

# UNIVERSIDAD DE CHILE FACULTAD DE CIENCIAS FISICAS Y MATEMATICAS DEPARTAMENTO DE GEOLOGÍA

### PETROLOGÍA Y EVOLUCIÓN GEODINÁMICA DEL COMPLEJO DENARO EN EL TERRENO MADRE DE DIOS (50°-53° S): AMBIENTE DE GÉNESIS Y DE ACRECIÓN AL MARGEN DE GONDWANA

# TESIS PARA OPTAR AL GRADO DE DOCTOR EN CIENCIAS MENCIÓN GEOLOGÍA

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#### Resumen

El Terreno Madre de Dios (TMD) corresponde a uno de los complejos metamórficos que forman el basamento occidental de la Patagonia (49°20'-53°25' S). Este complejo está constituido por tres unidades: el Complejo Denaro (CD), las Calizas Tarlton (CT) y el Complejo Duque de York (CDY), y ha sido interpretado como parte de un prisma de acreción construido en el margen paleo-Pacífico de Gondwana en el Paleozoico superior-Mesozoico inferior. Las características geológicas del TMD lo convierten en un elemento tectónico único en la Patagonia, por lo que descifrar su evolución geodinámica y el contexto paleogeográfico en que ésta se desarrolló es clave para comprender la evolución tectónica del margen paleo-Pacífico de Gondwana en el Paleozoico superior - Mesozoico inferior.

El análisis geoquímico de los metabasaltos del CD, junto con datos de microsonda electrónica de cromitas y clinopiroxenos primarios, confirma que estos corresponden a basaltos toleíticos tipo MORB y revela, además, que en este complejo predominan basaltos del tipo E-MORB, con limitados casos tipo N-MORB. Esto sugiere que las rocas del CD representan fragmentos del fondo oceánico del Pacífico ancestral formados en un centro de expansión oceánica. Diques y filones-manto que cortan al TMD presentan geoquímica de basaltos toleíticos de intraplaca, y son posiblemente producto de la etapa inicial del emplazamiento del Batolito Sur-Patagónico en el Jurásico Superior.

Datos palinológicos y dataciones U-Pb SHRIMP de circones detríticos en el CDY, confirman y restringen su edad de depósito al Pérmico, con una edad máxima de *ca*. 270 Ma. Los patrones de edades de circones detríticos confirman la existencia de dos poblaciones separadas de circones pérmicos, a *ca*. 270 Ma y *ca*. 290 Ma. La asociación palinológica en el CDY señala un ambiente húmedo durante su depósito. El CDY muestra notorias similitudes petrográficas, sedimentológicas, geoquímicas, isotópicas y geocronológicas, con otras sucesiones del margen de Gondwana, tales como el Trinity Peninsula Group y el Grupo LeMay oriental de la Península Antártica y el Terreno Rakaia de Nueva Zelandia. Los detritos de éstos, y del CDY, provienen de fuentes ígneas asociadas a un arco magmático activo Pérmico, situado en el margen occidental de Gondwana.

El estudio petrográfico y de microsonda electrónica de fases metamórficas en metabasaltos del CD muestra asociaciones minerales de la facies pumpellyita-actinolita. Pseudosecciones P-T calculadas para estas rocas indican condiciones del peak metamórfico a 290-310 °C y 4-6 kbar. Cálculos termodinámicos de equilibrios multivariantes usando las fases metamórficas en el CD y el CDY, indican un camino P-T prógrado desde  $4\pm 1$  kbar, 200-220°C a  $5\pm 1$  kbar, 290-330°C, reflejando trayectorias sub-horizontales de las partículas en el prisma de acreción frontal. Edades  ${}^{40}$ Ar/ ${}^{39}$ Ar por ablación láser UV *in situ* en fengitas, indican que la acreción del TMD ocurrió *ca.* 233 Ma. Además, una edad de *ca.* 201 Ma puede corresponder a un evento de acreción más joven o una etapa retrógrada. Un reajuste de edades a *ca.* 152 Ma es, probablemente, producto de la influencia de la etapa inicial del emplazamiento del Batolito Sur-Patagónico. Las condiciones y edad del metamorfismo del TMD son comparables con las del Terreno Rakaia, Grupo LeMay oriental y Trinity Peninsula Group, indicando el desarrollo de condiciones propias de subducción/acreción durante el Triásico Medio-Superior, a lo largo del margen paleo-Pacífico de Gondwana.

Consideraciones regionales permiten proponer un modelo geodinámico que involucra la acreción del TMD en el segmento Antártico del margen paleo-Pacífico de Gondwana. El arco magmático asociado con, y producto de, los procesos de subducción/acreción, estaría representado por granitoides del Pérmico y Triásico que afloran en el área de Marie Byrd Land (Antártica Occidental) y en la Península Antártica. Luego de su consolidación, el TMD habría sido transportado mediante movimientos de rumbo dextrales, antes del Jurásico Superior, desde el sector Antártico del margen de Gondwana hasta su posición actual en la placa Sudamericana, como parte de la Patagonia Austral.

En la Ciencia la única verdad sagrada, es que no hay verdades sagradas Carl Sagan

A mis padres

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#### <u>CAPÍTULO 1</u>: INTRODUCCIÓN

#### **1.1 ANTECEDENES GENERALES Y OBJETIVOS**

El basamento de los Andes Patagónicos incluye un conjunto de complejos metamórficos de edad pre-jurásica temprana que muestran historias estructurales y metamórficas muy diversas (e.g., Riccardi, 1971; Forsythe y Mpodozis, 1979; Forsythe, 1982; Dalziel y Forsythe, 1985; Hervé, 1988; Hervé et al., 1999a; Willner et al., 2000; Thomson y Hervé, 2002, Hervé et al., 2003; Ramírez-Sánchez et al., 2005; Augustsson et al., 2006; Calderón et al., 2007; Hervé et al., 2008; Hervé et al., 2010). Uno de estos complejos metamórficos, el Terreno Madre de Dios (TMD, Ramos, 1988; Hervé y Mpodozis, 2005, Sepúlveda et al., 2008) forma los afloramientos más occidentales del basamento Patagónico. Los afloramientos del TMD se extienden desde isla Mornigton (49°20'-50°00'S) hacia el sur, incluvendo el archipiélago Madre de Dios (50°00'-50°50'S), la isla Diego de Almagro (51°13'-51°40'S), las islas Ramírez y Contreras (51°40'-52°10'S), y las islas Recalada y Desolación (52°40'-53°25'S) en la boca occidental del Estrecho de Magallanes (Fig. 1A). El TMD ha sido descrito en publicaciones previas bajo los nombres de "Complejo Acrecionario Madre de Dios" (Thomson y Hervé, 2002; Lacassie, 2003; Sepúlveda, 2004; Hervé et al., 2007a; Hervé et al., 2008; Sepúlveda et al., 2010), "Complejo Madre de Dios" (Charrier et al., 2007), o "Complejo Metamórfico Madre de Dios" (Willner et al., 2009). En este trabajo, que incluye el estudio de los afloramientos en el archipiélago Madre de Dios, se ha elegido utilizar la denominación de "Terreno Madre de Dios" (TMD), ya que este concepto permite destacar de forma certera la individualidad propia de esta unidad geológica, que constituye un elemento tectónico único dentro de la Patagonia.

Aunque desde hace más de 50 años que se tiene conocimiento de la presencia de rocas paleozoicas en los archipiélagos de la Patagonia chilena (*e.g.*, Cecioni, 1955), aún persisten interrogantes en cuanto a la evolución geodinámica y al contexto paleogeográfico en que éstas se desarrollaron (*e.g.*, Hervé y Mpodozis, 2005). Si bien se considera que el TMD representaría parte de un prisma de acreción construido en el margen paleo-Pacífico de Gondwana en el Paleozoico superior - Mesozoico inferior (Forsythe y Mpodozis, 1979, Hervé *et al.*, 1981;

Dalziel, 1982; Forsythe y Mpodozis, 1983), se desconocen las conexiones/relaciones originales entre el TMD y el resto de las unidades presentes en la Patagonia extra-andina. Además, contribuye a esta incógnita la intrusión Meso-Cenozoica del Batolito Patagónico (Pankhurst *et al.*, 1999; Hervé *et al.*, 2007b), el que separa los diferentes dominios paleozoicos de la Patagonia austral.

Aunque se ha interpretado al TMD como parte de un complejo de subducción fósil, solamente se ha caracterizado cualitativamente el tipo de metamorfismo asociado a este régimen tectónico (Forsythe y Mpodozis, 1983; Hervé et al., 2000; Thomson y Hervé, 2002). A excepción del trabajo preliminar de Sepúlveda (2004) nunca se había efectuado un estudio detallado de las condiciones metamórficas en el TMD. Por esta razón, en esta tesis se utilizan metodologías que permiten cuantificar y comprender los procesos metamórficos que actuaron sobre estas rocas, en este caso particular, en el campo del metamorfismo en condiciones de muy bajo a bajo grado (temperaturas < ca. 300 °C). Lo anterior, unido a datos geocronológicos de minerales formados bajo estas condiciones metamórficas, permitirá establecer la modalidad y edad de acreción, lo que proporcionará una base para una comparación y eventual correlación a escala regional con otros complejos acrecionarios contemporáneos presentes a lo largo del margen paleo-Pacífico de Gondwana. Esto se complementa con información de los ambientes tectónicos donde se generaron las unidades ígneas del TMD, y con datos geocronológicos y palinológicos que permiten confirmar y precisar tanto la proveniencia como la edad de depósito del TMD. Estos datos, se emplean para analizar la evolución geodinámica de las rocas presentes en el archipiélago Madre de Dios, y posibles conexiones con otros complejos metamórficos del Paleozoico superior - Mesozoico inferior presentes tanto en la Península Antártica como en Patagonia.



**Figura 1.** A) Distribución de los afloramientos del TMD (tomado de Hervé *et al.*, 2006). B) Esquema geológico de la zona de estudio (modificado de Forsythe y Mpodozis, 1983 y Lacassie, 2003). 1: Depósitos Cuaternarios, 2: Batolito Sur-Patagónico, 3: Calizas Tarlton, 4: Complejo Denaro, 5: Complejo Duque de York, 6: Basamento indiferenciado, 7: Sill, 8: Cabalgamientos.

#### 1.1.1 Antecedentes Geológicos

Las rocas que constituyen el TMD en el archipiélago Madre de Dios y la isla Diego de Almagro fueron reconocidas inicialmente por Cecioni (1955, 1956), quien reconoció la presencia de grandes afloramientos de calizas portadoras de fusulínidos del Paleozoico superior, y señaló el carácter metamórfico de bajo grado de estas rocas. Con posterioridad, Forsythe y Mpodozis (1979, 1983) y Mpodozis y Forsythe (1983), efectuaron un estudio geológico regional del archipiélago Madre de Dios (Fig. 1B), indicando que el "basamento" allí aflorante está formado por tres unidades tectono-estratigráficas que, en muchos casos, presentan entre sí contactos tectónicos. Estas unidades son:

a) Complejo Denaro (CD), secuencia constituida por basaltos amigdaloidales de espesor indeterminado, recubiertos por delgadas capas de cherts metalíferos y lentes de sedimentos metalíferos, 30-60 m de cherts radiolaríticos bandeados rojos y verdes, los primeros con arcillolitas rojas intercaladas, y 20-50 m de lutitas silíceas negras y calcarenitas retrabajadas grises con fusulínidos. Los afloramientos de esta unidad corresponden en su mayoría a bloques limitados por fallas, lo que unido a probables cambios de facies laterales hace que esta secuencia no siempre se presente completa. En los basaltos se preservan estructuras primarias tales como almohadillas, hialoclastitas y *pillow-breccias*, mientras en las cercanías de estructuras mayores (fallas) los basaltos se presentan foliados (fig. 2). Radiolarios presentes en los cherts (género *Pseudoalbaillella*) permiten acotar la edad de este complejo entre el Carbonífero tardío y el Pérmico temprano (Ling *et al.*, 1985). Estos mismos autores reconocieron fósiles de foraminíferos fusulínidos en las calcarenitas, los que fueron asignados al Pérmico temprano (Wolfcampiano).



**Figura 2.** Metabasaltos del Complejo Denaro: A) estructura en almohadilla; B) hialoclastitas; C) foliación dinámica desarrollada en hialoclastitas; D) flujos basálticos amigdaloidales.

b) Calizas Tarlton (CT), unidad constituida por calizas macizas, parcialmente recristalizadas, y mármol, con un espesor mínimo estimado de 500 m. Sólo en una localidad (sitio IBGT, ver fig. 1) las CT yacen sobre una secuencia de basaltos almohadillados, sedimentos metalíferos y cherts rojos bandeados, potencialmente parte del CD. El contacto entre esta unidad y el CD es, generalmente, de naturaleza tectónica. Debido a la intensa recristalización, disolución y deformación (plegamiento) de esta unidad, son muy pocos los lugares donde se puede reconocer su estratigrafía original (fig. 3). Las calizas corresponden a calcarenitas y margas, y son portadoras de abundante fauna fósil, la que incluye foraminíferos (fusulínidos), gastrópodos, crinoídeos, corales y braquiópodos, además de abundantes trazas. Los fusulínidos presentes en estas rocas (géneros *Tricitites, Schwagerina, Pseudofusulina, Charloswagerina, Climacammina*,

entre otros) indican un rango de edad entre Pensilvaniano Medio a Pérmico temprano (Cecioni, 1956; Douglass y Nestell, 1972, 1976; Chisaka y Corvalán, 1979).



**Figura 3.** Calizas Tarlton: A) afloramientos en la costa norte de Isla Tarlton, donde se aprecia el aspecto masivo de esta unidad; B) estratificación primaria en las calizas, donde se aprecian capas métricas.

c) Complejo Duque de York (CDY), corresponde a la unidad más extendida del TMD, la que se encuentra complejamente imbricada y deformada, lo que impide reconocer certeramente su estratigrafía original. Está compuesta por una sucesión, de varios de miles de metros de espesor, de areniscas, lutitas y conglomerados (fig. 4). Las areniscas corresponden a grauwackas, con mala selección y granos subangulares de cuarzo, feldespatos y fragmentos líticos. Los conglomerados son, generalmente, matrizsoportados, con un dominio de clastos redondeados de volcanitas ácidas, lutitas, limolitas y areniscas, además de clastos de calizas y chert en menor proporción. Algunas capas de la sucesión presentan estructuras sedimentarias tales como bioturbación, estratificación cruzada, marcas de fondo, calcos de carga y sucesiones de Bouma. En dos localidades (Seno Palo-Pico York y extremo SE de fiordo Contreras) areniscas del CDY se apoyan en forma concordante sobre cherts radiolaríticos del CD. Por otro lado, en Seno Soplador una superficie paleo-kárstica separa en discordancia de erosión al CDY de las CT (Hervé et al., 1999b; Lacassie et al., 2006), mientras que en isla Tarlton el CDY parece suceder estratigráficamente a las CT (Forsythe y Mpodozis, 1983). Lo anterior apunta que el CDY se habría depositado con posterioridad a las unidades anteriores. Edades U-Pb SHRIMP de circones detríticos en areniscas pertenecientes al CDY revelan que la población de circones más joven y abundante es del Pérmico temprano (*ca*. 270 Ma) (Hervé *et al.*, 2003). Este dato es consistente con la edad pérmica temprana de radiolarios presentes en intercalaciones de cherts que ocurren dentro del CDY (A. Yoshiaki, comunicación escrita, 2002; en Hervé *et al.*, 2007a).



**Figura 4.** Complejo Duque de York: A) afloramientos en el extremo norte del Seno Eleuterio; B) estratificación cruzada en areniscas de este complejo.

Afloramientos de las mismas unidades se encuentran en la zona el Estrecho Nelson, 100 km al sur del archipiélago Madre de Dios, donde están en contacto tectónico con rocas jurásicas del Complejo Metamórfico Diego de Almagro a lo largo de la Zona de Cizalle del Seno Arcabuz (Forsythe *et al.*, 1981; Olivares *et al.*, 2003). Además, afloramientos de mármoles que aparecen al este del Batolito Sur-Patagónico a la misma latitud del archipiélago Madre de Dios (extremo oriental del Seno Andrés, 50°33'S-73°53'W) fueron asignados al TMD por Hervé *et al.* (2007b). Por otra parte, Hervé *et al.* (2010) señalan la presencia de rocas metasedimentarias con circones detríticos del Pérmico temprano, asignables al CDY, en las zonas noroeste (Caleta Murray) y suroeste (Seno Searle) de la Cordillera de Darwin, cerca del estrecho de Magallanes. Estos afloramientos corresponderían a bloques del CDY tectónicamente intercalados dentro del Complejo Metamórfico Cordillera de Darwin, el que fue afectado por metamorfismo de alto grado durante la deformación cretácica asociada al cierre de la "Cuenca de Rocas Verdes" (Kohn *et al.*, 1995; Klepeis *et al.*, 2010).

Forsythe y Mpodozis (1983) señalaron que, de acuerdo a datos geoquímicos, el CD representa fragmentos de fondo oceánico que migró a partir de una dorsal activa y fue cubierto,

progresivamente, por detritos planctónicos silíceos (cherts bandeados). Las CT corresponderían a una plataforma carbonatada intra-oceánica de aguas poco profundas, desarrollada sobre un sustrato volcánico, sincrónicamente con el depósito del CD (Ling *et al.*, 1985). Por otra parte, la potente secuencia detrítica que comprende el CDY constituiría depósitos turbidíticos, provenientes de erosión continental, acumulados en o cerca de una fosa. Este material detrítico se habría depositado sobre las CT y el CD a medida que estas últimas se acercaban a la zona de subducción en el margen continental de Gondwana (Forsythe y Mpodozis, 1983).

Estudios geoquímicos de metabasaltos del CD efectuados por Hervé *et al.* (1999b) comprueban que éstos corresponden a basaltos toleíticos E-MORB provenientes de una dorsal oceánica o de un plateau oceánico. Hervé *et al.* (2000) indicaron, sin embargo, que el origen probable para estas rocas sería un plateau oceánico o una dorsal asísmica. Por otro lado, datos geoquímicos de Faúndez *et al.* (2002) y Lacassie *et al.* (2006) en areniscas y fangolitas del CDY indican que estos sedimentos se acumularon en un margen continental activo a partir de una fuente en un arco volcánico de composición granodiorítica, situado relativamente próximo a su cuenca de depósito, y cuyas raíces plutónicas habían sido expuestas a la erosión.

En forma complementaria, Hervé et al. (2000) sugieren que los basaltos del CD habrían sido afectados, previamente a su acreción, por metamorfismo de fondo oceánico. Sin embargo, estudios más recientes (Sepúlveda, 2004; Sepúlveda et al., 2005) indican que la paragénesis mineral metamórfica presente en el CD se formó a temperaturas cercanas a los 300 °C y presiones mínimas de 4 kbar. Estas condiciones de presión y temperatura (P-T) son características de zonas de subducción, e indican que el metamorfismo del CD se desarrolló en la facies pumpellyitaactinolita, la cual ha sido documentada en rocas pertenecientes a otros prismas de acreción en Japón (Banno, 1998) y Chile (Hervé et al., 1999a; Willner et al., 2000). Las asociaciones de minerales metamórficos revelan que el metamorfismo está asociado a un gradiente geotermal entre 15 y 20 °C/km, lo cual ha sido atribuido a subducción lenta o subducción de litósfera oceánica joven y relativamente caliente (Hervé et al., 2007a). Las condiciones geodinámicas favorables para la instauración de esta facies pueden generarse durante procesos de acreción frontal u offscraping (Scholl et al., 1980; Moore et al., 1981; Platt, 1986), de manera similar a lo propuesto por Willner et al. (2000) para el cinturón oriental del Complejo Metamórfico de los Chonos, y por Richter et al. (2007) para la Serie Oriental del Complejo Acrecionario de la Cordillera de la Costa de Chile Central.

En cuanto a la edad del metamorfismo del TMD, Thomson y Hervé (2002) obtuvieron dos edades del Triásico superior en trazas de fisión en circones detríticos del CDY ( $209 \pm 19 \text{ y } 209 \pm 12$  Ma). Estas edades fueron interpretadas como edades de enfriamiento post-metamórfico y, por lo tanto, se infirió que la edad mínima de depósito y metamorfismo del CDY es de 195 Ma. Esto implica que el evento metamórfico ocurrió antes del inicio del emplazamiento del Batolito Sur-Patagónico Cretácico Temprano en esta área (episodio Cretácico 2 de Hervé *et al.*, 2007b), el cual tiene edades isotópicas cercanas al contacto con el TMD de 112-133 Ma (Rb-Sr roca total y biotita, Halpern, 1973), 130-143 Ma (K-Ar biotita, Duhart *et al.*, 2003) y *ca.* 133 Ma (U-Pb SHRIMP circón, Hervé *et al.*, 2007b).

#### 1.1.2 Origen y proveniencia del TMD: modelos alternativos

Las reconstrucciones paleogeográficas más recientes para el Carbonífero tardío y el Pérmico temprano (*e.g.*, Torsvik y Cocks, 2004; Veevers, 2004; Cocks y Torsvik, 2006; Cawood y Buchan, 2007; Blakey, 2007) posicionan el área del margen de Gondwana donde se emplaza actualmente el archipiélago Madre de Dios en una alta latitud austral, muy lejos de la zona tropical en donde se espera que se formen calizas marinas con asociaciones faunísticas similares a las encontradas en las CT (Douglass y Nestell, 1976; Lacassie, 2003). Este antecedente, junto al ambiente oceánico para el depósito coetáneo de las CT y del CD (Ling *et al.*, 1985; Ling y Forsythe, 1987), llevaron a Forsythe y Mpodozis (1983) a sugerir que tales unidades comenzaron a acumularse en latitudes menores siendo luego transportadas, debido al desplazamiento del fondo oceánico, hacia latitudes altas donde fueron incorporadas junto al CDY dentro de un prisma de acreción en el margen paleo-Pacífico de Gondwana.

Uno de los problemas existentes en cuanto al origen último del TMD es la ausencia en la Patagonia austral de un arco magmático calco-alcalino Pérmico (Triásico) que sea la fuente de los circones detríticos del CDY (Hervé *et al.*, 2003; Lacassie, 2003; Hervé y Mpodozis, 2005; Hervé *et al.*, 2006), y que además tenga una posición y geometría que permita ligarlo directamente a la subducción responsable de la construcción del prisma de acreción del que formaban parte las unidades del TMD. Esta situación ha llevado a algunos autores a sugerir que la generación de este prisma de acreción ocurrió en un segmento distinto del margen paleo-Pacífico de Gondwana

(Lacassie, 2003; Lacassie *et al.*, 2006), para después ser transportado por fallas de rumbo, o bien "en bloque" como parte de un terreno exótico, hasta alcanzar su posición actual antes del inicio del emplazamiento del Batolito Sur-Patagónico (Hervé *et al.*, 2007b). Entre los modelos propuestos destacan los siguientes (fig. 5):

Acreción en el segmento Antártico del margen de Gondwana: Lacassie et al. (2006) muestran que los metasedimentos del CDY comparten características petrográficas, geoquímicas y geocronológicas con metaturbiditas presentes en el Terreno Rakaia en Nueva Zelanda (MacKinnon, 1983) y con el Grupo LeMay oriental (Triásico) aflorante en la isla Alexander, Península Antártica (Burn, 1984). Estas semejanzas apuntan hacia fuentes ígneas similares para estas tres sucesiones, sugiriendo que éstas fueron depositadas simultáneamente a lo largo del mismo margen continental activo (Lacassie et al., 2006). Este margen podría estar localizado a lo largo del sector Antártico del margen paleo-Pacífico de Gondwana, como lo indican los estudios de Willan (2003) para el área fuente del Grupo LeMay, y los de Wandres et al. (2004) y Wandres y Bradshaw (2005) para la fuente del Terreno Rakaia. Los últimos dos trabajos indican que el origen de los detritos Pérmicos en el Terreno Rakaia estaría en las rocas plutónicas y volcánicas de las provincias de Amundsen y Ross, en Marie Byrd Land (Antártica Occidental), las que durante el Pérmico Tardío se encontraban cerca de los 60° latitud Sur (Veevers, 2004; Cawood y Buchan, 2007). En este contexto, Lacassie et al. (2006), siguiendo las interpretaciones de Hervé et al. (2000) y Cawood et al. (2002), proponen que la acreción de las CT y el CD habría ocurrido contra el segmento Antártico del margen de Gondwana, desde donde habrían sido desplazados por movimientos de traslación dextrales, junto con el CDY, como bloque coherente hasta su posición actual (Lacassie, 2003) (ver fig. 5). Un problema para este modelo deriva de la escasa información geocronológica disponible para los granitoides calco-alcalinos Pérmicos en las provincias de Amundsen y Ross (Pankhurst et al., 1998; Mukasa y Dalziel, 2000), junto al hecho que los afloramientos conocidos de estos cuerpos están geográficamente muy restringidos (< 1% del área total de Antártica, según Stump, 1995).

*Acreción en el segmento Sudamericano del margen de Gondwana*: datos paleomagnéticos obtenidos en las CT y el CD por Rapalini *et al.* (2001) indican que ambas unidades sufrieron una rotación anti-horaria de aproximadamente 117°, con una variación latitudinal despreciable, con posterioridad a la remagnetización producida por la influencia termal del Batolito Sur-Patagónico en el Cretácico temprano. Esta información permitió a estos autores concluir que la acreción de

estas unidades se habría llevado a cabo desde el NW (ver fig. 5), al contrario de lo señalado por Forsythe y Mpodozis (1979, 1983), quienes sugirieron una acreción desde el SW para las unidades que forman el TMD. La interpretación de Rapalini et al. (2001) concuerda con deformación asociada a cizalle sinistral en la parte norte de la Península Antártica, la que está restringida a fines del Triásico (A. Vaughan, comunicación escrita, Octubre 2006). Esta deformación afecta al Trinity Peninsula Group (Hyden y Tanner, 1981), unidad de edad y características sedimentológicas similares al CDY (Hervé et al., 2006). En este caso, el arco magmático Pérmico que dio origen a los circones detríticos del CDY podría estar representado por los granitos Permo-Triásicos del Macizo Nor-Patagónico (Pankhurst et al., 2006), y la acreción de las CT y el CD habría sucedido en las vecindades de estos cuerpos intrusivos. Sin embargo, este modelo presenta las siguientes falencias: (1) los datos paleomagnéticos de Rapalini et al. (2001) no son lo suficientemente concluyentes como para ser interpretados claramente como la rotación indicada por estos autores; (2) si tal rotación existiese, tendría que haberse rotado también parte del Batolito Sur-Patagónico, de lo cual no se tiene evidencia alguna; (3) ninguno de los granitos Pérmicos del Macizo Nor-Patagónico ha sido considerado como indicativo de subducción, sino más bien como el resultado de fusión cortical (Pankhurst et al., 2006); y (4) la disposición geométrica de los granitoides Pérmicos del Macizo Nor-Patagónico (faja E-W que atraviesa la Patagonia) hace prácticamente inviable que estos puedan ser considerados como un arco asociado a la subducción que originó el prisma del TMD.

Otras posibilidades a explorar, en el caso que no haya ocurrido traslación significativa del TMD después de la acreción de las unidades oceánicas (CT y CD) contra el margen paleo-Pacífico de Gondwana, son: (1) que los circones detríticos del CDY provengan, como lo sugiere recientemente Fanning *et al.* (2011), de la provincia magmática ácida Choiyoi (aunque esto no soluciona la falta de un arco Pérmico-Triásico en la posición adecuada para ligarlo a la subducción y acreción de las unidades del TMD); y (2) que exista un arco Pérmico bajo la cobertura Mesozoica de la Patagonia oriental, de modo similar a lo propuesto por Ramos (2008).



**Figura 5.** Reconstrucción paleogeográfica de Gondwana a los 260 Ma (modificada a partir de Cawood *et al.*, 2002 y Lacassie, 2003). Se muestran posiciones tentativas para el área de formación de las CT (cuadrados negros), así como las respectivas localizaciones probables para la acreción de las CT y el CD (círculos azules). En ambos casos se postula la traslación del TMD paralela al margen de Gondwana, desde el punto de acreción inicial hasta la posición actual respecto del margen de Gondwana (estrella roja). En verde está marcada la localización de las Provincias de Amundsen y Ross (Antártica Oriental), y en amarillo la extensión aproximada de granitos Permo-Triásicos de Macizo Nor-Patagónico (Pankhurst *et al.*, 2006). AF: África, ANT: Antártica, AUS: Australia, PA: Península Antártica, SUD: Sudamérica.

#### 1.1.3 Objetivos

Tomando en cuenta los antecedentes presentados, los objetivos principales de esta tesis son: (1) determinar el ambiente tectónico de formación del Complejo Denaro y la evolución metamórfica del TMD; (2) precisar la edad, lugar y mecanismo de acreción y emplazamiento final del TMD; (3) presentar un modelo geodinámico, que permita una mejor comprensión de la evolución tectónica del margen paleo-Pacífico de Gondwana en el Paleozoico superior - Mesozoico inferior.

Entre los objetivos específicos se cuentan los siguientes:

- Precisar el ambiente tectónico donde se generaron los basaltos del CD;

- Determinar las condiciones termo-barométricas y trayectorias P-T (presión-temperatura) del metamorfismo por medio de la aplicación de métodos termodinámicos (cálculo de reacciones multivariantes y pseudosecciones P-T);

- Establecer la edad del metamorfismo que afecta al TMD a través de la datación *in situ* de minerales que registren la acreción de las unidades que lo forman.

- Precisar tanto la edad del CDY como la proveniencia de los sedimentos que lo constituyen mediante el estudio geocronológico (U-Pb SHRIMP) de la población de circones detríticos y el análisis de su contenido palinológico.

#### Hipótesis de trabajo

- La amalgamación de las unidades oceánicas (CT y CD) con el CDY ocurrió durante su acreción al margen paleo-Pacífico de Gondwana (formación del TMD).
- Las condiciones metamórficas registradas en el TMD son resultado de la acreción frontal de estas rocas durante un régimen de subducción, el que probablemente ocurrió en el segmento Antártico del margen de Gondwana.

#### 1.2 METODOLOGÍA

#### 1.2.1 Trabajo en terreno

Se realizaron cuatro campañas a terreno, durante la temporada de verano en los años 2004, 2005, 2006 (archipiélago Madre de Dios) y 2007 (archipiélago Diego de Almagro), completando un total de 56 días efectivos de trabajo en terreno. Debido a la geografía del área, todas estas campañas involucraron navegación en pequeños barcos y/o botes zódiac para lograr acceder a los afloramientos, los que se presentan en general en la costa de islas e islotes del sector.

#### 1.2.2 Trabajo en laboratorio

Con el propósito de realizar una caracterización detallada de las unidades muestreadas, fue necesario desarrollar las siguientes actividades:

- Petrografía de las rocas recolectadas: estudio de cortes transparentes de las muestras.
- Geoquímica de roca total: Elementos Mayores, Trazas y Tierras Raras determinados a través de ICP-MS y/o XRF para precisar el ambiente de formación de rocas ígneas del TMD (metabasaltos del CD y diques que intruyen a las unidades del TMD).
- Análisis mineralógico por microsonda electrónica (Wave Dispersive Spectometer, WDS) para establecer las composiciones de los minerales que fueron utilizados en determinar condiciones de presión y temperatura.
- Geo-termo-barometría: se obtuvo información de las condiciones P-T de la evolución metamórfica de estas rocas a partir de:

- rangos P-T de la asociación metamórfica crítica (facies metamórfica) e información de las condiciones P-T mínimas para la cristalización de minerales específicos.

 geotermómetros y geobarómetros determinados experimentalmente, como los de Massonne y Schreyer (1987), Cathelineau (1988) y Massonne y Szpurka (1997).

- estimaciones de rangos de temperaturas del metamorfismo a partir de la determinación de la cristalinidad de fases minerales específicas (Índice de Cristalinidad de la Ilita o Índice de Kübler), utilizando difracción de rayos X (Departamento de Física, Universidad de Chile).

- cálculos termodinámicos de equilibrio mineral relevantes a las asociaciones minerales observadas (cálculo de reacciones multivariantes y pseudosecciones P-T utilizando software apropiado (Ge0-Calc y Perple\_X)).

• Geocronología: se utilizaron dos métodos de datación para obtener edades de depósito y de metamorfismo del TMD:

- U-Pb SHRIMP de circones detríticos en areniscas del CDY y sedimentos del CD (Australian National University).

- Ar-Ar *in situ* en micas blancas fengíticas en 4 muestras de roca mediante microsonda de ablación láser ultra-violeta (UV-LAMP) (Potsdam Universität, Alemania). Las edades obtenidas son interpretadas como edades del metamorfismo. Esta técnica ya ha sido aplicada con buenos resultados en la determinación de edades de acreción de terrenos en condiciones metamórficas de baja temperatura. En el caso en estudio, este método entrega restricciones de la llegada del TMD y, por lo tanto, detalles críticos del tiempo y magnitud de la traslación del terreno.

• Paleontología: estudio de los palinomorfos encontrados en areniscas y lutitas del CDY. Este tema se trabajó en conjunto con Sylvia Palma-Heldt especialista en Palinología del Paleozoico y Mesozoico de la Universidad de Concepción.

Todos estos resultados se integraron para así precisar la evolución geodinámica del TMD. De esta manera se puede enmarcar este estudio dentro del ámbito paleogeográfico y tectónico global del Paleozoico tardío en el margen paleo-Pacífico de Gondwana.

#### **1.3 ESTRUCTURA DE LA TESIS**

Esta tesis está organizada en cinco capítulos principales, donde el segundo, tercer y cuarto capítulo incluyen resúmenes en español e inglés al inicio de cada uno de éstos. Este primer capítulo incluye los antecedentes geológicos que justifican el estudio, los objetivos, hipótesis y metodología, además de una revisión general de la literatura en prismas de acreción, terrenos tectono-estratigráficos y pseudosecciones.

El segundo capítulo incluye bajo el título "*Petrological and geochemical characteristics of metamorphic and igneous units from the allochthonous Madre de Dios terrane, Southern Chile*", el estudio petrográfico de 34 muestras de rocas del TMD (metabasaltos y diques), además del análisis geoquímico de 19 de éstas por medio de fluorescencia de rayos X (XRF) e ICP-AES. También contiene el análisis por microsonda electrónica (EMPA) de 2 muestras de metabasaltos del Complejo Denaro. Como información complementaria al final de este capítulo se incluyen datos geoquímicos de tierras raras y elementos trazas de once muestras del Complejo Denaro. La información obtenida se utilizó para (1) precisar el ambiente tectónico de génesis de los basaltos del CD mediante el uso de varias metodologías, (2) establecer las composiciones de los minerales primarios y secundarios observados en las muestras, y (3) determinar cualitativamente condiciones termo-barométricas del metamorfismo que afectó a esta unidad.

En el tercer capítulo: "Conditions and timing of pumpellyite-actinolite facies metamorphism in the Early Mesozoic frontal accretionary prism of the Madre de Dios Archipelago (50°20'S; Southern Chile)", se usó información mineralógica (a partir de la utilización de microscopio óptico y microsonda electrónica), geoquímica y geocronológica (edades Ar-Ar in situ a partir de microsonda de ablación láser ultra violeta (UV-LAMP)) para (1) determinar la composición mineral y de roca total de trece muestras del CD y CDY, (2) realizar cálculos termodinámicos de equilibrio mineral utilizando reacciones multivariantes y pseudosecciones P-T mediante el uso de software apropiado (Ge0-Calc y Perple\_X), para de esta manera (3) cuantificar la evolución termal del TMD, y además, (4) determinar la edad del metamorfismo y/o acreción de estas rocas al margen paleo-Pacífico de Gondwana.

El cuarto capítulo "*Permian depositional age of metaturbidites of the Duque de York Complex, southern Chile: U-Pb SHRIMP data and palynology*" pretende (1) refinar la edad de depósito del CDY mediante la utilización de edades U-Pb SHRIMP en circones detríticos y el estudio de palinomorfos presentes en muestras pertenecientes a éste complejo, (2) entregar una síntesis de la información geocronológica y paleoambiental en relación con el lugar y edad de depósito de estas rocas, y (3) utilizar la información anterior para aportar nuevas hipótesis en cuanto al carácter alóctono de las rocas del CDY. Cabe destacar que este estudio palinológico correspondería al primer registro del Paleozoico tardío en Chile.

Tanto el segundo, tercer y cuarto capítulo siguen el formato de artículos enviados a revistas científicas internacionales. Por último, el quinto capítulo corresponde a la discusión y conclusiones generales.

# 1.4 PRISMAS DE ACRECIÓN, TERRENOS TECTONO-ESTRATIGRÁFICOS Y PSEUDOSECCIONES P-T: ESTADO DEL CONOCIMIENTO

#### 1.4.1 Prismas de acreción

Los márgenes de placas convergentes corresponden a las manifestaciones superficiales de las zonas de subducción, y están localizados donde una placa de litósfera oceánica desciende hacia el manto, a lo largo de la zona de Wadati-Benioff, bajo litósfera oceánica o continental (Underwood y Moore, 1995; Stern, 2002) (fig. 6).



**Figura 6.** A) Distribución global de los márgenes convergentes, indicados por triángulos negros. B) Sección esquemática de los 140 km superiores de una zona de subducción (tomado de Stern, 2002).

Aunque la mayoría de la litósfera oceánica es subductada hacia el manto, parte de cubierta sedimentaria y fragmentos de la corteza oceánica de la placa descendente pueden ser transferidos a la placa superior. De acuerdo a lo anterior, los márgenes convergentes (comúnmente llamados márgenes destructivos) se pueden dividir en aquellos que crecen por adición e imbricación de material a lo largo de la fosa oceánica (márgenes acrecionarios) y aquellos en que no hay adición de material (márgenes no-acrecionarios) (von Huene y Scholl, 1991; Stern, 2002). El balance entre acreción y no-acreción depende de la cantidad de sedimentos (oceánicos y continentales) que están siendo subductados, donde el espesor éstos tiene que superar los 500-1000 m (von Huene y Scholl, 1991; Le Pichon *et al.*, 1993) para que puedan ser raspados desde la placa que desciende y transferidos a la placa superior, generando así un *prisma de acreción* (fig. 7). Debido a lo anterior, los márgenes acrecionarios se sitúan comúnmente adyacentes a placas continentales donde el aporte de sedimentos es alto (Stern, 2002), aunque el volumen de detritos aportados a la fosa está determinado por las condiciones climáticas imperantes (*e.g.*, Bangs y Cande, 1997).

Un prisma de acreción (también conocido como prisma acrecionario, cuña acrecionaria o complejo acrecionario) es una estructura tridimensional en forma de cuña, constituida por material deformado acumulado mediante fallas inversas imbricadas en el borde de la placa superior cabalgante (Cloos y Shreve, 1988; Underwood y Moore, 1995) (fig. 7). El material que es añadido a la placa superior consiste en sedimentos marinos raspados desde la placa oceánica y sedimentos provenientes de la placa continental adyacente, pero en algunos casos también se incluye material de la corteza (piso oceánico) de la placa subductada (fig. 7A). Una superficie de despegue (décollement) (fig. 7) separa la parte superior de la sección acrecionada del material que está siendo subductado (Moore, 1989). Encima del nivel de despegue, el material "cepillado" es transferido al prisma acrecionario, el que muestra una morfología accidentada e irregular de su superficie, gobernada por numerosas dorsales tectónicas formadas por plegamiento y dislocación de fallas (Underwood y Moore, 1995). Estructuralmente, los prismas de acreción son esencialmente fajas plegadas y corridas compresionales, donde estas fallas y pliegues, en general, presentan una vergencia hacia la placa oceánica subductante, propagándose desde el nivel de despegue a través de la cuña (fig. 7). Modelos para la evolución de un prisma indican que la forma de éste depende dinámicamente de la resistencia del material que lo constituye y del stress de cizalle concentrado en la base de la cuña (e.g., Dahlen, 1984). No obstante, la corteza del antearco (compuesta principalmente por rocas ígneas y/o metamórficas) también influye en la forma y estructura interna del prisma de acreción al actuar como contrafuerte (*backstop*) al crecimiento de éste (*e.g.*, Byrne *et al.*, 1993).



**Figura 7.** Prisma de acreción. A) Esquema ilustrativo con las principales características de una zona de subducción acrecionaria y el prisma asociado (modificado de Moore *et al.*, 2007). B) Diagrama de bloque de prospección de reflexiones sísmicas 3D de parte de la cuña acrecionaria del margen sureste de la costa de Japón (Moore *et al.*, 2007).

En los prismas de acreción el transporte de sedimentos provenientes desde el continente es controlado por deslizamientos submarinos, flujos de detritos y corrientes de turbidez (Underwood y Moore, 1995) (fig. 7B). Cañones submarinos transportan sedimentos desde playas y ríos hacia la fosa. Estos cañones se forman por turbiditas canalizadas y, generalmente, pierden definición

con la profundidad debido a que el continuo fallamiento interrumpe los canales submarinos. Los sedimentos se mueven hacia abajo por la pared de la fosa por medio de canales y una serie de cuencas controladas por fallas. La fosa misma sirve como un eje para el transporte de sedimentos. Si suficiente sedimento se mueve por la fosa, esta puede ser completamente llenada de manera que las corrientes de turbidez sean capaces de llevar sedimentos más allá de la fosa, pudiendo incluso superar la pendiente externa (hacia el océano) de la fosa (*outer swell*) (Underwood y Moore, 1995).

#### Estilos de acreción

Los prismas de acreción crecen por medio de los procesos mecánicos de acreción frontal (offscraping) y acreción basal (underplating) (Karig y Sharman, 1975; Scholl et al., 1980; Moore et al., 1981; Platt, 1986; Cloos y Shreve, 1988). En la acreción frontal sedimentos y eventualmente corteza oceánica son raspados, a manera de *bulldozer*, y transferidos a la punta de la cuña acrecionaria (fig. 8). Esto resulta, a lo largo de la vida de un margen convergente, en el ensanchamiento del prisma, donde sedimentos más jóvenes definen la parte externa del prisma y sedimentos más viejos en las zonas más internas (Underwood y Moore, 1995). Las zonas más internas y antiguas del prisma están mucho más litificadas y tienen estructuras con más pendiente que las zonas más externas. Por otra parte, la acreción basal corresponde a la adición de masa en la base de la cuña acrecionaria (fig. 8), en una posición intermedia entre el arco magmático y la fosa, produciendo engrosamiento y alzamiento sin acortamiento adicional (Cloos y Shreve, 1988). En esencia, cualquier material adicionado bajo el material acrecionado frontalmente es considerado como acrecionado basalmente (Underwood y Moore, 1995). Este tipo de acreción es difícil de detectar en las zonas de subducción actuales, pero puede ser registrado en prismas de acreción antiguos (fósiles) en forma de mélanges tectónicos y duplex estructurales. Por otra parte, mientras que estudios estructurales y geocronológicos indican un relevo temporal entre los modos de acreción antes mencionados (e.g., Richter et al., 2007, Willner et al., 2008), modelos análogos muestran que ambos pueden coexistir durante el desarrollo de un sistema acrecionario (Kukowski et al., 2002; Glodny et al., 2005). Además, otros modelos muestran que la acreción basal ocurre sólo asociada a una alta fricción en la base del prisma (Kukowski et al., 1994; Gutscher et al., 1996; Contardo, 2008).



**Figura 8.** Estilos de acreción frontal y basal visualizados en A) ilustración esquemática basada en líneas sísmicas de la costa occidental de México de Moore *et al.* (1981), y en B) modelo análogo de Kukowski *et al.* (2002), donde se aprecia claramente el contraste estructural entre los ambos tipos de acreción, con pliegues subverticales para la acreción frontal y foliación subhorizontal para la acreción basal.

Los elementos estructurales desarrollados dentro de los complejos acrecionarios reflejan una historia de deformación específica y están relacionados a los modos de acreción, petrología, velocidad de convergencia y otros factores (Glodny *et al.*, 2005). De esta manera, y siguiendo los conceptos de campo de flujo de Feehan y Brandon (1999) y Ring *et al.* (1999), la acreción frontal causará un campo de flujo de engrosamiento, caracterizado por líneas de flujo convergentes y una extensa contracción horizontal (fig. 9). En contraste, la acreción basal producirá un campo de flujo de adelgazamiento, representado por líneas de flujo divergentes, las que indican una amplia extensión horizontal en la parte posterior de la cuña (Richter *et al.*, 2007) (fig. 9). Lo anterior se traduce en estilos estructurales contrastantes para cada modo de acreción, con foliación y pliegues subverticales para la acreción frontal, y foliación horizontal penetrativa para la acreción basal (ver fig. 8B). Además, cada estilo de acreción está asociado a condiciones metamórficas específicas, donde la acreción basal está relacionada a facies de esquistos verdes de alta presión,

y más raramente a esquistos azules y anfibolitas (*e.g.*, Willner *et al.*, 2000, 2004; Willner, 2005). A su vez, la acreción frontal estaría caracterizada por facies metamórficas de muy bajo grado (T < 300 °C) y condiciones de presión intermedias (*e.g.*, Willner *et al.*, 2000).



**Figura 9.** Ilustración esquemática de campos de flujo para los miembros extremos de las cuñas convergentes (tomado de Richter *et al.*, 2007). A) Durante la acreción frontal las líneas de flujo convergentes llevan a un campo de flujo de engrosamiento y amplia contracción horizontal; B) en la acreción basal líneas de flujo de adelgazamiento causan extensiva contracción vertical y extensión horizontal expresada como foliación subhorizontal.

En el caso del TMD, la asociación de unidades con características "oceánicas" (CT y CD) junto a una secuencia sedimentaria turbidítica de gran extensión (CDY), unido a la compleja imbricación tectónica entre estas unidades, ha llevado a proponer a este bloque como un "macro-mélange" representativo de un prisma de acreción construido en el margen continental paleo-Pacífico de Gondwana (Forsythe y Mpodozis, 1979; Dalziel, 1982). Además, el estilo estructural de la deformación en el TMD (cabalgamientos, pliegues subverticales) es similar al asociado al proceso de acreción frontal. Esto se ve apoyado por las características del metamorfismo que afectó a estas rocas, el que se enmarcaría dentro de las condiciones P/T asociadas a la facies pumpellyita-actinolita (Sepúlveda, 2004).

#### 1.4.2 Terrenos tectono-estratigráficos

El uso informal del término *terreno* se remonta a las décadas de 1920 y 1930 (Coombs, 1997), pero el significado geológico actual de esta expresión deriva de los trabajos de Irving (1964, 1972), quien los utilizó para diferenciar un conjunto de rocas con características específicas o con una relación genética, lo que las hace diferentes a su entorno. La expresión *terreno tectono-estratigráfico* especifica que un terreno es una entidad geológica definida en base a su estratigrafía, y cuya posición y dimensiones son resultado de procesos tectónicos (Howell, 1985).

#### Nomenclatura (tomado de Vaughan *et al.*, 2005)

De acuerdo a Coney *et al.* (1980), los terrenos son bloques geológicos discretos caracterizados por homogeneidad interna de su estratigrafía, estilo tectónico coherente y una historia geológica diferente a la de terrenos adyacentes. Los límites entre terrenos corresponden, generalmente, a fallas regionales o discontinuidades tectónicas mayores, y están marcados por quiebres en la estratigrafía que no pueden ser explicados por simples cambios de facies o discordancias. Estas características se resumen en la definición de terrenos como un conjunto de rocas limitado por fallas, los que poseen extensión regional y están caracterizados por una historia geológica que difiere de la de sus terrenos vecinos (Howell *et al.*, 1985; Friend *et al.*, 1988).

Un terreno es considerado como 'sospechoso' si existen dudas acerca de su emplazamiento paleogeográfico con respecto a terrenos adyacentes o a los márgenes continentales (Coney *et al.*, 1980; Coombs, 1997). Un terreno puede ser "exótico" o 'alóctono' (ambos significando casi lo mismo, según Vaughan *et al.*, 2005) si existen evidencia suficiente de que ellos se originaron lejos de su posición actual. A pesar de lo anterior, también se ha indicado que la diferencia entre terrenos alóctonos y terrenos exóticos es que mientras los primeros son aquellos bloques que se movieron desde su lugar de origen, los segundos corresponden a terrenos alóctonos que provienen de distancias muy grandes y que no coinciden paleogeográfica o biológicamente con ninguno de los terrenos o cratones cercanos (Howell, 1989; H. Bahlburg, comunicación escrita, Abril 2009). Un terreno 'autóctono' es aquel que no se ha movido desde su lugar de origen, con respecto al cratón adjunto, mientras que un terreno 'para-autóctono' implica desplazamientos
relativamente pequeños de éste, siempre dentro del dominio del continente (cratón) dentro del cual el fragmento cortical fue formado (Howell, 1989).

En cuanto al tamaño de los terrenos, es difícil definir límites que no sean arbitrarios, aunque estudios recientes (*e.g.*, Chang *et al.*, 2001) sugerirían que no existe un límite inferior en el tamaño de un terreno. Terrenos compuestos pueden ser muy grandes, y aunque no deberían ser más grandes que un continente, tampoco hay un límite superior arbitrario para su tamaño.

#### Procesos de terrenos (tomado de Howell et al., 1985; Howell, 1989; Vaughan et al., 2005)

Dos de los procesos claves en la formación de terrenos son la acreción y la dispersión. Acreción (o 'docking', según Twiss y Moore, 1992) es el proceso por el cual un terreno transportado junto a una placa oceánica es adicionado a un margen de subducción. Este proceso involucra colisión entre dos bloques corticales coherentes, y no debe ser confundido con el mecanismo de acreción por subducción (formación de un prisma de acreción) explicado en el subcapítulo anterior. La zona de contacto entre terrenos o entre un terreno y el núcleo de un continente corresponde a una estrecha zona de sutura, a lo largo de la cual se pueden encontrar ofiolitas desmembradas y rocas metamórficas de alta presión, aunque en otros casos, esta zona puede estar representada simplemente por fallas de rumbo, inversas o zonas de mélange tectónico. La formación de cubiertas sedimentarias y/o volcánicas discordantes sobre las zonas de sutura y el emplazamiento de complejos ígneos que 'cosen' las suturas ponen límites temporales a la acreción. La dispersión es el proceso por el cual fragmentos litosféricos se separan y son redistribuidos en la superficie terrestre a consecuencia de fenómenos de rifting y formación de nueva corteza oceánica, o bien debido a movimientos de gran magnitud a lo largo de fallas mayores. Un tercer proceso clave es la *amalgamación*, por el cual terrenos de distinto origen pueden combinarse formando un collage de terrenos o un terreno compuesto. Los más grandes de éstos, los súper-terrenos, pasan finalmente a formar parte de la corteza continental estable.

En el caso del TMD, este se ajusta a las definiciones de terreno de Coney *et al.* (1980) y Howell *et al.* (1985) por ser un conjunto de rocas con una historia geológica que lo hace claramente diferente a su entorno. La característica de la definición de Howell *et al.* (1985) que no se cumple completamente en el TMD, es que sus límites sean fallas de extensión regional. No obstante, esto podría deberse a que el Batolito Sur-Patagónico posiblemente utilizó la(s) estructura(s) que

limita(n) al TMD para emplazarse, o que estas estructuras no hayan sido reconocidas aún debido a la gruesa cubierta sedimentaria mesozoica en el área. Como ya se mencionó anteriormente, la ausencia en la Patagonia austral de un arco magmático Pérmico (Triásico) vinculado a la subducción responsable de la construcción del prisma de acreción del TMD, sugiere que la generación de este prisma ocurrió en un segmento distinto del margen paleo-Pacífico de Gondwana (*e.g.*, Hervé *et al.*, 2006). Los modelos propuestos hasta ahora para la localización del lugar de acreción de las unidades 'oceánicas' del TMD (*e.g.*, Lacassie, 2003; Lacassie *et al.*, 2006), involucran un extenso transporte de este bloque (700 km como mínimo, ver fig. 5) a lo largo del margen paleo-Pacífico de Gondwana, hasta alcanzar su posición actual. En este sentido, el TMD representaría un terreno alóctono y exótico, ya que las distancias deducidas son grandes, y la paleogeografía inferida para las unidades de este conjunto no coincide con la del cratón adyacente.

### 1.4.3 Pseudosecciones P-T

La determinación de condiciones de presión (P) y temperatura (T) para asociaciones minerales en equilibrio mediante el uso de programas computacionales, ha tenido un auge en los últimos veinte años gracias al incremento en la capacidad de procesamiento computacional y a la creación de bases termodinámicas exhaustivas y consistentes (e.g., Holland y Powell, 1985; Berman, 1988). Una manera para efectuar tales cálculos es a través de pseudosecciones, las que corresponden a secciones de diagramas de fases para la composición química específica de una roca, donde es posible visualizar las relaciones existentes entre complejas asociaciones minerales. Más en detalle, estas secciones son proyecciones en el campo P-T que se componen de diversos campos de fases caracterizados por una asociación mineral particular, donde dentro de cada uno de estos campos la composición química y las propiedades físicas de las fases estables puede variar continuamente, pero están inequívocamente determinadas en cada punto P-T (Connolly, 2005). Actualmente, existen diversos programas para calcular pseudosecciones, y si bien éstos difieren en el método de cálculo, la validez de las datos obtenidos dependen de los mismos factores: calidad de las bases de datos termodinámicos, seguridad de que la composición química elegida represente una composición en equilibrio de la roca (composición efectiva), y confiabilidad de las suposiciones de equilibrio termodinámico (Stüwe, 1997; de Capitani y Petrakakis, 2010). Por otra parte, la experiencia actual con la aplicación de cálculos computacionales para el desarrollo de diagramas de asociaciones minerales en equilibrio muestra que la mayor fuente de problemas y dificultades tiene que ver con las suposiciones de equilibrio y la composición química efectiva de la roca, por sobre la elección de la base de datos termodinámicos a ocupar (de Capitani y Petrakakis, 2010).

En esta tesis se utilizó el conjunto de programas computacionales conocido como PERPLE\_X (Connolly, 1990; Connolly, 2005). El método computacional usado por este programa emplea la minimización de la energía libre para proyectar (mapear) relaciones entre fases como función de las variables de interés. Según Connolly (2005), la estrategia del programa puede dividirse en dos componentes: la técnica de minimización y la táctica de mapeo:

- La minimización radica en encontrar las cantidades y composiciones de las fases que minimizan la energía libre de Gibbs de un sistema a presión y temperatura constante. La energía de Gibbs para una fase en solución es una función no-lineal de su composición, y por consiguiente, la solución exacta de los problemas de equilibrio de fase es complicada debido a la necesidad de refinar tanto las identidades como las composiciones de las fases estables por medio de iteración. Para sortear tales complicaciones, las variaciones composicionales de una solución pueden ser representadas por una serie de compuestos (pseudocompuestos), definidos de manera tal que cada compuesto tenga las propiedades termodinámicas de la solución a una composición específica.
- La estrategia de mapeo de relaciones de fases involucra el muestreo inicial del espacio de coordenadas de interés en una cuadrícula rectilínea. El mapeo se realiza por aplicación iterativa de una minimización de la energía libre de Gibbs. Una técnica de minimización efectiva provee la base para que las relaciones de fases y propiedades del equilibrio del sistema puedan ser mapeadas mediante diagramas de fases de un sistema termodinámico. Una consecuencia de la aproximación por pseudocompuestos es que la variación composicional continua de las fases individuales se vuelve discreta, por lo que los campos de un diagrama de fases se descomponen en una malla poligonal continua de campos pseudovariantes, cada uno de los cuales está definido por una asociación de pseudocompuestos única. Las ventajas de la estrategia de mapeo son que permite la elección de variables a proyectar, y que la resolución del mapeo es controlada por el usuario. Entonces, una proyección de baja resolución puede ser obtenida rápidamente y es

útil para muchas aplicaciones geodinámicas, así como una herramienta para la exploración de relaciones de fase petrológicas. Posteriormente, las proyecciones de baja resolución pueden ser refinadas al nivel de precisión requerido por aplicaciones específicas.

Actualmente se carecen de datos termodinámicos consistentes y compatibles entre sí para fases minerales formadas en condiciones metamórficas de muy bajo a bajo grado (*e.g.*, pumpellyita). Por lo anterior, para poder trabajar de forma adecuada con PERPLE\_X se modificó la base termodinámica de Holland y Powell (1998, actualizada 2002) adicionándole nuevos miembros extremos y modelos de actividades del trabajo de Massonne y Willner (2008). Aunque algunos de los datos termodinámicos de esta última publicación presentan un carácter preliminar, estos fueron especialmente diseñados para fases minerales típicamente formadas en condiciones metamórficas de muy bajo a bajo grado. Además, su utilización entrega resultados coherentes con otras relaciones entre fases minerales en esas condiciones metamórficas (Liou *et al.*, 1985; Evans, 1990; Frey *et al.*, 1991).

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## <u>CAPÍTULO 2</u>: PETROLOGICAL AND GEOCHEMICAL CHARACTERISTICS OF METAMORPHIC AND IGNEOUS UNITS FROM THE ALLOCHTHONOUS MADRE DE DIOS TERRANE, SOUTHERN CHILE

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#### RESUMEN

Características petrológicas y geoquímicas de unidades ígneas y metamórficas del Terreno alóctono Madre de Dios, Chile Austral. El Complejo Denaro, parte del Terreno Madre de Dios, está compuesto por basaltos almohadillados metamorfizados, metahialoclastitas, metacherts bandeados radiolaríticos y metalíferos, metapelitas y metaareniscas calcáreas redepositadas. Las rocas basálticas muestran texturas, minerales y estructuras primarias. Estas rocas se presentan foliadas especialmente en las cercanías de fallas inversas, las que han sido interpretadas como desarrolladas durante la acreción del terreno al margen de Gondwana. Las composiciones de cristales relictos de augita y cromita primarios se proyectan en el campo MORB de los diagramas discriminantes tectónicos. Lo mismo ocurre con los análisis de geoquímica de roca total, los que indican que estas rocas son similares a rocas volcánicas eruptadas a lo largo de un margen de placa constructivo (MORB tipo normal (N) y enriquecido (E)), probablemente en una dorsal o plateau oceánico centrado en un eje de expansión oceánica. La asociación metamórfica, característica de facies pumpellyita-actinolita, pone en evidencia metamorfismo en condiciones de elevada presión y baja temperatura desarrollado en una cuña acrecionaria. Estas características están probablemente relacionadas al evento Chónico del Triásico tardío-Jurásico temprano, el que ha sido reconocido en otros lugares de los Andes Patagónicos.

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# Petrological and geochemical characteristics of metamorphic and igneous units from the allochthonous Madre de Dios Terrane, Southern Chile

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#### Abstract

The Denaro Complex, part of the Madre de Dios Terrane is composed of metamorphosed pillow basalts, metahyaloclastites, banded metalliferous and radiolarian metacherts, metapelites and redeposited calcareous metasandstones. The basaltic rocks show primary textures, minerals and structures. They are foliated especially in the vicinities of thrust faults, interpreted to have developed during the accretion of the terrane to the Gondwana margin. Composition of relic primary augite and chromite crystals plots into the MORB field of tectonic discriminant diagrams, as do the analyses of whole rock geochemistry, which indicates that these rocks are akin to volcanic rocks erupted along a constructive plate margin (N- and E-type MORBs), probably in a spreading axis-centered oceanic plateau or ridge. The metamorphic assemblages of pumpellyite–actinolite facies bear witness of metamorphism in a frontal accretionary wedge at elevated *P* and low *T* conditions, probably related to the Late Triassic–Early Jurassic Chonide event, which has been recognized elsewhere in the Patagonian Andes. © 2007 International Association for Gondwana Research. Published by Elsevier B.V. All rights reserved.

Keywords: Metamorphism; Terrane accretion; Pumpellyite-actinolite facies; Seamount subduction; Frontal accretion

#### 1. Introduction

#### 1.1. Geological background

The basement of the Patagonian Andes is composed of an assemblage of accretionary complexes forming the palaeo-Pacific margin of Gondwana, mainly of pre-Early Jurassic age, but with different structural and metamorphic histories (Forsythe, 1982; Thomson and Hervé, 2002). However, this hypothesis has been difficult to demonstrate because the complexes were disrupted and separated by the intrusion of the Late Jurassic to Cenozoic Patagonian Batholith (Bruce et al., 1991; Pankhurst et al., 1999).

(50°-50°50'S), referred to by Hervé and Mpodozis (2005) as Madre de Dios Terrane (MDT), are an important portion of the western belt of outcrops of the Patagonian basement and consist of fragments of the accretionary complex built on the western margin of Gondwana during the Late Palaeozoic-Early Mesozoic (Fig. 1). The stratigraphical, geochemical and structural features of the units which comprise this macromelange were studied in detail by Forsythe and Mpodozis (1979, 1983) who distinguished: the Denaro Complex (DC) formed by fragments of ocean floor and its sedimentary cover (Late Carboniferous-Early Permian, see Ling et al., 1985), the Tarlton Limestone (TL) formed by massive marine limestone with an age between Middle Pennsylvanian and Early Permian (Ceccioni, 1956; Douglass and Nestell, 1976), and the Duque de York Complex (DYC), formed by a succession of pelite, greywacke and conglomerate of continental provenance, and deposited uncomformably on top of DC and TL when these units approached the Gondwana continental margin. U-Pb

The rocks which crop out at the Madre de Dios archipelago

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Fig. 1. Geological map of the studied area [modified from Forsythe and Mpodozis (1983) and Lacassie (2003)]. 1: Quaternary deposits. 2: South Patagonian Batholith (SPB). 3: Tarlton Limestone (TL). 4: Denaro Complex (DC). 5: Duque de York Complex (DYC). 6: Unmapped basement. 7: Sill.

SHRIMP detrital zircon ages from sandstones of the DYC reveal that the most abundant youngest population is late Early Permian (ca. 270 Ma) (Hervé et al., 2003). Zircon fission

track data have allowed Thomson and Hervé (2002) to infer that metamorphism that affects the DYC, and probably also the underlying TL and DC, took place during or before the

| Table 1                     |                           |                        |           |
|-----------------------------|---------------------------|------------------------|-----------|
| Geochemical whole rock data | for samples of the Denaro | Complex and cross-cutt | ing dykes |

|                                | 1                | 4                | 5                | 7                | 9                | 14               | 18      | 19      | 26            | 35                        | 36               | 04_3             | 04_4             | 04_5              | 05_13 | 05_18                  | 05_21 | 05_9  | 98_03J                    |
|--------------------------------|------------------|------------------|------------------|------------------|------------------|------------------|---------|---------|---------------|---------------------------|------------------|------------------|------------------|-------------------|-------|------------------------|-------|-------|---------------------------|
|                                | ICP-             | ICP-             | ICP-             | ICP-             | ICP-             | ICP-             | ICP-AES | ICP-AES | ICP-AES       | ICP-AES                   | ICP-AES          | XRF              | XRF              | XRF               | XRF   | XRF                    | XRF   | XRF   | XRF                       |
|                                | AES              | AES              | AES              | AES              | AES              | AES              |         |         |               |                           |                  |                  |                  |                   |       |                        |       |       |                           |
|                                | Pillow<br>basalt | Pillow<br>basalt | Pillow<br>basalt | Pillow<br>basalt | Pillow<br>basalt | Pillow<br>basalt | Basalt  | Dyke    | Hyaloclastite | Foliated<br>pillow basalt | Pillow<br>basalt | Pillow<br>basalt | Pillow<br>basalt | Pillow<br>breccia | Dyke  | Amigdaloidal<br>basalt | Dyke  | Dyke  | Foliated<br>hyaloclastite |
| $SiO_2$                        | 44.50            | 50.35            | 47.24            | 47.25            | 50.67            | 50.50            | 45.06   | 50.64   | 46.20         | 49.10                     | 50.50            | 43.00            | 49.87            | 49.90             | 51.79 | 41.09                  | 50.37 | 48.03 | 46.60                     |
| TiO <sub>2</sub>               | 1.67             | 1.85             | 0.96             | 1.14             | 2.19             | 1.08             | 1.28    | 1.86    | 0.41          | 1.15                      | 1.10             | 0.75             | 1.08             | 1.01              | 1.72  | 1.25                   | 1.98  | 2.29  | 0.62                      |
| $Al_2O_3$                      | 16.24            | 13.72            | 14.40            | 14.68            | 13.41            | 12.82            | 15.31   | 14.69   | 22.44         | 14.44                     | 13.35            | 13.16            | 11.16            | 9.85              | 12.45 | 15.33                  | 13.72 | 10.16 | 13.87                     |
| Fe <sub>2</sub> O <sub>3</sub> | 3.86             | 1.68             | 3.30             | 2.03             | 2.55             | 2.89             | 6.13    | 3.90    | 2.87          | 1.56                      | 3.34             |                  |                  |                   |       |                        |       |       |                           |
| FeO                            | 11.40            | 10.12            | 6.80             | 8.72             | 9.64             | 8.00             | 4.00    | 8.80    | 2.84          | 9.64                      | 6.48             | 12.25            | 13.27            | 13.94             | 14.33 | 9.74                   | 12.65 | 14.18 | 9.78                      |
| MnO                            | 0.20             | 0.14             | 0.16             | 0.16             | 0.14             | 0.16             | 0.11    | 0.26    | 0.08          | 0.13                      | 0.19             | 0.15             | 0.18             | 0.20              | 0.22  | 0.13                   | 0.21  | 0.11  | 0.15                      |
| MgO                            | 7.52             | 6.79             | 8.13             | 10.22            | 7.32             | 8.12             | 8.01    | 4.07    | 5.64          | 8.70                      | 9.78             | 14.85            | 11.74            | 11.17             | 5.51  | 24.15                  | 3.71  | 9.16  | 16.99                     |
| CaO                            | 5.38             | 4.52             | 12.32            | 6.45             | 6.33             | 10.50            | 7.38    | 3.09    | 8.37          | 8.19                      | 8.11             | 8.73             | 6.77             | 8.82              | 6.85  | 6.98                   | 7.28  | 6.32  | 6.12                      |
| Na <sub>2</sub> O              | 2.70             | 3.25             | 2.75             | 3.40             | 2.95             | 2.38             | 2.66    | 4.52    | 2.35          | 2.98                      | 1.82             | 1.68             | 2.38             | 2.40              | 3.55  | 0.76                   | 3.29  | 2.18  | 3.22                      |
| $K_2O$                         | 0.35             | 0.35             | 0.09             | 0.37             | 0.32             | 0.60             | 1.54    | 2.09    | 3.48          | 0.25                      | 0.17             | 1.18             | 0.87             | 0.19              | 0.86  | 0.29                   | 1.12  | 0.46  | 0.86                      |
| $P_2O_5$                       | 0.14             | 0.23             | 0.10             | 0.10             | 0.23             | 0.10             | 0.18    | 0.35    | 0.05          | 0.11                      | 0.10             | 0.09             | 0.09             | 0.08              | 0.36  | 0.15                   | 0.42  | 0.27  | 0.09                      |
| LOI                            | 5.94             | 6.78             | 3.84             | 5.31             | 4.43             | 3.38             | 8.77    | 4.77    | 5.21          | 4.33                      | 5.30             |                  |                  |                   |       |                        |       |       |                           |
| Total                          | 99.90            | 99.78            | 100.09           | 99.83            | 100.18           | 100.53           | 100.43  | 99.04   | 99.94         | 100.58                    | 100.24           | 96.09            | 97.56            | 97.68             | 97.79 | 99.87                  | 94.75 | 93.31 | 98.28                     |
| La                             | 3.50             | 3.50             | 2.00             | 1.00             | 14.00            | 1.00             | 8.00    | 14.00   | 1.00          | 1.00                      | 1.00             |                  |                  |                   |       |                        |       |       |                           |
| Ce                             | 14.00            | 15.00            | 7.00             | 6.00             | 18.00            | 6.00             | 21.00   | 36.00   | 4.00          | 5.00                      | 6.00             |                  |                  |                   |       |                        |       |       |                           |
| Nd                             | 12.00            | 12.00            | 7.00             | 7.00             | 14.00            | 7.00             | 15.00   | 24.00   | 4.00          | 7.00                      | 6.00             |                  |                  |                   |       |                        |       |       |                           |
| Sm                             | 3.47             | 3.25             | 1.89             | 2.02             | 4.59             | 2.00             | 3.74    | 5.97    | 0.88          | 2.20                      | 1.98             |                  |                  |                   |       |                        |       |       |                           |
| Eu                             | 1.29             | 1.24             | 0.78             | 0.79             | 1.37             | 0.73             | 1.21    | 1.83    | 0.15          | 0.74                      | 0.76             |                  |                  |                   |       |                        |       |       |                           |
| Gd                             | 4.54             | 4.62             | 2.79             | 3.35             | 6.51             | 3.05             | 4.60    | 6.61    | 1.16          | 3.27                      | 2.79             |                  |                  |                   |       |                        |       |       |                           |
| Dy                             | 5.70             | 5.65             | 3.51             | 3.97             | 7.27             | 3.70             | 5.31    | 5.94    | 1.20          | 3.63                      | 3.36             |                  |                  |                   |       |                        |       |       |                           |
| Но                             | 1.25             | 1.20             | 0.79             | 0.80             | 1.44             | 0.80             | 1.06    | 1.18    | 0.26          | 0.78                      | 0.68             |                  |                  |                   |       |                        |       |       |                           |
| Er                             | 3.50             | 3.00             | 2.10             | 2.33             | 4.90             | 2.33             | 3.17    | 3.31    | 0.79          | 2.20                      | 1.97             |                  |                  |                   |       |                        |       |       |                           |
| Yb                             | 3.66             | 2.90             | 2.11             | 2.45             | 4.27             | 2.33             | 312.00  | 3.26    | 0.90          | 2.25                      | 1.92             |                  |                  |                   |       |                        |       |       |                           |
| Lu                             | 0.56             | 0.44             | 0.33             | 0.35             | 0.71             | 0.35             | 0.50    | 0.54    | 0.14          | 0.35                      | 0.32             |                  |                  |                   |       |                        |       |       |                           |
| Y                              | 31               | 30               | 21               | 22               | 38               | 22               | 27      | 32      | 8             | 23                        | 18               | 18.2             | 23               | 18.1              | 24.3  | 20.4                   | 29.3  | 25.2  | 15.3                      |
| Sc                             | 52               | 48               | 45               | 52               | 48               | 51               | 41      | 36      | 31            | 49                        | 46               |                  |                  |                   |       |                        |       |       |                           |
| Hf                             | 2.51             | 3.4              | 1.5              | 2.4              | 3.9              | 1.8              | 1.7     | 3.6     | 1             | 1.7                       | 1.7              |                  |                  |                   |       |                        |       |       |                           |
| Th                             | 1                | 1                | 1                | 1                | 2                | 1                | 1       | 2       | 1             | 1                         | 1                |                  |                  |                   |       | 140                    | 0.6   | ~ -   |                           |
| Nb                             | 11               | 12               | 6                | 7                | 12               | 7                | 20      | 12      | 5             | 12                        | 6                | 3.2              | 4.9              | 2.4               | 7.6   | 16.9                   | 8.6   | 9.5   | 8.5                       |
| Zn                             | 108              | 124              | 90               | 76               | 106              | 92               | /4      | 110     | 45            | 87                        | 71               | 94.4             | 106.5            | 106.3             | 99.9  | 125.1                  | 116.9 | 151   | 100.3                     |
| Со                             | 50               | 50               | 38               | 40               | 48               | 38               | 31      | 33      | 18            | 34                        | 26               | 51.1             | 57.4             | 56.2              | 50.3  | 55                     | 48.2  | 46    | 54.2                      |
| N1                             | 54               | 48               | 95               | 70               | 43               | 63               | /9      | 16      | 53            | 52                        | /0               | 149.2            | 95.1             | 82.7              | 14    | 226.8                  | 16.9  | 10.9  | 281.3                     |
| Ba                             | 400              | 1970             | 103              | 210              | 185              | 312              | 100     | 10700   | 162           | 159                       | 137              | 845.5            | 574.8            | 107.2             | 246.7 | 77.6                   | 340.2 | 245.9 | 41.6                      |
| Cr                             | 19               | 112              | 293              | 258              | 58               | 126              | 249     | 20      | 226           | 77                        | 215              | 554.2            | 225.5            | 210               | 101.4 | 618.5                  | 99.3  | 74.1  | 1103.3                    |
| V                              | 440              | 400              | 274              | 290              | 400              | 315              | 227     | 351     | 141           | 290                       | 271              | 220.1            | 321.9            | 295               | 414.4 | 281.3                  | 351.8 | 482.3 | 202.5                     |
| Cu                             | 248              | 159              | 167              | 141              | 150              | 137              | 35      | 182     | 22            | 138                       | 128              | 89.8             | 153.6            | 198.4             | 175.8 | 102.3                  | 187   | 233.4 | 223.6                     |
| Kb                             | 2.46             | 1.60             | 226              | 115              | 226              | 225              |         | 227     | 400           | 017                       | 100              | 29               | 33.5             | 5.5               | 17.6  | 4.6                    | 33    | 12.7  | 12.1                      |
| Sr                             | 340              | 160              | 320              | 115              | 320              | 235              | 74      | 337     | 400           | 217                       | 108              | 446.5            | 81.2             | 232.9             | 322.7 | 487                    | 339.5 | 300.5 | 198.8                     |
| Zr                             | 71               | 95               | 45               | 54               | 120              | 50               | 76      | 133     | 26            | 55                        | 49               | 70.1             | 45.8             | 48.8              | 110.3 | 99.4                   | 128.9 | 124   | 39.4                      |



Fig. 2. Stratigraphic columns of the Denaro Complex from Isla Denaro and site IBGT (island between Guarello and Tarlton) (after Forsythe and Mpodozis, 1983). 1) pillow basalts; 2) hyaloclastites; 3) metalliferous cherts; 4) banded cherts; 5) siliceous shales and calcarenites; 6) reworked limestones; 7) limestones (TL); 8) metalliferous sediments.



earliest Jurassic, prior to the emplacement of the South Patagonian Batholith (SPB) in the Early Cretaceous in this area, which has isotopic ages closest to the contact with the MDT of 133–112 Ma (Rb–Sr whole rock and biotite isochron, Halpern, 1973), 130–143 Ma (K–Ar biotite, Duhart et al., 2003) and ca. 133 Ma (U–Pb SHRIMP zircon, Hervé et al., 2007a).

On the other hand, Forsythe and Mpodozis (1983) concluded that the DC is composed of fragments of oceanic floor that migrated from an active ridge and was progressively covered by silicic planktonic detritus (banded cherts). Hervé et al. (1999a) considered that the metabasalts of this complex correspond to E-MORB basalts coming from a mid-ocean ridge or an oceanic plateau. These interpretations point towards the idea that the DC basalts would have been affected by ocean floor metamorphism prior to their accretion. Sepúlveda (2004), however, concluded that the metamorphic mineral paragenesis was formed under a P-T regime typical of a subduction zone environment (accretionary prism), which implies that

Fig. 3. Microphotographs of selected samples. a) Back scattered electrons image of relic chromite crystals in metahyaloclastite sample. White horizontal line represents 50  $\mu$ m. b) Plane polarized view of the characteristic textures of dykes. White horizontal line represents 1 mm.

this process probably erased any early evidence of a seafloor metamorphism. The conditions of the metamorphism developed in the accretionary wedge may have been further modified by contact metamorphism produced by the intrusion of the SPB.

#### 1.2. Palaeogeographic setting

Current palaeogeographic reconstructions for the Late Carboniferous–Early Permian place the portion of the Gondwana margin where the Madre de Dios archipelago is presently

Table 2

Representative relic mineral analyses (chromite stoichiometry calculated using the procedure of Barnes and Roeder (2001), using the correction of C-J De Hoog)

|                                | Chromite  | 1      |        |        |        |        |        |       |          |        |         |         |
|--------------------------------|-----------|--------|--------|--------|--------|--------|--------|-------|----------|--------|---------|---------|
|                                | Rim       | Rim    | Core   | Rim    | Core   | Rim    | R      | im    | Core     | Rim    | Rim     | Rim     |
|                                | 983_1     | 983_58 | 983_59 | 983_69 | 983_70 | 983_71 | 9      | 84_57 | 984_58   | 984_59 | 984_116 | 984_117 |
| SiO <sub>2</sub>               | 0.04      | 0.10   | 0.12   | 0.10   | 0.05   | 0.11   |        | 0.12  | 0.10     | 0.09   | 0.13    | 0.11    |
| TiO <sub>2</sub>               | 0.22      | 0.22   | 0.21   | 0.26   | 0.22   | 0.43   |        | 0.18  | 0.15     | 0.19   | 0.11    | 0.17    |
| $Al_2O_3$                      | 20.99     | 20.87  | 21.23  | 22.51  | 22.84  | 22.57  |        | 20.44 | 20.19    | 20.56  | 20.72   | 21.13   |
| Cr <sub>2</sub> O <sub>3</sub> | 46.54     | 46.70  | 46.66  | 42.38  | 43.58  | 41.36  | 4      | 47.42 | 47.91    | 47.63  | 48.24   | 47.52   |
| Fe <sub>2</sub> O <sub>3</sub> | 4.12      | 4.40   | 3.97   | 5.67   | 4.44   | 6.08   |        | 4.17  | 4.21     | 3.93   | 2.98    | 3.15    |
| FeO                            | 14.26     | 14.36  | 13.91  | 16.54  | 17.08  | 16.72  |        | 13.67 | 13.56    | 13.79  | 13.15   | 13.75   |
| MnO                            | 0.27      | 0.29   | 0.30   | 0.27   | 0.23   | 0.24   |        | 0.18  | 0.31     | 0.25   | 0.31    | 0.25    |
| MgO                            | 13.74     | 13.71  | 13.98  | 12.35  | 12.17  | 12.31  |        | 14.07 | 14.09    | 14.01  | 14.22   | 14.00   |
| CaO                            | 0.01      | 0.03   | 0.00   | 0.10   | 0.04   | 0.13   |        | 0.03  | 0.02     | 0.00   | 0.01    | 0.02    |
| Na <sub>2</sub> O              | 0.01      | 0.01   | 0.00   | 0.01   | 0.03   | 0.02   |        | 0.00  | 0.00     | 0.02   | 0.00    | 0.01    |
| $K_2O$                         | 0.00      | 0.03   | 0.00   | 0.03   | 0.02   | 0.01   |        | 0.00  | 0.01     | 0.00   | 0.01    | 0.01    |
| Total                          | 99.79     | 100.27 | 99.98  | 100.22 | 100.27 | 99.97  | 10     | 00.27 | 100.54   | 100.48 | 99.87   | 100.12  |
| Si                             | 0.001     | 0.003  | 0.004  | 0.003  | 0.002  | 0.003  |        | 0.004 | 0.003    | 0.003  | 0.004   | 0.003   |
| Ti                             | 0.005     | 0.005  | 0.005  | 0.006  | 0.005  | 0.010  |        | 0.004 | 0.004    | 0.004  | 0.003   | 0.004   |
| Al                             | 0.762     | 0.755  | 0.768  | 0.820  | 0.828  | 0.825  |        | 0.741 | 0.732    | 0.744  | 0.752   | 0.765   |
| Cr                             | 1.133     | 1.133  | 1.131  | 1.036  | 1.059  | 1.013  |        | 1.154 | 1.164    | 1.156  | 1.174   | 1.154   |
| Fe <sup>3+</sup>               | 0.095     | 0.102  | 0.092  | 0.132  | 0.103  | 0.142  |        | 0.097 | 0.097    | 0.091  | 0.069   | 0.073   |
| Fe <sup>2+</sup>               | 0.367     | 0.369  | 0.357  | 0.428  | 0.439  | 0.434  |        | 0.352 | 0.349    | 0.354  | 0.338   | 0.353   |
| Mn                             | 0.007     | 0.007  | 0.008  | 0.007  | 0.006  | 0.006  |        | 0.005 | 0.008    | 0.006  | 0.008   | 0.006   |
| Mg                             | 0.630     | 0.627  | 0.639  | 0.569  | 0.558  | 0.569  |        | 0.645 | 0.645    | 0.641  | 0.652   | 0.641   |
| Total                          | 3.000     | 3.001  | 3.002  | 3.001  | 2.999  | 3.002  |        | 3.001 | 3.001    | 3.000  | 3.000   | 3.000   |
| #Fe <sup>3+</sup>              | 0.048     | 0.051  | 0.046  | 0.066  | 0.052  | 0.072  |        | 0.048 | 0.049    | 0.046  | 0.035   | 0.037   |
|                                | Clinopyrc | oxene  |        |        |        |        |        |       |          |        |         |         |
|                                | 983_12    | 983_14 | 983_15 | 983_21 | 983_23 | 983_44 | 983_47 | 983_5 | 1 983_56 | 983_62 | 983_67  | 983_96  |
| $SiO_2$                        | 49.96     | 51.76  | 50.70  | 51.01  | 50.55  | 51.56  | 51.33  | 52.41 | 50.98    | 51.71  | 51.31   | 51.28   |
| TiO <sub>2</sub>               | 0.59      | 0.46   | 0.55   | 0.52   | 0.53   | 0.59   | 0.24   | 0.19  | 0.31     | 0.26   | 0.22    | 0.37    |
| Al2O <sub>3</sub>              | 2.60      | 2.29   | 3.04   | 3.20   | 3.53   | 2.37   | 3.12   | 1.84  | 3.24     | 2.73   | 2.52    | 3.24    |
| $Cr_2O_3$                      | 0.09      | 0.16   | 0.38   | 0.28   | 0.63   | 0.05   | 1.23   | 0.80  | 1.52     | 1.31   | 1.10    | 0.45    |
| FeO                            | 12.48     | 8.55   | 7.82   | 7.35   | 6.29   | 11.69  | 5.60   | 5.54  | 5.69     | 6.42   | 5.28    | 7.40    |
| MnO                            | 0.37      | 0.24   | 0.15   | 0.18   | 0.17   | 0.30   | 0.16   | 0.15  | 0.18     | 0.21   | 0.17    | 0.18    |
| MgO                            | 15.74     | 17.43  | 16.89  | 17.31  | 16.37  | 15.37  | 17.28  | 18.72 | 16.92    | 17.33  | 17.74   | 18.52   |
| CaO                            | 16.24     | 18.06  | 19.16  | 18.89  | 20.38  | 18.17  | 19.88  | 19.55 | 20.14    | 19.23  | 19.77   | 17.57   |
| Na <sub>2</sub> O              | 0.16      | 0.14   | 0.21   | 0.28   | 0.20   | 0.19   | 0.35   | 0.21  | 0.40     | 0.40   | 0.20    | 0.17    |
| K <sub>2</sub> O               | 0.01      | 0.02   | 0.01   | 0.04   | 0.04   | 0.02   | 0.00   | 0.00  | 0.01     | 0.02   | 0.00    | 0.02    |
| Total                          | 98.24     | 99.08  | 98.90  | 99.06  | 98.70  | 100.30 | 99.17  | 99.40 | 99.38    | 99.61  | 98.31   | 99.20   |
| Si                             | 1.895     | 1.919  | 1.882  | 1.884  | 1.878  | 1.916  | 1.889  | 1.917 | 7 1.876  | 1.899  | 1.902   | 1.884   |
| Ti                             | 0.017     | 0.013  | 0.015  | 0.014  | 0.015  | 0.016  | 0.007  | 0.005 | 5 0.008  | 0.007  | 0.006   | 0.010   |
| Al                             | 0.116     | 0.100  | 0.133  | 0.139  | 0.155  | 0.104  | 0.135  | 0.079 | 0.141    | 0.118  | 0.110   | 0.140   |
| Cr                             | 0.003     | 0.005  | 0.011  | 0.008  | 0.018  | 0.001  | 0.036  | 0.023 | 0.044    | 0.038  | 0.032   | 0.013   |
| Fe <sup>3+</sup>               | 0.070     | 0.042  | 0.078  | 0.077  | 0.059  | 0.044  | 0.063  | 0.068 | 3 0.075  | 0.061  | 0.055   | 0.070   |
| Fe <sup>2+</sup>               | 0.328     | 0.224  | 0.166  | 0.151  | 0.138  | 0.321  | 0.111  | 0.102 | 2 0.101  | 0.137  | 0.109   | 0.158   |
| Mn                             | 0.012     | 0.007  | 0.005  | 0.006  | 0.005  | 0.010  | 0.005  | 0.005 | 5 0.006  | 0.007  | 0.005   | 0.006   |
| Mg                             | 0.890     | 0.963  | 0.934  | 0.953  | 0.906  | 0.851  | 0.947  | 1.021 | 0.928    | 0.948  | 0.980   | 1.014   |
| Ca                             | 0.660     | 0.717  | 0.762  | 0.747  | 0.811  | 0.724  | 0.784  | 0.766 | 6 0.794  | 0.757  | 0.786   | 0.692   |
| Na                             | 0.011     | 0.010  | 0.015  | 0.020  | 0.014  | 0.014  | 0.025  | 0.015 | 5 0.028  | 0.028  | 0.015   | 0.012   |
| Κ                              | 0.001     | 0.001  | 0.001  | 0.002  | 0.002  | 0.001  | 0.000  | 0.000 | 0.000    | 0.001  | 0.000   | 0.001   |
| Total                          | 4.002     | 4.001  | 4.002  | 4.001  | 4.001  | 4.001  | 4.001  | 4.001 | 4.001    | 4.001  | 4.001   | 4.001   |

For details see http://www.em.csiro.au/terrain\_studies/aboutus/people/stephen\_barnes/roeder\_spinels.htm.

<sup>1</sup> Fe<sup>3+</sup> content in chromites was determined by using stoichiometry and an ideal  $XY_2O_4$  formula, where  $X=(Fe^{2+}, Ni, Mn, Co, Zn)$  and  $Y=(Cr^{3+}, Fe^{3+}, Al)$ ; Fe is subdivided into Fe<sup>2+</sup> and Fe<sup>3+</sup> to satisfy the condition  $n_Y=2n_X$  where  $n_Y$  is total atoms of trivalent cations, and  $n_X$  is total divalent cations per unit cell.

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located at a high southern latitude, well outside the tropical zone where the TL is likely to have been deposited (Lacassie, 2003). This fact, together with the contemporaneity of the TL with the ocean floor deposit of the DC (Ling et al., 1985) lead to the conclusion that the MDT represents an allochthonous terrane originated at lower latitudes (around 20°S) and accreted via subduction processes to Gondwana after the Permian (Hervé et al., 2000). Lacassie (2003), following the interpretations of Hada et al. (2001) and Cawood et al. (2002), pointed out that the accretion of the TL and the DC would have occurred against a different sector of the Gondwana margin than the one occupied today, from where it would have been displaced by dextral translation, as a coherent block. The timing of the accretion of these units is bracketed between the age of deposition of the DYC, ca. 270 Ma (the youngest detrital zircon U-Pb SHRIMP age component) and the minimum age of metamorphism, 195 Ma (fission track detrital zircon age).

Palaeomagnetic data on the TL and the DC (Rapalini et al., 2001) indicate that, after Early Cretaceous remagnetization produced by the thermal influence of the SPB, both units underwent a counter-clockwise rotation of ca. 117° with an inappreciable latitudinal change. This evidence allowed Rapalini et al. (2001) to conclude (taking into account the structural studies of Forsythe and Mpodozis, 1979, 1983) that these rock units had been accreted to the Gondwana margin from the NW rather than from the SW as had been previously suggested (Forsythe and Mpodozis, 1983). This interpretation is consistent with the sinistral sense of shear of main structures parallel to the margin of South America, and is also coherent with the migration of the Antarctic Peninsula toward the South. It is, however, contrary to the hypothesis of Lacassie (2003). In addition, it is suggested that the end Triassic deformation in the northern Antarctic Peninsula, which affects the Trinity Peninsula Group accretionary complex, is associated with sinistral shearing, while dextral shearing is mainly a Cretaceous phenomenon in the Antarctic Peninsula (A. Vaughan, October 2006, written communication).

#### 1.3. Aims of this study

The purpose of this paper is to present information bearing on the tectonic setting of formation and metamorphism of the basalts of the DC, based on relic and metamorphic mineral chemistry, respectively. In addition, data on the geochemistry and petrography of dykes which crosscut the MDT constrain its evolution and possible connection with the SPB.

#### 2. Analytical methods

Eleven ICP-AES and eight wavelength-dispersive XRF analyses of metamorphosed pillow basalts and metahyaloclastites from the DC and cross-cutting dykes (Table 1) were performed at the Department of Geology, University of Chile and at the SPECTRAU Laboratory, Department of Geology, University of Johannesburg, South Africa, respectively.

The XRF analyses were carried out on Philips Magix Pro Spectrometer equipment. The major and the trace elements were analysed on lithium borate (Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>– LiBO<sub>2</sub>) fused glass beads and pressed powder pellets, respectively. The accuracy and precision of the data were estimated from repeated analyses of certified reference materials (basaltic rocks BE-N and JB-3). The accuracy was found to be better than  $\pm 5\%$  for SiO<sub>2</sub>, TiO<sub>2</sub>, A1<sub>2</sub>O<sub>3</sub>, CaO, MgO, MnO, K<sub>2</sub>O, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> and for total Fe<sub>2</sub>O<sub>3</sub>;  $\pm 4\%$  for Nb, Zn, Co, Ni, Ba, Cu, Rb, Sr and Zr; and  $\pm 10\%$  for Cr, V and Y. Precision for all major oxides was always better than 0.5%; for trace elements it was better than 3%.

EPMA analyses of two samples of metabasalts of the DC were obtained using a CAMECA SX 100 at Stuttgart Universität, Germany. Operation conditions were an acceleration voltage of 15 kV, a beam current of 15 nA, 20 s counting time per element and a defocused beam of 8  $\mu$ m in order to avoid loss of alkalies in mica and amphibole.

#### 3. Petrography and mineral chemistry

The Denaro Complex is constituted by a succession of unknown thickness of metamorphosed pillow basalts, metahyaloclastites, banded metalliferous and radiolarian metacherts, metapelites and redeposited calcarenites (Fig. 2). The metabasalts and metahyaloclastites have primary pillow structures with porphyritic to subophitic hypidiomorphic textures, frequently with amygdales. They are partly transformed to foliated greenschists in some localities. The samples analysed by EPMA are metabasaltic and hyaloclastitic semi-schists from an outcrop where DC and TL are in contact by a thrust fault. The rocks contain relic igneous clinopyroxene and chromite crystals preserved within a metamorphic mineralogy (Fig. 3a).

The cross-cutting dykes have an unaltered aspect in comparison with the metabasalts that belong to the DC, and display holocristaline, panidiomorphic, intergranular and porphyric textures. The phenocrystals present are pyroxenes and plagioclases in a groundmass composed of plagioclase, pyroxene, chloritised biotite and ilmenite crystals (Fig. 3b).



Fig. 4. Chromite plots.  $\#Fe^{3+}$  vs. TiO<sub>2</sub> (Arai, 1992).  $\#Fe^{3+}$  calculated as  $Fe^{3+}/(Al+Cr+Fe^{3+})$ .

#### 3.1. Tectonic discriminant diagrams

The relic igneous crystals in the analysed metabasalts are clinopyroxenes (augites) and chromites. Representative analy-

ses of relic igneous clinopyroxenes and chromites in metabasalts are shown in Table 2. The chromites plot in the MORB field of the discriminant diagram of Arai (1992) (Fig. 4), and in the ocean floor basalts field in the diagrams of Barnes and



Fig. 5. Chromite plots. a) Trivalent ions plot for tholeiitic basalts, b)  $Fe^{2+}/(Mg+Fe^{2+})$  vs.  $Fe^{3+}/(Al+Cr+Fe^{3+})$ . Heavy and dashed lines enclose the most densely packed 50% and 90% of all the data points taken from Barnes and Roeder (2001).

Roeder (2001) (Fig. 5a, b), while the augites plot in the nonalkaline basalts in the Leterrier et al. (1982) diagrams (Fig. 6a). Moreover, the (Ti+Cr) vs. Ca diagram of the latter authors permit to distinguish that the augites are more akin to those belonging to non-orogenic tholeiites (MORB and other tholeiites from spreading zones) (Fig. 6b).

The average of the DC metabasalts classifies as MORB in the trace element diagrams of Pearce and Norry (1979) and Pearce (1982) (Fig. 7a, b, c), although there is one sample (05– 18) that plots very close to the limit between MORB and intraplate basalt. The same sample shares characteristics of the within-plate tholeiites and within-plate alkali basalts in the diagram of Meschede (1986) (Fig. 7d). Even though MgO values have little meaning in such metamorphosed rocks, this sample is highly enriched in this oxide, and also in Ni and Cr relative to the other samples, and most likely represents a picritic basalt. The diagram of Meschede (1986) also allows the discrimination between the distinct types of ocean floor basalts, and although there is a strong scatter of the data between the N-MORB and E-MORB fields, the average of the DC analyses plot in the E-MORB field (Fig. 7d). It should be noted that there is concordance in the characterization of the schistose metabasaltic hyaloclastites classified as ocean floor basalts using the chemistry of their chromites, which also plot in the E-MORB field of Meschede (1986).



Fig. 6. Discrimination diagrams for clinopyroxenes (augites) phenocrystals in basalts (after Leterrier et al., 1982). Non-orogenic tholeiites includes MORB and other tholeiites from spreading zones (ocean-island tholeiites and back-arc basin tholeiites).

The whole rock analyses show that younger dykes cutting the whole MDT are tholeiitic andesites. On the diagrams of Pearce and Norry (1979) and Pearce (1982) they plot on the intra-plate field and the diagram of Meschede (1986) identify them as within-plate tholeiites or volcanic arc basalts (Fig. 7).

#### 3.2. Metamorphic paragenesis and conditions

The general metamorphic mineral assemblage present in the DC metabasalts is albite-chlorite-epidote-pumpellyite-stilpnomelane-titanite (grothite)-garnet (grandite)-white mica-actinolite-titanomagnetite-quartz. Representative analyses of the metamorphic minerals of the metabasites from the DC are presented in Table 3. Pumpellyite exhibits considerable variations between those replacing the groundmass and those occurring in veinlets: crystals that replace the groundmass have greenish-brown pleocroism and  $X_{Fe}^{3+}$  [Fe<sup>3+</sup>/Fe<sup>3+</sup>+Al<sub>total</sub>] of 10–19%, while those occurring in veinlets have bluish-green pleocroism and  $X_{\text{Fe}}^{3+}$  of 23–50%. Chlorite shows Si contents between 5.8 and 6.2 and XFe  $[Fe^{2+}/Fe^{2+}+Mg]$  of 0.3–0.2. The absence of zeolites and prehnite suggests P and T conditions above 2 kbar and 260 °C (Frey et al., 1991), while the presence of stilpnomelane indicates T below 280 °C at ca. 2.5 kbar and below 330 °C at ca. 5 kbar (Massonne and Szpurka, 1997). The use of chlorite geothermometry (Cathelineau, 1988; Jowett, 1991) on the samples yields an average temperature of 259±11 °C, and the use of the Massonne and Szpurka (1997) geobarometer in white micas with high phengitic contents (Si=3.44-3.69 p.f.u.) indicates minimum pressures of 5 kb (Table 3).

#### 4. Discussion and conclusions

Although the chromites have a more refractory and alteration resistant character than the clinopyroxenes (Barnes and Roeder, 2001) the tectonic discrimination diagrams based on the geochemistry of both relic igneous minerals give comparable results, indicating an environment of eruption of the DC basalts similar to the mid-ocean ridge basalts, in agreement with the whole rock geochemistry that indicates E-MORB characteristics. Interpretation of the whole rock chemical data is complicated by the metamorphic state of the samples, and for this reason only tectonic discrimination diagrams based on immobile trace elements were used, but it is probable that the scatter observed in these diagrams is produced by the fact that the concentrations of the more mobile elements were modified by open-system metamorphism. The results obtained for samples from different outcrops of the DC suggest that these basalts are similar to rocks formed as a bathymetrically elevated feature located at or near to a mid-oceanic spreading axis. An origin as an elevated ridge or plateau was also proposed for rocks with analogous characteristics in the Mino Terrane, Japan (Jones et al., 1993) and is additionally supported by the existence and extension of the coeval thick carbonate cover (TL).

The cross-cutting andesitic dykes have tholeiitic affinities and suggest an intra-continental plate origin. Structural field relationships and the unaltered and undeformed aspect indicate that these rocks were formed after the accretion and



Fig. 7. Selected trace element discrimination diagrams. a) Zr vs. Zr/Y (Pearce and Norry, 1979); b) Zr vs. Ti (Pearce, 1982); c) Nb/Y vs. Ti/Y, showing the subdivision of the within plate basalts (Pearce, 1982); d) Ti–Zr–Y (Meschede, 1986). 1—within plate alkali basalts and within plate tholeites, 2—E-type MORB, 3—within plate tholeites and volcanic arc basalts, 4—N-type MORB and volcanic arc basalts.

metamorphism of the MDT. Duhart et al. (2003) described similar basaltic dykes in the Madre de Dios archipelago that cut both the SPB and the basement units. Apparently, this will suggest that the occurrence of basaltic dykes in the area is linked to the end phases of the intrusive igneous activity of the Patagonian Batholith, as previously indicated by Halpern (1973). Further work on geochemistry and geochronology is needed to reach a more reliable conclusion.

The presence of two different kinds of pumpellyites with markedly contrasting chemistry is best explained as indicative of equilibration of the system at (at least two) different P-T conditions. The stability field of the metamorphic mineral paragenesis and the thermo-barometric determinations indicate that the metamorphism of the DC took place under conditions of the pumpellyite–actinolite facies (Fig. 8), which has been observed to be present in accretionary prisms in Japan (Banno, 1998) and Chile (Hervé et al., 1999b; Willner et al., 2000). The development of this facies reveals that metamorphism took place under geothermal gradients between 10 and 20 °C/km, which might suggests slow subduction or subduction of young, relatively hot oceanic lithosphere (Hervé et al., 2007b). The conditions favourable for the development of this facies may have been generated during frontal accretion (off-scraping) of

these rocks to the Gondwana margin, in a similar way as proposed by Willner et al. (2000) for the eastern belt of the Chonos Metamorphic Complex, which possibly formed during the same Late Triassic–Early Jurassic accretionary period as the DC. This period, known as Chonide event, has been attributed to a global reorganization of plates produced by the impact of mantle superplumes on the lithospheric plates (Vaughan and Livermore, 2005).

To prove the last hypothesis, it is necessary to have precise information on the time of docking of "suspect terranes" of similar lithology and depositional ages to the MDT, as the Le May Group in Alexander Island, Western Domain of the Antarctic Peninsula or the Torlesse Terrain in New Zealand (Lacassie et al., 2006; Hervé et al., 2006), clue areas along the Pacific margin of Gondwana. This will help to the evaluation of recently proposed hypotheses: that the accretionary events along the Gondwana margin are driven by oceanic subduction in a steady state mode, as suggested by Willner et al. (2004) for the Late Palaeozoic accretionary complex of south-central Chile, or that the accretionary events were episodic and related to the impact of superplumes (Vaughan and Livermore, 2005). Another aspect to be considered in future studies is that in spite of the indication by the metamorphic characteristics of the DC

| Table 3   |
|---|
| Representative microprobe analyses of selected metamorphic minerals |

|                     | White | mica <sup>1</sup> |       |       |       |       |                   | Chlorite   | 2          |             |             |             |            |             |             |             |              |                   | Pumpe     | ellyite <sup>3</sup> |             |             |             |             |
|---------------------|-------|-------------------|-------|-------|-------|-------|-------------------|------------|------------|-------------|-------------|-------------|------------|-------------|-------------|-------------|--------------|-------------------|-----------|----------------------|-------------|-------------|-------------|-------------|
|                     | 22    | 43                | 53    | 54    | 68    | 69    |                   | 9803-<br>6 | 9803-<br>8 | 9803-<br>42 | 9803-<br>63 | 9803-<br>80 | 9804-<br>7 | 9804-<br>14 | 9804-<br>26 | 9804-<br>76 | 9804-<br>119 |                   | 84_<br>26 | 9803_<br>3           | 9803_<br>32 | 9803_<br>85 | 9804_<br>12 | 9804_<br>84 |
| SiO <sub>2</sub>    | 53.71 | 53.47             | 55.06 | 53.82 | 53.75 | 54.11 | SiO <sub>2</sub>  | 29.44      | 29.66      | 29.98       | 27.90       | 29.16       | 30.18      | 29.71       | 31.10       | 30.47       | 28.88        | SiO <sub>2</sub>  | 37.75     | 35.88                | 35.17       | 36.32       | 34.91       | 37.20       |
| TiO <sub>2</sub>    | 0.04  | 0.02              | 0.02  | 0.01  | 0.03  | 0.02  | $Al_2O_3$         | 17.80      | 17.07      | 17.62       | 16.05       | 18.44       | 15.82      | 16.66       | 17.35       | 17.02       | 15.67        | TiO <sub>2</sub>  | 0.10      | 0.09                 | 0.01        | 0.03        | 0.12        | 0.04        |
| $Al_2O_3$           | 13.05 | 13.56             | 22.35 | 22.20 | 12.74 | 24.55 | FeO               | 17.30      | 16.98      | 16.71       | 16.78       | 16.43       | 12.71      | 12.45       | 12.03       | 12.16       | 12.35        | $Al_2O_3$         | 24.47     | 22.05                | 13.79       | 22.98       | 14.02       | 23.76       |
| $Cr_2O_3$           | 0.21  | 0.08              | 0.01  | 0.00  | 0.14  | 0.01  | MnO               | 0.19       | 0.20       | 0.19        | 0.23        | 0.17        | 0.19       | 0.24        | 0.20        | 0.20        | 0.20         | FeO*              | 4.13      | 8.38                 | 20.15       | 7.02        | 19.24       | 4.60        |
| FeO                 | 11.86 | 11.11             | 5.77  | 6.75  | 11.66 | 4.45  | MgO               | 22.10      | 22.31      | 22.50       | 20.42       | 22.53       | 25.38      | 24.84       | 25.74       | 26.07       | 24.79        | $Cr_2O_3$         | 0.00      | 0.09                 | 0.00        | 0.06        | 0.11        | 0.02        |
| MnO                 | 0.05  | 0.03              | 0.07  | 0.06  | 0.05  | 0.05  | CaO               | 0.17       | 0.09       | 0.38        | 0.22        | 0.12        | 0.13       | 0.14        | 0.14        | 0.07        | 0.06         | MnO               | 0.12      | 0.05                 | 0.00        | 0.10        | 0.10        | 0.15        |
| MgO                 | 6.11  | 6.29              | 4.35  | 4.03  | 6.39  | 4.05  | Na <sub>2</sub> O | 0.01       | 0.07       | 0.04        | 0.08        | 0.05        | 0.00       | 0.00        | 0.01        | 0.02        | 0.02         | MgO               | 3.11      | 4.29                 | 2.49        | 3.62        | 2.63        | 3.87        |
| CaO                 | 0.08  | 0.03              | 0.00  | 0.03  | 0.03  | 0.02  | $K_2O$            | 0.03       | 0.02       | 0.08        | 0.03        | 0.03        | 0.02       | 0.01        | 0.01        | 0.03        | 0.02         | CaO               | 22.15     | 21.59                | 22.12       | 22.67       | 21.99       | 23.46       |
| Na <sub>2</sub> O   | 0.02  | 0.02              | 0.01  | 0.01  | 0.00  | 0.02  | TiO <sub>2</sub>  | 0.02       | 0.02       | 0.01        | 0.03        | 0.02        | 0.02       | 0.03        | 0.07        | 0.02        | 0.01         | Na <sub>2</sub> O | 0.03      | 0.04                 | 0.02        | 0.03        | 0.02        | 0.04        |
| $K_2O$              | 10.32 | 9.95              | 10.51 | 10.34 | 10.30 | 9.28  | $Cr_2O_3$         | 0.06       | 0.07       | 0.06        | 4.46        | 0.00        | 2.97       | 2.05        | 0.29        | 0.15        | 3.89         | $K_2O$            | 0.58      | 0.00                 | 0.01        | 0.02        | 0.02        | 0.06        |
| Total               | 95.44 | 94.56             | 98.16 | 97.26 | 95.11 | 96.55 | Total             | 87.10      | 86.48      | 87.56       | 86.21       | 86.95       | 87.42      | 86.10       | 86.92       | 86.20       | 85.88        | Total             | 92.44     | 92.44                | 93.75       | 92.83       | 93.14       | 93.20       |
| Si                  | 7.36  | 7.33              | 7.18  | 7.10  | 7.37  | 7.04  | Si                | 5.87       | 6.04       | 5.88        | 5.93        | 5.81        | 6.01       | 5.99        | 6.13        | 6.00        | 6.05         | Si                | 6.07      | 5.86                 | 5.95        | 5.89        | 5.93        | 5.96        |
| $Al_{IV}$           | 0.64  | 0.67              | 0.82  | 0.90  | 0.63  | 0.96  | $Al_{IV}$         | 2.13       | 1.96       | 2.12        | 2.07        | 2.19        | 1.99       | 2.01        | 1.87        | 2.00        | 1.95         | Ti                | 0.01      | 0.01                 | 0.00        | 0.00        | 0.02        | 0.01        |
| Sum <sub>IV</sub>   | 8.00  | 8.00              | 8.00  | 8.00  | 8.00  | 8.00  | Al <sub>VI</sub>  | 2.05       | 2.14       | 1.95        | 1.96        | 2.13        | 1.72       | 1.95        | 2.16        | 1.96        | 1.92         | Al                | 4.64      | 4.24                 | 2.75        | 4.39        | 2.81        | 4.49        |
| $Al_{VI}$           | 1.46  | 1.53              | 2.61  | 2.56  | 1.43  | 2.80  | Fe <sup>2+</sup>  | 2.88       | 2.89       | 2.74        | 2.98        | 2.74        | 2.12       | 2.10        | 1.98        | 2.00        | 2.16         | Fe <sup>3+</sup>  | 0.50      | 1.03                 | 2.56        | 0.85        | 2.46        | 0.55        |
| Ti                  | 0.00  | 0.00              | 0.00  | 0.00  | 0.00  | 0.00  | Mn                | 0.03       | 0.03       | 0.03        | 0.04        | 0.03        | 0.03       | 0.04        | 0.03        | 0.03        | 0.03         | Cr <sup>3</sup>   | 0.00      | 0.01                 | 0.00        | 0.01        | 0.01        | 0.00        |
| Cr                  | 0.02  | 0.01              | 0.00  | 0.00  | 0.02  | 0.00  | Mg                | 6.57       | 6.78       | 6.57        | 6.47        | 6.69        | 7.53       | 7.46        | 7.56        | 7.66        | 7.74         | Mn <sup>2</sup>   | 0.02      | 0.01                 | 0.00        | 0.01        | 0.01        | 0.02        |
| Fe <sup>2+</sup>    | 0.42  | 0.35              | 0.63  | 0.61  | 0.37  | 0.48  | Са                | 0.04       | 0.02       | 0.08        | 0.05        | 0.03        | 0.03       | 0.03        | 0.03        | 0.01        | 0.01         | Mg                | 0.75      | 1.04                 | 0.63        | 0.88        | 0.67        | 0.93        |
| Fe                  | 0.94  | 0.92              | 0.00  | 0.14  | 0.97  | 0.00  | Na                | 0.00       | 0.03       | 0.02        | 0.03        | 0.02        | 0.00       | 0.00        | 0.00        | 0.01        | 0.01         | Ca                | 3.81      | 3.78                 | 4.01        | 3.94        | 4.00        | 4.03        |
| Mn                  | 0.01  | 0.00              | 0.01  | 0.01  | 0.01  | 0.01  | K                 | 0.01       | 0.00       | 0.02        | 0.01        | 0.01        | 0.00       | 0.00        | 0.00        | 0.01        | 0.00         | Na                | 0.01      | 0.01                 | 0.01        | 0.01        | 0.01        | 0.01        |
| Mg                  | 1.25  | 1.29              | 0.85  | 0.79  | 1.31  | 0.79  | Ti                | 0.00       | 0.00       | 0.00        | 0.00        | 0.00        | 0.00       | 0.00        | 0.01        | 0.00        | 0.00         | K T               | 0.12      | 0.00                 | 0.00        | 0.00        | 0.00        | 0.01        |
| Sum <sub>VI</sub>   | 4.10  | 4.10              | 4.10  | 4.10  | 4.10  | 4.08  | Cr<br>4TE (OC)    | 0.01       | 0.01       | 0.01        | 0.75        | 0.00        | 0.47       | 0.33        | 0.04        | 0.02        | 0.64         | Total             | 15.92     | 15.99                | 15.90       | 15.99       | 15.92       | 16.02       |
| Ca<br>N-            | 0.01  | 0.00              | 0.00  | 0.00  | 0.00  | 0.00  | 1 (°C)            | 266        | 253        | 256         | 291         | 278         | 259        | 263         | 239         | 249         | 280          | XFe               | 0.10      | 0.19                 | 0.48        | 0.16        | 0.47        | 0.11        |
| Na                  | 0.00  | 0.01              | 0.00  | 0.00  | 0.00  | 0.00  |                   |            |            |             |             |             |            |             |             |             |              |                   |           |                      |             |             |             |             |
| K.                  | 1.80  | 1.74              | 1.75  | 1.74  | 1.80  | 1.54  |                   |            |            |             |             |             |            |             |             |             |              |                   |           |                      |             |             |             |             |
| Sum <sub>VIII</sub> | 1.82  | 1./5              | 1.75  | 1.75  | 1.81  | 1.55  |                   |            |            |             |             |             |            |             |             |             |              |                   |           |                      |             |             |             |             |
| UH                  | 2.00  | 2.00              | 2.00  | 2.00  | 2.00  | 2.00  |                   |            |            |             |             |             |            |             |             |             |              |                   |           |                      |             |             |             |             |

<sup>1</sup> The amounts of cations are based on 42 valencies neglecting the interlayer cations; the sum of octahedrally coordinated cations is set to 4.1 to allow for an estimation of  $Fe^{3+}$ . <sup>2</sup> The amounts of cations are based on 28 oxygens; all Fe assumed to be  $Fe^{2+}$ . <sup>3</sup> The amounts of cations are based on 24.5 oxygens. FeO\* calculated by assuming FeO\*= (Fe<sub>2</sub>O<sub>3</sub>+1.11\*FeO); Fe<sup>3+</sup> determined by using stoichiometry and an ideal  $W_2XY_2Z_3O_{16.25}$  formula, where W=(Ca, Na, K, Mn); X = (Fe, Mg, Mn, Al, Cr); Y = (Ti, Fe, Al) and Z = (Si, Al).<sup>4</sup> Temperature obtained using the Cathelineau's (1988) geothermometer.



Fig. 8. Estimate of the P-T conditions of metamorphism. The black area is the supposed P-T conditions for the Denaro Complex (DC) (this work), and the dashed area is the P-T range for the eastern belt of Chonos Metamorphic Complex (CMC (E)) (taken from Willner et al. (2000)). The P-T field of ZEO (zeolite facies), PA (pumpellyite–actinolite facies), RA (prehnite–actinolite including prehnite–pumpellyite facies), and univariant reactions (3)–(5) (bold lines) are taken from Banno et al. (2000).

that it was emplaced in a subduction environment, there appears to be no coeval calc-alkaline magmatic arc in the Patagonian Andes or beyond.

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## 2.1 DATOS COMPLEMENTARIOS \*

### 2.1.1 Geoquímica (elementos trazas y tierras raras) de metabasaltos del Complejo Denaro

En esta sección se presentan datos geoquímicos de elementos trazas y tierras raras de once muestras de metabasaltos del CD (tabla 1). Se realizó el análisis de los datos de tierras raras y elementos trazas a través de su proyección en diagramas multi-elementos y *spiders* con el fin de establecer la geoquímica primaria de estas rocas. Elementos litófilos de grandes iones (LILE; Ba, Rb, Sr, K, U y Pb) no fueron considerados representativos de la composición primaria de estas rocas debido a que éstos se muestran sensibles a la alteración y metamorfismo.

La proyección de los datos en diagramas normalizados al manto primordial (Fig. 10) y a condritos (Fig. 11) (Sun & McDonough, 1989) muestra que la mayoría de los análisis (área sombreada) presentan un enriquecimiento en tierras raras livianas (LREE) en relación a las tierras raras pesadas (HREE). En ambos diagramas se destacan en color rojo dos muestras pertenecientes a Isla Denaro y un islote asociado (ver Fig. 1B), cuyos patrones de elementos trazas y tierras raras difieren del resto, y se presentan aproximadamente planos. Por otro lado, el comportamiento anómalo del Ba y el U que se observa en la figura 10 refleja la importante alteración (metamorfismo) que afecta a estas rocas.

Para poder contrastar los datos obtenidos con otros presentes en la literatura, se estudiaron razones entre tierras raras específicas normalizadas a condrito (denotado con el subíndice N). Las LREE tienen entre 10 y 40 veces los valores condríticos, mientras que las HREE poseen entre 6 y 15 veces esos valores. Los metabasaltos de la zona de Isla Denaro presentan razones (La/Yb)<sub>N</sub> entre 1,1 y 1,2, y razones (La/Sm)<sub>N</sub> cercanas a 0,9, indicando un muy leve enriquecimiento en LREE en relación a las HREE, y un muy ligero empobrecimiento de las primeras en comparación con las tierras raras intermedias (MREE). Las razones (La/Yb)<sub>N</sub> de las demás muestras del CD (área sombreada) están entre 2,0 y 4,3, mientras que la razón (La/Sm)<sub>N</sub> de éstas varía entre 1,6 y 3,5, apuntando hacia un enriquecimiento en LREE en relación a las HREE.

<sup>\*</sup> Los datos mostrados en esta sección no estuvieron disponibles al momento de realización de la publicación anterior, por lo que no alcanzaron a ser incorporados en esta.

| Denaro.    |
|------------|
| Complejo   |
| del        |
| asaltos    |
| metab      |
| s de       |
| muestras   |
| de         |
| raras      |
| y tierras  |
| trazas     |
| mentos     |
| ele        |
| s de       |
| Análisi    |
| <b>1</b> . |
| Tabl       |

| _      | MD04_3 ** | MD04_5 ** | MD05_18 ** | MD98-3 ** | MD98-4 | MD-22 | MD05_11 | MD06-3b | MD06-5a | MD06_12 | MD06-13b |
|--------|-----------|-----------|------------|-----------|--------|-------|---------|---------|---------|---------|----------|
| La     | 2,68      | 2,58      | 8,2        | 5,1       | 4      | 4,23  | 4,38    | 3,5     | 6,25    | 6,03    | 4,3      |
| ce     | 7,38      | 7,35      | 20         | 10,2      | 9,45   | 8,18  | 9,25    | 8,8     | 10,6    | 14,1    | 8,5      |
| ΡN     | 6,65      | 6,45      | 13         | 5,85      | 5,93   | 4,78  | 5,73    | 6,2     | 5,73    | 8,1     | 5        |
| Sm     | 1,91      | 1,89      | 3,4        | 1,39      | 1,52   | 1,2   | 1,2     | 1,36    | 1,17    | 2,02    | 1,39     |
| Eu     | 0,63      | 0,7       | 1,1        | 0,48      | 0,52   | 0,4   | 0,4     | 0,43    | 0,44    | 0,68    | 0,46     |
| Gd     | 2,2       | 2,43      | 4,43       | 1,8       | 2      | 1,56  | 1,5     | 1,71    | 1,53    | 2,57    | 1,79     |
| Dy     | 2,68      | с         | 4,09       | 2,1       | 2,48   | 1,87  | 1,78    | 2,11    | 1,72    | 2,83    | 2,16     |
| Чo     | 0,6       | 0,66      | 0,8        | 0,45      | 0,52   | 0,41  | 0,39    | 0,45    | 0,36    | 0,61    | 0,47     |
| Ъ      | 1,61      | 1,72      | 2,12       | 1,3       | 1,47   | 1,15  | 1,1     | 1,29    | 1,08    | 1,7     | 1,35     |
| ۲b     | 1,6       | 1,7       | 2,04       | 1,31      | 1,46   | 1,17  | 1,07    | 1,23    | 1,05    | 1,67    | 1,3      |
| Lu     | 0,25      | 0,26      | 0,31       | 0,2       | 0,23   | 0,18  | 0,16    | 0,19    | 0,16    | 0,25    | 0,2      |
| Ηf     | 1,5       | 1,1       | 1,4        | 1,2       | 1,9    | 0,9   | 0,9     | 0,9     | 1,2     | 1,5     | 0,9      |
| Sc     | 44        | 50        | 44         | 47        | 42     | 32    | 44      | 32      | 30      | 47      | 48       |
| Pb *   | 1,5       | 1,1       | 1,2        | 1,4       | 0,9    | 0,8   | 1,7     | 0,79    | 0,83    | 1,6     | 2,4      |
| *<br>D | 0         | 0         | 0,17       | 0,15      | 0      | 0,25  | 0,64    | 0,21    | 0       | 0       | 0,1      |
| Th *   | 0,38      | 0,3       | 1,1        | 0,63      | 1,5    | 0,92  | 0,71    | 0,47    | 0,44    | 0,74    | 0,71     |
| Ta *   | 0,19      | 0,15      | 0,72       | 0,4       | 0,28   | 0,24  | 0,33    | 0,2     | 0,24    | 0,52    | 0,34     |
| * dN   | 2,9       | 2,3       | 11,9       | 7         | 4,7    | 4,1   | 5,5     | 3,2     | 3,9     | 8,6     | 5,9      |
| Cs *   | 2,5       | 0,24      | 0,59       | 0,85      | 0,69   | 0,77  | 1,35    | 1,71    | 1,35    | 0,36    | 0,9      |
| Ξ      |           |           |            |           | 0,58   | 0,44  | 0,57    | 0,69    | 0,39    | ~       | 0,52     |
| ٩      |           |           |            |           | 0,1    | 0,19  | 0,27    | 0,24    | 0,16    | 0,18    | 0,12     |
| zr     |           |           |            |           | 40     | 30    | 44      | 44      | 40      | 71      | 55       |
| ≻      |           |           |            |           | 15     | 13    | 11      | 12      | 10      | 18      | 14       |
| Sr     |           |           |            |           | 153    | 53    | 44      | 75      | 140     | 107     | 106      |
| Ba     |           |           |            |           | 13     | 39    | 103     | 52      | 64      | 41      | 48       |
| >      |           |           |            |           | 145    | 175   | 207     | 145     | 201     | 243     | 196      |
| ບັ     |           |           |            |           | 1040   | 780   | 335     | 132     | 1070    | 270     | 656      |
| ပိ     |           |           |            |           | 34     | 27    | 28      | 27      | 28      | 35      | 31       |
| ïZ     |           |           |            |           | 237    | 149   | 101     | 63      | 196     | 102     | 183      |
| Cu     |           |           |            |           | 129    | 26    | 31      | 28      | 34      | 174     | 134      |
| Zn     |           |           |            |           | 73     | 60    | 69      | 06      | 56      | 82      | 69       |
|        |           |           |            |           |        |       |         |         |         |         |          |

Análisis (en ppm) realizados por medio de ICP-AES (Perkin–Elmer P-430) en el Departamento de Geología de la Universidad de Chile, salvo los indicados más abajo. Los límites de detección fueron: 1 ppm para Ba, Sr, Zr, Y, Cr, V, Ni, Co, Sc, Cu, Zn, Hf, La, Ce, Nd y Sm; 0,1 ppm para Eu, Gd, Dy, Ho, Er e Yb, y 0,05 ppm para Lu. Ti y P representan TiO2 y P2O5 (wt%).

\* Análisis de ICP-MS (Agilent 7500a) en el Laboratorio Químico del SERNAGEOMIN; límites de detección (ppm): Nb (0,1), Ta (0,01), Cs (0,05), Pb (0,01), U (0,01) y Th (0,01).

\*\* Zr, Y, Ti, P y Ba fueron tomados de la publicación anterior (Sepúlveda et al., 2008).

En la figura 10 se compara la información obtenida en los metabasaltos del CD con datos de basaltos tipo N-MORB promedio (Hofmann, 1988), con basaltos tipo E-MORB promedio (Sun y McDonough, 1989), y con basaltos tipo E-MORB lejos de la influencia de plumas mantélicas (*hotspots*), tanto de corteza oceánica atlántica "normal" (Donnelly *et al.*, 2004), como de montes oceánicos del Pacífico (Niu y Batiza, 1997; Niu *et al.*, 2002). Se aprecia que casi la totalidad de los análisis presentan patrones análogos a los basaltos tipo E-MORB, salvo dos muestras del área de Isla Denaro, las que presentan patrones planos similares a los basaltos tipo N-MORB. Lo anterior es aún más evidente en la figura 11, donde los patrones de tierras raras de estas últimas muestras se diferencian claramente de las demás del CD. En cuanto a las razones de (La/Sm)<sub>N</sub> y (La/Yb)<sub>N</sub>, los valores de casi la totalidad de las muestras del CD están en el rango de los basaltos de tipo E-MORB, mientras que los basaltos asociados a Isla Denaro presentan valores de (La/Sm)<sub>N</sub> semejantes a los de basaltos de tipo N-MORB (*e.g.*, Hofmann, 1988; Walker, 1991). Los valores de (La/Yb)<sub>N</sub> de las últimas muestras se encuentran levemente sobre aquellos registrados para basaltos del tipo N-MORB, pero muy por debajo de los valores para basaltos E-MORB (*e.g.*, Donnelly *et al.*, 2004).



**Figura 10.** Diagrama multi-elementos normalizado al manto primitivo (Sun & McDonough, 1989). En rojo las muestras de metabasaltos del área de Isla Denaro, mientras que el área sombreada corresponde a las demás muestras del CD. Los datos de basaltos N-MORB fueron tomados de Hofmann (1988), mientras que E-MORB1 corresponden a datos tomados de Sun & McDonough (1989), E-MORB2 de Donnelly *et al.* (2004), y E-MORB3 de Niu y Batiza (1997) y Niu *et al.* (2002).



**Figura 11.** Diagrama *spider* normalizado a condritos (Sun & McDonough, 1989). Las fuentes de los datos son las mismas mostradas en la figura anterior.

## 2.1.2 Conclusiones

El análisis de los datos de tierras raras y elementos trazas revela una similitud en la geoquímica primaria de la mayoría de los metabasaltos del CD con la de basaltos del tipo E-MORB. No obstante, algunas de las muestras (Isla Denaro e islotes asociados) exhiben una geoquímica que se asemeja más a la de basaltos del tipo N-MORB. En conclusión, el muestreo regional indica que tanto basaltos toleíticos del tipo E-MORB como N-MORB se encuentran formando parte del CD.

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# <u>CAPÍTULO 3:</u> CONDITIONS AND TIMING OF PUMPELLYITE-ACTINOLITE FACIES METAMORPHISM IN THE EARLY MESOZOIC FRONTAL ACCRETIONARY PRISM OF THE MADRE DE DIOS ARCHIPELAGO (LATITUDE 50°20`S; SOUTHERN CHILE)

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#### RESUMEN

Condiciones y edad del metamorfismo de facies pumpellyita-actinolita en el prisma de acreción frontal Mesozoico temprano del Archipiélago Madre de Dios (50°20' latitud S; Chile Austral). El Complejo Metamórfico Madre de Dios (CMMD) en Chile austral es un prisma de acreción frontal fósil, compuesto principalmente por rocas metapsamopelíticas, intercalaciones de rocas oceánicas (metabasitas y metacherts) y carbonatos de plataforma. Nos concentramos en las metabasitas para descifrar la evolución metamórfica. Este tipo de roca contiene asociaciones de la facies pumpellyita-actinolita: pumpellyita  $\pm$  actinolita-clorita  $\pm$  grandita  $\pm$  fengita  $\pm$  epidota-albita-cuarzo-titanita  $\pm$  K-feldespato  $\pm$  calcita. Las fases metamórficas crecieron esencialmente por reacciones de hidratación prógradas durante varios episodios de flujo restringido de fluidos. Relaciones fundamentales entre fases de la facies pumpellyita-actinolita y facies adyacentes fueron reproducidas por pseudosecciones calculadas para el sistema K<sub>2</sub>O-Na<sub>2</sub>O-CaO-FeO-O<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> a 200-400°C y 1-9 kbar. Los campos de estabilidad calculados para las asociaciones metamórficas presentes en las metabasitas del CMMD indican que las más altas condiciones metamórficas estuvieron restringidas a los 290-310 °C, 4-6 kbar para el CMMD, posiblemente como resultado del principal flujo de fluidos en esas condiciones. Sin embargo, equilibrios locales anteriores al *peak* metamórfico aún se preservan como resultado de

reacciones minerales controladas por cinemática, y por falta de recristalización y homogenización composicional a escala de sección transparente. Por otro lado, cálculos termodinámicos de equilibrios minerales multivariantes locales, usando toda la variación composicional de minerales del CMMD, muestran que el camino *PT* prógrado evolucionó desde  $4 \pm 1$  kbar, 200-220°C a  $5 \pm 1$  kbar, 290-330°C. El camino *PT* prógrado refleja trayectorias casi horizontales después de alcanzar una profundidad máxima, lo que es típico para partículas en prismas de acreción frontales. Una prolongada permanencia a profundidad máxima resultó en reequilibrio termal. Edades <sup>40</sup>Ar/<sup>39</sup>Ar fueron medidas por ablación láser UV *in situ* en concentraciones locales de fengita, obteniendo 233,2 ± 1,8 Ma en una metapelita deformada y 200,8 ± 2,4 Ma en una metabasita no deformada. Mientras que la primera edad representa una edad de acreción, la última edad puede ser atribuida a crecimiento mineral ya sea durante una etapa de acreción más joven o durante una etapa retrógrada. Análisis isotópicos <sup>40</sup>Ar/<sup>39</sup>Ar de dos muestras más de metabasitas reflejan un notorio reajuste de edades a 152,0 ± 2,2 Ma, y crecimiento de mica blanca durante acceso de fluidos externos gatillado por una intrusión local o por un período extensional Jurásico tardío.

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The Madre de Dios Metamorphic Complex (MDMC) in southern Chile is a fossil frontal accretionary prism, which is mainly composed of metapsammopelitic rocks, intercalations of oceanic rocks (greenstone and metachert) and platform carbonate. We concentrated on the metabasite to decipher the metamorphic evolution. This rock type contains assemblages of the pumpellyite-actinolite facies:  $pumpellyite \pm actinolite-chlorite \pm grandite \pm phengite \pm epidote$ albite-quartz-titanite  $\pm K$ -feldspar  $\pm$  calcite. The metamorphic phases mainly grew by prograde hydration reactions during various episodes of restricted fluid influx. Fundamental phase relations of the pumpellyite-actinolite facies and adjacent facies were reproduced by pseudosections calculated for the system  $K_2O-Na_2O-CaO FeO-O_2-MgO-Al_2O_3-TiO_2-SiO_2-H_2O-CO_2$  at 200-400°C and 1–9 kbar. The calculated stability fields of the metamorphic assemblages as realized in the MDMC metabasite indicate highest metamorphic conditions restricted to 290-310°C, 4-6 kbar for the MDMC, presumably as a result of the main fluid influx at these conditions. Nevertheless, earlier local equilibria are still preserved as a result of strongly kinetically controlled mineral reactions and a lack of recrystallization and compositional homogenization at thin-section

scale. Hence, thermodynamic calculations of local multivariant mineral equilibria using the entire compositional variation of minerals in the MDMC show that the prograde PT path evolved from  $4 \pm 1$ kbar,  $200-220^{\circ}C$  to  $5\pm1$  kbar,  $290-330^{\circ}C$ . The prograde PT path reflects nearly horizontal particle paths after reaching the maximum depth typical for frontal accretionary prisms. Long residence at maximum depth resulted in thermal re-equilibration.  ${}^{40}Ar/{}^{39}Ar$ spot ages were measured by in situ UV laser ablation of local phengite concentrations in a deformed metapelite at  $233 \cdot 2 \pm 1 \cdot 8$  Ma and in an undeformed metabasite at  $200.8 \pm 2.4$  Ma. Whereas the first age represents an age of accretion, the latter age can be attributed to mineral growth either during a younger stage of accretion or during a retrograde stage. <sup>40</sup>Ar/<sup>39</sup>Ar isotopic analyses of two further metabasite samples reflect a prominent resetting of ages at  $152.0 \pm 2.2$  Ma and white mica growth during external fluid access triggered by either a local intrusion or a late Jurassic extensional episode.

KEY WORDS: pumpellyite-actinolite facies; kinetically controlled mineral growth; frontal accretionary prism; prograde PT path; PT pseudosection; 40Ar/39Ar UV laser ablation

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### **INTRODUCTION**

The Patagonian Pacific margin between latitudes 42°S and 53°S is characterized by numerous Late Paleozoic-Mesozoic metamorphic complexes, which are generally referred to as fossil accretionary prisms (Hervé et al., 2003, 2007b; Fig. 1). These complexes vary in metamorphic grade, tectonic style, and age of metamorphism and accretion. The different basement complexes are generally separated from each other by the intrusion of the Late Jurassic to Cenozoic Patagonian Batholith (Hervé et al., 2007a, 2007b). Recent data have resulted in a better understanding of the formation of different types of accretionary prisms at the western margin of Gondwana. Two principal modes of accretion have been recognized in central Chile by Richter et al. (2007). Frontal accretion, involving subhorizontal convergence at shallow levels, changed in time to basal accretion involving underplating and subvertical flattening at deeper levels. In Patagonia such continuous relations can also be observed in basement rocks of the

Chonos Archipelago (Davidson et al., 1987; Willner et al., 2000). The different modes of accretion are also reflected by specific metamorphic conditions in the Chilean fossil accretionary systems. Basal accretion is clearly related to high-pressure (HP) greenschist-facies and more rarely to epidote-blueschist- and albite-amphibolite-facies conditions (Willner et al., 2000, 2004; Willner, 2005). However, areas showing frontal accretion are mostly overprinted by later high-temperature (HP), low-pressure (LP) metamorphism in central Chile (Willner, 2005). In Patagonia there are three major basement complexes, which are characterized by very low grade metamorphism, intermediate pressure conditions and an upper crustal deformation style that resembles that of frontal accretion, involving subvertical folds and brittle reverse faulting. These complexes comprise the Eastern Belt of the Chonos Archipelago (Willner et al., 2000; Fig. 1), the Eastern Andean Metamorphic Complex (Ramírez Sánchez et al., 2005) and the Madre de Dios Metamorphic Complex (MDMC; Thomson &



Fig. 1. Geological map and cross-section of the MDMC in the southern Madre de Dios Island and northern Duque de York Island of the Madre de Dios Archipelago after Forsythe & Mpodozis (1983) and Sepúlveda *et al.* (2008). Insert map shows the distribution of metamorphic complexes in Chilean Patagonia.

Hervé, 2002; Sepúlveda *et al.*, 2008). Such types of accretionary prism are, in general, predominantly composed of monotonous turbiditic successions. However, in the MDMC considerable amounts of oceanic crust and platform carbonate are also incorporated.

Focusing on the well-exposed MDMC, our aim is (1) to provide quantitative data for the thermal evolution of this example of a frontal accretionary prism using mainly metabasite as the lithology with the most variable assemblages, (2) to understand the nature of the low-temperature metamorphic reaction processes, (3) to apply new methods to study fundamental phase relations and metamorphic processes at very low grade conditions and (4) to date the very low grade metamorphic event so as to set an important time horizon for the evolution of the coastal accretionary systems of Chile as a whole.

## GEOLOGICAL SETTING AND FIELD RELATIONS

The MDMC is an isolated complex of metamorphic rocks in the Ultima Esperanza District of Chilean Patagonia between latitudes and longitudes of 50 and 53°S and 74 and 76°W, respectively, and is exposed on various remote islands (Mornington, Madre de Dios, Duque de York, Diego de Almagro, Ramírez, Contreras and Desolación Islands) along the Pacific margin. During their pioneering work, Forsythe & Mpodozis (1979, 1983) defined three units of the MDMC that are composed of distinct rock assemblages (Fig. 1): (1) the Denaro Unit (DU) is composed of large fragments of ocean floor rocks and their sedimentary cover (metalliferous chert, redeposited calcareous sandstone, black shale and banded radiolarian chert with a Late Carboniferous-Early Permian biostratigraphic age; see Ling et al., 1985). The metabasite of the DU shows geochemical affinities to enriched (E-) and normal (N-) mid-ocean ridge basalt (MORB) (Sepúlveda et al. 2008), whereas the metalliferous chert is comparable with exhalative precipitates at active spreading centers. Primary structures such as pillow and hyaloclastite relics are preserved and, generally, no internal deformation of the rocks is observed. (2) The Tarlton Limestone (TL) represents a marine carbonate platform of Middle Pennsylvanian to Early Permian age (Cecioni, 1956; Douglass & Nestell, 1976). (3) The Duque de York Unit (DYU) is the predominant unit and comprises a voluminous turbiditic metapsammopelitic succession of continental provenance, which also includes polymict conglomerates. The DYU was partly unconformably deposited on top of the DU and TL units, but is mostly in tectonic contact with its neighbouring units. A combination of the palynological record and geochronological data for the DYU suggests an earliest Middle Permian depositional age (Sepúlveda et al., 2009). Sensitive high-resolution ion microprobe (SHRIMP) U-Pb dating of detrital zircon from DYU metagreywacke yielded a youngest age population of c. 270 Ma that provides a maximum depositional age for the sequence (Hervé et al., 2003, 2006). These data also provide an uppermost limit for the age of metamorphism. Two fission-track (FT) ages were obtained from the same detrital zircon populations:  $209 \pm 14$  and  $209 \pm 12$  Ma (Thomson & Hervé, 2002). Considering annealing of zircon FT ages at  $\sim 280^{\circ}$ C for mean cooling rates (Rahn et al., 2004) the latter ages provide a minimum age of metamorphism. The DYU is regarded to have been deposited at an active continental margin on the basis of the composition of the detritus (Faúndez et al., 2002; Hervé et al., 2003; Lacassie et al., 2006). A prominent Early to Middle Permian (c. 270 Ma) population of detrital zircon in the DYU can be interpreted as the first input of detritus from an igneous complex that developed within the continental margin at this latitude (Hervé et al., 2003, 2006). However, such source rocks are apparently not exposed at the present margin of Southern Patagonia at the respective latitude. Thus, Lacassie et al. (2006) suggested that the MDMC may have been displaced and possibly originated at an extensive late Paleozoic active continental margin along the Antarctic sector of Gondwana. On the other hand, the late Permian zircon population might correspond to the widespread Permian(?)-Triassic Choiyoi acid magmatic province (Mpodozis & Kay, 1990) that extends from 28°S to 42°S, or to the Permian igneous rocks in the North Patagonian Massif (Pankhurst et al., 2006).

The MDMC was previously classified by Forsythe (1982) and Forsythe & Mpodozis (1983) as a forearc accretionary prism. Those workers described the predominant structures as follows: east-west-trending thrusts dipping north  $(D_1)$  were produced during north-to-south-directed (relative to present coordinates) tectonic emplacement of slices of the oceanic DU and TL within the continent-derived DYU. At the same time similarly trending tight to isoclinal folds formed as well as an early cleavage in the metapelitic rocks. Primary structures are generally preserved and no internal deformation occurs in the metagreywacke, metabasite and massive limestone.  $D_1$  structures were strongly overprinted during north-south-trending refolding with a prominent 1-100 m scale, slightly west-vergent chevron folds and associated axial plane cleavage in pelitic rocks. These  $D_2$  structures were thought to be related to a system of strike-slip faults. The prominent bedding folds and associated thrusts resemble structures formed during frontal accretion in shallow levels of an accretionary system as observed in analog experiments (Kukowski et al., 2002; Glodny et al., 2005) and rock units such as the Eastern Series of central Chile (Richter et al., 2007), which are interpreted in a similar fashion to a frontal accretionary prism.

After emplacement and development of a structural inventory, the units of the MDMC were intruded by the late Jurassic to Cenozoic South Patagonian Batholith (Hervé *et al.*, 2007*a*). In the study area this intrusion occurred at  $133 \pm 1$  Ma (Hervé *et al.*, 2007*a*). Late Jurassic silicic volcanic rocks of the Tobífera series represent the oldest cover sequence in the area, and unconformably overlie the metamorphic basement at Peninsula Staines (51°33'S; Allen, 1982).

Rapalini *et al.* (2001) provided paleomagnetic data on the TL and the DU, which suggest that both units rotated  $\sim 117^{\circ}$  in an anti-clockwise sense after an Early Cretaceous remagnetization caused by the thermal influence of the South Patagonian Batholith. Those workers concluded that both rock units were probably accreted to the Gondwana margin from the NW.

#### ANALYTICAL METHODS

Focusing on the lithologically most diverse Denaro Unit (DU), we selected representative rock types from different parts of its accessible outcrop (Fig. 1) for petrological and geochronological investigations. The mineralogy of the rock samples and their locations are given in Table 1.

Mineral compositions were obtained using a CAMECA SX 100 electron microprobe with five wavelengthdispersive systems at Universität Stuttgart, Germany. Operating conditions were an acceleration voltage of 15 kV, a beam current of 15 nA, 20 s counting time per element each on the peak and the background and a defocused beam of 8 µm to avoid loss of alkalis in mica and amphibole. We used natural minerals, glasses and pure oxides as standards. The PAP correction procedure provided by Cameca was used for matrix correction. Representative analyses and structural formulae of minerals used for PT calculations, together with the calculation procedure of the structural formulae, are presented in Table 2. The complete dataset is available as Supplementary Data, which can be downloaded from http://www.petrology.oxfordjournals.org. Abbreviations of minerals and end-member components in this paper are: ab, albite; ac, Mg-Al-celadonite; am, amphibole; bt, biotite; ca, calcic amphibole; cc, calcite; ch, chlorite; cl, clinochlore; cp, clinopyroxene; cz, clinozoisite; da, daphnite; ep, epidote; fc, Fe-Al-celadonite; gl, glaucophane; gt, grandite; kf, potassic feldspar; lm, laumontite; lw, lawsonite; mp, Mg-pumpellyite; na, sodic amphibole; pu, pumpellyite; pr, prehnite; qz, quartz; sb, stilbite; st, stilpnomelane; tt, titanite; tr, tremolite; v, H<sub>2</sub>O vapor; wk, wairakite; wm, potassic white mica.

Whole-rock major element analyses were obtained using Philips X-ray fluorescence spectrometers on glass disks at Ruhr-Universität Bochum and Universidad de Chile in Santiago. FeO was determined potentiometrically and  $Fe_2O_3$  was calculated by difference (Fe\_2O\_3tot -FeO\*1·1113). H<sub>2</sub>O was analysed by the coulometric Karl-Fischer titration method. Data are presented in Table 3.

Table 1: Assemblages of rock samples and their locations

|            | Metamorphic phases |       |      |      |    |    |      |    | Amygdules |      |    | Prim | ary ph | ases | Latitude | Longitude | Location | Ar/Ar age | Pseudo-      | Multivariant |                    |             |         |           |
|------------|--------------------|-------|------|------|----|----|------|----|-----------|------|----|------|--------|------|----------|-----------|----------|-----------|--------------|--------------|--------------------|-------------|---------|-----------|
|            | Ad                 | G G   | t Pi | и Ер | Ch | Wn | n Kf | Ab | Qz        | : Ti | Сс | St   |        |      |          | Срх       | Cr-sp    | Plag      |              |              |                    | (Ma)        | section | reactions |
| Metabasite |                    |       |      |      |    |    |      |    |           |      |    |      |        |      |          |           |          |           |              |              |                    |             |         |           |
| 04CH18c    | х                  |       | х    | х    | x  | x  |      | х  | х         | х    |    |      | Ch,    | Qz,  | Ep       | х         |          | x         | 50°27′57·9″  | 75°12′19·8″  | Isla Denaro        | 207-136     | x       | x         |
| 04CH17c    |                    |       |      |      | x  | x  |      | x  | х         | х    |    |      | Ch     |      |          | х         |          | x         | 50°28′10·6″  | 75°11′59·7″  | Isla Denaro        | $152\pm2$   |         |           |
| MD98-03    |                    | х     | х    | х    | x  |    |      | х  | х         | х    |    |      |        |      |          | х         | x        |           | 50°18′48·2″  | 75°16′50∙3″  | Seno Eleuterio     |             |         |           |
| MD98-04    | x                  | х     | х    | x    | x  | x  | x    | x  | х         | х    |    |      |        |      |          | х         | x        |           | 50°18′48·2″  | 75°16′50·3″  | Seno Eleuterio     |             | x       | x         |
| MD06-5B    | x                  | х     |      | x    | x  | x  |      | x  | х         | х    | x  |      | Qz,    | Ch,  | Сс       | х         | x        |           | 50°18′52·40″ | 75°16′50·57″ | Seno Eleuterio     |             |         | x         |
| MD5        | х                  |       | х    | х    | x  | x  |      | х  | х         | х    | x  |      | Ch,    | Qz   |          | х         |          |           | 50°28'36·4″  | 75°11′33·5″  | Islotes Roncas     |             | x       | x         |
| MD06-6A    | х                  |       |      |      | x  |    |      | х  |           | х    | x  |      | Ch,    | Сс   |          | х         |          |           | 50°18′52·40″ | 75°16′50·57″ | Seno Eleuterio     |             |         |           |
| MD26       | x                  |       | х    | x    | x  | x  |      | x  | х         | х    | x  |      | Ch,    | Сс   |          | х         |          |           | 50°22′42·1″  | 75°22′58·6″  | Seno Eleuterio     |             | x       | x         |
| MD05-18    |                    |       | х    | х    | x  |    | х    | х  | х         | х    |    |      |        |      |          |           |          |           | 50°23′31·7″  | 75°20′10·1″  | Isla Guarello      |             |         |           |
| MD05-11D   |                    |       |      | x    | x  | x  |      | x  | х         | х    | x  |      | Qz,    | Ch,  | Сс       | x         |          |           | 50°22'31.0″  | 75°22′46·9″  | Seno Eleuterio     | $201\pm\!2$ |         |           |
| MD06-3B    |                    |       | х    | х    | x  | х  | х    |    | х         | х    |    |      |        |      |          | x         |          |           | 50°22′44·67″ | 75°23′05·63″ | Seno Eleuterio     |             | x       |           |
| SLL853*    | х                  |       | х    | х    | x  | x  |      | х  | х         | х    |    | х    |        |      |          | х         |          |           | 45°20′56·1″  | 74°12′05·7″  | Isla Italia        |             | x       |           |
| Metapsami  | тор                | oelit | е    |      |    |    |      |    |           |      |    |      |        |      |          |           |          |           |              |              |                    |             |         |           |
| 04CH15     |                    |       |      |      | x  | x  |      | x  | х         |      | x  |      |        |      |          |           |          |           | 50°25′43·2″  | 75°19′33·1″  | Isla Madre de Dios | $233\pm3$   | x       |           |
| MD06-8     |                    |       |      |      | x  | x  | x    | x  | х         | x    |    |      |        |      |          |           |          |           | 50°17′41·41″ | 75°20′25·03″ | Isla Madre de Dios |             | x       |           |

\*Metabasite from the Chonos Archipelago (Hervé et al. 1999).
Table 2: Representative analyses of the peak metamorphic mineral compositions

|                                | Garnet |        |        |        |                                | White mic | в      |       |       |          |         |       |       |          |         |         |          |
|--------------------------------|--------|--------|--------|--------|--------------------------------|-----------|--------|-------|-------|----------|---------|-------|-------|----------|---------|---------|----------|
|                                | MD9803 | MD065B | MD9804 | MD9804 |                                | MD9804    | MD9804 | MD26  | MD26  | 04CH18c  | 04CH18c | MD5   | MD068 | 04CH15   | 04CH17c | MD0511D | MD065B   |
| SiO <sub>2</sub>               | 35.8   | 36·1   | 35.9   | calc.  | SiO <sub>2</sub>               | 55.3      | calc.  | 49.4  | calc. | 49.1     | calc.   | calc. | 50.4  | 51.6     | 50.3    | 52.7    | 50.3     |
| Al <sub>2</sub> O <sub>3</sub> | 8·11   | 6·15   | 6.39   |        | TiO <sub>2</sub>               | 0-01      |        | 0.03  |       | b.d.     |         |       | 0·14  | 0.03     | 0.04    | 0.02    | 0-52     |
| Ti0 <sub>2</sub>               | 0.38   | 0.42   | 06.0   |        | Al <sub>2</sub> O <sub>3</sub> | 21.7      |        | 28·0  |       | 27·3     |         |       | 27·2  | 26.7     | 26·8    | 24.7    | 24.1     |
| Fe <sub>2</sub> 0 <sub>3</sub> | 20.1   | 22·1   | 19-4   |        | FeO                            | 3·91      |        | 3·04  |       | 4.60     |         |       | 3·01  | 2·54     | 3·84    | 3·20    | 4.53     |
| $Cr_2O_3$                      | 0.03   | n.d.   | 1.69   |        | Fe <sub>2</sub> 0 <sub>3</sub> |           |        |       |       |          |         |       |       |          |         |         | 0.13     |
| MnO                            | 0·21   | 0.25   | 0-40   |        | MnO                            | 0.03      |        | 0.02  |       | 0.01     |         |       | b.d.  | 0.04     | 0·02    | b.d.    | 0.03     |
| MgO                            | 0.05   | 0.26   | 0.20   |        | MgO                            | 5.61      |        | 2.77  |       | 1.78     |         |       | 2.66  | 2.22     | 2·74    | 3·03    | 4.14     |
| CaO                            | 34.9   | 33·6   | 34·2   |        | CaO                            | 0.05      |        | 00.00 |       | 0-59     |         |       | 0.02  | 0.02     | 0·80    | 0·20    | 1.20     |
| Sum                            | 9.66   | 98·8   | 99·1   |        | Na <sub>2</sub> O              | 0.00      |        | 0·18  |       | 0.70     |         |       | 0.15  | 0.84     | 0.49    | 1·12    | 0-47     |
| Si                             | 5.850  | 5.966  | 5.920  | 6.00   | K <sub>2</sub> 0               | 10.5      |        | 10.9  |       | 9.8<br>8 |         |       | 10.3  | 9.8<br>8 | 9.4     | 9.6     | 10.2     |
| AIIV                           | 0.150  | 0.034  | 0.080  |        | H <sub>2</sub> 0               | 4.59      |        | 4.40  |       | 4.37     |         |       | 4.44  | 4.45     | 4.43    | 4-47    | 4.42     |
| Sum                            | 6·000  | 6·000  | 6·000  | 6·00   | Sum                            | 101·8     |        | 98·7  |       | 98·3     |         |       | 98·6  | 98·4     | 98·7    | 99·2    | 100.1    |
| AI <sup>VI</sup>               | 1-412  | 1·165  | 1.160  | 1.36   | Si                             | 7·226     | 6·90   | 6·693 | 06·90 | 6·744    | 6·86    | 6.94  | 6·801 | 6·951    | 6·802   | 7·078   | 6·827    |
| Fe <sup>3+</sup>               | 2.470  | 2.747  | 2.402  | 2.64   | AIV                            | 0·774     | 1.10   | 1·308 | 1.10  | 1·256    | 1·14    | 1·06  | 1.199 | 1·049    | 1.198   | 0.922   | 1.174    |
| Ξ                              | 0-046  | 0.052  | 0·111  |        | Sum                            | 8·000     | 8·00   | 8·000 | 8·00  | 8·000    | 8·00    | 8·00  | 8·000 | 8·000    | 8·000   | 8·000   | 8·000    |
| ŗ                              | 0.004  | n.d.   | 0·220  |        | AI <sup>VI</sup>               | 2·574     | 3·10   | 3·158 | 3·10  | 3·157    | 3·14    | 3·06  | 3·132 | 3·187    | 3·069   | 2.994   | 2.679    |
| Sum                            | 3·929  | 3·964  | 3·893  | 4·00   | Ξ                              | 0.001     |        | 0.003 |       |          |         |       | 0·014 | 0.003    | 0·004   | 0·002   | 0.053    |
| Mn                             | 0.030  | 0.035  | 0.055  |        | Fe <sup>2+</sup>               | 0-427     | 0·10   | 0.345 | 0·22  | 0.528    | 0·26    | 0.30  | 0.339 | 0·286    | 0.434   | 0·360   | 0-514    |
| Ca                             | 6·114  | 5.946  | 6-041  | 6·00   | Fe <sup>3+</sup>               |           |        |       |       |          |         |       |       |          |         |         | 0.014    |
| Mg                             | 0.013  | 0.064  | 0.049  |        | Mn                             |           |        |       |       |          |         |       |       | 0.005    | 0·002   | 0·00    | 0.003    |
| Sum                            | 6·156  | 6·046  | 6·145  | 6-00   | Mg                             | 0.004     | 0·80   | 0.003 | 0·68  | 0.001    | 0.60    | 0·64  | 0.534 | 0.446    | 0.552   | 0.607   | 0.837    |
| Grossular                      | 0-401  | 0.454  | 0·391  | 0·34   | Sum                            | 1·094     | 4·00   | 0.558 | 4·00  | 0.363    | 4·00    | 4·00  | 4·020 | 3·928    | 4·061   | 3·963   | 4·100    |
| Andradite                      | 0.592  | 0.529  | 0.556  | 0.66   | Са                             | 4.099     |        | 4.067 |       | 4.049    |         |       | 0.003 | 0.003    | 0.116   | 0.028   | 0.175    |
| Spessartine                    | 0.005  | 0·006  | 00·0   |        | Na                             | 0.007     | 0·04   | 0.000 | 0.04  | 0.087    | 0.04    | 0.40  | 0.040 | 0·219    | 0·129   | 0·292   | 0·125    |
| Pyrope                         | 0.002  | 0.011  | 0·008  |        | ⊻                              | 000.0     | 1.96   | 0.047 | 1.96  | 0·186    | 1.96    | 1.96  | 1·781 | 1·689    | 1·614   | 1·650   | 1·768    |
| Uvarovite                      | 0.001  | n.d.   | 0.036  |        | Sum                            | 1.751     | 2·00   | 1·887 | 2·00  | 1·723    | 2·00    | 2·00  | 1.835 | 1.919    | 1·885   | 1·973   | 2·068    |
|                                |        |        |        |        | НО                             | 1·758     | 4·00   | 1.934 | 4·00  | 1·996    | 4·00    | 4·00  | 4·000 | 4·000    | 4·000   | 4·000   | 4·000    |
|                                |        |        |        |        | $\chi_{Mg}$                    | 0·720     | 0·89   | 0.620 | 0.76  | 0.400    | 0.70    | 0·68  | 0.610 | 0.610    | 0.560   | 0.630   | 0.620    |
|                                |        |        |        |        | Muscovite                      | 0.330     |        | 0.584 |       | 0.423    |         |       | 0.546 | 0.433    | 0·347   | 0·300   | 0.277    |
|                                |        |        |        |        | Tri-oct. mica                  | 0.050     |        | 0.035 |       | 0.025    |         |       | 0.010 | 0.036    | 0.031   | 0.019   | 0-050    |
|                                |        |        |        |        | MgAI-celadonite                | 0.444     |        | 0.217 |       | 0.169    |         |       | 0.250 | 0·293    | 0·267   | 0·348   | 0.309    |
|                                |        |        |        |        | FeAI-celadonite                | 0.173     |        | 0·134 |       | 0·246    |         |       | 0.159 | 0·188    | 0·210   | 0·206   | 0.190    |
|                                |        |        |        |        | Paragonite                     | 000.0     |        | 0.024 |       | 0.093    |         |       | 0.022 | 0·114    | 0.069   | 0·148   | 0.060    |
|                                |        |        |        |        | Rest                           | 0.004     |        | 0·006 |       | 0-044    |         |       | 0.029 | 0-015    | 0.000   | 0-033   | 0.229    |
|                                |        |        |        |        |                                |           |        |       |       |          |         |       |       |          |         | (cor    | itinued) |

|                  | Chlorite |        |        |       |         |         |        |       |        |        |        |        |        |         |         |          |
|------------------|----------|--------|--------|-------|---------|---------|--------|-------|--------|--------|--------|--------|--------|---------|---------|----------|
|                  | MD9804   | MD9804 | MD26   | MD26  | 04CH18C | 04CH18C | MD5    | MD5   | MD9803 | MD068  | 04CH15 | MD066  | MD065B | 04CH17C | MD0511D | MD0518   |
| SiO <sub>2</sub> | 32·3     | calc.  | 28.0   | calc. | 29.1    | calc.   | 26-91  | calc. | 29.4   | 25:3   | 27:3   | 31.6   | 33.7   | 30-5    | 31.4    | 29.5     |
| $AI_2O_3$        | 15.8     |        | 19.2   |       | 16.1    |         | 18-59  |       | 17·8   | 17-5   | 14·3   | 15-9   | 14.0   | 15-5    | 17.0    | 19.3     |
| $TiO_2$          | 0.06     |        | 0-01   |       | 0.03    |         | 0-01   |       | 0.02   | 2.58   | 1.61   | b.d.   | 0.01   | b.d.    | b.d.    | b.d.     |
| FeO              | 13·3     |        | 18.6   |       | 25.8    |         | 24.55  |       | 17·3   | 32.3   | 31.0   | 13.9   | 13.5   | 22.2    | 11:3    | 11.9     |
| MgO              | 26·2     |        | 20.4   |       | 15.5    |         | 16·75  |       | 22·1   | ĿĿ     | 11.8   | 25-3   | 26.2   | 19-3    | 27·0    | 26.9     |
| MnO              | 0.16     |        | 0.22   |       | 0·28    |         | 0·20   |       | 0.19   | 0.37   | 0.11   | 0.17   | 0.22   | 0·20    | 0.15    | 0.25     |
| $H_2O'$          | 12·3     |        | 11-7   |       | 11·3    |         | 11·35  |       | 11·8   | 10.7   | 10.8   | 12.1   | 12·3   | 11-7    | 12·2    | 12·3     |
| Ц                | 100·2    |        | 98·2   |       | 98.1    |         | 98·35  |       | 98·7   | 96.4   | 97.0   | 0.66   | 6.66   | 99·3    | 99.1    | 100.2    |
| Si               | 6·321    | 6.00   | 5.759  | 6.00  | 6·171   | 6.00    | 5.689  | 6·00  | 5.968  | 5.685  | 6.059  | 6·263  | 6·592  | 6·265   | 6·154   | 5.757    |
| Al∾              | 1.680    | 2.00   | 2.241  | 2.00  | 1.830   | 2·00    | 2.311  | 2·00  | 2·032  | 2.315  | 1.941  | 1.737  | 1.408  | 1.735   | 1·846   | 2·244    |
| AI <sup>VI</sup> | 1.959    | 2.00   | 2.409  | 2.00  | 2·203   | 2.00    | 2.321  | 2.00  | 2·218  | 2·309  | 1.802  | 1.988  | 1·824  | 2.024   | 2·084   | 2.194    |
| ⊨                | 0.008    |        | 0.002  |       | 0.004   |         | 0.001  |       | 0.003  | 0.435  | 0·268  | 0.000  | 0.002  | 0.000   | 0.000   | 0.000    |
| Mn               | 0.027    |        | 3·199  |       | 0.050   |         | 0.036  |       | 0.033  | 0.071  | 0.020  | 0.028  | 0.036  | 0.035   | 0.024   | 0.041    |
| Fe               | 2.182    | 2·24   | 0.038  | 3·76  | 4·585   | 4·38    | 4·341  | 4.50  | 2·932  | 6.069  | 5.744  | 2·311  | 2·208  | 3·813   | 1·855   | 1.945    |
| Mg               | 7.646    | 7.76   | 6·258  | 6·24  | 4·914   | 4·91    | 5.278  | 5.50  | 6·677  | 2.572  | 3.913  | 7·488  | 7.633  | 5.903   | 7·872   | 7·821    |
| Sum              | 11.822   | 12·00  | 11.906 | 12·00 | 11.757  | 12·00   | 11-977 | 12·00 | 11·863 | 11-456 | 11·748 | 11·815 | 11·703 | 11.775  | 11·835  | 12·001   |
| НО               | 16·000   | 16-00  | 16·000 | 16.00 | 16·000  | 16·00   | 0.55   | 16·00 | 16·000 | 16·000 | 16·000 | 16·000 | 16·000 | 16·000  | 16-000  | 16·000   |
| $\chi_{Mg}$      | 0.78     | 0·78   | 0-66   | 0.62  | 0-51    | 0.56    | 0-55   | 0-55  | 0.695  | 0·298  | 0.405  | 0.764  | 0·776  | 0.608   | 0·814   | 0·801    |
|                  |          |        |        |       |         |         |        |       |        |        |        |        |        |         | (CO     | ntin.ed) |

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Table 2: Continued

|                                | Amphibol | <u>e</u> |        |        |        |       |                                | Epidote |       |         |         |       |       |         |        |        |
|--------------------------------|----------|----------|--------|--------|--------|-------|--------------------------------|---------|-------|---------|---------|-------|-------|---------|--------|--------|
|                                | MD5      | MD5      | MD065B | MD066  | MD9804 | MD26  |                                | MD26    | MD26  | 04CH18c | 04CH18c | MD5   | MD5   | MD0511D | MD0518 | MD9804 |
| SiO <sub>2</sub>               | 53.4     | calc.    | 57.5   | 56.4   | calc.  | calc. | $SiO_2$                        | 37·2    | calc. | 36.7    | calc.   | 37.3  | calc. | 37.8    | 37.8   | 36.8   |
| AI <sub>2</sub> 0 <sub>3</sub> | 0·48     |          | 0.52   | 0.70   |        |       | $TiO_2$                        | 0.13    |       | 60·0    |         | 00.0  |       | 0-01    | 0.10   | 0.02   |
| TiO <sub>2</sub>               | 0.06     |          | 0.01   | 0·13   |        |       | $AI_2O_3$                      | 23·1    |       | 23·5    |         | 21.9  |       | 22·2    | 23·8   | 20·8   |
| Fe <sub>2</sub> O <sub>3</sub> | 1·85     |          | 1.41   | 0·32   |        |       | Fe <sub>2</sub> O <sub>3</sub> | 13·3    |       | 13·3    |         | 14·8  |       | 14·3    | 12·1   | 14·8   |
| FeO                            | 14.0     |          | 6.60   | 7.73   |        |       | $Mn_2O_3$                      | 0.20    |       | 0.39    |         | 0·13  |       | 0.05    | 0.16   | 0.15   |
| MgO                            | 13·6     |          | 19-4   | 18·9   |        |       | MgO                            | 0.03    |       | 0.02    |         | 0.15  |       | 0.46    | 0.03   | 0.10   |
| CaO                            | 11.9     |          | 12.6   | 12.6   |        |       | CaO                            | 23·2    |       | 23·0    |         | 22.9  |       | 22.9    | 23·5   | 21·8   |
| MnO                            | 0.35     |          | 0·21   | 0.11   |        |       | $H_2O'$                        | 1.86    |       | 1.84    |         | 1.86  |       | 1.89    | 1·89   | 1·84   |
| BaO                            | 0.16     |          | b.d.   | 0.03   |        |       | Sum                            | 99·1    |       | 98·7    |         | 99.1  |       | 9.66    | 99·4   | 96-4   |
| Na <sub>2</sub> O              | 0.06     |          | 0.01   | 0.08   |        |       | Si                             | 3·000   | 3·00  | 3·000   | 3·00    | 3·000 | 3·00  | 3·000   | 3·000  | 3·000  |
| K <sub>2</sub> 0               | 0·18     |          | 0.30   | 0.40   |        |       | AI                             | 2.196   | 2·36  | 2·265   | 2.40    | 2.075 | 2·36  | 2·074   | 2·220  | 1·995  |
| H <sub>2</sub> 0'              | 2·02     |          | 2.16   | 2.13   |        |       | Fe <sup>3+</sup>               | 0·804   | 0.64  | 0.817   | 0.60    | 0.895 | 0.64  | 0.851   | 0·725  | 0-910  |
| Sum                            | 98·1     |          | 100·8  | 99·5   |        |       | $Mn^{3+}$                      | 0.012   |       | 0.024   |         | 0.008 |       | 0.003   | 0.010  | 600·0  |
| Si                             | 7·915    | 8·00     | 7·968  | 7.951  | 8·00   | 8·00  | Mg                             | 0.003   |       | 0.002   |         | 0.019 |       | 0.055   | 0.004  | 0-012  |
| AI <sup>IV</sup>               | 0·083    |          | 0.032  | 0.049  |        |       | ij                             | 0.008   |       | 0.005   |         | 000-0 |       | 0.001   | 0.006  | 0.001  |
| Sum                            | 7·998    | 8·00     | 8·000  | 8·000  | 8·00   | 8·00  | Sum                            | 3·022   | 3·00  | 3·113   | 3·00    | 2.996 | 3·00  | 2·983   | 2.964  | 2.927  |
| AI <sup>VI</sup>               | 000.0    | 0.04     | 0.052  | 0.067  | 0.08   | 0.06  | Ca                             | 2·000   | 2·00  | 2·011   | 2·00    | 1.973 | 2·00  | 1·944   | 1.994  | 1·904  |
| Ξ                              | 0.007    |          | 0.001  | 0.013  |        |       | НО                             | 1.000   | 1·00  | 1.000   | 1.00    | 1·000 | 1·00  | 1·000   | 1·000  | 1·000  |
| Mn                             | 0·044    |          | 0.025  | 0.013  |        |       |                                |         |       |         |         |       |       |         |        |        |
| Fe <sup>3+</sup>               | 0.206    | 0.17     | 0.147  | 0·034  |        |       |                                |         |       |         |         |       |       |         |        |        |
| Fe <sup>2+</sup>               | 1.735    | 1·69     | 0.765  | 0.911  | 1·02   | 1-40  |                                |         |       |         |         |       |       |         |        |        |
| Mg                             | 3·011    | 3·10     | 4-010  | 3.963  | 3·90   | 3.54  |                                |         |       |         |         |       |       |         |        |        |
| Sum                            | 13·000   | 13·00    | 13·000 | 13·000 | 13·00  | 13.00 |                                |         |       |         |         |       |       |         |        |        |
| Са                             | 1·893    | 1·80     | 1·875  | 1·898  | 1·88   | 1·84  |                                |         |       |         |         |       |       |         |        |        |
| Ba                             | 00·0     |          |        | 0.001  |        |       |                                |         |       |         |         |       |       |         |        |        |
| Na                             | 0.053    | 0·20     | 0.080  | 0·109  | 0·12   | 0·16  |                                |         |       |         |         |       |       |         |        |        |
| ¥                              | 0.012    |          | 0.001  | 0.014  |        |       |                                |         |       |         |         |       |       |         |        |        |
| Sum                            | 1.966    | 2.00     | 1·956  | 2·022  | 2.00   | 2·00  |                                |         |       |         |         |       |       |         |        |        |
| НО                             | 2·000    | 2.00     | 2·000  | 2·000  | 2.00   | 2.00  |                                |         |       |         |         |       |       |         |        |        |
| $X_{ m tremolite}$             | 0.946    |          | 0.938  | 0.949  |        |       |                                |         |       |         |         |       |       |         |        |        |
| $X_{glaucophane}$              | 000.0    |          | 0.016  | 0.034  |        |       |                                |         |       |         |         |       |       |         |        |        |
| $X_{ m riebeckite}$            | 0.054    |          | 0.046  | 0.017  |        |       |                                |         |       |         |         |       |       |         |        |        |
| $X_{Mg}$                       | 0.600    | 0.65     | 0·811  | 0.806  | 0.79   | 0.72  |                                |         |       |         |         |       |       |         |        |        |

(continued)

Table 2: Continued

| Model         Model <th< th=""><th></th><th>Pumpellyite</th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th></th><th>Clinopyro</th><th>xene</th><th></th><th></th><th></th></th<> |                                | Pumpellyite |         |        |        |       |       |       |       |        |         |                                | Clinopyro | xene    |       |         |       |
|--|--------------------------------|-------------|---------|--------|--------|-------|-------|-------|-------|--------|---------|--------------------------------|-----------|---------|-------|---------|-------|
| No.         333         onlo         334         334         335         515         515         515         515         515         515         515         515         515         515         523         523         523         523         523         523         523         523         523         523         523         523         523         523         523         523         523         523         523         524         523         524 <th></th> <th>04Ch18c</th> <th>04Ch18c</th> <th>MD9804</th> <th>MD9804</th> <th>MD5</th> <th>MD5</th> <th>MD26</th> <th>MD26</th> <th>MD9803</th> <th>MD05-18</th> <th></th> <th>MD5</th> <th>04CH18c</th> <th>MD5</th> <th>04CH17c</th> <th>MD066</th>               |                                | 04Ch18c     | 04Ch18c | MD9804 | MD9804 | MD5   | MD5   | MD26  | MD26  | MD9803 | MD05-18 |                                | MD5       | 04CH18c | MD5   | 04CH17c | MD066 |
| 10         000         001         001         002         103         003   | SiO <sub>2</sub>               | 35-9        | calc.   | 37.2   | calc.  | 36.6  | calc. | 36.3  | calc. | 35.8   | 36.8    | SiO <sub>2</sub>               | 50.7      | 51.5    | 50.7  | 53·2    | 52.4  |
| Mo.         101         238         245         244         191         260         Mo.         218         216         171         173         171         173         171         173         171         173         171         173         171         173         171         173         171         173         171         173         171         173         173         173         173         173         173         173         173         173         173         173         173         173         173         173         173         173         174         174         173         174 <td><math>TiO_2</math></td> <td>0.06</td> <td></td> <td>0.04</td> <td></td> <td>0.07</td> <td></td> <td>0.19</td> <td></td> <td>0.01</td> <td>0.02</td> <td>Ti0<sub>2</sub></td> <td>0-57</td> <td>0.48</td> <td>0.57</td> <td>0·28</td> <td>0.22</td>                 | $TiO_2$                        | 0.06        |         | 0.04   |        | 0.07  |       | 0.19  |       | 0.01   | 0.02    | Ti0 <sub>2</sub>               | 0-57      | 0.48    | 0.57  | 0·28    | 0.22  |
| Fey         738         426         262         577         104         251         Fey         151         151         133         133           600         38         0         32         0         37         104         37         103         547         133           M00         0.86         0.15         0.16         0.16         0.17         104         133         134         134         133           M10         280         387         280         37         106         137         106         137         133         134  | $AI_2O_3$                      | 21·0        |         | 23·8   |        | 24.5  |       | 24.4  |       | 19.1   | 26·0    | $AI_2O_3$                      | 2.16      | 3·04    | 2.16  | 1·87    | 3·11  |
| Fe0         346         0.23         271         162         273         647         673         847         647         647         647           Min         0.66         317         0.16         0.16         0.16         0.16         0.23         0.19         0.23         0.24         17.4   | Fe <sub>2</sub> O <sub>3</sub> | 7·38        |         | 4·26   |        | 2.62  |       | 5.37  |       | 10.54  | 2·51    | Fe <sub>2</sub> O <sub>3</sub> | 1.51      | 1.15    | 1.51  | 1.33    | 1.37  |
| Mid         08         15         010         013  | FeO                            | 3.46        |         | 0·32   |        | 2.77  |       | 1·62  |       | 2.72   | 0.57    | FeO'                           | 8·87      | 6·73    | 8·87  | 5.47    | 4·30  |
| Mg0         206         317         220         317         230         317         163         117         133         117         174         133           Mg0         227         034         036         235         236         236         236         236         232         103  | MnO                            | 0.08        |         | 0.15   |        | 0.10  |       | 0.16  |       | 0.03   | 0.15    | MnO                            | 0.23      | 0·19    | 0.23  | 0·24    | 0·15  |
| 0         27         24         25         25         25         26         37         39         39         30           Ng0         04         04         03         04         03         04         37         32 </td <td>MgO</td> <td>2.06</td> <td></td> <td>3·87</td> <td></td> <td>2.50</td> <td></td> <td>3·12</td> <td></td> <td>2.38</td> <td>3·77</td> <td>MgO</td> <td>14-7</td> <td>16.3</td> <td>14.7</td> <td>17-4</td> <td>18·3</td>  | MgO                            | 2.06        |         | 3·87   |        | 2.50  |       | 3·12  |       | 2.38   | 3·77    | MgO                            | 14-7      | 16.3    | 14.7  | 17-4    | 18·3  |
| Na         O 04         O 04         O 03         Na         Na         O 23         0.25         0.23         0.20         0.10           Va         D 04         D 05         D 1.1         O 05         D 1.1         D 1.1 <thd 1.1<="" th=""> <thd 1.1<="" th=""> <thd 1.1<="" th=""></thd></thd></thd>  | CaO                            | 22.7        |         | 23·4   |        | 23·5  |       | 22·5  |       | 22·6   | 23·2    | CaO                            | 19·2      | 19.3    | 19·2  | 20.4    | 19.6  |
| $(j_{0})$ <  | $Na_2O$                        | 0.04        |         | 0.04   |        | 0.03  |       | 0.02  |       | 0.01   | 0.03    | $Na_2O$                        | 0.23      | 0.25    | 0·23  | 0·20    | 0.15  |
| $\mu_{0}'$ $6.3$ $6.47$ $6.43$ $6.43$ $6.43$ $6.43$ $6.43$ $6.43$ $6.43$ $6.43$ $6.43$ $6.43$ $6.43$ $6.34$ $6.34$ $6.34$ $6.34$ $6.34$ $6.34$ $6.34$ $6.14$ $6.14$ $6.96$ $6.14$ $6.96$ $6.14$ $6.91$ $6.02$ $6.017$ $0.027$ $0.07$ $0.07$ $0.07$ $0.07$ $0.07$ $0.07$ $0.07$ $0.02$ $0.02$ $1.1$ $0.10$ $0.00$ $0.00$ $0.00$ $0.01$ $0.07$ $0.07$ $0.07$ $0.07$ $0.02$ $0.02$ $1.1$ $0.00$ $0.00$ $0.00$ $0.01$ $0.01$ $0.07$  | K <sub>2</sub> 0               | b.d.        |         | 0.06   |        | b.d.  |       | 0.06  |       | b.d.   | 0.01    | Sum                            | 98·2      | 0.66    | 98·2  | 100·4   | 9.66  |
| mm         m         mm         mm         mm<  | $H_2O'$                        | 6·33        |         | 6.47   |        | 6.43  |       | 6-44  |       | 6·14   | 6·54    |                                |           |         |       |         |       |
| Si         5 946         6 00         6 034         6 00         5 946         6 01         6 01         6 071         0 071         0 087         0 071         0 087         0 071         0 087         0 087           1         4 111         474         4 544         4 950         4 713         4 72         4 688         4 76         3 854         4 920         5 000         2 000   | Sum                            | 0.66        |         | 9·66   |        | 99·2  |       | 100.1 |       | 99·4   | 9.66    | Si                             | 1·923     | 1.913   | 1·923 | 1-941   | 1·913 |
|  | Si                             | 5.948       | 6·00    | 6·034  | 6·00   | 5.985 | 6·00  | 5.915 | 6·00  | 6·114  | 5·911   | Al∾                            | 0-077     | 0.087   | 0-077 | 0.059   | 0.087 |
|  | A                              | 4·111       | 4·74    | 4·544  | 4.96   | 4·713 | 4·72  | 4·688 | 4·76  | 3·854  | 4·920   | Sum                            | 2·000     | 2·000   | 2·000 | 2·000   | 2·000 |
|  | Ξ                              | 0·008       |         | 0.005  |        | 0.00  |       | 0.024 |       | 0.002  | 0·002   | Al <sup>vi</sup>               | 0.020     | 0-046   | 0.020 | 0-021   | 0.047 |
| Sun         503         500         508         500         504         500         537         500         5210         526 $Fe^{3+}$ 0033         0032         0033         0033         0033           M         0509         058         0937         086         0508         054         0757         064         0607         0933         542         033         0037         0033           Mn         011         010         020         014         022         0757         064         0607         0933         5729         0733         0167         013           Ke <sup>2+</sup> 0430         040         070         100         100         100         100         070         070         070         070         070           Ke <sup>2+</sup> 0430         040         070         100         100         100         100         070         070         070         070           Ke <sup>2+</sup> 043         040         033         034         033         040         100         070         070         070         070         070         070         070         070         070         070         070         070  | Fe <sup>3+</sup>               | 0.920       | 0·26    | 0·520  | 0·04   | 0·322 | 0·38  | 0.659 | 0·24  | 1.355  | 0·303   | Ħ                              | 0.016     | 0.013   | 0.016 | 0.008   | 0.006 |
| Mg         0500         058         037         036         054         057         060         060         028         028         0167         017           Mn         0011         0010         002         002         005         005         020         010         0007         0001         001         001         001         0010         001         001         001<  | Sum                            | 5.039       | 5.00    | 5.068  | 5.00   | 5-044 | 5.00  | 5.370 | 5.00  | 5·210  | 5·226   | Fe <sup>3+</sup>               | 0.043     | 0.032   | 0-043 | 0.037   | 0·038 |
|  | Mg                             | 0.509       | 0.58    | 0·937  | 0·86   | 0.608 | 0.54  | 0.757 | 0.64  | 0.607  | 0·903   | Fe <sup>2+</sup>               | 0·283     | 0·209   | 0·283 | 0.167   | 0·131 |
|  | Мл                             | 0-011       |         | 0·020  |        | 0.014 |       | 0.022 |       | 0.005  | 0.020   | Мп                             | 0.007     | 0.006   | 0.007 | 0.007   | 0.005 |
| Sum         1-00         1-00         1-00         1-00         1-00         1-00         1-00         1-00         1-00         1-00         0-780         0-780         0-790         0-700         0-700         0-700         0-700         0-700  | Fe <sup>2+</sup>               | 0.480       | 0-40    | 0.043  | 0·14   | 0·379 | 0·36  | 0·221 | 0.36  | 0·388  | 0.077   | Mg                             | 0·833     | 906·0   | 0·833 | 0.949   | 0-997 |
|  | Sum                            | 1·000       | 1·00    | 1·000  | 1·00   | 1·000 | 1.00  | 1.000 | 1·00  | 1.000  | 1.000   | Ca                             | 0·781     | 0·770   | 0.780 | 0.796   | 0.766 |
| Na $0.012$ $0.013$ $0.013$ $0.010$ $0.010$ $0.000$ $2$   | Ca                             | 4·035       | 4·00    | 4·074  | 4·00   | 4·113 | 4·00  | 3·923 | 4·00  | 4·132  | 3·985   | Na                             | 0-017     | 0.018   | 0.017 | 0-014   | 0.010 |
| K $0.012$ $0.012$ $0.012$ $0.012$ Sum $4.047$ $4.00$ $4.099$ $4.00$ $4.127$ $4.00$ $3.941$ $4.00$ $4.136$ $3.995$ $M_{Mg}$ $0.510$ $7.00$ $7.00$ $7.00$ $7.00$ $7.00$ $7.00$ $7.00$ $7.00$ $X_{Mg}$ $0.510$ $0.690$ $0.620$ $0.60$ $0.700$ $7.00$ $7.00$ $7.00$ $X_{Mg}$ $0.510$ $0.620$ $0.60$ $0.700$ $7.00$ $7.00$ $7.00$ $X_{Mg}$ $0.510$ $0.620$ $0.60$ $0.700$ $7.00$ $7.00$ $7.00$ $X_{Mg}$ $0.730$ $0.641$ $0.610$ $0.920$ $0.920$   | Na                             | 0.012       |         | 0·013  |        | 0.010 |       | 0·00  |       | 0.004  | 0.008   | Sum                            | 2·000     | 2·000   | 2·000 | 2·000   | 2·000 |
| Sum $4.047$ $4.00$ $4.09$ $4.127$ $4.00$ $3.941$ $4.00$ $4.136$ $3.955$ OH $7.000$ $7.00$ $7.00$ $7.00$ $7.00$ $7.00$ $7.00$ $X_{M_g}$ $0.510$ $0.980$ $0.620$ $0.60$ $0.700$ $7.00$ $7.00$ $X_{M_g}$ $0.510$ $0.520$ $0.60$ $0.700$ $7.00$ $7.00$ $X_{M_g}$ $0.510$ $0.980$ $0.620$ $0.60$ $0.610$ $0.920$ $X_{M_g}$ $0.280$ $0.83$ $0.470$ $0.740$ $0.520$ $0.720$   | ⊻                              |             |         | 0·012  |        |       |       | 0.012 |       |        | 0.001   |                                |           |         |       |         |       |
| OH         7-00  | Sum                            | 4·047       | 4·00    | 4·099  | 4·00   | 4·127 | 4·00  | 3.941 | 4·00  | 4·136  | 3·995   |                                |           |         |       |         |       |
| $X_{Mg}$ 0.510 0.59 0.980 0.86 0.620 0.60 0.780 0.64 0.610 0.920 $X_{Mg}^{*}$ 0.280 0.47 0.630 0.83 0.47 0.460 0.52 0.260 0.700  | НО                             | 7·000       | 7·00    | 7·000  | 7·00   | 7·000 | 7·00  | 7·000 | 7·00  | 7·000  | 7·000   |                                |           |         |       |         |       |
| $X_{M_9}^*$ 0.280 0.47 0.630 0.83 0.470 0.47 0.460 0.52 0.260 0.700  | $X_{\rm Mg}$                   | 0.510       | 0.59    | 0·980  | 0·86   | 0-620 | 0.60  | 0.780 | 0.64  | 0.610  | 0.920   |                                |           |         |       |         |       |
|  | $X_{Mg}^*$                     | 0·280       | 0.47    | 0.630  | 0·83   | 0.470 | 0-47  | 0.460 | 0·52  | 0·260  | 0.700   |                                |           |         |       |         |       |

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(continued)

Table 2: Continued

#### Table 2: Continued

|                                | Feldspar |        |        |         |       |        |        |
|--------------------------------|----------|--------|--------|---------|-------|--------|--------|
|                                | MD26     | MD9804 | MD9804 | 04CH18c | MD5   | MD0518 | MD0518 |
| SiO <sub>2</sub>               | 68·9     | 65·3   | 69·4   | 68·3    | 67·3  | 63·3   | 64·88  |
| Al <sub>2</sub> O <sub>3</sub> | 19·5     | 19·5   | 20.3   | 19·5    | 19.2  | 19·6   | 17.84  |
| TiO <sub>2</sub>               | 0.38     | 0.01   | 0.01   | 0.01    | b.d.  | b.d.   | b.d.   |
| FeO                            | 0.26     | 0.11   | 0.02   | 0.26    | 0.36  | 1.75   | 0.29   |
| MgO                            | 0.56     | 0.01   | b.d.   | 0.03    | n.d.  | 2.88   | 0.01   |
| MnO                            | 0.04     | 0.01   | b.d.   | b.d.    | n.d.  | b.d.   | 0.01   |
| CaO                            | 0.76     | b.d.   | 0.04   | 0.27    | 0.39  | 0.31   | b.d.   |
| BaO                            | n.d.     | n.d.   | n.d.   | n.d.    | b.d.  | b.d.   | 0.40   |
| Na <sub>2</sub> O              | 10.8     | 0.06   | 10.9   | 11·3    | 11·5  | 10.8   | 0.07   |
| K <sub>2</sub> O               | 0.14     | 15·99  | 0.06   | 0.00    | 0.02  | 0.27   | 16.21  |
| Sum                            | 101.1    | 101·0  | 100.8  | 99·7    | 99.0  | 98.9   | 99.7   |
| Si                             | 2.981    | 2.977  | 2.992  | 2.993   | 2.979 | 2.844  | 3·015  |
| Al <sup>IV</sup>               | 0.019    | 0.023  | 0.008  | 0.007   | 0.022 | 0.156  | 0.000  |
| Sum                            | 3.000    | 3.000  | 3.000  | 3.000   | 3.000 | 3.000  | 3.015  |
| Al <sup>VI</sup>               | 0.975    | 1.024  | 1.026  | 1.000   | 0.978 | 0.882  | 0.977  |
| Fe                             | 0.010    | 0.004  | 0.002  | 0.010   | 0.012 | 0.066  | 0.011  |
| Mg                             | 0.017    |        |        | 0.002   |       | 0.193  | 0.001  |
| Mn                             | 0.002    |        |        |         |       |        |        |
| Sum                            | 1.016    | 1.029  | 1.029  | 1.012   | 0.990 | 1.142  | 0.990  |
| Са                             | 0.035    |        | 0.002  | 0.013   | 0.085 | 0.015  |        |
| Ва                             |          |        |        |         |       |        | 0.007  |
| Na                             | 0.909    | 0.005  | 0.912  | 0.957   | 0.984 | 0.945  | 0.007  |
| К                              | 0.008    | 0.930  | 0.003  | 0.000   | 0.001 | 0.015  | 0.961  |
| Sum                            | 0.952    | 0.935  | 0.917  | 0.970   | 0.997 | 0.975  | 0.975  |
| Ο′                             | 8.000    | 8.000  | 8.000  | 8.000   | 8.000 | 8.000  | 8.000  |
| Albite                         | 0.038    | 0.000  | 0.002  | 0.013   | 0.079 | 0.015  | 0.000  |
| Anorthite                      | 0.955    | 0.005  | 0.995  | 0.987   | 0.919 | 0.969  | 0.007  |
| Orthoclase                     | 0.008    | 0.995  | 0.004  | 0.000   | 0.001 | 0.016  | 0.986  |

calc., calculated with PERPLE\_X (at 300°C, 5.6 kbar); b.d., below detection limit; n.d., not determined. For garnet, cations are based on 48 negative charges, including 10 cations in the tetrahedral and octahedral site to calculate  $Fe^{3+}$ . For white mica, the proportion of cations is based on 42 negative charges neglecting the interlayer cations; the sum of octahedrally coordinated cations is set at 4.1 to allow for an estimation of  $Fe^{3+}$ . For chlorite, cations are based on 56 negative charges;  $H_2O$  is calculated on the basis of OH = 16. For amphibole, proportion of cations is based on the sum of cations = 13, except for Ca, Na and K for estimation of  $Fe^{3+}$ , and on 46 negative charges. For epidote, proportion of cations is based on the sais of OH = 4; estimation of  $Fe^{2+}$  by assuming the X-position filled with divalent cations. For clinopyroxene, normalization to four cations is used to calculate  $Fe^{3+}$ . For feldspar, normalization is on the basis of 16 negative charges.

\*Calculated with Fetotal.

Preparation and measurements for determination of the Kübler Index of white mica were carried out at the Universidad de Chile in Santiago. The <2  $\mu$ m fraction of pelitic rocks was separated using a HERMLE centrifuge and measured with a SIEMENS D5000 X-ray powder diffractometer using quartz as a standard, Cu K $\alpha$  radiation and automatic primary as well as secondary divergence

slits. Operating conditions were 40 kV acceleration voltage and 30 mA current. Each specimen was scanned from 2 to  $23^{\circ}2\theta$  in steps of  $0.02^{\circ}2\theta$  and an integration time of 5 s. Peaks were analyzed using the EVA software provided by SIEMENS.

 $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$  dating was performed in the  $^{40}\mathrm{Ar}/^{39}\mathrm{Ar}$  geochronology laboratory at the Universität Potsdam after JOURNAL OF PETROLOGY VOLUME 50 NUMBER 11 NOVEMBER 2009

Table 3: Whole-rock analyses and simplified compositions (also corrected for clinopyroxene content) used for the calculation of pseudosections (Figs 6–9)

|                                | Whole-roo | k analyses | 6      |       |       |        |       |         |                   | Simplified | compositi | ons    |       |       |        |
|--------------------------------|-----------|------------|--------|-------|-------|--------|-------|---------|-------------------|------------|-----------|--------|-------|-------|--------|
| Sample:                        | 04CH18A   | MD9804     | MD063B | MD26  | MD5   | SLL853 | MD066 | MD0511D |                   | 04CH18A    | MD9804    | MD063B | MD26  | MD5   | SLL853 |
| SiO <sub>2</sub>               | 48·1      | 45·8       | 47·9   | 50·5  | 47·2  | 49·0   | 43·5  | 43·4    | SiO <sub>2</sub>  | 47·4       | 45·9      | 48·3   | 50·5  | 46·6  | 49·0   |
| TiO <sub>2</sub>               | 1.01      | 0.53       | 0.64   | 1.10  | 0.96  | 1.16   | 0.57  | 0.53    | TiO <sub>2</sub>  | 1.17       | 0.53      | 0.65   | 1.14  | 1.12  | 1.23   |
| $AI_2O_3$                      | 13·6      | 14·5       | 16.1   | 13·4  | 14.4  | 14·2   | 15.6  | 16·7    | $Al_2O_3$         | 16.3       | 14·5      | 16.2   | 13·9  | 19·2  | 15.7   |
| FeO                            | 7·91      | 6.56       | 4.60   | 6.48  | 6.80  | 9.56   | 8.48  | 8·52    | $\rm FeO_{tot}$   | 11.7       | 9·15      | 8·75   | 9·71  | 8.04  | 11·5   |
| Fe <sub>2</sub> O <sub>3</sub> | 3.25      | 2.85       | 4·52   | 3.34  | 3.30  | 1.74   | 0.96  | 4.00    | MgO               | 8·14       | 16·6      | 8.04   | 9.39  | 5·77  | 4.49   |
| MgO                            | 9.60      | 16.49      | 7·97   | 9.78  | 8·13  | 5.49   | 15·16 | 7.39    | CaO               | 5.53       | 3.29      | 5.95   | 7.51  | 9.90  | 10.1   |
| MnO                            | 0.16      | 0.14       | 0.09   | n.d.  | 0.16  | 0.17   | 0.13  | 0.10    | Na <sub>2</sub> O | 3·27       | 0.91      | 2.21   | 1.91  | 3.73  | 3.64   |
| CaO                            | 8·24      | 3.28       | 5.90   | 8·11  | 12·3  | 10.9   | 1.49  | 7.04    | K <sub>2</sub> 0  | 0.36       | 0.68      | 2.26   | 0.18  | 0.12  | 0.06   |
| Na <sub>2</sub> O              | 2.72      | 0.91       | 2·19   | 1.82  | 2.75  | 3.28   | 2.65  | 3.07    | H <sub>2</sub> O  | 5·97       | 8·15      | 6.96   | 5.06  | 5·19  | 4·21   |
| K <sub>2</sub> 0               | 0.29      | 0.68       | 2.24   | 0.17  | 0.09  | 0.02   | 0.23  | 1.57    | CO <sub>2</sub>   | 0.00       | 0.00      | 0.45   | 0.53* | 0·14* | 0.00   |
| P <sub>2</sub> O <sub>5</sub>  | 0.06      | 0.09       | 0.22   | n.d.  | 0.10  | 0.21   | 0.08  | 0.25    | 0 <sub>2</sub> †  | 0.15       | 0·15      | 0.15   | 0.15  | 0.15  | 0.15   |
| H <sub>2</sub> O/LOI           | 4·74      | 8·13‡      | 6·90‡  | 5·30‡ | 3·84‡ | 3·77‡  | 9.67  | 7·20‡   |                   | 100.0      | 100.0     | 100.0  | 100.0 | 100.0 | 100.0  |
| CO <sub>2</sub>                | 0.00      | n.d.       | 0.45   | n.d.  | n.d.  | n.d.   | 0.39  | n.d.    |                   |            |           |        |       |       |        |
| Sum                            | 99.6      | 99.9       | 99.8   | 100.0 | 96.3  | 99.6   | 98.6  | 99·7    |                   |            |           |        |       |       |        |
| FeO <sub>tot</sub>             | 10.8      | 9·13       | 8·67   | 9.49  | 9.77  | 11.1   | 9.34  | 12·1    |                   |            |           |        |       |       |        |
| Cpx§                           | 0.22      | 0.00       | 0.00   | 0.05  | 0.27  | 0.10   | 0.00  | 0.00    |                   |            |           |        |       |       |        |

SLL853 is a metabasite from the Chonos Archipelago (Hervé et al., 1999). n.d., not determined.

\*CO<sub>2</sub> estimated according to calcite content in the rock.

<sup>†</sup>Content of O<sub>2</sub> used for calculation.

‡Loss on ignition.

Scontent of clinopyroxene as a fraction of 1.

neutron activation of polished sections (1 cm diameter) at the Geesthacht Neutron Facility (GeNF) of the GKSS in Geesthacht, Germany. The polished thick sections were wrapped in commercial Al foils and set into a 99.999% pure Al holder of 20 mm diameter and 88 mm height consisting of 18 stacked Al disks. The package was Cd-shielded and irradiated with fast neutrons with a flux of  $1 \times 10^{12}$ n/cm<sup>2</sup>/s for 97 h. The Fish Canyon Tuff sanidine (age 27.5 Ma; Uto et al., 1997; Ishizuka et al., 2002) was used as a flux monitor during irradiation to obtain the I values, which reflect the degree of neutron activation for the irradiated samples. K<sub>2</sub>SO<sub>4</sub> and CaF<sub>2</sub> crystals were also irradiated to correct interference of Ar isotopes produced by the reactions on K or Ca in the samples. The Ar isotopic analytical system at Universität Potsdam consists of (1) a New Wave Gantry Dual Wave laser ablation system with a  $50 \text{ W CO}_2$  laser (wavelength 10.6 µm) and 6 mJ UV pulse laser (wavelength 266 nm, frequency-quadrupled) for heating and extracting gas from the samples, (2) an ultrahigh-vacuum purification line with SAES getters and a cold trap and (3) a Micromass 5400 noble gas mass spectrometer with a high sensitivity and an ultralow background. The mass spectrometer has a pulse counting system with an electron multiplier, which works effectively for the analysis of very small amounts of gas. Fish Canyon Tuff sanidine and the K<sub>2</sub>SO<sub>4</sub> and CaF<sub>2</sub> crystals were heated using a defocused continuous CO<sub>2</sub> laser beam with a similar diameter to the grain size for 1 min. The samples of unknown age were ablated by a UV pulse laser at the following conditions: 50 µm beam size, 2 min pulse duration and 10 Hz repetition rate. The extracted gas was exposed to SAS getters and a cold trap, in which the metal fingertube was cooled to the freezing temperature of ethanol for 10 min to purify the sample gas to pure Ar gas. Finally, the purified Ar gas was introduced into the Micromass 5400 noble gas mass spectrometer to determine the Ar isotopic ratios. The Ar isotopic ratios of the sample gas were finally obtained after corrections of blank, mass discrimination by the analytical results of atmospheric argon, interference of the Ar isotopes derived from Ca and K by the irradiation, and the decay of the radiogenic Ar isotopes (<sup>37</sup>Ar and <sup>39</sup>Ar) produced by the irradiation. The calculation of the ages and errors was performed according to Uto et al. (1997). The data are presented in Table 4.

#### **RESULTS Petrographic and mineral chemical characteristics**

A conspicuous feature of most MDMC rocks is the preservation of primary fabrics even at microscopic scale as a result of a general lack of penetrative internal deformation. In most metabasite samples a former subophitic texture of intergrown clinopyroxene and plagioclase crystals or a porphyritic texture with clinopyroxene phenocrysts (0.5-3 mm) in a feldspar-rich groundmass is variably preserved, although generally partly to completely pseudomorphed (Fig. 2). Amygdales with a mono- or bimineralic fill of quartz, chlorite, calcite and/or epidote (0.5-4.0 mm diameter; Fig. 2d) represent an additional common primary feature in the metabasites.

Clinopyroxene is augite with a widely variable composition (diopside<sub>36-58</sub>, hedenbergite<sub>7-15</sub>, enstatite<sub>18-49</sub>, acmite<sub>0-7</sub>, Tschermak component<sub>0-1</sub>) including traces of Ti (0·004-0·019 a.p.f.u.) and Mn (0·003-0·011 a.p.f.u.). According to Sepúlveda *et al.* (2008) its composition is typical for non-alkaline basalts. Relict plagioclase compositions range between 48 and 79 and 19 and 27 mol % anorthite. Some samples contain chromite crystals in the groundmass, which are typically reddish brown, anhedral to euhedral grains (0·02-0·4 mm), commonly with an alteration halo. Internal deformation in the metabasites is represented only by fissures, mostly with a monomineralic fill of pumpellyite, chlorite, epidote, white mica or calcite.

The metamorphic assemblages in the metabasite are (Table 1):

- (l) actinolite-pumpellyite-epidote-chlorite-white micaalbite-quartz-titanite ± calcite;
- (2) pumpellyite-epidote-chlorite-albite-quartz-titanite ± calcite ± white mica ± K feldspar;
- (3) garnet (grandite)-pumpellyite-epidote-chloritealbite-quartz-titanite ± white mica;
- (4) actinolite-garnet (grandite) epidote-chloritewhite mica-albite-quartz-titanite ± pumpellyite ± K-feldspar ± calcite.

The metabasites of the MDMC appear to lack stilpnomelane, although this mineral was observed in the metachert of the DU (Sepúlveda, 2004). Metamorphic minerals are heterogeneously distributed and can form small monomineralic clusters of 0.2-1 nm size of chlorite, pumpellyite, epidote, titanite-chlorite intergrowths, garnet, actinolite or white mica (Fig. 2). The crystal size within the clusters is generally between 10 and 30 µm, but may be up to 100 µm for chlorite or actinolite. Titanitechlorite intergrowths form pseudomorphs probably after primary ilmenite. Actinolite, chlorite and pumpellyite mainly replace clinopyroxene, whereas white mica and to a lesser degree also epidote form pseudomorphs after plagioclase (Fig. 2).

In the metapsammopelitic rocks of the DU and DYU the relic clastic fabric is preserved without or with only a very low degree of recrystallization of quartz in the matrix. The size of the newly grown quartz grains in the matrix is <0.02 mm. Whereas a cleavage is well developed in the metapelites, the metapsammites show only an incipient banding of phyllosilicate and quartz-rich domains of millimetre spacing. Metamorphic white mica and chlorite grew parallel to the incipient cleavage. Detrital phyllosilicates are mechanically rotated parallel to the cleavage and bent. Some quartz clasts in contact with white mica show incipient pressure solution effects causing a slight shape-preferred orientation. The metapsammopelitic rocks still exhibit relic clastic components, predominantly angular to subrounded clasts of quartz, albite, white mica, biotite and minor K-feldspar. Lithic clasts are mainly shale, siltstone, quartzite, mylonite, rare basalt and rhyolite. Heavy minerals are mainly zircon and tourmaline as well as minor titanite, garnet, apatite, pyrite and Fe-Ti oxides.

The composition of white mica in the metabasite samples varies considerably, but the range is similar between samples (Fig. 3; Table 2): Si 3.07-3.54 a.p.f.u. with phengite compositions (Si >3·2 a.p.f.u.) predominating, very low Ti (0.00–0.02 a.p.f.u.) and intermediate  $X_{Mg}$  [Mg/  $(Fe^{2+} + Mg); 0.30-0.64]$ . Notably, a considerable margarite component may occur in some white mica grains within samples 04CH18c, 04CH17c, MD06-5B, MD06-11D and MD06-8 (Ca 0.02-0.14 a.p.f.u.), whereas most grains are devoid of Ca. Similarly, the Na content varies considerably between grains of a single sample and between the studied samples (Na 0.005-0.150 a.p.f.u.). The erratic and occasionally high Ca and Na contents are incompatible with the low metamorphic grade as a result of the known solvus relationships (e.g. Chatterjee & Froese, 1975; Höck, 1974). It is assumed that small domains of margarite and paragonite are intergrown with potassic white mica and that the occasionally high Ca and Na contents actually represent mixed analyses of such domains. In sample MD9804 two generations of phengite with significant compositional differences, particularly regarding the calculated Fe<sup>3+</sup> contents, were detected (Fig. 3, Table 2): white mica I (Si 3.68-3.73 a.p.f.u., Fe<sup>3+</sup> 0.97-1.11 a.p.f.u.,  $X_{Mg}$  0.74-0.81and white mica II (Si 3.45-3.59 a.p.f.u., Fe<sup>3+</sup> 0.00-0.36a.p.f.u.,  $X_{Mg}$  0.55–0.78). White mica I appears to be almost glauconite in composition according to the definition of Bailey (1980). In all metabasite samples occasional high calculated Fe<sup>3+</sup> contents occur (0.06-0.14 a.p.f.u.). Mixtures of chlorite and phengite can be excluded as an explanation, because the white mica was analysed in clusters devoid of chlorite.

White mica in the metapsammopelites always occurs in two generations: detrital mica is characterized by larger grain size (0.05-4 mm), lower Si content (3.03-3.38 a.p.f.u.), higher Ti content (0.005-0.075 a.p.f.u.), higher Na content



**Fig. 2.** Photomicrographs showing clustering phenomena. (a, b) Former subophitic texture of clinopyroxene (Cpx) and plagioclase replaced by an assemblage of clusters of chlorite (Cll) growing at the expense of clinopyroxene, of titanite-chlorite intergrowths (TtCl) replacing ilmenite and of white mica (Wm) replacing plagioclase. On the left-hand side, chlorite (Cl2) fills a fissure that opened twice (see arrow); widths of images are 175 mm (sample 04CH17); (a) crossed polars' (b) parallel polars. (c) White mica cluster (Wm) replacing a plagioclase phenocryst cut by a late chlorite-filled fissure (arrows); in the upper part of the image white mica replaces smaller randomly oriented former plagioclase with interstices filled by titanite-chlorite clusters (TtCl); width of image is 0.7 mm (sample MD26); crossed polars. (d) Epidote clusters (Ep) replacing former plagioclase in an assemblage with clusters of chlorite (Cl) and titanite-chlorite intergrowths (TtCl); an amygdule filled by quartz and chlorite occurs in the upper left corner; width of image is 0.7 mm (sample MD9); crossed polars.

(0.02-0.16 a.p.f.u.) and more variable  $X_{Mg}$  (0.34-0.66)compared with metamorphic white mica (0.01-0.05 mm), which is invariably phengite (Si 3·35-3·50 a.p.f.u.; Ti 0.001-0.010 a.p.f.u.; Na 0.00-0.02 a.p.f.u.;  $X_{Mg}$  0.52-0.62). White mica compositions in all samples mostly plot close to the ideal line of the Tschermak's substitution except for sample MD 9804 and partly MD 06-8 with considerable Fe<sup>3+</sup> substitution (Fig. 3a). Only a few samples contain some metamorphic white mica grains (particularly sample MD 9804) with a reduced interlayer occupancy between 0.8 and 0.9 a.p.f.u., whereas most of the studied white mica have identical interlayer occupancies to those formed during low-grade conditions (e.g. Willner, 2005). The observed minor reduction of interlayer occupancy may be due to some substitution of the pyrophyllite component towards illite as a result of the

 $KAl^{IV} \square_{-1}Si_{-1}$  and  $KR^{2+}Al^{VI} \square_{-1} \square_{-1}$ substitutions (R = Mg, Fe). According to an IMA recommendation the term illite should only be used for interlayer-cationdeficient micas with K + Na < 0.85 a.p.f.u. (Rieder *et al.*, 1998) and illite usually has an interlayer occupancy of c. 0.75 (Srodon & Eberl, 1984). Thus, at most, a small amount of illite is actually present in our samples. This concurs with similar observations made by the systematic study of Abad et al. (2006) that true illite compositions are rather rare with respect to muscovite-phengite compositions at very low grade and low-grade conditions. Similarly, muscovite and phengite has been reported from pumpellyite-actinolite-facies schists in the Swiss Alps and in New Zealand (e.g. Coombs et al., 1976, 1977). Interestingly, there is a systematic major element correlation in white micas: generally, a systematic variation of



Fig. 3. Si vs Al and Si vs  $X_{Mg}$  variations of white mica in the metabasite and metapsammopelite samples of the MDMC.

increasing  $X_{Mg}$ , a temperature-dependent parameter, with increasing Si content, a pressure-dependent parameter, can be observed (Fig. 3b).

Chlorite is ubiquitous in all samples. Chlorite generally shows a wide range of Si contents compared with a restricted  $X_{\rm Mg}$  range within single samples (Table 2; Fig. 4). Conversely,  $X_{\rm Mg}$  varies widely between samples (0·3–0·85) because of the variation in whole-rock composition, but also the range of Si contents within the samples varies considerably (5·4–6·8 a.p.f.u.). Mn is the only trace element with significant contents (0·02–0·06 a.p.f.u.; rarely up to 0·08–0·14 a.p.f.u.). No distinct chlorite generations as a result of compositional differences were detectable.

Garnet occurs as clusters of crystals (10–20  $\mu$ m size) in the metabasite samples MD98-03, MD98-04 and MD06-5B and is invariably grandite in composition (andradite<sub>37–46</sub>, grossular<sub>50–6b</sub> spessartine<sub>0.2-1.b</sub>, pyrope<sub>0.1-1.7</sub>, almandine<sub>0.0-2.4</sub>, uvarovite<sub>0.0-2.0</sub>). Rare elevated Cr contents of 0.1-0.5 a.p.f.u. were locally detected in some grains in samples MD98-03 and MD98-04.

Epidote contains 67–98 mol % (mostly above 80 mol %) pistacite component (Table 2). The distribution of Fe within the grains is rather patchy. A different population of epidote was detected in three samples with considerably lower pistacite contents of 41–58 mol % (04CH18, MD26, MD05-18) or 25–27 mol % (MD26). The only notable minor element is Mn (0.005–0.018 a.p.f.u., occasionally up to 0.05 a.p.f.u.).

Amphibole is actinolite (Si 7·83–8·00 a.p.f.u.) with some calculated Fe<sup>3+</sup> (0·03–0·59 a.p.f.u.), some Na<sup>B</sup> contents (0·03–0·20 a.p.f.u.) and a high  $X_{\rm Mg}$  (0·60–0·82).  $X_{\rm Fe}^{2+}$  [Fe<sup>2+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>); 0·38–0·96] varies considerably, possibly as a result of variable oxidation fugacities.

Pumpellyite shows a positive correlation between  $X_{\rm Fe}^{3+}$  [Fe<sup>3+</sup>/(Fe<sup>3+</sup> + Al); 0·38–0·92] and  $X_{\rm Mg}$  (0·62–0·94) as well as some trace elements; for example,



Fig. 4. Si vs  $X_{Mg}$  variation of chlorite in metabasite and metapsammopelite samples of the MDMC.

Ti (0·001–0·147 a.p.f.u.), Mn (0·000–0·025 a.p.f.u.) and Na (0·003–0·023 a.p.f.u.). Metamorphic feldspar is pure albite and/or K-feldspar. The latter mineral was observed in the metabasite samples MD98-04, MD05-18 and MD06-3B (Table 2).

# General phase relations and metamorphic conditions

The prevalence of very low grade metamorphism in the MDMC is evident from the following observations. The general lack of quartz recrystallization in the matrix of the metagreywackes and preservation of datable radiolarians in the cherts (Ling *et al.*, 1985) associated with the DU metabasites suggest that maximum temperatures would not have significantly exceeded 300°C. Quartz fabrics in the metagreywackes resemble those of type C of Brix *et al.* (2002) that are shown to have prevailed at a temperature of  $300-320^{\circ}$ C. In addition, a temperature of about  $280^{\circ}$ C, at which fission tracks in zircon anneal at mean cooling rates (Rahn *et al.*, 2004), must have been reached or overstepped, because all detrital zircon in the two metagreywacke samples studied has been entirely reset (Thomson & Hervé, 2002).

The Kübler Index (KI; Kübler, 1968) is a common semiquantitative temperature indicator at very low grade to low-grade metamorphism that integrates over the strongly variable compositions of potassic white mica present in the rock. For the determination of the KI, four metapelite samples from a transitional contact zone between the DU and the DYU were analyzed. Samples MD04-1A and MD04-1B were taken from the DYU and samples MD04-8A and MD04-8AB represent red siliceous argillite from the DU intercalated within the chert. All samples were composed of white mica, chlorite, quartz and hematite. KI values vary as follows: 0.28  $\Delta^{\circ}2\theta$  for MD04-8AB and MD048A; 0.30  $\Delta^{\circ}2\theta$  for MD04-1A; 0.32  $\Delta^{\circ}2\theta$  for MD04-1B. These values correspond to anchizonal conditions representing temperatures between 200° and 300°C. No break of metamorphic conditions appears to exist between the major units of the MDMC.

An obvious lack of very low grade minerals such as laumontite and prehnite precludes metamorphism at LP conditions, including ocean-floor metamorphism. This agrees with the ubiquitous occurrence of metamorphic indicators of elevated pressure such as phengite. On the other hand, typical HP phases, such as lawsonite and Na-amphibole, are absent. The prevalent assemblages in the DU metabasites define conditions of the pumpellyite-actinolite facies at intermediate pressures. Figure 5 indicates the approximate limits of the actinolite-pumpellyite facies for the MDMC. The multivariant boundary reactions were calculated with averaged activities of end members of solid solutions in the system CMASH as realized in the rocks of the DU (for the method see below). The extent of the stability field of the actinolite-pumpellyite facies is largely defined by the presence of pumpellyite + chlorite. At the transition to the lawsonite-blueschist facies a subfacies field exists where both minerals coexist with glaucophane. It is notable that the pumpellyite-actinolite facies occupies an intermediate pressure field, corresponding to a geothermal gradient of  $\sim 11-25^{\circ}$ C/km (calculated using 2.8 g/cm<sup>3</sup> as the mean crustal density). This field also extends into the



**Fig. 5.** Petrogenetic grid for the pumpellyite–actinolite facies with limiting multivariant reactions calculated with mean activities of the following end-members in the system CNMASH as realized in the studied rocks (in parentheses): lw, lawsonite (1 0); gl, glaucophane (0·4); cl, chlinochlor (0·1); pu, Mg-pumpellyite (0·7); cz, clinozoisite (0·2); tr, tremolite (0·7); qz, quartz (1 0); ab, albite (1 0); v, H<sub>2</sub>O fluid (1 0); pr, prehnite (1 0). Shaded area indicates the field of metamorphic gradients between 11 and  $25^{\circ}$ C/km.

field of HP greenschist facies (Fig. 5). It deviates strongly from the metamorphic geotherm of  $8-10^{\circ}$ C/km typically deduced from HP–LT rocks that were overprinted directly above a subducting slab (e.g. Agard *et al.*, 2009) and presumably represents a hotter region of the subduction system.

### Phase relations observed in *PT* pseudosections

For an advanced assessment of phase relations, geothermobarometric constraints and equilibrium conditions at very low to low grade we calculated PT pseudosections in the system K<sub>2</sub>O-Na<sub>2</sub>O-CaO-FeO-O<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> at 200-400°C and 1-9 kbar with the PERPLEX software package (Connolly, 1990, 2005; version of August 2006 downloaded from www.perplex .ethz.ch). The thermodynamic dataset of Holland & Powell (1998, updated 2002) for minerals and aqueous fluid was used. This dataset was recently enlarged using end-member data for Fe<sup>2+</sup>- and Fe<sup>3+</sup>-pumpellvite, Fe<sup>2+</sup>and Mg-stilpnomelane, actinolite and magnesioriebeckite (Massonne & Willner, 2008). Calculations were performed using the following solid-solution models: for white mica, epidote, chlorite and biotite by Holland & Powell (2003) and Powell & Holland (1999), grandite by Engi & Wersin (1987) and amphibole, sodic clinopyroxene, pumpellyite and stilpnomelane by Massonne & Willner (2008). The selected amphibole model provides a better adaptation to very low grade and low-grade conditions, whereas the selected clinopyroxene model is the Holland & Powell (1996) model supplemented by the aegirine component, which is often enhanced at very low grade conditions. The solid-solution models of white mica, epidote, chlorite, biotite and grandite were selected from the distributed version of the PERPLEX solution model file. The solid-solution models of amphibole, sodic clinopyroxene, pumpellyite and stilpnomelane are added to this file as described by Massonne & Willner (2008). Albite, K-feldspar, quartz, titanite,  $H_2O$  and paragonite were considered as pure phases.

We selected five metabasite samples from the MDMC (MD5, MD26, MD98-04, 04CH18 and MD06-3) covering the entire range of observed assemblages (Table 1), and an additional metabasite sample (SLL853) from the very low grade Eastern Belt of the Chonos Archipelago for comparison. This sample contains a stilpnomelane-bearing assemblage that was not observed in the MDMC (Tables 1 and 3). In some samples a considerable amount of magmatic clinopyroxene remains despite complete reaction of this phase to form metamorphic phases in other samples. This amount was subtracted from the original bulk-rock analyses. Furthermore, for an optimal reproducibility of the

assemblages realized in the MDMC we used a slightly reduced oxygen content (uniformly 0.15 wt % O2, which is related to Fe<sup>3+</sup> by the PERPLEX software) compared with the determined Fe<sub>2</sub>O<sub>3</sub> contents of the rock. These Fe<sub>2</sub>O<sub>3</sub> contents were higher than that of the metamorphic mineral assemblage because of the presence of hematite along grain boundaries formed by weathering. On the other hand, we kept the water content at the amount measured in the samples, because calculations with the PERPLEX software shows that at water excess conditions the entire rocks would have reacted to a higher quantity of hydrous minerals than observed. Although we included  $CO_2$  as a component to calculate calcite, we did not consider it as a volatile component. Hence a pure H<sub>2</sub>O fluid was used in the calculations for simplicity. However, corresponding calculations with a H<sub>2</sub>O-CO<sub>2</sub> mixture have shown that the fluid is virtually entirely composed of H<sub>2</sub>O at the selected PT conditions.

The *PT* pseudosections obtained (Figs 6–10; summary in Fig. 6) for the selected six metabasite compositions show a successful reproduction of the stability fields of the actual mineral assemblages within the pumpellyite–actinolite facies and also display the varying stability fields of critical very low grade phases that are consistent with phase relations as proposed and calculated by Katagas & Panagos (1979), Evans (1990), Frey *et al.* (1991) and Banno (1998) in the NC(F)MASH system (see also Massonne & Willner, 2008). Furthermore, selected calculated compositions of solid solutions (at approximate peak conditions of  $5\cdot 6$  kbar,  $300^{\circ}$ C) concur well with analyzed compositions that are probably representative for peak metamorphic conditions (see Table 2).

Chlorite, amphibole and titanite are present at all calculated *PT* conditions. Pumpellyite in the presence of chlorite is stable within a very low grade field between 2 and 9 kbar and up to 300-350°C, whereas prehnite occurs below 3 kbar and 300–320°C.  $X_{Mg}$  $=X_{Mg}$  $(X_{Mg} + X_{Fetotal})$ ] in pumpellyite rises with pressure and temperature with minimum values (0.40-0.46) below 3 kbar and 250°C (Figs 7 and 9). Lawsonite appears above 4-5 kbar and below 300-350°C. Laumontite occurs below 4-5 kbar and 300°C. Stilpnomelane can be stable in the entire very low grade field up to 300°C; biotite appears above 300-350°C. Epidote generally is a stable phase at very low grade conditions already between 200 and 250°C. Calculated Fe<sup>3+</sup> contents are somewhat lower (0.6-0.64 a.p.f.u.) than those in the measured grains (0.8-0.9 a.p.f.u.). Grandite may be stable in the entire very low grade to low-grade field up to 350°C (Fig. 8) and has identical grossular/andradite compositions to those in the measured garnets (Table 2). K-feldspar and wairakite in metabasite occur below 3 kbar and 300-350°C and 2 kbar and 300-320°C, respectively. Amphibole is actinolite with Na contents up to 0.2 a.p.f.u. at 5 kbar and

 $X_{\rm Mg} = 0.6 - 0.8$  as observed in all studied MDMC metabasite samples. At low-grade conditions and at 6-8 kbar an intermediate Na-Ca-amphibole (0.2-0.5 Na p.f.u.; Figs 7–9) is stable. This mineral occurs within all regions of the Chilean basement that are interpreted to be accretionary complexes (e.g. Willner et al., 2001; Willner, 2005). Na-amphibole appears above 5-7 kbar at very low grade conditions and above 8 kbar at low-grade conditions. At very low grade conditions, two amphiboles may be present in the LP part of the lawsonite-blueschist facies (Figs 7 and 9), but one amphibole for Fe-rich bulk-rock compositions (Fig. 8). White mica is invariably phengite in the calculated PT field with Si contents increasing with pressure and decreasing with temperature. There appears to be a maximum of Si content of 3.4-3.5 a.p.f.u., particularly in the field of the pumpellvite-actinolite facies (Figs 7 and 9), coinciding with the analyzed phengite. Whereas  $X_{Mg}$ values of calculated and measured white mica grains deviate (e.g. 0.76 and 0.62, respectively, at 300°C and 5.6 kbar), those of chlorite are comparable (Table 2).

There is a remarkably good agreement of the metamorphic assemblages in the studied rocks with the six calculated assemblages at 290–310°C, 4–6 kbar (Fig. 10a). The appearance of stilpnomelane at these conditions was calculated and observed only for sample SLL853 from the Eastern Belt of the Chonos Archipelago. On the other hand, according to the pseudosections the former presence of stilpnomelane during the prograde PT path can be predicted for samples 04CH18, MD06-3 and MD5. Stilpnomelane disappeared at maximum PT conditions outside its stability field or never nucleated as a result of overstepping of reactions. Sample MD98-04 contains some epidote, which, however, appears at the high-temperature boundary of the field marked in Fig. 10a.

The conditions of the observed mineral assemblages appear to be realized at the high-temperature end of the pumpellyite-actinolite facies. Four samples show the stable assemblage actinolite-pumpellyite. Three *PT* fields concur with the approximate outline of the pumpellyiteactinolite facies as shown in Fig. 5. It should be noted that for two metabasite samples no realistic assemblages could be calculated. The whole-rock compositions are ultrabasic (MD066 and MD05-11D; Table 3) and the number of phases in the rocks is restricted (Table 1). This shows that considerable metasomatism, presumably caused by enhanced fluid flow, affected these two rocks at some stage, causing the low number of phases.

# Geothermobarometry using multivariant equilibria

We also calculated PT conditions for the peak of metamorphism and different prograde equilibration stages using the entire range of variation of analyzed mineral compositions. We calculated multivariant reactions using the Ge0-Calc software of Brown *et al.* (1989) and derivations



Fig. 6. PT fields of minerals extracted from calculated pseudosections for the whole-rock compositions of the metabasite samples (see Table 3).



Fig. 7. Pseudosection calculated for the whole-rock composition of metabasite sample MD26 (see Table 3) with isopleths of Si a.p.f.u. in white mica, Na a.p.f.u. in amphibole and  $X_{Mg}$  in pumpellyite. Shading indicates degree of variance: white, divariant; light grey, trivariant; dark grey, quadrivariant.

(TWQ) with the thermodynamic dataset of Berman (1988) augmented by compatible thermodynamic data for the end-members glaucophane and Mg-pumpellyite by Evans (1990),clinochlore, Mg-Al-celadonite and Fe-Alceladonite by Massonne (1995a) and daphnite and muscovite by Massonne & Szpurka (1997). The activity formulations used for non-ideal solid solutions of garnet were those of Berman (1990), for chlorite and amphibole those of Massonne (1995a, 1995b), for white mica those of Massonne (1995a, 1997) and pumpellyite those of Evans (1990), whereas an ideal solution model was chosen for epidote  $(a_{\text{clinozoisite}} = 1 - X_{\text{pistacite}})$ . We preferred these data to those of Holland & Powell (1998) used for the calculation of pseudosections (see previous section) in order to obtain independent information on the maximum PT conditions

recorded. We have widely and successfully applied this approach to other low- and medium-grade rocks of the Chilean accretionary systems (e.g. Willner *et al.*, 2000, 2001, 2004; Willner, 2005). Hence, a better basis for comparison between the various Chilean accretionary complexes is given.

Because the above-described phase relations demonstrate adaptation to the conditions of the upper pumpellyite-actinolite facies without homogenization of mineral compositions, it is likely that transient prograde equilibria are locally preserved. Although it is difficult to find coexisting phases in mutual contact because of clustering of the phases, we tried to calculate local equilibria considering the wide compositional range of the relevant phases. Calculation results are shown in Fig. 11. For three samples



Fig. 8. Pseudosection calculated for the whole-rock composition of metabasite sample MD9804 (see Table 3) with isopleths of Si a.p.f.u. in white mica and Na a.p.f.u. in amphibole. Shading as in Fig. 7, and black, quintvariant.

 $(04\mathrm{CH18},\ \mathrm{MD26}$  and  $04\mathrm{CH15})$  we applied the water-independent thermometer reaction

$$daphnite_{Ch}+5 Mg-Al-celadonite_{Wm}$$
(E1)  
= 5 Fe-Al-celadonite\_{Wm}+clinochlore\_{Ch}.

This indicated a temperature range of  $200-330^{\circ}$ C during metamorphic mineral growth. Similarly, application of the water-dependent thermometer reactions

and

to samples MD05-06B and MD5, respectively, gave the same range, supporting our assumption that the fluid consists predominantly of  $H_2O$ .

A water-dependent barometer reaction

$$5 \text{ Mg-Al-celadonite}_{wm}$$
+muscovite<sub>wm</sub>  
= 2 quartz + 6 K-feldspar + clinochlore<sub>cl</sub>+2 water  
(E4)

was applied only to two K-feldspar-bearing samples (metapsammite MD06-8 and metabasite MD9804). In these samples calcite is absent and hence the water activity can be assumed to be unity. Although the pressure ranges for the two samples do not overlap, it is likely that the full range of compositions was not observed. Hence, a pressure range of 3–5 kbar at 200°C and 4–6 kbar at 300°C appears likely for the growth of minerals of the MDMC rocks also according to the *PT* calculation of mineral equilibria.

In sample MD9804 the *PT* intersection of 24 multivariant equilibria was calculated in the KCMASH system including K-feldspar and quartz and mineral end-members muscovite, Mg–Al-celadonite, Mg-pumpellyite, clinochlore, clinozoisite and grossular. Eight of these 24 equilibria are water-independent. The corresponding



Fig. 9. Pseudosection calculated for the whole-rock composition of metabasite sample 04CH18 (see Table 3) with isopleths of Si a.p.f.u. in white mica, Na a.p.f.u. in amphibole and  $X_{Mg}$  in pumpellyite. Shading as in Fig. 7, and black, quintvariant.

intersections calculated for three different local mineral assemblages vary between  $230^{\circ}$ C, 4.5 kbar and  $240^{\circ}$ C, 3.5 kbar.

For metabasite samples 04CH18 and MD26 the intersection of four multivariant reactions was calculated in the system KCFMASH including the mineral end-members muscovite, Mg–Al-celadonite, Fe–Al-celadonite, Mgpumpellyite, clinochlore, daphnite, clinozoisite and quartz. Only one of the four equilibria is waterindependent. The resulting PT intersections for each of the samples fall in the range 245–330°C, 3·9–5·8 kbar.

Summarizing the results of different but logical combinations of mineral equilibria to reconstruct transient local PT domains based on thermodynamic calculations, it can be shown that the observed variation in the chemical composition of the minerals reflects a range of temperatures that by far exceeds the narrow range of 290–310°C estimated for the peak metamorphic assemblage. Temperatures calculated for the local *PT* domains are up to 100°C lower at a similar pressure range. Some local PT domains, which are firmly constrained by the intersection of 24 multivariant equilibria, show temperatures that are  $60^{\circ}$ C lower than the derived peak T conditions. Considering an estimated error of  $\leq \pm 30^{\circ}$ C for the geothermometers at relatively low temperatures, a common assumption (e.g. Holland & Powell, 1998), this temperature difference would be significant within error Hence, we interpret the local PT domains as prograde relics indicating that the late prograde PT path evolved from  $4 \pm 1$  kbar, 200–220°C to  $5 \pm 1$  kbar, 290–330°C and, thus, in the medium-pressure part of the pumpellyite-actinolite facies related to metamorphic geotherms between  $13^{\circ}C/km$  (at the beginning) and  $25^{\circ}C/km$ . Maximum PT conditions are broadly identical to those derived from the



Fig. 10. (a) Calculated PT fields of the peak metamorphic assemblages observed in six selected metabasite samples. (b) PT fields of actinolite-pumpellyite for four selected metabasite samples.



Fig. 11. PT diagram showing the maximum PT spread of calculated reactions and equilibria. The approximate prograde PT path is shown (grey arrow).

calculation of the pseudosections. This result is, however, based on the assumption that all rocks in the study area evolved along similar PT paths, at least within the given PT range.

#### Ar/Ar geochronology

We analyzed the  ${}^{40}\text{Ar}/{}^{39}\text{Ar}$  systematics of white mica in three metabasite samples (MD0511D, 04CH17c, 04CH18)

and one metapelite sample (04CH15) using the *in situ* UV laser ablation technique to obtain the age of the very low grade metamorphism. We selected this method because peak metamorphic temperatures in the MDMC are considerably below the commonly accepted value ( $\sim$ 350–420°C) of the white mica Ar closure temperature (McDougall & Harrison, 1999, and references therein) and, thus, the ages reflect white mica growth ages rather

than cooling ages. The UV laser ablation technique of Kelley *et al.* (1994) allows detection of age heterogeneities at thin-section scale. Although the beam size of 50  $\mu$ m exceeded the size of single crystals, clusters of only a few adjacent white mica crystals were analyzed. The white mica clusters in the metabasite are monomineralic, whereas the white mica in the metapelite is always intergrown with some chlorite. The presence of detrital mica in the metapelite is unlikely, because the selected slate 04CH15 represents a pelagic clay deposited on top of oceanic crust before metamorphism. The results are presented in Fig. 12 and Table 4. An earlier attempt to date titanite-chlorite clusters by U/Pb laser ablation failed because of the low U concentrations.

Three samples show a distribution of single-spot ages at thin-section scale with identical ages within the limits of the  $1\sigma$  errors: a weighted mean age of  $200.8 \pm 2.4$  Ma results for metabasite MD0511D,  $233 \cdot 2 \pm 1.8$  Ma for metapelite 04CH15 and  $152.0 \pm 2.2$  Ma for metabasite 04CH17c. The rather homogeneous spot ages in metapelite 04CH15 again demonstrate that no detrital white mica is present in the sample. On the other hand, metabasite 04CH18c shows a rather wide scatter of ages at thin-section scale ranging from  $127.5 \pm 32.4$  to  $206.9 \pm 16.0$  Ma, including substantial errors for the single-spot ages. Analyses of the metabasite samples generally show relatively high  ${}^{37}\text{Ar}/{}^{39}\text{Ar}$  and  ${}^{37}\text{Ar}_{\text{Ca}}/{}^{39}\text{Ar}_{\text{K}}$  values. We suggest that this is due to some contamination of the measured spots with titanite. Because titanite belongs to the same metamorphic assemblage as the dated white mica, no mixture of ages should be expected.

The weighted mean age of  $200.8 \pm 2.4$  Ma for the metabasite MD0511D is identical to the normal and inverse isochron ages (196.4 ± 8.0 Ma and 199.3 ± 7.5 Ma respectively; Fig. 12) and its initial  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio of  $302 \pm 28$  in the inverse isochron plot is close to that of atmospheric Ar (295.5). The inverse isochron plot reveals a simple mixture of radiogenic and 21–41% atmospheric Ar. Also, the weighted mean age of  $233.2 \pm 1.8$  Ma for the metapelite 04CH15 is identical to the normal and inverse isochron ages (239.5 ± 8.6 Ma and  $243.0 \pm 8.3$  Ma respectively) within the 1 $\sigma$  error.

Both samples with considerably younger ages (04CH17c and 04CH18c) also show rather high contents of atmospheric Ar (52–93%) and their initial  ${}^{40}$ Ar/ ${}^{36}$ Ar ratios of 291 ±3 and 305 ±3 are close to that of atmospheric Ar. In sample 04CH17c the weighted mean age of 152·0±2·2 Ma is nearly identical to the normal and inverse isochron ages (both 156·8±3·7). In sample 04CH18 the weighted mean age is calculated as 151.6±4·4 Ma, although single age values vary significantly from 128 to 207 Ma. Isochron ages of 128·6±7·8 Ma (normal isochron) and 128·5±7·6 Ma (inverse isochron) were obtained with an initial  ${}^{40}$ Ar/ ${}^{36}$ Ar ratio of 305±3 for both isochrons. This

means that the Ar/Ar ages are variable or dispersed among spots against the initial atmospheric <sup>40</sup>Ar/<sup>36</sup>Ar ratio of 295.5, or the Ar/Ar ages are identical or homogeneous around 129 Ma against the higher initial <sup>40</sup>Ar/<sup>36</sup>Ar ratio of 305. Although the possibility of excess Ar cannot be excluded, we prefer the former interpretation, because the strong scatter of ages in sample 04CH18c appears to be due to a variable age resetting, with age values between those similar to samples MD0511 and 04CH15 and young ages as in sample 04CH17c that can be interpreted as a consequence of complete resetting. The weighted mean ages in samples 04CH17c and 04CH18c are identical, in accordance with their neighbouring outcrops, and can best be interpreted to date an age resetting event. During the retrograde PT path atmospheric Ar may have been introduced, presumably by meteoric fluids, which caused the resetting of the ages when a relatively shallow crustal level was reached. Because of a lack of internal deformation in the metabasite samples, any effect of deformation on age resetting can be excluded. Consequently, only the two older ages obtained from samples MD0511  $(200.8 \pm 2.4 \text{ Ma})$  and 04 CH15  $(233.2 \pm 1.8 \text{ Ma})$  can be related to the very low grade metamorphic event.

#### DISCUSSION Kinetically controlled metamorphic reactions

At present, much petrological work is focused on understanding the kinetic controls on mineral formation under variable metamorphic conditions as a result of dynamic disequilibrium processes (e.g. Carlson, 2002; Müller et al., 2009). Apparent disequilibria are ubiquitous phenomena at all metamorphic grades, but particularly during very low grade metamorphism of metabasic rocks. Considering a prograde PT path for basic rocks (which contain a significant proportion of unaltered magmatic minerals) hydrous fluid influx is required to enhance the progress of reactions, producing dominant hydrous phases such as amphibole, chlorite, white mica, pumpellyite or stilpnomelane. This is essentially due to fluid flux from adjacent dehydrating metapsammopelites. However, reactions proceeding locally within the metabasite during prograde metamorphism can also release hydrous fluids as a result of dehydration. A number of non-equilibrium effects are associated with the hydration and dehydration reactions. The incomplete, heterogeneous consumption of protolith phases such as clinopyroxene or plagioclase (Fig. 2) within and between samples could point to restricted availability of water. It was because of this assumption that the wholerock compositions for the calculation of pseudosections were corrected for the protolith phases and the amount of water was limited. The very small grain size of the reaction products particularly in the clusters reflects high

Table 4: Results of isotopic analysis for  ${}^{40}Ar{}^{\beta9}Ar$  dating

| Age (Ma)    | ±1σ      | <sup>40</sup> Ar <sup>*</sup> / <sup>39</sup> Ar <sub>K</sub> | ±1σ       | <sup>40</sup> Ar/ <sup>39</sup> Ar | ±1σ    | <sup>38</sup> Ar/ <sup>39</sup> Ar | ±1σ   | <sup>37</sup> Ar/ <sup>39</sup> Ar | ±1σ    | <sup>36</sup> Ar/ <sup>39</sup> Ar | ±1σ    | % <sup>40</sup> Ar <sub>atm</sub> | $^{37}\mathrm{Ar}_{\mathrm{Ca}}/^{39}\mathrm{Ar}_{\mathrm{K}}$ |   |                    |
|-------------|----------|---|-----------|------------------------------------|--------|------------------------------------|-------|------------------------------------|--------|------------------------------------|--------|-----------------------------------|--|---|--------------------|
| Sample MDU  | J511D; J | = 0.001698, m   | etabasite |                                    |        |                                    |       |                                    |        |                                    |        |                                   |  |   |                    |
| 197-46      | 4.35     | 68·120  | 1.561     | 97.407                             | 0.729  | 0.042                              | 0·007 | 0.1951                             | 0.0043 | 0·1024                             | 0.0050 | 30-40                             | 0.82   | normal isochron age:                              | 196·4±8·0 Ma       |
| 204-41      | 7.18     | 70.654  | 2.608     | 119-741                            | 1·202  | 0.037                              | 0.007 | 0.3495                             | 0.0113 | 0.1711                             | 0.0086 | 41·31                             | 1-47   | MSWD  | 0.94               |
| 199·32      | 6·72     | 68·798  | 2.435     | 95·738                             | 0·783  | 0.032                              | 0.007 | 0.3836                             | 0.0069 | 0.0948                             | 0.0080 | 28·54                             | 1.62   | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $309\pm29$         |
| 194·16      | 6.94     | 66·920  | 2.510     | 84·716                             | 1·081  | 0.034                              | 600·0 | 0·2980                             | 0.0115 | 0.0631                             | 0.0079 | 21.42                             | 1·26   | inverse isochron age:                             | 199·3±7·5 Ma       |
| 207·53      | 4.65     | 71·797  | 1.678     | 90·528                             | 0·810  | 0.039                              | 0.004 | 0.0626                             | 0·0032 | 0.0657                             | 0.0052 | 21·03                             | 0·26   | MSWD  | 1.00               |
| 199·16      | 7·23     | 68·739  | 2·621     | 98·504                             | 1.450  | 0.041                              | 0.006 | 0·2098                             | 0.0070 | 0·1041                             | 0.0081 | 30.55                             | 0·89   | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $302\pm28$         |
|             |          |   |           |                                    |        |                                    |       |                                    |        |                                    |        |                                   |  | weighted mean                                     | 200.8 $\pm$ 2.4 Ma |
| Sample 04Ci | H15; J=  | 0-001707, meti  | apelite   |                                    |        |                                    |       |                                    |        |                                    |        |                                   |  |   |                    |
| 230-96      | 3·09     | 80·010  | 1.093     | 115·535                            | 0.757  | 0·048                              | 0·004 | 0·0677                             | 0·0042 | 0.1237                             | 0.0033 | 31·04                             | 0.30   | normal isochron age:                              | 239·5±8·6 Ma       |
| 235·58      | 4.96     | 81·719  | 1·808     | 111·175                            | 0·876  | 0.037                              | 0.004 | 0.0884                             | 0.0069 | 0·1029                             | 0.0057 | 26·81                             | 0.39   | MSWD  | 1.48               |
| 246·13      | 5.29     | 85·631  | 1.938     | 111·119                            | 0.950  | 0.039                              | 0.003 | 0.0290                             | 0.0047 | 0·0891                             | 0.0061 | 23·25                             | 0·13   | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $272\pm27$         |
| 229-47      | 4·32     | 79-461  | 1.562     | 105·112                            | 0.696  | 0.029                              | 0.004 | 0.0376                             | 0.0040 | 0.0896                             | 0.0050 | 24·71                             | 0.16   | inverse isochron age:                             | 243·0±8·3 Ma       |
| 223·96      | 5.79     | 77·432  | 2·105     | 125·297                            | 1.151  | 0.050                              | 0.006 | 0·0342                             | 0.0043 | 0·1661                             | 0.0068 | 38.45                             | 0·15   | MSWD  | 1.58               |
| 236.87      | 4·86     | 82·194  | 1.769     | 119·547                            | 1-400  | 0.039                              | 0.006 | 0.0353                             | 0.0051 | 0·1299                             | 0.0052 | 31.53                             | 0·15   | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $264 \pm 27$       |
|             |          |   |           |                                    |        |                                    |       |                                    |        |                                    |        |                                   |  | weighted mean                                     | 233·2±1·8 Ma       |
| Sample 04Ci | H17; J=  | 0-001707, met   | abasite   |                                    |        |                                    |       |                                    |        |                                    |        |                                   |  |   |                    |
| 143·47      | 5·84     | 48·491  | 2·045     | 279-976                            | 2.575  | 0·172                              | 0·008 | 0.5578                             | 0·0122 | 0.7996                             | 0·008  | 82·79                             | 2.39   | normal isochron age:                              | 156·8±3·7 Ma       |
| 155·05      | 5.94     | 52·573  | 2·092     | 141·501                            | 1.117  | 0·082                              | 0.007 | 0·4106                             | 0·0082 | 0·3082                             | 0.0070 | 63·06                             | 1-77   | MSWD  | 0.56               |
| 143·98      | 14.61    | 48·670  | 5.133     | 373·883                            | 5·164  | 0·222                              | 0.015 | 0.6585                             | 0.0206 | 1·1228                             | 0·0221 | 87·07                             | 2·84   | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $291 \pm 3$        |
| 155·00      | 11·68    | 52.556  | 4·127     | 285·332                            | 2·282  | 0·178                              | 600·0 | 0.5030                             | 0·0133 | 0·8040                             | 0·0149 | 81.69                             | 2.17   | inverse isochron age:                             | 156·8±3·7 Ma       |
| 143·85      | 11·08    | 48·625  | 3·892     | 204·786                            | 2.372  | 0·126                              | 0.011 | 0·2639                             | 0·0104 | 0.5394                             | 0·0132 | 76·38                             | 1.14   | MSWD  | 0.57               |
| 153·96      | 2.79     | 52·191  | 0-965     | 108·232                            | 0.606  | 0.049                              | 0.005 | 0·2341                             | 0.0046 | 0·1944                             | 0·0032 | 52·02                             | 1·01   | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $291 \pm 3$        |
|             |          |   |           |                                    |        |                                    |       |                                    |        |                                    |        |                                   |  | weighted mean                                     | 152·0±2·2 Ma       |
| Sample 04Ci | H18c; J= | = 0·001697, me  | etabasite |                                    |        |                                    |       |                                    |        |                                    |        |                                   |  |   |                    |
| 196·16      | 24.48    | 67·687  | 8-911     | 438·379                            | 9·719  | 0.296                              | 0.018 | 0.9554                             | 0.0298 | 1·2809                             | 0.0407 | 84·69                             | 4·27   | normal isochron age:                              | 126.6 $\pm$ 7.8 Ma |
| 171·76      | 13·21    | 58·861  | 4.740     | 528·686                            | 10·748 | 0·344                              | 0.020 | 2·0982                             | 0.0507 | 1.6255                             | 0·0363 | 89-01                             | 9-43   | MSWD  | 1.42               |
| 127·50      | 32.37    | 43·153  | 11·347    | 402·531                            | 10·744 | 0·344                              | 0.026 | 4·7883                             | 0·1380 | 1·2513                             | 0.0500 | 89-55                             | 21.80  | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $305\pm3$          |
| 142·44      | 6·88     | 48·412  | 2.425     | 166·784                            | 2.676  | 0·114                              | 0.007 | 0·9394                             | 0.0212 | 0.4110                             | 0.0100 | 71·21                             | 4·21   | inverse isochron age:                             | 128·5±7·6 Ma       |
| 136·76      | 7.94     | 46·407  | 2.792     | 215·763                            | 3·721  | 0·131                              | 0.015 | 0·2919                             | 0.0128 | 0.5849                             | 0.0133 | 78·60                             | 1·31   | MSWD  | 2.8                |
| 167·41      | 18·94    | 57·299  | 6·785     | 762·850                            | 18·989 | 0·472                              | 0.028 | 2·6483                             | 0.0765 | 2·4391                             | 0.0640 | 92·61                             | 11-97  | initial <sup>40</sup> Ar/ <sup>36</sup> Ar ratio: | $305\pm3$          |
| 206·92      | 16·00    | 71·616  | 5.856     | 544.518                            | 11-612 | 0.348                              | 0·022 | 2·6402                             | 0.0607 | 1.6383                             | 0.0395 | 87·05                             | 11.95  | weighted mean                                     | 151·6±4·4 Ma       |



Fig. 12. Probability curves and weighted average ages for Ar/Ar spot ages of four samples. Dots indicate single *in situ* spot ages (with  $1\sigma$  error bars).

nucleation and growth rates, with nucleation rates exceeding growth rates because of a high reaction affinity, which is a measure of the departure from equilibrium or the degree of overstepping (Roselle *et al.*, 1997).

Erratic compositional variations, such as margarite and paragonite domains in white mica, occasional elevated Cr contents in garnet or occasional elevated Mn contents in epidote, may be due to local variations in the whole-rock composition that were not homogenized during the metamorphic reactions. Intergranular diffusion rates are particularly low at very low temperature and those for elements such as Ca, Mn and trivalent elements such as Cr are considerably more sluggish than for common elements such as Fe and Mg (Carlson, 2002).

Variable Fe<sup>3+</sup> contents in amphibole, white mica and pumpellyite are expressions of variable local buffering of fluids and/or diverse generation of external fluids. This may also explain different filling of fissures. For instance, Massonne & Willner (2008) noted that at 5 kbar, metapsammopelite and MORB mostly dehydrate at 230–250°C and 270–300°C, respectively. This means that at very low grade conditions the source and amount of the fluids may be variable and the amount restricted to specific *PT* conditions.

Mineral phases are not randomly distributed, but occur in nearly monomineralic clusters. The size of these clusters is generally controlled by the size and distribution of the protolith phases (Fig. 2). Clustering means that the distance between reaction partners varies strongly and hence influences intergranular diffusion and reaction progress.

The composition of the fine-grained metamorphic phases varies considerably, even within clusters. The  $X_{Mg}$  ratios of white mica, chlorite, amphibole and pumpellyite, as well as the Si contents of white mica and chlorite, show systematic variation within a restricted compositional range (Figs 3 and 4). This points to a temporary and local approach to equilibrium conditions.

It should be emphasized that the observed fine-grained fabric and the compositional variation strongly contrast with those of low-grade rocks in other Chilean accretionary systems metamorphosed at  $\sim$ 350–400°C (e.g. Willner *et al.*, 2000, 2001; Willner, 2005). Here recrystallization and compositional homogenization occurred throughout the rocks. Similarly, Brix *et al.* (2002) pointed out that above 320°C the grain size of the quartz fabric rapidly rises by an order of magnitude by complete recrystallization.

The described compositional variation and fabric effects may be explained by channelized and episodic infiltration of hydrous fluids that are heterogeneous in terms of composition including oxygen fugacity and amount, even at thin-section scale, as well as by kinetic control of mineral reactions. Of course, such processes appear to contradict and complicate the use of the applied geothermobarometric methods, challenging any attempt to define their precision. However, similar to mineral-zoning phenomena at higher metamorphic grade, the apparent nonequilibrium conditions provide a chance to decipher the PT conditions of prograde metamorphism. Hence, consideration of some locally preserved transient equilibria results in a reasonably consistent variation of conditions of mineral growth within a restricted PT range from about  $4 \pm 1$  kbar, 200–220°C to  $5 \pm 1$  kbar, 290–330°C. The strong scatter of mineral compositions must at least partly be due to dynamic equilibration along the prograde PT path leading to mineral growth over about 100°C within a narrow pressure range. This reflects near-isobaric prograde heating. There is little indication of retrograde mineral growth as is common under low-grade conditions in deeper (basally accreted) levels of other Chilean accretionary systems (e.g. Willner, 2005). The existence of potassic feldspar with a stability field at low pressure (Fig. 5) and some indication of late replacement by white mica as partly indicated by the Ar/Ar ages (see also below) may be taken as evidence that fluid flow and hence mineral growth did not entirely cease at peak metamorphic conditions.

The observed metamorphic assemblages can be reproduced within a rather limited PT range (290-310°C, 4-6 kbar) by calculation of PT pseudosections, although the modal amount of the produced phases varies significantly. The calculated compositions of minerals within this PT space reasonably coincide with those in nature. This demonstrates that adaptation of the metamorphic assemblage to the prevailing PTX conditions in fact took place on a thin-section scale, at least in the higher temperature part of the very low grade metamorphic range. This may be partly due to the fact that fluid infiltration was rapid and strongest around 300°C, in agreement with the findings of Massonne & Willner (2008) that in metapsammopelitic rocks of accretionary prism complexes a maximum amount of dehydration must have occurred at 230-250°C releasing hydrous fluids for reactions in the metabasic rocks. Müller et al. (2009) showed that a fluid infiltration controlled, carbonate thermometer reaction advanced rapidly to the recorded maximum temperatures, thus, preserving 'frozen in' lower temperature compositions. Stilpnomelane that should occur at the intermediate temperatures of the pumpellyite-actinolite facies according to the calculated pseudosections probably did not nucleate, as a result of overstepping of reactions or reduced availability of fluids at that stage. However, it grew at 300°C in the rocks of the Eastern Belt of the neighbouring Chonos Metamorphic Complex, where identical peak PT conditions to those in the MDMC were previously deduced by Willner et al. (2000). For the same reason the pseudosections can successfully be used as a petrogenetic grid

showing the growth of the actual assemblages in the metabasites of the MDMC within the pumpellyite–actinolite facies, bounded by the stability fields of lawsonite, laumontite, prehnite and biotite.

#### Significance of the prograde PT path

The proposed partial, nearly isobaric, prograde PT path points to a long-term adjustment to thermal conditions outside the subduction zone during subhorizontal particle paths at maximum depth (Fig. 13). Subhorizontal particle paths in frontal accretionary prisms at maximum depths are implied by the flow field concept of Ring et al. (1999) and are also observed in analog modelling (Kukowski et al., 2002; Glodny et al., 2005). They result from duplex stacking during build-up of the frontal accretionary prism. The subhorizontal particle flow paths cross the isotherms of the temperature field of the convergent margin towards higher temperatures, resulting in a finally preserved relatively high metamorphic gradient that strongly deviates from a geotherm realized along the top of the subducting slab. The peak conditions derived here approximate to an intermediate metamorphic geotherm of 17°C/ km. As subduction in the Phanerozoic has commonly occurred with plate velocities >3 cm/a, causing rather low geothermal gradients of  $\leq 10^{\circ}$  C/km, rising geotherms at the deepest levels reached imply temporal residence and thermal re-equilibration over a certain period of time, before exhumation and cooling started (Fig. 13). The extraction of subhorizontal PT paths from frontally accreted parts of subduction systems produced by thermomechanical modelling proves the deduced relationship (Willner et al., 2008). However, it should be noted that the described effect is not the only possibility leading to elevated metamorphic geotherms. Such geotherms may also result, for example, from very slow subduction or subduction of hot young oceanic crust, according to numerical experiments by Peacock (1996). However, these alternative heating effects are special cases that would mainly affect the temperature field of the subduction channel, whereas the proposed thermal re-equilibration at depth after accretion appears to be a process characteristic of frontal accretionary prisms. It appears unlikely that geotherms as high as those observed in the studied metabasite will develop in the subduction channel.

#### Significance of the Ar/Ar ages

Compositional heterogeneity at a thin-section scale could also imply Ar/Ar age heterogeneity, because all derived Ar/Ar ages should be interpreted as ages of mineral formation owing to mineral growth considerably below the closure temperature of the K/Ar system. Age heterogeneities at thin-section scale, even in very low grade rocks, can be much better resolved with the *in situ* Ar/Ar UV laser ablation technique than by analyses of bulk concentrates. We obtained two ages related to very low grade



Fig. 13. Simplified schematic visualization of the possible thermal field around a growing frontal accretionary prism indicated by thrusts and folds. Grey area, subducting oceanic slab; dotted grey lines, isotherms; black arrows, active thrusts; grey arrows, inactive thrusts. Subhorizontal mass flow paths (black dashed arrows) result during the build-up of the prisms that cross the isotherms towards higher temperatures.

metamorphism in the DU by demonstrating homogeneous white mica age distributions at thin-section scale of  $200.8 \pm 2.4$  Ma and  $233.2 \pm 1.8$  Ma (Fig. 12). The measured single-spot ages of white mica in each sample did not vary within the  $1\sigma$  error. Mineral growth was evidently timerestricted and this behaviour contrasts with results in lowgrade rocks of the metamorphic basement of the Coastal Cordillera in central Chile, where an age scatter results from continuing mineral growth along the retrograde PT paths (Willner et al., 2005). The homogeneous age distribution in sample 04CH15  $(233 \cdot 2 \pm 1 \cdot 8 \text{ Ma})$  is presumably caused by prograde growth of oriented white mica during deformation of the rock. This deformation represents the accretion process. The resultant age is compatible with the maximum depositional age of the DYU of about 270 Ma revealed by the youngest detrital zircon SHRIMP age (Hervé et al., 2003) and two fission-track zircon ages of  $209 \pm 14/12$  Ma (Thomson & Hervé, 2002). The latter ages reflect a time of cooling after the peak of metamorphism, because the temperature of fission-track annealing in zircon of around 280°C was just overstepped. The age of  $200.8 \pm 2.4$  Ma of the unoriented white mica clusters replacing plagioclase in sample MD0511 is younger than the FT zircon ages. This Ar/Ar white mica age may represent growth at peak PT conditions during a later stage of build-up of the accretionary prism, because sample MD0511 occurs about 4 km west of the samples used for FT dating and the older sample 04CH15. Alternatively, it may represent a retrograde stage of mineral growth.

Thomson & Hervé (2002) detected a similar peak metamorphic age in the Eastern Belt of the Chonos Metamorphic Complex (Fig. 1), bracketed by a young detrital zircon SHRIMP age of  $207 \pm 6$  Ma and a fissiontrack zircon age of  $210 \pm 12$  Ma. Here, very low grade metamorphic conditions identical to those in the MDMC

prevailed (Willner et al., 2000). Therefore in the two Patagonian accretionary systems (MDMC and CMC) metamorphism in the upper, frontally accreted, levels is about 100 Myr younger than in central Chile, where the equivalents (Eastern Series) were accreted before 300 Ma (Willner et al., 2005). This also appears to apply to the accretionary systems to the east of the Patagonian batholith, the East Andean Metamorphic Complex, where at least in its northern part maximum depositional ages of 311-353 Ma (Augustsson et al., 2006) and zircon fissiontrack ages of 253-267 Ma (Thomson & Hervé, 2002) point to similar ages of accretionary activity to those in central Chile. Hence the younger ages of metamorphism of the CMC and the MDMC point to a coherent Late Triassic-Early Jurassic event and thus the youngest fossil accretionary system exposed along the coast of Chilean Patagonia. On the other hand, the age of the structurally underlying and hence younger, basally accreted Western Belt of the CMC is as yet unknown. The MDMC is at least in tectonic contact with a rather small, basally accreted complex, the Diego de Almagro Metamorphic Complex (DAMC). The age of the peak of metamorphism in the DAMC is considered to be around  $117 \pm 28$  Ma (K/ Ar; Willner et al., 2004). Volcanic rocks formed at  $157 \pm 2$ Ma were overprinted within the DAMC (Hervé et al., 2003). The age relations between the MDMC and the DAMC confirm that in this region frontal accretion also occurred prior to basal accretion as has been recognized in central Chile (Richter et al., 2007).

The basement rocks were partly overprinted at  $152.5 \pm 2.2$  Ma over a short distance (c. 2 km) from the Patagonian batholith (04CH17c and 04CH18c; Fig. 1). In sample 04CH18c relict ages as old as 207 Ma and a scatter of younger ages prove an incomplete resetting of ages originally similar to those of the peak of HP metamorphism. The overprinted metabasite samples also contain a little muscovite in addition to phengite, which might indicate, at least partly, new mineral growth during a partial LP overprint. This overprint, however, appears to be incompatible with heating by the closest pluton of the Patagonian batholith, which intruded later at  $133 \pm 1$  Ma (Hervé et al., 2007a). Also, contact metamorphic effects are observed only at the immediate contact of the pluton and there is no indication that the maximum temperature of  $\sim 300^{\circ}$ C was exceeded in sample 04CH18c. Additionally, deformation is not a factor, because internal deformation is absent within the analyzed samples. It is proposed that access of variable amounts of external hydrous fluids at some stage after the peak of metamorphism caused the local resetting of ages. McDowell & Elders (1980) reported 'illitization' of muscovite in the Salton Sea System at temperatures  $\leq 280^{\circ}$ C, causing an apparent younging of ages. This process would imply partial or complete replacement of white mica. If the spacing of the replacement zones or lamellae is smaller than the beam size of the UV laser, a mixed age between the intrusion age of the nearby pluton and that of the replacement lamellae would be feasible. On the other hand, the obtained late Jurassic overprint age, if replacement of white mica is complete, could be related to the first bimodal intrusive activity of the South Patagonian batholith at 157–145 Ma (Hervé *et al.*, 2007*a*). This activity was due to an extensional event causing crustal thinning, an increase of the geothermal gradient and finally advection of hydrothermal fluids at shallow crustal levels.

#### CONCLUSIONS

In the Madre de Dios Metamorphic Complex mineral assemblages of the intermediate-pressure and hightemperature part of the actinolite-pumpellyite facies are formed. Different peak metamorphic assemblages observed in six metabasite samples suggest equilibration on a thin-section scale at 290-310°C and around 5 kbar. Furthermore, it has been shown that local equilibria are preserved despite strong compositional heterogeneity of the metamorphic phases, because of restricted availability of hydrous fluids, with presumably variable compositions and a lack of later compositional homogenization owing to the low temperatures attained. Calculated PT data indicate metamorphism along a nearly isobaric, prograde PT path, which in turn reflects a subhorizontal particle path in the frontal accretionary prism and a long-term thermal re-equilibration at maximum depths. This is in agreement with current concepts about the formation of frontal accretionary prisms. The prograde information preserved in the very low grade rocks strongly contrasts with that from the low-grade rocks of other Chilean accretionary systems, where recrystallization and compositional homogenization is complete and retrograde PT information is recorded.

The Ar/Ar spot ages do not vary at thin-section scale in three samples, but reflect ages of rapid growth of white mica at very different stages of the evolution of the accretionary prism. Only the age of  $233 \cdot 2 \pm 1.8$  Ma can unambiguously be related to accretion, indicating that accretion in the MDMC started shortly before or around that time. Growth of white mica at  $200 \cdot 8 \pm 2 \cdot 4$  Ma may be due to an advanced stage of accretion or a retrograde resetting effect. Much younger growth of white mica at  $152 \cdot 0 \pm 2 \cdot 2$  Ma is clearly a later local resetting effect caused by access of external fluids, which were generated either during a postaccretionary extensional event or by a nearby igneous intrusion.

The Late Triassic age of accretion in the MDMC is identical to that of the upper part of the Chonos Metamorphic Complex in the north but in contrast to the Carboniferous frontal accretion in central Chile and to the east of the Patagonian batholith. This could be in line with migration of accretion mass flow processes with time from east to west as well as from north to south.

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#### SUPPLEMENTARY DATA

Supplementary data for this paper are available at *Journal* of *Petrology* online.

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### <u>CAPÍTULO 4:</u> PERMIAN DEPOSITIONAL AGE OF METATURBIDITES OF THE DUQUE DE YORK COMPLEX, SOUTHERN CHILE: U-Pb SHRIMP DATA AND PALYNOLOGY

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### Permian depositional age of metaturbidites of the Duque de York Complex, southern Chile: U-Pb SHRIMP data and palynology

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**ABSTRACT.** The Duque de York Complex (DYC) is part of the low grade metamorphic accretionary complexes of the pre-Andean Patagonian 'basement'. It is a sedimentary succession exposed along the western margin of southernmost South America. New U-Pb zircon ages and palynological data restrict the maximum depositional age of the DYC to the limit between the early Permian (Kungurian) and the middle Permian (Roadian). The palynological association recorded in the DYC, characterized mainly by Gymnospermopsida pollen, indicates a humid environment of forest with an undergrowth of ferns. Regional paleogeographic correlations point out that an interpretation of DYC as an autochthonous terrane cannot be discarded, contrasting with previous hypotheses which suggest an allochthonous character for this complex.

Keywords: Palynology, U-Pb dating, Duque de York Complex, Terranes, Gondwana, Chile.

**RESUMEN. Edad pérmica de sedimentación de las metaturbiditas del Complejo Duque de York, sur de Chile:** datos mediante U-Pb SHRIMP y palinología. El Complejo Duque de York (CDY) forma parte de los complejos metamórficos acrecionarios del 'basamento' pre-Andino de la Patagonia, correspondiendo a una sucesión sedimentaria que aflora a lo largo del margen occidental austral de Sudamérica. Nuevas edades U-Pb en circón, en combinación con información palinológica, permiten acotar la máxima edad de depósito posible del CDY al límite entre el Pérmico temprano (Kunguriano) y el Pérmico medio (Roadiano). La asociación palinológica registrada en el CDY está caracterizada por Gymnospermopsida, e indica un ambiente húmedo de bosque con sotobosque de helechos. Las correlaciones paleogeográficas apuntan a que la condición de terreno autóctono del CDY no puede ser descartada, lo que se contrapone a hipótesis anteriores, las que sugieren un carácter alóctono para este complejo.

Palabras clave: Palinología, Datación U-Pb, Complejo Duque de York, Terrenos, Gondwana, Chile.

#### 1. Introduction

The Duque de York Complex (DYC) is one of the metamorphic complexes that form the pre-Andean Patagonian 'basement' rocks, which crop out extensively along the western edge of South America south of 50°S. These rocks have been generally considered as part of the late Paleozoic-early Mesozoic accretionary prism built at the paleo-Pacific (Panthalassan) margin of Gondwana (e.g., Hervé et al., 1981; Forsythe, 1982). The accretionary orogenic belt that formed on this margin is one of the largest known orogenic belts in Earth history, and now occupies the eastern third of Australia, New Zealand, West Antarctica, the Transantarctic Mountains and large parts of southern South America (Vaughan et al., 2005). This orogenic belt has been termed in two different ways depending on the interval considered: the Proterozoic and Paleozoic Terra Australis orogen (Cawood, 2005), and the Paleozoic and Mesozoic Australides (Vaughan et al., 2005). It has been regarded as a collage of accreted terranes-terranes being fault-bounded packages of rocks of regional extent characterized by a geological history that differs from that of neighboring terranes (Howell et al., 1985; Vaughan et al., 2005).

The DYC corresponds to a widespread low grademetasedimentary succession that crops out along the Madre de Dios and Diego de Almagro archipelagos (50°00'-51°50'S) and at the Ramírez, Contreras and Desolación islands (51°50'-53°00'S), in southern Chile (Fig. 1A). Forsythe and Mpodozis (1979, 1983) interpreted the DYC as a continent-derived detrital succession that was deposited over two coeval late Paleozoic exotic oceanic units, as they approached the continental margin of Gondwana. The DYC together with the oceanic units, defined as the Madre de Dios Accretionary Complex (MDAC) by Thomson and Hervé (2002), were then tectonically amalgamated to the forearc of this margin by subduction processes, resulting in an intricate tectonic interweaving. These complexes were intruded by the South Patagonian Batholith (SPB) in the Early Cretaceous (Halpern, 1973; Duhart et al., 2003; Hervé et al., 2007a).

For a long time, the accretionary complexes that compose the MDAC have been considered of exotic or allochthonous origin, or at least, as suspect terranes. Terranes are 'suspect' if there is doubt about their paleogeographical setting with respect to adjacent terranes or continental margin (Coney *et al.*, 1980; Coombs, 1997), and may be described as 'exotic', 'far-travelled' or 'allochthonous' (all meaning about the same thing) if there is sufficient evidence that they originated far from their present locations, often assumed to be hundreds or thousands of kilometers away (Vaughan et al., 2005). The consideration of the MDAC as suspect and potentially exotic is based mainly on its fossil content and the inferred depositional setting for them (in the case of the TL and the coeval DC) (e.g., Ling et al., 1985; Ramos, 1988) and on the impossibility to find a contemporaneous magmatic arc as the source of Permian zircons for the DYC anywhere at a similar latitude in southern Patagonia (Hervé et al., 2003; Hervé and Mpodozis, 2005; Hervé et al., 2006). The latter has led to propose that the deposition of the DYC took place at high southern latitudes along the Antarctic sector of the Gondwana margin (Lacassie, 2003; Lacassie et al., 2006). However, derivation of the DYC from lower and warmer latitudes is a hypothesis that cannot be ruled-out.

The lack of index fossils in the DYC has prevented an accurate determination of the depositional age of this complex. In consequence, a late early Permian maximum depositional age has been established by the use of the youngest detrital zircon population in these metasediments (Hervé et al., 2003). Nevertheless, the use of the youngest detrital zircon age or population in a sediment as a limit for the age of deposition has been questionable for both geological (there is no necessary connection between the timing of zircon-generating events in a source region and the age of final deposition of a sediment eroded from this source) and statistical reasons (Andersen, 2005). In this context, this paper presents the first palynological study in rocks of the DYC and it also corresponds to the first record of late Paleozoic palynomorphs in Chile. The aim of this work is to restrict the age range of the DYC by the combination of the palynological results with new U-Pb SHRIMP ages in key samples, and also gives a revision of the paleoenvironmental and geochronological data regarding the place and timing of deposition of the DYC. The conclusions derived from this work allow giving some new considerations focused on the supposed allochthonous character of the MDAC, and especially of the DYC.

#### 2. Geological background

The rocks of the studied area were first recognized by Cecioni (1955, 1956), who determined the presence of upper Paleozoic sediments in the Patagonian archipelago, distinguishing fusulinids as well as the low grade-metamorphic character of these rocks. The geology of the Madre de Dios Archipelago was studied in detail by Forsythe and Mpodozis (1979, 1983) and Mpodozis and Forsythe (1983), who distinguished three metamorphic complexes that made up the MDAC (Fig. 1B):

**a**. the Denaro Complex (DC), formed by tholeiitic basalts with E- and N-MORB signatures (Hervé *et al.*, 1999; Sepúlveda *et al.*, 2008), banded radiolarian and metalliferous cherts, pelites and calcarenites. This complex represents fragments of ocean floor and its sedimentary cover (late Carboniferous-early Permian, according to Ling *et al.*, 1985), **b**. the Tarlton Limestones (TL), formed by fusulinid-bearing massive limestones, deposited in an intra-oceanic carbonate platform during Middle Pennsylvanian-early Permian times (Cecioni, 1956; Douglass and Nestell, 1972, 1976),

c. the Duque de York Complex (DYC), formed by a thick succession of greywackes, pelites, and minor conglomerates of continental provenance, and deposited on top of DC and TL. Based on field observation, Faúndez *et al.* (2002) described the DYC as being formed by metaturbidites. Also, it has been indicated that this succession has early Permian radiolarian cherts at Desolación Island (A. Yoshiaki, written communication, 2002; in Hervé *et al.*, 2007b). Owing to the accretionary processes, most contacts among these units are of tectonic



FIG. 1. A. Sketch map showing the distribution of the DYC; B. Geological map of the Madre de Dios Archipelago (after Forsythe and Mpodozis, 1983; Lacassie *et al.*, 2006; Sepúlveda *et al.*, 2008). 1. Quaternary deposits; 2. South Patagonian Batholith (SPB);
3. Tarlton Limestones (TL); 4. Denaro Complex (DC); 5. Duque de York Complex (DYC); 6. Unmapped basement; 7. Sill. Sampling sites are marked with black circles; all for palynology except FO04-21; FO04-21 and FO04-22 for U-Pb Shrimp dating.

origin (Fig. 2), but few examples of depositional contacts have been recognized. In fact, the preserved stratigraphic relations confirm that the DYC has both unconformable and conformable depositional contacts with the other complexes (*e.g.*, Lacassie *et al.*, 2006).

All these units where metamorphosed under the conditions of pumpellyite-actinolite facies in a frontal accretionary wedge (Sepúlveda, 2004; Sepúlveda *et al.*, 2008) during Middle Triassic to earliest Jurassic times, as indicated by *in situ* Ar/Ar UV-LAMP ages on phengites (Willner *et al.*, 2009). Thomson and Hervé (2002) used zircon fission track data to point out that the metamorphism that affects the DYC, and also the underlying TL and DC, took place during or before the earliest Jurassic (*ca.* 195 Ma). This information constrains the minimum probable age of deposition for the DYC, and demonstrates that, in this area, the metamorphism occurred prior to the emplacement of the SPB in the Early Cretaceous. The isotopic ages of the SPB, in the outcrops ad-



FIG. 2. Outcrops at Madre de Dios Island, where tectonic contact (dashed line) between deformed metasediments of the DYC (brown) and massive limestones of the TL (white) is partly observed.

jacent to the contact with the MDAC, are 133-112 Ma (Rb-Sr whole rock and biotite isochron, Halpern, 1973), 130-143 Ma (K-Ar biotite, Duhart *et al.*, 2003) and *ca.* 133 Ma (U-Pb SHRIMP zircon, Hervé *et al.*, 2007a).

U-Pb SHRIMP detrital zircon ages from sandstones of the DYC reveal that the youngest main opulation, and hence the maximum possible depositional age, is late early Permian (ca. 270 Ma) (Hervé et al., 2003). The geochemical study of Lacassie et al. (2006), complementing the data and refining the conclusions of Faúndez et al. (2002), indicates that the DYC sandstones and mudstones had their source in a volcanic arc of granodioritic average composition located relatively proximal to the depositional basin, and whose plutonic roots had been exposed by erosion. Also, they propose that the DYC was deposited in a tectonic setting corresponding to an active continental margin, possibly located along the Antarctic segment of the Panthalassan Gondwana margin.

#### 2.1. Paleogeographic setting

The fusulinid fauna in the TL shows that these carbonate sedimentary rocks must have been deposited in marine warm water (Douglass and Nestell, 1976). Similarities between the fossil content of the TL with those of the backarc marine carbonate deposits of the late Paleozoic Copacabana Formation in Peru and Bolivia (Cabrera La Rosa and Petersen, 1936; Chamot, 1965; Mamet, 1996), indicates that deposition of TL occurred in low latitude zones (ca. 20°S) during the late Carboniferous-early Permian (Lacassie, 2003). However, recent paleogeographic reconstructions for those periods (Torsvik and Cocks, 2004; Veevers, 2004; Cocks and Torsvik, 2006; Cawood and Buchan, 2007) locate the portion of the Gondwana margin where the Madre de Dios archipelago is presently situated at a high southern latitude, well outside the tropical zone where the TL is likely to have been deposited. Also, it is indicated that the late Paleozoic Ice Age in Gondwana was active between the Carboniferous and the early Permian (Isbell et al., 2003; Isbell et al., 2005; López-Gamundí, 2005; Buatois et al., 2006; Fielding et al., 2008; Rocha Campos et al., 2008). These facts, together with the contemporaneity of the TL with the ocean floor deposit of the DC (Ling et al., 1985; Ling

and Forsythe, 1987) lead to the conclusion that the MDAC represents an allochthonous or exotic terrane derived from lower latitudes and accreted via subduction processes to Gondwana (Ramos, 1988). The timing of the accretion of these units would be bracketed between the maximum age of deposition of the DYC (*ca.* 270 Ma; Hervé *et al.*, 2003) and the minimum age of metamorphism (195 Ma; Thomson and Hervé, 2002).

The apparent lack of a Permian magmatic arc in southernmost Patagonia allowed Lacassie (2003) and Lacassie et al. (2006), following Hervé et al. (2000) and Cawood *et al.* (2002), to propose that the accretion of the TL and the DC would have occurred against the Antarctic-Australian segment of the Gondwana margin, from where both would have been displaced by dextral translation, together with the DYC, as a coherent block to their current position. In addition, Lacassie et al. (2006) show that the DYC metasediments share important petrographic, geochemical and geochronological characteristics with metaturbidites present in the Rakaia Terrane in New Zealand and with the eastern (Triassic) Le May Group in Alexander Island. These similarities point towards similar igneous sources for the three successions, suggesting that they were coevally deposited along the same active continental margin (Lacassie et al., 2006). This margin was probably located along the Antarctic sector of the Panthalassan Gondwana margin, as favored by the studies of Willan (2003) for the source area of the Le May Group, and of Wandres et al. (2004) and Wandres and Bradshaw (2005) for the source area of the Rakaia terrane. The last two studies indicate that the origin of the Permian detritus in the Rakaia terrane would be in the igneous rocks of the Amundsen and Ross Provinces, East Antarctica, which during the Permian were close to 60°S (Veevers, 2004; Cawood and Buchan, 2007). If the source of Permian detritus was the same for these three successions (DYC, Rakaia Terrane and Le May Group), this would imply dextral strikeslip displacement of the MDAC along the SW Gondwana margin from these high latitude to its present position.

On the other hand, paleomagnetic information on the TL and the DC demonstrate that, after Early Cretaceous remagnetization produced by the thermal influence of the SPB, both units underwent a counter-clockwise rotation of ca. 117° with an inappreciable latitudinal change (Rapalini *et al.*, 2001). This evidence, coupled to the structural data of Forsythe and Mpodozis (1979, 1983), allowed Rapalini et al. (2001) to propose that the former units have been accreted to the Gondwana margin from the NW rather than from the SW, as had been previously considered (Forsythe and Mpodozis, 1983; Ling and Forsythe, 1987). That agrees with the early hypothesis of Ozawa and Kanmera (1984), which suggested the north-western Pacific area for the origin of the exotic oceanic units of the MDAC, and is also consistent with the sinistral sense of shear of main structures parallel to the margin of South America (Cunningham, 1993; Olivares et al., 2003). These interpretations are coherent with the migration of the Antarctic Peninsula towards the south starting in the latest Jurassic (Hervé et al., 2006; König and Jokat, 2006; Miller, 2007), which was situated parallel to the west of Patagonia at that time (Miller, 2007, and references therein). Moreover, it is suggested that the late Triassic deformation in northern Antarctic Peninsula (Peninsula Orogeny), which affects the Trinity Peninsula Group accretionary complex (TPG, Hyden and Tanner, 1981), is associated with sinistral strike-slip movements, while dextral strike-slip is mainly a Cretaceous phenomenon in the Antarctic Peninsula (written communication, A. Vaughan, October 2006).

The deposition of sediments of the DYC in high southern latitudes (Lacassie, 2003; Lacassie *et al.*, 2006), contrasts with the second scenario, which involves deposition of the DYC in lower and warmer latitudes, perhaps associated with subsequent sinistral strike-slip movements of the entire MDAC along the Panthalassan margin of Gondwana.

#### 3. Sampling and Methods

Palynological data were acquired from one sample of limestone of the TL and seven samples of metasediments of the DYC: five from Madre de Dios Archipelago and two from Diego de Almagro Archipelago (Table 1; Fig. 1). All samples were processed by standard palynological methods. All but one of the samples (MD05-20 from Guarello Island) yielded poorly preserved palynomorphs. The study and the description of the specimens were made with an optical microscope. The slides are housed at the Laboratory of Paleopalynology of the Departamento de Ciencias de la Tierra, Universidad de Concepción under codes 1396 to 1401.

Two metasedimentary samples (FO04-21 and FO04-22) from the units of the MDAC were collected for U-Pb zircon dating by SHRIMP RG (sensitive high resolution ion microprobe, reverse geometry) at the Research School of Earth Sciences, The Australian National University. Zircon grains were separated from total rock samples using standard crushing, washing, heavy liquid and paramagnetic procedures. The zircon-rich heavy mineral concentrates were poured onto double-sided tape, mounted in epoxy together with chips of the reference zircons (FC1 and SL13), sectioned approximately in half, and polished. Reflected and transmitted light photomicrographs were prepared for all zircons. Cathodoluminescence (CL) Scanning Electron Microscope (SEM) images were prepared for all zircon grains. The CL images were used to decipher the internal structures of the sectioned grains and to ensure that the  $\sim 20 \ \mu m$  SHRIMP spot was wholly within a single age component (usually the youngest) within the sectioned grains.

The U-Th-Pb analyses were made using SHRIMP RG. The zircon grains were analyzed sequentially and randomly. Each analysis consisted of 4 scans through the mass range, with a reference zircon analyzed for every five unknown zircon analyses; SHRIMP analytical method follows Williams (1998, and references therein). The data have been reduced using the SQUID Excel Macro of Ludwig (2001). The U-Pb ratios have been normalized relative to a value of 0.01859 for the FC1 reference zircon, equivalent to an age of 1,099 Ma (Paces and Miller, 1993). Uncertainties given for individual analyses (ratios and ages) are at the one sigma level (Tables 2 and 3). Tera-Wasserburg concordia plots, probability density plots with stacked histograms and weighted mean <sup>206</sup>Pb/<sup>238</sup>U age calculations were carried out using ISOPLOT/EX (Ludwig, 2003). The 'Mixture Modelling' algorithm of Sambridge and Compston (1994), via ISOPLOT/EX, was used to un-mix statistical age populations or groupings; from these groups weighted mean <sup>206</sup>Pb/<sup>238</sup>U ages were calculated and the uncertainties are reported as 95% confidence limits.

An estimate for the maximum age for the deposition of the sediment sample may be determined from the weighted mean age of the youngest peak in these distributions, where  $\geq 3$  analyses are within analytical uncertainty. Such an age grouping has taken into account isolated cases of inferred radiogenic Pb-loss, which can produce minor scatter to younger ages. Ages for individual grains are reported at the 68% confidence level, and Geological Time Scale referred throughout the text is that of Gradstein *et al.* (2004).

| Sample             | Lithology (unit)           | Location (coordinates)                   |
|--------------------|----------------------------|--|
| · · · · <b>k</b> · |                            |  |
| MD04-1             | black shale (DYC)          | 50°25'43.2"'S; 75°19'33.1"W              |
|                    |                            |  |
| FO04-22            | sandstone (DYC)            | 50°25'43.2"'S; 75°19'33.1"W              |
|                    |                            |  |
| MD05-3             | calcareous sandstone (DYC) | 50°21'54.1''S; 75°19'53.8''W             |
| ND05-20            |                            | 50022246 4220 25010201 12004             |
| MD05-20            | sandstone (DYC)            | 50°22 46.4 °S; 75°19 01.1 °W             |
| MD06-7             | limestone (TL)             | 50°18'14 2''S <sup>.</sup> 75°20'17 2''W |
|                    |                            | 00 10 112 0, 70 20 172 1                 |
| MD06-10            | sandstone (DYC)            | 50°19'07.6''S; 75°21'50.1''W             |
|                    |                            |  |
| DA-28              | sandstone (DYC)            | 51°30'40.5''S; 75°06'21.3''W             |
|                    |                            |  |
| DA-29              | shale (DYC)                | 51°30′40.5″S; 75°06'21.3"W               |

TABLE 1. SAMPLES ANALYZED BY PALYNOLOGICAL METHODS.

|           | ,<br>isc                                | 6       |         |          |         | ,       |         |             |          |          |         |         |         |         |         |          |          |         |          | ,       |         |         |            |          |         |          |         |          |         |         |        |
|-----------|---|---------|---------|----------|---------|---------|---------|-------------|----------|----------|---------|---------|---------|---------|---------|----------|----------|---------|----------|---------|---------|---------|------------|----------|---------|----------|---------|----------|---------|---------|--------|
|           | D %                                     | 3 19    |         |          | 7 4     |         |         |             |          |          |         |         |         |         |         |          |          |         |          |         |         |         |            |          |         |          |         |          |         |         |        |
|           | ₽<br>₽                                  | 0 5     |         |          | 1       |         |         |             |          |          |         |         |         |         |         |          |          |         |          |         |         |         |            |          |         |          |         |          |         |         |        |
| (Ma)      | 205P                                    | 986     |         | '        | 87      | '       | '       | '           | '        | '        | '       | '       |         | '       | '       | '        | '        | 1       | '        | '       | '       | '       | 1          | '        | '       | '        | '       | '        | '       | '       |        |
| Age       | +1                                      | Ξ       | U       | (1)      | 0,      | (,)     | (1)     | (,          |          | 7        | 43      | (,      | U       |         | (,)     | ,        | ,        | Û       | 7        | (1)     | 43      | 7       | U          | 0,       |         | 41       | 61      | (,)      | (1)     | 61      | (      |
|           | <sup>206</sup> Pb/                      | 797     | 527     | 285      | 833     | 261     | 279     | 277         | 273      | 315      | 374     | 270     | 378     | 271     | 264     | 270      | 291      | 466     | 342      | 282     | 397     | 283     | 532        | 678      | 266     | 296      | 274     | 265      | 274     | 279     | i<br>i |
|           | C                                       | 0.477   |         | ,        | 0.802   |         | ,       |             | ,        |          |         |         |         | ,       |         |          |          | ·       |          | ,       |         |         |            |          |         | ,        |         |          |         | ·       |        |
|           | +1                                      | 0.0019  |         |          | 0.0006  |         |         |             |          |          |         | ,       |         |         |         |          |          |         |          | ı       | ,       | ,       |            |          |         | ·        |         |          |         | ,       |        |
|           | <sup>207</sup> Pb/<br><sup>206</sup> Pb | 0.0718  |         |          | 0.0681  |         |         |             | ·        | ·        | ,       | ,       | ,       | ·       | ,       | ,        | ,        | ı       |          | ı       | ,       | ,       |            |          | ·       | ·        | ı       | ,        |         | ,       |        |
| Ratios    | +1                                      | 0.039   |         |          | 0.018   |         |         |             | '        | ,        | ,       | ,       | ,       | '       | ,       | ,        | ,        | ·       |          | ,       | ,       | ,       | ,          | ,        | ,       | ,        | ,       | ,        |         |         |        |
| adiogenic | <sup>207</sup> Pb/                      | 1,302   | ·       | ı        | 1,295   | ı       |         | ,           | ,        | ·        |         |         |         | ,       |         |          |          | ı       | ·        | ,       |         |         |            |          | ,       | ·        | ·       |          | ı       | ı       |        |
| R         | +1                                      | 0.0019  | 0.0010  | 0.0005   | 0.0016  | 0.0005  | 0.0005  | 0.0005      | 0.0005   | 0.0007   | 0.0009  | 0.0005  | 0.0011  | 0.0005  | 0.0005  | 0.0006   | 0.0005   | 0.0010  | 0.0007   | 0.0005  | 0.0007  | 0.0006  | 0.0010     | 0.0015   | 0.0005  | 0.0007   | 0.0005  | 0.0005   | 0.0005  | 0.0005  | -0000  |
|           | <sup>206</sup> Pb/<br><sup>238</sup> U  | 0.1316  | 0.0853  | 0.0452   | 0.1380  | 0.0413  | 0.0442  | 0.0439      | 0.0433   | 0.0500   | 0.0597  | 0.0428  | 0.0603  | 0.0429  | 0.0417  | 0.0428   | 0.0461   | 0.0750  | 0.0545   | 0.0447  | 0.0636  | 0.0448  | 0.0860     | 0.1109   | 0.0422  | 0.0470   | 0.0435  | 0.0419   | 0.0434  | 0.0442  |        |
|           | +1                                      | 0.0013  | 0.0008  | 6000.0   | ).0006  | .0008   | 6000.0  | .0008       | 0008     | 0.0038   | 0.0032  | 0.0019  | 0.0028  | 0008    | .0009   | 0.0013   | 6000.0   | 0.0010  | 0.0010   | 0.0022  | 0.0010  | 0.0012  | ).0006     | 0.0005   | 0.0012  | 0.0018   | 0.0010  | 0.0014   | 6000.0  | 0.0008  | 0000   |
| tios      | <sup>207</sup> Pb/<br><sup>206</sup> Pb | .0743 ( | .0609   | 0.0584 ( | .0681 ( | .0519 ( | 0560 (  | .0590 (     | 0.0522 ( | ).1186 ( | .1056 ( | .0945 ( | .0973 ( | .0529 ( | .0539 ( | 0.0651 ( | 0.0723   | .0556 ( | 0.0584 ( | .0777 ( | .0951 ( | .0588 ( | .0569 (    | 0.0656 ( | .0893 ( | 0.0631 ( | .0579 ( | 0.1087 ( | .0534 ( | .0506 ( | 01-0   |
| Total Ra  | +1                                      | 0.107 0 | ).139 ( | ).258 (  | ).082 ( | 0.276 0 | ).265 ( | ).265 (     | ).265 (  | ).237 (  | 0.215 0 | 0.272 0 | ).266 ( | 0.270 0 | 0.304 0 | ).296 (  | ).239 (  | ).168 ( | 0.215 0  | ).252 ( | 0.171 0 | 0.287 0 | 0.129 0    | 0.116 0  | ).268 ( | ).322 (  | 0.278 0 | ).263 (  | 0.271 0 | ).260 ( | 0.00   |
|           | <sup>238</sup> U/                       | 7.576 ( | 1.687 ( | 1.953 (  | 7.249 ( | 4.213 ( | 2.506 ( | 2.559 (     | 3.092 (  | 8.354 (  | 5.673 ( | 2.121 ( | 5.691 ( | 3.279 ( | 3.890 ( | 2.987 (  | 1.130 (  | 3.351 ( | 8.224 (  | 1.650 ( | 4.941 ( | 2.118 ( | 1.644 (    | 8.977    | 2.608 ( | 0.973 (  | 2.824 ( | 2.140 (  | 2.998 ( | 2.675 ( |        |
|           | f_ <sup>206</sup><br>%                  | 0.30    | 0.36 1  | 0.80 2   | 0.01    | 0.06 2  | 0.52 2  | 0.90 2      | 0.06 2   | 8.20 1   | 6.39 1  | 5.34 2  | 5.35 1  | 0.16 2  | 0.29 2  | 1.68 2   | 2.52 2   | 0.01 1  | 0.63 1   | 3.21 2  | 5.01 1  | 0.86 2  | 0.01 1     | 0.43     | 4.70 2  | 1.35 2   | 0.77 2  | 7.12 2   | 0.21 2  | 0.01 2  | 0 10   |
|           | <sup>204</sup> Pb/<br><sup>206</sup> Pb | .000174 | .000071 | .001414  | v<br>1  | .000092 | 001116  | .000741     | .000093  | .006618  | .005147 | .003302 | .003231 | .000033 | .000162 | .000832  | .001689  | ·<br>·  | .000255  | .002074 | .000408 | .000298 | > 000059 < | .000021  | .002652 | .000390  | .000503 | .004512  | .000172 | V<br>I  | 000000 |
|           | %Pb*                                    | 14.1 0  | 35.6 0  | 29.8 0   | 68.9    | 29.8 0  | 30.0 (  | 33.4 0      | 29.0 0   | 25.6 0   | 36.8 0  | 25.4 0  | 24.4 0  | 27.5 0  | 19.5 0  | 13.6 0   | 42.2 0   | 20.7    | 28.4 0   | 29.4 0  | 38.9 0  | 14.2 0  | 58.1 0     | 82.3 0   | 23.2 0  | 8.2 0    | 21.6 0  | 25.2 0   | 25.8 0  | 31.3    |        |
|           | ZIN/U                                   | 0.71    | 0.26    | 0.55     | 0.31    | 0.66    | 0.64    | 0.63        | 0.59     | 0.90     | 0.79    | 1.07    | 0.73    | 0.48    | 0.49    | 0.65     | 0.65     | 0.01    | 0.31     | 0.57    | 0.50    | 0.69    | 0.17       | 0.19     | 0.52    | 0.67     | 0.53    | 0.72     | 0.56    | 0.70    | 0.00   |
|           | Th<br>ppm)                              | 88      | 128     | 419      | 181     | 551     | 507     | 556         | 460      | 493      | 528     | 702     | 328     | 360     | 265     | 237      | 674      | 3       | 186      | 425     | 342     | 250     | 137        | 167      | 315     | 134      | 306     | 467      | 389     | 576     |        |
|           | ÷<br>F                                  | 4       | 5       | 52       | 81      | 41      | 87      | <i>LL</i> : | 780      | 546      | 572     | 554     | 446     | 744     | 542     | 363      | 037      | 322     | 602      | 742     | 676     | 365     | 787        | 860      | 611     | 201      | 575     | 650      | 069     | 827     | 100    |
|           | U<br>U                                  | 12      | 48      | 2        | ŝ       | ×       | ~       | œ           | •        |          | -       | ~       |         | •       |         |          | <u> </u> |         |          |         |         |         | ÷          |          |         |          |         |          |         |         |        |
|           | Grain. U<br>spot (ppn                   | 1.1 12  | 2.1 48  | 3.1 70   | 4.1 5   | 5.1 8   | 7.1 7   | 8.1 8       | 9.1      | 10.1     | 13.1    | 14.1 (  | 15.1    | 16.1    | 17.1    | 18.1     | 21.1 1,  | 22.1    | 23.1     | 24.1    | 25.1    | 26.1    | 27.1       | 28.1     | 29.1    | 30.1     | 31.1    | 32.1     | 33.1    | 34.1    |        |

TABLE 2. ANALYTICAL DATA FOR SAMPLE F004-21 (SUMMARY OF SHRIMP U-Pb ZIRCON RESULTS FOR SAMPLE F004-21).

|                         |                      |                                  |                                      |                             |   |  |  | Total ]                           | Ratios                                  |                            |  | R                              | adiogenic ]               | Ratios                |   |                                   |                                     |                                 | Age (N              | <b>[a</b> )                                      |                        |           |
|-------------------------|----------------------|----------------------------------|--------------------------------------|-----------------------------|---|--|--|-----------------------------------|---|----------------------------|--|--------------------------------|---------------------------|-----------------------|---|-----------------------------------|-------------------------------------|---------------------------------|---------------------|--|------------------------|-----------|
| Grain.<br>spot          | U<br>( <b>udd</b> )  | Th<br>(ppm)                      | Th/U                                 | <sup>206</sup> Pb*<br>(ppm) | <sup>204</sup> Pb/<br><sup>206</sup> Pb         | f <sub>206</sub><br>%  | <sup>238</sup> U/<br><sup>206</sup> Pb   | +1                                | <sup>207</sup> Pb/<br><sup>206</sup> Pb | ++                         | <sup>206</sup> Pb/<br><sup>238</sup> U | +1                             | 207 <b>Pb/</b>            | +1                    | <sup>207</sup> Pb/<br><sup>206</sup> Pb | +1                                | d                                   | <sup>206</sup> Pb/              | +1                  | <sup>207</sup> Pb/                               |                        | %<br>Disc |
| 36.1                    | 636                  | 291                              | 0.46                                 | 25.0                        | 0.001799  | 2.96   | 21.821   | 0.260                             | 0.0756                                  | 0.0011                     | 0.0445                                 | 0.0005                         |                           |                       | ı                                       |                                   |                                     | 280                             | ŝ                   |  |                        |           |
| 37.1                    | 583                  | 300                              | 0.51                                 | 21.7                        | 0.000215  | 0.21   | 23.073   | 0.280                             | 0.0534                                  | 0.0010                     | 0.0432                                 | 0.0005                         |                           | ,                     |   |                                   | ,                                   | 273                             | 3                   |  |                        |           |
| 38.1                    | 871                  | 562                              | 0.64                                 | 32.0                        | 0.000364  | 0.01   | 23.365   | 0.267                             | 0.0518                                  | 0.0008                     | 0.0428                                 | 0.0005                         |                           | ,                     |   | ,                                 | ,                                   | 270                             | б                   | ,  | ,                      |           |
| 40.1                    | 883                  | 453                              | 0.51                                 | 33.9                        | 0.000032  | 0.07   | 22.399   | 0.361                             | 0.0525                                  | 0.0008                     | 0.0446                                 | 0.0007                         |                           | ,                     | ,                                       |                                   | ,                                   | 281                             | 4                   | ,  | ,                      |           |
| 41.1                    | 551                  | 332                              | 0.60                                 | 20.5                        | 0.000145  | <0.01  | 23.101   | 0.284                             | 0.0516                                  | 0.0010                     | 0.0433                                 | 0.0005                         |                           | ,                     |   |                                   |                                     | 273                             | З                   |  |                        |           |
| 42.1                    | 663                  | 408                              | 0.62                                 | 25.1                        | 0.000693  | 1.02   | 22.727   | 0.290                             | 0.0600                                  | 0.0010                     | 0.0436                                 | 0.0006                         |                           | ,                     |   |                                   |                                     | 275                             | 3                   |  |                        |           |
| 43.1                    | 257                  | 124                              | 0.48                                 | 9.7                         | 0.000159  | 0.10   | 22.823   | 0.331                             | 0.0526                                  | 0.0015                     | 0.0438                                 | 0.0006                         |                           | ,                     |   |                                   |                                     | 276                             | 4                   |  |                        |           |
| 44.1                    | 1,081                | 984                              | 0.91                                 | 43.2                        | 0.001981  | 2.62   | 21.529   | 0.248                             | 0.0730                                  | 0.0009                     | 0.0452                                 | 0.0005                         |                           |                       | ,                                       |                                   |                                     | 285                             | 3                   |  |                        |           |
| 45.1                    | 685                  | 419                              | 0.61                                 | 25.2                        |   | <0.01  | 23.388   | 0.280                             | 0.0509                                  | 0.0009                     | 0.0428                                 | 0.0005                         |                           |                       | ,                                       |                                   |                                     | 270                             | 3                   |  |                        |           |
| 46.1                    | 398                  | 372                              | 0.94                                 | 14.1                        | 0.000162  | 0.12   | 24.316   | 0.294                             | 0.0524                                  | 0.0009                     | 0.0411                                 | 0.0005                         |                           | ,                     | ,                                       |                                   |                                     | 260                             | 3                   |  |                        |           |
| 47.1                    | 161                  | 98                               | 0.61                                 | 6.2                         | 0.002612  | 4.12   | 22.090   | 0.304                             | 0.0848                                  | 0.0021                     | 0.0434                                 | 0.0006                         |                           | ,                     | ,                                       | ī                                 | ,                                   | 274                             | 4                   |  |                        |           |
| 48.1                    | 678                  | 406                              | 0.60                                 | 25.0                        | 0.000017  | 0.17   | 23.350   | 0.272                             | 0.0530                                  | 0.0006                     | 0.0428                                 | 0.0005                         |                           |                       | ,                                       |                                   |                                     | 270                             | ŝ                   |  |                        |           |
| 49.1                    | 471                  | 193                              | 0.41                                 | 17.2                        | 0.000050  | 0.18   | 23.511   | 0.283                             | 0.0531                                  | 0.0008                     | 0.0425                                 | 0.0005                         |                           |                       | ,                                       |                                   |                                     | 268                             | 3                   |  |                        |           |
| 50.1                    | 789                  | 272                              | 0.34                                 | 35.5                        | 0.000032  | 0.21   | 19.092   | 0.229                             | 0.0547                                  | 0.0006                     | 0.0523                                 | 0.0006                         |                           |                       | ,                                       |                                   |                                     | 328                             | 4                   |  |                        |           |
| 51.1                    | 300                  | 65                               | 0.22                                 | 16.2                        | 0.000259  | 0.03   | 15.946   | 0.196                             | 0.0548                                  | 0.0008                     | 0.0627                                 | 0.0008                         | ,                         |                       | ,                                       |                                   |                                     | 392                             | 5                   |  |                        |           |
| 52.1                    | 126                  | 134                              | 1.06                                 | 4.7                         |   | <0.01  | 23.209   | 0.342                             | 0.0509                                  | 0.0015                     | 0.0431                                 | 0.0006                         |                           |                       |   |                                   |                                     | 272                             | 4                   |  |                        |           |
| 53.1                    | 586                  | 288                              | 0.49                                 | 21.5                        | 0.000029  | 0.06   | 23.471   | 0.271                             | 0.0521                                  | 0.0006                     | 0.0426                                 | 0.0005                         |                           |                       | ,                                       |                                   |                                     | 269                             | б                   |  |                        |           |
| 54.1                    | 455                  | 324                              | 0.71                                 | 17.0                        | 0.001647  | 2.82   | 23.028   | 0.271                             | 0.0742                                  | 0.0009                     | 0.0422                                 | 0.0005                         | ı                         | ,                     | ,                                       |                                   |                                     | 266                             | б                   |  |                        |           |
| 55.1                    | 684                  | 401                              | 0.59                                 | 25.4                        | 0.000077  | <0.01  | 23.123   | 0.265                             | 0.0511                                  | 0.0006                     | 0.0433                                 | 0.0005                         | ı                         | ,                     | ,                                       |                                   |                                     | 273                             | б                   |  |                        |           |
| 56.1                    | 601                  | 260                              | 0.43                                 | 21.5                        | 0.000064  | 0.02   | 24.071   | 0.282                             | 0.0517                                  | 0.0007                     | 0.0415                                 | 0.0005                         | ,                         |                       | ,                                       |                                   |                                     | 262                             | ŝ                   |  |                        |           |
| 57.1                    | 733                  | 436                              | 0.60                                 | 26.4                        | 0.000083  | 0.11   | 23.838   | 0.282                             | 0.0524                                  | 0.0007                     | 0.0419                                 | 0.0005                         |                           |                       |   |                                   |                                     | 265                             | б                   |  |                        |           |
| 58.1                    | 940                  | 193                              | 0.21                                 | 35.2                        | 0.001162  | 1.98   | 22.941   | 0.265                             | 0.0675                                  | 0.0013                     | 0.0427                                 | 0.0005                         |                           |                       | ,                                       |                                   |                                     | 270                             | ŝ                   |  |                        |           |
| 59.1                    | 1,770                | 2,148                            | 1.21                                 | 60.3                        | 0.000014  | 0.11   | 25.237   | 0.283                             | 0.0521                                  | 0.0004                     | 0.0396                                 | 0.0004                         |                           |                       | ,                                       |                                   |                                     | 250                             | 3                   |  |                        |           |
| 60.1                    | 629                  | 374                              | 0.59                                 | 21.6                        | 0.000130  | 0.22   | 25.012   | 0.495                             | 0.0530                                  | 0.0007                     | 0.0399                                 | 0.0008                         |                           | ,                     |   | ,                                 | ,                                   | 252                             | 5                   | ,  | ,                      |           |
| Notes: <b>1.</b><br>dif | Uncertai<br>ferent m | nties givel<br>ounts); <b>3.</b> | n at the o<br>f <sub>206</sub> % den | me σ leve<br>lotes the p    | l; 2. Error ir<br>bercentage of<br>the measured | 1 FC1 rei<br>? <sup>206</sup> Pb th:<br>1 <sup>2381 1/2061</sup> | The second structure is common at is common and some other second solutions at 18,000 and 19,000 at 19,0000 at 19,0000 at 19,0 | on calibra<br>on Pb; <b>4</b> . F | ttion was 0.<br>or areas ol             | 38% & 0.77<br>der than ~80 | 2% for the a<br>0 Ma corre             | unalytical se<br>ction for cor | ssions (not<br>nmon Pb rr | included<br>ade using | in above er<br>g the measur             | rors but<br>ed <sup>204</sup> Pb. | required<br>/ <sup>206</sup> Pb rat | when com<br>io; <b>5.</b> For a | nparing<br>treas yo | <sup>206</sup> Pb/ <sup>238</sup> U<br>anger tha | J data fr<br>in ~800 ] | om<br>Ma  |

Permian depositional age of metaturbidites of the Duque de York Complex, southern Chile...

Table 2 continued.

|             | %<br>Disc  |   |  |  | -  |  |   |  |  |   |  |   |   |  |  |   | -                                       |  | ٢  |  |   |  |  |   |  |                                       |
|-------------|--|---|--|--|--|--|---|--|--|---|--|---|---|--|--|---|---|--|--|--|---|--|--|---|--|---------------------------------------|
|             | +  |   |  |  | 56   |  |   |  |  |   |  |   |   |  |  |   | 20                                      |  | 7  |  |   |  |  |   |  |                                       |
| Ia)         | <sup>207</sup> Pb/   |   | ,  |  | 1,073  | ·  |   |  |  |   |  |   |   |  |  |   | 2,071                                   | ,  | 1,380  |  |   |  |  |   | ·  | ,                                     |
| Age (A      | +1   | 7   | 3  | 9                                      | 14   | 9  | 4   | 5  | 4  | 4   | 9  | 5   | 4   | 6  | 3  | 5   | 27                                      | з  | 13   | 9                                      | 4   | 4  | 5  | 8   | 5  | 4                                     |
|             | <sup>206</sup> Pb/<br><sup>238</sup> U   | 432   | 264  | 315                                    | 1,089  | 469  | 307   | 398                                      | 280                                      | 287                                       | 528  | 377                                       | 284   | 757  | 261  | 353   | 2,089                                   | 296  | 1,287  | 373                                    | 301                                       | 292                                      | 405  | 642   | 363  | 293                                   |
|             | C  |   | ,  |  | 0.448  | ,  |   |  |  |   | ,  |   |   | ,  | ,  |   | 0.808                                   | ,  | 0.947  |  |   |  |  |   | ,  |                                       |
|             | +1   |   | ŀ  |  | 0.0021   | ı  |   |  |  |   | ,  |   |   | ,  | ,  |   | 0.0014                                  |  | 0.0003   |  |   |  |  |   | ı  |                                       |
|             | <sup>207</sup> Pb/<br><sup>206</sup> Pb  |   |  |  | 0.0752   | ,  |   |  |  |   | ,  | ,   | ,   |  | ·  | ,   | 0.1280                                  |  | 0.0879   |  | ,   |  |  |   | ,  | ,                                     |
| atios       | +1   |   | ı  |  | 0.059  | ı  |   |  |  |   | ı  |   |   | ı  | ı  | ,   | 0.128                                   |  | 0.032  |  |   |  |  |   | ı  | ,                                     |
| ndiogenic R | <sup>207</sup> Pb/<br><sup>235</sup> U   |   | ·  |  | 1,906  | ı  | ,   | ,  | ,  | ,   | ı  | ı   | ı   | ı  | ı  | ·   | 6,756                                   | ı  | 2,678  | ,                                      | ı   |  |  |   | ı  |                                       |
| R           | +1   | 0.0011  | 0.0005   | 0.0009                                 | 0.0026   | 0.0009   | 0.0006  | 0.0008                                   | 0.0006                                   | 0.0006                                    | 0.0011   | 0.0007                                    | 0.0006  | 0.0016   | 0.0005   | 0.0008  | 0.0058                                  | 0.0006   | 0.0025   | 0.0009                                 | 0.0007                                    | 0.0006                                   | 0.0008   | 0.0013                                      | 0.0009   | 0.0006                                |
|             | <sup>206</sup> Pb/<br><sup>238</sup> U   | 0.0693  | 0.0418   | 0.0501                                 | 0.1840   | 0.0754   | 0.0487  | 0.0637                                   | 0.0444                                   | 0.0456                                    | 0.0854   | 0.0603                                    | 0.0450  | 0.1245   | 0.0413   | 0.0564  | 0.3827                                  | 0.0470   | 0.2210   | 0.0596                                 | 0.0479                                    | 0.0464                                   | 0.0649   | 0.1047                                      | 0.0580   | 0.0466                                |
| ĺ           | +1   | 0.0017  | 0.0010   | 0.0011                                 | 0.0019   | 0.0007   | 0.0008  | 0.0007                                   | 0.0010                                   | 0.0018                                    | 0.0008   | 0.0009                                    | 0.0012  | 0.0008   | 0.0010   | 0.0013  | 0.0014                                  | 0.0007   | 0.0003   | 0.0015                                 | 0.0010                                    | 0.0011                                   | 0.0006   | 0.0007                                      | 0.0012   | 0.0011                                |
| tios        | <sup>207</sup> Pb/<br><sup>206</sup> Pb  | 0.0552  | 0.0527   | 0.0540                                 | 0.0743   | 0.0564   | 0.0536  | 0.0555                                   | 0.0522                                   | 0.0525                                    | 0.0570   | 0.0544                                    | 0.0530  | 0.0642   | 0.0522   | 0.0552  | 0.1280                                  | 0.0511   | 0.0879   | 0.0559                                 | 0.0517                                    | 0.0516                                   | 0.0552   | 0.0613                                      | 0.0544   | 0.0516                                |
| Total Ra    | +1   | 24 (  | 03   | 51 (                                   | 75 (   | 59 (   | 11  | 00                                       | ~  |   | -<br>-   | е<br>Э                                    | 5   | 00   | 08   | 46 (  | t0                                      | 5  | 52 (   | 250 (                                  | 87 (                                      | 284 (                                    | .183 (   | .117 (                                      | .250 (   | 0.273 (                               |
|             |  | 0.2   | 0.3  | 0.3(                                   | 0.07   | 0.1  | 0.25  | 0.19                                     | 0.28                                     | 0.278                                     | 0.14   | 0.20                                      | 0.29  | 0.1  | 0.3  | 0.2   | 0.0                                     | 0.25   | 0.0  | 0.2                                    | 0.2                                       | 0.                                       | 0  | $\circ$                                     | 0  | _                                     |
|             | <sup>238</sup> U/<br><sup>206</sup> Pb   | 14.427 0.2  | 23.866 0.3                                     | 19.939 0.30                            | 5.442 0.07   | 13.261 0.1   | 20.488 0.25                                     | 15.693 0.19                              | 22.522 0.28                              | 21.915 0.278                              | 11.728 0.14  | 16.590 0.20                               | 22.190 0.25                                     | 8.033 0.1  | 24.174 0.3   | 17.709 0.2  | 2.613 0.04                              | 21.297 0.25  | 4.525 0.0  | 16.726 0.3                             | 20.909 0.2                                | 21.588 0.                                | 15.404 0   | 9.547 (                                     | 17.240 0   | 21.483                                |
|             | f <sub>206</sub> 2.38U/<br>%206 <b>Pb</b>  | <0.01 14.427 0.2  | 0.14 23.866 0.3                                | 0.17 19.939 0.30                       | <0.01 5.442 0.07   | <0.01 13.261 0.1   | 0.13 20.488 0.25                                | 0.10 15.693 0.19                         | 0.04 22.522 0.28                         | 0.05 21.915 0.278                         | <0.01 11.728 0.14  | 0.03 16.590 0.20                          | 0.13 22.190 0.25                                | <0.01 8.033 0.1  | 0.10 24.174 0.3  | 0.20 17.709 0.2   | <0.01 2.613 0.02                        | <0.01 21.297 0.25  | <0.01 4.525 0.0  | 0.23 16.726 0.2                        | <0.01 20.909 0.2                          | <0.01 21.588 0.                          | 0.04 15.404 0  | 0.03 9.547 (                                | 0.07 17.240 (  | <0.01 21.483                          |
|             | м-Ph/ f <sub>206</sub> <sup>238</sup><br><sup>206</sup> Pb % <sup>206</sup> Pb   | - <0.01 14.427 0.2  | 0.000063 0.14 23.866 0.3                       | - 0.17 19.939 0.3                      | - <0.01 5.442 0.07   | - <0.01 13.261 0.1   | 0.000109 0.13 20.488 0.25                       | - 0.10 15.693 0.19                       | - 0.04 22.522 0.28                       | - 0.05 21.915 0.278                       | 0.000037 <0.01 11.728 0.14   | - 0.03 16.590 0.20                        | 0.000141 0.13 22.190 0.29                       | 0.000063 <0.01 8.033 0.1   | - 0.10 24.174 0.3  | 0.000019 0.20 17.709 0.2  | - <0.01 2.613 0.02                      | - <0.01 21.297 0.25  | 0.000002 <0.01 4.525 0.0   | - 0.23 16.726 0.2                      | - <0.01 20.909 0.2                        | - <0.01 21.588 0.                        | 0.000019 0.04 15.404 0   | 0.000067 0.03 9.547 (                       | 0.000236 0.07 17.240 0   | - <0.01 21.483                        |
|             | <sup>206</sup> Pb <sub>8</sub> * <sup>206</sup> Db f <sub>206</sub> <sup>236</sup> <sup>236</sup> <sup>206</sup> Db <sup>90</sup> Pb   | 5.0 - <0.01 14.427 0.2  | 10.9 0.000063 0.14 23.866 0.3                  | 9.7 - 0.17 19.939 0.3                  | 14.1 - <0.01 5.442 0.07  | 28.5 - <0.01 13.261 0.1  | 20.0 0.000109 0.13 20.488 0.25                  | 22.6 - 0.10 15.693 0.19                  | 11.0 - 0.04 22.522 0.28                  | 12.4 - 0.05 21.915 0.278                  | 17.6 0.000037 <0.01 11.728 0.14  | 21.1 - 0.03 16.590 0.20                   | 8.0 0.000141 0.13 22.190 0.29                   | 26.9 0.000063 <0.01 8.033 0.1  | 11.6 - 0.10 24.174 0.3   | 7.4 0.000019 0.20 17.709 0.2  | 17.1 - <0.01 2.613 0.02                 | 26.3 - <0.01 21.297 0.25   | 204.7  0.000002  < 0.01  4.525  0.0  | 5.6 - 0.23 16.726 0.2                  | 11.5 - <0.01 20.909 0.2                   | 10.1 - <0.01 21.588 0.                   | 35.8 0.000019 0.04 15.404 0  | 29.7 0.00067 0.03 9.547 (                   | 9.9 0.000236 0.07 17.240 0   | 13.7 - <0.01 21.483                   |
|             | Th/U         f         f         f         2%         2%         2%         1% <th1%< th="">         1%         1%         1%<td>0.80 5.0 - &lt;0.01 14.427 0.2</td><td>0.43 10.9 0.000063 0.14 23.866 0.3</td><td>0.47 9.7 - 0.17 19.939 0.3</td><td>0.54 14.1 - &lt;0.01 5.442 0.07</td><td>0.40 28.5 - &lt;0.01 13.261 0.1</td><td>0.33 20.0 0.000109 0.13 20.488 0.25</td><td>0.84 22.6 - 0.10 15.693 0.19</td><td>0.50 11.0 - 0.04 22.522 0.28</td><td>0.29 12.4 - 0.05 21.915 0.278</td><td>0.62 17.6 0.000037 &lt;0.01 11.728 0.14</td><td>0.31 21.1 - 0.03 16.590 0.20</td><td>0.61 8.0 0.000141 0.13 22.190 0.29</td><td>0.34 26.9 0.000063 &lt;0.01 8.033 0.1</td><td>0.61 11.6 - 0.10 24.174 0.3</td><td>0.98 7.4 0.000019 0.20 17.709 0.2</td><td>0.45 17.1 - &lt;0.01 2.613 0.02</td><td>0.41 26.3 - &lt;0.01 21.297 0.25</td><td>0.60  204.7  0.000002  &lt;0.01  4.525  0.0</td><td>0.44 5.6 - 0.23 16.726 0.2</td><td>0.38 11.5 - &lt;0.01 20.909 0.2</td><td>0.65 10.1 - &lt;0.01 21.588 0.</td><td>0.29 35.8 0.000019 0.04 15.404 0</td><td>0.23 29.7 0.000067 0.03 9.547 0</td><td>1.42 9.9 0.000236 0.07 17.240 0</td><td>0.39 13.7 - &lt;0.01 21.483</td></th1%<> | 0.80 5.0 - <0.01 14.427 0.2   | 0.43 10.9 0.000063 0.14 23.866 0.3             | 0.47 9.7 - 0.17 19.939 0.3             | 0.54 14.1 - <0.01 5.442 0.07   | 0.40 28.5 - <0.01 13.261 0.1   | 0.33 20.0 0.000109 0.13 20.488 0.25             | 0.84 22.6 - 0.10 15.693 0.19             | 0.50 11.0 - 0.04 22.522 0.28             | 0.29 12.4 - 0.05 21.915 0.278             | 0.62 17.6 0.000037 <0.01 11.728 0.14   | 0.31 21.1 - 0.03 16.590 0.20              | 0.61 8.0 0.000141 0.13 22.190 0.29              | 0.34 26.9 0.000063 <0.01 8.033 0.1   | 0.61 11.6 - 0.10 24.174 0.3  | 0.98 7.4 0.000019 0.20 17.709 0.2   | 0.45 17.1 - <0.01 2.613 0.02            | 0.41 26.3 - <0.01 21.297 0.25  | 0.60  204.7  0.000002  <0.01  4.525  0.0   | 0.44 5.6 - 0.23 16.726 0.2             | 0.38 11.5 - <0.01 20.909 0.2              | 0.65 10.1 - <0.01 21.588 0.              | 0.29 35.8 0.000019 0.04 15.404 0   | 0.23 29.7 0.000067 0.03 9.547 0             | 1.42 9.9 0.000236 0.07 17.240 0  | 0.39 13.7 - <0.01 21.483              |
|             | Th <sup>246</sup> Pb* <sup>244</sup> Pb/ f <sub>266</sub> <sup>238</sup> U/<br>(ppm) <sup>246</sup> Pph % <sup>266</sup> Ph  | 66         0.80         5.0         -         <0.01   | 131 0.43 10.9 0.000063 0.14 23.866 0.3         | 106 0.47 9.7 - 0.17 19.939 0.3         | 48 0.54 14.1 - <0.01 5.442 0.07  | 178 0.40 28.5 - <0.01 13.261 0.1   | 156 0.33 20.0 0.000109 0.13 20.488 0.25         | 347 0.84 22.6 - 0.10 15.693 0.19         | 146 0.50 11.0 - 0.04 22.522 0.28         | 91 0.29 12.4 - 0.05 21.915 0.275          | 150         0.62         17.6         0.000037         <0.01         11.728         0.14                           | 127 0.31 21.1 - 0.03 16.590 0.20          | 125 0.61 8.0 0.000141 0.13 22.190 0.25          | 86 0.34 26.9 0.000063 <0.01 8.033 0.1  | 199         0.61         11.6         -         0.10         24.174         0.3                          | 149 0.98 7.4 0.000019 0.20 17.709 0.2   | 23 0.45 17.1 - <0.01 2.613 0.02         | 269 0.41 26.3 - <0.01 21.297 0.25  | $651 \qquad 0.60 \qquad 204.7 \qquad 0.000002  <0.01 \qquad 4.525 \qquad 0.0$              | 49 0.44 5.6 - 0.23 16.726 0.2          | 107 0.38 11.5 - <0.01 20.909 0.2          | 166 0.65 10.1 - <0.01 21.588 0.          | 189 0.29 35.8 0.000019 0.04 15.404 0   | 77 0.23 29.7 0.000067 0.03 9.547 0          | 281 1.42 9.9 0.000236 0.07 17.240 0  | 133 0.39 13.7 - <0.01 21.483          |
|             | $ \begin{array}{cccccccccccccccccccccccccccccccccccc$  | 83 66 0.80 5.0 - <0.01 14.427 0.2   | 304 131 0.43 10.9 0.000063 0.14 23.866 0.3     | 226 106 0.47 9.7 - 0.17 19.939 0.3     | 89 48 0.54 14.1 - <0.01 5.442 0.07   | 440         178         0.40         28.5         -         <0.01         13.261         0.1 | 477 156 0.33 20.0 0.000109 0.13 20.488 0.25     | 413 347 0.84 22.6 - 0.10 15.693 0.19     | 289 146 0.50 11.0 - 0.04 22.522 0.28     | 317 91 0.29 12.4 - 0.05 21.915 0.276      | 241 150 0.62 17.6 0.000037 <0.01 11.728 0.14   | 407 127 0.31 21.1 - 0.03 16.590 0.20      | 205 125 0.61 8.0 0.000141 0.13 22.190 0.25      | 251         86         0.34         26.9         0.000063         <0.1         8.033         0.1               | 327 199 0.61 11.6 - 0.10 24.174 0.3  | 152         149         0.98         7.4         0.000019         0.20         17.709         0.2 | 52 23 0.45 17.1 - <0.01 2.613 0.02      | 652 269 0.41 26.3 - <0.01 21.297 0.25  | $1,078 \qquad 651 \qquad 0.60 \qquad 204.7 \qquad 0.000002  <0.01 \qquad 4.525 \qquad 0.0$ | 110 49 0.44 5.6 - 0.23 16.726 0.2      | 280 107 0.38 11.5 - <0.01 20.909 0.2      | 255 166 0.65 10.1 - <0.01 21.588 0.      | 642         189         0.29         35.8         0.000019         0.04         15.404         0 | 330 77 0.23 29.7 0.000067 0.03 9.547 0      | 198         281         1.42         9.9         0.000236         0.07         17.240         0              | 342 133 0.39 13.7 - <0.01 21.483      |
|             | Grain. U Th <sup>206</sup> Pb* <sup>204</sup> Pb/ f <sub>266</sub> <sup>238</sup> U/<br>spot (ppm) (ppm) <sup>206</sup> Pph % <sup>206</sup> Pb  | 1.1         83         66         0.80         5.0         -         <0.01         14.427         0.2 | 2.1 304 131 0.43 10.9 0.000063 0.14 23.866 0.3 | 3.1 226 106 0.47 9.7 - 0.17 19.939 0.3 | 4.1         89         48         0.54         14.1         -         <0.01         5.442         0.07 | 5.1 440 178 0.40 28.5 - <0.01 13.261 0.1   | 7.1 477 156 0.33 20.0 0.000109 0.13 20.488 0.25 | 8.1 413 347 0.84 22.6 - 0.10 15.693 0.19 | 9.1 289 146 0.50 11.0 - 0.04 22.522 0.28 | 10.1 317 91 0.29 12.4 - 0.05 21.915 0.276 | 11.1         241         150         0.62         17.6         0.000037         <0.01         11.728         0.14' | 12.1 407 127 0.31 21.1 - 0.03 16.590 0.20 | 13.1 205 125 0.61 8.0 0.000141 0.13 22.190 0.25 | 14.1         251         86         0.34         26.9         0.000063         <0.01         8.033         0.1 | 15.1         327         199         0.61         11.6         -         0.10         24.174         0.3 | 16.1 152 149 0.98 7.4 0.000019 0.20 17.709 0.2  | 17.1 52 23 0.45 17.1 - <0.01 2.613 0.04 | 18.1         652         269         0.41         26.3         -         <0.01         21.297         0.25 | 19.1  1,078  651  0.60  204.7  0.000002  <0.01  4.525  0.0                                 | 20.1 110 49 0.44 5.6 - 0.23 16.726 0.2 | 21.1 280 107 0.38 11.5 - <0.01 20.909 0.2 | 22.1 255 166 0.65 10.1 - <0.01 21.588 0. | 23.1 642 189 0.29 35.8 0.00019 0.04 15.404 0   | 24.1 330 77 0.23 29.7 0.000067 0.03 9.547 ( | 25.1         198         281         1.42         9.9         0.000236         0.07         17.240         0 | 26.1 342 133 0.39 13.7 - <0.01 21.483 |

| continued. |
|------------|
| ŝ          |
| Table      |

|                |       |             |      |                             |   | I                     |                        | Total R: | atios                                   |        |  | R      | adiogenic F        | atios |   |        | I     |                    | Age (N | (a)                |             |
|----------------|-------|-------------|------|-----------------------------|---|-----------------------|------------------------|----------|---|--------|--|--------|--------------------|-------|---|--------|-------|--------------------|--------|--------------------|-------------|
| Grain.<br>spot | (mqq) | Th<br>(ppm) | Th/U | <sup>206</sup> Pb*<br>(ppm) | <sup>204</sup> Pb/<br><sup>206</sup> Pb | f <sup>206</sup><br>% | 238U/<br>206 <b>Pb</b> | +1       | <sup>207</sup> Pb/<br><sup>206</sup> Pb | +I     | <sup>206</sup> Pb/<br><sup>238</sup> U | +1     | <sup>207</sup> Pb/ | +1    | <sup>207</sup> Pb/<br><sup>206</sup> Pb | +1     | ٩     | <sup>206</sup> Pb/ | +1     | <sup>207</sup> Pb/ | •` <b>I</b> |
| 27.1           | 406   | 91          | 0.22 | 22.7                        | 0.000046                                | 0.02                  | 15.337                 | 0.186    | 0.0550                                  | 0.0014 | 0.0652                                 | 0.0008 |                    |       |   |        |       | 407                | s      |                    |             |
| 28.1           | 195   | 98          | 0.50 | 7.8                         | 0.000187                                | <0.01                 | 21.495                 | 0.295    | 0.0509                                  | 0.0012 | 0.0466                                 | 0.0006 | ,                  |       |   | ,      |       | 294                | 4      |                    |             |
| 29.1           | 96    | 55          | 0.57 | 3.9                         |   | <0.01                 | 21.389                 | 0.341    | 0.0521                                  | 0.0018 | 0.0468                                 | 0.0008 |                    |       |   |        |       | 295                | 5      |                    |             |
| 30.1           | 639   | 450         | 0.70 | 24.9                        | 0.000019                                | 0.05                  | 22.066                 | 0.265    | 0.0524                                  | 0.0007 | 0.0453                                 | 0.0005 | ,                  |       |   |        |       | 286                | 3      |                    | ,           |
| 31.1           | 163   | 35          | 0.21 | 12.1                        | ,                                       | 0.17                  | 11.523                 | 0.207    | 0.0595                                  | 0.0011 | 0.0866                                 | 0.0016 | ·                  |       |   |        |       | 536                | 6      |                    |             |
| 32.1           | 262   | 282         | 1.08 | 20.1                        | 0.000066                                | 0.03                  | 11.174                 | 0.141    | 0.0589                                  | 0.0009 | 0.0895                                 | 0.0012 | ,                  |       |   |        |       | 552                | ٢      |                    |             |
| 33.1           | 161   | 115         | 0.71 | 6.5                         | 0.000183                                | 0.19                  | 21.340                 | 0.311    | 0.0537                                  | 0.0016 | 0.0468                                 | 0.0007 | ,                  |       |   |        |       | 295                | 4      |                    |             |
| 34.1           | 341   | 152         | 0.45 | 15.3                        |   | <0.01                 | 19.186                 | 0.247    | 0.0526                                  | 0.0011 | 0.0521                                 | 0.0007 | ,                  |       |   |        |       | 328                | 4      |                    |             |
| 35.1           | 161   | 104         | 0.64 | 6.9                         | 0.000148                                | -0.14                 | 20.105                 | 0.298    | 0.0515                                  | 0.0015 | 0.0498                                 | 0.0007 | ·                  | ,     |   |        |       | 313                | 5      | ·                  | ,           |
| 36.1           | 404   | 248         | 0.61 | 16.0                        | ·                                       | <0.01                 | 21.699                 | 0.275    | 0.0515                                  | 0.0009 | 0.0461                                 | 0.0006 | ı                  | ,     |   | ī      |       | 291                | 4      | ı                  |             |
| 37.1           | 405   | 170         | 0.42 | 15.6                        | ,                                       | 0.10                  | 22.272                 | 0.277    | 0.0528                                  | 0.0009 | 0.0449                                 | 0.0006 | ·                  |       |   |        |       | 283                | 3      |                    |             |
| 38.1           | 173   | 114         | 0.66 | 8.9                         | 0.000065                                | <0.01                 | 16.631                 | 0.226    | 0.0531                                  | 0.0011 | 0.0602                                 | 0.0008 | ı                  | ,     |   | ,      | ,     | 377                | 5      |                    | ,           |
| 39.1           | 172   | 59          | 0.34 | 6.8                         | ,                                       | 0.05                  | 21.824                 | 0.305    | 0.0525                                  | 0.0013 | 0.0458                                 | 0.0006 | ı                  | ,     |   | ,      | ,     | 289                | 4      | ,                  | ,           |
| 40.1           | 196   | 146         | 0.74 | 8.0                         | 0.000090                                | <0.01                 | 20.915                 | 0.294    | 0.0517                                  | 0.0013 | 0.0479                                 | 0.0007 | ,                  |       |   |        |       | 301                | 4      |                    |             |
| 41.1           | 151   | 80          | 0.53 | 5.9                         | 0.000236                                | <0.01                 | 22.004                 | 0.318    | 0.0516                                  | 0.0014 | 0.0455                                 | 0.0007 | ·                  |       |   | ,      |       | 287                | 4      |                    | ,           |
| 42.1           | 102   | 72          | 0.70 | 17.9                        | 0.000009                                | 0.02                  | 4.903                  | 0.072    | 0.0851                                  | 0.0011 | 0.2039                                 | 0.0030 | 2,389              | 0.046 | 0.0850                                  | 0.0011 | 0.761 | 1, 196             | 16     | 1,315              | 24          |
| 43.1           | 25    | 6           | 0.35 | 1.0                         | 0.001193                                | <0.01                 | 21.965                 | 0.539    | 0.0502                                  | 0.0033 | 0.0456                                 | 0.0011 | ,                  | ,     | ,                                       | ı      | ı     | 288                | ٢      | ı                  |             |
|                |       |             |      |                             |   |                       |                        |          |   |        |  |        |                    |       |   |        |       |                    |        |                    |             |

mounts); 3.  $f_{26}$ % denotes the percentage of <sup>206</sup>Pb that is common Pb; 4. For areas older than ~800 Ma correction for common Pb made using the measured <sup>204</sup>Pb/<sup>206</sup>Pb ratio; 5. For areas younger than ~800 Ma correction Notes: 1. Uncertainties given at the one  $\sigma$  level; 2. Error in FC1 reference zircon calibration was 0.72% for the analytical sessions (not included in above errors but required when comparing <sup>206</sup>Pb/<sup>73U</sup> data from different for common Pb made using the measured <sup>234</sup>U/<sup>266</sup>Pb and <sup>207</sup>Pb/<sup>306</sup>Pb ratios following Tera and Wasserburg (1972) as outlined in Williams (1998); 6. For % Disc, 0% denotes a concordant analysis.
## 4. Results

### 4.1. Palynology

The palynological analysis revealed a palynoflora composed predominantly by Gymnospermopsida monosaccate pollen grains, although Gymnospermopsida bisaccate pollen grains were also observed. Selected species are illustrated in figure 3. The samples show a very low frequency of palynomorphs, and in most cases an exact identification of the species is impossible because of the bad preservation state of the palynomorphs. The palynomorphs detected within the TL are *Punctatisporites punctatus* (Ibrahim) Ibrahim, a Pteridophyta known from the Carboniferous to Triassic in New Zealand, Australia, Asia, Europe and South America (Alpern and Doubinger, 1973; Owens *et al.*, 2002; Pérez Loinaze, 2008).

The palynological association observed in the metasediments of the DYC (sampled in the Madre de Dios Archipelago and in the Diego de Almagro Island) is characterized by Gymnospermopsida pollen. In addition, Pteridophyta spores as well as rare green algae (Botryococcus braunii Kützing, Lower Carboniferous to Recent) and epiphyllous fungal spores (Granatisporites and Multicellaesporites spp.) have been observed. The Gymnospermopsida include Coniferales and Cordaitales. The more frequent monosaccate pollens are Plicatipollenites and Cannanoropollis spp., which are also represented in the Carboniferous-Permian of Gondwana (e.g., Vergel, 2008; Di Pasquo, 2009). The bisaccate pollen grains of Gymnospermopsida are assigned to the Protohaploxypinus sp., also known in middle Carboniferous successions of Argentina, but recognized also in the Permian of Brazil, South Africa, India, Antarctica, Australia and North America (Césari and Gutiérrez, 2000, and reference therein). Remnants of polyplicate and monocolpate pollen grains, of 80-95 µm, assigned to Praecolpatites sinuosus (Balme and Hennelly) Bharadwaj and Srivastava, have been observed (sample FO04-22, Fig. 4). They have broad distribution in the Permian of Argentina, Brazil, Australia, Africa, Antarctica and New Zealand (e.g., Lindström, 1995). Therefore, a Permian age for the deposition of the sediments of the DYC is inferred.



FIG. 3. Selected pollen grains, spores and algae from the studied samples. Black line represents 10 μm. A. Granatisporites sp.; B. Protohaploxypinus sp.; C. Cannanoropollis sp.; D. Botryococcus braunii; E. Punctatisporites punctatus; F. Plicatipollenites sp.

In addition, a humid environment of conifer and/ or cordaitales forests with an undergrowth of ferns (probably developed on wet shaded slopes) is proposed from the palynological association recorded in the DYC.

## 4.2. Petrography

The metasedimentary samples collected for U-Pb zircon dating were obtained from an outcrop where the DC and the DYC are in conformable and intercalated stratigraphic contact (Fig. 4). Significantly, this site corresponds to one of only two localities were this type of contact between these complexes is recorded. The samples were spatially associated, stratigraphically separated by ca. 10 m. The first sample (FO04-21) comes from a deformed (folded) metasedimentary horizon (0.04 to 0.06 m thick) of tuffaceous character, interbedded in metacherts of the DC. The microscopic petrographic description of this sample shows that it is mainly composed by very angular fragments (0.01-0.2 mm) of quartz (55%), altered feldspars (30%) and biotite flakes (15%) in a cryptocrystalline siliceous matrix. Accessory minerals include zircon, garnet, sphene, apatite and Fe-oxides. Scarce small and highly altered shard fragments were also observed. The biotites are oriented parallel to the contacts with the underlying radiolarian chert. This last feature coupled with the normal grading observed in this bed agrees with subaquatic conditions of deposition. The second sample (FO04-22) is a quartz rich metasandstone of the DYC previously analyzed by palynological methods. The sample was extracted from a massive and structureless sandstone bed (20 m of minimum thickness) nearly 3 m above the contact with the banded cherts of the DC. It is a feldspathic arenite formed by well to moderately sorted subangular and highly spherical fragments, with sizes between 0.02 and 1.2 mm (0.3 mm in average). Main fragments are quartz (60%), feldspars (30%), biotite (8%) and white mica (2%). Accessories include zircon, apatite, lithic fragments (basalts and rhyolites), garnet, pyrite and Fe-oxides.

### 4.3. U-Pb SHRIMP ages of detrital zircons

The Tera-Wasserburg diagrams plot the total ratios, uncorrected for common Pb, and show that the data generally plot close to Concordia (Fig. 5). Relative probability spectra of the detrital zircon ages are presented in figure 5. For sample FO04-21 54 grains were analyzed, whereas 42 grains were examined for sample FO04-22.



FIG. 4. A. Outcrops at Seno Contreras, where the stratigraphical contact between deformed banded cherts of the DC (above the white line) and shales and sandstones of the DYC (below) is observed; B. Stratigraphic column showing the disposition of the samples analyzed by U-Pb SHRIMP and by palynological methods. 1. Sandstones; 2. Banded cherts; 3. Shales; 4. Tuffaceous layer.

FO04-21. The zircons of this sample are prismatic and euhedral crystals, with zoned magmatic internal structures as seen under CL imaging (Fig. 6). This is compatible with its textural and mineralogical characteristics, which are indicative of the tuffaceous character of the metasediment. Although some of the youngest individual ages involve significant common Pb correction (Fig. 5); a correction has been applied to derive the radiogenic ratios and age of these analyses (Table 2). The age spectrum shows a narrow range of provenance ages with a major peak in the early middle Permian, representing *ca*.



FIG. 5. Tera-Wasseburg diagrams for zircon U-Pb data. Analyses are plotted as total ratios calibrated for U-Pb, but uncorrected for common Pb. The error ellipses are 68.3% confidence limits. The dotted arrow in FO04-21 shows the direction of common Pb at 270 Ma. Alignment along this arrow suggests a real inferred age on Concordia with variable degrees of incorporated common Pb at the time of crystallization.

76% of the analyses. Minor peaks are observed in the Carboniferous, Devonian, Ordovician, Cambrian and Neoproterozoic, each one equivalent to less than 8% of the total analyzed grains. The Permian analyses yield a weighted mean  $^{206}Pb/^{238}U$  age of 270.4±2.7 Ma (MSWD=1.2), interpreted as the maximum possible depositional age of the analyzed metasediment.

FO04-22. The zircon grains show zoned internal structures (Fig. 6), and subrounded to subangular shapes with high sphericity are predominant, although prismatic grains are observed as well. The grains analyzed from this sample are very low in common Pb. The relative probability plots of the detrital zircon ages display a prominent component in the early Permian (ca. 40% of the analyses), with other subordinate peaks in the Carboniferous and Devonian (ca. 17% of the analyses each one). There are scattered older ages ranging from Early Paleozoic to Neo and Mesoproterozoic aged noise and one Paleoproterozoic aged zircon. A weighted mean <sup>206</sup>Pb/<sup>238</sup>U age of 289.7±2.1 Ma (MSWD=1.3) place a constraint on the maximum age of deposition of this metasediment.

#### 5. Discussion

#### 5.1. Regional paleoenvironmental conditions

As pointed out by Cúneo (1996) and Buatois et al. (2006), it seems that the end of the late Paleozoic Ice Age in Gondwana is diachronous, waning first in South America, as revealed by litho- and biostratigraphic records (ca. 280 Ma; Iannuzzi et al., 2007), and then in Australia (ca. 260 Ma; Fielding et al., 2008). This diachronism has been habitually attributed to the Gondwana drift across the South Pole (López-Gamundí et al., 1994; Visser, 1996), but the possibility of more than one glacial event cannot be ruled out (Limarino et al., 2006). Roscher and Schneider (2006) show that there is a general trend of aridization in the Permo-Carboniferous interrupted by wet phases related to the waxing and waning of the Gondwana icecap. Lindström and McLoughlin (2007) indicate that during the middle to late Permian a gradual warming trend is evident from the western to the eastern parts of Gondwana. Furthermore, semiarid and arid climatic conditions in middle Permian times appear like a common feature in many western Gondwana basins (López-Gamundí et al., 1992; Limarino et al., 2006; Spalletti



FIG. 6. U-Pb zircon age provenance patterns (age versus relative probability) of the analyzed samples. Insets show the entire population of zircon ages. Montages of representative portions of the cathode-luminescence images for each sample, with individual spot ages.

and Limarino, 2006; Souza *et al.*, 2007), while the start of arid conditions in western Gondwana has been situated towards the end of the early Permian by Césari *et al.* (2007).

Palynomorphs documented in this study are comparable to those recorded in Carboniferous and Permian strata of other late Paleozoic Gondwanan basins, such as those exposed in the Chaco-Paraná Basin in Argentina and Uruguay (Césari et al., 1995; Beri et al., 2006), and at Rio Grande do Sul in Paraná Basin, Brazil (Souza and Marques-Toigo, 2005). It is noteworthy to emphasize that the only palynomorph with exclusive Permian record (Praecolpatites sinuosus) is in one of the samples with a Permian maximum depositional age (Fig. 4). Regarding the paleoenvironmental background mentioned above and the Permian age obtained in the DYC, the proposed paleoclimatic setting for the deposition of the late Paleozoic basins of southwestern Gondwana, in particular those situated in Patagonia, helps to

establish regional correlations and some paleoclimatic inferences. Archangelsky et al. (1996) and Limarino et al. (1996) suggested a specially humid and temperate climate, even subtropical, for the deposition of the La Golondrina Formation (the lower member in the La Golondrina Basin, Patagonia), whose age would be restricted between the Sakmarian and the Kungurian (Limarino and Spalletti, 2006). The age and paleoclimatic features of this formation are remarkable, particularly because it crops out in a relatively close position (ca. 500 km apart) to the present-day position of the outcrops of the DYC (Fig. 7). Another late Paleozoic Patagonian basin that shares similar paleoclimatic characteristics and also an adjacent location to the deposits of the DYC is the Tepuel-Genoa Basin (López-Gamundí and Limarino, 1984; Andreis et al., 1987) (Fig. 7), likely related to metamorphic rocks outcropping in the Coastal Range of Chile (Hervé, 1988; Duhart et al., 2001). The early Permian component of this basin (Sakmarian-Artinskian, according to Césari et al., 2007) is represented by the Río Genoa Formation, whose sediments have also been interpreted as deposited in a humid and subtropical climate (Archangelsky et al., 1996; Limarino et al., 1996). However, it is not possible to determine a more precise paleoclimatic connection with the La Golondrina Formation, mostly because late early Permian (Kungurian) sedimentary rocks have not been identified in the Tepuel-Genoa Basin (Limarino and Spalletti, 2006). If it is assumed a fixed position of the DYC with respect to Patagonia since its deposition, and considering the previous examples and the age obtained for the DYC, it would be probable that warm paleoclimatic conditions were recorded in the metasediments of this complex. This was, however, impossible to register in this study, mainly due to the very low proportion of palynological material in the samples.

Even though we cannot precise the paleoclimatic conditions during the deposition of the DYC, some observations can be done. The types of deposits accumulated as a consequence of ice activity are very varied, and several non-glacially related mechanisms can produce similar deposits. The recognition of these accumulations is more difficult if we consider that glacial deposits are frequently reworked in outwashes or by mass flow. For these reasons, the assignment of a glacial origin to any deposit, or its refutation, needs the combination of the properties of the deposit itself, the adjacent rocks units, as well as climatic and paleogeographic conditions at the time of deposition (*e.g.*, Charrier, 1986). Additionally, to establish that a sedimentary succession, or part of it,



FIG. 7. Paleogeographic reconstruction for South America in the early Permian, based on the pole of Rapalini et al. (2006). Positions of the late Paleozoic basins (from Limarino and Spalleti, 2006), Choiyoi deposits (modified from Kay et al., 1989; Ramos, 2000), and the current location of the outcrops of the Madre de Dios Accretionary Complex (MDAC) and the Trinity Peninsula Group (TPG) are shown, as well as the probable position of the Antarctic Peninsula (AP). The southern extension of the Río Chico-Punta Dúngenes high is taken from Ramos (2008), and the distribution of Permian igneous rocks of the North Patagonian Massif is from Pankhurst et al. (2006).

preserves a record of glacial, proglacial or periglacial depositional environments, multiple facies criteria are needed (diamictites, chaotic fabrics, rhythmites, laminated mudrocks with outsized dispersed clasts (lonestones), striated pavement, and faceted, bulletshaped and striated clasts, among others; Miller, 1996), or it is required a single criterion that unambiguously appears to indicate glacial influence by virtue of its occurrence out of context with enclosing facies (e.g., Fielding et al., 2008). In this context, even though there have been records of diamictites in the DYC (Cecioni, 1956; Forsythe and Mpodozis, 1983), this does not give conclusive evidence of a glacial environment of deposition. Moreover, there are only few localities in the whole extension of this accretionary complex (more than 1,000 km<sup>2</sup>) where diamictites have been identified, but the existence of glacial characteristics sensu stricto like lonestones (dropstones), striated pavements or faceted clasts have never been reported.

The large extension and volume of the DYC could be attributed to the great volume of fresh water produced by ice-melting during the waning of the glaciation in Gondwana (Buatois *et al.*, 2006). This huge volume of water probably reworked large amounts of sediments that were subsequently deposited at the margins of the continent. The ichnofaunas registered in DYC (Scalarituba isp., Chondrites isp., Planolites isp., Palaeophycus isp. and Ancorichnus isp.; in Lacassie, 2003), are distinctive of marine environments (written communication, L. Buatois, January 2008), and the low content of palynological material in the samples suggests a marine offshore environment of deposition of the host rocks. Both proposals match with the interpretation of the DYC rocks as turbidites, and would exclude a fjord-like setting for the origin of this succession and indicate that the place of deposition of the DYC was located far away from the direct influence of fresh water formed during the Gondwanan deglaciation.

## 5.2. Age and sources of metasediments

The detrital zircon data for sample FO04-21 of the DC reveal a maximum possible depositional age of this tuff-rich sediment of 270.4 $\pm$ 2.7 Ma, roughly in the limit between the early Permian (Kungurian) and the middle Permian (Roadian). This result is identical to the youngest predominant detrital zircon U-Pb SHRIMP age component previously reported for samples of the DYC (*ca.* 270 Ma, Hervé *et al.*, 2003; Hervé *et al.*, 2006), and suggests that this peak is probably linked to a significant contribution of volcanic (tuffaceous) material deposited near the continental margin. This is also in agreement with the age of widespread ash fall deposits and tuffaceous horizons present in basins of the west Gondwana (Turner, 1999; Stollhofen *et al.*, 2000; López-Gamundí, 2006; Santos *et al.*, 2006, Tohver *et al.*, 2007), commonly correlated with the peak of the Choiyoi silicic volcanism during the late early Permian and middle Permian along the Andean Cordillera and its equivalents in Patagonia (López-Gamundí, 2006).

The data obtained for sample FO04-22 of the DYC (289.7±2.1 Ma) indicate an early Permian (Sakmarian) maximum possible depositional age. This is nearly 20 m.y. older than the youngest U-Pb SHRIMP ages component recorded for detrital zircons in the DYC (Hervé et al., 2003). Nonetheless, the former authors have recognized this Sakmarian peak (ca. 290 Ma) as an individual Permian population in the age spectrum of the detrital zircons in the DYC. The apparent inverted stratigraphical position of the analyzed samples (Fig. 4) can be explained as FO04-21 being the airborne volcanic material deposited near the continental margin of Gondwana, and FO04-22 as resedimented detritus, formerly deposited somewhere between its local source area and the final depositional site, and then redeposited as turbidite flows above the cherts which include the tuffaceous layer represented by FO04-21.

Augustsson *et al.* (2006) suggest that the Permian sediments present in the metasedimentary complexes of Patagonia were probably largely supplied from local Patagonian and West Antarctic sources. Furthermore, Pankhurst *et al.* (2006) claim that the Permo-Triassic granites present in the North Patagonian Massif (extending between 41° and 44°S, approximately) can be identified as the most important source so far recognized for the provenance of detritus in the late Paleozoic metasedimentary rocks along the Pacific margin of Gondwana. This would imply transport by a system of long rivers over a wide and relatively flat pre-Andean platform (Hervé *et al.*, 2003), or even eolian transport over hundreds of kilometers (*e.g.*, Dickinson and Gehrels, 2009).

The widespread abundance of radiometric data from ash fall deposits within the range of 280 to 260 Ma has been commonly attributed to a period of intense silicic volcanism along the continental margin of southwestern Gondwana that peaked

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around the 270 Ma (López-Gamundí, 2006). Besides the model of Pankhurst et al. (2006), until now no analogous magmatic process responsible for the ubiquitous Sakmarian peak (ca. 290 Ma) in the U-Pb spectrum from samples of the DYC has been clearly identified. Similar and equivalent radiometric ages have been obtained from adjacent late Paleozoic basins of southwestern Gondwana. In the southernmost Karoo Basin of South Africa, Bangert et al. (1999) reported 288.0±3.0 and 289.6±3.8 Ma from bentonitic tuff beds intercalated in sedimentary rocks of the Prince Albert Formation, lower Ecca Group. Rocha-Campos et al. (2006) and Guerra-Sommer et al. (2008) acquired comparable Permian ages from ash-fall deposits interbedded in coal successions of the southern Paraná Basin in Brazil. The last authors claim that this information supports the presence of an active and extensive volcanic event in western Gondwana around the Carboniferous-Permian boundary (ca. 299 Ma). It is, however, difficult to restrict the magmatic activity in southwestern Gondwana to a single instant in Permian times, since most of the limited available data are in the range of 270 to 290 Ma and usually they overlap within their analytical uncertainty. Instead, the entire early Permian could be regarded as a period of active and geographically widespread magmatism in this region of Gondwana. This scenario would also explain the strong coincidence of the main Permian peaks in the detrital zircon U-Pb spectrum of the metasediments of the DYC, the Rakaia Terrane (New Zealand) and the eastern Le May Group (Alexander Island, Antarctica) (Lacassie et al., 2006). Nevertheless, the cause of the petrographic and geochemical similarities between these three metasedimentary units is an issue not discussed here as it is beyond the scope of this work.

#### 5.3. Paleogeographic correlations

So far, there has been no consensus in the place of accretion of the TL and DC and the supposed subsequent sense of movement of the MDAC (as a coherent block) along the southwestern Gondwana margin. Lacassie *et al.* (2006) proposed accretion of the DC-TL assemblage at the Antarctic-Australian portion of the Gondwana margin, followed by dextral translation of the MDAC (and hence of the DYC) parallel to the margin. On the other hand, the possibility of a virtually fixed position for the DYC since its deposition (with Patagonia as reference) is hampered by the fact that there is no clear indication of a coeval Permian magmatic arc at latitude similar to the current position of the MDAC in southern Patagonia (e.g., Hervé et al., 2006). This magmatic arc could be represented either by the Choiyoi acid magmatic province (Kay et al., 1989; Mpodozis and Kay, 1990) or by the Permian igneous rocks in the North Patagonian Massif (Pankhurst et al., 2006), both sources currently located north of the 40° and 44°S, respectively. However, the Choiyoi Formation presents ages of ca. 281 Ma near its base (Rocha-Campos et al., 2006; Suárez et al., 2009), and thus cannot account for the 290 Ma peak in the U-Pb age spectrum. Conversely, it is well known that the subduction of bathymetrically elevated oceanic features such as ridges or plateau (DC and TL in this case) can flatten the subducting slab and prevent the magmatic activity in the vicinity of the continental margin. According to the above-mentioned situation, the DYC would not have had displacement since its deposition and the remnants of the associated Permian magmatic arc could still be hidden below the Mesozoic sedimentary cover somewhere in the southeastern Patagonia or even farther eastward. This option has been recently explored by Ramos (2008), who proposes a late Paleozoic magmatic arc with a southern extension in the NNE trending Río Chico-Punta Dúngenes High (Fig. 7). This hypothesis would preclude defining the DYC as an allochthonous terrane. A precedent that supports this hypothesis is the presence of metasedimentary rocks with detrital zircons with U-Pb SHRIMP ages similar (ca. 290 Ma) to the ones recorded in the DYC to the east of the South Patagonian Batholith, at almost the same latitude of the MDAC (Augustsson et al., 2006). In brief, additional and more detailed paleomagnetic, geochronological and isotopic work is needed to give more convincing arguments supporting one of the proposed hypotheses, an autochthonous or an allochthonous origin of the DYC.

Little is known about the exact paleogeographic configuration of the Antarctic Peninsula during the late Paleozoic, though one of the most accepted current paleogeographic reconstructions locate the Antarctic Peninsula lying west of Patagonia in the Middle Jurassic (König and Jokat, 2006). Therefore, the possibility of a geological correlation between the geologic units present in western Patagonia and those exposed in the Antarctic Peninsula must be considered. In this context, it has been suggested based on the similarity of lithology and detrital zircon age patterns, that the Trinity Peninsula Group (TPG) is the equivalent counterpart of the DYC in the Antarctic Peninsula (Hervé et al., 2006) (Fig. 7). Willan (2003) assumed that the TPG could have been derived from a glaciated continental margin, though his result is based only on indirect evidence (geochemical weathering) and, at this time, there are no palynological reports on this unit. According to the paleogeographic reconstructions for the late Paleozoic (e.g., Cawood and Buchan, 2007), the TPG was supposedly located in a higher paleolatitudinal position than the late Paleozoic Patagonian basins, and therefore the paleoclimatic conditions would have been colder during its deposition. However, caution must be taken with this interpretation, mainly because the TPG is part of the Western Domain of the Antarctic Peninsula (Vaughan and Storey, 2000), which has been regarded as a suspect terrane and even as allochthonous to the rest of the terranes of the Antarctic Peninsula (Willan, 2003).

## 6. Conclusions

This contribution presents the first palynological record for the late Paleozoic in Chile. The palynological assemblage recorded in the DYC is composed mainly of Gymnospermopsida pollen, with also Pteridophyta and fungal spores. The studied association indicates a humid environment of forests with an undergrowth of ferns.

The palynological data indicate a Permian age for the deposition of the DYC. This age is also supported by new U-Pb SHRIMP detrital zircon ages, which constrain the maximum depositional age of the DYC to the limit between the early Permian and the middle Permian (*ca.* 270 Ma), confirming the maximum depositional age obtained by previous geochronological data (Hervé *et al.*, 2003).

The available data indicate that the allochthonous hypothesis for the DYC is not completely proved, and an autochthonous tectonic setting (with respect to Patagonia) could also be a possible interpretation.

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# <u>CAPÍTULO 5</u>: DISCUSIÓN Y CONCLUSIONES

## 5.1 ORIGEN DEL TERRENO MADRE DE DIOS (TMD)

## 5.1.1 Metabasaltos del Complejo Denaro

Los resultados obtenidos a partir del estudio de la geoquímica de cromitas y clinopiroxenos primarios relictos, y la geoquímica de roca total de los metabasaltos del Complejo Denaro (CD) (Sepúlveda *et al.*, 2008 y datos complementarios) confirman que estos corresponden a basaltos toleíticos tipo MORB. Los análisis de elementos trazas y tierras raras indican que en el CD predominan metabasaltos con geoquímica primaria tipo E-MORB, con algunos casos de metabasaltos tipo N-MORB. Los metabasaltos ocurren como basaltos almohadillados, hialoclastitas y *pillow-breccias* que subyacen a capas de cherts bandeados, o como *pillow-breccias*, hialoclastitas y flujos basálticos altamente amigdaloidales que se encuentran como lentes estructurales limitados por fallas.

Hervé et al. (1999a) señalaron que la geoquímica tipo E-MORB de los metabasaltos del CD apunta a que éstos se habrían generado en una dorsal o en un plateau oceánico, ya que las lavas submarinas generadas en estos ambientes presentarían características geoquímicas similares a basaltos tipo MORB (e.g., Batiza, 1991; Mahoney et al., 1995). Sin embargo, la mayoría de los basaltos de plateaus oceánicos presentan características isotópicas que se asemejan más a basaltos de isla oceánica (ocean island basalts, OIB), cuya generación está asociada a plumas mantélicas (hotspots), en contraste con la tradicional signatura MORB de las dorsales oceánicas (Batiza, 1991; Frey et al., 2000). En este sentido, la geoquímica de cromitas del CD (Sepúlveda et al., 2008) muestra una afinidad mayor con basaltos tipo MORB que a una fuente de tipo OIB, lo que descartaría que su génesis esté vinculada a una pluma mantélica. Esto se ve apoyado por la correlación entre los patrones de tierras raras y elementos trazas de metabasaltos del CD y aquellos de basaltos E-MORB producidos lejos de la influencia de plumas mantélicas (ver figs. 10 y 11). Se debe señalar que la generación de basaltos de tipo E-MORB, cuando no está asociada a hotspots, ha sido atribuida a la presencia de heterogeneidades geoquímicas (enriquecimientos) de pequeña escala dispersas en el manto superior (e.g., Hanson y Langmuir, 1978; Batiza y Vanko, 1984; Zindler et al., 1984).

La determinación precisa del ambiente tectónico donde se formaron de los metabasaltos E-MORB del CD no es, sin embargo, fácil. Esta variedad geoquímica está asociada a diversos dominios del piso oceánico, presentándose tanto en diferentes tipos de centros de expansión oceánica (*e.g.*, Niu *et al.*, 1999; Cooper *et al.*, 2004; Janney *et al.*, 2005), como en regiones tectónicamente complejas en las dorsales (*e.g.*, Kamenetsky *et al.*, 2000), o bien en montes oceánicos fuera del eje de la dorsal pero distribuidos aleatoriamente en sus vecindades (*near-axis* o *off-axis seamounts*) (*e.g.*, Batiza *et al.*, 1990; Batiza, 1991). No obstante, la asociación de estas rocas con sedimentos oceánicos de aguas profundas (cherts radiolaríticos bandeados) y la presencia de metabasaltos con geoquímica N-MORB dentro de este complejo, sugieren que estas rocas representan fragmentos del fondo oceánico formado en un centro de expansión oceánica. Esto se ve apoyado por estudios geoquímicos detallados que han revelado la coexistencia de basaltos tipo E-MORB y N-MORB en diversos segmentos de dorsales actuales (*e.g.*, Langmuir *et al.*, 1986; Mühe *et al.*, 1997; Donnelly *et al.*, 2004) y en montes oceánicos asociados espacialmente a éstas (*e.g.*, Niu y Batiza, 1997).

Los metabasaltos que afloran en el sitio IBGT (ver fig. 1) fueron originalmente interpretados por Forsythe y Mpodozis (1983) como parte del sustrato volcánico de una "isla" o monte submarino intra-oceánico, sobre el cual se acumularon las Calizas Tarlton (CT). Se debe señalar que, al igual que la mayoría de los metabasaltos del CD, las rocas de esta localidad presentan geoquímica tipo E-MORB y subyacen a capas de cherts bandeados rojos, sobre los cuales se apoyan las calizas asignadas a las CT por Forsythe y Mpodozis (1983). Estos autores propusieron que los basaltos de este sitio deben ser producto de volcanismo oceánico de intraplaca, más joven que la mayoría de los demás basaltos del CD. Pero, como de acuerdo a sus rasgos geoquímicos este no es el caso, es más probable que los basaltos del sitio IBGT representen parte de un monte oceánico asociado espacialmente a la dorsal donde se formaron los metabasaltos del CD.

Las edades de "acreción" obtenidas en el CD (Willner *et al.*, 2009), son más jóvenes hacia la parte exterior (hacia el océano) del prisma de acreción (*ca.* 201 Ma para metabasaltos del sitio IBGT, en comparación con *ca.* 233 Ma para metasedimentos asociados a metacherts del CD) (ver figura A2-1). Teniendo esto en consideración, y el hecho de que algunos afloramientos del CD ocurren como lentes estructurales, no se puede descartar totalmente que parte de los metabasaltos

del CD provengan de dominios tectónicos distintos a una dorsal oceánica (*e.g.*, un monte oceánico asociado a una dorsal).

## 5.1.2 Calizas Tarlton

Tal como fue indicado por Douglass y Nestell (1976), la presencia de fusulínidos en las CT sugiere que éstas se depositaron en un paleoambiente de aguas cálidas y someras (subtropicales a tropicales) (Betzler *et al.*, 1997). Esto concuerda con la abundancia de radiolarios en cherts del CD, depositados en forma sincrónica con las CT (Ling *et al.*, 1985), ya que éstos actualmente dominan el fango pelágico de aguas tropicales (Prothero y Schwab, 2004). Considerando tanto el contenido faunístico (fusulínidos y corales, principalmente) y el carácter macizo de las CT, Forsythe y Mpodozis (1983) propusieron que éstas representan una plataforma carbonatada depositada en un ambiente similar a un arrecife. La gran extensión y potencia de las calizas sugiere que éste correspondería a un arrecife en etapas de evolución avanzada (ver Field *et al.*, 2002). La recristalización y deformación que afecta a estas rocas dificulta el análisis de las facies sedimentarias y condiciones de depositación. No obstante, el rango de edad de los fusulínidos (Douglass y Nestell, 1976) coincide con un período de proliferación de arrecifes de aguas cálidas en el lapso Carbonífero inferior tardío (Serpukhoviano) - Pérmico inferior temprano (Sakmariano) (*e.g.*, Beauchamp y Desrochers, 1997; Beauchamp y Bauld, 2002; Weidlich, 2002; Reid *et al.*, 2007).

Considerando que la orientación de los cinturones climáticos durante el Carbonífero tardío -Pérmico temprano era similar a la actual (*e.g.*, Tabor y Poulsen, 2008; Shi y Waterhouse, 2010), es posible estimar la paleolatitud relativa para la formación de las CT al compararla con otros sedimentos carbonáticos depositados en el margen occidental de Gondwana. Al respecto, se ha indicado que las faunas fósiles de las unidades carbonatadas marinas del Paleozoico tardío en el norte y centro de Chile (formaciones Juan de Morales, Cerros de Cuevitas, Cerro del Árbol y Huentelauquén) presentan afinidades de aguas templadas a frías (Díaz-Martínez *et al.*, 2000). Estos datos indican que las CT se habrían depositado en aguas más cálidas y, por lo tanto, a una paleolatitud menor que la supuesta para la más septentrional de las formaciones carbonatadas acumuladas sobre el margen de Gondwana en el norte de Chile (*i.e.*, Formación Juan de Morales), la que estaría cercana a 30°S según datos paleomagnéticos (Rakotosolofo *et al.*, 2006),

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y entre los 30° y 40° S de acuerdo a las reconstrucciones para el Pérmico temprano de Blakey (2007) y Lawver *et al.* (2007).

Considerando la similitud entre los fusulínidos presentes en las CT y las rocas de la Formación Copacabana de Perú y Bolivia (Douglass y Nestell, 1976), Lacassie (2003) propuso que ambas unidades se acumularon a una paleolatitud equivalente, siendo la Formación Copacabana el depósito calcáreo de aguas templadas a cálidas más austral reconocido para la región occidental de los Andes (Díaz-Martínez *et al.*, 2000). Los datos paleomagnéticos de la Formación Copacabana (Rakotosolofo *et al.*, 2006) sitúan a esta unidad cerca de los 20° S durante el Pérmico temprano, concordando con las reconstrucciones de Gondwana para este período (*e.g.*, Blakey, 2007). Aunque las CT representarían una plataforma carbonatada intra-oceánica (Forsythe y Mpodozis, 1983) y no depósitos "autóctonos" acumulados sobre el margen de Gondwana, las relaciones anteriores indicarían que las CT se habrían depositado a una latitud menor que la supuesta para la más septentrional de las formaciones carbonatadas del norte de Chile (*i.e.*, Formación Juan de Morales), o sea, por sobre los 30° S.

# 5.1.3 Complejo Duque de York

La información palinológica obtenida indica que el Complejo Duque de York (CDY) se habría depositado en el Pérmico (Sepúlveda *et al.*, 2010). Esta determinación está de acuerdo con las dataciones U-Pb SHRIMP de circones detríticos, las que confirman y restringen la edad máxima de depósito del CDY cerca del límite entre el Pérmico temprano y el Pérmico medio (*ca.* 270 Ma) (Hervé *et al.*, 2003; Hervé *et al.*, 2006; Sepúlveda *et al.*, 2010). Los palinomorfos presentes en el CDY indican un ambiente húmedo durante el depósito de los sedimentos (Sepúlveda *et al.*, 2010). Ello es consistente con el hecho de que en los metasedimentos del CDY no se presentan evidencias de condiciones glaciales durante su depósito, ya que el predominio global de condiciones climáticas frías, asociadas a la glaciación del Paleozoico tardío, se mantuvo sólo hasta el Pérmico inferior temprano (Sakmariano) (Roscher y Schneider, 2006; Montañez *et al.*, 2007).

Los patrones de edades de circones detríticos obtenidos en este estudio confirman la presencia de dos poblaciones principales de circones (*ca*. 270 Ma y *ca*. 290 Ma), tal como lo indicaron Hervé *et al*. (2003), y como ha sido recientemente comprobado por Fanning *et al*. (2011).

Lacassie (2003) indicó que la edad de las poblaciones de circones detríticos del CDY es comparable a las que aparecen en sedimentitas clásticas del Terreno Rakaia (parte del Terreno Torlesse) en Nueva Zelandia y del Grupo LeMay oriental de la Península Antártica. Semejanzas petrográficas y geoquímicas apuntan a que estas secuencias derivan de fuentes ígneas de composición similar, y sugieren que éstas fueron depositadas a lo largo del mismo margen continental activo (Willam, 2003; Wandres *et al.*, 2004; Wandres y Bradshaw, 2005; Lacassie *et al.*, 2006). Trabajos más recientes indican, además, que el CDY comparte similitudes en sus características geoquímicas y sedimentológicas con el Trinity Peninsula Group, aflorante en la zona norte de la Península Antártica (Castillo, 2008; Quezada, 2010; Castillo *et al.*, 2009), y que también muestran similares rasgos isotópicos de Lu-Hf (Fanning *et al.*, 2011) y patrones de edad de circones detríticos (Hervé *et al.*, 2006; Castillo *et al.*, 2009; Barbeau *et al.*, 2010; Fanning *et al.*, 2011). Estos estudios proponen que ambas sucesiones tuvieron una fuente común correspondiente, también, a un arco magmático ubicado en un margen continental activo.

Intrusivos pérmicos que pueden representar a remanentes preservados de una fuente común en un arco magmático ubicado en un margen continental activo, aparecen en el segmento Antártico del margen paleo-Pacífico de Gondwana. Dentro de éstos se pueden incluir los granitoides calcoalcalinos pérmicos en las provincias de Amundsen y Ross en Marie Byrd Land (Antártica Occidental) (Pankhurst *et al.*, 1998; Mukasa y Dalziel, 2000), y eventualmente algunos granitos tipo "S" de la Península Antártica (Millar *et al.*, 2002). Sin embargo, Fanning *et al.* (2011) han sugerido también, en base a datos isotópicos de Lu-Hf asociados a edades U-Pb SHRIMP, que una fuente probable para los circones detríticos pérmicos del CDY serían la provincia magmática ácida del Choiyoi y los granitoides pérmicos del Macizo Nor-Patagónico (Pankhurst *et al.*, 2006).

# 5.1.4 Edad mínima del TMD: magnetización remanente e intrusivos básicos

Rapalini *et al.* (2001) señalaron que la fase mineral portadora de la magnetización en las CT corresponde a titanomagnetita secundaria, que se habría generado durante la intrusión del

Batolito Sur-Patagónico en el Cretácico Inferior. No obstante, nuevas edades obtenidas en el Batolito Sur-Patagónico por Hervé et al. (2007), en conjunto con el rejuvenecimiento de las edades de metamorfismo en los basaltos del CD cercanos al contacto con el Batolito (Willner et al., 2009) indican un evento termal significativo durante el Jurásico Superior (ca. 152 Ma en la zona de estudio). Este evento jurásico corresponde a la etapa inicial del emplazamiento del Batolito Sur-Patagónico, y ha sido explicado como resultado de actividad magmática bi-modal relacionada a extensión (Hervé et al., 2007). En este contexto, es posible que este evento sea el generador de diques y filones-manto que cortan al TMD, los que presentan geoquímica afín a basaltos toleíticos de intraplaca (Sepúlveda et al., 2008). Estos cuerpos hipabisales abundan en los afloramientos del TMD lejanos al contacto con el Batolito (ver fig. 1), y es altamente probable que sean los responsables del crecimiento de titanomagnetita en las CT. El efecto termal producido por estos cuerpos podría haber provocado movilización de Fe (y Ti, en menor medida) para generar titanomagnetita en las CT, pero no habría sido lo suficientemente potente como para ocasionar un rejuvenecimiento de las edades de acreción de las muestras del CD lejos del contacto con el Batolito. Esto puede ser explicado por la elevada tasa de difusión del Fe a bajas temperaturas (Carlson, 2002), en conjunto con la alta retención de Ar en micas blancas en condiciones metamórficas de bajo grado (Kirschner et al., 1996).

## **5.2 CONDICIONES DE METAMORFISMO**

Los resultados del estudio efectuado en muestras de metabasaltos del CD indican que estas presentan asociaciones minerales de la zona de presión intermedia y alta temperatura de la facies pumpellyita-actinolita (Willner *et al.*, 2009). Dado el carácter del metamorfismo y las texturas observadas en las rocas del TMD, es difícil establecer si estas asociaciones minerales representan situaciones de equilibrio químico del peak metamórfico. Sin embargo, las fases minerales muestran variaciones sistemáticas dentro de rangos de composición restringidos, sugiriendo una aproximación local y temporal a condiciones de equilibrio, por lo menos en algunos subdominios texturales. Debido a ello se consideró que las asociaciones minerales representan equilibrios locales generados durante o cerca del peak metamórfico. Basándose en esta premisa, Willner *et al.* (2009) utilizaron pseudosecciones P-T para calcular los campos de estabilidad de la asociación metamórfica en metabasaltos del CD, las que indican que las condiciones del peak

metamórfico se alcanzaron a 290-310 °C y 4-6 kbar, lo cual concuerda con las asociaciones metamórficas observadas en las metabasitas.

Por otra parte, Willner *et al.* (2009) señalan que, a pesar de la composición heterogénea de las fases metamórficas, equilibrios locales anteriores al peak metamórfico estarían preservados en algunas de las muestras debido, probablemente, a las bajas temperaturas alcanzadas y a una disponibilidad de fluidos limitada. Así, cálculos termodinámicos de equilibrios minerales multivariantes locales usando todo el rango de composiciones de los minerales metamórficos en el TMD (en este caso CD y CDY) muestran que la trayectoria P-T prógrada evolucionó desde  $4 \pm 1$  kbar, 200-220 °C hasta  $5 \pm 1$  kbar, 290-330 °C (Willner *et al.*, 2009). Esta trayectoria P-T refleja un transporte subhorizontal de las partículas en el prisma de acreción frontal y un reequilibrio termal de largo plazo a profundidad máxima, lo que concuerda con conceptos actuales de formación de prismas de acreción frontales y con modelos numéricos de subducción que involucran generación de un sistema de cuña acrecionaria (*e.g.*, Gorczyk *et al.*, 2007).

Las determinaciones P-T por medio de equilibrios multivariantes son concordantes otros cálculos efectuados, esto a pesar de que los análisis de microsonda de los minerales de la asociación metamórfica fueron incorporados a modelos de actividades genéricos. En este sentido, las temperaturas calculadas por Sepúlveda *et al.* (2008), usando el geotermómetro de Cathelineau (1988), están dentro del rango del las obtenidas para las mismas muestras por Willner *et al.* (2009). Además, aunque en algunos casos las temperaturas determinadas por reacciones multivariantes son ligeramente menores a las obtenidas con pseudosecciones para una misma muestra, éstas son congruentes entre sí.

# 5.2.1 Pseudosecciones y estado de oxidación

Los análisis realizados indican una fuerte dependencia entre los datos obtenidos en las pseudosecciones y el estado de oxidación de la muestras, el que se estableció a partir del contenido de hierro férrico (trivalente) y se traduce en el contenido de oxigeno ( $O_2$ ). Los resultados conseguidos usando el contenido de  $O_2$  medido en cada muestra fueron incongruentes con la paragénesis mineral observada (ausencia de fases de la asociación y/o campos de estabilidad muy restringidos y/o composiciones de las fases del peak metamórfico no

comparables con las obtenidas por microsonda). Esto fue atribuido por Willner *et al.* (2009) a un proceso de alteración (oxidación) posterior al peak metamórfico, lo que se tradujo en un aumento sustancial de los valores de  $O_2$ . Debido a lo anterior, el contenido de  $O_2$  fue seleccionado para obtener composiciones y cantidades similares de minerales metamórficos entre los entregados por las pseudosecciones y los observados en las muestras. Luego de comprobar la coherencia de las pseudosecciones (*i.e.*, presencia de todas las fases de la asociación) con contenidos menores de  $O_2$ , se lograron resultados congruentes en el rango de 0,1% a 0,2% de  $O_2$ , y se asumió un valor constante de 0,15% para este parámetro en todas las muestras (ver fig. 12). Se apreció también que la presencia de algunas fases minerales (*e.g.*, estilpnomelano) depende en gran medida de los valores de  $O_2$  de 0,12% propuesto por Massonne y Willner (2008) para un basalto tipo N-MORB. Además, este método constituye una forma empírica de contrastar la coherencia de los resultados de las pseudosecciones con la mineralogía metamórfica cuando se dispone de un conjunto de rocas con distintos grados de oxidación, lo que es usual en rocas metamórficas de muy bajo a bajo grado.



**Figura 12.** Diagrama P-T con el campo de estabilidad de la asociación metamórfica de la muestra MD26, extraído desde la pseudosección de esta muestra a partir de distintos valores del contenido de  $O_2$ . La línea punteada naranja indica el campo de estabilidad calculado con el valor de  $O_2$  obtenido del análisis de roca total. El área verde corresponde al campo de estabilidad calculado para el valor promedio de 0,15%.

## 5.2.2 Validez de la interpretación de la trayectoria prógrada

La interpretación de la trayectoria prógrada casi isobárica de las rocas del TMD se hizo en base a las condiciones P-T obtenidas a partir de equilibrios multivariantes, asumiendo la existencia de equilibrios prógrados transitorios debido a la falta de homogeneidad composicional mineral a escala de sección transparente (Willner *et al.*, 2009). Al considerar la variación composicional de las fases involucradas, las reacciones multivariantes muestran temperaturas del metamorfismo entre 200 y 330 °C, obteniéndose además equilibrios P-T locales transitorios dentro de este rango. No obstante, este intervalo de temperatura puede interpretarse como el resultado de variaciones en la concentración de hierro férrico (*X*Fe<sup>3+</sup>) en las fases minerales al incluir el hierro (Fe) como componente dentro del cálculo de condiciones P-T usando equilibrios multivariantes, tal como lo proponen Cho *et al.* (1986) y Cho y Liou (1987) para metabasitas de muy bajo grado. Sin embargo, la obtención del rango de temperatura antes señalado se realizó tanto incorporando como excluyendo Fe como componente en los cálculos, por lo que éste no es un factor preponderante en los resultados obtenidos.

También se ha señalado que variaciones en la concentración del CO<sub>2</sub> (*X*CO<sub>2</sub>) en la fase fluida podría ocasionar un movimiento de puntos invariantes dentro de las facies metamórficas de muy bajo grado y, en particular, causar modificaciones en los campos de estabilidad de fases como prehnita y pumpellyita (Cho y Liou, 1987; Digel y Ghent, 1994). Sin embargo, el cálculo de los equilibrios multivariantes involucra reacciones subordinadas a la temperatura (reacciones termómetros) que son dependientes e independientes del H<sub>2</sub>O, ambas entregando el mismo rango de temperaturas antes indicado, por lo que Willner *et al.* (2009) infirieron que el fluido estaba compuesto predominantemente por H<sub>2</sub>O. Además, en el cálculo de pseudosecciones se varió la proporción de CO<sub>2</sub> como componente en la fase fluida sin obtener cambios substanciales en los resultados, por lo que se dedujo que el fluido estaba compuesto casi íntegramente por H<sub>2</sub>O. Por otro lado, no se apreciaron cambios notorios en el campo de estabilidad de la pumpellyita al variar *X*CO<sub>2</sub> en la fase fluida, lo que también apoya el hecho de que la fase fluida estaba compuesta casi exclusivamente de H<sub>2</sub>O.

En resumen, el rango de temperatura a presión casi constante determinado por medio de reacciones multivariantes no puede ser explicado por variaciones en  $XFe^{3+}$  en las fases minerales

ni por cambios de  $XCO_2$  en la fase fluida. Esto refuerza la validez de la interpretación de este intervalo (y de los equilibrios locales preservados) como la trayectoria prógrada casi horizontal de las partículas asociada a procesos de acreción frontal dentro de un prisma de acreción.

# 5.2.3 Generación y disponibilidad de fluidos durante la trayectoria prógrada

Willner *et al.* (2009) indican que evidencias texturales y composicionales en las rocas del CD (*e.g.*, fases primarias relictas, falta de homogeneidad composicional) sugieren que el acceso de fluidos durante el metamorfismo fue limitado. Esto no es del todo coherente con la evolución metamórfica de un bloque dentro de un prisma de acreción, donde se asume una alta disponibilidad y flujo de fluidos. En este contexto, los fluidos pueden provenir de su liberación por compactación de sedimentos en la región más somera de la zona de subducción (von Huene y Scholl, 1991; Moore y Vrolijk, 1992), o ser producto de reacciones de deshidratación que afectan a los fases hidratadas presentes tanto en la corteza oceánica alterada como en los metasedimentos que la cubren, al ingresar a zonas más profundas del prisma (Moore y Vrolijk, 1992; Hacker *et al.*, 2003, Massonne y Willner, 2008). Al respecto, Massonne y Willner (2008) muestran que para un gradiente geotermal cercano a 15 °C/km ocurre un importante evento de deshidratación de metasedimentos alrededor de 220-240 °C, y lo mismo sucede en metabasaltos a 240-300 °C.

En la figura 13 se pueden observar las isópletas de H<sub>2</sub>O en el diagrama P-T de una muestra representativa de metabasaltos del CD. Aquí se puede apreciar que para el gradiente geotermal calculado en las muestras del TMD (*ca.* 17 °C/km, Willner *et al.*, 2009), existe un notorio frente de deshidratación concentrado en el intervalo 290-310 °C, el que es generado por el quiebre de pumpellyita. También se aprecia que el mismo frente ocurre a mayor y menor gradiente geotermal, y está asociado al quiebre de ceolitas (laumontita-wairakita) y lawsonita, respectivamente. En el caso del gradiente calculado para el TMD, el evento de deshidratación libera aproximadamente el 10% del H<sub>2</sub>O contenida en sólidos, y estaría ocurriendo durante el peak metamórfico (ver fig. 13).

Lo anterior implicaría que los metabasaltos del CD sufrieron un episodio de deshidratación al llegar a la temperatura máxima de su evolución metamórfica, y que esta fase de deshidratación fue posterior a la que habría afectado a los metasedimentos del TMD, de acuerdo al modelo de

Massonne y Willner (2008). Por otro lado, esta situación es concordante con la observación hecha en Willner *et al.* (2009) acerca de la posibilidad de diversas fuentes de generación de fluidos acuosos de composición heterogénea.



**Figura 13.** Diagrama P-T con las isópletas de  $H_2O$  (líneas punteadas negras) y el campo de estabilidad de la asociación metamórfica de la muestra MD26 (en naranja). El contenido de  $H_2O$  en sólidos inicial para esta muestra es de 5,06%, y las isópletas varían cada 0,1%. Se muestran los campos de estabilidad de wairakita (amarillo), laumontita (celeste), pumpellyita (verde) y lawsonita (azul).

Dados estos antecedentes, una forma de explicar que los fluidos producidos durante la evolución metamórfica del TMD no hayan afectado extensivamente la textura y mineralogía de las rocas del CD es que éstos se hayan canalizado por discontinuidades estructurales o zonas restringidas dentro del CD, las que actuarían como conductos para el flujo de estos fluidos. Estas zonas pueden haber permitido la circulación de los fluidos producidos en las distintas etapas de deshidratación, pero circunscribiendo la interacción fluido-roca mayormente dentro de estas zonas. Una evidencia de esta canalización de fluidos podría ser el incremento de la deformación y metasomatismo asociado en algunos de los contactos tectónicos entre las rocas del CD y las CT, y en zonas de deformación (asociadas a recristalización) dentro de bloques del CD.

# 5.3 EDAD DEL METAMORFISMO: COMPARACIÓN CON OTROS COMPLEJOS DE SUBDUCCIÓN DEL MARGEN DE GONDWANA

Las edades de metamorfismo obtenidas en el TMD (<sup>40</sup>Ar/<sup>39</sup>Ar UV-LAMP *in situ* en fengitas) se interpretan como distintas fases de la evolución del prisma de acreción, donde la edad de *ca*. 233 Ma corresponde a la edad de acreción de las unidades del TMD, mientras que la edad de *ca*. 201 Ma puede representar una etapa de acreción avanzada o un efecto de reajuste retrógrado (Willner *et al.*, 2009). Las condiciones P-T y la edad del metamorfismo obtenida en el TMD pueden contrastarse con aquellas determinadas para otros complejos de subducción formadores del margen paleo-Pacífico de Gondwana.

Desde este punto de vista, el TMD se puede comparar con el Trinity Peninsula Group, expuesto en el extremo norte de la Península Antártica. Esta unidad presenta asociaciones metamórficas en facies prehnita-pumpellyita, pumpellyita-actinolita y esquistos verdes (Smellie, 1991; Smellie y Millar, 1995; Smellie *et al.*, 1996). Smellie y Millar (1995) obtuvieron edades K-Ar (roca total) de esquistos asignados a este complejo, las que indican que el metamorfismo que afectó a esta unidad tiene una edad Triásica temprana (245-250 Ma). Ya que se ha propuesto que el Trinity Peninsula Group es el equivalente del CDY en la Península Antártica (*e.g.*, Hervé *et al.*, 2006), entonces estas edades deberían interpretarse como de metamorfismo asociado a subducción/acreción.

Las edades y el tipo de metamorfismo que afectan al TMD también se pueden comparar con aquellas que se presentan en parte del Grupo LeMay, en el Dominio Occidental de la Península Antártica (Vaughan y Storey, 2000), el cual incluye rocas con asociaciones minerales propias de metamorfismo de subducción, algunas de las cuales se formaron en facies pumpellyita-actinolita (Doubleday y Tranter, 1994; Doubleday *et al.*, 1994). Esta unidad presenta amplio rango de edad bioestratigráfica (Jurásico Inferior - Cretácico medio, Thomson y Tranter, 1986; Holdsworth y Nell, 1992), indicando que puede estar constituida por rocas de distinta edad yuxtapuestas durante eventos tectónicos (*e.g.*, Storey *et al.*, 2005). Dataciones U-Pb SHRIMP en circones detríticos de la parte más antigua (oriental) de esta unidad presentan una edad Triásica (Millar *et al.*, 2003). Dentro de esta porción de este complejo, Storey *et al.* (2005) obtuvieron una edad de *ca.* 218 Ma (Ar-Ar en micas blancas), la que fue asociada a la acreción de este bloque al margen de Gondwana durante el Triásico tardío.

Aún más al sur, estudios efectuados en el Terreno Rakaia (parte del Terreno Torlesse), en Nueva Zelandia, indican que éste fue afectado por condiciones metamórficas similares a las que ocurren en prismas de acreción, y que alcanzaron hasta la facies pumpellyita-actinolita (Coombs y Cox, 1991; Hada y Landis, 1995). Cawood *et al.* (2002) indican, en base a edades U-Pb de zonas recristalizadas en circones detríticos, que la edad de deformación y metamorfismo para el Terreno Te Akatarawa (parte del Terreno Rakaia) es de  $230 \pm 11$  Ma. Además, de lo anterior, Adams (2003) pudo determinar, en afloramientos separados para rocas del Pérmico tardío y Triásico Medio-Superior del Terreno Torlesse en facies prehnita-pumpellyita y pumpellyita-actinolita, edades de metamorfismo K-Ar (roca total de pizarras y esquistos) de  $250 \pm 10$  Ma y  $210 \pm 10$  Ma, sugiriendo que probablemente indicarían dos eventos de metamorfismo triásicos.

En la Patagonia chilena occidental, el complejo de subducción más cercano al norte del Archipiélago Madre de Dios corresponde al Complejo Metamórfico de los Chonos (Davidson *et al.*, 1987). La porción oriental de este complejo, al igual que el TMD, se formó en un régimen P/T típico de ambientes de subducción en facies pumpellyita-actinolita (Hervé *et al.*, 1994; Hervé *et al.*, 1999b; Willner *et al.*, 2000), y presenta una edad mínima de metamorfismo de *ca.* 210 Ma (Thomson y Hervé, 2002). Sin embargo, este complejo tiene edades de depósito del Triásico tardío, indicada tanto por fósiles (Fang *et al.*, 1998), como por edades U-Pb SHRIMP en circones detríticos (Hervé y Fanning, 2001; Hervé *et al.*, 2003), por lo representaría una porción más joven del margen de Gondwana.

Por consiguiente, el estado actual del conocimiento de los complejos acrecionarios formadores del margen paleo-Pacífico de Gondwana permite correlacionar las condiciones y edades del metamorfismo/acreción del TMD con las determinadas para el Trinity Peninsula Group y el Grupo LeMay oriental de la Península Antártica, y el Terreno Rakaia de Nueva Zelandia. A pesar de que los tipos de dataciones geocronológicas utilizados en cada caso no son totalmente comparables, todo apunta a que estas unidades sobrellevaron condiciones metamórficas asociadas a procesos de subducción/acreción ocurridos durante el Triásico en el margen paleo-Pacífico de Gondwana.

# 5.4 CONSIDERACIONES PALEOGEOGRAFICAS Y TECTÓNICAS

Las asociaciones litológicas, geoquímica, estilo estructural y condiciones del metamorfismo del Terreno Madre de Dios (TMD) indican que este complejo representa parte de un prisma de acreción construido en el margen paleo-Pacífico de Gondwana (*e.g.*, Forsythe y Mpodozis, 1979). Los datos obtenidos en este trabajo indican que las unidades con características oceánicas de este complejo (CD y CT) comenzaron a acumularse en latitudes tropicales/sub-tropicales (probablemente sobre los 30° S) siendo luego transportadas hacia latitudes más altas, donde al acercarse al margen continental paleo-Pacífico de Gondwana fueron cubiertas por depósitos turbidíticos del Pérmico temprano-medio, representados por el CDY. Subsiguientemente, todas estas unidades fueron incorporadas dentro de un prisma de acreción en el margen de Gondwana durante el Triásico Medio - Triásico Superior (fig. 14). Un problema aún no resuelto, sin embargo, es el lugar del margen donde se produjo originalmente la construcción de ese prisma. Esto se debe a que la formación de un sistema de este tipo requiere, necesariamente, de la existencia de un arco magmático constituido por rocas intrusivas y volcánicas, propias de un margen activo, cuya geometría y posición sea compatible con la construcción de un prisma de acreción sincrónico.

En el caso específico del TMD, la ausencia en la Patagonia austral de un arco magmático calcoalcalino Pérmico (Triásico) que pueda ser considerado como fuente indiscutible de los circones detríticos del CDY (*e.g.*, Lacassie, 2003; Hervé *et al.*, 2006) y, sobre todo, como evidencia de la subducción de corteza oceánica durante la construcción del prisma, plantea dudas en cuanto a que la construcción del prisma del TMD haya ocurrido en el segmento de la costa de Chile austral donde actualmente aflora. Ramos (2008) plantea una configuración tectónica para el Paleozoico superior que supone la existencia de un arco Pérmico que se extendería, en la Patagonia oriental, a través del Macizo del Deseado hasta alcanzar hacia el sur el Alto de Punta Dúngenes. Según este autor, ese arco (ubicado de todos modos a un distancia muy grande de una zona de subducción pérmica, la que se habría situado en el borde occidental de la Patagonia) podría encontrarse, actualmente, bajo la cobertura sedimentaria Meso-Cenozoica de la Patagonia extraandina (ver fig. A3-7). Cabe mencionar que Hervé *et al.* (2010) obtuvieron una edad pérmica en el borde recristalizado de un circón proveniente de gneisses cámbricos del basamento de Tierra del Fuego, la que interpretan como el producto de un evento metamórfico de alta temperatura. Estos autores correlacionan este evento con el efecto metamórfico-termal de las raíces de un arco

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magmático como el sugerido por Ramos (2008). Sin embargo, la existencia de un sistema de este tipo, altamente hipotético, no ha podido a la fecha ser demostrada en forma concluyente y permanece en el campo de los modelos a ser testeados.

La falta de datos y argumentos concluyentes acerca de la existencia de un arco Pérmico (Triásico) en la Patagonia Austral ha llevado a algunos autores a sugerir que la acreción del TMD ocurrió en un segmento distinto del margen paleo-Pacífico de Gondwana (segmento Australiano: Lacassie, 2003; segmento Antártico: Lacassie *et al.*, 2006), desde donde fue posteriormente transportado como terreno exótico, hasta alcanzar su posición actual antes del inicio del emplazamiento del Batolito Sur-Patagónico en el Jurásico Superior (Hervé *et al.*, 2007b) (ver fig. 14).



**Figura 14.** Sección esquemática del margen de Gondwana. A) Configuración inicial de las unidades del TMD previo a la acreción inicial del CD y las CT (pre-270 Ma). B) Incorporación de las unidades (CD, CT y CDY) al prisma de acreción y consolidación del TMD, con la subsecuente traslación de este bloque (como un terreno alóctono) mediante movimientos de rumbo dextrales hasta alcanzar su posición actual durante el Jurásico Superior.

Evidencias sedimentológicas, petrográficas, geoquímicas, isotópicas y geocronológicas muestran que sucesiones metasedimentarias correlacionables o que se pueden comparar específicamente con el Complejo Duque de York (Trinity Peninsula Group, Grupo LeMay oriental, Terreno Rakaia) derivaron desde fuentes ígneas de composición y edad similar, el que correspondería a un arco magmático pérmico ubicado en un margen continental activo (Willam, 2003; Wandres *et al.*, 2004; Wandres y Bradshaw, 2005; Lacassie *et al.*, 2006; Hervé *et al.*, 2006; Castillo, 2008; Castillo *et al.*, 2009; Quezada, 2010). Como se indicó en párrafos previos, rocas que podrían representar remanentes de este arco magmático se encontrarían en los granitoides calco-alcalinos pérmicos en las provincias de Amundsen y Ross en Marie Byrd Land (Antártica Occidental) (Pankhurst *et al.*, 1998; Mukasa y Dalziel, 2000), y en los granitos tipo "S" pérmicos de la Península Antártica (Millar *et al.*, 2002). Estas áreas pertenecían en ese período al segmento Antártico del margen paleo-Pacífico de Gondwana (ver fig. 15).

Si se supone que la fuente de detritos del CDY se ubicaba en el margen Antártico de Gondwana, esto necesariamente implica un desplazamiento de rumbo dextral del CDY (y del TMD en su conjunto), desde una alta latitud austral (cerca del círculo polar Antártico) hasta su posición actual en la placa Sudamericana (Lacassie *et al.*, 2006) (fig. 15). Un desplazamiento dextral de bloques a lo largo del margen paleo-Pacífico de Gondwana ha sido propuesto recientemente por Adams (2010) para explicar la ausencia de cuencas del Paleozoico tardío en la corteza continental asociada a Nueva Zelandia ("Zealandia"). Esta hipótesis es aparentemente consistente con el estudio estructural de Storey *et al.* (2005), quienes sugieren que la subducción responsable de la acreción del Grupo LeMay oriental era oblicua e incluía una componente de movimiento dextral. De igual manera, Kleiman y Japas (2009) postulan convergencia oblicua en sentido NNE de la placa paleo-Pacífica bajo la placa Sudamericana durante el Pérmico. Lo anterior también es concordante con la trayectoria oblicua al margen austral de Gondwana y posterior movimiento dextral propuesto por Cawood *et al.* (2002) para el emplazamiento de las calizas con fusulínidos del Pérmico incluidas en el Terreno Te Akatarawa en Nueva Zelandia (ver fig. 15).

Si el arco pérmico del cual provienen los detritos del CDY estuviera localizado en las provincias de Amundsen y Ross de Marie Byrd Land (o en sus vecindades) (ver fig. 15), y la acreción del TMD ocurrió en el Triásico, entonces es válido preguntarse por la localización del arco magmático activo asociado a esta acreción. Si se acepta que la placa paleo-Pacífica tuvo una

dirección de convergencia oblicua en sentido NNE (coordenadas actuales) (Kleiman y Japas, 2009), entonces el arco magmático simultáneo (y más cercano) para el régimen de subducción antes mencionado podría estar representado por los intrusivos triásicos ubicados en la Península Antártica e Isla Thurston.

A este respecto se puede indicar que, efectivamente, varios autores han obtenido edades triásicas en rocas ígneas y metamórficas tanto en la Península Antártica (Hole et al., 1991; Wever et al., 1994, Scarrow et al., 1996; Millar et al., 2002; Flowerdew et al., 2006) como en la Isla Thurston (Pankhurst et al., 1993). Sin embargo, la mayoría de los cuerpos intrusivos triásicos corresponden a granitoides tipo "S" (Wever et al., 1994; Scarrow et al., 1996; Millar et al., 2001), los que difieren del carácter calco-alcalinos tipo "I" típicamente producido por magmatismo mantélico en una zona de subducción activa. A pesar de lo anterior, Millar et al. (2001) sostuvieron, en base a datos isotópicos de intrusivos del área nor-oriental de Palmer Land, que el emplazamiento sincrónico de granitoides tipo "I" y granitoides tipo "S" durante el Triásico - Jurásico Medio indica que, en ese lapso, la subducción en el margen paleo-Pacífico de Gondwana parece haber coincidido con una fase de extensión cortical intermitente. Millar et al. (2002) indican que la predominancia de granitoides pérmicos y triásicos tipo "S" en la Península Antártica, aparentemente refleja un largo período de alto flujo calórico cortical y anatexia. Esta hipótesis parece estar de acuerdo con los datos de Millar et al. (2002) y Flowerdew et al. (2006), quienes obtuvieron edades triásicas (ca. 230-200 Ma) para sobre-crecimientos en circones de gneisses y migmatitas de la Península Antártica. No obstante, según Flowerdew et al. (2006), estos sobrecrecimientos fueron generados desde fundido producido por metamorfismo de alta temperatura, probablemente ligado al calentamiento magmático en niveles profundos de un arco. Estas edades podrían representar un evento termal producido por la influencia de un arco Permo-Triásico resultante de la subducción de la placa paleo-Pacífica bajo el margen de Gondwana (Leat et al., 1995; Millar et al., 2001). En relación con esta propuesta, Millar et al. (2003) concluyen en base a isótopos de Hf, que la parte Triásica (oriental) del Grupo LeMay se formó como un prisma de acreción asociado con al arco magmático coetáneo ubicado en la Península Antártica.

Una hipótesis alternativa para la proveniencia de los circones detríticos del CDY ha sido presentada recientemente por Fanning *et al.* (2011), quienes han propuesto que las fuentes más probables para los circones detríticos pérmicos del CDY son la provincia magmática ácida del Choiyoi y los granitoides pérmicos del Macizo Nor-Patagónico (Pankhurst *et al.*, 2006). Esto

implicaría que el ensamblaje del TMD se habría llevado a cabo cerca de ese sector del margen de Gondwana, para posteriormente ser transportado mediante desplazamiento de rumbo sinistral hasta su posición actual (ver fig. 15). Sin embargo, el sentido de este desplazamiento se contrapone con la convergencia oblicua en sentido NNE de la placa paleo-Pacífica bajo la placa Sudamericana durante el Pérmico (Kleiman y Japas, 2009). Además, el modelo formulado por Fanning *et al.* (2011) no soluciona la falta de un arco Pérmico-Triásico con una configuración adecuada para ligarlo directamente a la subducción y acreción de las unidades del TMD.

Los granitoides pérmicos del Macizo Nor-Patagónico, que derivan de fusión cortical a gran escala y cuya geoquímica no incluye una componente de subducción (ver Pankhurst et al., 2006), forman una faja E-W que atraviesa la Patagonia, lo cual hace inviable que estos puedan ser considerados como el arco asociado a la subducción que originó el prisma del TMD. Por otro lado, las edades del Grupo Choiyoi, que incluye cerca de su base tobas y lavas con edades de *ca*. 281 Ma (e.g., Rocha-Campos et al., 2011), no pueden dar cuenta del prominente peak de ca. 290 Ma presente en los patrones de edad de los circones detríticos del CDY. Las evidencias más cercanas de magmatismo en la parte que eventualmente podría estar asociada a la acreción del TMD, serían algunos pequeños stocks de granitoides triásicos presentes en la Cordillera de la Costa del centro-sur de Chile (34°-37°S, Vásquez et al., 2011 y referencias allí citadas). Estos cuerpos ígneos están expuestos discontinuamente a lo largo del margen continental actual, presentan una geoquímica híbrida entre granitoides "tipo-A" y "tipo-I", y han sido interpretados por Vásquez et al. (2011) como generados durante subducción. No obstante, otros autores han indicado que estos cuerpos se habrían emplazado como consecuencia de los procesos de extensión y rifting que afectaron gran parte del centro y norte de Argentina y Chile durante el Triásico - Jurasico Inferior (e.g., Ramos y Kay, 1991; Parada, et al., 1999).

Considerando los antecedentes descritos y los datos disponibles a la fecha, el modelo geodinámico propuesto más coherente y consistente es el que involucra la acreción de las unidades del TMD en el segmento Antártico del margen paleo-Pacífico de Gondwana, donde existen evidencias de la presencia de un arco magmático Pérmico-Triásico, probablemente ligado a subducción, que estaría representado por las rocas ígneas que afloran en Marie Byrd Land y en la Península Antártica. La aceptación de este modelo implica que el TMD habría sido desplazado, mediante movimientos de rumbo dextrales, desde el sector Antártico del margen paleo-Pacífico de Gondwana hasta su posición actual en la placa Sudamericana (ver figs. 14 y 15).



Figura 15. A) Reconstrucción paleogeográfica de Gondwana de Cawood et al. (2002), donde se muestra la trayectoria propuesta para el Terreno Te Akaterawa (línea negra). B) Reconstrucción paleogeográfica de Gondwana a los 270 Ma, centrada en el Polo Sur (Lawver et al., 2007). La trayectoria del bloque formado por las CT y el CD en línea azul. El área azul es la probable zona de acreción inicial de este bloque, donde ocurre la imbricación con los detritos que forman el CDY y consolidación del TMD. La línea roja es la subsecuente trayectoria del TMD en forma paralela al margen de Gondwana hasta su posición anterior al quiebre de Gondwana (óvalo naranja), como continuación hacia el norte del Trinity Peninsula Group. La línea roja punteada representa el movimiento posterior del TMD hasta su posición actual (estrella roja). En verde la localización estimada del arco pérmico (fuente de los detritos del CDY), con líneas punteadas su extensión sugerida hacia Patagonia. En amarillo los granitoides pérmicos del Macizo Nor-Patagónico (Pankhurst et al., 2006). La flecha gris indica el sentido de convergencia de la placa paleo-Pacífica (de Kleinman y Japas, 2009). AF: África; ANT: Antártica; AUS: Australia; CP: Campbell Plateau (incluye Chatham Rise y margen Paleozoico de Nueva Zelandia); CHP: Challenger Plateau (incluye basamento de Nueva Zelandia); EWM: Ellsworth-Withmore Mountain; IM: Islas Malvinas; IT: Isla Thurston; MBL-A: Mary Byrd Land-Amundsen; MBL-R: Mary Byrd Land-Ross; PA-GL: Graham Land, Península Antártica; PA-PL: Palmer Land, Península Antártica; SUD: Sudamérica.

No obstante, para poder verificar esta hipótesis serían necesario efectuar nuevas determinaciones geocronológicas (*e.g.*, U-Pb SHRIMP con cátodo-luminiscencia) en Marie Byrd Land, ya que: (1) los datos de esta zona son escasos, y (2) los datos geocronológicos existentes incluyen una isócrona Rb-Sr combinada de varias muestras (Pankhurst *et al.*, 1998), y dataciones U-Pb convencional, sin un control en la zonación de los circones datados (Mukasa y Dalziel, 2000). Además, dado que los datos paleomagnéticos disponibles para Gondwana Occidental en el Paleozoico tardío - Mesozoico temprano pertenecen a las áreas estables (cratónicas) de Sudamérica (*e.g.*, Rapalini *et al.*, 2006; Tomezzoli, 2009), la adquisición de información paleomagnética de las unidades que conformaron el margen paleo-Pacífico de Gondwana (Patagonia, Península Antártica, Antártica Occidental), permitiría la elaboración de reconstrucciones paleogeográficas detalladas y confiables para el período geológico aquí considerado.

Una nueva hipótesis a evaluar con los datos obtenidos en esta tesis podría ser el modelo recientemente propuesto por Boger (2011). La reconstrucción presentada por este autor (fig. 16) implica que el TMD formaría parte de una "constelación de terrenos" que se habrían incorporado a Gondwana durante la orogénesis Terra Australis (Cawood, 2005) y/o la orogénesis Gondwánica, indicando que la movilidad y el desplazamiento de los diferentes bloques y terrenos tectono-estratigráficos que forman parte del margen de Gondwana occidental puede ser aún mayor de la que, hasta la fecha, se ha supuesto.



**Figura 16.** Reconstrucción de Gondwana de Boger (2011). Terrenos acrecionados a Gondwana incluyen: AP(e)=eastern domain Antarctic Peninsula, B=Bowers Terrane, Ch=Chilenia Terrane, ChP=Challenger Plateau (western domain New Zealand (NZ(w)),CP(w)=Campbell Plateau (western domain New Zealand), Cu=Cuyania Terrane, D=Deseado Terrane, LH=Lord Howe Rise, MB(r)=Ross Province Marie Byrd Land, NEFB=New England Fold Belt, P=Pampean Terrane, RBT=Robertson Bay Terrane and T=Tasmanides, AP(cw)=central and western domains of the Antarctic Peninsula, CP(e)=Campbell Plateau (eastern domain New Zealand) and MB(a)=Amundsen Province Marie Byrd Land.

## **5.5 CONCLUSIONES**

Dentro de los constituyentes del Terreno Madre de Dios (TMD), el Complejo Denaro (CD) está compuesto por metabasaltos toleíticos, metacherts bandeados radiolaríticos y metalíferos, metapelitas y metaareniscas calcáreas. La composición geoquímica de cristales de augita y cromita primarios, y la geoquímica de roca total de los metabasaltos confirma que estos corresponden a basaltos toleíticos tipo MORB. Los análisis geoquímicos (elementos trazas y tierras raras) revelan una similitud con basaltos del tipo E-MORB y, en algunos casos, con basaltos tipo N-MORB. Lo anterior, junto a la asociación de estas rocas con sedimentos oceánicos de aguas profundas (cherts radiolaríticos bandeados), sugiere que la mayoría de estos metabasaltos representan fragmentos del fondo oceánico del Pacífico ancestral formados en un centro de expansión oceánica activo.

La gran extensión y espesor de las Calizas Tarlton (CT) indica que estas se acumularon en un arrecife, probablemente en una etapa avanzada de su evolución. Su edad (Pensilvaniano Medio - Pérmico temprano) coincide con la de un período global de proliferación de arrecifes de aguas cálidas. La comparación de las CT con otros depósitos calcáreos contemporáneos en el margen occidental de Gondwana, sugiere que esta unidad pudo haberse depositado en una zona subtropical a tropical ubicada a una latitud menor que los 30° S.

Datos palinológicos y nuevas dataciones U-Pb SHRIMP de circones detríticos en el Complejo Duque de York (CDY), confirman y restringen la edad de depósito al Pérmico, con una edad máxima de depósito cerca del límite entre el Pérmico temprano y el Pérmico medio (*ca.* 270 Ma). Los patrones de edades de circones detríticos obtenidos en este estudio confirman la existencia de dos poblaciones separadas de circones pérmicos (*ca.* 270 Ma y *ca.* 290 Ma). La asociación palinológica en el CDY, compuesta principalmente por polen de *Gymnospermopsida*, con esporas de *Pteridofita* y hongos, señala un ambiente húmedo durante el depósito de los sedimentos. La petrografía, sedimentología, geoquímica, y los datos isotópicos y geocronológicos del CDY muestran grandes similitudes con otras sucesiones expuestas a lo largo del margen paleo-Pacífico de Gondwana, tales como el Trinity Peninsula Group y el Grupo LeMay oriental de la Península Antártica y el Terreno Rakaia de Nueva Zelandia. La fracción detrítica dominante de éstos, y del CDY, deriva de fuentes ígneas asociadas a un arco magmático activo durante el Pérmico, situado en el margen occidental de Gondwana.

Diques y filones-manto que cortan al TMD presentan geoquímica de basaltos toleíticos de intraplaca, y son posiblemente producto de la etapa inicial del emplazamiento del Batolito Sur-Patagónico en el Jurásico Superior.

El TMD presenta un metamorfismo caracterizado por asociaciones minerales de la zona de presión intermedia y alta temperatura de la facies pumpellyita-actinolita. La utilización de pseudosecciones P-T para calcular los campos de estabilidad de la asociación metamórfica en metabasaltos del CD, indica que las condiciones del peak metamórfico alcanzaron a los 290-310 °C y 4-6 kbar. La información P-T calculada a partir de equilibrios minerales multivariantes locales indica metamorfismo a lo largo de una trayectoria prógrada casi isobárica (desde  $4 \pm 1$  kbar y 200-220 °C hasta  $5 \pm 1$  kbar y 290-330 °C), la que a su vez refleja una trayectoria subhorizontal de las partículas en el prisma de acreción frontal y un re-equilibrio termal de largo plazo a profundidad máxima. Esto concuerda con los conceptos actuales de formación de prismas de acreción frontales.

Las edades  ${}^{40}$ Ar/ ${}^{39}$ Ar obtenidas por ablación láser UV *in situ* en fengitas reflejan edades de crecimiento de mica blanca en diferentes etapas de la evolución del prisma de acreción. Mientras la edad de *ca*. 233 Ma corresponde probablemente a una edad de metamorfismo de las rocas incorporadas dentro del prisma de acreción, el crecimiento de mica blanca a *ca*. 201 Ma puede ser el reflejo de una etapa de acreción avanzada o a un efecto de reajuste retrógrado. El crecimiento de mica blanca a los *ca*. 152 Ma es evidentemente un efecto de reajuste local causado por el acceso de fluidos externos, probablemente ligados a las primeras etapas del emplazamiento del Batolito Sur-Patagónico en el Jurásico Superior.

Las condiciones metamórficas y edad de metamorfismo del TMD son comparables con las determinadas para el Terreno Rakaia, Grupo LeMay oriental y Trinity Peninsula Group, lo cual indica que estas unidades presentan condiciones propias de sistemas de subducción/acreción desarrollado, durante el Triásico Medio-Superior, a lo largo del margen paleo-Pacífico de Gondwana.

Consideraciones regionales, con los datos disponibles a la fecha, permiten proponer un modelo geodinámico que involucra la acreción del TMD en el segmento Antártico del margen paleo-
Pacífico de Gondwana. El arco magmático asociado con, y producto de, los procesos de subducción/acreción, estaría representado por granitoides del Pérmico y Triásico que afloran en el área de Marie Byrd Land (Antártica Occidental) y en la Península Antártica. Después de haberse formado y consolidado, el TMD habría sido transportado, mediante movimientos de rumbo dextrales ocurridos con anterioridad al Jurásico Superior (*ca.* 152 Ma), desde el sector Antártico del margen de Gondwana hasta su posición actual en el borde occidental de la placa Sudamericana, como parte de la Patagonia Austral.

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# APÉNDICES

## FE DE ERRATA

Las secciones c) y d) de la figura 7 del Sepúlveda *et al.* (2008) (Capítulo 2 de esta tesis), deben modificarse por las siguientes:



## i) Clinopiroxenos

| Clinopyroxe  | ne         |           |         |        |       |      |       |       |      |        |       |       |       |       |       |       |       |       |       |       |       |       |
|--------------|------------|-----------|---------|--------|-------|------|-------|-------|------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Sample       | SiO2       | TiO2      | AI2O3   | Fe2O3  | FeO'  | MnO  | MgO   | CaO   | Na2O | Sum    | Si    | Alt   | sum   | Alo   | Ti    | Fe3+  | Fe2+  | Mn    | Mg    | Ca    | Na    | SU2   |
| 04CH17c      | 51,49      | 0,28      | 3,14    | 0,72   | 8,45  | 0,22 | 16,66 | 17,51 | 0,22 | 98,71  | 1,921 | 0,079 | 2,000 | 0,059 | 0,008 | 0,020 | 0,264 | 0,007 | 0,927 | 0,700 | 0,016 | 2,000 |
| 04CH17c      | 53,17      | 0,28      | 1,87    | 1,33   | 5,47  | 0,24 | 17,45 | 20,36 | 0,20 | 100,37 | 1,941 | 0,059 | 2,000 | 0,021 | 0,008 | 0,037 | 0,167 | 0,007 | 0,949 | 0,796 | 0,014 | 2,000 |
| 04CH17c      | 53,20      | 0,34      | 1,64    | 2,44   | 5,26  | 0,19 | 17,38 | 20,75 | 0,20 | 101,39 | 1,929 | 0,070 | 1,999 | 0,000 | 0,009 | 0,067 | 0,159 | 0,006 | 0,939 | 0,806 | 0,014 | 2,001 |
| 04CH17c      | 51,46      | 0,33      | 3,42    | 2,07   | 3,52  | 0,17 | 16,81 | 21,13 | 0,24 | 99,17  | 1,896 | 0,104 | 2,000 | 0,045 | 0,009 | 0,058 | 0,109 | 0,005 | 0,923 | 0,834 | 0,017 | 2,000 |
| 04CH18c      | 51,49      | 0,48      | 3,04    | 1,15   | 6,73  | 0,19 | 16,35 | 19,34 | 0,25 | 99,03  | 1,913 | 0,087 | 2,000 | 0,046 | 0,013 | 0,032 | 0,209 | 0,006 | 0,906 | 0,770 | 0,018 | 2,000 |
| 04CH18c      | 52,66      | 0,26      | 3,44    | 0,00   | 7,64  | 0,25 | 14,90 | 18,19 | 0,95 | 98,31  | 1,967 | 0,033 | 2,000 | 0,119 | 0,007 | 0,000 | 0,239 | 0,008 | 0,830 | 0,728 | 0,069 | 2,000 |
| MD5          | 50,69      | 0,57      | 2,16    | 1,51   | 8,87  | 0,23 | 14,72 | 19,23 | 0,23 | 98,21  | 1,923 | 0,077 | 2,000 | 0,020 | 0,016 | 0,043 | 0,283 | 0,007 | 0,833 | 0,782 | 0,017 | 2,002 |
| MD5          | 50,29      | 0,44      | 1,53    | 2,29   | 9,93  | 0,26 | 14,94 | 17,70 | 0,22 | 97,63  | 1,927 | 0,069 | 1,997 | 0,000 | 0,013 | 0,066 | 0,318 | 0,009 | 0,854 | 0,727 | 0,016 | 2,003 |
| MD5          | 51,47      | 0,32      | 1,56    | 1,45   | 6,56  | 0,18 | 16,45 | 19,57 | 0,15 | 97,72  | 1,941 | 0,059 | 2,000 | 0,011 | 0,009 | 0,041 | 0,207 | 0,006 | 0,925 | 0,791 | 0,011 | 2,000 |
| MD5          | 49,74      | 0,53      | 2,52    | 3,03   | 5,50  | 0,24 | 15,36 | 20,23 | 0,20 | 97,40  | 1,882 | 0,109 | 2,000 | 0,005 | 0,015 | 0,087 | 0,175 | 0,008 | 0,871 | 0,824 | 0,015 | 2,000 |
| MD5          | 49,86      | 0,45      | 2,57    | 3,26   | 4,53  | 0,16 | 15,53 | 20,92 | 0,18 | 97,55  | 1,889 | 0,111 | 2,000 | 0,004 | 0,013 | 0,093 | 0,144 | 0,005 | 0,877 | 0,849 | 0,013 | 2,000 |
| MD26.        | 51,75      | 0,32      | 3,27    | 0,59   | 5,00  | 0,17 | 17,48 | 19,74 | 0,12 | 99,24  | 1,905 | 0,095 | 2,000 | 0,046 | 0,009 | 0,016 | 0,154 | 0,005 | 0,959 | 0,778 | 0,009 | 2,000 |
| MD26.        | 52,19      | 0,34      | 3,06    | 0,24   | 5,59  | 0,15 | 17,71 | 19,36 | 0,13 | 99,47  | 1,916 | 0,084 | 2,000 | 0,048 | 0,010 | 0,007 | 0,172 | 0,005 | 0,969 | 0,762 | 0,010 | 2,000 |
| MD26.        | 51,69      | 0,30      | 3,03    | 0,47   | 4,12  | 0,15 | 17,31 | 20,60 | 0,12 | 98,87  | 1,908 | 0,092 | 2,000 | 0,040 | 0,008 | 0,013 | 0,127 | 0,005 | 0,953 | 0,815 | 0,009 | 2,000 |
| MD26.        | 51,23      | 0,24      | 3,52    | 1,34   | 4,96  | 0,11 | 18,36 | 18,03 | 0,13 | 98,51  | 1,894 | 0,106 | 2,000 | 0,047 | 0,007 | 0,037 | 0,153 | 0,003 | 1,012 | 0,714 | 0,009 | 2,000 |
| MD26.        | 50,04      | 0,66      | 3,34    | 1,66   | 6,15  | 0,17 | 15,33 | 20,20 | 0,20 | 97,97  | 1,888 | 0,112 | 2,000 | 0,037 | 0,019 | 0,047 | 0,194 | 0,006 | 0,862 | 0,816 | 0,014 | 2,000 |
| MD26.        | 51,95      | 0,26      | 2,33    | 0,68   | 5,26  | 0,15 | 16,48 | 20,84 | 0,19 | 98,80  | 1,930 | 0,070 | 2,000 | 0,032 | 0,007 | 0,019 | 0,164 | 0,005 | 0,913 | 0,829 | 0,014 | 2,000 |
| MD26.        | 52,08      | 0,32      | 2,32    | 0,66   | 5,31  | 0,22 | 16,14 | 21,31 | 0,21 | 99,10  | 1,932 | 0,068 | 2,000 | 0,034 | 0,009 | 0,019 | 0,165 | 0,007 | 0,893 | 0,847 | 0,015 | 2,000 |
| MD26.        | 50,87      | 0,44      | 2,80    | 1,14   | 5,39  | 0,13 | 15,70 | 20,93 | 0,19 | 98,02  | 1,911 | 0,089 | 2,000 | 0,035 | 0,012 | 0,032 | 0,169 | 0,004 | 0,879 | 0,843 | 0,014 | 2,000 |
| MD26.        | 52,22      | 0,35      | 1,68    | 0,15   | 6,77  | 0,15 | 16,25 | 20,28 | 0,19 | 98,20  | 1,956 | 0,044 | 2,000 | 0,030 | 0,010 | 0,004 | 0,212 | 0,005 | 0,908 | 0,814 | 0,014 | 2,000 |
| MD05-11D     | 52,96      | 0,26      | 2,51    | 0,66   | 5,04  | 0,13 | 18,71 | 19,04 | 0,14 | 99,44  | 1,935 | 0,065 | 2,000 | 0,043 | 0,007 | 0,018 | 0,154 | 0,004 | 1,019 | 0,745 | 0,010 | 2,000 |
| MD06-5B      | 50,86      | 0,54      | 4,21    | 0,13   | 12,15 | 0,34 | 14,55 | 15,45 | 0,67 | 98,903 | 1,914 | 0,086 | 2,000 | 0,101 | 0,015 | 0,004 | 0,383 | 0,011 | 0,816 | 0,623 | 0,049 | 2,000 |
| MD06-5B      | 53,87      | 0,15      | 1,80    | 0,82   | 7,06  | 0,34 | 21,95 | 13,40 | 0,18 | 99,575 | 1,953 | 0,047 | 2,000 | 0,030 | 0,004 | 0,023 | 0,214 | 0,011 | 1,186 | 0,520 | 0,013 | 2,000 |
| MD06-6.      | 52,41      | 0,22      | 3,11    | 1,37   | 4,30  | 0,15 | 18,31 | 19,59 | 0,15 | 99,61  | 1,913 | 0,087 | 2,000 | 0,047 | 0,006 | 0,038 | 0,131 | 0,005 | 0,997 | 0,766 | 0,010 | 2,000 |
| MD06-6.      | 52,12      | 0,23      | 3,49    | 1,35   | 4,57  | 0,18 | 18,64 | 18,65 | 0,14 | 99,40  | 1,905 | 0,095 | 2,000 | 0,055 | 0,006 | 0,037 | 0,140 | 0,006 | 1,015 | 0,731 | 0,010 | 2,000 |
| MD06-6.      | 53,26      | 0,21      | 2,26    | 0,43   | 4,94  | 0,20 | 19,14 | 18,99 | 0,06 | 99,49  | 1,942 | 0,058 | 2,000 | 0,039 | 0,006 | 0,012 | 0,151 | 0,006 | 1,041 | 0,742 | 0,005 | 2,000 |
| Normalisatio | n to 4 cat | ions to c | alculat | e Fe3+ |       |      |       |       |      |        |       |       |       |       |       |       |       |       |       |       |       |       |

### ii) Feldespatos

| Feldspar |       |       |      |      |      |      |       |      |       |       |        |       |        |       |       |       |       |       |       |       |       |        |        |        |       |        |           |            |
|----------|-------|-------|------|------|------|------|-------|------|-------|-------|--------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|--------|--------|--------|-------|--------|-----------|------------|
| Sample   | SiO2  | AI2O3 | TiO2 | FeO  | MgO  | MnO  | CaO   | BaO  | Na2O  | K20   | Sum    | Si    | Alt    | sum   | Alo   | Fe    | Mg    | Mn    | sum   | Ca    | Ba    | Na     | к      | sum (  | 0'    | Albite | Anorthite | Orthoclase |
| 04CH17c  | 52,31 | 26,05 | 0,08 | 2,31 | 0,07 | 0,11 | 14,59 | 0,00 | 2,14  | 0,04  | 97,70  | 2,452 | 0,548  | 3,000 | 0,891 | 0,091 | 0,005 | 0,005 | 0,994 | 0,733 | 0,000 | 0,194  | 0,003  | 0,930  | 8,000 | 20,91  | 78,81     | 0,27       |
| 04CH17c  | 52,84 | 24,63 | 0,06 | 2,97 | 0,06 | 0,07 | 13,12 | 0,00 | 5,37  | 0,00  | 99,12  | 2,469 | 0,531  | 3,000 | 0,825 | 0,116 | 0,004 | 0,003 | 0,950 | 0,657 | 0,000 | 0,487  | 0,000  | 1,144  | 8,000 | 42,56  | 57,44     | 0,00       |
| 04CH17c  | 56,28 | 26,40 | 0,05 | 0,87 | 0,06 | 0,00 | 10,00 | 0,00 | 5,98  | 0,09  | 99,74  | 2,548 | 0,452  | 3,000 | 0,957 | 0,033 | 0,004 | 0,000 | 0,996 | 0,485 | 0,000 | 0,525  | 0,005  | 1,015  | 8,000 | 51,73  | 47,77     | 0,50       |
| 04CH17c  | 52,78 | 28,30 | 0,07 | 0,97 | 0,12 | 0,01 | 12,65 | 0,00 | 4,56  | 0,05  | 99,51  | 2,417 | 0,583  | 3,000 | 0,944 | 0,037 | 0,009 | 0,000 | 0,993 | 0,621 | 0,000 | 0,405  | 0,003  | 1,028  | 8,000 | 39,39  | 60,35     | 0,26       |
| 04CH18c  | 65,48 | 18,90 | 0,03 | 2,49 | 1,44 | 0,03 | 0,32  | nd   | 10,04 | 0,00  | 98,74  | 2,930 | 0,070  | 3,000 | 0,927 | 0,093 | 0,096 | 0,001 | 1,119 | 0,016 | nd    | 0,871  | 0,000  | 0,887  | 8,000 | 98,23  | 1,75      | 0,02       |
| 04CH18c  | 68,32 | 19,51 | 0,01 | 0,26 | 0,03 | 0,00 | 0,27  | nd   | 11,27 | 0,00  | 99,68  | 2,993 | 0,007  | 3,000 | 1,000 | 0,010 | 0,002 | 0,000 | 1,012 | 0,013 | nd    | 0,957  | 0,000  | 0,970  | 8,000 | 98,69  | 1,31      | 0,00       |
| 04CH18c  | 64,87 | 20,20 | 0,04 | 0,72 | 0,11 | 0,00 | 3,55  | nd   | 7,67  | 0,82  | 97,97  | 2,915 | 0,085  | 3,000 | 0,985 | 0,027 | 0,008 | 0,000 | 1,021 | 0,171 | nd    | 0,668  | 0,047  | 0,886  | 8,000 | 75,43  | 19,28     | 5,29       |
| 04CH18c  | 59,45 | 19,84 | 0,02 | 4,96 | 0,96 | 0,08 | 5,67  | nd   | 8,32  | 0,06  | 99,38  | 2,736 | 0,264  | 3,000 | 0,812 | 0,191 | 0,066 | 0,003 | 1,073 | 0,280 | nd    | 0,743  | 0,004  | 1,026  | 8,000 | 72,39  | 27,24     | 0,37       |
| MD-5.    | 67,34 | 19,22 | nd   | 0,36 | nd   | nd   | 0,39  | 0,00 | 11,47 | 0,02  | 99,03  | 2,979 | 0,022  | 3,000 | 0,978 | 0,012 | nd    | nd    | 0,990 | 0,085 | 0,000 | 0,984  | 0,001  | 1,003  | 8,000 | 0,98   | 0,08      | 0,00       |
| MD-5.    | 69,22 | 17,82 | nd   | 0,36 | nd   | nd   | 0,24  | 0,03 | 10,99 | 0,00  | 98,88  | 3,051 | -0,051 | 3,000 | 0,926 | 0,019 | nd    | nd    | 0,945 | 0,012 | 0,001 | 0,939  | 0,000  | 0,951  | 8,000 | 0,99   | 0,01      | 0,00       |
| MD-5.    | 65,77 | 19,24 | nd   | 0,46 | nd   | nd   | 0,44  | 0,00 | 11,34 | 0,08  | 97,70  | 2,956 | 0,045  | 3,000 | 0,975 | 0,016 | nd    | nd    | 0,991 | 0,021 | 0,000 | 0,988  | 0,005  | 1,014  | 8,000 | 0,97   | 0,02      | 0,00       |
| MD-5.    | 66,46 | 19,38 | nd   | 0,81 | nd   | nd   | 0,63  | 0,00 | 11,27 | 0,08  | 98,86  | 2,954 | 0,046  | 3,000 | 0,970 | 0,027 | nd    | nd    | 0,997 | 0,030 | 0,000 | 0,971  | 0,005  | 1,006  | 8,000 | 0,97   | 0,03      | 0,00       |
| MD-5.    | 64,39 | 19,39 | nd   | 1,90 | nd   | nd   | 0,97  | 0,13 | 10,47 | 0,08  | 98,47  | 2,889 | 0,111  | 3,000 | 0,989 | 0,064 | nd    | nd    | 1,053 | 0,047 | 0,002 | 0,912  | 0,005  | 0,966  | 8,000 | 0,94   | 0,05      | 0,00       |
| MD-5.    | 62,98 | 19,53 | nd   | 0,83 | nd   | nd   | 3,26  | 0,00 | 10,41 | 0,03  | 97,39  | 2,872 | 0,128  | 3,000 | 0,972 | 0,028 | nd    | nd    | 1,000 | 0,160 | 0,000 | 0,920  | 0,002  | 1,081  | 8,000 | 0,85   | 0,15      | 0,00       |
| MD05-11D | 60,44 | 24,73 | 0,00 | 0,22 | 0,05 | 0,00 | 6,74  | 0,05 | 8,16  | 0,09  | 100,50 | 2,685 | 0,315  | 3,000 | 0,980 | 0,008 | 0,004 | 0,000 | 0,992 | 0,321 | 0,001 | 0,703  | 0,005  | 1,030  | 8,000 | 0,68   | 0,31      | 0,01       |
| MD05-11D | 60,82 | 24,71 | 0,00 | 0,22 | 0,01 | 0,01 | 6,48  | 0,00 | 8,48  | 0,05  | 100,78 | 2,692 | 0,308  | 3,000 | 0,981 | 0,008 | 0,001 | 0,000 | 0,991 | 0,307 | 0,000 | 0,728  | 0,003  | 1,038  | 8,000 | 0,70   | 0,30      | 0,00       |
| MD05-11D | 59,09 | 25,79 | 0,00 | 0,14 | 0,01 | 0,00 | 8,59  | 0,00 | 6,80  | 0,10  | 100,53 | 2,630 | 0,370  | 3,000 | 0,982 | 0,005 | 0,001 | 0,000 | 0,988 | 0,410 | 0,000 | 0,587  | 0,006  | 1,002  | 8,000 | 0,59   | 0,41      | 0,01       |
| MD05-18. | 63,26 | 19,59 | 0,00 | 1,75 | 2,88 | 0,00 | 0,31  | 0,01 | 10,84 | 0,27  | 98,91  | 2,844 | 0,156  | 3,000 | 0,882 | 0,066 | 0,193 | 0,000 | 1,142 | 0,015 | 0,000 | 0,945  | 0,015  | 0,975  | 8,000 | 96,90  | 1,52      | 1,57       |
| MD05-18. | 64,88 | 17,84 | 0,00 | 0,29 | 0,01 | 0,01 | 0,00  | 0,40 | 0,07  | 16,21 | 99,71  | 3,015 | 0,000  | 3,015 | 0,977 | 0,011 | 0,001 | 0,000 | 0,990 | 0,000 | 0,007 | 0,007  | 0,961  | 0,975  | 8,000 | 0,67   | 0,00      | 98,58      |
| MD05-18. | 59,88 | 18,14 | 0,00 | 1,97 | 3,64 | 0,00 | 0,09  | 0,65 | 0,15  | 13,37 | 97,89  | 2,853 | 0,148  | 3,000 | 0,871 | 0,079 | 0,259 | 0,000 | 1,209 | 0,004 | 0,012 | 0,013  | 0,812  | 0,842  | 8,000 | 1,60   | 0,53      | 96,43      |
| MD05-18. | 64,72 | 17,85 | 0,00 | 0,06 | 0,02 | 0,00 | 0,00  | 0,74 | 0,13  | 15,94 | 99,46  | 3,016 | 0,000  | 3,016 | 0,981 | 0,002 | 0,001 | 0,000 | 0,984 | 0,000 | 0,014 | 0,011  | 0,948  | 0,973  | 8,000 | 1,18   | 0,00      | 97,43      |
| MD05-18. | 64,58 | 17,71 | 0,00 | 0,25 | 0,01 | 0,00 | 0,00  | 0,55 | 0,13  | 16,05 | 99,28  | 3,016 | 0,000  | 3,016 | 0,975 | 0,010 | 0,001 | 0,000 | 0,986 | 0,000 | 0,010 | 0,012  | 0,956  | 0,978  | 8,000 | 1,22   | 0,00      | 97,75      |
| MD06-6.  | 65,64 | 18,74 | 0,07 | 1,73 | 2,64 | 0,03 | 0,08  | 0,01 | 11,22 | 0,04  | 100,19 | 2,903 | 0,097  | 3,000 | 0,879 | 0,064 | 0,174 | 0,001 | 1,121 | 0,004 | 0,000 | 0,962  | 0,002  | 0,968  | 8,000 | 99,37  | 0,41      | 0,20       |
| MD06-6.  | 68,34 | 18,90 | 0,06 | 0,56 | 0,73 | 0,00 | 0,06  | 0,00 | 12,00 | 0,08  | 100,71 | 2,980 | 0,020  | 3,000 | 0,951 | 0,021 | 0,047 | 0,000 | 1,021 | 0,003 | 0,000 | 1,015  | 0,004  | 1,021  | 8,000 | 99,34  | 0,26      | 0,41       |
| MD06-6.  | 69,14 | 19,25 | 0,00 | 0,11 | 0,01 | 0,00 | 0,04  | 0,01 | 11,73 | 0,05  | 100,33 | 3,008 | 0,000  | 3,008 | 0,987 | 0,004 | 0,001 | 0,000 | 0,992 | 0,002 | 0,000 | 0,990  | 0,003  | 0,995  | 8,000 | 99,53  | 0,20      | 0,26       |
| MD06-8.  | 60,33 | 17,40 | 0,02 | 0,08 | 0,01 | 0,00 | 0,05  | 0,54 | 2,89  | 15,29 | 96,61  | 2,982 | 0,018  | 3,000 | 0,996 | 0,003 | 0,001 | 0,000 | 1,001 | 0,003 | 0,010 | 0,028  | 0,964  | 1,005  | 8,000 | 2,75   | 0,26      | 95,96      |
| MD26     | 66 33 | 20.84 | 0.12 | 1 74 | 2 39 | 0.00 | 0.37  | nd   | 9 34  | 1 15  | 101 60 | 2 861 | 0 139  | 3 000 | 0.932 | 0.064 | 0 156 | 0.000 | 1 155 | 0.017 | nd    | 0 7895 | 0.0640 | 0.8709 | 8 000 | 90.64  | 2.00      | 7 35       |
| MD26     | 65 24 | 19.97 | 0.03 | 2.66 | 3.97 | 0.04 | 0.27  | nd   | 9.64  | 0.03  | 101.87 | 2 842 | 0 159  | 3,000 | 0.867 | 0.097 | 0.258 | 0.002 | 1 225 | 0.013 | nd    | 0.8137 | 0.0015 | 0.8277 | 8,000 | 98 31  | 1.51      | 0.19       |
| MD26.    | 68.88 | 19.48 | 0.38 | 0.26 | 0.26 | 0.04 | 0.76  | nd   | 10.83 | 0.14  | 101.06 | 2,981 | 0.019  | 3,000 | 0.975 | 0.010 | 0.017 | 0.002 | 1.016 | 0.035 | nd    | 0.9087 | 0.0078 | 0.9517 | 8,000 | 95.48  | 3,70      | 0.82       |
|          | ,     | ,     | .,   | 0,20 | -,   | .,   | .,    |      | ,     | .,    | ,      | _,    | -,     | -,    | -,    | -,    | -,    | -,    | .,    | -,    |       | .,     | .,     | -,     | .,    | ,      |           | -,         |
| MD9804.  | 63,3  | 18,76 | 0,07 | 0,11 | 0,01 | 0,00 | 0,01  | nd   | 0,09  | 16,01 | 98,33  | 2,972 | 0,028  | 3,000 | 1,012 | 0,004 | 0,000 | 0,000 | 1,016 | 0,000 | 0,000 | 0,008  | 0,960  | 0,969  | 8,000 | 0,009  | 0,000     | 0,99       |
| MD9804.  | 65,3  | 19,48 | 0,01 | 0,11 | 0,01 | 0,01 | 0,00  | nd   | 0,06  | 15,99 | 100,98 | 2,977 | 0,023  | 3,000 | 1,024 | 0,004 | 0,000 | 0,000 | 1,029 | 0,000 | 0,000 | 0,005  | 0,930  | 0,935  | 8,000 | 0,005  | 0,000     | 0,99       |
| MD9804.  | 69,3  | 20,37 | 0,00 | 0,53 | 0,86 | 0,00 | 0,05  | nd   | 9,37  | 0,06  | 100,55 | 3,006 | 0,000  | 3,000 | 1,041 | 0,019 | 0,000 | 0,000 | 1,060 | 0,002 | 0,000 | 0,788  | 0,003  | 0,793  | 8,000 | 0,993  | 0,003     | 0,00       |
| MD9804.  | 69,1  | 21,21 | 0,01 | 0,62 | 0,75 | 0,02 | 0,06  | nd   | 9,99  | 0,04  | 101,83 | 2,967 | 0,033  | 3,000 | 1,040 | 0,022 | 0,000 | 0,001 | 1,063 | 0,003 | 0,000 | 0,831  | 0,002  | 0,836  | 8,000 | 0,994  | 0,003     | 0,00       |
| MD9804.  | 69,4  | 20,35 | 0,01 | 0,07 | 0,00 | 0,00 | 0,04  | nd   | 10,91 | 0,06  | 100,82 | 2,992 | 0,008  | 3,000 | 1,026 | 0,002 | 0,000 | 0,000 | 1,029 | 0,002 | 0,000 | 0,912  | 0,003  | 0,917  | 8,000 | 0,994  | 0,002     | 0,00       |

Normalisation on the basis of 16 negative charges

### iii) Granates

| Garnet       |                    |              |           |           |         |            |          |         |            |          |            |            |       |       |       |       |       |       |       |       |       |       |           |           |             |        |           |           |
|--------------|--------------------|--------------|-----------|-----------|---------|------------|----------|---------|------------|----------|------------|------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-----------|-----------|-------------|--------|-----------|-----------|
| Sample       | SiO2               | AI2O3        | TiO2      | Fe2O3     | FeO'    | Cr2O3      | MnO      | MaO     | CaO Su     | n Si     | Alt        | sum        | Alo   | Fe3+  | Ti    | Cr    | sum   | Fe2+  | Mn    | Ca    | Ma    | sum   | Andradite | Grossular | Spessartine | Pyrope | Almandine | Uwarowite |
| MD9303       | 35,83              | 9,11         | 0,39      | 18,76     | 0,00    | 0,12       | 0,07     | 0,35    | 34,64 99   | 27 5,84  | 0,160      | 6,000      | 1,591 | 2,301 | 0,047 | 0,015 | 3,945 | 0,000 | 0,010 | 6,051 | 0,084 | 6,144 | 0,375     | 0,610     | 0,002       | 0,014  | 0,000     | 0,003     |
| MD9303       | 35,86              | 8,29         | 0,72      | 19,04     | 0,00    | 0,69       | 0,20     | 0,31    | 33,75 98   | 86 5,90  | 4 0,096    | 6,000      | 1,512 | 2,358 | 0,089 | 0,090 | 3,993 | 0,000 | 0,027 | 5,954 | 0,076 | 6,057 | 0,389     | 0,594     | 0,005       | 0,013  | 0,000     | 0,015     |
| MD9303       | 35,41              | 8,60         | 0,61      | 18,35     | 0,00    | 0,93       | 0,18     | 0,44    | 33,51 98   | 03 5,88  | 6 0,115    | 6,000      | 1,571 | 2,295 | 0,077 | 0,122 | 3,988 | 0,000 | 0,025 | 5,968 | 0,108 | 6,101 | 0,376     | 0,602     | 0,004       | 0,018  | 0,000     | 0,020     |
| MD9303       | 35,79              | 8,11         | 0,38      | 20,08     | 0,00    | 0,03       | 0,21     | 0,05    | 34,91 99   | 56 5,85  | 0,150      | 6,000      | 1,412 | 2,470 | 0,046 | 0,004 | 3,929 | 0,000 | 0,030 | 6,114 | 0,013 | 6,156 | 0,401     | 0,592     | 0,005       | 0,002  | 0,000     | 0,001     |
| MD9303       | 35,18              | 6,95         | 0,16      | 22,07     | 0,00    | 0,01       | 0,10     | 0,05    | 35,00 99   | 51 5,80  | 5 0,195    | 6,000      | 1,155 | 2,741 | 0,019 | 0,001 | 3,915 | 0,000 | 0,014 | 6,188 | 0,011 | 6,213 | 0,441     | 0,555     | 0,002       | 0,002  | 0,000     | 0,000     |
| MD9303       | 35,57              | 7,17         | 0,26      | 21,29     | 0,00    | 0,00       | 0,25     | 0,02    | 34,55 99   | 11 5,86  | 7 0,134    | 6,000      | 1,260 | 2,642 | 0,033 | 0,000 | 3,935 | 0,000 | 0,034 | 6,106 | 0,006 | 6,146 | 0,430     | 0,564     | 0,006       | 0,001  | 0,000     | 0,000     |
| MD9303       | 35,55              | 8,00         | 0,80      | 19,86     | 0,00    | nd         | 0,18     | 0,27    | 34,05 98   | 76 5,84  | 6 0,154    | 6,000      | 1,396 | 2,458 | 0,099 | nd    | 3,954 | 0,000 | 0,025 | 6,000 | 0,066 | 6,090 | 0,404     | 0,582     | 0,004       | 0,011  | 0,000     | nd        |
|              |                    |              |           |           |         |            |          |         |            |          |            |            |       |       |       |       |       |       |       |       |       |       |           |           |             |        |           |           |
| MD065B       | 35,84              | 6,43         | 0,46      | 21,79     | 0,00    | nd         | 0,22     | 0,22    | 33,55 98   | 51 5,94  | 0,060      | 6,000      | 1,196 | 2,718 | 0,057 | nd    | 3,972 | 0,000 | 0,032 | 5,958 | 0,054 | 6,044 | 0,450     | 0,536     | 0,005       | 0,009  | 0,000     | nd        |
| MD065B       | 36,09              | 6,22         | 0,38      | 22,03     | 0,00    | nd         | 0,23     | 0,42    | 33,09 98   | 46 5,97  | 3 0,022    | 6,000      | 1,192 | 2,746 | 0,047 | nd    | 3,986 | 0,000 | 0,033 | 5,873 | 0,104 | 6,009 | 0,457     | 0,520     | 0,006       | 0,017  | 0,000     | nd        |
| MD065B       | 36,09              | 6,15         | 0,42      | 22,08     | 0,00    | nd         | 0,25     | 0,26    | 33,57 98   | 82 5,96  | 5 0,034    | 6,000      | 1,165 | 2,747 | 0,052 | nd    | 3,964 | 0,000 | 0,035 | 5,946 | 0,064 | 6,046 | 0,454     | 0,529     | 0,006       | 0,011  | 0,000     | nd        |
| MD065B       | 35,71              | 6,38         | 0,42      | 21,85     | 0,00    | nd         | 0,30     | 0,11    | 33,55 98   | 31 5,93  | 7 0,063    | 6,000      | 1,187 | 2,734 | 0,053 | nd    | 3,973 | 0,000 | 0,042 | 5,977 | 0,027 | 6,046 | 0,452     | 0,536     | 0,007       | 0,005  | 0,000     | nd        |
| MD065B       | 35,91              | 8,65         | 0,28      | 19,34     | 0,00    | nd         | 0,22     | 5,16    | 27,48 97   | 04 5,87  | 5 0,125    | 6,000      | 1,543 | 2,381 | 0,035 | nd    | 3,959 | 0,000 | 0,031 | 4,817 | 1,259 | 6,107 | 0,390     | 0,399     | 0,005       | 0,206  | 0,000     | nd        |
|              |                    |              |           |           |         |            |          |         |            |          |            |            |       |       |       |       |       |       |       |       |       |       |           |           |             |        |           |           |
| MD9304       | 35,94              | 6,39         | 0,90      | 19,38     | 0,00    | 1,69       | 0,40     | 0,20    | 34,23 99   | 11 5,92  | 0,080      | 6,000      | 1,160 | 2,402 | 0,111 | 0,220 | 3,893 | 0,000 | 0,055 | 6,041 | 0,049 | 6,145 | 0,391     | 0,556     | 0,009       | 0,008  | 0,000     | 0,036     |
| MD9304       | 34,60              | 6,82         | 0,80      | 18,10     | 1,04    | 4,03       | 0,47     | 0,24    | 32,49 98   | 61 5,76  | 2 0,238    | 6,000      | 1,101 | 2,268 | 0,101 | 0,530 | 4,000 | 0,145 | 0,066 | 5,796 | 0,061 | 6,067 | 0,374     | 0,494     | 0,011       | 0,010  | 0,024     | 0,087     |
| Cations band | ased on<br>ermined | 48 nega<br>I | ative cha | arges inc | uding 1 | 10 cation: | s in the | tetrahe | dral and o | tahedral | site to ca | ilculate f | -e3+  |       |       |       |       |       |       |       |       |       |           |           |             |        |           |           |

### iv) Micas blancas

| White Mic<br>Metabasit   | a<br>9<br>9000  | TIO2  | 1202   | En0 -   | ~2O2 •   |  | 140 ·  | · • •  | 1220 1   | · ^  | 1201   |  | AH   |  | т  | En2-   | E02. •   | un •   | Ma   | eum -  |  | Na "  | <i>.</i> .  |  | tri  | ioctahedral M   | g-Al- Fe   | -Al-   |  |  |
|--|---|---|--|---|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|---|---|--|--|---|--|--|--|--|
| Sample<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c<br>04CH18c   | SiO2<br>44,46<br>45,85<br>45,88<br>45,86<br>48,02<br>49,13<br>46,67<br>49,20<br>48,15<br>49,05<br>48,05<br>51,61<br>49,59   | TiO2 0,33<br>0,19<br>0,13<br>0,29<br>0,04<br>0,00<br>0,04<br>0,00<br>0,04<br>0,00<br>0,08<br>0,06<br>0,02<br>0,03<br>0,03   | Al2O3 1<br>34,04<br>34,19<br>34,22<br>34,88<br>28,78<br>27,28<br>28,36<br>28,32<br>27,68<br>25,56<br>28,35<br>24,66<br>25,04   | FeO F<br>1,33<br>1,22<br>1,16<br>1,22<br>4,48<br>4,60<br>4,68<br>4,25<br>4,36<br>4,94<br>4,25<br>5,01<br>4,61   | e2O3 N<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,   | InO N<br>0,01<br>0,00<br>0,02<br>0,05<br>0,01<br>0,05<br>0,05<br>0,05<br>0,04<br>0,00<br>0,03<br>0,05<br>0,03                                | 190 0<br>0,81<br>0,96<br>0,93<br>0,66<br>1,37<br>1,78<br>1,39<br>1,22<br>1,99<br>2,23<br>1,34<br>2,37<br>2,83  | CaO N<br>0,00<br>0,02<br>0,02<br>0,00<br>0,02<br>0,59<br>1,88<br>0,06<br>0,26<br>0,11<br>1,11<br>0,02<br>0,01  | Va2O F<br>0,67<br>0,69<br>0,71<br>0,87<br>0,26<br>0,70<br>0,16<br>0,82<br>0,17<br>0,57<br>0,62<br>1,14<br>0,09   | (20 F<br>9,73<br>10,34<br>10,24<br>9,91<br>10,57<br>9,84<br>9,58<br>10,02<br>10,54<br>10,26<br>9,76<br>9,62<br>10,68   | 4,34<br>4,42<br>4,42<br>4,45<br>4,36<br>4,37<br>4,27<br>4,39<br>4,34<br>4,31<br>4,34<br>4,42<br>4,37   | Sim         Si           95,71         6,146           97,88         6,217           97,71         6,224           98,16         6,180           97,96         6,599           98,30         6,744           97,71         6,652           97,10         6,652           97,10         6,652           97,10         6,652           97,10         6,647           98,92         7,009           98,49         6,808 | Alt sun<br>1,854 8,0<br>1,783 8,0<br>1,776 8,0<br>1,821 8,0<br>1,821 8,0<br>1,401 8,0<br>1,401 8,0<br>1,404 8,0<br>1,447 8,0<br>1,348 8,0<br>1,171 8,0<br>1,348 8,0<br>0,991 8,0<br>1,192 8,0  | Alo           00         3,691           00         3,680           00         3,695           00         3,719           00         3,261           00         3,261           00         3,261           00         3,262           00         3,269           00         3,269           00         3,223           00         3,223           00         3,263           00         3,264           00         3,269           00         3,269           00         3,263           00         3,264           00         3,269           00         3,269           00         3,263           00         3,264           00         3,263           00         3,263           00         2,859   | Ti 0,034<br>0,019<br>0,014<br>0,030<br>0,004<br>0,000<br>0,004<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000   | Fe2+<br>0,153<br>0,138<br>0,132<br>0,137<br>0,514<br>0,528<br>0,549<br>0,549<br>0,504<br>0,504<br>0,576<br>0,504<br>0,579<br>0,529   | Fe3+ 1<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000   | Mn 0,002<br>0,000<br>0,000<br>0,002<br>0,006<br>0,001<br>0,006<br>0,006<br>0,005<br>0,000<br>0,005<br>0,000<br>0,004<br>0,006<br>0,003   | VIg<br>0,167<br>0,195<br>0,187<br>0,133<br>0,282<br>0,363<br>0,292<br>0,248<br>0,411<br>0,464<br>0,276<br>0,479<br>0,580   | sum (<br>4,047<br>4,032<br>4,027<br>4,021<br>4,067<br>4,049<br>4,097<br>4,008<br>4,086<br>4,086<br>4,068<br>4,041<br>4,014<br>4,100  | Ca P<br>0,000<br>0,003<br>0,002<br>0,000<br>0,003<br>0,087<br>0,282<br>0,009<br>0,038<br>0,017<br>0,164<br>0,003<br>0,001  | Na P<br>0,179<br>0,181<br>0,186<br>0,228<br>0,070<br>0,186<br>0,043<br>0,217<br>0,047<br>0,154<br>0,167<br>0,299<br>0,023   | 1,716<br>1,788<br>1,772<br>1,704<br>1,854<br>1,723<br>1,715<br>1,715<br>1,715<br>1,744<br>1,857<br>1,823<br>1,722<br>1,667<br>1,871   | sum         OH         m           1,894         4,000           1,972         4,000           1,931         4,000           1,927         4,000           1,927         4,000           2,041         4,000           1,932         4,000           1,934         4,000           1,935         4,000           1,942         4,000           2,054         4,000           1,983         4,000           1,983         4,000           1,984         4,000           1,985         4,000   | uscovite m<br>0,792<br>0,771<br>0,771<br>0,767<br>0,626<br>0,423<br>0,375<br>0,520<br>0,563<br>0,455<br>0,414<br>0,332<br>0,500  | ica ce<br>0,024<br>0,016<br>0,014<br>0,010<br>0,033<br>0,025<br>0,048<br>0,004<br>0,043<br>0,043<br>0,043<br>0,020<br>0,007<br>0,050  | Hadonite ce<br>0,038<br>0,064<br>0,066<br>0,044<br>0,106<br>0,169<br>0,144<br>0,122<br>0,155<br>0,189<br>0,145<br>0,231<br>0,212   | ladonite par<br>0,035<br>0,046<br>0,046<br>0,046<br>0,194<br>0,246<br>0,271<br>0,240<br>0,190<br>0,234<br>0,258<br>0,275<br>0,193  | agonite         rest           0,094         0,017           0,092         0,011           0,095         0,008           0,118         0,015           0,037         0,003           0,033         0,044           0,021         0,140           0,110         0,005           0,024         0,024           0,077         0,011           0,082         0,081           0,152         0,006           0,012         0,067 |  |
| MD26<br>MD26<br>MD26<br>MD26<br>MD26<br>MD26<br>MD26<br>MD26   | 47,73<br>47,63<br>50,47<br>47,19<br>49,06<br>49,51<br>49,14<br>49,14<br>49,46<br>48,51<br>48,20<br>47,59<br>48,20<br>47,55<br>47,40<br>48,20<br>47,55<br>47,40<br>48,20<br>47,55<br>47,40<br>48,51<br>46,88 | 0,02<br>0,00<br>0,01<br>0,02<br>0,01<br>0,02<br>0,02<br>0,03<br>0,03<br>0,03<br>0,03<br>0,03<br>0,03  | 33,01<br>33,59<br>33,15<br>27,58<br>31,94<br>28,90<br>31,58<br>30,59<br>28,90<br>32,46<br>32,95<br>32,46<br>32,68<br>34,43<br>31,13<br>31,87<br>34,42<br>33,23<br>31,17<br>34,13 | 2,40<br>1,99<br>2,29<br>3,37<br>2,46<br>3,01<br>3,00<br>2,31<br>3,00<br>2,31<br>3,04<br>2,36<br>1,59<br>1,50<br>3,14<br>2,36<br>1,59<br>1,52<br>2,33<br>2,30<br>2,11<br>1,17<br>1,172<br>2,47<br>1,53 | 0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,0  | 0,00<br>0,05<br>0,00<br>0,02<br>0,01<br>0,02<br>0,02<br>0,02<br>0,02<br>0,02   | $\begin{array}{c} 1,21\\ 1,08\\ 1,06\\ 2,83\\ 1,14\\ 2,16\\ 2,43\\ 1,48\\ 1,98\\ 2,77\\ 1,99\\ 1,16\\ 3,14\\ 1,32\\ 0,92\\ 1,42\\ 1,58\\ 1,19\\ 0,57\\ 0,85\\ 1,70\\ 0,61\\ \end{array}$ | 0,01<br>0,00<br>0,00<br>0,03<br>0,00<br>0,00<br>0,00<br>0,00   | 0,22<br>0,26<br>0,18<br>0,12<br>0,22<br>0,21<br>0,12<br>0,20<br>0,23<br>0,23<br>0,18<br>0,32<br>0,32<br>0,32<br>0,32<br>0,32<br>0,32<br>0,32<br>0,32   | 11,10<br>10,68<br>11,04<br>10,98<br>11,08<br>11,08<br>11,08<br>11,08<br>11,08<br>10,92<br>10,87<br>10,85<br>8,83<br>10,53<br>10,53<br>10,73<br>10,84<br>10,71<br>10,91<br>11,07<br>10,91<br>11,07<br>10,95 | $\begin{array}{c} 4,48\\ 4,49\\ 4,42\\ 4,45\\ 4,34\\ 4,44\\ 4,43\\ 4,44\\ 4,43\\ 4,44\\ 4,43\\ 4,41\\ 4,52\\ 4,52\\ 4,53\\ 4,54\\ 4,54\\ 4,54\\ 4,54\\ 4,54\\ 4,47\\ 4,50\\ 4,42\\ 4,46\\ 4,47\end{array}$ | 100,18 6,358<br>99,77 6,332<br>99,04 6,314<br>99,82 6,761<br>98,47 6,408<br>99,83 6,652<br>99,83 6,652<br>99,83 6,652<br>98,73 6,693<br>100,19 6,571<br>100,04 6,429<br>98,56 6,473<br>100,36 6,856<br>99,00 6,527<br>100,36 6,434<br>99,04 6,319<br>97,90 6,328<br>99,74 6,300<br>98,64 6,302   | 1,642 8,0<br>1,668 8,0<br>1,240 8,0<br>1,240 8,0<br>1,240 8,0<br>1,349 8,0<br>1,534 8,0<br>1,534 8,0<br>1,524 8,0<br>1,524 8,0<br>1,527 8,0<br>1,527 8,0<br>1,527 8,0<br>1,528 8,0<br>1,602 8,0<br>1,618 8,0<br>1,618 8,0<br>1,671 8,0<br>1,671 8,0              | 00 3,540<br>00 3,596<br>00 3,517<br>00 3,114<br>00 3,519<br>00 3,279<br>00 3,279<br>00 3,229<br>00 3,229<br>00 3,2465<br>00 3,342<br>00 3,158<br>00 3,516<br>00 3,550<br>00 3,550<br>00 3,550<br>00 3,550<br>00 3,550<br>00 3,550<br>00 3,550<br>00 3,550<br>00 3,250<br>00 3, | 0,002<br>0,000<br>0,001<br>0,002<br>0,001<br>0,002<br>0,003<br>0,003<br>0,002<br>0,003<br>0,004<br>0,006<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,001<br>0,002 | 0,268<br>0,222<br>0,257<br>0,378<br>0,279<br>0,338<br>0,378<br>0,259<br>0,349<br>0,345<br>0,262<br>0,348<br>0,167<br>0,348<br>0,262<br>0,254<br>0,254<br>0,254<br>0,254<br>0,254<br>0,254<br>0,258<br>0,278<br>0,172 | 0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000 | 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| 4,050<br>4,036<br>4,047<br>4,055<br>4,055<br>4,052<br>4,026<br>4,090<br>4,067<br>4,028<br>3,996<br>4,047<br>4,028<br>3,998<br>4,046<br>4,046<br>4,024<br>4,024<br>4,035<br>4,013<br>4,046<br>3,998 | 0,001<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,002<br>0,035<br>0,002<br>0,017<br>0,000<br>0,000<br>0,004<br>0,004<br>0,004<br>0,004<br>0,002<br>0,008<br>0,000 | 0,056<br>0,068<br>0,047<br>0,032<br>0,057<br>0,056<br>0,032<br>0,052<br>0,061<br>0,047<br>0,072<br>0,082<br>0,049<br>0,076<br>0,076<br>0,076<br>0,075<br>0,102<br>0,068<br>0,071<br>0,068<br>0,071<br>0,069<br>0,091<br>0,046 | 1,885<br>1,811<br>1,876<br>1,918<br>1,899<br>1,923<br>1,899<br>1,840<br>1,887<br>1,840<br>1,887<br>1,843<br>1,494<br>1,778<br>1,843<br>1,494<br>1,778<br>1,836<br>1,774<br>1,836<br>1,836<br>1,837<br>1,823 | 1,942,4,000<br>1,879,4,000<br>1,879,4,000<br>1,908,4,000<br>1,980,4,000<br>1,984,4,000<br>1,985,4,000<br>1,985,4,000<br>1,991,4,000<br>1,994,4,000<br>1,282,4,000<br>1,284,4,000<br>1,284,4,000<br>1,284,4,000<br>1,284,4,000<br>1,943,4,000<br>1,943,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974,4,000<br>1,974 | 0,755<br>0,776<br>0,782<br>0,564<br>0,739<br>0,641<br>0,621<br>0,760<br>0,584<br>0,584<br>0,584<br>0,584<br>0,584<br>0,567<br>0,742<br>0,613<br>0,522<br>0,721<br>0,808<br>0,681<br>0,818    | 0,025<br>0,018<br>0,026<br>0,030<br>0,077<br>0,029<br>0,028<br>0,015<br>0,045<br>0,035<br>0,014<br>0,035<br>0,014<br>0,035<br>0,014<br>0,003<br>0,003<br>0,003<br>0,003<br>0,003<br>0,001<br>0,003<br>0,001                   | 0,088<br>0,082<br>0,073<br>0,230<br>0,167<br>0,195<br>0,126<br>0,217<br>0,173<br>0,173<br>0,173<br>0,179<br>0,276<br>0,171<br>0,089<br>0,387<br>0,097<br>0,078<br>0,135<br>0,064                   | 0.097<br>0.086<br>0.154<br>0.154<br>0.131<br>0.135<br>0.111<br>0.135<br>0.111<br>0.135<br>0.112<br>0.134<br>0.134<br>0.197<br>0.098<br>0.157<br>0.008<br>0.107<br>0.068<br>0.112<br>0.096<br>0.088<br>0.110<br>0.088 | 0.029 0.007<br>0.036 0.002<br>0.024 0.007<br>0.017 0.005<br>0.029 0.006<br>0.028 0.004<br>0.028 0.004<br>0.028 0.004<br>0.027 0.005<br>0.027 0.005<br>0.024 0.003<br>0.024 0.003<br>0.024 0.003<br>0.024 0.007<br>0.040 0.007<br>0.045 0.007<br>0.045 0.007<br>0.045 0.007<br>0.045 0.007  |  |
| 04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c<br>04CH17c      | 47,02<br>50,27<br>48,23<br>48,51<br>50,14<br>47,92<br>50,05<br>48,55<br>51,38<br>48,12<br>48,93<br>48,26<br>49,40<br>48,71<br>48,78<br>47,30<br>49,31   | 0,02<br>0,04<br>0,02<br>0,02<br>0,03<br>0,05<br>0,04<br>0,06<br>0,02<br>0,03<br>0,04<br>0,05<br>0,02<br>0,07<br>0,00<br>0,08<br>0,04  | 31,02<br>26,76<br>29,13<br>28,35<br>30,33<br>27,83<br>26,83<br>30,66<br>27,20<br>28,36<br>30,55<br>30,96<br>28,43<br>28,01<br>27,68<br>30,78<br>30,78<br>30,26                   | 2,43<br>3,84<br>3,66<br>4,11<br>3,94<br>3,66<br>4,11<br>4,23<br>3,45<br>4,11<br>4,27<br>3,30<br>3,40<br>4,02<br>4,25<br>4,22<br>3,56<br>3,25  | 1,78<br>0,00<br>0,84<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,0  | 0,02<br>0,02<br>0,02<br>0,01<br>0,09<br>0,05<br>0,07<br>0,04<br>0,05<br>0,02<br>0,01<br>0,02<br>0,00<br>0,00<br>0,09<br>0,00<br>0,07<br>0,05 | 1,95<br>2,74<br>2,19<br>2,15<br>1,75<br>2,21<br>1,79<br>2,83<br>1,23<br>2,11<br>2,05<br>1,39<br>1,16<br>2,46<br>2,38<br>2,18<br>1,11<br>1,69   | 0,01<br>0,80<br>0,02<br>0,12<br>0,07<br>0,09<br>0,47<br>0,30<br>0,04<br>1,53<br>0,08<br>0,02<br>0,03<br>0,56<br>0,00<br>0,04<br>0,04<br>0,016  | 0,09<br>0,49<br>0,04<br>0,09<br>0,03<br>0,04<br>0,43<br>0,17<br>0,20<br>1,58<br>0,16<br>0,22<br>0,09<br>0,16<br>0,43<br>0,11<br>0,09<br>0,87   | 9,70<br>9,35<br>9,84<br>10,22<br>10,33<br>10,21<br>10,04<br>10,60<br>9,39<br>9,88<br>10,45<br>10,63<br>10,45<br>10,63<br>10,32<br>9,76<br>10,77<br>10,58<br>9,48   | 4,46<br>4,43<br>4,44<br>4,39<br>4,47<br>4,45<br>4,37<br>4,44<br>4,46<br>4,50<br>4,37<br>4,48<br>4,45<br>4,46<br>4,44<br>4,38<br>4,39<br>4,50   | 98,51 6,329<br>98,73 6,802<br>98,44 6,516<br>98,74 6,506<br>98,74 6,506<br>98,74 6,506<br>99,31 6,763<br>99,30 6,530<br>99,30 6,500<br>99,946 6,650<br>99,46 6,650<br>99,46 6,650<br>99,46 6,650<br>99,46 6,650  | 1,671 8,0<br>1,198 8,0<br>1,484 8,0<br>1,378 8,0<br>1,478 8,0<br>1,495 8,0<br>1,495 8,0<br>1,470 8,0<br>1,470 8,0<br>1,470 8,0<br>1,470 8,0<br>1,470 8,0<br>1,500 8,0<br>1,363 8,0<br>1,445 8,0<br>1,418 8,0<br>1,418 8,0<br>1,418 8,0<br>1,418 8,0<br>1,418 8,0 | 00 3,251<br>00 3,069<br>00 3,155<br>00 3,183<br>00 3,240<br>00 3,240<br>00 3,240<br>00 3,240<br>00 3,125<br>00 3,125<br>00 3,145<br>00 3,1415<br>00 3,043<br>00 3,043<br>00 3,153<br>00 3,333  | 0,002<br>0,004<br>0,003<br>0,002<br>0,002<br>0,003<br>0,005<br>0,004<br>0,005<br>0,002<br>0,003<br>0,004<br>0,005<br>0,002<br>0,008<br>0,000<br>0,009<br>0,004   | 0,274<br>0,434<br>0,413<br>0,469<br>0,442<br>0,471<br>0,478<br>0,388<br>0,458<br>0,490<br>0,370<br>0,383<br>0,452<br>0,481<br>0,484<br>0,406<br>0,363  | 0,180<br>0,000<br>0,085<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,015<br>0,080<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000  | 0,003<br>0,002<br>0,002<br>0,001<br>0,011<br>0,016<br>0,008<br>0,004<br>0,006<br>0,002<br>0,001<br>0,002<br>0,000<br>0,000<br>0,000<br>0,000<br>0,008<br>0,005   | 0,391<br>0,552<br>0,441<br>0,438<br>0,351<br>0,46<br>0,570<br>0,247<br>0,420<br>0,419<br>0,278<br>0,278<br>0,492<br>0,479<br>0,446<br>0,226<br>0,337   | 4,100<br>4,061<br>4,100<br>4,095<br>4,095<br>4,095<br>4,097<br>4,088<br>4,097<br>4,035<br>4,011<br>4,102<br>4,030<br>4,030<br>4,100<br>4,082<br>4,100<br>4,082<br>4,058<br>4,041                   | 0,002<br>0,116<br>0,002<br>0,018<br>0,010<br>0,012<br>0,070<br>0,044<br>0,009<br>0,005<br>0,226<br>0,011<br>0,003<br>0,005<br>0,881<br>0,000<br>0,005<br>0,023   | 0,023<br>0,129<br>0,011<br>0,023<br>0,008<br>0,010<br>0,114<br>0,044<br>0,043<br>0,043<br>0,043<br>0,043<br>0,043<br>0,023<br>0,023<br>0,021<br>0,112<br>0,028<br>0,023<br>0,023<br>0,226                                     | 1,666<br>1,614<br>1,696<br>1,779<br>1,768<br>1,757<br>1,786<br>1,818<br>1,596<br>1,730<br>1,785<br>1,825<br>1,825<br>1,829<br>1,683<br>1,882<br>1,842<br>1,613  | 1,726 4,000<br>1,885 4,000<br>1,868 4,000<br>1,817 4,000<br>1,868 4,000<br>1,817 4,000<br>1,873 4,000<br>1,873 4,000<br>1,873 4,000<br>1,853 4,000<br>1,853 4,000<br>1,815 4,000<br>1,817 4,000<br>1,817 4,000   | 0,684<br>0,347<br>0,621<br>0,558<br>0,549<br>0,556<br>0,556<br>0,498<br>0,678<br>0,360<br>0,360<br>0,678<br>0,360<br>0,633<br>0,713<br>0,599<br>0,603<br>0,603<br>0,720<br>0,544             | 0,050<br>0,031<br>0,050<br>0,048<br>0,048<br>0,048<br>0,048<br>0,044<br>0,048<br>0,044<br>0,048<br>0,051<br>0,051<br>0,051<br>0,050<br>0,050<br>0,050<br>0,050  | 0,109<br>0,267<br>0,144<br>0,167<br>0,222<br>0,206<br>0,141<br>0,220<br>0,105<br>0,205<br>0,191<br>0,122<br>0,095<br>0,167<br>0,167<br>0,164<br>0,083<br>0,145                                     | 0,077<br>0,210<br>0,135<br>0,179<br>0,153<br>0,191<br>0,182<br>0,185<br>0,223<br>0,165<br>0,223<br>0,166<br>0,156<br>0,154<br>0,154<br>0,178<br>0,178<br>0,149<br>0,156  | 0,014 0,000<br>0,069 0,000<br>0,012 0,000<br>0,005 0,000<br>0,005 0,000<br>0,059 0,000<br>0,023 0,000<br>0,023 0,000<br>0,023 0,000<br>0,023 0,000<br>0,023 0,000<br>0,013 0,000<br>0,015 0,000<br>0,015 0,000<br>0,015 0,000  |  |
| MD05_110<br>MD05_110<br>MD05_110<br>MD05_110<br>MD05_110<br>MD05_110<br>MD05_110<br>MD05_110   | 52,70<br>51,80<br>50,25<br>50,83<br>49,47<br>50,81<br>50,69<br>49,96  | 0,02<br>0,03<br>0,04<br>0,03<br>0,02<br>0,04<br>0,03  | 24,74<br>27,29<br>27,94<br>25,74<br>29,37<br>26,67<br>25,06<br>27,69   | 3,20<br>3,45<br>2,90<br>3,46<br>3,09<br>3,35<br>3,85<br>3,85<br>3,22  | 0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,0  | 0,00<br>0,02<br>0,00<br>0,00<br>0,00<br>0,03<br>0,03<br>0,03   | 3,03<br>2,83<br>2,79<br>3,35<br>2,09<br>3,08<br>3,80<br>2,70   | 0,20<br>0,09<br>0,07<br>0,14<br>0,05<br>0,06<br>1,26<br>0,02   | 1,12<br>0,19<br>0,10<br>0,11<br>0,10<br>0,28<br>0,09<br>0,13   | 9,63<br>9,72<br>10,98<br>10,92<br>10,69<br>10,40<br>10,01<br>10,79   | 4,47<br>4,54<br>4,47<br>4,43<br>4,47<br>4,46<br>4,42<br>4,44   | 99,17 7,078<br>99,96 6,842<br>99,56 6,742<br>99,08 6,882<br>99,42 6,634<br>99,22 6,831<br>99,30 6,883<br>99,06 6,741   | 0,922 8,0<br>1,158 8,0<br>1,258 8,0<br>1,118 8,0<br>1,366 8,0<br>1,169 8,0<br>1,117 8,0<br>1,259 8,0   | 00 2,994<br>00 3,090<br>00 3,160<br>00 2,990<br>00 3,276<br>00 3,056<br>00 2,894<br>00 3,144   | 0,002<br>0,003<br>0,004<br>0,003<br>0,002<br>0,002<br>0,004<br>0,003   | 0,360<br>0,381<br>0,325<br>0,392<br>0,347<br>0,377<br>0,437<br>0,363   | 0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000   | 0,000<br>0,003<br>0,000<br>0,000<br>0,000<br>0,004<br>0,003<br>0,000   | 0,607<br>0,557<br>0,558<br>0,676<br>0,418<br>0,617<br>0,770<br>0,543   | 3,963<br>4,032<br>4,046<br>4,060<br>4,043<br>4,055<br>4,108<br>4,054   | 0,028<br>0,012<br>0,010<br>0,021<br>0,008<br>0,009<br>0,184<br>0,003   | 0,292<br>0,048<br>0,026<br>0,029<br>0,025<br>0,072<br>0,023<br>0,033  | 1,650<br>1,638<br>1,879<br>1,886<br>1,828<br>1,784<br>1,784<br>1,734  | 1,973 4,000<br>1,700 4,000<br>1,916 4,000<br>1,939 4,000<br>1,864 4,000<br>1,869 4,000<br>1,943 4,000<br>1,898 4,000   | 0,300<br>0,518<br>0,579<br>0,487<br>0,636<br>0,505<br>0,299<br>0,575   | -0,019<br>0,016<br>0,023<br>0,030<br>0,021<br>0,028<br>0,054<br>0,027   | 0,348<br>0,255<br>0,238<br>0,287<br>0,176<br>0,262<br>0,343<br>0,224   | 0,206<br>0,174<br>0,139<br>0,166<br>0,146<br>0,160<br>0,195<br>0,150   | 0,148 0,033<br>0,028 0,017<br>0,014 0,015<br>0,015 0,029<br>0,014 0,014<br>0,039 0,014<br>0,012 0,195<br>0,018 0,011   |  |
| MD06_5B<br>MD06_5B<br>MD06_5B<br>MD06_5B<br>MD06_5B  | 48,97<br>49,50<br>50,86<br>49,74<br>50,31   | 0,02<br>0,04<br>0,18<br>0,02<br>0,52  | 30,13<br>29,16<br>24,30<br>25,99<br>24,09  | 2,48<br>3,18<br>5,04<br>1,73<br>4,53  | 0,00<br>0,00<br>0,00<br>2,74<br>0,13   | 0,07<br>0,10<br>0,08<br>0,02<br>0,03   | 2,35<br>2,49<br>3,69<br>4,04<br>4,14   | 0,06<br>0,06<br>1,22<br>0,10<br>1,20   | 0,11<br>0,43<br>0,10<br>0,06<br>0,47   | 11,01<br>10,42<br>9,86<br>11,01<br>10,21   | 4,48<br>4,48<br>4,42<br>4,46<br>4,42   | 99,75 6,556<br>99,90 6,618<br>99,74 6,902<br>99,89 6,693<br>100,07 6,827   | 1,444 8,0<br>1,382 8,0<br>1,098 8,0<br>1,308 8,0<br>1,174 8,0  | 00 3,309<br>00 3,214<br>00 2,789<br>00 2,814<br>00 2,679   | 0,002<br>0,004<br>0,019<br>0,002<br>0,053  | 0,278<br>0,356<br>0,572<br>0,195<br>0,514  | 0,000<br>0,000<br>0,000<br>0,277<br>0,014  | 0,008<br>0,011<br>0,010<br>0,002<br>0,003  | 0,469<br>0,496<br>0,747<br>0,811<br>0,837  | 4,066<br>4,080<br>4,136<br>4,100<br>4,100  | 0,008<br>0,009<br>0,177<br>0,014<br>0,175  | 0,028<br>0,112<br>0,026<br>0,015<br>0,125   | 1,881<br>1,777<br>1,706<br>1,889<br>1,768   | 1,921 4,000<br>1,899 4,000<br>1,909 4,000<br>1,918 4,000<br>2,068 4,000  | 0,661<br>0,579<br>0,273<br>0,512<br>0,277  | 0,033<br>0,040<br>0,068<br>0,050<br>0,050   | 0,179<br>0,183<br>0,308<br>0,285<br>0,309  | 0,106<br>0,132<br>0,236<br>0,069<br>0,190  | 0,014 0,015<br>0,059 0,015<br>0,013 0,204<br>0,008 0,154<br>0,060 0,229  |  |
| MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804<br>MD9804   | 53,23<br>53,71<br>54,61<br>53,47<br>53,82<br>53,75<br>54,11<br>54,42<br>53,92<br>54,16<br>54,11<br>53,59<br>54,81<br>55,31<br>53,70<br>53,72<br>52,91<br>54,55<br>54,57<br>53,58<br>54,26                   | 11,46<br>13,04<br>11,20<br>13,56<br>22,20<br>12,74<br>24,55<br>23,04<br>23,47<br>11,04<br>23,85<br>12,77<br>23,74<br>21,74<br>25,37<br>25,40<br>23,20<br>23,81<br>24,90<br>23,13                          | 0,03<br>0,04<br>0,02<br>0,01<br>0,03<br>0,02<br>0,00<br>0,02<br>0,03<br>0,00<br>0,01<br>0,01<br>0,01<br>0,01<br>0,01<br>0,01   | 10,63<br>9,03<br>10,09<br>8,90<br>1,37<br>9,33<br>0,00<br>0,89<br>0,08<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00  | 2,86<br>3,74<br>3,70<br>5,52<br>3,26<br>4,45<br>2,83<br>4,00<br>3,44<br>5,31<br>3,91<br>3,91<br>3,91<br>3,92<br>2,86<br>3,35<br>4,70<br>4,93<br>3,76<br>3,84 | 6,64<br>6,11<br>6,63<br>6,29<br>4,03<br>6,39<br>4,05<br>5,56<br>6,70<br>5,70<br>6,70<br>5,61<br>4,72<br>4,02<br>4,42<br>4,11<br>4,21<br>4,78 | 0,01<br>0,05<br>0,06<br>0,05<br>0,05<br>0,03<br>0,00<br>0,01<br>0,02<br>0,03<br>0,03<br>0,03<br>0,03<br>0,05<br>0,05<br>0,01<br>0,04<br>0,04<br>0,05                                     | 0,06<br>0,08<br>0,04<br>0,03<br>0,03<br>0,02<br>0,03<br>0,02<br>0,03<br>0,01<br>0,04<br>0,04<br>0,04<br>0,05<br>0,02<br>0,03<br>0,02<br>0,03<br>0,02<br>0,03<br>0,02<br>0,03<br>0,02<br>0,03<br>0,02<br>0,03<br>0,02 | 0,00<br>0,01<br>0,02<br>0,01<br>0,02<br>0,01<br>0,02<br>0,01<br>0,02<br>0,01<br>0,00<br>0,03<br>0,02<br>0,01<br>0,00<br>0,02<br>0,01<br>0,02<br>0,01<br>0,02<br>0,01<br>0,02<br>0,01<br>0,02<br>0,01 | 10,27<br>10,32<br>10,27<br>9,95<br>10,34<br>10,30<br>9,89<br>10,65<br>10,23<br>9,37<br>10,02<br>10,48<br>10,51<br>9,56<br>10,54<br>9,56<br>10,54<br>9,73<br>10,54<br>9,73<br>10,54                         | $\begin{array}{c} 4.31\\ 4.37\\ 4.38\\ 4.54\\ 4.54\\ 4.54\\ 4.54\\ 4.56\\ 4.58\\ 4.36\\ 4.58\\ 4.63\\ 4.59\\ 4.62\\ 4.63\\ 4.60\\ 4.59\\ 4.61\\ 4.59\\ 4.56\end{array}$                                    | 99.51 7,388<br>100,50 7,370<br>100,98 7,472<br>99,73 7,340<br>101,94 7,103<br>100,14 7,103<br>101,14 7,039<br>101,211 7,053<br>100,13 7,471<br>102,96 7,381<br>101,11 6,959<br>101,11 6,959<br>101,23 6,888<br>102,14 7,130<br>101,31 7,085<br>100,12 7,130  | 0,602 8,0<br>0,630 8,0<br>0,528 8,0<br>0,619 8,0<br>0,619 8,0<br>0,619 8,0<br>0,948 8,0<br>0,948 8,0<br>0,948 8,0<br>0,948 8,0<br>0,948 8,0<br>0,774 8,0<br>1,044 8,0<br>1,041 8,0<br>0,871 8,0<br>0,905 8,0<br>0,995 8,0  | 00 1,275<br>00 1,279<br>00 1,279<br>00 1,532<br>00 2,555<br>00 1,433<br>00 2,623<br>00 2,623<br>00 2,623<br>00 1,265<br>00 1,265<br>00 2,745<br>00 2,845<br>00 2,841<br>00 2,713   | 0,003<br>0,004<br>0,002<br>0,001<br>0,002<br>0,000<br>0,002<br>0,000<br>0,000<br>0,000<br>0,001<br>0,001<br>0,001<br>0,001<br>0,000<br>0,000<br>0,000<br>0,000   | 0,333<br>0,429<br>0,356<br>0,609<br>0,375<br>0,484<br>0,308<br>0,437<br>0,397<br>0,581<br>0,315<br>0,427<br>0,328<br>0,310<br>0,366<br>0,514<br>0,536<br>0,516   | 1,112<br>0,932<br>1,039<br>0,920<br>0,965<br>0,000<br>0,087<br>0,073<br>1,058<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000                            | 0,002<br>0,006<br>0,007<br>0,006<br>0,006<br>0,003<br>0,000<br>0,001<br>0,012<br>0,003<br>0,004<br>0,004<br>0,004<br>0,004<br>0,004<br>0,005<br>0,002<br>0,004<br>0,004<br>0,004<br>0,004  | 1,376<br>1,250<br>1,353<br>1,287<br>0,793<br>1,308<br>0,785<br>1,079<br>0,917<br>1,377<br>0,723<br>1,298<br>1,023<br>1,094<br>0,913<br>0,774<br>0,833<br>0,862<br>0,796<br>0,820<br>0,936  | 4,100<br>4,100<br>4,100<br>4,100<br>4,100<br>4,078<br>4,100<br>4,100<br>4,100<br>4,078<br>4,092<br>4,042<br>4,042<br>4,042<br>4,080<br>4,077<br>4,077  | 0,009<br>0,012<br>0,004<br>0,005<br>0,005<br>0,002<br>0,004<br>0,001<br>0,019<br>0,006<br>0,004<br>0,007   | 0,000<br>0,004<br>0,005<br>0,003<br>0,000<br>0,005<br>0,003<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000          | 1,821<br>1,806<br>1,792<br>1,742<br>1,742<br>1,539<br>1,642<br>1,778<br>1,804<br>1,759<br>1,759<br>1,759<br>1,752<br>1,751<br>1,583<br>1,712<br>1,779<br>1,758<br>1,614<br>1,779                            | 1.830         4.000           1.822         4.000           1.798         4.000           1.798         4.000           1.751         4.000           1.754         4.000           1.754         4.000           1.754         4.000           1.754         4.000           1.546         4.000           1.824         4.000           1.784         4.000           1.774         4.000           1.784         4.000           1.784         4.000           1.784         4.000           1.774         4.000           1.684         4.000           1.784         4.000           1.774         4.000           1.618         4.000           1.618         4.000           1.618         4.000           1.618         4.000           1.618         4.000           1.628         4.000  | -0,039<br>0,015<br>-0,054<br>0,057<br>0,011<br>0,435<br>0,379<br>0,401<br>-0,052<br>0,391<br>0,009<br>0,400<br>0,330<br>0,460<br>0,480<br>0,470<br>0,378<br>0,473<br>0,473<br>0,453<br>0,483 | 0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050<br>0,050 | 0,567<br>0,515<br>0,563<br>0,514<br>0,314<br>0,329<br>0,424<br>0,357<br>0,531<br>0,424<br>0,357<br>0,532<br>0,424<br>0,307<br>0,444<br>0,359<br>0,444<br>0,359<br>0,344<br>0,358<br>0,336<br>0,393 | 0.137<br>0.177<br>0.141<br>0.241<br>0.154<br>0.121<br>0.154<br>0.121<br>0.165<br>0.247<br>0.157<br>0.137<br>0.129<br>0.138<br>0.213<br>0.213<br>0.213<br>0.213<br>0.213  | 0,000 0,285<br>0,002 0,241<br>0,000 0,264<br>0,003 0,233<br>0,002 0,037<br>0,000 0,245<br>0,003 0,002<br>0,002 0,024<br>0,003 0,012<br>0,000 0,266<br>0,005 0,012<br>0,003 0,248<br>0,000 0,024<br>0,003 0,044<br>0,000 0,004<br>0,000 0,004<br>0,003 0,007<br>0,001 0,002<br>0,003 0,007  |  |
| Metapsam<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15<br>04CH15 | mopelit<br>52,46<br>50,79<br>48,72<br>51,60<br>46,70<br>51,22<br>44,86<br>45,28<br>50,42<br>52,27<br>45,61<br>49,65<br>50,39<br>44,25<br>50,39<br>44,25<br>50,75<br>49,81<br>50,67<br>50,05<br>45,53        | e<br>0,02<br>0,03<br>0,71<br>0,03<br>0,28<br>0,04<br>0,25<br>0,45<br>0,03<br>0,04<br>0,03<br>0,04<br>0,03<br>0,02<br>0,79<br>0,02<br>0,79<br>0,02<br>0,79<br>0,02<br>0,79<br>0,02<br>0,03<br>0,04<br>0,03 | 26,54<br>27,55<br>33,28<br>29,47<br>26,36<br>34,87<br>30,24<br>26,34<br>25,59<br>33,25<br>25,80<br>25,33<br>35,06<br>26,19<br>28,90<br>26,76<br>26,67<br>35,37                   | 3,49<br>2,88<br>0,93<br>2,54<br>2,14<br>3,81<br>1,05<br>3,70<br>2,90<br>3,40<br>2,19<br>3,73<br>3,96<br>0,86<br>3,39<br>2,08<br>3,23<br>3,48<br>0,98  | 0,00<br>0,00<br>0,00<br>2,30<br>0,00<br>1,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00<br>0  | 0,00<br>0,05<br>0,00<br>0,04<br>0,05<br>0,03<br>0,00<br>0,02<br>0,00<br>0,00<br>0,00<br>0,00<br>0,00   | 2,35<br>2,20<br>0,74<br>2,22<br>2,32<br>2,44<br>0,58<br>1,08<br>2,34<br>1,95<br>1,00<br>2,40<br>2,41<br>0,61<br>2,53<br>2,25<br>2,38<br>2,25<br>0,52                                     | 0,02<br>0,04<br>0,00<br>0,02<br>0,06<br>0,03<br>0,00<br>0,01<br>0,01<br>0,00<br>0,00<br>0,00<br>0,00   | 0,01<br>0,14<br>0,68<br>0,84<br>0,12<br>0,07<br>0,63<br>0,48<br>0,09<br>1,16<br>0,36<br>0,05<br>1,18<br>0,07<br>0,17<br>0,03<br>0,04<br>1,01   | 9,75<br>9,99<br>9,22<br>9,83<br>9,57<br>10,37<br>10,08<br>10,13<br>8,47<br>9,55<br>10,25<br>8,65<br>10,05<br>10,07<br>10,37<br>9,97<br>8,89  | 4,52<br>4,46<br>4,55<br>4,45<br>4,39<br>4,45<br>4,38<br>4,44<br>4,33<br>4,35<br>4,38<br>4,44<br>4,43<br>4,34<br>4,44<br>4,43<br>4,39<br>4,44   | 99.37 6,959<br>98,23 6,842<br>99,20 6,842<br>97,60 6,374<br>98,32 6,807<br>97,10 6,138<br>96,81 6,312<br>96,81 6,312<br>96,82 6,904<br>97,55 7,055<br>96,50 6,939<br>96,34 6,875<br>96,50 6,939<br>98,31 6,704<br>98,03 6,867<br>97,03 6,844<br>97,03 6,155  | 1,041 8,0<br>1,166 8,0<br>1,575 8,0<br>1,049 8,0<br>1,627 8,0<br>1,048 8,0<br>1,068 8,0<br>1,068 8,0<br>1,076 8,0<br>1,771 8,0<br>1,125 8,0<br>1,061 8,0<br>1,061 8,0<br>1,133 8,0<br>1,136 8,0<br>1,136 8,0   | 00 3,110<br>00 3,204<br>00 3,599<br>00 3,187<br>00 3,114<br>00 3,081<br>00 3,260<br>00 3,280<br>00 3,280<br>00 3,280<br>00 3,096<br>00 3,096<br>00 3,288<br>00 3,2141<br>00 3,791  | 0,002<br>0,003<br>0,071<br>0,028<br>0,004<br>0,025<br>0,047<br>0,003<br>0,004<br>0,029<br>0,003<br>0,002<br>0,002<br>0,002<br>0,002<br>0,002<br>0,003<br>0,004<br>0,001  | 0,387<br>0,324<br>0,102<br>0,286<br>0,245<br>0,429<br>0,120<br>0,432<br>0,384<br>0,250<br>0,432<br>0,456<br>0,099<br>0,385<br>0,234<br>0,366<br>0,398<br>0,111   | 0,000<br>0,000<br>0,236<br>0,000<br>0,105<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000  | 0,000<br>0,006<br>0,005<br>0,005<br>0,004<br>0,000<br>0,011<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,002<br>0,002<br>0,002<br>0,002   | 0,465<br>0,442<br>0,146<br>0,472<br>0,490<br>0,119<br>0,224<br>0,477<br>0,393<br>0,203<br>0,496<br>0,494<br>0,152<br>0,512<br>0,452<br>0,452<br>0,452<br>0,452<br>0,458<br>0,104   | 3,964<br>3,978<br>3,917<br>3,928<br>4,100<br>4,008<br>4,025<br>4,100<br>3,968<br>3,906<br>4,017<br>4,003<br>4,027<br>4,001<br>3,990<br>3,993<br>4,004<br>4,016                                     | 0,003<br>0,005<br>0,000<br>0,003<br>0,004<br>0,000<br>0,003<br>0,001<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000  | 0,003<br>0,036<br>0,174<br>0,219<br>0,033<br>0,017<br>0,168<br>0,025<br>0,003<br>0,015<br>0,003<br>0,015<br>0,003<br>0,015<br>0,003<br>0,015<br>0,003<br>0,014<br>0,043<br>0,048<br>0,048<br>0,040                            | 1,650<br>1,715<br>1,552<br>1,667<br>1,667<br>1,810<br>1,792<br>1,769<br>1,459<br>1,663<br>1,805<br>1,749<br>1,514   | 1,667 4,000<br>1,745 4,000<br>1,745 4,000<br>1,745 4,000<br>1,919 4,000<br>1,934 4,000<br>1,824 4,000<br>1,824 4,000<br>1,824 4,000<br>1,771 4,000<br>1,826 4,000<br>1,787 4,000<br>1,876 4,000<br>1,876 4,000<br>1,876 4,000<br>1,876 4,000<br>1,876 4,000  | 0,519<br>0,652<br>0,672<br>0,433<br>0,648<br>0,521<br>0,815<br>0,669<br>0,538<br>0,323<br>0,770<br>0,538<br>0,571<br>0,712<br>0,551<br>0,557<br>0,560<br>0,750                               | -0.018<br>-0.011<br>-0.041<br>-0.036<br>0.050<br>0.004<br>0.013<br>0.050<br>-0.016<br>-0.047<br>0.033<br>0.008<br>0.001<br>0.010<br>0.000<br>-0.005<br>-0.005<br>0.002<br>0.002<br>0.002                                      | 0,267<br>0,245<br>0,132<br>0,293<br>0,131<br>0,243<br>0,035<br>0,273<br>0,055<br>0,273<br>0,255<br>0,236<br>0,226<br>0,227<br>0,259<br>0,237<br>0,259<br>0,248<br>0,228<br>0,248<br>0,228          | 0,222<br>0,179<br>0,092<br>0,188<br>0,068<br>0,213<br>0,036<br>0,106<br>0,186<br>0,267<br>0,207<br>0,227<br>0,227<br>0,221<br>0,195<br>0,129<br>0,198<br>0,198<br>0,044  | 0,002 0,019<br>0,020 0,016<br>0,100 0,033<br>0,114 0,015<br>0,019 0,170<br>0,010 0,019<br>0,085 0,032<br>0,067 0,108<br>0,014 0,014<br>0,074 0,014<br>0,054 0,043<br>0,056 0,043<br>0,056 0,043<br>0,062 0,007<br>0,169 0,115<br>0,010 0,010<br>0,024 0,031  |  |
| MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8                       | 52,55<br>50,26<br>50,26<br>48,83<br>48,64<br>49,81<br>48,38<br>49,17<br>47,71<br>49,46<br>49,34<br>46,33<br>46,24<br>46,33<br>46,22<br>46,16  | 0,12<br>0,03<br>0,14<br>0,03<br>0,22<br>0,05<br>0,33<br>1,46<br>0,43<br>0,08<br>0,04<br>0,02<br>0,47<br>0,59<br>0,90<br>0,73  | 24,19<br>26,27<br>27,24<br>25,74<br>25,38<br>27,34<br>29,29<br>25,70<br>27,51<br>27,77<br>24,94<br>26,20<br>35,50<br>30,76<br>35,50<br>30,761<br>31,05<br>34,45                  | 4,01<br>3,74<br>3,01<br>3,98<br>3,47<br>3,34<br>2,55<br>3,03<br>3,74<br>2,79<br>3,91<br>3,10<br>0,80<br>3,56<br>1,01<br>3,18<br>1,17  | 0,00<br>0,00<br>0,63<br>2,26<br>0,00<br>0,00<br>0,00<br>0,64<br>0,00<br>2,23<br>0,00<br>0,00<br>1,04<br>0,00<br>0,00<br>0,00                                 | 0,06<br>0,00<br>0,00<br>0,01<br>0,04<br>0,02<br>0,03<br>0,00<br>0,00<br>0,00<br>0,04<br>0,01<br>0,00<br>0,00<br>0,00                         | 2,72<br>2,95<br>2,66<br>2,75<br>3,15<br>2,82<br>2,03<br>2,53<br>2,44<br>2,42<br>3,09<br>2,65<br>0,50<br>1,30<br>0,79<br>1,30<br>0,52   | 0,11<br>0,04<br>0,02<br>0,07<br>0,19<br>0,02<br>0,06<br>1,52<br>0,02<br>0,03<br>0,09<br>0,05<br>0,00<br>0,02<br>0,01<br>0,04<br>0,02   | 0,11<br>0,04<br>0,03<br>0,03<br>0,15<br>0,17<br>0,13<br>0,11<br>0,02<br>0,00<br>0,69<br>0,21<br>0,95<br>0,35<br>0,61   | 9,82<br>9,88<br>10,34<br>10,28<br>9,72<br>10,21<br>10,15<br>9,63<br>10,62<br>10,42<br>9,46<br>10,38<br>9,97<br>10,73<br>9,68<br>10,45<br>10,40   | 4,44<br>4,41<br>4,37<br>4,36<br>4,43<br>4,40<br>4,35<br>4,40<br>4,38<br>4,33<br>4,49<br>4,49<br>4,49<br>4,49<br>4,37<br>4,46   | 98,45 7,096<br>97,89 6,828<br>98,61 6,801<br>97,57 6,687<br>98,25 6,746<br>97,55 6,582<br>97,75 6,582<br>97,72 6,741<br>97,65 6,582<br>97,72 6,741<br>98,79 6,171<br>98,79 6,172<br>99,05 6,322<br>99,05 6,322   | 0,904 8,0<br>1,172 8,0<br>1,199 8,0<br>1,306 8,0<br>1,255 8,0<br>1,412 8,0<br>1,412 8,0<br>1,219 8,0<br>1,219 8,0<br>1,428 8,0<br>1,243 8,0<br>1,638 8,0<br>1,629 8,0<br>1,629 8,0<br>1,679 8,0<br>1,779 8,0   | 00 2,946<br>00 3,035<br>00 3,132<br>00 3,140<br>00 2,799<br>00 3,110<br>00 3,289<br>00 2,957<br>00 3,055<br>00 3,202<br>00 2,783<br>00 3,114<br>00 3,754<br>00 3,265<br>00 3,682<br>00 3,674   | 0,013<br>0,003<br>0,014<br>0,003<br>0,022<br>0,005<br>0,034<br>0,05<br>0,008<br>0,004<br>0,002<br>0,048<br>0,004<br>0,002<br>0,048<br>0,049<br>0,060<br>0,093  | 0,453<br>0,425<br>0,339<br>0,457<br>0,399<br>0,290<br>0,349<br>0,431<br>0,318<br>0,447<br>0,359<br>0,089<br>0,406<br>0,113<br>0,366<br>0,132   | 0,000<br>0,000<br>0,065<br>0,234<br>0,000<br>0,000<br>0,066<br>0,000<br>0,230<br>0,000<br>0,000<br>0,000<br>0,107<br>0,000<br>0,000  | 0,007<br>0,000<br>0,000<br>0,001<br>0,005<br>0,003<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000<br>0,000   | 0,548<br>0,597<br>0,534<br>0,561<br>0,645<br>0,570<br>0,412<br>0,500<br>0,493<br>0,631<br>0,546<br>0,100<br>0,264<br>0,100<br>0,264<br>0,267<br>0,103  | 3,966<br>4,066<br>4,020<br>4,100<br>4,068<br>4,028<br>3,980<br>4,100<br>4,021<br>4,021<br>4,022<br>3,990<br>4,100<br>4,012<br>4,073<br>3,984   | 0,016<br>0,003<br>0,010<br>0,028<br>0,003<br>0,024<br>0,003<br>0,004<br>0,014<br>0,007<br>0,000<br>0,003<br>0,002<br>0,006   | 0,029<br>0,010<br>0,040<br>0,008<br>0,008<br>0,008<br>0,035<br>0,028<br>0,005<br>0,000<br>0,180<br>0,025<br>0,246<br>0,092<br>0,158   | 1,691<br>1,713<br>1,781<br>1,798<br>1,705<br>1,764<br>1,764<br>1,764<br>1,869<br>1,811<br>1,652<br>1,834<br>1,697<br>1,867<br>1,867<br>1,867<br>1,832<br>1,785  | 1,753 4,000<br>1,740 4,000<br>1,833 4,000<br>1,748 4,000<br>1,748 4,000<br>1,748 4,000<br>1,748 4,000<br>1,835 4,000<br>1,835 4,000<br>1,856 4,000<br>1,858 4,000<br>1,833 4,000<br>1,933 4,000<br>1,940 4,000   | 0,409<br>0,526<br>0,546<br>0,551<br>0,492<br>0,574<br>0,619<br>0,595<br>0,582<br>0,483<br>0,585<br>0,784<br>0,699<br>0,734<br>0,699<br>0,734   | -0,017<br>0,033<br>0,010<br>0,050<br>0,050<br>0,014<br>-0,010<br>0,050<br>0,010<br>0,050<br>0,010<br>0,050<br>0,010<br>0,050<br>0,050<br>0,050<br>0,050<br>0,036<br>0,036   | 0,310<br>0,248<br>0,250<br>0,225<br>0,228<br>0,228<br>0,228<br>0,228<br>0,228<br>0,228<br>0,231<br>0,229<br>0,260<br>0,047<br>0,065<br>0,055<br>0,055  | 0,256<br>0,176<br>0,159<br>0,161<br>0,139<br>0,151<br>0,129<br>0,206<br>0,136<br>0,149<br>0,162<br>0,149<br>0,162<br>0,149<br>0,042<br>0,042<br>0,000<br>0,039<br>0,098  | 0.017 0.049<br>0.006 0.023<br>0.022 0.029<br>0.004 0.180<br>0.005 0.017<br>0.005 0.017<br>0.021 0.069<br>0.023 0.333<br>0.018 0.085<br>0.015 0.026<br>0.003 0.146<br>0.000 0.026<br>0.028 0.114<br>0.129 0.073<br>0.048 0.109<br>0.081 0.081   | metamorphic<br>metamorphic<br>metamorphic<br>metamorphic<br>metamorphic<br>metamorphic<br>detrital<br>metamorphic<br>metamorphic<br>detrital<br>detrital<br>detrital<br>detrital |

The proportion of cations is based on 42 negative charges neglecting the interlayer cations; the sum of octahedrally coordinated cations is set at 4.1 to allow for an estimation of Fe3+

## v) Cloritas

| Sample<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C<br>04CH18C  | SiO2<br>25,84<br>28,28<br>29,20<br>29,05<br>28,74<br>27,86<br>28,39<br>28,24<br>27,07<br>26,41<br>27,65<br>28,40<br>28,79<br>28,40<br>28,79<br>28,84<br>28,28<br>29,20<br>28,84<br>28,28<br>29,20<br>28,74<br>30,80<br>31,26   | AI2O3<br>18,04<br>16,49<br>16,36<br>16,11<br>16,27<br>17,12<br>16,21<br>16,17<br>16,54<br>18,04<br>17,95<br>16,83<br>17,89<br>15,99<br>16,34<br>18,04<br>16,49<br>16,49<br>16,49<br>16,49<br>16,27<br>15,51<br>15,51<br>14,31   | TiO2         Fe           0,05         2           0,01         2           0,03         2           0,00         2           0,05         2           0,001         2   | eO N<br>28,566<br>25,665<br>25,45<br>25,45<br>25,45<br>25,45<br>26,01<br>24,78<br>24,78<br>25,06<br>26,63<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,65<br>26,61<br>26,64<br>26,64<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>26,66<br>25,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,65<br>26,66<br>25,65<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>25,66<br>22,67<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>22,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,07<br>20,00 | Igo         13,79           13,79         15,11           15,11         15,15           15,52         15,53           16,25         16,31           16,14         14,64           16,41         14,64           16,63         13,79           15,11         15,15           15,52         15,53           16,21         15,25           15,52         15,25           15,25         19,26           19,36         20,37  | MnO<br>0,33<br>0,30<br>0,28<br>0,25<br>0,26<br>0,24<br>0,23<br>0,26<br>0,25<br>0,27<br>0,28<br>0,26<br>0,25<br>0,27<br>0,28<br>0,23<br>0,20<br>0,30<br>0,20<br>0,30<br>0,20 | CaO 0,06<br>0,08<br>0,11<br>0,10<br>0,09<br>0,18<br>0,06<br>0,08<br>0,06<br>0,05<br>0,03<br>0,05<br>0,03<br>0,05<br>0,03<br>0,06<br>0,06<br>0,06<br>0,06<br>0,06<br>0,06<br>0,08<br>0,08     | Va2O<br>0,04<br>0,02<br>0,09<br>0,15<br>0,06<br>0,09<br>0,12<br>0,07<br>0,05<br>0,26<br>0,12<br>0,07<br>0,05<br>0,26<br>0,12<br>0,09<br>0,43<br>0,14<br>0,09<br>0,13<br>0,04<br>0,04<br>0,02<br>0,09<br>0,15<br>0,09<br>0,12<br>0,09<br>0,12<br>0,09<br>0,12<br>0,09<br>0,12<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,15<br>0,09<br>0,09<br>0,15<br>0,09<br>0,09<br>0,15<br>0,09<br>0,09<br>0,15<br>0,09<br>0,09<br>0,09<br>0,09<br>0,09<br>0,09<br>0,09<br>0,0 | <b>K2O</b> 0,00 0,04 0,04 0,04 0,04 0,04 0,04 0,0  | H2O'<br>11,04<br>11,14<br>11,27<br>11,29<br>11,19<br>11,27<br>11,27<br>11,27<br>11,27<br>11,27<br>11,21<br>11,24<br>11,28<br>11,22<br>11,35<br>11,22<br>11,35<br>11,32<br>11,35<br>11,29<br>11,29<br>11,27<br>11,29<br>11,19<br>11,67<br>11,75  | SUMK<br>97,71<br>97,12<br>97,94<br>98,36<br>97,32<br>98,41<br>97,06<br>97,04<br>97,06<br>97,04<br>97,05<br>97,54<br>97,54<br>99,15<br>97,54<br>99,15<br>97,71<br>97,12<br>97,34<br>97,34<br>97,34  | Si<br>5,633<br>6,088<br>6,214<br>6,161<br>5,933<br>6,053<br>6,072<br>6,028<br>5,911<br>6,072<br>6,028<br>5,911<br>6,071<br>6,150<br>6,140<br>5,633<br>6,074<br>6,171<br>6,161<br>6,265<br>6,337  | Alt<br>2,367<br>1,912<br>2,067<br>1,947<br>1,928<br>1,973<br>2,189<br>2,284<br>1,973<br>2,189<br>2,284<br>2,089<br>1,999<br>1,850<br>2,367<br>1,912<br>1,786<br>1,830<br>1,839<br>1,735<br>1,665<br>1,621   | Alo<br>2,269<br>2,273<br>2,315<br>2,271<br>2,229<br>2,155<br>2,148<br>2,386<br>2,294<br>2,155<br>2,386<br>2,294<br>2,156<br>2,386<br>2,294<br>2,156<br>2,456<br>2,174<br>2,219<br>2,269<br>2,273<br>2,271<br>2,229<br>2,273<br>2,271<br>2,203<br>2,271<br>2,203<br>2,271<br>2,204<br>1,995<br>2,273<br>2,271<br>2,299<br>2,275<br>2,273<br>2,271<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,279<br>2,315<br>2,279<br>2,315<br>2,279<br>2,315<br>2,279<br>2,315<br>2,279<br>2,315<br>2,315<br>2,279<br>2,315<br>2,315<br>2,279<br>2,315<br>2,315<br>2,279<br>2,315<br>2,315<br>2,279<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,315<br>2,329<br>2,315<br>2,329<br>2,315<br>2,329<br>2,329<br>2,329<br>2,329<br>2,329<br>2,329<br>2,329<br>2,329<br>2,329<br>2,329<br>2,279<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,297<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2,299<br>2, 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 | Fe<br>5,206<br>4,620<br>4,528<br>4,562<br>4,632<br>4,450<br>4,459<br>4,474<br>4,459<br>4,474<br>4,474<br>4,478<br>4,4877<br>4,415<br>4,693<br>4,583<br>4,693<br>4,693<br>4,620<br>4,620<br>4,620<br>4,528<br>4,562<br>3,813<br>3,791   | Mg<br>4,480<br>4,850<br>4,791<br>4,914<br>4,874<br>4,931<br>5,201<br>5,202<br>5,137<br>4,604<br>4,723<br>5,305<br>4,463<br>4,463<br>4,463<br>4,463<br>4,4850<br>4,4850<br>4,850<br>4,850<br>4,874<br>5,903<br>5,932<br>5,933<br>5,932<br>5,932<br>5,932<br>5,937  | sum 12,024<br>12,024<br>11,797<br>11,689<br>11,757<br>11,753<br>11,845<br>11,850<br>11,850<br>11,855<br>11,821<br>11,920<br>11,666<br>11,920<br>11,678<br>11,778<br>11,779<br>11,753<br>11,775<br>11,775  | Na         K           0,018         0,000           0,017         0,012           0,038         0,016           0,061         0,007           0,023         0,011           0,038         0,011           0,038         0,011           0,032         0,012           0,030         0,013           0,022         0,010           0,023         0,011           0,071         0,002           0,074         0,004           0,075         0,001           0,076         0,012           0,036         0,011           0,036         0,011           0,036         0,014           0,037         0,012           0,038         0,012           0,038         0,012           0,038         0,012           0,038         0,012           0,041         0,020   | Ca<br>0,013<br>0,018<br>0,025<br>0,025<br>0,020<br>0,042<br>0,015<br>0,018<br>0,013<br>0,016<br>0,013<br>0,016<br>0,027<br>0,014<br>0,027<br>0,014<br>0,021<br>0,018<br>0,025<br>0,023<br>0,020<br>0,018<br>0,025  | OH<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16   | XMg<br>0,46<br>0,51<br>0,51<br>0,52<br>0,52<br>0,52<br>0,52<br>0,54<br>0,54<br>0,54<br>0,53<br>0,49<br>0,49<br>0,49<br>0,49<br>0,49<br>0,55<br>0,52<br>0,52<br>0,52<br>0,52<br>0,52<br>0,52<br>0,52  |
|--|--|---|--|--|--|---|--|---|--|---|--|--|---|---|--|---|--|---|---|--|--|--|--|
| 04CH17C<br>04CH17C<br>04CH17C<br>04CH17C<br>04CH17C<br>04CH17C<br>04CH17C<br>04CH17C<br>04CH17C<br>04CH17C   | 31,11<br>31,78<br>31,32<br>31,37<br>31,52<br>29,18<br>31,28<br>31,57<br>30,06<br>27,32<br>29,45  | 14,24<br>14,58<br>15,28<br>14,40<br>13,62<br>17,01<br>13,11<br>12,83<br>15,57<br>14,32<br>19,88   | 0,00 2<br>0,00 2<br>0,02 2<br>0,02 2<br>0,02 2<br>0,02 2<br>0,02 2<br>0,02 2<br>0,06 2<br>0,06 2<br>1,61 3<br>0,09 2   | 22,05<br>21,97<br>21,94<br>21,57<br>21,21<br>22,63<br>21,70<br>21,80<br>22,09<br>30,96<br>24,08  | 20,03<br>20,01<br>18,99<br>19,77<br>20,17<br>17,84<br>20,53<br>20,72<br>18,53<br>11,83<br>13,41  | 0,23<br>0,20<br>0,17<br>0,22<br>0,29<br>0,16<br>0,14<br>0,23<br>0,21<br>0,11<br>0,34  | 0,22<br>0,17<br>0,20<br>0,17<br>0,20<br>0,38<br>0,10<br>0,07<br>0,40<br>0,15<br>0,03   | 0,08<br>0,11<br>0,43<br>0,15<br>0,07<br>0,26<br>0,05<br>0,04<br>0,13<br>0,04<br>0,28  | 0,03<br>0,11<br>0,06<br>0,01<br>0,05<br>0,03<br>0,00<br>0,02<br>0,02<br>0,02   | 11,67<br>11,83<br>11,75<br>11,67<br>11,60<br>11,55<br>11,55<br>11,55<br>11,59<br>11,53<br>10,81<br>11,61  | 99,67<br>100,76<br>100,17<br>99,40<br>98,70<br>99,09<br>98,48<br>98,91<br>98,58<br>97,24<br>100,06   | 6,395<br>6,444<br>6,393<br>6,446<br>6,515<br>6,061<br>6,498<br>6,532<br>6,255<br>6,059<br>6,087  | 1,605<br>1,556<br>1,607<br>1,554<br>1,485<br>1,939<br>1,502<br>1,468<br>1,745<br>1,941<br>1,913   | 1,844<br>1,930<br>2,071<br>1,933<br>1,832<br>2,225<br>1,707<br>1,660<br>2,072<br>1,802<br>2,930   | 0,000<br>0,003<br>0,001<br>0,002<br>0,003<br>0,002<br>0,009<br>0,010<br>0,268<br>0,014   | 0,040<br>0,034<br>0,030<br>0,050<br>0,050<br>0,025<br>0,040<br>0,036<br>0,020<br>0,059  | 3,791<br>3,726<br>3,745<br>3,707<br>3,666<br>3,931<br>3,769<br>3,773<br>3,844<br>5,744<br>4,163  | 6,137<br>6,050<br>5,779<br>6,055<br>6,214<br>5,523<br>6,358<br>6,390<br>5,747<br>3,913<br>4,132   | 11,811<br>11,740<br>11,627<br>11,735<br>11,764<br>11,710<br>11,861<br>11,871<br>11,709<br>11,748<br>11,298  | 0,032 0,009<br>0,045 0,027<br>0,172 0,015<br>0,060 0,015<br>0,028 0,003<br>0,015 0,013<br>0,019 0,008<br>0,017 0,000<br>0,052 0,005<br>0,017 0,006<br>0,110 0,231  | 0,049<br>0,037<br>0,043<br>0,039<br>0,045<br>0,085<br>0,022<br>0,015<br>0,089<br>0,036<br>0,036  | 16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000   | 0,62<br>0,62<br>0,61<br>0,62<br>0,63<br>0,58<br>0,63<br>0,63<br>0,63<br>0,60<br>0,41<br>0,50   |
| 04CH15<br>04CH15<br>MD5<br>MD5<br>MD5<br>MD5<br>MD5<br>MD5<br>MD5<br>MD5<br>MD5<br>MD  | 27,177<br>25,92<br>26,68<br>28,670<br>27,26<br>28,90<br>27,26<br>28,90<br>27,26<br>28,90<br>27,26<br>28,90<br>27,26<br>28,90<br>27,26<br>28,90<br>27,26<br>28,90<br>29,00<br>28,90<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,00<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,000<br>29,0000<br>29,0000<br>29,0000<br>29,0000000000 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19,12<br>19,20<br>17,07<br>18,56<br>17,07<br>18,55<br>16,67<br>17,07<br>16,95<br>17,09<br>17,07<br>18,50<br>16,67<br>17,07<br>17,07<br>18,50<br>16,57<br>17,07<br>17,70<br>18,50<br>16,57<br>17,07<br>19,10<br>16,57<br>16,95<br>16,74<br>16,58<br>16,74<br>17,57<br>17,71<br>17,57<br>17,71<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,74<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57<br>17,57 | 0.03         2           0.11         2           0.12         2           0.02         2           0.02         2           0.02         2           0.02         2           0.02         2           0.02         2           0.03         2           0.04         2           0.05         2           0.06         2           0.07         2  | 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|
| MD05_11D<br>MD05_11D<br>MD05_11D<br>MD05_11D<br>MD05_11D<br>MD05_11D   | 31,41<br>31,17<br>31,12<br>30,72<br>32,59<br>29,52   | 17,02<br>17,36<br>17,16<br>17,41<br>15,52<br>19,31  | 0,00 1<br>0,01 1<br>0,00 1<br>0,00 1<br>0,00 1<br>0,00 1   | 11,32<br>11,37<br>10,87<br>11,19<br>10,61<br>11,93   | 26,95<br>26,94<br>27,11<br>27,22<br>27,90<br>26,90   | 0,15<br>0,21<br>0,10<br>0,13<br>0,17<br>0,25  | 0,10<br>0,10<br>0,10<br>0,13<br>0,15   | 0,07<br>0,03<br>0,01<br>0,03<br>0,07<br>0,00  | 0,11<br>0,08<br>0,09<br>0,07<br>0,12<br>0,06   | 12,24<br>12,26<br>12,19<br>12,21<br>12,30<br>12,30  | 99,36<br>99,52<br>98,74<br>99,11<br>99,44<br>100,35  | 6,154<br>6,099<br>6,122<br>6,037<br>6,358<br>5,757   | 1,846<br>1,901<br>1,878<br>1,963<br>1,643<br>2,244  | 2,084<br>2,104<br>2,100<br>2,069<br>1,926<br>2,194  | 0,000<br>0,001<br>0,000<br>0,000<br>0,000<br>0,000   | 0,024<br>0,035<br>0,016<br>0,021<br>0,029<br>0,041  | 1,855<br>1,861<br>1,789<br>1,839<br>1,730  | 7,872<br>7,860<br>7,950<br>7,975<br>8,113<br>7,821  | 11,835<br>11,861<br>11,855<br>11,905<br>11,798<br>12,001  | 0,025 0,027<br>0,010 0,020<br>0,003 0,022<br>0,011 0,018<br>0,027 0,031<br>0,000 0,016   | 0,020<br>0,022<br>0,021<br>0,028<br>0,031<br>0,016   | 16,000<br>16,000<br>16,000<br>16,000<br>16,000   | 0,81<br>0,81<br>0,81<br>0,82<br>0,81<br>0,80   |
| MD05_18<br>MD05_18<br>MD05_18<br>MD05_18<br>MD05_18<br>MD05_18   | 32,37<br>29,22<br>27,90<br>29,53<br>31,28<br>30,14   | 16,40<br>18,47<br>19,75<br>18,65<br>17,24<br>17,38  | 0,01 1<br>0,05 1<br>0,02 1<br>0,01 1<br>0,03 1<br>0,20 1   | 11,60<br>12,06<br>17,16<br>15,94<br>11,05<br>10,87   | 26,30<br>26,46<br>22,10<br>21,82<br>26,95<br>27,31   | 0,18<br>0,24<br>0,20<br>0,25<br>0,22<br>0,21  | 0,42<br>0,09<br>0,04<br>0,45<br>0,15<br>0,17   | 0,03<br>0,02<br>0,06<br>0,00<br>0,02<br>0,01  | 0,40<br>0,04<br>0,02<br>0,33<br>0,18<br>0,06   | 12,30<br>12,08<br>11,85<br>11,89<br>12,25<br>12,13  | 100,02<br>98,72<br>99,09<br>98,87<br>99,38<br>98,50  | 6,315<br>5,801<br>5,648<br>5,957<br>6,126<br>5,963   | 1,685<br>2,199<br>2,352<br>2,043<br>1,874<br>2,037  | 2,085<br>2,122<br>2,360<br>2,390<br>2,105<br>2,016  | 0,001<br>0,007<br>0,003<br>0,002<br>0,005<br>0,029   | 0,030<br>0,040<br>0,034<br>0,043<br>0,037<br>0,036  | 1,892<br>2,002<br>2,906<br>2,689<br>1,809<br>1,799   | 7,647<br>7,833<br>6,669<br>6,562<br>7,868<br>8,055  | 11,654<br>12,004<br>11,971<br>11,685<br>11,823<br>11,934  | 0,012 0,099<br>0,006 0,010<br>0,022 0,006<br>0,000 0,085<br>0,008 0,045<br>0,003 0,016   | 0,089<br>0,019<br>0,008<br>0,098<br>0,031<br>0,037   | 16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000   | 0,80<br>0,80<br>0,70<br>0,71<br>0,81<br>0,82   |
| MD06_5B<br>MD06_5B<br>MD06_5B<br>MD06_6<br>MD06_6<br>MD06_6<br>MD06_6<br>MD06_6<br>MD06_6<br>MD06_6<br>MD06_6  | 33,70<br>32,99<br>29,84<br>31,16<br>31,56<br>31,56<br>31,33<br>32,10<br>31,32<br>29,71<br>31,59  | 14.02<br>13.77<br>17.32<br>16.54<br>15.92<br>16.41<br>15.84<br>15.79<br>16.22<br>16.49<br>15.97   | 0,01 1<br>0,00 1<br>0,00 1<br>0,00 1<br>0,01 1<br>0,01 1<br>0,01 1<br>0,05 1<br>0,05 1<br>0,00 1   | 13,50<br>13,66<br>15,00<br>14,13<br>13,92<br>14,84<br>14,32<br>13,83<br>13,85<br>14,37<br>14,37  | 26,18<br>26,22<br>24,50<br>25,54<br>25,31<br>25,27<br>25,59<br>25,47<br>25,00<br>24,77<br>25,32  | 0,22<br>0,17<br>0,26<br>0,17<br>0,18<br>0,15<br>0,19<br>0,15<br>0,15<br>0,19  | 0,22<br>0,30<br>0,20<br>0,09<br>0,15<br>0,11<br>0,12<br>0,12<br>0,16<br>0,30<br>0,03   | 0,05<br>0,01<br>0,00<br>0,05<br>0,01<br>0,03<br>0,01<br>0,03<br>0,01<br>0,03  | 0,26<br>0,10<br>0,13<br>0,00<br>0,14<br>0,09<br>0,11<br>0,20<br>0,14<br>0,08<br>0,28   | 12,26<br>12,11<br>11,98<br>12,14<br>12,09<br>12,21<br>12,09<br>12,17<br>12,05<br>11,85<br>12,13   | 100.43<br>99,33<br>99,22<br>99,83<br>100,70<br>99,58<br>99,88<br>99,88<br>97,95<br>99,91   | 6,592<br>6,533<br>5,974<br>6,155<br>6,263<br>6,199<br>6,215<br>6,327<br>6,235<br>6,235<br>6,248  | 1,408<br>1,467<br>2,026<br>1,845<br>1,737<br>1,802<br>1,785<br>1,673<br>1,765<br>1,988<br>1,752   | 1,824<br>1,748<br>2,060<br>2,006<br>1,988<br>1,997<br>1,919<br>1,994<br>2,039<br>1,945<br>1,971   | 0,002<br>0,000<br>0,000<br>0,000<br>0,002<br>0,002<br>0,002<br>0,002<br>0,007<br>0,034<br>0,000  | 0,036<br>0,028<br>0,044<br>0,029<br>0,028<br>0,030<br>0,025<br>0,031<br>0,026<br>0,026<br>0,031   | 2,208<br>2,263<br>2,510<br>2,334<br>2,311<br>2,437<br>2,375<br>2,279<br>2,307<br>2,432<br>2,377  | 7,633<br>7,743<br>7,310<br>7,522<br>7,488<br>7,399<br>7,567<br>7,481<br>7,419<br>7,473<br>7,464   | 11,703<br>11,781<br>11,925<br>11,891<br>11,815<br>11,865<br>11,865<br>11,887<br>11,787<br>11,798<br>11,910<br>11,843  | 0.021 0.064<br>0.002 0.026<br>0.000 0.032<br>0.019 0.000<br>0.018 0.036<br>0.003 0.022<br>0.010 0.027<br>0.002 0.051<br>0.010 0.036<br>0.004 0.019   | 0,046<br>0,064<br>0,042<br>0,019<br>0,033<br>0,024<br>0,026<br>0,024<br>0,034<br>0,034<br>0,036<br>0,007   | 16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000   | 0.78<br>0.77<br>0.74<br>0.76<br>0.76<br>0.75<br>0.76<br>0.77<br>0.76<br>0.77<br>0.76<br>0.75<br>0.76   |
| MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8<br>MD06_8   | 26,48<br>26,67<br>25,31<br>24,04<br>25,16<br>27,58<br>23,68<br>25,05<br>25,26<br>26,95<br>26,89  | 17,23<br>16,33<br>17,46<br>19,03<br>19,60<br>14,54<br>19,41<br>18,38<br>19,10<br>16,46<br>15,19   | 0,01 3<br>2,01 3<br>2,58 3<br>0,06 3<br>0,06 3<br>0,84 3<br>0,04 3<br>0,04 3<br>0,04 3<br>0,10 3<br>1,58 3<br>1,70 3   | 33,04<br>32,27<br>32,30<br>33,38<br>32,36<br>30,98<br>31,28<br>32,14<br>31,92<br>32,09<br>33,45  | 8,61<br>8,57<br>7,68<br>8,21<br>8,22<br>10,04<br>9,19<br>7,79<br>10,54<br>9,88<br>10,25  | 0,36<br>0,32<br>0,37<br>0,42<br>0,42<br>0,32<br>0,41<br>0,32<br>0,41<br>0,32<br>0,42<br>0,34<br>0,25  | 0,14<br>0,14<br>0,34<br>0,10<br>0,05<br>0,10<br>0,05<br>0,18<br>0,03<br>0,18<br>0,11   | 0,06<br>0,00<br>0,06<br>0,01<br>0,00<br>0,00<br>0,00<br>0,02<br>0,00<br>0,00  | 0,35<br>0,19<br>0,18<br>0,20<br>0,63<br>0,13<br>0,31<br>0,05<br>0,21<br>0,03   | 10,68<br>10,76<br>10,68<br>10,50<br>10,70<br>10,61<br>10,46<br>10,43<br>10,90<br>10,93<br>10,86   | 96,95<br>97,33<br>96,95<br>95,98<br>96,74<br>95,68<br>94,65<br>94,65<br>94,64<br>98,37<br>98,64<br>98,77   | 5,949<br>5,947<br>5,685<br>5,491<br>5,642<br>6,237<br>5,431<br>5,758<br>5,556<br>5,916<br>5,937  | 2,052<br>2,053<br>2,315<br>2,509<br>2,358<br>1,763<br>2,569<br>2,242<br>2,445<br>2,084<br>2,063   | 2,512<br>2,239<br>2,309<br>2,613<br>2,822<br>2,113<br>2,677<br>2,738<br>2,508<br>2,175<br>1,889   | 0,001<br>0,338<br>0,435<br>0,011<br>0,002<br>0,144<br>0,007<br>0,007<br>0,016<br>0,260<br>0,283  | 0,069<br>0,061<br>0,071<br>0,081<br>0,062<br>0,079<br>0,063<br>0,078<br>0,064<br>0,047  | 6,208<br>6,018<br>6,069<br>6,376<br>6,070<br>5,859<br>6,000<br>6,179<br>5,872<br>5,891<br>6,176  | 2,884<br>2,848<br>2,572<br>2,794<br>2,747<br>3,385<br>3,143<br>2,668<br>3,457<br>3,231<br>3,375   | 11,674<br>11,504<br>11,456<br>11,875<br>11,722<br>11,563<br>11,907<br>11,655<br>11,931<br>11,621<br>11,771  | 0,024 0,101<br>0,000 0,053<br>0,026 0,053<br>0,006 0,056<br>0,001 0,181<br>0,000 0,040<br>0,000 0,091<br>0,010 0,015<br>0,000 0,058<br>0,000 0,009   | 0,033<br>0,081<br>0,023<br>0,013<br>0,014<br>0,012<br>0,045<br>0,045<br>0,045<br>0,042<br>0,026  | 16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000   | 0,32<br>0,32<br>0,30<br>0,31<br>0,37<br>0,34<br>0,30<br>0,37<br>0,35<br>0,35   |
| MD26<br>MD26<br>MD26<br>MD26<br>MD26<br>MD26<br>MD26<br>MD26   | 27,97<br>28,26<br>28,41<br>28,64<br>32,94<br>28,11<br>28,03<br>28,57<br>27,41  | 18,82<br>18,32<br>18,08<br>18,03<br>15,20<br>19,37<br>19,21<br>18,76<br>19,00   | 0,02 1<br>0,00 1<br>0,00 1<br>0,01 1<br>0,02 1<br>0,01 1<br>0,01 1<br>0,05 1<br>0,03 1   | 15,63<br>14,95<br>16,70<br>16,74<br>13,40<br>15,32<br>18,62<br>16,11<br>17,14  | 22,73<br>23,72<br>22,74<br>24,89<br>22,82<br>20,44<br>22,56<br>21,02   | 0,21<br>0,18<br>0,28<br>0,12<br>0,22<br>0,16<br>0,22<br>0,19<br>0,26  | 0,00<br>0,02<br>0,11<br>0,11<br>0,04<br>0,04<br>0,10<br>0,08   | 0,04<br>0,10<br>0,02<br>0,02<br>0,19<br>0,01<br>0,00<br>0,07<br>0,07  | 0,01<br>0,00<br>0,03<br>0,09<br>0,02<br>0,01<br>0,01<br>0,02   | 11,69<br>11,74<br>11,73<br>11,76<br>12,13<br>11,77<br>11,67<br>11,76<br>11,46   | 97,11<br>97,27<br>97,98<br>98,21<br>99,18<br>97,72<br>98,28<br>98,27<br>96,64  | 5,741<br>5,775<br>5,809<br>5,839<br>6,512<br>5,723<br>5,723<br>5,759<br>5,805<br>5,707   | 2,259<br>2,225<br>2,191<br>2,161<br>1,489<br>2,277<br>2,241<br>2,195<br>2,293   | 2,294<br>2,187<br>2,166<br>2,173<br>2,052<br>2,371<br>2,409<br>2,298<br>2,368   | 0,003<br>0,000<br>0,002<br>0,002<br>0,002<br>0,002<br>0,002<br>0,002<br>0,008<br>0,005   | 0,037<br>0,031<br>0,049<br>0,021<br>0,036<br>0,027<br>0,038<br>0,033<br>0,046   | 2,682<br>2,556<br>2,857<br>2,855<br>2,216<br>2,609<br>3,199<br>2,738<br>2,984  | 6,954<br>7,225<br>6,932<br>6,910<br>7,336<br>6,926<br>6,258<br>6,833<br>6,523   | 11,970<br>11,998<br>12,004<br>11,961<br>11,644<br>11,934<br>11,906<br>11,909<br>11,926  | 0.016 0.003<br>0.039 0.003<br>0.008 0.001<br>0.009 0.007<br>0.072 0.022<br>0.005 0.005<br>0.000 0.004<br>0.027 0.003<br>0.029 0.005  | 0,000<br>0,005<br>0,024<br>0,024<br>0,008<br>0,009<br>0,021<br>0,017   | 16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000   | 0,72<br>0,74<br>0,71<br>0,71<br>0,77<br>1,00<br>0,99<br>1,00<br>0,99   |
| 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| 11,56 (3,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0   | 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25,770<br>25,380<br>25,760<br>25,384<br>25,745<br>25,665<br>25,012<br>25,565<br>25,021<br>25,575<br>26,245<br>26,25,25<br>26,25,26<br>26,25,26<br>26,26,27<br>26,26,27<br>26,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,20<br>22,2 | 0.21<br>0.17<br>0.19<br>0.20<br>0.22<br>0.22<br>0.22<br>0.22<br>0.22<br>0.22<br>0.2   | 0.21<br>0.39<br>0.32<br>0.32<br>0.14<br>0.24<br>0.14<br>0.24<br>0.25<br>0.24<br>0.15<br>0.24<br>0.10<br>0.23<br>0.15<br>0.24<br>0.13<br>0.13<br>0.13<br>0.13<br>0.13<br>0.13<br>0.13<br>0.13 | 0.00<br>0.01<br>0.02<br>0.01<br>0.01<br>0.01<br>0.01<br>0.01  | 0.02<br>0.04<br>0.04<br>0.04<br>0.04<br>0.00<br>0.02<br>0.02   | 11.87<br>12.26<br>11.76<br>12.21<br>11.76<br>12.74<br>12.74<br>12.74<br>12.74<br>12.74<br>12.76<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>12.97<br>11.90<br>12.97<br>12.97<br>11.90<br>12.97<br>12.97<br>11.90<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80<br>11.80 | 96,61<br>99,67<br>96,20<br>98,72<br>98,78<br>98,78<br>98,78<br>99,07<br>98,49<br>99,07<br>98,49<br>99,07<br>98,49<br>98,52<br>100,56<br>98,88<br>99,52<br>99,53<br>99,53<br>99,53<br>99,54<br>99,53<br>99,54<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57<br>99,57 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| $\begin{array}{c} 11,773\\ 11,827\\ 11,827\\ 11,826\\ 11,786\\ 11,786\\ 11,786\\ 11,786\\ 11,740\\ 11,866\\ 11,740\\ 11,862\\ 11,762\\ 11,700\\ 11,700\\ 11,700\\ 11,700\\ 11,700\\ 11,700\\ 11,700\\ 11,823\\ 11,823\\ 11,863\\ 11,823\\$ |  | 0.466 0.082 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.087 0.083 0.022 0.084 0.081 0.083 0.027 0.024 0.083 0.027 0.024 0.083 0.027 0.024 0.083 0.027 0.025 0.083 0.027 0.025 0.083 0.027 0.025  | 16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000<br>16,000   | 0.800<br>0.79 0.78 0.78 0.78 0.78 0.78 0.78 0.78 0.78  |

## vi) Epidotas

| Epidote  |       |      |       |       |       |      |       |       |       |       |       |       |       |       |       |       |       |       |
|----------|-------|------|-------|-------|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Sample   | SiO2  | TiO2 | AI2O3 | Fe2O3 | Mn2O3 | MgO  | CaO   | H2O'  | sum   | Si    | AI    | Fe3+  | Mn3+  | Mg    | Ti    | sum   | Ca    | он    |
| 04CH18c  | 36,77 | 0,00 | 22,92 | 14,13 | 0,75  | 0,03 | 22,51 | 1,84  | 98,95 | 3,000 | 2,204 | 0,868 | 0,047 | 0,004 | 0,000 | 3,122 | 1,968 | 1,000 |
| 04CH18c  | 36,74 | 0,00 | 21,67 | 15,35 | 0,24  | 0,18 | 22,84 | 1,84  | 98,87 | 3,000 | 2,085 | 0,943 | 0,015 | 0,022 | 0,000 | 3,065 | 1,998 | 1,000 |
| 04CH18C  | 36,79 | 0,15 | 21,87 | 14,92 | 0,29  | 0,05 | 23,08 | 1,84  | 99,04 | 3,000 | 2,102 | 0,915 | 0,018 | 0,006 | 0,009 | 3,052 | 2,017 | 1,000 |
| 04CH18C  | 30,00 | 0,09 | 23,49 | 13,28 | 0,39  | 0,02 | 22,95 | 1,84  | 98,75 | 3,000 | 2,200 | 0,817 | 0,024 | 0,002 | 0,005 | 3,113 | 2,011 | 1,000 |
| 0400180  | 30,07 | 0,09 | 21,98 | 15,23 | 0,22  | 0,10 | 23,00 | 1,84  | 99,22 | 3,000 | 2,120 | 0,937 | 0,014 | 0,020 | 0,006 | 3,090 | 2,010 | 1,000 |
| 04011100 | 39,23 | 0,00 | 25 17 | 0.87  | 0,20  | 0,10 | 22,01 | 1,50  | 08.63 | 3,000 | 2,441 | 0,400 | 0,012 | 0,012 | 0,000 | 2,071 | 1,030 | 1,000 |
| 04CH18c  | 37 20 | 0,03 | 21,90 | 14.82 | 0,14  | 0.30 | 22,01 | 1.86  | 98 77 | 3,000 | 2,323 | 0,302 | 0,003 | 0.037 | 0,003 | 3 031 | 1,936 | 1,000 |
| 04CH18c  | 36.60 | 0 11 | 21 90 | 14.58 | 0 11  | 0.04 | 22.95 | 1.83  | 98.18 | 3,000 | 2 116 | 0,899 | 0.007 | 0.005 | 0.007 | 3 034 | 2 016 | 1,000 |
| 04CH18c  | 36.87 | 0.20 | 22.15 | 14.14 | 0.10  | 0.13 | 23.13 | 1.84  | 98.58 | 3.000 | 2.124 | 0.866 | 0.006 | 0.016 | 0.012 | 3.023 | 2.017 | 1.000 |
| 04CH18c  | 37.09 | 0.05 | 23.33 | 13.71 | 0.76  | 0.01 | 22.09 | 1.85  | 98,90 | 3,000 | 2.224 | 0.835 | 0.047 | 0.002 | 0.003 | 3.110 | 1.915 | 1.000 |
| 04CH18c  | 36,98 | 0,05 | 21,71 | 15,36 | 0,13  | 0,14 | 22,56 | 1,85  | 98,81 | 3,000 | 2,076 | 0,938 | 0,008 | 0,017 | 0,003 | 3,041 | 1,961 | 1,000 |
|          |       |      |       |       |       |      |       |       |       |       |       |       |       |       |       |       |       |       |
| MD-5.    | 37,20 | 0,02 | 24,25 | 11,58 | 0,58  | 0,22 | 22,73 | 1,86  | 98,44 | 3,000 | 2,305 | 0,703 | 0,036 | 0,027 | 0,001 | 3,071 | 1,964 | 1,000 |
| MD-5.    | 37,04 | 0,09 | 22,48 | 14,62 | 0,17  | 0,09 | 23,34 | 1,85  | 99,79 | 3,000 | 2,146 | 0,891 | 0,010 | 0,011 | 0,005 | 3,063 | 2,026 | 1,000 |
| MD-5.    | 36,67 | 0,07 | 22,44 | 14,57 | 0,10  | 0,25 | 22,83 | 1,83  | 98,83 | 3,000 | 2,164 | 0,897 | 0,006 | 0,030 | 0,004 | 3,102 | 2,002 | 1,000 |
| MD-5.    | 37,20 | 0,06 | 23,10 | 13,66 | 0,11  | 0,01 | 23,39 | 1,86  | 99,49 | 3,000 | 2,196 | 0,829 | 0,007 | 0,001 | 0,004 | 3,036 | 2,021 | 1,000 |
| MD-5.    | 37,30 | 0,00 | 21,89 | 14,79 | 0,13  | 0,15 | 22,90 | 1,86  | 99,11 | 3,000 | 2,075 | 0,895 | 0,008 | 0,019 | 0,000 | 2,996 | 1,973 | 1,000 |
| MD-5.    | 37,37 | 0,03 | 22,29 | 14,16 | 0,11  | 0,03 | 22,65 | 1,87  | 98,61 | 3,000 | 2,109 | 0,856 | 0,007 | 0,004 | 0,002 | 2,977 | 1,948 | 1,000 |
| MD-5.    | 37,50 | 0,04 | 23,26 | 12,60 | 0,13  | 0,26 | 21,73 | 1,87  | 97,70 | 3,000 | 2,193 | 0,759 | 0,008 | 0,031 | 0,003 | 2,993 | 1,862 | 1,000 |
| MD05-11D | 37 94 | 0.05 | 24 24 | 12 07 | 0.21  | 0.04 | 23 30 | 1 896 | 99.83 | 3 000 | 2 259 | 0 718 | 0.013 | 0.005 | 0.003 | 2 998 | 1 974 | 1 000 |
| MD05-11D | 37.40 | 0.02 | 22.07 | 14.24 | 0.15  | 0.16 | 23.07 | 1,869 | 99.08 | 3.000 | 2,087 | 0.860 | 0.009 | 0.020 | 0.001 | 2,976 | 1,982 | 1,000 |
| MD05-11D | 37.80 | 0.01 | 22.17 | 14.25 | 0.05  | 0.46 | 22.86 | 1.889 | 99.57 | 3.000 | 2.074 | 0.851 | 0.003 | 0.055 | 0.001 | 2.983 | 1.944 | 1.000 |
|          |       |      |       |       |       |      |       |       |       |       |       |       |       |       |       |       |       |       |
| MD05-18. | 37,14 | 0,03 | 25,32 | 10,96 | 0,15  | 0,02 | 23,41 | 1,856 | 98,89 | 3,000 | 2,410 | 0,666 | 0,009 | 0,002 | 0,002 | 3,089 | 2,026 | 1,000 |
| MD05-18. | 37,37 | 0,02 | 24,12 | 12,19 | 0,15  | 0,04 | 23,31 | 1,867 | 99,16 | 3,000 | 2,282 | 0,737 | 0,009 | 0,004 | 0,001 | 3,033 | 2,005 | 1,000 |
| MD05-18. | 39,90 | 0,05 | 25,46 | 9,08  | 0,21  | 0,16 | 21,90 | 1,994 | 99,78 | 3,000 | 2,256 | 0,514 | 0,012 | 0,018 | 0,003 | 2,802 | 1,764 | 1,000 |
| MD05-18. | 37,76 | 0,07 | 23,30 | 13,29 | 0,14  | 0,04 | 23,47 | 1,887 | 99,96 | 3,000 | 2,181 | 0,794 | 0,009 | 0,004 | 0,004 | 2,993 | 1,998 | 1,000 |
| MD05-18. | 37,62 | 0,15 | 23,56 | 12,70 | 0,14  | 0,03 | 23,50 | 1,880 | 99,63 | 3,000 | 2,215 | 0,762 | 0,009 | 0,004 | 0,009 | 2,998 | 2,008 | 1,000 |
| MD05-18. | 37,53 | 0,09 | 23,86 | 12,27 | 0,14  | 0,01 | 23,64 | 1,876 | 99,52 | 3,000 | 2,248 | 0,738 | 0,009 | 0,001 | 0,005 | 3,001 | 2,024 | 1,000 |
| MD05-18. | 37,83 | 0,10 | 23,75 | 12,14 | 0,16  | 0,03 | 23,46 | 1,891 | 99,38 | 3,000 | 2,220 | 0,725 | 0,010 | 0,004 | 0,006 | 2,964 | 1,994 | 1,000 |
| MD26     | 37 25 | 0.13 | 23 13 | 13.26 | 0.20  | 0.03 | 23 17 | 1 861 | 99.09 | 3 000 | 2 196 | 0 804 | 0.012 | 0.003 | 0.008 | 3 022 | 2 000 | 1 000 |
| MD26.    | 37.64 | 0.12 | 24.81 | 4.14  | 0.14  | 3.32 | 23.03 | 1,881 | 95.35 | 3.000 | 2,331 | 0.248 | 0.008 | 0.395 | 0.007 | 2,989 | 1,967 | 1,000 |
| MD26.    | 37.07 | 0.09 | 24.61 | 4.26  | 0.18  | 3.22 | 23.15 | 1.853 | 94.52 | 3.000 | 2.347 | 0.259 | 0.011 | 0.388 | 0.005 | 3.011 | 2.008 | 1.000 |
| MD26.    | 37.52 | 0.01 | 25.09 | 10.76 | 0.16  | 0.03 | 22.80 | 1.875 | 98,50 | 3.000 | 2.364 | 0.647 | 0.010 | 0.004 | 0.001 | 3.026 | 1.953 | 1.000 |
| MD26.    | 37,23 | 0,04 | 24,35 | 4,52  | 0,08  | 3,30 | 23,39 | 1,861 | 94,84 | 3,000 | 2,312 | 0,274 | 0,005 | 0,397 | 0,003 | 2,990 | 2,019 | 1,000 |
|          |       |      |       |       |       |      |       |       |       |       |       |       |       |       |       |       |       |       |
| MD9804   | 36,83 | 0,02 | 20,78 | 14,84 | 0,15  | 0,10 | 21,82 | 1,84  | 96,38 | 3,000 | 1,995 | 0,910 | 0,009 | 0,012 | 0,001 | 2,927 | 1,904 | 1,000 |
| MD9804   | 36,77 | 0,01 | 19,64 | 15,90 | 0,17  | 0,03 | 21,71 | 1,84  | 96,07 | 3,000 | 1,889 | 0,976 | 0,010 | 0,003 | 0,001 | 2,879 | 1,898 | 1,000 |

Proportions of cations are based on normalization of Si to three cations

# vii) Anfíbolas

| Amphihole     |           |          |        |         |         |          |          |         |          |          |          |          |         |           |            |       |       |       |       |       |       |       |        |       |       |       |       |       |       |            |              |             |       |       |
|---------------|-----------|----------|--------|---------|---------|----------|----------|---------|----------|----------|----------|----------|---------|-----------|------------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|------------|--------------|-------------|-------|-------|
| Sample        | SiO2      | AI2O3    | TiO2   | Fe2O3 I | eO N    | laO (    | CaO      | BaO     | K20 I    | Va20     | MnO      | H20 S    | um :    | Si        | Alt s      | sum / | Alo   | ті і  | Mn    | Fe3+  | Fe2+  | Ma    | sum    | Ca    | Ba N  | a I   | ĸ s   | um    | он :  | Ktremolite | Xolauconhane | Xriebeckite | XMa   | XFe   |
| MD06-5B       | 56.83     | 0.81     | 0.03   | 5.28    | 4.95    | 18.63    | 11.32    | 0.00    | 0.07     | 0.74     | 0.21     | 2.17 1   | 101.03  | 7.871     | 0.129      | 8.000 | 0.003 | 0.003 | 0.024 | 0.550 | 0.574 | 3.846 | 13.000 | 1.680 | 0.000 | 0.199 | 0.012 | 1.890 | 2.000 | 0.840      | 0.001        | 0.159       | 0.770 | 0.511 |
| MD06-5B       | 55.21     | 1.07     | 0.93   | 5.60    | 3.05    | 19.53    | 11.91    | 0.03    | 0.06     | 0.26     | 0.19     | 2.15     | 99.99   | 7,700     | 0.176      | 7.876 | 0.000 | 0.097 | 0.022 | 0.587 | 0.356 | 4.061 | 13.000 | 1,779 | 0.002 | 0.070 | 0.010 | 1.861 | 2.000 | 0.890      | 0.000        | 0.110       | 0.808 | 0.377 |
| MD06-5B       | 57,22     | 0,92     | 0,00   | 4,04    | 4,04    | 19,80    | 12,14    | 0,00    | 0,04     | 0,32     | 0,21     | 2,18 1   | 100,90  | 7,879     | 0,121      | 8,000 | 0,028 | 0,000 | 0,025 | 0,418 | 0,465 | 4,064 | 13,000 | 1,791 | 0,000 | 0,086 | 0,006 | 1,883 | 2,000 | 0,896      | 0,007        | 0,098       | 0,817 | 0,526 |
| MD06-5B       | 57,50     | 0,52     | 0,01   | 1,41    | 6,60    | 19,41    | 12,63    | 0,00    | 0,01     | 0,30     | 0,21     | 2,16 1   | 100,77  | 7,968     | 0,032      | 8,000 | 0,052 | 0,001 | 0,025 | 0,147 | 0,765 | 4,010 | 13,000 | 1,875 | 0,000 | 0,080 | 0,001 | 1,956 | 2,000 | 0,938      | 0,016        | 0,046       | 0,811 | 0,839 |
| MD06-5B       | 57,22     | 0,92     | 0,00   | 4,04    | 4,04    | 19,80    | 12,14    | 0,00    | 0,04     | 0,32     | 0,21     | 2,18 1   | 100,90  | 7,879     | 0,121      | 8,000 | 0,028 | 0,000 | 0,025 | 0,418 | 0,465 | 4,064 | 13,000 | 1,791 | 0,000 | 0,086 | 0,006 | 1,883 | 2,000 | 0,896      | 0,007        | 0,098       | 0,817 | 0,526 |
|               |           |          |        |         |         |          |          |         |          |          |          |          |         |           |            |       |       |       |       |       |       |       |        |       |       |       |       |       |       |            |              |             |       |       |
| MD06-6.       | 56,28     | 0,65     | 0,08   | 2,25    | 6,34    | 18,89    | 12,23    | 0,06    | 0,06     | 0,37     | 0,18     | 2,13     | 99,52   | 7,917     | 0,084      | 8,000 | 0,024 | 0,009 | 0,021 | 0,238 | 0,746 | 3,962 | 13,000 | 1,844 | 0,003 | 0,101 | 0,010 | 1,957 | 2,000 | 0,922      | 0,007        | 0,071       | 0,798 | 0,758 |
| MD06-6.       | 57,07     | 0,50     | 0,01   | 4,42    | 3,83    | 20,09    | 12,45    | 0,00    | 0,02     | 0,14     | 0,15     | 2,17 1   | 100,87  | 7,869     | 0,082      | 7,951 | 0,000 | 0,001 | 0,018 | 0,459 | 0,442 | 4,130 | 13,000 | 1,840 | 0,000 | 0,037 | 0,003 | 1,880 | 2,000 | 0,920      | 0,000        | 0,080       | 0,818 | 0,490 |
| MD06-6.       | 57,15     | 0,25     | 0,02   | 0,71    | 6,75    | 19,77    | 13,02    | 0,03    | 0,02     | 0,20     | 0,19     | 2,15 1   | 100,25  | 7,966     | 0,035      | 8,000 | 0,006 | 0,002 | 0,022 | 0,074 | 0,787 | 4,108 | 13,000 | 1,944 | 0,002 | 0,055 | 0,003 | 2,004 | 2,000 | 0,972      | 0,002        | 0,026       | 0,823 | 0,914 |
| MD06-6.       | 56,71     | 0,57     | 0,11   | 0,44    | 8,46    | 18,21    | 12,26    | 0,11    | 0,08     | 0,42     | 0,22     | 2,13     | 99,72   | 7,996     | 0,005      | 8,000 | 0,089 | 0,012 | 0,027 | 0,047 | 0,997 | 3,828 | 13,000 | 1,851 | 0,006 | 0,115 | 0,015 | 1,988 | 2,000 | 0,926      | 0,049        | 0,026       | 0,781 | 0,955 |
| MD06-6.       | 56,21     | 0,52     | 0,01   | 3,29    | 4,64    | 19,57    | 12,32    | 0,03    | 0,01     | 0,15     | 0,12     | 2,13     | 98,99   | 7,904     | 0,086      | 7,989 | 0,000 | 0,001 | 0,014 | 0,348 | 0,545 | 4,103 | 13,000 | 1,856 | 0,002 | 0,041 | 0,002 | 1,901 | 2,000 | 0,928      | 0,000        | 0,072       | 0,819 | 0,610 |
| MD06-6.       | 56,43     | 0,70     | 0,13   | 0,32    | 7,73    | 18,87    | 12,57    | 0,03    | 0,08     | 0,40     | 0,11     | 2,13     | 99,47   | 7,951     | 0,049      | 8,000 | 0,067 | 0,013 | 0,013 | 0,034 | 0,911 | 3,963 | 13,000 | 1,898 | 0,001 | 0,109 | 0,014 | 2,022 | 2,000 | 0,949      | 0,034        | 0,017       | 0,806 | 0,965 |
| MD06-6.       | 56,13     | 0,73     | 0,04   | 3,84    | 5,13    | 18,80    | 11,91    | 0,02    | 0,08     | 0,24     | 0,20     | 2,13     | 99,24   | 7,897     | 0,103      | 8,000 | 0,018 | 0,004 | 0,023 | 0,407 | 0,604 | 3,944 | 13,000 | 1,795 | 0,001 | 0,064 | 0,014 | 1,874 | 2,000 | 0,898      | 0,004        | 0,098       | 0,792 | 0,597 |
| MD06-6.       | 55,54     | 1,31     | 0,34   | 1,27    | 7,30    | 18,55    | 12,48    | 0,02    | 0,11     | 0,45     | 0,20     | 2,13     | 99,69   | 7,830     | 0,170      | 8,000 | 0,048 | 0,036 | 0,023 | 0,135 | 0,860 | 3,898 | 13,000 | 1,885 | 0,001 | 0,122 | 0,021 | 2,029 | 2,000 | 0,942      | 0,015        | 0,043       | 0,793 | 0,864 |
| MD06-6.       | 57,12     | 0,37     | 0,06   | 1,88    | 6,32    | 19,67    | 13,00    | 0,00    | 0,02     | 0,10     | 0,19     | 2,16 1   | 100,89  | 7,919     | 0,061      | 7,979 | 0,000 | 0,006 | 0,022 | 0,196 | 0,733 | 4,064 | 13,000 | 1,932 | 0,000 | 0,027 | 0,004 | 1,963 | 2,000 | 0,966      | 0,000        | 0,034       | 0,810 | 0,789 |
| MD06-6.       | 55,97     | 0,24     | 0,02   | 0,93    | 7,13    | 19,48    | 12,98    | 0,02    | 0,03     | 0,21     | 0,15     | 2,15 1   | 100,31  | 7,955     | 0,039      | 7,994 | 0,000 | 0,002 | 0,018 | 0,098 | 0,833 | 4,000 | 13,000 | 1,942 | 0,001 | 0,058 | 0,005 | 2,000 | 2,000 | 0,971      | 0,000        | 0,029       | 0,811 | 0,895 |
| MD06-6.       | 57,01     | 0,45     | 0,07   | 1,30    | 0,37    | 19,70    | 12,00    | 0,02    | 0,02     | 0,20     | 0,10     | 2,10     | 100,42  | 7,931     | 0,069      | 8,000 | 0,004 | 0,008 | 0,019 | 0,143 | 0,741 | 4,086 | 13,000 | 1,917 | 0,001 | 0,069 | 0,003 | 1,990 | 2,000 | 0,958      | 0,001        | 0,041       | 0,819 | 0,839 |
| MD06-6.       | 57,08     | 0,28     | 0,01   | 1,41    | 0,09    | 19,69    | 12,97    | 0,00    | 0,04     | 0,10     | 0,14     | 2,10 1   | 00.02   | 7,949     | 0,046      | 7,990 | 0,000 | 0,001 | 0,016 | 0,148 | 0,710 | 4,130 | 13,000 | 1,936 | 0,000 | 0,028 | 0,006 | 1,909 | 2,000 | 0,965      | 0,000        | 0,032       | 0,820 | 0,828 |
| MD00-0.       | 51,21     | 0,19     | 0,00   | 0,20    | 7,00    | 19,02    | 12,91    | 0,07    | 0,00     | 0,20     | 0,17     | 2,10     | 99,92   | 8,005     | 0,000      | 8,005 | 0,031 | 0,000 | 0,021 | 0,029 | 0,020 | 4,009 | 13,000 | 1,934 | 0,004 | 0,005 | 0,001 | 1,992 | 2,000 | 0,907      | 0,017        | 0,010       | 0,024 | 0,900 |
| MD5           | 53,40     | 0,48     | 0,06   | 1,85    | 14,00   | 13,63    | 11,92    | 0,16    | 0,06     | 0,18     | 0,35     | 2,02     | 98,11   | 7,915     | 0,083      | 7,998 | 0,000 | 0,007 | 0,044 | 0,206 | 1,735 | 3,011 | 13,000 | 1,893 | 0,009 | 0,053 | 0,012 | 1,966 | 2,000 | 0,946      | 0,000        | 0,054       | 0,603 | 0,894 |
| Proportion of | cations i | is based | on the | sum of  | cations | s = 13 e | xcept fo | r Ca, M | la and H | C for es | stimatio | n of Fe3 | + and o | n 46 nega | ative char | ges   |       |       |       |       |       |       |        |       |       |       |       |       |       |            |              |             |       |       |

viii) Pumpellyitas

| Pumpellyite | 5:02  | TiO2 | AI2O3 | Ee2O3 | Fa0 1 | MnO  | MaO  | C 90 1 | 1220 | K20  | H2O'         | eum (          | si .  |       | т; і  | Fo3+  | eum            | Ma    | Mn    | Fo?+  | eum   | <b>C</b> a | Na    | ĸ     | eum   | он    | YEo3+ | YMa   | XMa   |
|-------------|-------|------|-------|-------|-------|------|------|--------|------|------|--------------|----------------|-------|-------|-------|-------|----------------|-------|-------|-------|-------|------------|-------|-------|-------|-------|-------|-------|-------|
| 04Ch18c     | 36.24 | 0.05 | 22 73 | 4 67  | 2 92  | 0.06 | 2 40 | 23.09  | 0.03 | 0.00 | 6.38         | 98 57          | 5 966 | 4 409 | 0.006 | 0.579 | 4 993          | 0 589 | 0.009 | 0 402 | 1 000 | 4 071      | 0.010 | 0.000 | 4 081 | 7 000 | 0.590 | 0.589 | 0.375 |
| 04Ch18c     | 36.12 | 0.08 | 23.52 | 5.13  | 2.29  | 0.14 | 2.74 | 22.38  | 0.05 | 0.02 | 6.42         | 98,90          | 5,903 | 4.531 | 0.010 | 0.631 | 5,172          | 0.667 | 0.020 | 0.313 | 1.000 | 3,920      | 0.017 | 0.005 | 3,941 | 7.000 | 0.668 | 0.667 | 0.414 |
| 04Ch18c     | 36.14 | 0.06 | 22.95 | 4.21  | 3.01  | 0.09 | 2.33 | 23.18  | 0.01 | 0.00 | 6.37         | 98.35          | 5,958 | 4,460 | 0.007 | 0.523 | 4,990          | 0.572 | 0.013 | 0.415 | 1,000 | 4.094      | 0.004 | 0.000 | 4.098 | 7.000 | 0.558 | 0.572 | 0.379 |
| 04Ch18c     | 35.88 | 0.06 | 21.04 | 7.38  | 3.46  | 0.08 | 2.06 | 22.71  | 0.04 | 0.00 | 6.33         | 99.04          | 5,948 | 4,111 | 0.008 | 0.920 | 5.039          | 0.509 | 0.011 | 0.480 | 1.000 | 4.035      | 0.012 | 0.000 | 4.047 | 7.000 | 0.657 | 0.509 | 0.267 |
| 04Ch18c     | 36.70 | 0.07 | 23.76 | 3,98  | 2.70  | 0.09 | 2.51 | 22.66  | 0.03 | 0.03 | 6.38         | 98,90          | 6.039 | 4.607 | 0.008 | 0.492 | 5.108          | 0.616 | 0.012 | 0.372 | 1.000 | 3,995      | 0.011 | 0.007 | 4.012 | 7.000 | 0.570 | 0.616 | 0.416 |
| 04Ch18c     | 36.70 | 0.14 | 23.63 | 3.99  | 2.29  | 0.19 | 2.69 | 23.00  | 0.02 | 0.02 | 6.39         | 99.05          | 6.029 | 4.575 | 0.017 | 0.493 | 5.085          | 0.659 | 0.027 | 0.314 | 1.000 | 4.048      | 0.006 | 0.004 | 4.059 | 7.000 | 0.611 | 0.659 | 0.449 |
| 04Ch18c     | 36,57 | 0,10 | 22,89 | 5,25  | 2,30  | 0,10 | 2,71 | 22,86  | 0,05 | 0,01 | 6,35         | 99,18          | 6,042 | 4,456 | 0,012 | 0,653 | 5,121          | 0,669 | 0,013 | 0,318 | 1,000 | 4,046      | 0,016 | 0,002 | 4,064 | 7,000 | 0,673 | 0,669 | 0,408 |
| 04Ch18c     | 36,48 | 0,06 | 23,15 | 3,91  | 3,00  | 0,11 | 2,29 | 22,68  | 0,03 | 0,01 | 6,31         | 98,03          | 6,069 | 4,539 | 0,008 | 0,490 | 5,036          | 0,567 | 0,016 | 0,417 | 1,000 | 4,042      | 0,011 | 0,003 | 4,056 | 7,000 | 0,540 | 0,567 | 0,385 |
| 04Ch18c     | 36,61 | 0,08 | 22,80 | 4,45  | 2,94  | 0,14 | 2,30 | 22,60  | 0,02 | 0,01 | 6,31         | 98,26          | 6,092 | 4,470 | 0,010 | 0,557 | 5,037          | 0,571 | 0,020 | 0,409 | 1,000 | 4,030      | 0,005 | 0,002 | 4,037 | 7,000 | 0,577 | 0,571 | 0,372 |
| 04Ch18c     | 36,49 | 0,04 | 23,18 | 5,10  | 2,41  | 0,10 | 2,65 | 22,55  | 0,05 | 0,01 | 6,34         | 98,92          | 6,036 | 4,519 | 0,005 | 0,635 | 5,159          | 0,653 | 0,015 | 0,333 | 1,000 | 3,996      | 0,016 | 0,002 | 4,013 | 7,000 | 0,656 | 0,653 | 0,403 |
| MD5         | 36,72 | 0,06 | 24,34 | 2,88  | 2,89  | 0,12 | 2,40 | 22,86  | 0,07 | 0,02 | 6,40         | 98,80          | 6,021 | 4,704 | 0,007 | 0,355 | 5,066          | 0,587 | 0,016 | 0,397 | 1,000 | 4,016      | 0,023 | 0,004 | 4,046 | 7,000 | 0,472 | 0,587 | 0,438 |
| MD5         | 36,64 | 0,07 | 24,49 | 2,62  | 2,77  | 0,10 | 2,50 | 23,51  | 0,03 | 0,00 | 6,43         | 99,21          | 5,985 | 4,713 | 0,009 | 0,322 | 5,044          | 0,608 | 0,014 | 0,379 | 1,000 | 4,113      | 0,010 | 0,000 | 4,127 | 7,000 | 0,460 | 0,608 | 0,464 |
| MD5         | 36,58 | 0,05 | 24,36 | 3,23  | 2,39  | 0,11 | 2,68 | 22,72  | 0,01 | 0,01 | 6,39         | 98,53          | 6,007 | 4,715 | 0,006 | 0,400 | 5,121          | 0,656 | 0,015 | 0,329 | 1,000 | 3,999      | 0,002 | 0,002 | 4,002 | 7,000 | 0,549 | 0,656 | 0,474 |
| MD5         | 35,75 | 0,03 | 24,00 | 5,15  | 1,40  | 0,09 | 3,26 | 22,01  | 0,03 | 0,01 |              | 91,73          | 5,836 | 4,620 | 0,004 | 0,615 | 5,239          | 0,586 | 0,014 | 0,400 | 1,000 | 4,077      | 0,009 | 0,000 | 4,087 | 7,000 | 0,399 | 0,586 | 0,366 |
| MD5         | 36,27 | 0,06 | 24,73 | 2,27  | 2,90  | 0,10 | 2,43 | 23,53  | 0,03 | 0,00 |              | 92,32          | 5,866 | 4,720 | 0,007 | 0,266 | 4,993          | 0,617 | 0,015 | 0,368 | 1,000 | 4,052      | 0,003 | 0,002 | 4,057 | 7,000 | 0,431 | 0,617 | 0,493 |
| MD5         | 36,38 | 0,11 | 24,47 | 2,36  | 2,66  | 0,11 | 2,55 | 23,32  | 0,01 | 0,01 |              | 91,98          | 5,900 | 4,680 | 0,013 | 0,279 | 4,972          | 0,707 | 0,016 | 0,276 | 1,000 | 4,002      | 0,006 | 0,002 | 4,010 | 7,000 | 0,612 | 0,707 | 0,560 |
| MD5         | 36,21 | 0,05 | 24,34 | 3,62  | 2,01  | 0,12 | 2,93 | 23,07  | 0,02 | 0,01 |              | 92,38          | 5,862 | 4,850 | 0,006 | 0,435 | 5,291          | 0,707 | 0,016 | 0,712 | 1,000 | 4,002      | 0,006 | 0,002 | 4,010 | 7,000 | 0,379 | 0,707 | 0,381 |
| MD05-18     | 36,81 | 0,02 | 26,00 | 2,51  | 0,57  | 0,15 | 3,77 | 23,17  | 0,03 | 0,01 | 6,54         | 99,57          | 5,911 | 4,920 | 0,002 | 0,303 | 5,226          | 0,903 | 0,020 | 0,077 | 1,000 | 3,985      | 0,008 | 0,001 | 3,995 | 7,000 | 0,798 | 0,903 | 0,704 |
| MD05-18     | 36,97 | 0,06 | 25,36 | 2,10  | 0,77  | 0,17 | 3,63 | 23,50  | 0,02 | 0,00 | 6,50         | 99,09          | 5,965 | 4,822 | 0,008 | 0,256 | 5,085          | 0,873 | 0,024 | 0,103 | 1,000 | 4,062      | 0,007 | 0,000 | 4,069 | 7,000 | 0,712 | 0,873 | 0,709 |
| MD05-18     | 36,49 | 0,04 | 24,24 | 3,42  | 2,97  | 0,04 | 2,40 | 23,03  | 0,03 | 0,01 | 6,39         | 99,06          | 5,990 | 4,689 | 0,005 | 0,422 | 5,116          | 0,587 | 0,005 | 0,408 | 1,000 | 4,051      | 0,009 | 0,001 | 4,060 | 7,000 | 0,509 | 0,587 | 0,414 |
| MD05-18     | 37,33 | 0,18 | 24,36 | 2,76  | 1,39  | 0,09 | 3,31 | 23,50  | 0,00 | 0,01 | 6,49         | 99,42          | 6,039 | 4,645 | 0,022 | 0,336 | 5,003          | 0,799 | 0,013 | 0,189 | 1,000 | 4,074      | 0,000 | 0,002 | 4,076 | 7,000 | 0,641 | 0,799 | 0,603 |
| MD05-18     | 37,17 | 0,08 | 24,57 | 2,48  | 1,45  | 0,14 | 3,24 | 23,26  | 0,02 | 0,00 | 6,46         | 98,88          | 6,036 | 4,703 | 0,010 | 0,303 | 5,016          | 0,784 | 0,020 | 0,197 | 1,000 | 4,047      | 0,006 | 0,001 | 4,054 | 7,000 | 0,607 | 0,784 | 0,611 |
| MD26        | 36,30 | 0,19 | 24,41 | 5,37  | 1,62  | 0,16 | 3,12 | 22,47  | 0,02 | 0,06 | 6,44         | 100,15         | 5,915 | 4,688 | 0,024 | 0,659 | 5,370          | 0,757 | 0,022 | 0,221 | 1,000 | 3,923      | 0,006 | 0,012 | 3,941 | 7,000 | 0,749 | 0,757 | 0,463 |
| MD26        | 37,60 | 0,11 | 24,38 | 2,37  | 1,63  | 0,18 | 3,14 | 22,31  | 0,03 | 0,58 |              | 92,33          | 6,048 | 4,622 | 0,013 | 0,284 | 4,919          | 0,753 | 0,025 | 0,223 | 1,000 | 3,845      | 0,009 | 0,119 | 3,973 | 7,000 | 0,560 | 0,753 | 0,598 |
| MD26        | 37,75 | 0,10 | 24,47 | 2,20  | 1,74  | 0,12 | 3,11 | 22,15  | 0,03 | 0,58 |              | 92,25          | 6,067 | 4,635 | 0,012 | 0,260 | 4,907          | 0,745 | 0,016 | 0,238 | 1,000 | 3,814      | 0,009 | 0,119 | 3,943 | 7,000 | 0,522 | 0,745 | 0,599 |
| MD9803      | 36,54 | 0,01 | 19,17 | 10,43 | 1,34  | 0,02 | 3,21 | 22,72  | 0,06 | 0,00 | 6,22         | 99,72          | 6,167 | 3,814 | 0,001 | 1,325 | 5,140          | 0,808 | 0,002 | 0,190 | 1,000 | 4,108      | 0,020 | 0,001 | 4,129 | 7,000 | 0,875 | 0,808 | 0,348 |
| MD9803      | 35,17 | 0,01 | 13,79 | 17,66 | 2,26  | 0,00 | 2,49 | 22,12  | 0,02 | 0,01 | 5,88         | 99,41          | 6,273 | 2,900 | 0,001 | 2,370 | 5,271          | 0,663 | 0,000 | 0,337 | 1,000 | 4,228      | 0,008 | 0,001 | 4,236 | 7,000 | 0,876 | 0,663 | 0,197 |
| MD9803      | 35,79 | 0,01 | 19,14 | 10,54 | 2,72  | 0,03 | 2,38 | 22,58  | 0,01 | 0,00 | 6,14         | 99,36          | 6,114 | 3,854 | 0,002 | 1,355 | 5,210          | 0,607 | 0,005 | 0,388 | 1,000 | 4,132      | 0,004 | 0,000 | 4,136 | 7,000 | 0,777 | 0,607 | 0,258 |
| MD9803      | 36,04 | 0,01 | 19,01 | 10,74 | 2,20  | 0,02 | 2,69 | 22,63  | 0,05 | 0,00 | 6,17         | 99,57          | 6,134 | 3,814 | 0,001 | 1,376 | 5,190          | 0,683 | 0,003 | 0,314 | 1,000 | 4,126      | 0,017 | 0,000 | 4,143 | 7,000 | 0,814 | 0,683 | 0,288 |
| MD9803      | 34,77 | 0,02 | 13,43 | 18,51 | 1,44  | 0,03 | 2,91 | 22,04  | 0,01 | 0,00 | 5,84         | 99,00          | 6,244 | 2,843 | 0,003 | 2,501 | 5,346          | 0,779 | 0,004 | 0,217 | 1,000 | 4,240      | 0,004 | 0,000 | 4,244 | 7,000 | 0,920 | 0,779 | 0,223 |
| MD9803      | 36,82 | 0,01 | 19,62 | 10,29 | 1,40  | 0,03 | 3,21 | 22,61  | 0,25 | 0,00 | 6,28         | 100,51         | 6,156 | 3,867 | 0,001 | 1,294 | 5,162          | 0,801 | 0,004 | 0,195 | 1,000 | 4,051      | 0,082 | 0,000 | 4,133 | 7,000 | 0,869 | 0,801 | 0,350 |
| MD9803      | 36,44 | 0,06 | 21,30 | 7,62  | 2,08  | 0,08 | 2,81 | 22,79  | 0,02 | 0,01 | 6,29         | 99,49          | 6,082 | 4,191 | 0,007 | 0,957 | 5,155          | 0,699 | 0,012 | 0,290 | 1,000 | 4,076      | 0,007 | 0,001 | 4,084 | 7,000 | 0,767 | 0,699 | 0,359 |
| MD9803      | 36,19 | 0,03 | 22,98 | 6,27  | 0,68  | 0,10 | 3,62 | 22,67  | 0,03 | 0,02 | 6,35         | 98,93          | 5,985 | 4,479 | 0,004 | 0,781 | 5,264          | 0,893 | 0,013 | 0,094 | 1,000 | 4,017      | 0,010 | 0,003 | 4,031 | 7,000 | 0,893 | 0,893 | 0,505 |
| MD9804      | 34,91 | 0,12 | 14,02 | 17,11 | 1,89  | 0,10 | 2,63 | 21,99  | 0,02 | 0,02 | 5,86         | 98,66          | 6,251 | 2,958 | 0,016 | 2,305 | 5,279          | 0,701 | 0,015 | 0,284 | 1,000 | 4,218      | 0,006 | 0,004 | 4,228 | 7,000 | 0,890 | 0,701 | 0,213 |
| MD9804      | 35,08 | 0,88 | 16,88 | 11,99 | 1,01  | 0,07 | 3,23 | 22,30  | 0,02 | 0,00 | 6,00         | 97,47          | 6,139 | 3,483 | 0,116 | 1,579 | 5,178          | 0,842 | 0,011 | 0,148 | 1,000 | 4,183      | 0,008 | 0,000 | 4,190 | 7,000 | 0,914 | 0,842 | 0,328 |
| MD9804      | 35,69 | 0,57 | 15,55 | 14,01 | 1,38  | 0,07 | 3,01 | 22,03  | 0,03 | 0,01 | 5,98         | 98,32          | 6,263 | 3,216 | 0,075 | 1,850 | 5,142          | 0,788 | 0,010 | 0,203 | 1,000 | 4,142      | 0,009 | 0,003 | 4,154 | 7,000 | 0,901 | 0,788 | 0,277 |
| MD9804      | 34,29 | 1,08 | 13,56 | 16,09 | 1,57  | 0,11 | 2,74 | 21,44  | 0,02 | 0,01 | 5,77         | 96,71          | 6,232 | 2,905 | 0,147 | 2,201 | 5,254          | 0,743 | 0,018 | 0,239 | 1,000 | 4,176      | 0,009 | 0,003 | 4,188 | 7,000 | 0,902 | 0,743 | 0,233 |
| MD9804      | 35,40 | 0,32 | 14,13 | 15,65 | 2,29  | 0,11 | 2,40 | 21,78  | 0,05 | 0,00 | 5,87         | 98,00          | 6,330 | 2,978 | 0,043 | 2,106 | 5,127          | 0,641 | 0,017 | 0,342 | 1,000 | 4,173      | 0,017 | 0,001 | 4,190 | 7,000 | 0,860 | 0,641 | 0,207 |
| MD9804      | 35,54 | 0,27 | 16,52 | 13,36 | 1,63  | 0,13 | 2,85 | 22,09  | 0,01 | 0,00 | 6,00         | 98,42          | 6,213 | 3,404 | 0,035 | 1,758 | 5,197          | 0,742 | 0,020 | 0,238 | 1,000 | 4,138      | 0,003 | 0,001 | 4,142 | 7,000 | 0,881 | 0,742 | 0,271 |
| MD9804      | 34,95 | 0,16 | 17,62 | 12,26 | 1,73  | 0,12 | 2,79 | 21,87  | 0,05 | 0,01 | 5,98         | 97,54          | 6,128 | 3,643 | 0,021 | 1,619 | 5,282          | 0,729 | 0,018 | 0,253 | 1,000 | 4,110      | 0,018 | 0,002 | 4,129 | 7,000 | 0,865 | 0,729 | 0,280 |
| WD9804      | 37,20 | 0,04 | 23,76 | 4,26  | 0,32  | 0,15 | 3,87 | 23,44  | 0,04 | 0,06 | 0,4/         | 99,60          | 6,034 | 4,544 | 0,005 | 0,520 | 5,068          | 0,937 | 0,020 | 0,043 | 1,000 | 4,074      | 0,013 | 0,012 | 4,099 | 7,000 | 0,924 | 0,937 | 0,625 |
| MD0804      | 34,70 | 0,06 | 14,11 | 10,41 | 1,55  | 0,05 | 2,82 | 21,84  | 0,02 | 0,01 | 5,81         | 97,39          | 6,202 | 3,001 | 0,008 | 2,229 | 5,238<br>5,270 | 0,758 | 0,008 | 0,235 | 1,000 | 4,224      | 0,008 | 0,003 | 4,234 | 7,000 | 0,905 | 0,758 | 0,235 |
| MD09004     | 34,41 | 0,09 | 13,22 | 17.00 | 1,46  | 0,10 | 2,02 | 21,0/  | 0,01 | 0,01 | 0,00         | 30,43          | 6 427 | 2,022 | 0,012 | 2,037 | 5,370          | 0,700 | 0,015 | 0,225 | 1,000 | 4,243      | 0,005 | 0,003 | 4,202 | 7,000 | 0,919 | 0,700 | 0,210 |
| MD9804      | 36,50 | 0,14 | 10.00 | 10.02 | 2,14  | 0,10 | 2,40 | 21,10  | 0,01 | 0,00 | 5,00<br>6 13 | 97,00<br>07,83 | 6 177 | 2,717 | 0,010 | 2,440 | 5,1/5          | 0,001 | 0,016 | 0,323 | 1,000 | 4,093      | 0,003 | 0,000 | 4,095 | 7,000 | 0,003 | 0,001 | 0,193 |
|             | 50,10 | 0,01 | 13,09 | 10,02 | 0,04  | 0,04 | 0,04 | 22,22  | 0,02 | 0,02 | 5,15         | 31,03          | 3,177 | 3,030 | 0,001 | 1,230 | 5,141          | 3,302 | 3,000 | 0,032 | 1,000 | 4,074      | 3,007 | 5,004 | 4,000 | .,000 | 0,000 | 0,002 |       |

Cations are based on 49 negative valencies; H2O is calculated on the basis of OH = 4; estimation of Fe2+ by assuming half of X-position filled with divalent cations

#### PUBLICACIONES GENERADAS A PARTIR DE ESTA TESIS

#### i) Revistas ISI

- Sepúlveda, F.A.; Palma-Held, S.; Hervé, F.; Fanning, C.M. 2010. Permian depositional age of metaturbidites of the Duque de York Complex, southern Chile: U-Pb SHRIMP data and palynology. Andean Geology, vol. 37 (2), pp. 375-397.
- Willner, A.P.; Sepúlveda, F.A.; Hervé, F.; Massonne, H.-J.; Sudo, M. 2009. Conditions and timing of pumpellyite-actinolite facies metamorphism in the Early Mesozoic frontal accretionary prism of the Madre de Dios Archipelago (50°20`S; S-Chile). *Journal of Petrology*, vol. 50 (11), pp. 2127-2155.
- Sepúlveda, F.A.; Hervé, F.; Calderón, M.; Lacassie, J.P. 2008. Petrology of igneous and metamorphic units from the allocthonous Madre de Dios Terrane, Magallanes, Chile. *Gondwana Research*, v. 13 (2), pp. 238-249.

#### ii) Congresos Internacionales

- Septiembre, 2008: Willner, A.P.; Massonne, H.-J.; **Sepúlveda, F.A.**; Hervé, F. Phase relationships at pumpellyite-actinolite facies conditions within fossil frontal accretionary prisms in southern Chile. 86th Annual Meeting of the German Mineralogical Society (Deutsche Mineralogische Gesellschaft), Berlin.
- Noviembre, 2007: **Sepúlveda, F.A.**; Palma-Heldt, S.; Hervé, F.; Fanning, C.M. First palynological record in the allochtonous Madre de Dios Terrane, Southern Chile: constraints for the age of the Duque de York Complex. Geosur 2007 – International Geological Congress on the Southern Hemisphere, Santiago, Chile.
- Noviembre, 2007: Willner, A.P.; **Sepúlveda, F.A.**; Hervé, F.; Massonne, H.-J.; Sudo, M. The Madre de Dios Metamorphic Complex of Southern Chile: evolution of a frontal accretionary prism during Triassic times. Geosur 2007 International Geological Congress on the Southern Hemisphere, Santiago, Chile.
- Noviembre, 2005: **Sepúlveda, F**.; Hervé, F. and Calderón, M. Petrology of the Late Paleozoic Denaro complex, Madre de Dios archipelago, Magallanes, Chile. Gondwana 12: *Geological and biological heritage of Gondwana*, Mendoza, Argentina.
- Septiembre, 2005: **Sepúlveda, F.**; Hervé, F. y Calderón, M. Condiciones de metamorfismo del Complejo Denaro, Archipiélago Madre de Dios, Magallanes, Chile. XVI Congreso Geológico Argentino, La Plata, Argentina.

#### *iii) Congresos Nacionales*

Noviembre, 2009: **Sepúlveda, F.A.**; Willner, A; Hervé, F.; Sudo, M. El Complejo Metamórfico Madre de Dios: condiciones PT y edad del metamorfismo de un prisma de acreción frontal fósil. XII Congreso Geológico Chileno Santiago, Chile.

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