Geochronology of very low-grade Mesozoic Andean metabasites; an approach through the K–Ar, $^{40}Ar/^{39}Ar$ and U–Pb LA-MC-ICP-MS methods

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Abstract: Multiple geochronological methods using different metamorphic minerals were combined to date the regional, very low-grade metamorphism affecting Upper Jurassic–Lower Cretaceous volcano-sedimentary successions in the Andes of central Chile. Early Late Cretaceous metamorphic ages (between 82 and 108 Ma) were obtained by the K–Ar and U–Pb methods for celadonite and titanite. A much younger thermal event is responsible for actinolite formation at 8 Ma, most probably related to the intrusion of proximal Miocene granitoids. Previous models for the metamorphism should be reinterpreted taking into account the absence of a greenschist-facies event. The combination of different metamorphic minerals and chronometers is regarded as a powerful analytical tool to date the very low-grade metamorphism associated with the Mesozoic extensional regime developed within the Andes.

A recent advance in the study of very low-grade metabasites is the quantitative approach to the intensive *P–T–X* conditions using internally consistent thermodynamic databases (e.g. Powell *et al*. 1993; Robinson *et al*. 2004, 2005; Day & Springer 2005). However, the accurate timing of the very low-grade metamorphic processes has been a subject scarcely investigated, largely as a consequence of the small number and size of newly formed minerals suitable for dating. In burial-type processes, dating of metamorphic minerals would record the time of the different stages in the development of a basin, as shown by Aguirre *et al*. (1999) and Fuentes *et al*. (2005).

Present knowledge of the geodynamic evolution of the Andes during the Late Jurassic and Early Cretaceous is poorly constrained because of the absence of a precise chronostratigraphic framework. However, these epochs are of the utmost importance in the development of the orogen, as they coincide with major planetary events; for example, intense volcanic activity and formation of several large igneous provinces accompanied the opening of the Atlantic Ocean. Widespread rifting occurred along the western border of South America during the Late Jurassic–Early Cretaceous (Åberg *et al*. 1984), and has been attributed to asthenospheric mantle upwelling leading to extension, crustal attenuation and subsidence (Aguirre *et al*. 1999).

During those epochs, large volumes of volcanic rocks were deposited in central Chile between 25° and 36°S along a 1200 km string of ensialic basins characterized by alternating marine and terrestrial conditions (Vergara *et al*. 1995). The Upper Jurassic–Lower Cretaceous successions are displayed as two parallel belts at the western and eastern flanks of a Mesozoic synclinorium (Fig. 1); the western belt along the Coastal Range and the eastern one along the Andes, near the border with Argentina. The rocks in both belts are affected by burial metamorphism at upper zeolite, prehnite–pumpellyite and lower greenschist facies (Levi *et al*. 1989; Fig. 1). In the central Chilean Andes (33–35°S), these epochs are characterized by alternating cycles of marine transgression, basin generation and continental uplift, which have given rise to thick successions of volcaniclastic rocks, limestone–shale units, and intermediate to basic lava flows. Palaeontological ages are known for the marine carbonate units but isotopic dates do not exist for documenting the episodes of volcanism, or the very low-grade metamorphism. Two different metamorphic events took place, one during the early Late Cretaceous and the other in early Miocene; these events explain the metamorphic pattern found in the Upper Jurassic–Lower Cretaceous and the Cenozoic volcanic sequences (Fig. 1), which unconformably overlie the Mesozoic units (Robinson *et al*. 2004).

Here we report K–Ar, Ar–Ar, and laser ablation inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) U–Pb ages that suggest the occurrence of at least two metamorphic events. These new data provide insights into the geodynamic evolution of this segment of the Andean Cordillera.

Geological framework

A typical section of the Upper Jurassic–Lower Cretaceous volcano-sedimentary successions is well exposed in the Andes of central Chile, east of Santiago (Fig. 1). The Rio Damas Formation consists of *c*. 3 km of red continental volcanogenic sedimentary rocks and porphyritic lavas of basic composition. A Late Jurassic age has been assigned to this formation based on biostratigraphic data relating to both the underlying and overlying marine sequences (Thiele 1980). A *c*. 1.4 km thick unit, the Lo Valdés Formation, concordantly overlies the Rio Damas Formation. The former consists of a 700 m basal section of basic lavas, partly pillowed, andesitic hyaloclastites, and a marine fossiliferous sequence of limestones and shales. Based on its palaeontological record, the age of the Lo Valdés Formation covers the interval Early–Mid-Tithonian to Hauterivian (Hallam *et al*. 1986). Both formations have been affected by regional, very low-grade, burial-type metamorphism. Common secondary mineral assemblages in metabasites of the Rio Damas Formation

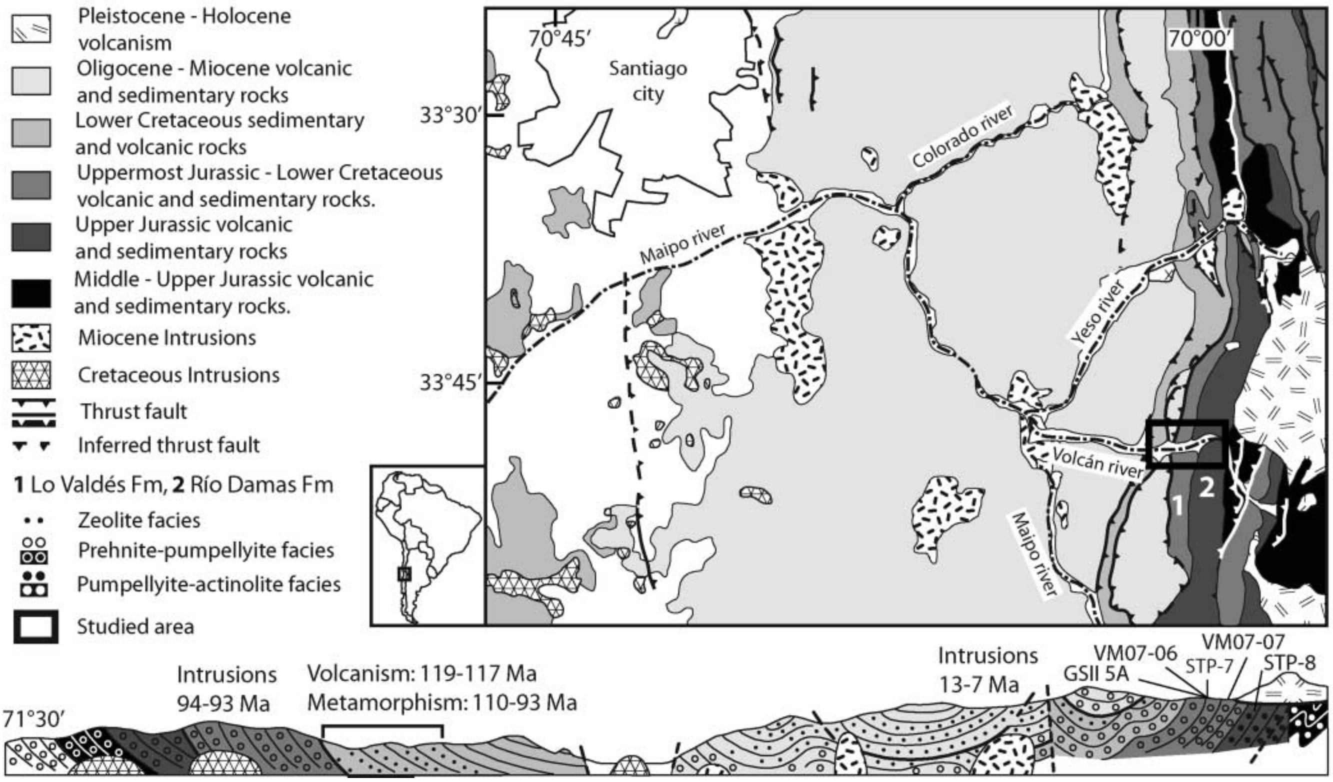

Fig. 1. Simplified geological map of central Chile (modified from SERNAGEOMIN 2003; Fock *et al*. 2006). Schematic geological profile (*c*. 33°45′S) showing the Mesozoic–Cenozoic sequences both in the Coastal Range and in the Andean Cordillera (modified after Levi *et al*. 1989). Ages are from Åberg *et al*. (1984), Aguirre *et al*. (1999), SERNAGEOMIN (2003), Wilson *et al*. (2003), Fuentes *et al*. (2004) and Parada *et al*. (2005).

are: (1) epidote + actinolite + chlorite ± titanite; (2) chlorite + epidote ± pumpellyite ± calcite; (3) actinolite + prehnite + epidote with ubiquitous chalcedony. Previous workers have assigned these mineral associations to the pumpellyite–actinolite facies and, based on mineral chemistry and thermodynamic modelling on the $Na_2O–CaO–MgO–Al_2O_3–SiO_2–H_2O$ (NCMASH) basaltic system, a minimum value for the invariant CHEPPAQ (chlorite–water–epidote–prehnite–pumpellyite–actinolite–quartz) point was established as 260 °C and 1.1 kbar (Robinson *et al*. 2004). Metabasites of the Lo Valdés Formation contain assemblages with pumpellyite, prehnite, chlorite, mixed-layer smectite–chlorite, celadonite, titanite, quartz, K-feldspar, calcite and minor epidote (actinolite absent), which are characteristic of the prehnite–pumpellyite facies (Levi *et al*. 1989). Based on facies distribution and regional tectonics, the metamorphism of the Upper Jurassic–Lower Cretaceous successions described here has been attributed to an early Late Cretaceous event (Levi *et al*. 1989; Robinson *et al*. 2004). Age determinations for the main secondary minerals from this section have not been determined; however, the occurrence of a Cretaceous event is supported by ages of 105 ± 3 Ma and 101.3 ± 2.9 Ma obtained by K–Ar analysis of celadonite from basic lavas of the Río Damas Formation at its type locality in Termas del Flaco, some 200 km south from the Maipo area (Belmar 2000).

Minerals dated and analytical methods

A systematic investigation of the timing of metamorphism affecting the Upper Jurassic–Lower Cretaceous metabasites of the Andean successions between latitudes 33 and 35°S was undertaken. Our approach includes isotopic age determinations using the K–Ar, $^{40}Ar/^{39}Ar$ and *in situ* U–Pb LA-MC-ICP-MS methods. The K–Ar and $^{40}Ar/^{39}Ar$ analyses were performed at the Laboratorio de Geocronología, Servicio Nacional de Geología y Minería, Chile (analytical specifications have been given by Arancibia *et al*. 2006); laser ablation analyses were conducted at the Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Canada.

Minerals selected for dating include celadonite, titanite, and actinolite (Fig. 2). Analytical results are given in Table 1, Figure 3 and in the Supplementary Publication, available online at http://ww.geolsoc.org.uk/SUP18304. Large celadonite aggregates (individual grains <2 μm) are present infilling amygdales (Fig. 2a and b); consequently, their hand-picking separation under the binocular microscope for K–Ar dating was relatively easy. Titanite is a very common metamorphic phase in the mineral assemblages of the Lo Valdés and Río Damas metabasites; infilling amygdales accompanied by Ca–Al hydrated silicates (Fig. 2b), in the groundmass (Fig. 2c), and replacing previous Ti-rich oxides. The titanite crystals present in the metamorphic assemblages of these two formations are typically <200 μm in size (very often <100 μm). The U–Pb isotopic compositions of titanite were determined in standard petrographic thin sections by LA-MC-ICP-MS using a novel *in situ* technique. Titanite grains were ablated using a spot size of either 60 or 120 μm (dependent on the size of the crystal). A typical laser ablation analysis consists of a 60 s baseline measurement (prior to ablation) followed by a 30 s interval for data acquisition. A Tera–Wasserburg plot is used to determine the isotopic compositions of both the common and radiogenic Pb components, the end-members of well-defined mixing lines (Fig. 3a and b). The reader is referred

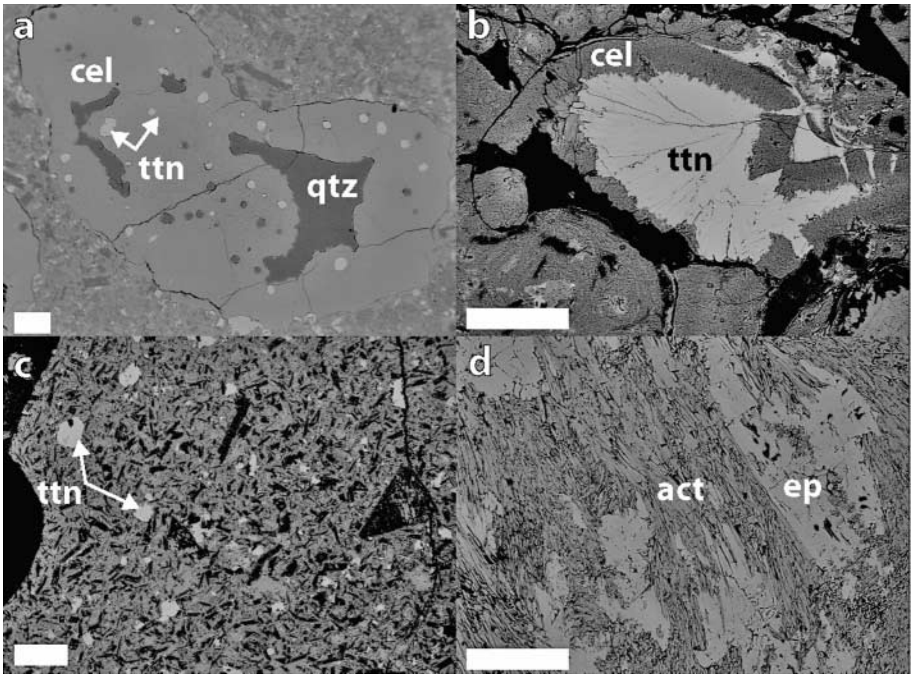

Fig. 2. SEM images of altered metabasites from the Andes of central Chile: (**a**) amygdale with celadonite, quartz and titanite; (**b**) titanite and celadonite infilling amygdale, sample GSII5A; (**c**) small anhedral crystals of titanite in the groundmass, sample STP-8; (**d**) fibrous actinolite and epidote infilling amygdale, sample STP-8. Scale bar represents 200 µm. ttn, titanite; cel, celadonite; qtz, quartz; act, actinolite; ep, epidote.

Table 1. *K–Ar, U–Pb and Ar–Ar ages for metamorphic minerals from metabasites of the Lo Valdés and Río Damas Fms, central Chile; datum SA56*

K–Ar ages

Sample	Coordinates	Mineral	% K	Ar rad. (nl g^{-1})	% Atm Ar	Age (Ma ± 2σ)
VM06-07	70°02′27″S, 33°49′30″W	Celadonite	0.988	3.202	24	82 ± 3
VM07-07	70°01′24″S, 33°47′08″W	Celadonite	6.504	28.351	5	109 ± 3
STP-7	33°49′42″S, 70°02′45″W	Celadonite	3.392	12.433	43	92 ± 3

U–Pb ages

Sample	Coordinates	Mineral	Spot size (µm)	Number of analyses	Lower intercept age (Ma ± 2σ)	MSWD	Mean age (Ma ± 2σ)	MSWD	Probability
GSII5A	33°49′33″S, 70°02′31″W	Titanite	120, 60	17	84.3 ± 3.0	0.9	84.6 ± 4.4	1.4	0.15
STP-8	33°48′42″S, 69°59′57″W	Titanite	60	8	106.0 ± 21.0	2.0	108.0 ± 15.0	1.4	0.02

Ar–Ar ages

Sample	Coordinates	Mineral	Run	Integrated age (Ma ± 2σ)	Plateau age (Ma ± 2σ)	Number of steps/ total	MSWD	Probability	% Gas
STP-8	33°48′42″S, 69°59′57″W	Actinolite	11375-01	10.0 ± 4.0	8.7 ± 1.9	8/8	0.4	0.93	100.0
STP-8	33°48′42″S, 69°59′57″W	Actinolite	11375-02	9.9 ± 1.9	8.2 ± 0.8	5/6	0.0	1.00	98.7
STP-8	33°48′42″S, 69°59′57″W	Actinolite	11445-01	7.0 ± 4.0	7.0 ± 3.0	7/7	0.1	1.00	100.0
STP-8	33°48′42″S, 69°59′57″W	Actinolite	11445-02	9.0 ± 3.0	8.4 ± 1.6	6/6	0.3	0.90	100.0

to Simonetti *et al*. (2006) for a more detailed description of the instrumentation, analytical protocol, and data reduction and validation procedures. Actinolite is abundant but in a rather restricted area, as it occurs in vesicular basaltic lavas from the Upper Jurassic sequences in paragenetic association with epidote–quartz–chlorite (Fig. 2d). Fibrous crystals up to 10 mm long are well developed and easy to separate under the binocular microscope.

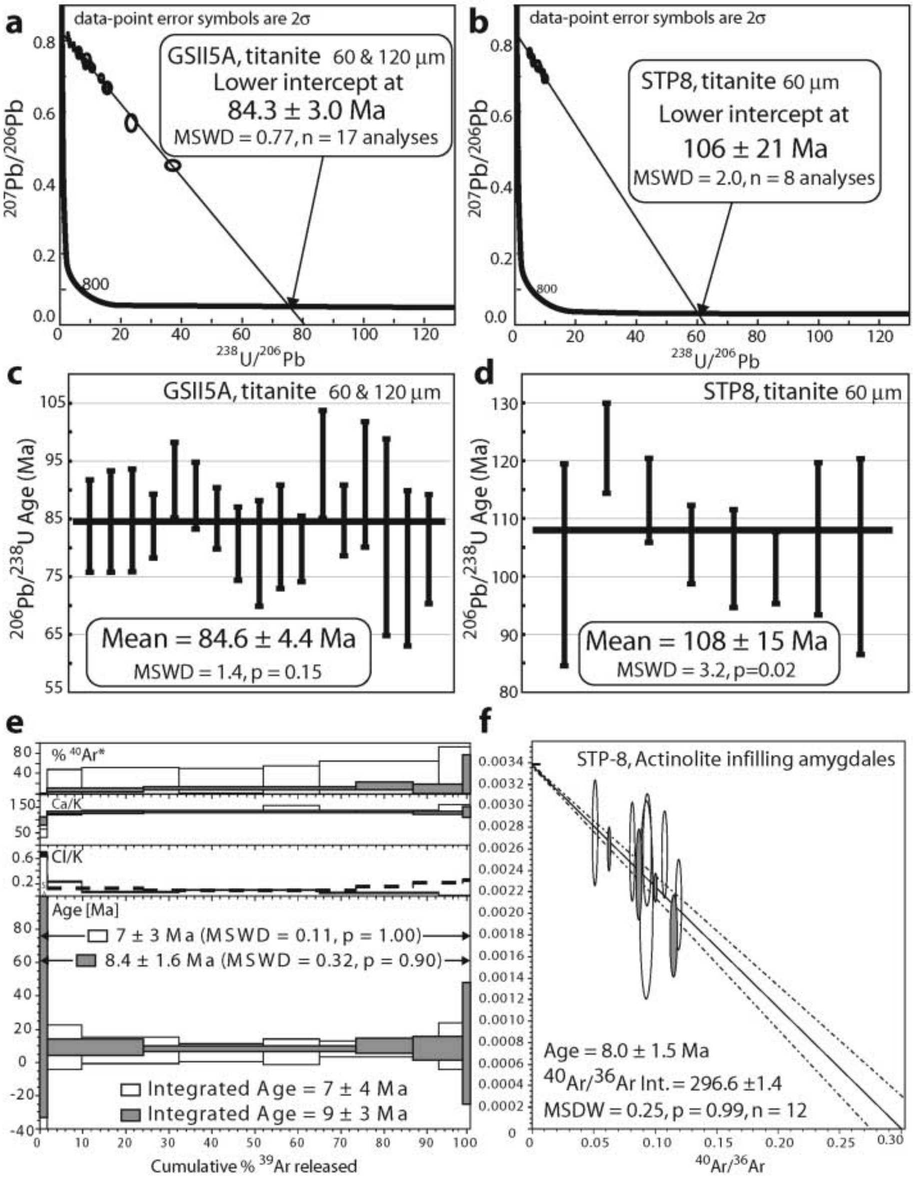

Fig. 3. Tera–Wasserburg diagrams (**a**, **b**) and weighted average $^{206}Pb/^{238}U$ (**c**, **d**), for laser ablation results obtained from titanite infilling amygdales and in the groundmass. Ages are given at 2σ confidence level. $^{40}Ar/^{39}Ar$ age, Ca/K, Cl/K and %$^{40}Ar^*$ spectra (**e**) and inverse isochron diagram (**f**) were obtained for actinolite from a metamorphosed andesitic lava (sample STP-8). Plateau and integrated ages are given at the 2σ confidence level; apparent ages of individual step and ellipses are given at the 1σ level.

Geochronological results

Celadonite separates from metabasites of the Lo Valdés Formation (Fig. 1) yielded K–Ar ages of 82 ± 3, 93 ± 3 and 109 ± 3 Ma (Table 1). Titanite infilling amygdales in a highly altered hyaloclastic andesitic rock (Lo Valdés Fm, sample GSII5A) and titanite in the groundmass of an amygdaloidal lava (Río Damas Formation, sample STP-8) were analysed; the former yielded a weighted mean $^{206}Pb/^{238}U$ age of 84.6 ± 4.4 Ma (2σ level; Fig. 3c, Table 1). In contrast, the small and anhedral titanite crystals within the groundmass yielded a weighted mean $^{206}Pb/^{238}U$ age of 108.0 ± 15.0 Ma (Fig. 3d, Table 1). Both ages are considered reliable, as they are in the range of the K–Ar ages obtained for metamorphic celadonite in the same rocks.

Four $^{40}Ar/^{39}Ar$ runs in two samples of amygdale-hosted actinolite of the Río Damas metabasites (sample STP-8) analysed yielded high-quality degassing spectra, giving unexpected plateau ages of 7.0 ± 3.0, 8.4 ± 1.6, 8.2 ± 0.8 and 8.7 ± 1.9 Ma (Fig. 3e, Table 1) and an inverted composite isochron age of 8.0 ± 1.4 Ma (Fig. 3f).

Significance of the age data and geodynamic implications

The U–Pb titanite ages seem to indicate two different metamorphic Cretaceous events, one at 108.0 ± 15.0 Ma and the other at 84.6 ± 4.4 Ma. The occurrence of these two events may also be supported based on the K–Ar dates for celadonite (Table 1). However, it is not clear whether the K–Ar age of 93 Ma has geological meaning, or if it represents a mixture of different mineral phases, or resetting as a result of thermal overprint. Further radiometric data are needed to determine if more than one Cretaceous metamorphic event is recorded in these metabasites; however, at the very least, the existence of Cretaceous metamorphism has been confirmed. Moreover, $^{40}Ar/^{39}Ar$ ages between 110 and 93 Ma are known for secondary mineral (K-feldspar and sericite) in rocks belonging to the Lower Cretaceous volcanic formation in the Coastal Range of central Chile at 33°S. These ages have been interpreted as representing a very low-grade burial metamorphic event that occurred under extensional conditions and partly contemporaneous with plutonic activity

(Fig. 1). An interval of *c*. 20–25 Ma exists between the volcanism and subsequent metamorphism (Aguirre *et al*. 1999; Wilson *et al*. 2003; Fuentes *et al*. 2005).

The inverted composite isochron age of 8.0 ± 1.4 Ma obtained from two ^{40}Ar/^{39}Ar runs of amygdale-hosted actinolite of the Río Damas metabasites clearly indicates that actinolite was not formed during the Mesozoic prehnite–pumpellyite metamorphic event. This suggests that a much younger metamorphic event could have been superimposed on the regional prehnite–pumpellyite Cretaceous pattern. Some microtextural relationships observed in thin sections would support partial replacement of pumpellyite by actinolite according to the reaction pumpellyite + quartz + chlorite = actinolite + epidote + H_2O. Moreover, chemographic and algebraic analysis suggests that the presence of actinolite is controlled by high-variance continuous reactions that produce actinolite + epidote at the expense of pumpellyite-(Mg) + minor chlorite, with excess albite, quartz and H_2O (Day & Springer 2005). In fact, the presence of actinolite together with prehnite + chlorite + epidote + pumpellyite is necessary to calculate the invariant CHEPPAQ point. In contrast, the disappearance of pumpellyite and the occurrence of actinolite mark the greenschist-facies boundary. However, as stated above, actinolite developed in a later, low-T event independent to the one responsible for the prehnite–pumpellyite-facies metamorphism. This result is of major relevance because actinolite was considered paragenetic with prehnite and pumpellyite in these Mesozoic volcanic rocks (Levi *et al*. 1989; Robinson *et al*. 2004), and hence thermodynamic modelling of that paragenesis was carried out with the principal aim of establishing $P–T$ conditions (minimum values 260 °C and 1.1 kbar; Robinson *et al*. 2004). According to the ^{40}Ar/^{39}Ar ages obtained for actinolite, this thermodynamic modelling based on the equilibrium actinolite–prehnite–pumpellyite–epidote–chlorite has no geological significance; calculated $P–T$ conditions and the assignment of that assemblage to the pumpellyite–actinolite facies are both incorrect. Moreover, thermodynamic modelling of the reaction pumpellyite + quartz + chlorite = actinolite + epidote + H_2O indicates T values around 300 °C for an assumed $P < 2$ kbar. Here we suggest that a thermal event associated with the intrusion of neighbouring Miocene granodioritic bodies, emplaced between 13 and 7 Ma (Fig. 1; SERNAGEOMIN 2003), may account for the local presence of actinolite and the partial obliteration of the metamorphic minerals formed during the Cretaceous. This late Miocene thermal event exerted only a local influence and is not related to the early Miocene regional, very low-grade metamorphism that affected the Cenozoic volcano-sedimentary units in central Chile at 15–22 Ma (Belmar 2000).

Conclusions

This geochronological research applies a methodological approach to dating very low-grade metamorphism in rocks of the Andes and reports *in situ* U–Pb age determinations of metamorphic titanite. The results from this study both enlarge and complement the ^{40}Ar/^{39}Ar data previously obtained for the Lower Cretaceous volcanic formations of the Coastal Cordillera west of Santiago. The main conclusions are as follows.

(1) One or two metamorphic event(s) occurred during the Early Late Cretaceous, which affected both the Upper Jurassic and Lower Cretaceous volcanic successions in the Andes. This is evidenced by the K–Ar and U–Pb ages (82 ± 3 and 84.6 ± 4.4 Ma; 108.0 ± 15.0 and 109 ± 3 Ma) and the age interval of the prehnite–pumpellyite metamorphism affecting similar Lower Cretaceous volcanic rocks exposed in the Coastal Range (*c*. 93–110 Ma, Fig. 1).

(2) The occurrence of a younger event, partly overprinting the Cretaceous paragenesis, is recorded by the 8 Ma age for the actinolite present in the metabasites of the Rio Damas Formation. This age conflicts with the 108 Ma date obtained for titanite present in assemblages of the same sample, and invalidates the former hypothesis of a pumpellyite–actinolite-facies metamorphism affecting the Rio Damas volcanic rocks.

(3) The ages obtained for the minerals analysed confirm the occurrence of regional, burial-type metamorphism during the Cretaceous; however, these do not result from the thermal overprint associated with the emplacement of granitoids, as all intrusions in this region of the Andes have a Miocene age.

(4) Cross-verification of metamorphic ages using both different minerals and chronometers helps to accurately decipher the formational histories of complex (very low-grade) metamorphic mineral assemblages. Moreover, we demonstrate the possibility of dating different low-grade metamorphic events within a single sample (e.g. STP-8).

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