

UNIVERSIDAD DE CHILE FACULTAD DE CIENCIAS FÍSICAS Y MATEMÁTICAS DEPARTAMENTO DE GEOLOGÍA

## UNDERSTANDING OF ACTIVE PINNACLES OF PORCELANA GEYSERS (NORTHERN PATAGONIA) BY MEANS OF MINERALOGY, HYDROGEOLOGY AND MICROBIOLOGY APPROACH

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

BÁRBARA SALOMÉ RUIZ VELÁSQUEZ

PROFESOR GUÍA: DIEGO MORATA CÉSPEDES

PROFESORA CO-GUÍA: LINDA DANIELE

MIEMBRO DE LA COMISIÓN: BEATRIZ DÍEZ MORENO

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"George, muy serio, observó: – No es ninguna broma. En realidad, el sistema de las cintas es malo. Con las cintas se aprende demasiado, y sin el menor esfuerzo. Los que se acostumbran a aprender de esta manera ya no saben hacerlo de otra. Sólo saben lo que les han inculcado las cintas. Pero si a una persona no se le facilitasen cintas, sino que se le obligase a aprender por sí sola desde el primer momento, en ese caso adquiriría el hábito del estudio, y no le costaría seguir asimilando conocimientos. Me parece que esta idea no puede ser más razonable. Una vez haya conseguido desarrollar bien esa costumbre, no niego que pueda aprender algunas cosas mediante cintas, para llenar ciertas lagunas o fijar algunos detalles. Luego seguiría progresando solo."

Profesión (1957). Cuentos Completos Vol. I - Isaac Asimov

#### Abstract

Porcelana Geysers is the only place known in the world with a system of active travertine pinnacles that are currently precipitating, because of this they can be considered a singularity. Another reason is because they are the only geysers registered in Patagonia, located in Los Lagos District, Chile, specifically on the slopes of the Barranco Colorado volcano, in the Huequi peninsula, where a high frequency of faults is present due to the convergence of the Arc oblique Long-lived basement (ALFS) and Liquiñe-Ofqui (LOFS) Fault Systems.

Inactive pinnacles (that are nor currently precipitating) are formed by a thick inner section formed by aragonite crystals and an external coverage made of calcite and silica associated to the presence of biofilms. In the paleo-duct of these pinnacles several zoned crystals of calcite are found.

The genesis of this singularity could be answered by clarifying the possible origins of the carbon that generates high ratios of  $HCO_3/Ca$ , greater than 2 in the thermal waters, showing that the calcium carbonate dissolution would not correspond to the main source of carbon. Stable carbon isotope ratios showed negative values with -3.6‰ and -1.4‰ VPDB on average for aragonite and calcite, respectively. These negative ratios are not usually common for carbonates with hydrothermal source of CO<sub>2</sub> and they are not negative enough to be solely attributed to soil processes. By the study of the conditions of the paleo-fluids that generated the travertine precipitation, intermediate values of  $\delta^{13}C_{\text{(original CO2)}}$  were obtained, with a range from -15.1 to -9.4% VPDB, which indicates that CO<sub>2</sub> gas that participated in carbonate precipitation had a mixed origin, formed by an atmospheric and a magmatic or deep source. This was corroborated by high Ar/He and N<sub>2</sub>/CO<sub>2</sub> ratios measured in geysers gases corresponding to an atmospheric influence; while thermal water geochemistry suggests magmatic/deep, meteoric and fjord sources. Negative values of redox potential and high B/CI, F/CI, Rb/CI and Cs/CI ratios support a magmatic/deep source; on the other hand, Na/CI, Br/CI and Sr/CI ratios that are similar to those measured in the fjord, while  $\delta^{18}$ O and  $\delta$ D show a meteoric source. The oscillations of these conditions over time are registered in zoned calcite crystals founded in the internal conduit of fluid emission of inactive pinnacles that agree with the variations of redox potential values measured in thermal waters.

The inactive cones have much higher resistance respect to active pinnacles that showed great height changes within a period of just one year. The main differences were that active pinnacles lack a calcite-silica coverage and they have much lesser biotic presence. Also, temperatures of the water that precipitated the inner section of all pinnacles were warmer (73.8°C) than those that formed by calcite in their external coverage (69.5°C) and distal calcite deposits (68°C). The bacterial presence correlates both calcite deposits both calcite deposits are correlated between.

Therefore, the reasons why these geysers can precipitate high and resistant travertines is due to the high CO<sub>2</sub> input from mixed sources (atmospheric and volcanic) and to the coexistence of bacteria processes.

#### Resumen

Los Géiseres de Porcelana corresponden al único lugar conocido en el mundo con un sistema de pináculos de travertino activo, por lo que pueden considerarse una singularidad geológica. Estos son los únicos géiseres registrados en la Patagonia, ubicados en la Región de Los Lagos, Chile, específicamente en las laderas del volcán Barranco Colorado, en la península de Huequi, donde existe una alta frecuencia de fallas y estructuras tectónicas debido a la convergencia de Sistemas de Fallas reactivadas de basamento de larga vida (ALFS) y Liquiñe-Ofqui (LOFS).

Los pináculos inactivos están constituidos por una sección interna gruesa formada por cristales de aragonito y una cobertura externa hecha de calcita y sílice asociada a la presencia de tapete microbiológico.

La génesis de esta singularidad podría aclararse estableciendo los posibles orígenes del carbono que genera altas razones de HCO<sub>3</sub>/Ca en las aguas termales, (>2), lo que demuestra que la disolución de CaCO<sub>2</sub> no correspondería a la principal fuente de carbono. Las razones isótopos estables de C mostraron valores negativos con promedios de -3.6% y -1.4% VPDB para aragonito y calcita, respectivamente. Estas razones negativas son comunes para los carbonatos con una fuente hidrotermal de CO2 y tampoco pueden relacionarse directamente con un componente del suelo porque no son suficientemente negativos. Mediante el estudio de las condiciones de los paleo-fluidos que habrían precipitado el travertino, se obtuvieron valores intermedios de  $\delta^{13}$ C del CO<sub>2</sub>, con un rango de -15.1 a -9.4‰ VPDB, lo que indica que el CO<sub>2</sub> tenía un origen mixto, formado por una fuente atmosférica y una magmática/profunda. Esto fue corroborado por altos índices Ar/He y N<sub>2</sub>/CO<sub>2</sub> medidos en gases de los géiseres correspondientes a una influencia atmosférica; mientras que la geoquímica de aguas termales sugiere fuentes profundas, meteóricas y de fiordos. Los valores negativos de potencial redox y las altas relaciones B/CI, F/CI, Rb/CI y Cs/CI respaldan una fuente magmática/profunda; por otra parte, las relaciones Na/Cl, Br/Cl y Sr/Cl son similares a los medidos en el fiordo, mientras que  $\delta^{18}$ Ο y  $\delta$ D muestran una fuente meteórica. Las oscilaciones de estas condiciones a lo largo del tiempo se registran en cristales de calcita zonados que se encuentran en el conducto interno de emisión de fluidos de los pináculos inactivos que coinciden con las variaciones de los valores de potencial redox medidos en aguas termales.

Los conos inactivos tienen una resistencia mucho mayor con respecto a los pináculos activos, los que mostraron grandes cambios de altura entre un año y otro. Las principales diferencias fueron que estos últimos carecen de una cobertura de calcita-sílice y tienen una menor presencia biótica. Además, las temperaturas del agua que habría precipitado la sección interna de los pináculos habrían sido más cálidas (73.8°C) que las que formaron calcita de la cobertura externa (69.5°C) y depósitos de calcita distal (68°C). Estos dos últimos estarían correlacionados entre ellos por la presencia bacteriana.

Por lo tanto, las razones por las que estos géiseres pueden precipitar travertinos altos y resistentes se deben a un fuerte aporte de CO<sub>2</sub> de fuentes mixtas (atmosférica y volcánica) y la coexistencia de procesos de bacterias.

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#### 1 Introduction

Precipitation around hot springs is controlled by several of intrinsic and extrinsic factors that are still, in many respects, poorly understood. Calcium carbonate precipitated in spring pools could be related to numerous complex factors, including water temperature, pH, geochemistry, calculated saturation indices, CO<sub>2</sub> degassing rates, and isotope rates (Renaut and Jones, 1997; Guo and Riding, 1998; Bonny and Jones, 2003; Peng *et al.*, 2010; Hailei *et al.*, 2012; Peng and Jones, 2013; Zhang *et al.*, 2014) and also biological variables, in particular bacteria (Pentecost, 2003; Okumura *et al.*, 2011, 2013; Kawano and Obokata, 2007; Fouke, 2011; Della Porta *et al.*, 2015). In many cases the biotic presence is related to the precipitation process, driven by photosynthesis, mutual influence between different organisms or their interaction with liquid and solid phases, generates new textures in the final carbonate deposits.

Porcelana Geysers are located in Northern Patagonia, where no other geysers are known. The study area is a singular geothermal manifestation where several travertine deposits, some of them with pinnacle morphologies, are currently active which makes them unique in the world. These travertine pinnacles or cones reach heights above 2 metres in some cases, which counteracts even the erosive effects of the climate of this zone of Patagonia, where high annual rainfall averages about 2,000 mm have been measured (Figure 1.4; DGA, 2017; INE, 2017). Porcelana geysers is located at on the northern coast of the Huegui peninsula, in Los Lagos District, about 2 kilometres from Comau fjord shore, more specifically in the northern bank of the Punta Calle River. The geysers rise at temperatures above 80°C through aligned fractures in diorites rocks which seem to drive the river incision. On the opposite river bank, a small thermal spring outflows at lower temperatures, in correspondence of hydrothermal breccias with no carbonate deposit. Another thermal spring called Punta Calle is found about 700 metres downstream in the southern river bank, with an average temperature of 53.4°C. According to their chemical composition, the thermal waters and Porcelana Geysers could have a common origin.

Despite Porcelana Geysers are called "geysers" it is important to take into account that a "geyser" is defined as a thermal water in which the eruptive activity is induced by boiling at depth that forces the fluid outflow through the duct intermittently over an exhaust system (Bryan, 2008; Glennon and Pfaff, 2005; Peterson, 1959; White, 1967). However, Porcelana Geysers present a constant flow of gas and liquid, which is why they should be strictly called "perpetual spouters" or pulsating springs (Bryan, 2008; Allen and Day, 1935; White, 1967). In spite of the aforementioned, they can still be called "geysers", since it can be considered that the pulses occur in a very high or low frequency that is not visible to the naked eye or at human scale, thus this is the way they will be called in this study and the way they are popularly recognized.



#### 1.1 Travertines

Travertines are defined as chemically precipitated continental carbonates, regardless of the temperature of the water, accumulated around seepages, slopes, estuaries and rivers, and occasionally lakes (Pentecost and Viles, 1994). This precipitation is derived from the evasion or invasion of CO<sub>2</sub> from or to a groundwater source, leading to a supersaturation of calcium carbonate, with or without biogenic

influence (Della Porta, 2015; Pentecost, 2005). Calcium carbonate deposits are very common in the terrestrial environment, especially in areas with surface thermal waters, as in Porcelana Geysers, where the contribution of CO<sub>2</sub> comes from geothermal processes and travertine is precipitated by the fluids, thus these deposits can be classified as "thermogenic travertines" (Jones and Renaut, 2010).

Several factors that favour the increase in the precipitation rate are found in hydrothermal environments. Considering that the predominant thermodynamic factor to generate a high rate of calcium carbonate precipitation corresponds to the high degassing of carbon dioxide from thermal waters (Pentecost, 2005), high temperatures, high gas concentration, low hydrostatic pressure, turbulence and bubble formation, which increase the exposure surface of the flow, correspond to triggers that increase the insolubility of CO<sub>2</sub> (Ladd and Ryan, 2016; Pentecost, 2005; Roy and Ryan, 2013; Ryan *et al.*, 2000).

According to the variation of those factors, carbonates present varied morphologies at small and large scale (Della Porta, 2015; Fouke et al., 2000; Jones, 2017; Pentecost, 2005; Pentecost and Viles, 1994), but there are few documented cases that show conical morphologies such as those present in Porcelana Geysers. So far no deposits have been found with similar characteristics within the country or within South America, however, one of the few exceptions in the world corresponds to the travertines of the Mammoth Hot Springs, Yellowstone National Park, USA, where a cone of 14 meters high stands out. This was built through the precipitation of calcium carbonate with the addition of siliceous volcanic ash that together with the bacterial activity during its genesis would be the causes of its morphology (Fouke, 2011). Additionally, in China it is possible to find some similar examples, like the travertines from Rongma Hot Springs, located in the northern Tibet, whose precipitated cones have dimensions and shapes similar to those of Porcelana Geysers but, unlike these, all of them are inactive, like the cone from Mammoth Hot Springs (Gao et al., 2013); or the case of the Jifei Geothermal Field, from Yunnan Province, southwestern China, also known as the "Female Tower" vent that has an inactive travertine cone formed by greater spring activity in the past, which is characterized by the presence of sulphur-oxidizing bacteria (Jiang et al., 2017).

Since the bacterial presence usually affects these aspects and the growth of travertine deposits product of cellular respiration and photosynthesis processes in many cases (Capezzuoli *et al.*, 2014; Della Porta, 2015; Fouke *et al.*, 2003; Okumura *et al.*, 2011, 2013), the favourable conditions mentioned above could be promoted by the presence of biotic diversity, which increases the amount of  $CO_2$  disposed in the hydrothermal fluid and releases pre-bonded HCO<sub>3</sub><sup>-2</sup> and Ca<sup>2+</sup> promoting the precipitation of these travertines.

Stable carbon isotope ratios in carbonates

Carbonate deposits record the carbon isotope ratios generated by isotopic fractionation according to the precipitating agents that participate during its precipitation, which can be both inorganic and organic (Della Porta *et al.*, 2015; Della Porta, 2015; Jones

and Peng, 2014; Kanellopoulos, 2012; Fouke, 2011; Jones and Renaut, 2010; Pentecost, 2007; Pentecost, 2005; Friedman, 1970). Isotopic fractionation allows to correlate different ranges isotope ratios with various agents and sources that can be contributing to the carbonate deposition. The negative values reflect the contribution of soil respired carbon dioxide and biogenic processes involved in carbonate precipitation (Jones and Peng, 2014; Radha *et al.*, 2010), while thermogene travertines values are displaced to more positive values with median is 4.3‰. However, there is no well-defined mode, because 90% of the travertines fall within the range –1 and +10‰ (Della Porta, 2015; Pentecost, 2005; Craig, 1953); this becomes necessary to analyse the carbon isotope ratios from the water and original CO<sub>2</sub> gas that were involved in the carbonate precipitation of each deposit and compare to the values of known sources (Minissale, *et al.*, 2002).

In this way, it is possible to assess the main carbon source contribution generated by magmatic source, limestone decarbonation reactions (Turi, 1986; Pentecost 1995) or if there is some biotic influence generating high resistant and, therefore, the morphology of the travertine pinnacles of Porcelana Geysers.

#### 1.2 Groundwater mixing processes

It is very common that mixing processes among different sources of fluids (magmatic, hydrothermal, and meteoric) occur in groundwater. Due to that is not easy to assess all the fluid circulation model without an extended and complete geochemical data of all end-members.

Mixed origin of the fluids are reflected in changes of major and trace elements, physicochemical conditions and isotopic ratios present in the fluids, such as  $\delta^{13}$ C,  $\delta^{34}$ S,  $\delta^{7}$ Li or  $\delta^{11}$ B, which may derive from a magmatic, metamorphic, meteoric, biogenic, marine or lithological source or more likely from a mixture of them (Nicholson, 1992; Giggenbach, 1992; Pichler, 2005; Pichler *et al.*, 1999; Richard *et al.*, 2019; Stefánsson *et al.*, 2015; Purnomo *et al.*, 2016; Pistiner and Henderson, 2003).

The Porcelana Geysers rise in a peninsula with the presence of three volcanoes and surrounded by fjord waters. Thus some possible source could be meteoric, magmatic and marine or a mixed of all them.

#### 1.2.1 Meteoric and hydrothermal contribution

When a relevant meteoric input is feeding a groundwater system, stable isotope  $(\delta^{18}O, \delta D \text{ and } \delta^{16}C)$  ratios are often used to evaluate the isotopic fractionation that occurs in water and carbon cycles. These isotope ratios are fractionated by water cycle (in particular boiling) as a mass-dependent process (Gat and Gonfiantini, 1981; Li and Garzione, 2017) and by the rocks composition considering volcanic or deep interactions. Hydrogen isotopic fractionation occurs also due to deuterium escape from the atmosphere following the photo-dissociation of water molecules in the upper atmosphere (Suess, 1953), converting the atmospheric and meteoric environment into a medium depleted in deuterium.

Stable oxygen and hydrogen isotope ratios are seen as natural tracers, since they form the water molecules (Kendall and McDonnell, 1998). The isotope ratios in sampled water represent the relative difference of their values with respect to the ratios of heavy/light isotopes of a sample of a standard water, the Vienna Standard Mean Ocean Water (VSMOW) (Craig, 1961; Gonfiantini *et al.*, 1995). In order to detect a meteoric or different contribution, these values must be compared to local rainwater stable isotope ratios to identify additional processes.

In the case of volcanic zones it is common to find some mixing processes between hydrothermal and magmatic gases in the groundwater circulation (Begué *et al.*, 2017; Giroud, 2008; Nuccio *et al.*, 1999; Giggenbach, 1992; Henley and Ellis, 1983), with an important meteoric component.

Volcanic gases are mainly composed by H<sub>2</sub>O, CO<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S, HCI, native S, HF, H<sub>3</sub>BO<sub>3</sub>, HBr, CH<sub>4</sub>, Ar, O<sub>2</sub>, Ne, H<sub>2</sub>, He, CO (Tamburello *et al.*, 2015; Shinohara and Witter, 2005; Sepúlveda *et al.*, 2007; Tassi *et al.*, 2009).

Thus, even though stable isotope ratios in water are an undeniable tool to identify sources different from meteoric one. The geochemical composition of the gas emitted by a geysers system also helps to identify the existence of a meteoric or magmatic source by deep gas input. Ar and N<sub>2</sub> contents can be derived from the atmosphere or meteoric water saturated with air. Additionally, the helium concentration in air is very low, so its presence must be explained from magmatic or crustal sources, the same occurs with CO<sub>2</sub> inputs.

Carbon dioxide is a good tracer recording the variations of stable carbon isotope ratios in all fluids, produced mainly by mass-depending fractionation and temperature changes. Specifically, gas  $\delta^{13}$ C ratios can be classified according to the main source (Figure 1.2). Therefore,  $\delta^{13}$ C<-20.0‰ is almost entirely related to a biogenic source of CO<sub>2</sub>, while -7.0< $\delta^{13}$ C<-4.0‰ is characteristic of mantle CO<sub>2</sub> and -2.0<  $\delta^{13}$ C<-4.0‰ is commonly found in gases from a hydrothermal source (Minissale *et al.*, 2002; Rollinson, 1993; Deines *et al.*, 1974; Rose and Davisson, 1996).



Figure 1.2. Various sources of CO2 with different carbon isotope ratios belonging to Tiber Valey, central Italy (obtained from Minissale et al., 2002).

Regarding hydrothermal and magmatic contributions, some trace elements commonly present in hot fluids tend to show higher concentrations in the final upwelling water compared to other surface waters, as B, Br, As, F, Hg, Cs and Rb. In particular, B and Br are good tracers because they are conservative as chloride, and additionally because of the volatile behaviour of their common species (Risacher *et al.*, 2011; Giroud, 2008; Aiuppa *et al.*, 2005; Vengosh, 2003; Aiuppa *et al.*, 2002; Giggenbach, 1991; Glover, 1988).

Absolute concentrations may vary due to dilution with freshwater occurred during the flow to the upwelling zone, therefore the ratios of constituents are preferred to search for possible sources because they are lesser affected during fluid transport. However, chemical reactions, such as boiling, precipitation, dissolution and ion exchange may change ionic ratios, in this case, it is recommended to compare the variation of concentrations of some abundant ions (such as CI and HCO<sub>3</sub>) between known end-members (Richter and Kreitler, 1993).

#### 1.2.2 Marine contribution

Although many hot springs outflows in a continental environment, several studies have recognized seawater feeding continental systems and thermal waters (Risacher *et al.*, 2011; Giroud, 2008; Custodio, 2010; Park *et al.* 2012; Sebben *et al.*, 2015; Negri *et al.*, 2018), even at great distance from coastline.

This marine recharge is usually related to high permeability zones that connect coastal areas with groundwater systems. High permeability is favoured by faults presence (Adler *et al.*, 2013), and depending on the fault and fractures geometry, the extension of the sea-freshwater interface is generated in different ways (Sebben *et al.*, 2015):

*Vertical fractures:* The mixing zone thickness is increased only when the fractures are in contact with seawater edge.

*Horizontal fractures:* The seawater edge is pushed offshore in the deep portion of the aquifer. Whereas fractures intersect the discharge zone of meteoric waters tend to enhance inland extent of the wedge.

*Inclined fractures:* When these are approximately parallel to sea-freshwater interface, marine influence extend inland. Otherwise, when the fractures are perpendicular to the interface this is inhibited.

The identification of a marine contribution can be assessed using an analysis f major and trace elements analysis: (i) observing chlorides concentration present in endmembers, (ii) comparing element contents respect to temperatures values and, in particular, (iii) calculating ion-chloride ratios selecting those ions that are highly present in seawater (Negri *et al.*, 2018). Thus, high presence in groundwater *a priori* could indicate a marine intrusion if they also show similar ratios among them as it was explained above. The ions that usually have highlighted concentrations in the seawater are CI and Na (both as NaCI), Mg, S, K, Ca, Br, B, Sr, F, Rb, Cs, I and Ba (

Table 1.1), which have higher concentrations respect other elements of similar atomic weight (Turekian, 1968).

Element	Symbology	Atomic weight	Concentration
			ppm
Sodium	as NaCl	22.9898	10,800
Chlorine	as NaCl	35.453	19,400
Magnesium	Mg	24.312	1,290
Sulfur	S	32.064	904
Potassium	К	39.102	392
Calcium	Ca	40.08	411
Bromine	Br	79.909	67.3
Lithium	Li	6.939	0.170
Boron	В	10.811	4.450
Fluorine	F	18.998	13
Rubidium	Rb	85.47	0.120
Strontium	Sr	87.62	8.1
lodine	1	166.904	0.064
Cesium	Cs	132.905	0.0003
Barium	Ва	137.34	0.021

Table 1.1. Chemical composition corresponding to main elements present in the seawater at 3.5% salinity (obtained from Turekian, 1968).

#### 1.3 Geologic background

Plate boundaries frequently generate complex accommodation fault systems which act like weakness zones that facilitate the ascent and infiltration of fluids (Person and Baumgartner, 1995; Kerrick, 2001; Minissale, 2004; Sánchez et al., 2013; Tardani et al., 2016). Porcelana Geysers are located in the Los Lagos District (42° 25'S, 72° 30'W), belonging to the southern zone of continental Chile (Figure 1.1), where the tectonic geometry is due to the subduction of the Nazca plate under the South American plate that favours the fusion of rocks located at the base of the continental crust and the upper part of the mantle generating its consequent rise, which makes this territory an area with a high frequency of thermal anomalies. In the case of Los Lagos District, these are numerous, located in the South Volcanic Zone (ZVS: 33° - 46 °S), specifically at its southern end (Stern, 2004; Stern et al., 2007). The permanent stress caused by subduction generates the formation of large fault systems with dynamics adapted to the subduction conditions, which directly influence the location of fluids, both magmatic and hydrothermal. Two major tectonic structures define the study area (Figure 1.3), one corresponds to a NNE-SSW trending dextral-reverse faults of the Liquiñe-Ofqui Fault System (LOFS) (Cembrano et al., 2000; Cembrano and Lara, 2009). Since this fault system is produced by oblique stress, there are transtensive basins that allow fluid ascent (Cembrano and Lara, 2009). The second group consists of WNW-ESE trending, primarily sinistral faults of the Arc oblique Long-lived basement Fault System (ALFS) that were formed by the reactivation of pre-Andean faults (López-Escobar et al., 1995; Lara et al., 2006; Rosenau et al., 2006; Sánchez et al., 2013). Regarding the high permeability that is generated by high frequency of faults and fractures, Los Lagos District stands out for its numerous representations of volcanic and hydrothermal activity, where there are more than 15 volcanoes and 36 thermal water sources (Hauser, 1997; Ruiz and Morata, 2016; Ruiz, 2015; Risacher et al., 2011).

In particular, Porcelana Geysers zone is located along an intersection of both fault systems, LOFS and ALFS, that put two different lithologies in contact: the North Patagonian Batholith (NPB), which consists of tonalites and granodiorites from the Upper Jurassic and Lower Cretaceous; and lava and pyroclastic and laharic deposits of Pleistocene (Rosenau, *et al.*, 2006; SERNAGEOMIN-BRGM, 1995; SERNAGEOMIN, 2014; Ruiz, 2015).

The Huequi peninsula has three important volcanoes (Figure 1.3), one of them, Huequi volcano, has been recognized as an active system but the rest, Porcelana and Barranco Colorado volcanoes, do not have published research and are catalogued as inactive. Nevertheless, the entire peninsula and fjord seem to be formed over fault systems, which would be connecting these three volcanoes, for this reason the existence of a large volcanic connected system cannot be discarded. Because Porcelana Geysers are found in the foothills of the Barranco Colorado volcano and the high frequency of faults in the peninsula, it is presumed that very mixed sources could be participating in the formation of its thermal fluids, with volcanic and fjord components, both due to its



proximity, and with an atmospheric input due to the high permeability generated by high frequency of structural faults.

Figure 1.3. Local geology of southern end of the Comau fjord (modified from SERNAGEOMIN, 2014). Por: Porcelana Geysers; HS: Punta Calle Hot Springs; CHS: Comau Hot Springs; PHS: Porcelana Hot Springs.



Figure 1.4. Annual rainfall averages per month of Los Lagos District (measured at the Puerto Montt weather station) (DGA, 2017; INE, 2017).

### 1.4 Objectives of the study

The main aim of this thesis is to generate a model of travertine formation recognizing different sources that recharge the water system including the participation of coexisting biota in the precipitation of calcium carbonates.

To obtain this final model it is necessary to carry out the following objectives:

i. Obtain the characteristics of the fluids that allowed the precipitation of the existing pinnacles and other carbonate deposits and compare them with the current conditions of the fluids that are present in the area.

ii. Recognize ionic ratios that may be important in the geochemical composition of surface waters found in the area, especially those that can be related to the carbonate anomalous deposition and the source of its carbon dioxide.

iii. Obtain a record of the activity of the Porcelana Geysers in different years, specifically their superficial physicochemical characteristics.

iv. Identify the relations between biotic presences and carbonate deposits of the studied area and obtain a distribution of this biota around the geysers zone.

## 2 Methods

For the development of this study the following methods were used: (1) sampling and analytical procedures (water, carbonate, gas and microbiologic samples), (2) analytical and geochemical tools (major and trace elements, stable isotope ratios), (3) calculation of carbon and oxygen isotope ratios, and (4) estimation of the carbon isotope ratio of  $CO_2$  gas from travertine data.

## 2.1 Sampling and analytical procedures

Different samples were collected in the studied area, trying to include all the aspects in which the geothermal system influences or leaves a record: hot and cold surface waters, carbonate precipitated from hot water, river and fjord water, geothermal gas and organic mat present in the same places as carbonate deposits and hot water tables.

Some physicochemical parameters were measured *in situ* in surface waters from the study area: temperature, pH, electric conductivity and reduction potential. According to these parameters and the observable characteristics in the area, different places were chosen to collect water, travertine, steam and microbiological samples, specifically as follow.

### 2.1.1 Water samples

Five points in the studied area were selected to be measured and sampled, classified by surface temperature and type of water. Major, minor and trace elements were analysed as well as the silica concentration and the ratios  $\delta^{18}$ O,  $\delta D \delta^{13}$ C, for geothermal waters, rivers and fjords. The geothermal water that is present in the studied area is found as 3 different springs, (1) an upwelling of water and gas with the highest measured temperature (85.2°C) sampled in 2014, 2016 and 2017, (2) another one with an intermediate temperature (65.7°C) sampled in 2016, and a warm spring pool (56°C) sampled in 2016 and 2017. Respect to cold waters, Punta Calle River was sampled in 2014, 2016 and 2017, and also water from Comau Fjord was collected in 2014 from the middle of the fjord from a boat.

The bottles were previously washed and rinsed with purified water by reverse osmosis and with ultrapure water (Milli-Q®). Finally, they were dried at room temperature. The bottles for the analysis of cations and trace elements were additionally treated with nitric acid Suprapur® for 48 hours and rinsed again with purified and ultrapure water several times.

On field, all samples were filtered using 0.45  $\mu$ m Millipore filters, they stayed unacidified for anion analysis, and were acidified with HNO<sub>3</sub> (Suprapur®) only for cations and trace elements analysis. Additionally, unfiltered samples were collected for isotopic analysis. All samples were stored from the field to the laboratories at 4 °C.

The samples that were collected in 2014 were analysed in the chemical laboratory of Chilean National Geology and Mining Service (SERNAGEROMIN) and those collected in 2016 and 2017 were sent to the laboratories of the Andean Geothermal Centre of Excellence (CEGA).

The analysis made at CEGA laboratories were performed by the use of:

- a) Anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Br<sup>-</sup> and NO<sub>3</sub><sup>-</sup>): Ion Chromatography (IC) Thermo Scientific Dionex ICS-2100, which has a detection limit of 0.03 mg/L.
- b) Cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>3+</sup>): Atomic Absorption Spectrophotometry (AAS, Perkin-Elmer PinAAcle 900F) with detection limits of 0.05, 0.12, 0.15 and 0.003 mg/L, respectively.
- c) Trace elements (Li, B, Sr): Inductively Coupled Plasma Mass Spectrometry (ICP-MSQ), Thermo Scientific (Thermo iCAP Q), with detection limits of 0.20, 0.07 and 0.001 ppb respectively.
- d) Bicarbonates (HCO<sub>3</sub><sup>-</sup>) and pH: Volumetric Titration using Giggenbach and Goguel (1989) method.
- e) pH: Automatic titrator Hanna HI-902C, with a precision of ±0.001 pH.
- f) Silica (SiO<sub>2</sub>): Portable Photometer for measurement of silica Hanna Instruments HI 96705, with detection limits of 0.03 mg/L and a precision of ±3%.
- g) Stable isotopes: analysis was carried out in the Estación Experimental de Zaidín (CSIC, Spain).  $\delta^{18}$ O and  $\delta^{2}$ H were analysed by Finnigan Delta Plus XL mass spectrometer. Oxygen isotopes were measured using the CO<sub>2</sub>-H<sub>2</sub>O equilibration method (Epstein and Mayeda, 1953). Hydrogen isotopic ratios were determined from H<sub>2</sub> after the reaction of 10 ml of water with metallic zinc at 500°C (Coleman *et al.*, 1982). The experimental error was ±0.1% and ±1.1% for  $\delta^{18}$ O and  $\delta^{2}$ H values, respectively.

### 2.1.2 Carbonate samples

Big deposits of calcium carbonate rises in the northern bank of Punta Calle River, presenting various morphologies and mineral compositions (mainly aragonite and calcite). Thus, pinnacles and cascades were sampled both inactive and active deposits as follows:

a) Inactive pinnacle: One inactive pinnacle was selected to be sampled in 2016, it was a small specimen (30 cm long approximately) and it was stored into a rigid plastic box to be carried to the laboratory, where a cross section was obtained. The cross

section allows to observe the concentric layers of different colours which were isolated with the use of a rotary tool for geochemical and optical analysis.

- b) Active pinnacle: Small pieces (about 1 cm diameter) were collected in 2018 from a short new active pinnacle, with continuous discharge of gas and water. These pieces were removed from the top, the middle section and the bottom of the pinnacle, and they were stored and sealed in new plastic bags.
- c) Wall cascades: Small pieces from carbonate efflorescence were collected in 2018 from different curved surfaces covering the rock walls. They were also stored, as well as the pieces of the active pinnacle.

The samples were subjected to various analysis in different laboratories:

- 1) X-ray diffraction: The layers of the inactive pinnacle were sent to Crystallography and X-ray Diffraction Laboratory of the Department of Physics of the University of Chile, using a diffractometer Siemens model D5000 for crystalline powder of Bragg-Brentano geometry with Cu radiation of 1.5406 A. The measurements were made at a sweep speed of 0.02% with a tube power of 40 kV and 30 mA. Then, the results were analysed by using the software XPowder and the database file *PDF2.dat* of the 'The International Centre for Diffraction Data (ICDD)'.
- 2) Stable isotopes: All carbonate samples were powdered until <200 μm into a clean porcelain mortar. δ<sup>18</sup>O (V-PDB) and δ<sup>2</sup>H (V-SMOW) values were determined in 2016 using a Finnigan DELTAplus XP mass spectrometer at the Stable Isotope Laboratory of the Instituto Andaluz de Ciencias de la Tierra CSIC-UGR (Granada, Spain). In 2018 active and inactive pinnacle samples and cascade deposits on rock walls were taken to the chemical laboratory of the Department of Earth Science of the University of Milan (UNIMI) in 2018, were a Delta V Advantage isotope ratio mass spectrometer (IRMS) was used with a precision of 0.006‰. These samples were cleaned with helium injection and acidified with H<sub>4</sub>PO<sub>3</sub> at 70°C for 1 hour. Finally, helium was hydrated and removed as water, while CO<sub>2</sub> was collected to be analysed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Final δ<sup>18</sup>O (V-PDB) and δ<sup>2</sup>H (V-SMOW) values were calculated using Kim *et al.* 2007 and Paul *et al.* 2007 equations.
- 3) Cathodoluminescence (CL): Thin sections were obtained from the inactive pinnacle in rock laboratory of the Department of Geology, University of Chile, and they were



Figure 2.1. (a) Weight and distribution of all powdered samples and carbonate standards, with an amount of 100 mg per glass tube, for IRMS analysis. (b) Samples with  $H_4PO_5$  solution being heated in the IRSM.

analysed by optical cathodoluminescence in the microscopy laboratory of the Department of Earth Sciences, University of Milan (UNIMI).

- 4) Microprobe: Inactive pinnacle thin sections were analysed using a microprobe SuperProbe Electron Probe Microanalyzer (EPMA), JEOL 8200 Super Probe JXA-8230 belonging to Department of Earth Science of the University of Milan (UNIMI), with a detectable element range of 4Be to 92U, and detectable wavelength: 0.087 to 9.3 nm.
- 5) Scanning Electron Microscopy (SEM): Carbonate samples displayed as thin sections and small pieces were covered by graphite by a Scan COAT SIX to be analysed by a Scanning Electron Microscopy (SEM), Cambridge Stereoscan 360 LaB6, with Energy Dispersive X-Ray Spectroscopy (EDS), EDS Link ISIS Microanalysis, in the Laboratory of Electron Microscopy and Microanalysis of the Department of Earth Science of the University of Milan.

#### 2.1.3 Gas samples

An isolated point was chosen at the top of a growing travertine pinnacle, actively precipitating, with high gas flow to be sampled in 2017. Different materials were needed to perform the sampling for non-condensable gases analysis. Giggenbach bottles (with a valve) were prepared in the laboratory before field work, as it follows.

The volume of the glass bottles was calculated measuring their weight by filling them with purified water, then they were prevailed and filled with sodium hydroxide Suprapur® 4.0 N solution (1/3 of the bottle volume). Later they were completely emptied, except for NaOH solution. To reduce the risks of air intake, the nozzles were filled by ultrapure water Milli-Q® and covered with plastic paraffin film.



On field, each bottle was connected to a sterile silicone tube 1.8 m long, which was also connected by the other end to a plastic funnel. The funnel covered the upper half of the spitting pinnacle and its edges were covered by local warm mud, to avoid the entry of atmospheric air.

Figure 2.2. Emptying of Giggenbach bottle (right) with a vacuum pump (left).

Finally, the valve was opened slowly until the bottle was filled and no more gas entered, wrapped with paper towel, moistened with ultrapure water Milli-Q®. Glass bottles was stored in a padded box.

Three bottles were carried to the study area but only one bottle was correctly filled, because the atmospheric air entered inside the second one and the third bottle broke.

The only bottle with sample was sent to the laboratories of the Andean Geothermal Centre of Excellence (CEGA) and the non-condensable gases of the gas sample were analysed. This analysis was performed with a Gas Chromatograph Agilent Technologies 7890A modified with injection system for volcanic gases and Wasson-ECE Instrumentation additional oven, two thermal conductivity detectors (TCD) and a flame ionization detector (FID).

#### 2.1.4 Microbiologic samples.

Abundant organic mat was found in the carbonate deposition area (northern bank of Punta Calle River). To look for biologic interaction between carbonates and their precipitation process, many samples of organic mat and carbonate were collected.

To be able to recognize the possible microorganisms, two sample duplicates were taken for each carbonate type texture and visible organic mat, for DNA analysis and microscopic observation.

- a) DNA analysis: Samples were taken with metal spoon, previously rinsed with ethanol. Each carbonate and mat sample were stored in a cryotube and submerged in the own geothermal water or RNA*later* solution (1 – 1.5 mL), respectively, to stabilize and protect cellular RNA in situ in unfrozen specimens without jeopardizing the quality or quantity of RNA. The suffix "L" was added at the end of the code of these samples.
- b) Microscopic observation: Samples were also taken with metal spoon (previously rinsed with ethanol) and were stored in cryotubes with 2.5% glutaldehyde solution

dissolved into with Milli-Q® water. These tubes were transported under dark and cold conditions (4°C).

This samples were sent to the laboratories of the Department of Molecular Genetics and Microbiology of the Pontifical Catholic University of Chile, in charge of Dr. Beatriz Díez. They were analysed by the researcher Jaime Alcorta.

From an organic mat sample that was grown in BG-11 medium at room temperature, two subcultured populations were separated, corresponding to a green and a purple population that could be separated by serial dilution (Figure 2.3). The culture medium is BG-11-NO<sub>3</sub> except in the last well, where BG-11-0 is used, which lacks a combined nitrogen source.



Figure 2.3. Culture in a multiple plate. In A is shown the culture of cyanobacteria from green colonies of Porcelana Geysers. In B the cultivation of cyanobacteria from purple colonies is shown. M indicates manual disintegration and homogenization, while a S indicates a sonicator treatment.

Two extraction protocols were used according to the type of sample: xanthogenate buffer for organic mats and the PowerSoil® DNA isolation kit (Qiagen) for carbonates.

DNA quantification was performed using a spectrophotometer (NanoDrop®, Thermo Scientific) and a fluorometer (Qubit®, TermoFisher). Many of the results delivered by the spectrophotometer indicated a low DNA content, with low purity values for the presence of sugars and phenol (most samples with a ratio of 260/230 (sugars) and 260/280 (phenol) less than 1.8). In the analysis by the fluorometer, many of the data showed values of <1  $\mu$ g/mL. For polymerase chain reaction (PCR) to increase the specific amount of DNA from the region of the ribosomal gene 16S rRNA, universal primers for bacteria 358F-GC and 907R were used. Checking of the product of the PCR was made by visualizing of agarose gel and staining with GelRed® (Biotium).

With the aim of separating the fragments of the amplified gene, a Denaturing Gradient Gel Electrophoresis (DGGE) was made. This is made according to the resistance of the fragments to denaturation along the gradient (the separation of the double strand of DNA), which is dependent on the sequence or the content of G+C (amount of differential hydrogen bonds for hybrid pairs GC = 3 or AT = 2). For the 6% acrylamide electrophoresis

gel a gradient of 50 to 75% denaturation was performed, which is used for general bacterial samples.

For future reamplification and sequencing for the identification of populations, some bands were cut and eluted in nuclease-free water.

#### 2.2 Analytical and geochemical tools

Major elements were plotted in different binary and ternary diagrams to analyse the compared distribution on these parameters, classify the surface waters and identify possible processes (sources mixture, fractionation, boiling, etc.), *i.e.* using the Langelier–Ludwig (Langelier and Ludwig, 1942) Piper and Giggenbach anions diagrams (Giggenbach, 1991).

Characterization of waters also was done plotting their major and trace elements and stable isotope ratios. Respect to water values it is useful to compare cations and anions that are involved in the precipitation of carbonate. In this study the relation among calcium, strontium, magnesium and bicarbonate was observed in detail. For these binary diagrams the ratio among bicarbonate and the cations was considered as 2:1, considering the molality of each component in the carbonate precipitation reaction:

$$Ca^{2+} 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2$$

Also, correlation index among major and trace elements and physicochemical parameters were calculated using the tools of Microsoft Excel 2013.

The results of compositions that were obtained with the water samples were used in the application of different geochemical tools: geochemical speciation using Phreeq-C version 3.3.12 (Parkhurst and Appelo, 2013) and the database file *LLNL.dat*, derived from databases for EQ3/6 and Geochemist's Workbench that uses thermodynamic data compiled by the Lawrence Livermore National Laboratory, which contents equilibrium constants of several aqueous, mineral and gaseous species in a large temperature range  $(0.01 - 300^{\circ}C)$ ; thus it is possible to identify and compare the presence of various mineral phases and saturation index.

In the case of gas data, this can be used to determine gas sources, as comparing  $He - N_2 - Ar$  concentrations, which indicates gaseous input from the mantle, crust or atmospheric air (Giggenbach, 1992). Also, it is possible to distinguish concentrations comparatively of meteoric or magmatic (or deeper) source of gas through the Lowenstern *et al.* diagram (2015).

### 2.3 Calculation of carbon and oxygen isotope ratios

Isotopic fractionation in the carbon cycle generates important differences in the <sup>13</sup>C/<sup>12</sup>C ratios in different environments as in gas originated from the magma,

decarbonation, organic matter or dissolved CO<sub>2</sub> in meteoric waters, which is recorded in water, deposits and gas present in various parts of the system.

To obtain  $\delta^{13}$ C and  $\delta^{18}$ O the carbonate samples these were dissolved, and the resulting CO<sub>2</sub> gas emitted was measured using IRMS for each sample. Two different standards were used for calculating: IAEA-603 ( $\delta^{13}$ C = 2.46,  $\sigma$  = 0.01;  $\delta^{18}$ O = -2.37,  $\sigma$  = 0.04) and NBS-18 ( $\delta^{13}$ C = -5.014,  $\sigma$  = 0.035;  $\delta^{18}$ O = -23.2,  $\sigma$  = 0.1), resulting a calculated error of 0.0093‰ and 0.0092‰ for  $\delta^{13}$ C and  $\delta^{18}$ O, respectively.

To calculate  ${}^{13}C/{}^{12}C$  ratios the values obtained from the CO<sub>2</sub> gas were replaced in equation developed by Paul *et al.* (2007), which is expressed by:

$$\delta^{13}C_{[V-PDB]} = (\delta^{13}C_{S1} + \delta^{13}C_{S2}) / (\delta^{13}C_{S1_m} - \delta^{13}C_{S2_m}) \times (\delta^{13}C_{measured} - \delta^{13}C_{S2_m}) + \delta^{13}C_{S2_m}$$

Where  $\delta^{13}C_{S1}$  and  $\delta^{13}C_{S2}$  correspond to the known values of the standards IAEA-603 and NBS-18, respectively;  $\delta^{13}C_{S1_m}$  and  $\delta^{13}C_{S2_m}$  correspond to the measured values of the standards IAEA-603 and NBS-18, respectively; and  $\delta^{13}C_{measured}$  represents the measured value from the sample.

Oxygen isotope fractionation is related not only to temperatures but also to mineralogy (Grossman and Ku, 1986; Valley, 2001; Kim *at al.*, 2007; Dietzel *et al.*, 2009; Kele *et al.*, 2015; Kim *et al.*, 2015). In this case, the equation presented in the work of Kim *et al.* (2015) was used because this considers different mineral phases, which is defined as:

$$\delta^{18}O$$
 [V-PDB] = m ·  $\delta^{18}O$  CO2 (ACID) + b

With:

$$m = \frac{\left[\left(\delta^{18}O_{|AEA-603,VPDB} + 1\right) \cdot \frac{\alpha CO_{2(ACID)\text{-calcite}}}{\alpha CO_{2(ACID)\text{-carbonate}}} - 1\right] - \left[\left(\delta^{18}O_{|NBS-18,VPDB} + 1\right) \cdot \frac{\alpha CO_{2(ACID)\text{-calcite}}}{\alpha CO_{2(ACID)\text{-carbonate}}}\right]}{\delta^{18}O_{|AEA-603\text{-}CO2(ACID)} + \delta^{18}O_{|NBS-18\text{-}CO2(ACID)}}$$
$$b = \left[\left(\delta^{18}O_{|AEA-603,VPDB} + 1\right) \frac{\alpha CO_{2(ACID)\text{-calcite}}}{\alpha CO_{2(ACID)\text{-calcite}}} - 1\right] - m \cdot \delta^{18}O_{|AEA-603\text{-}CO2(ACID)}$$

Values of NBS–19 were replaced by IAEA–603 in 2016 because it is the first stable isotope RM with well characterised uncertainty (IAEA, 2016). This equation considers the acid fractionation factor of both calcite  $\alpha$  CO<sub>2(ACID)-calcite</sub> (1.00856) and that of the carbonate sample (1.00898 for aragonite), determined for 75°C (Kim *et al.*, 2007; Kim *et al.*, 2015). Also, official values of NBS–18 and IAEA–603 are taken into account ( $\delta^{18}$ O<sub>NBS-18,VPDB</sub> =

-23.01% and  $\delta^{18}O_{IAEA-603,VPDB} = -2.37\%$ ). The measured oxygen isotopic compositions of the CO<sub>2</sub> generated from NBS–18 and IAEA–603 were included as  $\delta^{18}O_{NBS-18-CO2(ACID)} = 23.17\%$  and  $\delta^{18}O_{IAEA-603-CO2(ACID)} = -2.45\%$ , respectively.

Thus, the final equation used to calculate <sup>18</sup>O/<sup>16</sup>O ratios from aragonite samples is as it follows:

$$\delta^{13}C$$
 [V-PDB]-aragonite = 1.003196 ·  $\delta^{13}C$  CO2 (ACID) + 0.008144

For calcite, replacing  $\alpha$  CO\_2(ACID)-carbonate por  $\alpha$  CO\_2(ACID)-calcite, the equation is as follows:

 $\delta^{18}O$  [V-PDB]-calcite = 1.005115 ·  $\delta^{18}O$  CO2 (ACID) + 0.087506

2.4 Estimation of the carbon isotope ratio of CO<sub>2</sub> gas from travertine data

 $CO_2$  degassing is a trigger for carbonate precipitation (Pentecost, 2005) and generates an isotope fractionation process between  $CaCO_3$  and residual  $CO_2$  during degassing, thus this gas can show possible sources of carbon, which influence the carbon isotope ratios obtained in the travertine samples and this lets formulate an idea about the mix of carbon sources.

As it was not possible to obtain gas samples for isotope analysis, these carbon isotope ratios were recalculated using  $\delta^{13}C$  values of travertine samples through the following formula:

$$\delta^{13}C_{(CO2)} = 1.2 \cdot \delta^{13}C_{(trav)} - 10.5$$

This equation was proposed by Panichi and Tongiorgi (1975) to correlate  $\delta^{13}$ C values of several active travertine deposits and their respective  $\delta^{13}$ C values of CO<sub>2</sub> emitted. Also, this equation was used by Minissale *et al.* (2002) to analyse different sources of carbon for travertine formation in the Tiber Valley.

## 3 Results

## 3.1 Water

Porcelana Geysers area is located along Punta Calle River. On the northern bank the fluids with highest temperature (85.1°C) are found as a mixing of hot water and steam (Por-1). Across the river only hot water (65.7°C) is emerging through rocks fractures (Por-2). Finally, a hot spring pool (56.0°C) was found 1.2 km downstream, on the southern bank of the river (Por-4). These three sites showed similar physicochemical conditions as neutral pH (6.78-8.05), high electric conductivity (from 847  $\mu$ S/m in Por-4 to 2510  $\mu$ S/m in Por-1) and reducing conditions.

## i. Water from geysers vents (Por-1):

These samples were collected from the vent where the highest temperature of water was measured (85.1°C). It emerges from the bottom of an inactive pinnacle, which seems to have been slightly dissolved. This water flows down a 20-90° slope with an approximate flow rate of 2 to 3 litres per second and dispersed steam, descending 2.8 m until reaching the river waters. The areas of this slope which are covered by the water flow present surfaces fractions with no visible organic mat on it and others with dark brown and orange organic mat and algae (Figure 3.1), at the central axis of the water layer the surface is light orange and on the external edges of the flow sheet it has dark orange colour with some calcite efflorescence (Figure 3.1.a). Long filaments of green algae cover the surface bordering the water flow.

The water is practically neutral (pH values between 7.79 and 8.04) and reductive, varying Eh from -284 mV (in 2014), -118.2 mV (in 2015) and finally -71.5 mV (in 2017), all these measurements were made on the same date in different years. This shows a large range of possible values with respect to redox conditions over time.

Also, high conductivity values were measured in these waters, over 2000  $\mu\text{S/m}$  in all cases.

## ii. Water from southern river bank (Por-2):

This water emerges on the southern bank of Punta Calle River (15 m across the river) through a fracture in granitic rocks percolating among them until reaching the river, forming no water table. It is colder than Por-1 (51.2 - 65.7°C), there is no presence of vapor emission or deposit of carbonates throughout the bank or presence of organic matter close to the flow visible to the naked eye.

Also, this fluid corresponds to a neutral water with a pH value equal to 6.8 and it shows reducing conditions (Eh = -133 mV; measured in 2016), similar to Por-1. High conductivity
Table 3.1. Summary of physicochemical parameters and chemical and isotopic measurement data of thermal and cold surface waters samples from Porcelana Geysers area. The letter of each sample ID indicates the year of sampling (A: 2014; B: 2016; C: 2017).

.( / L(															
Sample	East	North	Elevatic	Hd u	Eh	Temp	Condutivity	Na	¥	Mg	Ca	Sr	Mn	Fe	SiO2
₽	WGS84 18	S	(m.a.s.l	(;	(mV)	(°C)	(mS/cm)	(mqq)							
Geysers a	area														
1A_	706312	5300883	370	8.04	-284.00	85.10	2170	383	39.0	0.20	49.0	0.180	0.183	0.188	201
<del>6</del> 6	706312	5300883	205	7.79	-118.20	81.40	2510 2210	403	42.8	3.73 2.23	38.7 2	0.165	0.179	0.051 2.251	226
	101010	5301180	180	/.88	0 <u>c</u> .r/-	82.30	2340	402	39.6	3.80	37.4	0.164	0.097	<0.004	20102
River wat	ter														
2A	706312	5300883	370	6.96	n.m.	10.00	101	12.0	1.1	0.20	7.5	0.017	0.004	0.024	6.4
2B	706312	5300883	203	6.95	33.70	11.70	210	13.6	1.6	1.05	7.5	0.025	0.004	0.004	19.0
2C	707010	5301180	179	7.17	n.m.	10.50	n.m.	26.3	2.8	0.90	6.9	0.022	0.011	<0.004	n.m.
Southern	bank therma	l spring													
3B	706312	5300883	203	6.78	-133.00	65.70	2440	392	40.4	3.07	39.0	0.181	0.197	0.064	222
Geothem	al pool														
4B	707568	5388788	130	6.93	-73.70	56.00	973	143	13.6	2.20	28.1	0.147	0.065	<0.010	107
4C	707766	5389070	142	6.99	-11.90	50.80	847	128	9.7	2.10	24.4	0.122	0.000	<0.004	87.0
Fjord wat	er														
5A	710859	5294831	0	7.50	n.m.	19.80	11010	2200	78.0	25.0	108	1.280	0.004	0.326	2.1
Rain wate	er														
6A	709370	5302513	42	6.43	n.m.	10	83	2.6	23.1	0.10	2.8	<0.001	<0.003	<0.01	<1.0
Sample	S04	HCO3	Ū	Ba	ш		As	S	В	В	Rb	δ18O	۵D	Balance	Depth temp*
۵												% (VSMC	(MC	(%)	(°C)
Geysers	area														
1A	19.0	227	528	<0.005	0.53	2.30	0.203	0.515	16.00	1.373	0.464	-8.65	n.m.	2.8	195.6
1B	21.3	227	617	0.0045	0.69	3.010	0.219	0.499	18.18	1.440	0.448	-7.21	-51.04	-1.7	200.2
10	15.2	224	551	0.0037	. 0.66	0.264	0.203	0.479	16.40	1.390	0.417	-3.66	-47.51	2.9	192.0
River wat	ter														
2A	7.3	16.0	15.0	<0.05	0.03	0.10	0.005	0.011	0.29	0.033	0.010	-8.95	n.m.	5.8	n.m.
2B	11.4	17.3	18.3	0.0020	<0.03	0.086	0.006	0.013	0.55	<0.03	0.014	-7.60	-57.76	2.7	n.m.
2C	8.6	28.8	51.1	0.0013	0.14	0.156	0.012	0.028	0.96	0.200	0.026	-1.22	-38.04	-12.3	n.m.
Southern	bank therma	l spring													
3B	20.7	219	615	0.0061	0.71	2.834	0.170	0.520	17.88	1.470	0.424	-7.74	-56.80	-2.6	196.9
Geothem	al pool														
4B	32.8	153	182	0.0014	0.30	0.821	0.138	0.122	5.74	0.820	0.123	-7.99	-59.82	-1.0	188.2
4C	26.2	137	150	0.0013	0.28	0.710	0.012	0.096	4.41	0.370	0.101	-2.09	-41.78	1.3	165.5
Fjord wat	ter														
5A	473	30.0	3330	<0.05	0.18	<0.02	0.011	0.001	0.57	11.96	0.019	-8.57	n.m.	0.4	n.m.
Rain wate	er														
6A	1.5	31.0	3.3	<0.005	<0.03	<0.02	<0.005	0.001	<0.06	0.009	0.005	-8.17	n.m.	14.8	n.m.

\* Depth temperature calculated by using the equation of Santoyo and Díaz-González (2010). "n.m." refers to data that could not be measured

values were also recorded in both the field work and the laboratory (2.44 and 2.34, respectively).

## iii. Hot spring pool (Por-3)

An elongated hot spring pool is located 1.2 km downstream, where the hot fluids (water and bubbles) are rising from the pool floor through the sediments at 56°C (2016), 50.8°C (2017) and 46.8°C (2018) with mostly neutral pH values (6.78-6.99). No carbonate deposit is found but abundant algae are present as floor cover and in suspension.

Is important to notice that an increase of Eh values is also recorded between 2016 and 2017 (-73.7 and -11.9, respectively), showing a more oxidizing environment over time.

Por-1 is especially higher in chlorides, bicarbonate, sodium and silica respect to the rest of water samples, presenting concentrations higher than 500 mg/l of chlorides. Given these results it seems important to contrast different elements concentrations with chlorides, with the aim to understand some correlations and processes that could be happening among different components. Regarding trace elements, the most highlighting is Boron, which forms high B/Cl ratios (over 0.3), with concentrations between 16 and 18.2 mg/l. Considering the information that can be obtained from chemical compositions, different diagrams will be used.

### 3.1.1 Speciation calculation

With the geochemical data it was possible to calculate the saturation index (SI) of all water samples for different mineral phases (Table 3.2), of which the most relevant ones were chosen (aragonite, calcite, dolomite, halite and quartz). These indexes indicate that the only thermal waters that have conditions for precipitate carbonates are those from Por-1, and that all thermal waters that could precipitate quartz.

Also an inverse modelling was made by using Phreeq-C version 3.3.12 (Parkhurst and Appelo, 2013) considering all common minerals present in the intrusive and metamorphic rocks seen in studied area to elucidate which minerals were dissolved and precipitated during the subsurface flow from meteoric recharge (rainwater) and the rising of the geothermal water (Por-1), even though hundreds of possibilities were displayed by the program in which aragonite and calcite are excluding as phase mole transfers, both indicated as negative input. Other very common mineral phases resulted from the models were CO<sub>2</sub>, pyrite and tremolite as product, and H<sub>2</sub>S, dolomite and halite as input phases.

Sample	Saturation					
ID	Index (SI)	Aragonite	Calcite	Dolomite	Halite	Quartz
Geysers ar	ea					
1A		1.06	1.20	1.66	-5.35	0.68
1B		0.72	0.86	2.33	-5.27	0.78
1C		0.79	0.94	2.51	-5.32	0.73
River water						
2A		-2.65	-2.50	-5.26	-8.22	-
2B		-2.60	-2.46	-4.45	-8.09	-
2C		-2.23	-2.08	-3.73	-7.36	-
Southern b	ank thermal	spring				
3B		-0.42	-0.27	-0.09	-5.28	0.97
Geothemal	pool					
4B		-0.74	-0.59	-0.64	-6.19	0.77
4C		-1.00	-0.85	-1.27	-6.32	0.76
Fjord water						
5A		-1.02	-0.88	-1.01	-3.84	-
Rain water						
6A		-3.30	-3.16	-6.45	-9.54	-

Table 3.2. Saturation	Index of	samples	waters	for the	main	mineral	S
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#### 3.1.2 Major and trace elements analysis

#### 3.1.2.1 Ion comparison

Major and trace elements allow classifying and grouping the waters present in the study area (Table 3.1). It is interesting to see that the Piper and anion ternary diagrams describe thermals and cold waters as chlorinated (Figure 3.2) which could be related to a long fluid transport (Sanchez *et al.* 2010), and an external chloride source (e.g. deep geothermal fluid, fjord water intrusion) (Negri *et al.* 2018; Nicholson, 1993; Giggenbach, 1991).

With the analysis of major ions concentrations, different source of water, and mixing and dilution processes could be recognized. The first thing is to notice how enriched the water samples are respect to different elements, searching for some existing correlation among them. When the main elements concentrations are compared among them, it is possible to observe that all the sampled waters, including fjord and river waters, tend to be subparallel, following a trend with high concentrations of Na, CI and low values of Mg and SO<sub>4</sub> (Figure 3.4). The outstanding difference is the high concentration of bicarbonate ions present only in groundwaters, not only the water that emerges from the pinnacles but also the rest of the thermal waters sampled.

In general, all the thermal water seems to come from the same source, but they look more diluted the farther they are from the area of the pinnacles. As it happens with major elements compositions, a common trend is observed for trace elements of all water samples. The main differences observed between subparallel trends of trace elements of thermal and cold waters correspond to Sr, Mn, As and Br concentrations, The first two

related to the dissolution and precipitation of carbonates (Veizer, 1983; Pingitore and Eastman, 1986; Morse and Bender, 1990; Budd *et al.*, 2000; Hiatt and Pufahl, 2014) and the two last are related to a evaporitic, marine and volcanic sources (Carroll and Holloway, 1994; Hedenquist and Lowenstern, 1994; Edmunds, 1996; Aiuppa *et al.*, 2009).

Respect to boron contents they are anomaly high for all the samples, around 17.1 mg/l average in Por-1 and Por-2. Considering at the same time the high contents of lithium it could be indicating a volcanic origin (Giggenbach, 1988, 1997; Arnórsson *et al.*, 2007). In particular, this is explained by the moderately (Li) to strongly (B) incompatible but volatile behaviour of these elements (Ryan and Langmuir, 1987, 1993; Giggenbach, 1991; Brenan *et al.*, 1998), whose high concentrations use to indicate a short fluid transport (Giggenbach, 1991; Sánchez *et al.*, 2010; Ruiz and Morata, 2016).

To elucidate the possible sources of these cations, they were plotted against some anions (Figure 3.5). Chloride compositions form linear trends from rain to fjord water with sodium, bromine and strontium values (Figure 3.7) and, also form linear trends from rain water to geysers waters with boron, lithium, rubidium, fluorine and caesium values (Figure 3.8).



Figure 3.1. Place where the highest temperature water emerges. a) The thermal water emerges from the left side of the carbonate pinnacle (white circle). b) Closer picture from the white square in a); under the water flow no organic mat is observable, there is only orange surface with rounded microterracettes.

This generates different mixing lines using different end-members that will be reviewed deeper within the discussions of this study.



Figure 3.2. Classification diagrams with thermal and cold-water samples. Left: anion diagram (Nicholson, 1993; Giggenbach, 1991). Right: Piper diagram. Each sample is indicated by a number and a letter, where the number indicates the place of sampling (1: geysers area; 2: river water; 3: southern bank hot spring; 4: hot spring pool) and the letter the year of sampling (A: 2014; B: 2016; C: 2017).

It is possible to see that HCO<sub>3</sub> contents deviate upward respect CI concentrations (Figure 3.5), over the line formed by the correlation between rain and fjord waters that could be possibly indicating an additional HCO<sub>3</sub> input unrelated to the contribution from the fjord. Depending on the possible sources found in the area and the available isotopic ratios information, an idea could be proposed about the phase that is responsible of HCO<sub>3</sub> recharge.

Regarding conservative behaviour of chlorides, the linear trend formed between rain and fjord water for chlorine versus other elements contents has been considered, halite could be taken as the main mean of transport of Cl<sup>-</sup> by the aqueous medium, thus Na/Cl ratios were compared for different water samples. This diagram shows that geothermal and fjord waters content similar molar ratios (Figure 3.9.b) that could be related to a fjord input to the groundwater system (Negri *et al.*, 2018). Following the possibilities of a marine intrusion (Pulido-Lebœuf, 2004; Daniele *et al.* 2013; Negri *et al.*, 2018) the mixing between meteoric and fjord water is analysed through the equation 3.1.

$$f_{s} = \frac{(C_{Cl,sample} - C_{Cl,mw})}{(C_{Cl,sw} - C_{Cl,mw})} \cdot 100$$
(3.1)





Figure 3.3. a) Major and b) trace compositions of sampled waters. Different types of lines represent the year in which the water samples were taken: dotted line, 2014; dashed line, 2016; solid line, Langelier-Ludwig 2017. C) diagram. Each sample is indicated by a number and a where the letter. number indicates the place of sampling (1: geysers area; 2: river water; 3: southern bank hot spring; 4: hot spring pool) and the letter the year of sampling (A: 2014; B: 2016; C: 2017).



Figure 3.5. Concentrations of chloride versus. Each sample is indicated by a number and a letter, where the number indicates the place of sampling (1: geysers area; 2: river water; 3: southern bank hot spring; 4: hot spring pool) and the letter the year of sampling (A: 2014; B: 2016; C: 2017).



Figure 3.6 Relationship between the sum of Ca, Mg and Sr and the concentrations of HCO<sub>3</sub>.

The content of Cl<sup>-</sup> measured in geothermal waters is represented by  $C_{Cl,sample}$ , Cl<sup>-</sup> contents of the most diluted meteoric water by  $C_{Cl,mw}$  and that obtained for the fjord is included as  $C_{Cl,sw}$ . In this case, fjord contribution percentage was calculated for Por-1 considering it as the less diluted thermal water, with an average concentration of 577.8 mg/L, rainwater data was use as  $C_{Cl,mw}$  (3.3 mg/L), and the value obtained for fjord water was 3330 mg/L. With these data, the percentage of fjord contribution calculated is 17.3%.



Nevertheless, it is useful to estimate the possible sources of chlorides. The results plotted in the diagram made by Vengosh (2003) seem to show a hydrothermal source for chlorides (Figure 3.9.a).

Respect to the rest of cations, whose bicarbonate concentrations do not show a linear trend with respect to that of the fjord water, it is possible to notice that they show an enrichment in HCO<sub>3</sub> contents, in particular for waters of highest temperatures. Some of these cations are those involved in the carbonate dilution/precipitation process; thus, they were be compared to HCO<sub>3</sub> composition.

 $Ca^{2+}/HCO_{3}$  and ( $Ca^{2+}+Mg^{2+}+Sr^{2+}$ )/  $HCO_{3}$  ratios are not close to the expected ratio of 1:2 (Figure 3.5) that they could show in the case of assuming that the bicarbonate comes from the carbonate dissolution. These ratios are lower as the water temperature is higher and form a linear trend when compared to  $HCO_{3}$ contents.

Figure 3.7. Diagrams comparing chloride sodium with and trace elements concentrations. Each sample is indicated by a number and a letter, where the number indicates the place of sampling (1: geysers area; 2: river water; 3: southern bank

hot spring; 4: hot spring pool) and the letter the year of sampling (A: 2014; B: 2016; C: 2017).



Figure 3.8. Diagrams comparing chloride with sodium and trace elements concentrations. Each sample is indicated by a number and a letter, where the number indicates the place of sampling (1: geysers area; 2: river water; 3: southern bank hot spring; 4: hot spring pool) and the letter the year of sampling (A: 2014; B: 2016; C: 2017).



Figure 3.9. (a) Elucidation of saline sources by using the variations of Br/Cl and B/Cl molar ratios (Vengosh, 2003). (b) Na/Cl vs. Cl<sup>-</sup>, concentrations in meq/l. Each sample is indicated by a number and a letter, where the number indicates the place of sampling (1: geysers area; 2: river water; 3: southern bank hot spring; 4: hot spring pool; 5: Comau fjord) and the letter the year of sampling (A: 2014; B: 2016; C: 2017).



Figure 3.10. Comparison between Ca/HCO3 and Sr/HCO3 ratios. Each sample is indicated by a number and a letter, where the number indicates the place of sampling (1: geysers area; 2: river water; 3: southern bank hot spring; 4: hot spring pool) and the letter the year of sampling (A: 2014; B: 2016; C: 2017).

#### 3.1.2.2 Geothermometers

To estimate the depth conditions, Na/K geothermometer was used because. This geothermometer is based on the variation of Na and K as a temperature dependent reaction and is produced by ion exchange. This equilibrium is represented by the concentrations of albite and potassium feldspar (Nicholson, 1993; Giggenbach, 1988):

(3.2)

The equilibrium constant ( $K_{eq}$ ) of this reaction is given in terms of the thermodynamic activities:

$$K_{eq} = \frac{a_{K-feldspar} \cdot a_{Na+}}{a_{Na-feldspar} \cdot a_{K+}}$$
(3.3)

Considering K and Na feldspar as pure mineral phases, a  $_{\rm K-feldspar}$  and a  $_{\rm K-feldspar}$  are equal to 1, thus:

$$K_{eq} = \frac{a_{Na+}}{a_{K+}}$$
(3.4)

Using the Van't Hoff equation the temperature dependence can be defined as:

$$\log K_{eq} = \frac{\Delta H^{\circ}}{2.303 \text{ RT}} + C$$
(3.5)

Where  $\Delta H^{\circ}$  corresponds to standard enthalpy of reaction, T is the temperature at which the reaction occurs, and R is the universal gas constant. If eq. (3.4) is considered, eq. (3.5) becomes:

$$\log \frac{a_{Na^{+}}}{a_{K^{+}}} = \frac{\Delta H^{\circ}}{2.303 \text{ R}} \frac{1}{T(^{\circ}K)} + C$$
(3.6)

Approximating the activity of the cations to their compositions in the eq. (3.6) and obtaining the temperature in Celsius degrees, the temperature is defined as it follows:

T(°C) = 
$$\frac{b}{-273.15}$$
 (3.7)  
Log  $\frac{a_{Na+}}{a_{K+}} + a$ 

In eq. (3.7) a and b coefficients are inferred from linear regression between log  $K_{eq}$  and 1/T. For the selected geothermometer their values are 0.8775 (±0.0508) and 876.3 (±26.26), respectively (Santoyo and Díaz-González, 2010), which were determined from 103 geothermal wells from worldwide to improve the result of Díaz-González *et al.* equation (2008) developed for a database with temperatures from 30 to 350°C. Na and K concentrations have to be included in mg/L or mg/kg.

With these values of a and b, and Na and K compositions from Por-1 in 2014, 2016 and 2017 (which is consider the less diluted water) the estimated temperature for the geothermal reservoir is 195.9°C on average (Table 3.1).

#### 3.1.3 Stable isotopes

Oxygen, hydrogen and carbon isotopes ratios were obtained for thermal and river water samples collected in 2016 and 2017. With the first two it is possible to see that the main origin of the geysers corresponds to meteoric water (Figure 3.11). Nevertheless, for 2016 samples a slight displacement is observed in 2016 samples respect to global and local meteoric water lines (GMWL and LMWL, respectively): Por-1: +0.57‰, Por-2:



Figure 3.11.  $\delta^{18}$ O and  $\delta$ D values of water samples. GMWL (Global Meteoric Water Line; Craig, 1961); LMWL (Local Meteoric Water Line; IAEA, 2017).

+1.06‰, Por-3: +0.80‰ and Por-4: +0.95, differences with LMWL, which are higher for lower temperatures. This could due to an error range of the analysis or sampling method, an increase of <sup>18</sup>O/<sup>16</sup>O ratio in an external water source or a depletion of <sup>16</sup>O due to boiling during the flow of water.

Respect to data of samples collected in 2017, this is much further from the line, that could be the result of oxygen isotope equilibrium exchange between CO<sub>2</sub> and water, boiling processes or high temperature reactions (Karolyte *et al.*, 2017; D'Amore and Panichi, 1987). However, this difference was most likely caused by an error made during the storage of the samples because these samples could not be analysed until several months later and also because no significant changes in chemical concentration were found between the data obtained from samples from 2016 and 2017. Considering the aspects mentioned above, this data should be seen with caution.

The values obtained from the samples in 2016 are -4.90, -4.79 and -5.83‰ (VPDB) for Por-1, Por-2 and Por-4, respectively.  $\delta^{13}$ C data was used to study the possible sources of CO<sub>2</sub>, from deep or shallow origin, by the diagram presents by Frondini *et al.* (2009) that contrasts them with Total Dissolved Inorganic Carbon values. This diagram shows that possibly the CO<sub>2</sub> source is mixed with a slightly deeper influence for thermal waters. In this context it is necessary to review the data of the precipitated solid.



#### 3.2 Travertine

In the studied area there are some singular and unique travertine pinnacles, both inactive and current precipitants.

Inactive pinnacles have an outer coverage of white to dark brown, with tops that vary from conical to rounded blunt, showing smooth surfaces and microterracettes. Their dimensions are from 20 cm to 2 m of height and 10 to 70 cm in diameter. Some of them are covered by a dark green or brown organic mat of a few millimetres thick.

There are also some currently forming pinnacles, which are current vent of the geothermal system, spouting energetically hot water and steam. These pinnacles are orange, with white flatter tops and microterracettes on their surfaces. They do not present any organic mat and do not exceed 35 cm in height or 20 cm in diameter at each vent. The presence of this type of pinnacles is very variable because they tend to "appear" and "disappear" between one year and another, indicating high rates of precipitation and erosion.

The travertine pinnacles are all surrounded by calcite deposits forming cascades geometries, located downstream in a distal location respect to the vents. The area covered by this calcite layers is close to 150 m<sup>2</sup> and is very steep, actually it is formed by two planes in contact: an upper one with a 15-20° slope and a lower one of 60-90° of slope.

This calcite deposits form smooth and rough surfaces. The first ones are covered by organic green and dark green mat, except for those surfaces covered by hot water flow, which are orange coloured and do not have any organic mat on them. The rough calcite layers show white efflorescence and a high hardness (~5-6 on the Mohs scale).

Many samples were collected from inactive and active pinnacles and from calcite cascades. They were grouped according to their main mineralogy, deposit morphology and the location into the geysers area, as follows:

i. Calcite deposits: The external layers of the pinnacles are from a few millimetres to 1 cm thick and, in conjunction with the precipitated crust formed in the cascades, the calcite is presented compactly and with abundant presence of microbial mats.

Calcite deposits can be classified as follows:

CC1: Dendritic calcite currently growing over a smooth slope portion of a cascade (Figure 3.13.a).

CC2: Dendritic calcite currently growing over a steep slope cascade (Figure 3.13Figure 3.13.b).

PF1E: External layer of inactive travertine pinnacle (25 cm high). External layer has a thick and dark brown organic coverage (Figure 3.13.c).

PF2E: External layer of inactive travertine pinnacle (22 cm high). This presents an orange external surface (Figure 3.13.d).

ii. Aragonite and mixed deposits: Both, inactive and active travertine pinnacles present aragonite acicular crystals with high aspect ratios, growing not only parallel to the flux direction but also with a radial orientation. Lacking microbial mat or presence of organisms. Few isolated crystals of calcite are found among the aragonite crystals.



Figure 3.13. Outcrops of sampled travertine in northern river bank. (a) and (b) CC1 and CC2 have been precipitated on cascades with different slope angles. (c) and (d) PF1 and PF2 are inactive travertine pinnacles, both covered by dark organic mat; in particular (d) show microterracettes (specifically d). (e) PA1 and PA2 belong to a pinnacle that is currently formed by rapid CO<sub>2</sub> degassing. (f) Native sulphur found on the southern river bank.

Aragonite deposits can be classified as follows:

PA1: Top of travertine pinnacle in current formation, with hot water and steam emission (Figure 3.13.e).

PA2: Base of travertine pinnacle in current formation, with hot water and steam emission (Figure 3.13.e).

PF1I: Portion of an inactive travertine pinnacle (the same as PC1), mainly formed by acicular aragonite crystals.

PF2I: Portion of an inactive travertine pinnacle (the same as PC2), mainly formed by acicular aragonite crystals.



Figure 3.14. Height variation of a travertine pinnacle between 2016 and 2016 and between 2017 and 2018 due to erosion and precipitation. (a) Decrease of 30 cm and morphology change between March 15<sup>th</sup> (2016) and March 14<sup>th</sup> (2017). (b) Increase of 83 cm height and colour change of the same travertine pinnacle between March 14<sup>th</sup> (2017) and January 23<sup>rd</sup> (2018).

On the southern river bank no carbonate precipitation is seen, but a small presence of native sulphur was found, according to the XRD results, which indicate that the sediment was formed entirely by native sulphur.

These deposits present high precipitation and erosion rates, which do not allow the use of a small-scale method such as the one developed by Nicolau (2013); actually to measure the height variations between one year and another as Figure 3.14 shows was easier. Over 30 cm height of erosion and up to 90 cm of growth were measured.

#### 3.2.1 Mineralogy

A transversal section of the inactive travertine pinnacle PF1 (Figure 3.13.c) was studied, where 5 zones were differentiated according to their colours (Figure 3.15). These layers were analysed by X-Ray diffraction and two groups were recognized: (i) One composed mainly by calcite, (ii) and the rest of layers composed by aragonite and other components as calcite, Fe and MgO (Table 3.3). This agrees with the previous division made between PF1I and PF1E.

Table 3.3. Mineralogical compositions of the different zones identified in the transversal section of the inactive pinnacle PF1 (Figure 3.15). \*Areas indicated in Figure 3.13.

Sample	Carbonate	CaCO <sub>3</sub> (calcite)	CaCO <sub>3</sub> (aragonite)	SiO <sub>2</sub> (tridymite)	MgO (periclase)	Fe0.9 Si0.09	Fe
ID	deposit*	(%)					
A1	PF1E	88	-	12	-	-	-
A2	PF1I	-	100	-	-	-	-
A3	PF1I	-	97.4	-	-	2.6	-
A4	PF1I	-	85.7	-	14.3	-	-
A5	PF1I	17.7	75.3	-	-	7	-
A6	PF1I (vesicle)	43.5	55.6	-	-	0.9	-
A7	PF1I (amygdale)	9.7	85.5	-	-	-	4.8

### 3.2.2 Calcite deposits

## 3.2.2.1 Polarized light



Figure 3.15. Distribution of distinguishable layers of the travertine column obtained in the field (Figure 3.13.c).

The section transversal (Figure 3.15) were divided on three thin sections which were analysed under polarized light (PL) microscopy, where the laver external is easv to recognize.

Different parallel layers are distinguishable in the most external portion of the pinnacle – the upper part of thin sections – all of them with mostly constant thickness and formed by micritic or crystalline calcite with small oxidized areas and well-defined borders (Figure 3.16 and Figure 3.17).

From outer to inner layers, it is possible to identify a first more chaotic and heterogeneous portion with clear calcite crystals and an area with thin micritic stripes tending to form diagonal lines (Figure 3.16.c and 3.24.d). A high-density band lays under this chaotic layer, which is limited by brown oxidized borders up and down closing a grey micritic portion. Under this dark layer a

thick and chaotic zone is distinguishably (ca. 1 mm thick), with the presence of diagonal oxidizing lines across it. Finally, next to the aragonite crystal fans, the calcite crystals seem to form two well-defined and less micritic stripes, from 0.05 to 0.3 mm thick (Figure 3.16.c and 3.24.d), with darker and thinner borders, showing a more crystalline, mosaic and homogenous fabric.

In all the described layers it is possible to find filamentous organic structures, which will be studied in detail by the rest of the analysis (Figure 3.16.d).



Figure 3.16. a) and b) Different views of the outermost portion of external layer of the inactive travertine pinnacle PF1 (A1 and A2 (Figure 3.15)) in plane-polarized light (PPL). Three of the four descripted layers are visible. c) and d) Inner edge of the external layer of the travertine pinnacle in PPL, showing two well-defined layers next to the aragonite crystal fans, formed by euhedral and clear crystals and separated by dark oxidizing lines. e) Vesicle into the thicker layer with oxidized edges (in PPL). It is possible to recognize filamentous structures presents in all layers of this external segment of the inactive travertine pinnacle.

# 3.2.2.2 Cathodoluminescence

In the external layer of the inactive pinnacle it is possible to distinguish many euhedral calcite crystals (up to 0.5 mm on diameter) with bright red and orange luminescence, finding two main types of crystals: (1) red crystals growing parallel to the external edge with bright red and orange luminescence areas towards the centre of them. They form stripes which are surrounded by dark red luminescence above and below them (Figure 3.17a). (2) Also, is possible to find many small euhedral calcite crystals around the big red strip and along the dark zones, showing a clear zonation of the luminescence described above, varying their luminescence colours thought the zonation among bright red, dark red and black colours (Figure 3.17c).



Figure 3.17. Calcite external layer of travertine pinnacle. a) Red luminescence strip made of calcite crystals. It is possible to recognize the presence of brighter luminescence colours towards the centre of the strip. b) Same area in PPL. c) and d) Calcite crystals presenting zonation with different luminescence colours, from dark red to bright red. White arrow indicates an area with a high density of crystals with zonal structure.

From Figure 3.17.a and Figure 3.17.b it is not possible to establish a clear correlation between the crystal settings observed in PPL image and the distribution of the luminescence colours.

### 3.2.2.3 Scanning Electron Microscope (SEM)

The external calcite layer of the inactive travertine pinnacle was not the only calcite deposit which was analysed by using the SEM, but also some samples of travertine from carbonate draped cascades with calcite microterracettes and dendritic fabrics, located in a more distal area from the vents, where the hot spring waters have lost a great portion of dissolved CO<sub>2</sub>. At first a review of the fabric and structures present on the external layer of inactive travertine pinnacles will be described. Then, the same details will be developed for the distal deposits.



Figure 3.18. Microbial structures present in external face of aragonite crystals portion from the inactive travertine pinnacle. (a) Abundant microbial organisms over the coverage of smooth silica and biofilm EPS. (b) and (c) Microbial mat growing among the aragonite crystals. (d) White arrows point to alveolar EPS, and black arrows show amorphous silica substance. (e) The white arrows indicate some elongated microbial organisms (possibly filamentous cyanobacteria), and the black arrows show EPS. (f) Spheroidal morphology that could be authigenic clay minerals or EPS growing among aragonite crystals.

a) External layer of inactive travertine pinnacle

Abundant aragonite crystals from the external portion of the travertine pinnacle are covered by microbial mats, biofilm Extracellular Polymeric Substances (EPS), silica coatings, bacteria structures and minor calcite crystals (Figure 3.19).

Also, it is possible to recognize some areas with crystalline calcite (Figure 3.19.b). These crystalline packaging clearly show the calcite angles ca. 60 and 120°. Numerous organic spheres are also found over and around them, composed mainly by calcic phosphate (41.8% O; 29.9% Ca; 21.2% P; 7.1% Na) (Figure 3.19.c).



Figure 3.19. Crystalline agglomerates of calcite among acicular crystals of aragonite. The white arrow (a) shows semi-spheroidal substance growing over a calcite crystal, while the black arrow indicates a concave amorphous silica over calcite and aragonite crystals. (b) Rhomboidal cleavage of calcite crystals in an agglomerate. (c) Euhedral calcite crystal with spheroidal organic structures.

### b) Distal deposits

Almost no aragonite crystal is present in these facies, but dendritic calcite forms an irregular and rough surface (Figure 3.20.a) with abundant presence of microbes, biofilm EPS (Figure 3.20.b, c, d and e) and siliceous material. The microbial organisms are abundant, as fragmented cyanobacteria, coccoides and diatoms covering a large part of the surface (Figure 3.20 and Figure 3.21). Silica is usually overlaying the rough external face of calcite, also it is found as concentric growths, characterized by smooth surface textures, acting as a coating of carbonate crystals and organic matter (Figure 3.22 and Figure 3.23).





Figure 3.21. Different diatoms found in the calcite layers from the smooth slope cascade (CC1).



Figure 3.22. Concentric layers formed by aragonite crystals, coccoides and silica coverages, present in the smooth slope cascade (CC1). (a) Frontal view of concentric crusts. (b) External edge of central and outer portions, white arrow points a smooth silica blanket, which has the same composition as the spheroid structures present around it.



Figure 3.23. (a) Hexagonal concentric crystal, which is composed mostly for silica (44.3% Si and 52.3% O), formed on the cascade with steep slope. (b) Isolated silica shield covering the rough calcite and silica surface.

### 3.2.2.4 Electron microprobe

A thin section was analysed by the Electron microprobe, belonging to PF1, which included the external calcite layer.

The fabrics recognized using PPL and cathodoluminescence images are also identified using the Electron Microprobe, where it was possible to corroborate the existence of high concentrations of silica associated to this layer (Figure 3.24). Silica-enriched areas form vermicular shapes across all the external layer, growing inside the calcite crystals and in the spaces among them (Figure 3.25).



Figure 3.24. External layer of inactive pinnacle PF1. (1) Lighter crystals composed by CaCO<sub>3</sub>. (2) Darker crystals with a siliceous composition.





## 3.2.3 Aragonite and mixed deposits

### 3.2.3.1 Polarized light

Aragonite crystals from inner portion of the inactive travertine pinnacle PF1 show a homogenous distribution, forming radial acicular fans, interrupted by perpendicular short fine lines and a few cavities, which seems to generate oxidation in their edges and an irregular arrangement of the crystals (Figure 3.27). Closer to the calcite layer is possible to find only homogenous aragonite fans (Figure 3.26), nevertheless, towards the axial axis of the pinnacle the aragonite crystals become smaller and many euhedral calcite crystals are found, grown among the aragonite crystals (Figure 3.28).



Figure 3.26. PPL image of a thick thin section (core is up, and rim is down) where is possible to see the outer edge of aragonite crystals fans limiting down with the calcite external layer of the inactive travertine pinnacle PF1.



Figure 3.27. (a) Irregular arrangement of aragonite crystals around a cavity presenting oxidation on the edge. Area corresponding to inner portion of the inactive travertine pinnacle PF1. (b) Aragonite crystals with fine perpendicular lines (fractures).



Figure 3.28. Aragonite crystals located close to the centre of the axial axis of the inactive travertine pinnacle (PF1). (a) Image in plane-polarized light (PPL). (b) Same imagen in cross-polarized light (CPL)). (c) Calcite crystals at the centre of the axial axis of the inactive travertine pinnacle, lacking aragonite crystals.

It is possible to observe that crystals of aragonite that are present in the axial axis have lower aspect ratios and lacking radial distribution (Figure 3.28) than those close to the rim (Figure 3.27).

# 3.2.3.2 Cathodoluminescence

Aragonite crystals from the inner part of the pinnacles do not show a great variety of fabrics and luminescence colours, they are all dark green with some light green crystals among them (Figure 3.29). However, at the centre of the axial axis of the travertine pinnacle it is possible to find numerous calcite crystals with clear zonal structure (Figure 3.30, Figure 3.31 and Figure 3.32), varying interspersed from dark red to bright orange, grown behind the aragonite crystals. Some anomalies are observed as an increase of the size of calcite crystals, which seem to be recrystallizing inside vesicles (Figure 3.31).



Figure 3.29. Aragonite crystals viewed by cathodoluminescence (left) and PPL (right), belonging to the inner portion of an inactive travertine pinnacle (PF1).



Figure 3.30. Area close to the axial axis of an inactive travertine pinnacle (PF1). Calcite crystals with red luminescence are replacing aragonite crystals and present a clear zonation (left). Calcite crystals look colourless in PPL image (right).



Figure 3.31. Close to the axial axis of an inactive travertine pinnacle (PF1) greater calcite crystals are found inside some differential spaces among aragonite crystals, all of them showing a clear zonation (left). The space in which they are located seems to have been a cavity (dotted line) filled by aragonite and calcite crystals (right).



Figure 3.32. Mosaic of calcite crystals located along the axial axis of an inactive travertine pinnacle (PF1). All the crystals are showing zonation (left), while the brighter look opaquer at the PPL image (right).

Also, it is possible to suggest that a relation between brighter luminescence colours and opaque minerals in PPL exists, considering that the most of brighter crystals in the CL images look opaquer than the rest of minerals in PPL image, but this implication is not observed clearly in the opposite direction (Figure 3.32).

### 3.2.3.3 Scanning Electron Microscope (SEM)

Samples from three travertine pinnacles were analysed using SEM images: two inactive travertine pinnacles (PF1 and PF2) and one in current formation (PA). From the first only internal parts were considered to analyse the aragonite precipitated crystals (PF1I and PF2I), and 2 samples were collected from the one that is active: from the top of its vent (PA1) and from its bottom (PA2).

## a) Inactive pinnacles

Acicular aragonite crystals belonging to the internal parts of inactive pinnacles have the greatest aspect ratios (up to 40) (Figure 3.33.b). They have parallel and radial arrangement (Figure 3.33.a). Some of the crystals show broken faces and most of them lacking microbial mat and EPS (Figure 3.34 and Figure 3.35). However, several crystals located close to external face of the pinnacle content on their surface some biotic structures (Figure 3.34, Figure 3.35 and Figure 3.36) and several calcite euhedral crystals (Figure 3.37). Biotic structures are found as organic filaments that form bridges between the surfaces of crystals and also as amorphous substances that wrap crystals (Figure 3.34).



Figure 3.33. (a) Fragment of an inactive pinnacle (PF2I) showing the longitudinal arrangement of aragonite crystals. (b) Aragonite crystal with an aspect ratio of ca. 35, showing the wide variety of crystal lengths.



Figure 3.34. Broken faces of aragonite crystals belonging to PF2I. Right: It is possible to observe some microbial mat (white arrow) and some small biotic structures (visible as light dots over the aragonite faces).



Figure 3.35. (a) Aragonite twins located into an inactive pinnacle (PF2I), growing in different directions. Ruptures of faces and EPS are visible. (b) Aragonite fans grown in radially (c) and in opposite directions (right). Microbial structures are present, but they are very scarce (white arrow). Also, a calcite crystal was found at the centre of a fan (black arrow).



Figure 3.36. Organic and amorphous substance covering an aragonite crystal into an inactive pinnacle (PF2I).

Figure 3.37. Aragonite (long) and calcite (hexagonal) crystals are present near the axial axis of the inactive pinnacle PF1I.

#### b) Pinnacle in current formation

The main difference found between inactive pinnacles and those in formation is the existence of an external calcite and silica coverage which are much more present in the first ones. Organic filaments (biofilm EPS and cyanobacteria) and crystals of euhedral calcite are also found in the outer coating and among aragonite crystals near it, especially towards the base of the pinnacle (Figure 3.38), but in less quantity than in PF1 and PF2. While the top of the vent of the pinnacle lacks organic matter, only long aragonite crystals are found.



Figure 3.38. Part of the upper part of the vent of the travertine pinnacle in current formation (PA1).

The crystalline arrangements are less ordered on the bottom respect to the top of the pinnacle, changing from a mainly parallel to a radial and chaotic arrangement (Figure 3.39) accompanied also by a greater presence of calcite and organic components in the outermost portions (Figure 3.40).



Figure 3.39. Radial arrangement of aragonite crystals from the bottom of the pinnacle (PA2).



Figure 3.40. Presence of microbes, biofilm EPS and calcite observed on the external surface of the bottom of a pinnacle in formation (PA2). (a) Presence of EPS among the aragonite crystals connecting deteriorated aragonite crystals. (b) Silica coverage related to a great concentration of cyanobacteria. (d) Pyramidal structure made of calcite crystals grown over aragonite crystals.

# 3.2.3.4 Electron microprobe

As seen above, inactive pinnacles can be divided into 3 well defined parts from outside to the axial axis: (i) a crust formed by a calcite mosaic, (ii) a thick portion composed mainly of fans of aragonite crystals, and (iii) a mixed area with aragonite needles overlapping zoned calcite crystals. Parts (i) and (ii) are visible in Figure 3.41.

Two thin sections belonging to one of the inactive travertine pinnacles (PF1) were analysed using the electron microprobe, especially to identify the composition variations across the zoned crystals of calcite located along the axial axis of the pinnacle.

It was possible to identify two types of zoned crystals (from Figure 3.42 to Figure 3.47): (i) a group with a remarkable light rim that is very thin and surrounds the core, enriched mainly in Fe and slightly in Mn, and (ii) another set of crystals with a core enriched in Mn in the centre and with positive peaks of Fe, particularly at the edge of these cores. In both groups SO<sub>3</sub> generally tends to elevate its concentration towards the edge of the core, presenting less define rims in the rest of the crystal.

Most of fractures, aragonite needles and amorphous silica (dark grey zones) seem to have been formed after zoned crystals interrupting the rims, and few small vesicles show a light-coloured edge.



Figure 3.41. Aragonite crystal in contact with the calcite external and intermediate layers of an inactive pinnacle (PF1). (i) External crust formed by a calcite mosaic; (ii) internal portion composed mainly of fans of aragonite crystals.



Figure 3.42. (a) Calcite crystal showing a clear zoning, present among aragonite crystals. Black line (L1) indicates the transect made of 20 points separated by 7.51  $\mu$ m between them from the core (9) to the edge (28) of the crystal, which was analysed to know the composition variation. (b) Diagram with the chemical composition of the transect L1.



Figure 3.43. (a) Calcite crystal showing a clear zoning, present among aragonite crystals. Black line (L2) indicates the transect made of 10 points separated by 6.43  $\mu$ m between them from the core (32) to the edge (41) of the crystal, which was analysed to know the composition variation. (b) Diagram with the chemical composition of the transect L2.


Figure 3.44. (a) Calcite crystal showing a clear zoning, present among aragonite crystals. Black line (L3) indicates the transect made of 8 points separated by 5.89  $\mu$ m between them from the core (44) to edge (51) of the crystal, which was analysed to know the composition variation. (b) Diagram with the chemical composition of the transect L3.



Figure 3.45. (a) Calcite crystal showing a clear zoning, present among aragonite crystals. Black lines (L4 and L5) indicate the transects analysed to know the composition variation. The dark grey area bordering aragonite and calcite crystals is composed of silica, as filling spaces. (b) Diagram with the chemical composition of the transect L4, made of 15 points from the core (65) to the edge (79) of the calcite crystal. All points are separated by 5.51 µm between them. (c) Diagram with the chemical composition of a transect L5, made of 11 points from the core (80) to the edge (90) of the calcite crystal. All points are separated by 5.64 µm between them.



Figure 3.46. (a) Calcite crystal showing a clear zoning, present among aragonite crystals. Black lines (L6 and L7) indicate the transects analysed to know the composition variation. The dark grey area bordering aragonite and calcite crystals (in the upper area of the image) is composed of silica, as filling spaces. (b) Diagram with the chemical composition of the transect L6 made of 11 points from the core (91) to the edge (101) of the calcite crystal. All points are separated by 5.94 µm between (c) them. Diagram with the chemical composition of the transect L7, made of 8 points from the core (102) to the edge (109) of the calcite crystal. All points are separated by 5.31 µm between them.



Figure 3.47. Calcite crystal showing a clear zoning, present among aragonite crystals. Black line (L8) indicates the transect made of 20 points separated by 5.90  $\mu$ m between them from the core (119) to the edges (110 and 229), which was analysed to know the composition variation. (b) Diagram with the chemical composition of the transect L8.

## 3.2.4 Stable isotopes

## 3.2.4.1 Stable isotopes from samples

Samples from all travertine deposits were prepared in different ways (dried at room temperature and treated with peroxide) to be analysed using Isotope-Ratio Mass Spectrometry (IRMS).

The values are normalized according to the experiments developed by Kim *et al.*, 2015 for calcite and aragonite precipitated at 75°C (Table 3.4).

Is possible to differentiate two main groups according to  $\delta^{13}$ C values: calcite and aragonite deposits (Figure 3.48). They coincide with the groups defined above, where the highest values correspond to calcite deposits and the most negative values to aragonite deposits, with one exception: the most negative values of calcite correspond to outer layers of an inactive pinnacle (PF1E), not from the cascading deposits, as do the rest of the results of this group.



Figure 3.48. Plot of  $\delta^{18}O$  and  $\delta^{13}C$  [V-PDB] of carbonate deposits from the Porcelana Geysers area.

Carbonate deposit*	Sample ID	Type of deposit	Mineralogy	<u>δ180</u> ‰(VPDB)	_δ13C	δ13C (CO2)**	Calculated T*** (°C)
CC1	31T1	Eflorescences in cascade	Calcite	-17.5	-2	-12.7	73.2 <sup>(b)</sup>
CC2	G3B	Eflorescences in cascade	Calcite	-16.5	-1.2	-11.7	65.8 <sup>(b)</sup>
CC2	G3A	Eflorescences in cascade	Calcite	-15	0.8	-9.4	56.7 <sup>(b)</sup>
CC2	G3C	Eflorescences in cascade	Calcite	-16.2	-2.7	-13.5	64.5 <sup>(b)</sup>
CC2	3GT3	Eflorescences in cascade	Calcite	-16.2	-1.4	-11.9	63.8 <sup>(b)</sup>
PF1E	01-A1	Fossil pinnacle, exterior	Calcite	-17.7	-3.4	-14.4	73.6 <sup>(b)</sup>
PF2E	1-211B	Fossil pinnacle, exterior	Aragonite	-20.5	-3.8	-14.8	76.1 <sup>(a)</sup>
PF2E	31T2II	Fossil pinnacle, exterior	Aragonite	-20.2	-3.7	-14.7	74.8 <sup>(a)</sup>
PF2E	31T2-B	Fossil pinnacle, exterior	Aragonite	-20.5	-3.8	-14.9	76.7 <sup>(a)</sup>
PF2E	31T2-C	Fossil pinnacle, exterior	Aragonite	-20.5	-3.8	-14.8	76.7 <sup>(a)</sup>
PA1	3GT1	Active pinnacle, top	Aragonite	-20.4	-3.8	-14.8	75.9 <sup>(a)</sup>
PA2	G2A	Active pinnacle, bottom	Aragonite	-20.2	-4	-15.0	74.4 <sup>(a)</sup>
PA2	G2B	Active pinnacle, bottom	Aragonite	-19.9	-4	-15.1	72.9 <sup>(a)</sup>
PA2	G2C	Active pinnacle, bottom	Aragonite	-19.8	-3.6	-14.5	71.9 <sup>(a)</sup>
PA2	3GT2	Active pinnacle, bottom	Aragonite	-19.5	-3.6	-14.6	70.2 <sup>(a)</sup>
PF1I	01-A2	Fossil pinnacle, interior	Aragonite	-19.5	-3.1	-14.0	71.7 <sup>(a)</sup>
PF1I	01-A3	Fossil pinnacle, interior	Aragonite	-19.3	-3.3	-14.3	70.5 <sup>(a)</sup>
PF1I	01-A4	Fossil pinnacle, interior	Aragonite	-19.3	-3.5	-14.5	70.4 <sup>(a)</sup>
PF1I	01-A5	Fossil pinnacle, interior	Aragonite	-19.9	-3.9	-15.0	73.7 <sup>(a)</sup>
PF1I	01-A6	Fossil pinnacle, vesicle	Calcite	-16.8	-2	-12.7	68.4 <sup>(b)</sup>
PF1I	01-A7	Fossil pinnacle, amygdale	Mixed	-19.5	-3	-13.9	71.6 <sup>(a)</sup>
PF2I	1-21	Fossil pinnacle, interior	Aragonite	-20.4	-3.8	-14.8	75.7 <sup>(a)</sup>
PF2I	1-211A	Fossil pinnacle, interior	Aragonite	-20.1	-3.7	-14.7	73.9 <sup>(a)</sup>
PF2I	31T2-D	Fossil pinnacle, interior	Aragonite	-20.6	-3.6	-14.6	76.8 <sup>(a)</sup>
PF2I	31T2I	Fossil pinnacle, interior	Aragonite	-20.3	-3.7	-14.7	74.9 <sup>(a)</sup>
PF2I	31T2-A	Fossil pinnacle, interior	Aragonite	-20.5	-3.8	-14.8	76.3 <sup>(a)</sup>

Table 3.4. Stable isotopes values belonging to all different carbonate deposits present in Porcelana Geysers zone.

\* Areas indicated in Figure 3.13. \*\* Values obtained with the equation:  $\delta^{13}C_{(CO2)} = 1.2 \cdot \delta^{13}C_{(trav)} - 10.5$  (Panichi and Tongiorgi, 1975; Minissale *et al.* 2002). \*\*\* Calculated isotopic temperature from  $\delta^{18}O$  data on the travertine. <sup>(a)</sup> Zhou and Zheng, 2003. <sup>(b)</sup> Kim and O'Neil, 1997.

#### 3.2.4.2 Paleotemperatures of precipitating water

It is possible to estimate the temperature of saturated water that precipitated the carbonate deposits from  $\delta^{18}$ O, based on the isotopic fractionation occurred during the process which is temperature dependant (Urey, 1947). Two equations have been used according to the mineral phase. For aragonite, the calculus was made with the equation developed by Zhou and Zheng (2003):

$$T (^{\circ}C) = (20.44 \cdot 1000/(10^{3} \ln \alpha + 41.48)) - 273.25$$
(3.8)

Where  $\alpha$  is defined as:

$$\alpha = \frac{\frac{\delta^{18}O_{\text{travertine}} \cdot 2005.2}{1000}}{\frac{\delta^{18}O_{\text{water}} \cdot 2005.2}{1000}}$$
(3.9)

In this case,  $\delta^{18}O_{water}$  was taken from the data obtained for sample Por-1 collected in 2016 (Table 3.2), where  $\delta^{18}O_{water-1B}$  is equal to 7.21 ‰.

For calcite, according to the work of Kim and O'Neil (1997), the equation 3.8 is as follow:

$$T (^{\circ}C) = (18.03 \cdot 1000/(10^{3} \ln \alpha + 32.17)) - 273.25$$
(3.10)

The obtained values do not cover a very wide range (from 56.7 to 76.8°C). The lowest values were obtained with calcite data with an average of 69.5°C, while the values calculated for aragonite have an average of 73.8°C.

### 3.2.4.3 Carbon isotope ratios for original CO<sub>2</sub>

With the carbon isotope ratios of active and inactive travertine deposits it is possible to have an estimate of the original conditions of the gas that participated in the precipitation of this carbonate. For this calculation, the equation developed by Panichi and Tongiorgi (1975) and used by Minissale *et al.* (2002) was used with all the values measured from travertine deposits, which are shown the Table 3.4.

Estimated  $\delta^{13}$ C values for original CO<sub>2</sub> range from -15.1 to -9.4‰ VPDB, with an average of -14.0‰ VPDB (Table 3.4), which are not negative enough to be considered from biogenic or organic source and neither positive enough to be explained only by a magmatic-volcanic source (Minissale *et al.* 2002; Rose and Davisson, 1996; Rollinson, 1993; Panichi and Tongiorgi, 1975; Deines *et al.*, 1974).

### 3.3 Gas

A unique gas sample was obtained from an active travertine pinnacle due to the difficulty of the accessibility, which was analysed to obtain the concentration of non-condensable gases (Table 3.5). These analyses are useful to know about the steam fraction and to analyse the atmospheric content of geothermal gases.

Table 3.5. Results of non-condensable gases from gas sample collected from an active travertine pinnacle.

Sample	Ar	O2	N2	CH4	CO	He	H2	CO2	H2S	Gas fraction
ID	(mmol/mol)									(%)
PA	1.44	8.20	105.49	0.256	n.d.	0.008	29.19	853.8	1.62	1.16

The gas chemical composition indicates that the main source of gas corresponds to atmospheric air origin because of its low He content (Figure 3.49), generally associated to magmatic deep source.



Figure 3.49. Ternary diagram of He, Ar and N<sub>2</sub> compositions of gas geothermal samples (Giggenbach, 1983).

Although, the origin of the gas seems to correspond to a mixed source, not only because of the N<sub>2</sub>/Ar ratio (PA sample is slightly displaced respect air in the Figure 3.49) but also because the gas fraction and the N<sub>2</sub>/CO<sub>2</sub> ratio are not high enough to be related only to the meteoric source (Figure 3.50; Lowenstern *et al.* 2015).



Figure 3.50. Log (% Gas) versus log (N<sub>2</sub>/CO<sub>2</sub>), and bubble diameter scaled according to log (Ar/He) (Lowenstern *et al.* 2015).

### 3.4 Microbiology

Some samples of organic mat and carbonates were analysed to have an idea about filamentous microorganisms that are visible by optical microscopy (Figure 3.16.e), SEM (Figure 3.18, Figure 3.19, Figure 3.20 and Figure 3.21) and electron microprobe (Figure 3.25). The most of samples correspond to carbonate deposits with low biomass presence.

DNA quantification and visual confirmation were made, where it is possible to observe that samples do not present a great amount of genetic material (Figure 3.55), except for sample 1-C2 (Figure 3.52.b) that showed a lot of degraded DNA. After the Polymerase Chain Reaction (PCR), it is observed that there was an amplification of the ribosomal gene except in the sample 1-C1-L (1-C1 with RNA*later* solution), and in the sample 1-C2, where the genetic material is slightly degraded (Figure 3.56). For the other samples fragment amplification is observed.

Then, in the results of the DGGE similar band patterns are observed for the samples, but with some unique bands (Figure 3.57). In the third lane there is a continuum of DNA without clear bands, which agrees with what was observed in the PCR gel of the sample 1-C2 (Figure 3.56).

Subsequently, based on the image of Figure 3.57, an identification of the common bands among the samples was performed in order to make a matrix of presence and absence of these. In Figure 3.58.a the most evident bands superimposed on Figure 3.57 were selected and are observed Figure 3.58.b, which were ordered to analyse correlations among them. The samples were grouped based on this identification of common bands in a Bray-Curtis dendrogram (Figure 3.59), the similarity among the samples is given according to the band patterns as a percentage.

Therefore, two groups of bacteria with similarity percentages over a 50% can be recognized:

- Group A: 1-C1, 1-C2 and G-C4 with a 51.4% of similarity, where both 1-C1 and G-C4 (subgroup A.1) present an efflorescence texture (with a 69.9% of similarity between them) and are correlated to CC1 and CC2 calcite samples (Figure 3.13, Figure 3.52.b and Figure 3.54), respectively, which are the carbonate samples with more biotic presence and silica structures, while 1-C2 is closer to the level of hot water, which suggests that its temperature would be higher, generating a decrease in the amount of certain groups of specimens and favouring others.
- Group B: G-C1 and G-C2, with a 60% of similarity, that is coherent with the location of the sample, where the hot water runs down from the top (G-C1) to the base of the pinnacle (G-C2), these samples are correlated to PA1 and PA2 aragonite samples (Figure 3.13.e and Figure 3.53), respectively. Sample G-C3 cannot be grouped with a high similarity percentage, probably due to the lower presence of biomass due to the higher temperatures of the hot water flow.





Figure 3.51. (a) Sampling areas, where (i) corresponds to the place of the samples with index 1 and (ii) to those with index G. (b) Close view of area pointed out in the square (i) in Fig. (a).





Figure 3.52. (a) Frontal view of selected area in Figure 3.51. (b) Close view of the white square indicated in Figure (a), with the location of the samples.







Figure 3.54. (a) Calcite cascade located between two areas with travertine pinnacles. (b) Eflorescences texture of calcite cascade.



Figure 3.55. DNA extraction confirmation. Low genetic material available in most of the samples.



Figure 3.56. Polymerase Chain Reaction (PCR) of the rRNA gene 16S. It is observed that there is no amplification in the samples 1-C1-L and 1-C2.



Figure 3.57. Denaturing Gradient Gel Electrophoresis (DGGE) of environmental samples of Porcelana Geysers and crops. Different bands of interest were marked to later cut and sequence.

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Figure 3.58. Bands selected for presence-absence matrix based on the Denaturing Gradient Gel Electrophoresis (DGGE) obtained for all the samples.



Figure 3.59. Bray-Curtis similarity dendrogram according to the matrix of presence and absence of bands for each sample (Figure 3.58).

### 4 Discussion

As for many geothermal systems of Chile, Porcelana Geysers has travertine precipitation associated to its water flow, nevertheless the resistant morphology and the high precipitation rates are anomalous, presenting a growth only measurable through changes in pinnacles dimensions. A characteristic that it is expected to be found in this type of waters is a high CO<sub>2</sub> concentration, not only in the waters (as HCO<sub>3</sub>) but also in the exsolved gas which can come from an atmospheric, biogenic, volcanic or lithological source, depending on the processes that occur underground. This can be studied reviewing the geochemical analysis and it is possible to propose some processes occurring in subsurface to explain this anomaly, involving the high permeability estimated in this area.

### 4.1 Bicarbonate sources

When the contents of calcium and strontium are compared with those of bicarbonate, it is observed that they do not have a 1:2 ratio between them because the HCO<sub>3</sub> ion exceeds them widely, reaching a ratio of 1:4., even joining the concentrations of both cations they are not enough to reach HCO<sub>3</sub> values. This high presence of bicarbonate could be the main cause of high precipitation of carbonates, whose origin can explain the existence of the travertine pinnacles formed by the geyser fluids. However, despite the high bicarbonate content, hot water has higher chloride contents, taking into consideration its conservative and hydrophilic behaviour it may be useful to use these concentrations as an instrument to elucidate possible sources from water, gas and rock. In addition, the characteristics of CO<sub>2</sub> are also good markers to detect different processes that are responsible for the final composition and, in particular, the high concentrations of bicarbonate in the emitted fluids, these processes can come from both deep and superficial sources, therefore, the depth of the sources can finally indicate some factors that make the precipitation rate so high and this area so special.

## 4.1.1 Chlorides source

The geochemical concentrations of sampled waters show that the southern bank thermal spring (Por-3), the thermal pool (Por-4) and the river water (Por-2) correspond to more diluted versions of the hot spring located in the geysers area (Por-01), therefore this can be considered as the most proximal sample and that with the geochemistry closest to the original reservoir.

The water geochemistry of all these samples indicates that the reservoir waters are chlorinated, even the river water, that *a priori* does not agree with the assumption that these waters were bicarbonate. To understand this situation, the origin of chlorides can be useful.

It is unknown which is the mineral phase in which the chlorides are added in the waters because of the hundreds of models generated by the inverse modelling, where the only mentioned phase that contains CI is halite. To have a proposal about some source of chlorides it is useful to observe that chloride contents tend to increase with temperature but not in a perfect linear trend where fjord water escapes from the trend (Figure 4.1). This could mean that it exists magmatic or deep source of chlorides but that this is not the only one. Therefore, analysis of major and trace elements and comparisons of the water with highest concentration of chlorides with the rest of the samples where studied. In this case, fjord water corresponds to the most saline water which shows similar rates of Na and Cl with respect to the rest of the waters, in particular the thermal ones. Fjord water has similar Na/Cl ratio with respect to the rest of the rest of the waters, in particular the thermal ones. Compositions of other elements than sodium as bromine and strontium have also been highlighted, thus Br/Cl, Sr/Cl, B/Cl, Rb/Cl and Cs/Cl ratios were compared to those of thermal waters and show similar values in the most of cases among them (Figure 4.2 and Figure 4.3).





Fjord water is depleted respect to standard seawater respect all elements (Turekian, 1968), but this was expected regarding that it consists of a mixed system and also that the samples were collected from the water surface. Nevertheless, some elements have higher concentrations respect to the river and thermal waters, which were considered to be compared. Fjord water and the rest of the waters have similar Na/Cl, Br/Cl and Sr/Cl ratios among them, as it is possible to see in Figure 4.4. These elements have a more or less positive relationship with respect to the temperature of the water surface, but this trend is interrupted by the fjord water and a slight negative relationship between the waters located along the geyser area, which could be generated by fjord contribution.





Although, there are other trace elements that do not show this similarity, such as boron, rubidium and caesium, where B/Cl, Rb/Cl and Cs/Cl ratios are much higher for thermal and even river water than for fjord water (Figure 4.4). In addition, the pattern of the concentrations versus temperature are positive, but again there is a chaotic distribution of the waters located along the area of geysers (grey circles in Figure 4.4).

Furthermore, considering lithium for being a conservative constituent, the Li-Cl-B ternary plot shows that all thermal waters fall between areas of absorption of steam (Figure 4.2), suggesting a possible mixture of a volcanic steam input and an external source that could be a fjord water intrusion and a small lithological contribution.

Another result that indicates a mixed origin of fluids is the tendency generated by the concentrations of fluorine with respect to chloride, where the contents of F tend to increase by one order of magnitude (molar concentrations) among the waters of the geysers, hot springs, rivers and fjord, while the Cl increases to almost two orders of magnitude. Fluorine usually comes from evaporite dissolution and volcanic gases, thus, considering the evaporite lack in the area, is expected that this anion increases slowly, while chlorides seem to have an additional source that change the F/Cl molar ratios (Figure 4.5).

Some diagrams and data seem to support the idea of a fjord water input and others indicate the opposite, while the relationship among some conservative elements do not show any clear trend. This contradictory behaviour suggests that a fjord contribution should not be discarded considering that the coast of the fjord is only 2 km northeast and that there are many fractured aquifers studied which are located further away from the coast that have a marine contribution (Kim *et al.* 2006; Sebben *et al.* 2015). However, the main source of chlorides seems to be related to a geothermal source because of the classification obtained by B/CI and Br/CI ratios displayed in the Vengosh diagram (Figure

3.9.a and Figure 4.4) and because of the slight proximity of the waters to the crustal weathering in the CI-Li-B ternary plot. In both cases, the structural complex that has been observed (intersection between LOFS and ALFS) could be responsible for generating a high enough permeability to connect the geothermal and fjord systems and making them contribute to the system that origins the hot springs and the geysers, evidence of this is the knowledge of fishermen who have seen thermal fluids and bubbles emerging from the fjord floor, that would talk about a very deep mix of waters.



Figure 4.3. Left: Na/Cl, Br/Cl and Sr/Cl molar ratios compared to Cl contents of thermal, river and fjord waters. ("r" means in meq/L). Right: Concentrations (ppm) versus temperatures measured on the surface.



Figure 4.4. Left: B/Cl, Rb/Cl and Cs/Cl molar ratios compared to Cl contents of thermal, river and fjord waters. ("r" means in meq/L). Right: Concentrations (ppm) versus temperatures measured on the surface.



Figure 4.5. Left: F/CI molar ratio compared to CI contents of thermal, river and fjord waters. ("r" means in meq/L). Right: Concentrations (ppm) versus temperatures measured on the surface.

#### 4.1.2 Depth of the sources

Chlorides seem to indicate that at least geothermal and fjord components could be feeding the system, but the depth information allows to create a more detailed model of fluid dynamics.

When a deep source it is involved it is normal to find reducing conditions in the waters, even sometimes on the surface, but this implication is not correct in the opposite sense. In this case, all thermal waters presented negative values of redox potential (Eh: from -284 to -71.5 mV), which is consistent with the great depletion of sulphate ions. That Eh values have been increasingly positive over the years it does not mean that there could necessarily exist an oxidizing trend over time, because there was no relationship with rainfall rates, but it is a good example of its high variability.

Reducing conditions can be generated by several factors, not only by great depth reservoir, but also by a volcanic contribution, bacterial reduction or organic input (Tan *et al.*, 2017; Reguera, 2012; Pfeffer *et al.*, 2012; Christensen *et al.*, 2000; Fritz *et al.*, 1989).

An option that supports the deep source possibility is the high B/CI ratios in thermal waters, especially in Por-1 and Por-3 that, as was mentioned above, is not explained by a fjord contribution but a volcanic steam.

Another larger redox record corresponds to that evidenced in zoning of calcite crystals present in the axial axis of the inactive travertine pinnacles. These crystals are considered representative because of two reasons: (i) they would correspond to long time of precipitation process (tens of years), because during the period 2014 - 2018 no euhedral crystal of calcite was found in a new pinnacle, but they were formed only by aragonite needles were found with few isolated anhedral calcite crystals, which had grown

only from one year to the next; and (ii) also it is coherent to establish that these calcite crystals would have been precipitated by the last fluids that flow through the pinnacle before it became inactive, because these crystals are located in the middle of their paleoduct.

Zoning in calcite crystals observed both with cathodoluminescence and with microprobe analysis, should reflect the redox conditions of the fluids that precipitated the calcite (Figure 4.6, Hiatt and Pufahl, 2014; Kyser *et al.*, 2002; Vahrenkamp and Swart, 1994; Cander, 1994; Barnaby and Rimstidt, 1989; Amieux, 1982; Frank *et al.*, 1982; Meyers, 1978; Meyers, 1974). These rims are not only on the axial axis of the inactive pinnacle, but also are in the external calcite layer (Figure 3.17), where they form a dense light orange area.

It is not possible to stablish a clear correlation among all light zoning within the crystals both cathodoluminescence and microprobe, but with cathodoluminescence images (Figure 3.17, Figure 3.30, Figure 3.31 and Figure 3.32) three statements can be made: (i) considering a stable pH value generated by a constant carbonate precipitation and a quasi-stationary acid input, allows to reaffirm that redox conditions of water are mostly reducing (Figure 4.4; Hiatt and Pufahl, 2014), (ii) thin light orange rims might represent quick changes in water redox conditions, particularly oxidizing; and (iii) a more oxidizing environment would be present during the formation of the calcite layer (A1 in Figure 3.15).

Moreover, few microbiologic studies have been written about Porcelana geysers and nearby areas (Mackenzie *et al.*, 2013 and Alcorta *et al.*, 2018), where none of the identified organisms, particularly cyanobacteria, represent a great reducing factor to justify such negative values. But, regarding that all filamentous bacteria observed were found among calcite crystals, specifically in the brighter crystals (in CL images), it is reasonable to propose that they grow at more oxidizing conditions respect to the forming characteristics of the rest of carbonate precipitation.

Regarding the carbonate deposits, carbon isotope ratios are mostly negative, which is not common for hydrothermal travertines (Della Porta, 2015; Capezzuoli *et al.* 2014; Pola *et al.*, 2014; Minissale, 2004; Fouke *et al.*, 2000; Manfra *et al.*, 1976; Friedman, 1970; Fritz, 1965), particularly they tend to have a certain closeness to values of calcites associated with modern freshwater cyanobacteria and algae (Pentecost and Spiro, 1990).



Figure 4.6. Eh / pH diagram for the aqueous species of Mn and Fe superimposed by idealized CL colours that would be expected from calcite under those conditions. Obtained from Hiatt and Pufahl, 2014.

Aragonite <sup>13</sup>C/<sup>12</sup>C ratios have an average value of -3.6‰, while calcite samples have an average of -1.4‰. At first, these values, as it was mentioned above, are more negative than it was expected because the high temperatures measured in field and those calculated by the use of  $\delta^{18}$ O values. These can be related to different processes as: (i) injection of water that contains dissolved CO<sub>2</sub> from older rocks weathering (Sarg et al., 2013), (ii) exchange of CO<sub>2</sub> atmosphere-hydrosphere, where CO<sub>2</sub> depleted in  $^{13}$ C is incorporated in the water (Sarg et al., 2013), (iii) organic CO<sub>2</sub> input through organic matter alteration (Minissale et al., 2004), or (iv) dilution and reprecipitation of metamorphic limestones (marble) (Minissale et al., 2004); in this case the only possibility of existence of this type of lithology is very deep in the crust and as a small portion, because there is no presence of carbonate lithology in geological maps or observed on the surface, also because metamorphic rocks (Bahía Mansa Metamorphic Complex) are outcropping in the studied area, making this last option very unlikely. In the same way, water that contains dissolved CO<sub>2</sub> from older rocks weathering tends to be related to a water-soil interaction (Prado-Pérez et al., 2013) generated by the occurrence of a greater soil development generated from rock weathering. Nevertheless, the soil thickness along the water rising zones is very thin (less than 1 metre on the surfaces with more vegetation) because faults and fractures not only favour the high permeability but also river erosion, forming steep slopes banks in which geysers and hot spring rise, which does not allow to form a thick soil layer, which is actually only a few tens of centimetres thick over intrusive rocks belonging to the North Patagonian Batholith; it can only be considered as a possibility for the thermal waters of Por-4 that are located downstream and are surrounded by a more developed vegetation and soil, and for some recharge area upstream. Therefore, another factor that can be ruled out as a significant local reducing factor is the existence of an anoxic organic environment derived from the degradation of organic material, but this is unknown for recharge areas upstream.

Regarding gas contribution, these can come from a meteoric (atmospheric or shallow levels) or magmatic (deep levels) sources that can be recognized through the comparison with other components and the analysis of carbon isotope ratios. In this way, gas fraction, N<sub>2</sub>, He, Ar and particularly CO<sub>2</sub> gas contents and carbon isotope ratios help to elucidate the main source of gas. The problem is that the diagrams that compare  $\delta^{13}C_{water}$  versus TDIC (Frondini *et al.*, 2009), He, Ar, N<sub>2</sub> gas compositions (Figure 3.49, Giggenbach *et al.*, 1983) and gas fraction versus N<sub>2</sub>/CO<sub>2</sub> (Figure 3.50, Lowenstern *et al.*, 2015) suggest different sources. On the one hand, Giggenbach *et al.* (1983) ternary diagram indicates an atmospheric source, at least for N<sub>2</sub> and Ar. On the other hand, Frondini *et al.* (2009) and Lowenstern *et al.* (2015) diagrams suggest a mixed or undefined source for CO<sub>2</sub>.

Because CO<sub>2</sub> occurs within the aquifer as a free gas phase, (HCO<sub>3</sub>)<sub>aq</sub>, and as a component in precipitating carbonate, the isotopic composition of CO<sub>2</sub> in gas, can elucidate the origin of the fluids that form travertine. Although it was not possible to obtain  $\delta^{13}$ CcO<sub>2</sub> data from gas samples, these values could be estimated from samples of active and inactive carbonate (Table 3.4). The ratios calculated from aragonite samples have an average value for the original CO<sub>2</sub> of -14.6 ‰ [VPDB], while those calculate from calcite average -12.0‰ [VPDB]. Such negative <sup>13</sup>C/<sup>12</sup>C ratios could arise from mixing between a deeply derived CO<sub>2</sub> generated by the input of deep hydrothermal solutions with a  $\delta^{13}$ CcO<sub>2</sub> = [-2.0, 3.0]‰ (VPDB) (Chiodini *et al.*, 2008; Minissale *et al.*, 2002; Rollinson, 1993) and descending organic derived CO<sub>2</sub> with  $\delta^{13}$ CcO<sub>2</sub> < -20‰ (VPDB) (Chiodini *et al.*, 2008; Deines *et al.*, 1974; Rose and Davisson, 1996), which agrees with Lowenstern *et al.* (2015) about a mixed source of gas.

The small difference between the values of aragonite and calcite for <sup>13</sup>C/<sup>12</sup>C ratios of CO<sub>2</sub> could be explained by the isotopic fractionation generated by carbonate precipitation downstream, thus heavier C-isotopes remain in the water that precipitates calcite at lower temperatures (Minissale *et al.*, 2004, 2002).

#### 4.2 External coverage travertine pinnacles

Two types of travertine pinnacles can be identified according to their life period: active and inactive pinnacles, all of them located on the northern river bank. Active pinnacles seem to have high erosion and grow rates whose changes are easily visible between one year and another, instead of the inactive pinnacles that keep their morphology over time.

The main different found between these two groups is the existence of a calcite layer covering an aragonite core in inactive pinnacles, while active pinnacles do not present that coverage that seem to be the product of the cessation of flow and a decrease in temperature, because zoned calcite crystals are found in both the outer layer and the axial axis of the pinnacle, which may be its paleo-conduit that may have precipitated calcite crystals during several dissolution and precipitation stages, generating a high presence of cavity filling textures (Figure 3.27, Figure 3.28, Figure 3.31 and Figure 3.32).

Also, external calcite coverage is characterized by a high biomass presence (even in the active pinnacle but to a lesser extent) such as diatoms, filamentous bacteria and abundant biofilms that seem to fill spaces among the calcite and aragonite crystals and inside of some fractures and cavities of them. Also, it is possible to recognize some textures that could talk about biomineralization during the last stage of crystallization, because of the high presence of spherulitic and amorphous silica covering calcite and aragonite crystals, even with microorganisms as part of their own structure (Figure 3.22 and Figure 3.23).

Table 4.1. Microbiological samples related to the precipitation temperatures of the carbonates in which they were collected.

Sample	Carbonate	Type of deposit	Precipitation T**	High similarity
ID	deposit*		(°C)	Group
1-C1	CC1	Calcite eflorescence	73.2	A (A.1)
1-C2	n.c.	Organic mat	-	А
1-C3	n.c.	Organic mat	-	-
G-C1	PA1	Aragonite from pinnacle	75.9	В
G-C2	PA2	Aragonite from pinnacle	72.4	В
G-C3	n.c.	Organic mat	-	-
G-C4	CC2	Calcite eflorescence	62.7	A (A.1)

\*Areas indicated in Figure 3.13. \*\* Precipitation temperatures of the carbonates calculated from δ<sup>18</sup>O values (Table 3.4). "n.c." refers to samples of bacteria that were not found in carbonate rocks.

In this context, microbiologic samples were collected from organic matter and carbonates from the geysers area, to find some special correlation.

Group A.1 is the one with highest similarity percentage (69.9%) that was found for calcite efflorescences, one formed on the base of a fossil pinnacle under an active hot water flow and another sample from several metres away forming a calcite cascade (Figure 3.52, Figure 3.54 and Figure 3.59). While Group B with lower similarity index (60%) is formed by the two samples collected from an active pinnacle, which as a group has a 46.1% of similarity with the first group the rest of bacteria group, except for green mat that was collected on the base of the active pinnacle. The temperatures cannot be measured *in situ*, but temperature of carbonate precipitation was calculated by using oxygen isotope ratios obtained for travertine samples.

According to the crossing of data from travertine and microbiological samples, it is possible to create a correlation between the groups of bacteria and the calculated temperature of carbonate precipitation (table 4.1). The difference between precipitation temperatures related to samples of group A.1 is more than 10°C, despite the great similarity between them, while members of the group B show less similarity but closer temperatures. Therefore, three different statements can be formulated: (i) there is no a

direct relationship between bacteria distribution and temperatures of carbonate precipitation, (ii) that a group of bacteria can prevail during the cooling of the waters from proximal to distal zones and (iii) that most of the bacteria present in group A are favoured by the existence of a minimum flow of water but they cannot be present near a point with emission of gas and water at high pressure as in PA1 and PA2; therefore, it could be a good assumption to say that they can grow on a surface like the fossil pinnacles, but they cannot do it on those that are currently precipitating, especially because of the high temperatures, which are underestimated for aragonite, because it is known that the water spouted from pinnacles has temperatures over 80°C (measured in field), however the maximum estimated temperature obtained for the active travertine was 75.9°C for the top of the new pinnacle in current formation. This means that the microorganisms that are present in calcite develop better under lower temperatures.

# 5 Conclusions

At a glance, Porcelana Geysers is not a simple geothermal system, which involves different processes at different scales and depth. This complexity is given by the presence of several faults and fractures generating high permeability along the entire peninsula and it is very likely that this is responsible for the existence not only of the thermal manifestations but also of the volcanic arc.

Therefore, the following sequence can be understood from the geochemical construction made above:

- 1) The system is recharged by fluvial water which percolates through the fractures along all faults present from the higher area to the geysers, following the topography.
- 2) During the water flow, this reach great depth through the rock fractures reaching anoxic and reducing environments, receiving high temperature volcanic fluids rich in H<sub>2</sub>O, CO<sub>2</sub>, chlorides, boron, rubidium and caesium, and maybe some content of sulphur, bringing the system temperature to values that surround the 196°C.
- 3) At high depths, some saline intrusions of the fjord are mixed with the thermal fluids of the system, mainly adding chlorides, bromine, sodium and strontium.
- 4) When heavy rain occurs, the high permeability allows meteoric bicarbonate water interacts with thermal system, adding additional atmospheric CO<sub>2</sub>. This could dilute the contribution of the fjord to values lower than 17.3%, since this value only considers the fjord water as a chloride contributor, taking the data from the final geochemistry resulting from surface water.
- 5) The hot water highly charged in CO<sub>2</sub> rises to the surface due to the high pressure existing underground (lithostatic and hydrostatic) at different points along the fault that cut the Northern Patagonian Batholith. During the water flow the thermal fluids are diluted downstream until reach Punta Calle Hot Springs and depleted in CO<sub>2</sub>. The water reaches the surface in the area of Porcelana Geysers with temperatures around 76.9°C (from 70.2 to 85.1°C), and an average probably higher, because of the underestimation of precipitations temperatures for aragonites.
- 6) The reducing environment causes the sulphate to be reduced to H<sub>2</sub>S and native sulphur, which is emitted directly as a gas through the geysers and as a solid deposit composed only of native sulphur on the southern river bank. Simultaneously, pH and redox potential changes occurs in the system, depending on the volcanic and meteoric input variations. The decrease in pH may be related to a higher volcanic contribution and/or long periods of drier weather, and is recorded by sporadic deposition of native sulphur on the southern river bank, where there is no relevant or visible carbonate precipitation that acts as a pH buffer, contrary to the northern river bank. While the redox potential changes, according to the variation of the deep and superficial contribution, are registered in zoned calcite crystals, as seen below.



Figure 5.1. Schematic S-N section across the northeast shore of the Huequi peninsula, illustrating the various sources of fluids with different characteristics (isotopic ratios, redox potential and geochemical composition) involved in the crustal circulation of fluids in an area with convergence of fault systems.

- 7) During periods of high carbon dioxide degassing, the aragonite pinnacles are precipitated with a large vertical component due to the vertical emission of saturated water (geysers). These pinnacles are very fragile and tend to grow and break in periods of time less than a year.
- 8) The water that flows from the geysers pinnacles downstream cools to temperatures between 56.7 and 73.6°C and is depleted in CO<sub>2</sub> and <sup>12</sup>C, allowing calcite formation with heavier  $\delta^{13}$ C ratios and the development of bacteria and several microorganisms on the lowest surfaces of the pinnacles and in cascades with thermal water flow, forming efflorescence textures. Among these crystals abundant EPS, bacteria and silica grow, where specifically bacteria with amorphous silica coverage are spatially correlated, especially in more proximal areas, which makes calcite deposits highly resistant to erosion. During this process, rainwater favours the flow of water to distal areas, which helps to decrease its temperature and dilute the water.
- 9) Because of changes in local permeability due to dissolution and precipitation processes, sometimes the flux of water and gas that rises through an aragonite pinnacle reduces its flow, generating lower temperatures, similar to the water that

precipitates the external efflorescence of calcite. Therefore, a mosaic of calcite crystals is formed in the pinnacle duct and also an external cover is formed, which is rounded by rainwater during its formation. The calcite crystallized in the conduit is more protected from rainwater, thus, they register the variations of the redox potential of the water in their zoning. When the flow of water almost stops, the outer calcite cover becomes favourable for biotic development helping the precipitation of silica probably driven by microorganisms, which creates a shield for the pinnacle increasing its resistance.

The DNA sequencing of this community of bacteria is proposed for future studies, for a better understanding of the interaction between biota and calcite and silica mineralization. A correction of the estimated temperatures of the travertine precipitating fluids by could be essential for this purpose. Finally, a more detailed source analysis is proposed by measuring different ratios of isotopes, such as strontium, bromine, boron, chloride, stable carbon and helium from gas and water samples, not only from Porcelana Geysers but also from other thermal manifestations existing in the peninsula and under the fjord waters.

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## 7 Appendix

Table 7.1. Mass	percent com	position obta	ained for thin	sections from	the inactive	pinnacle
PF1						

	1	0																										1												
Total	57.5377	110.304	57.3973	57.5083	58.5700	71.1883	89.8251	96.5075	59.2513	58.0248	58.2050	58.1595	58.1816	58.1571	57.8736	57.2957	58.5355	58.3524	58.4989	57.9822	57.5440	57.9104	57.7889	58.0270	57.9552	58.3603	57.4437	58.5993	59.3932	62.1077	59.4519	59.7337	60.3934	59.7903	60.1944	59.3103	59.7732	60.4335	59.7499	59.7468
P205	0.1901	0.0000	0.2149	0.1899	0.1988	0.1533	0.0005	0.0000	0.2013	0.1786	0.2497	0.2176	0.2147	0.2265	0.2114	0.1892	0.1865	0.2203	0.2356	0.1832	0.1863	0.2192	0.2148	0.2185	0.2258	0.1542	0.2267	0.1591	0.2076	0.5173	0.2321	0.3370	0.3499	0.3278	0.4326	0.4180	0.3482	0.3267	0.2800	0.2622
ō	0.0141	0.1728	0.0065	0.0000	0.0056	0.0150	0.0158	0.0428	0.0000	0.0000	0.0000	0.0000	0.0027	0.0029	0.0095	0.0000	0.0058	0.0040	0.0117	0.0005	0.0010	0.0027	0.0045	0.0093	0.0074	0.0040	0.0164	0.0101	0.0136	0.0106	0.0085	0.0056	0.0133	0.0114	0.0026	0.0000	0.0010	0.0000	0.0054	0.0000
CoO	0.0000	0.0000	0.0101	0.0000	0.0000	0.0209	0.0533	0.0119	0.0764	0.0000	0.0000	0.0265	0.0354	0.0151	0.0000	0.0215	0.0000	0.0018	0.0000	0.0451	0.0000	0.0000	0.0088	0.0053	0.0000	0.0000	0.0217	0.0119	0.0209	0.0213	0.0000	0.0097	0.0000	0.0000	0.0000	0.0026	0.0446	0.0215	0.0000	0.0000
Cr203	0.0000	0.0080	0.0557	0.0000	0.0000	0.0000	0.0000	0.0126	0.0000	0.0000	0.0000	0.0213	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0163	0.0000	0.0343	0.0000	0.0076	0.0368	0.0000	0.0000	0.0081	0.0000	0.0000	0.0187	0.0000	0.0000	0.0000	0.0000	0.0644	0.0000	0.0000	0.0000
SiO2	0.0921	106.9200	0.2830	0.0906	0.1923	38.3500	87.4900	90.0100	0.0249	0.0079	0.0186	0.0083	0.0000	0.0000	0.0092	0.0005	0.0000	0.0126	0.0422	0.0194	0.0020	0.0284	0.0368	0.0145	0.0174	0.0059	0.0143	0.0261	0.0201	0.0198	0.0000	0.0000	0.0248	0.0000	0.0245	0.0226	0.0111	0.0239	0.0135	0.0254
AI2O3	0.0000	0.1316	0.0048	0.0020	0.0115	0.0161	0.0301	3.6000	0.0094	0.0136	0.0000	0.0140	0.0192	0.0030	0.0020	0.0084	0.0103	0.0172	0.0000	0.0000	0.0000	0.0068	0.0000	0.0040	0.0036	0.0000	0.0000	0.0227	0.0008	0.0248	0.0000	0.0086	0.0000	0.0000	0.0000	0.0530	0.0000	0.0000	0.0296	0.0092
CaO	56.4700	0.8855	56.5000	56.7200	57.6000	31.7600	1.4100	1.7800	57.0500	55.8100	56.2600	56.1900	56.0100	55.5700	52.4300	52.4300	55.9200	54.9700	55.8900	55.9300	56.0800	56.6300	56.3600	56.8800	56.5800	56.8900	56.1800	56.1000	56.5100	52.4300	57.3100	56.8100	56.5200	56.5800	56.6700	54.8800	56.4300	57.8000	57.6900	57.9600
FeO	0.0333	1.4900	0.0756	0.1057	0.0911	0.0395	0.0630	0.0859	0.2145	0.3793	0.2698	0.2654	0.4581	0.8292	3.2800	2.5000	0.2832	1.5900	1.1292	0.5871	0.4163	0.3504	0.3749	0.2080	0.3122	0.2495	0.2025	0.0889	0.0654	5.2800	0.3393	0.7192	0.4258	0.2123	0.3242	1.3400	0.5495	0.7543	0.5556	0.3733
SO3	0.0579	0.1020	0.0321	0.0161	0.0000	0.0296	0.0530	0.0774	0.1321	0.1320	0.0967	0.1353	0.0773	0.0676	0.0324	0.0713	0.0388	0.0355	0.1741	0.2096	0.1124	0.1286	0.0644	0.0739	0.1191	0.1417	0.0932	0.0193	0.0323	0.0622	0.0225	0.0775	0.1489	0.1518	0.0873	0.1488	0.0775	0.2258	0.1706	0.2155
As205	0.0035	0.0000	0.0000	0.0000	0.0154	0.0000	0.0000	0.0000	0.0565	0.0267	0.0000	0.0167	0.0387	0.0000	0.0000	0.0000	0.0000	0.0400	0.0000	0.0000	0.0000	0.0000	0.0216	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0340	0.0000	0.0379	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MgO	0.3091	0.0762	0.0190	0.0022	0.0303	0.4140	0.3345	0.5066	0.4116	0.3558	0.2896	0.3383	0.3851	0.4217	0.3943	0.4259	1.0644	0.4439	0.2258	0.2382	0.2059	0.1865	0.2933	0.2492	0.2415	0.2482	0.2637	0.3613	0.3574	0.2417	0.3208	0.2703	0.2858	0.2487	0.2535	0.3176	0.4516	0.1609	0.1311	0.1296
K20	0.0021	0.0999	0.0000	0.0017	0.0000	0.0000	0.0438	0.0322	0.0055	0.0096	0.0000	0.0000	0.0020	0.0000	0.0019	0.0000	0.0042	0.0060	0.0000	0.0000	0.0000	0.0000	0.0000	0.0032	0.0000	0.0067	0.0088	0.0000	0.0000	0.0167	0.0000	0.0017	0.0027	0.0000	0.0000	0.0000	0.0117	0.0000	0.0000	0.0000
Ohn	0.2231	0.0862	0.1318	0.0973	0.0966	0.1388	0.2082	0.2500	1.0690	1.0951	0.9079	0.8903	0.9192	1.0211	1.4900	1.6400	0.8713	0.9900	0.7705	0.6403	0.4962	0.3578	0.3341	0.3517	0.3656	0.4329	0.4016	1.7900	2.0000	3.4600	1.1680	1.3900	2.3100	2.0700	2.1800	2.1200	1.7600	1.0122	0.8741	0.7716
SrO	0.0751	0.0240	0.0000	0.2618	0.2122	0.2326	0.0722	0.0000	0.0001	0.0000	0.1127	0.0251	0.0000	0.0000	0.0000	0.0000	0.1510	0.0000	0.0001	0.1252	0.0000	0.0000	0.0249	0.0000	0.0750	0.1750	0.0000	0.0000	0.1383	0.0000	0.0000	0.0502	0.2388	0.1381	0.1885	0.0000	0.0000	0.0625	0.0000	0.0000
Ā	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Na2O %	0.0673	0.3078	0.0638	0.0210	0.1162	0.0185	0.0507	0.0981	0.0000	0.0162	0.0000	0.0107	0.0192	0.0000	0.0129	0.0089	0.0000	0.0211	0.0197	0.0036	0.0276	0.0000	0.0165	0.0094	0.0000	0.0154	0.0148	0.0099	0.0187	0.0233	0.0167	0.0352	0.0355	0.0502	0.0312	0.0077	0.0236	0.0457	0.0000	0.0000
Line			•		•				-	-	-	-	-	-	-	-	-	~	-	-	-	-	-	-	-	-	-	-	•		2	2	2	2	2	2	2	2	7	2
N° point	-	2	с	4	5	9	7	8	6	10	1	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	32	33	34	35	36	37	38	39	40	41

	74	95	37	68 6 68 6	00	94	24	80	66	34	64	92	81	91	15	29	25	73	32	92	02	84	49	69	94	17	21	76	84	71	44	13	81	36	60	60	88	75	84	yo Yo
Total	61.64	61.71	59.81	60.34 1	59.39 59.39	58.63	59.51	59.89	59.65	63.50	58.08	58.25	59.89	60.04	59.07	58.99	60.16	60.35	59.83	57.77	91.79	57.28	55.95	56.28	56.68	55.85	56.88	58.62	58.90	58.72	58.61	58.33	58.28	56.53	58.56	58.16	58.19	56.39	55.97	55.99
P205	0.4832	0.3610	0.4065	0.4337	0.3460	0.3791	0.3220	0.3219	0.3853	0.5232	0.2445	0.2512	0.2580	0.3331	0.2234	0.2530	0.2257	0.2096	0.2906	0.2246	0.0372	0.1956	0.0717	0.0649	0.1237	0.1182	0.1691	0.2257	0.2543	0.2371	0.1866	0.2021	0.1933	0.1578	0.2293	0.2353	0.2333	0.1341	0.1139	0.1613
ū	0.0146	0.0051	0.0064	0.0096	0.0061	0.0000	0.0000	0.0018	0.0019	0.0042	0.0115	0.0130	0.0133	0.0266	0.0000	0.0000	0.0005	0.0095	0.0101	0.0041	0.0056	0.0000	0.0052	0.0140	0.0077	0.0070	0.0052	0.0000	0.0129	0.0056	0.0032	0.0000	0.0045	0.0493	0.0082	0.0000	0600.0	0.0003	0.0000	0.0109
C00	0.0117	0.0227	0.0000	0.0000	0.0011	0.0713	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0419	0.0000	0.0291	0.0700	0.0024	0.0000	0.0011	0.0000	0.0279	0.0069	0.0172	0.0000	0.0278	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0145	0.0130	0.0000	0.0000	0.0000	0.0287	0.0000	0.0000	0.0000
Cr203	0.0000	0.0000	0.0100	0.0000	0,0000	0.0017	0.0330	0.0104	0.0158	0.0199	0.0000	0.0329	0.0000	0.0000	0.0070	0.0000	0.0000	0.0000	0.0406	0.0000	0.0000	0.0321	0.0000	0.0000	0.0000	0.0000	0.0477	0.0000	0.0233	0.0000	0.0014	0.0158	0.0420	0.0376	0.0162	0.0000	0.0026	0.0000	0.0000	0.0000
SiO2	0.0195	0.0202	0.0366	0.0003	0.0329	0.0000	0.0325	0.0156	0.0311	0.0086	0.0000	0.0277	0.0115	0.0109	0.0425	0.0244	0.0588	0.0399	0.0835	0.0901	91.2300	0.0156	0.0903	0.1435	0.1008	0.2228	0.0469	0.0834	0.1608	0.1942	0.0661	0.0464	0.0740	1.6461	0.0953	0.0607	0.1537	0.0441	0.0552	0.0438
AI2O3	0.0105	0.0130	0.0000	0.0267	0.0000	0.0041	0.0098	0.0232	0.0444	0.0160	0.0102	0.0120	0.0104	0.0362	0.0000	0.0170	0.0190	0.0358	0.0182	0.0135	0.0394	0.0054	0.0000	0.0254	0.0205	0.0000	0.0197	0.0213	0.0203	0.0055	0.0000	0.0000	0.0000	0.0072	0.0228	0.0136	0.0164	0.0053	0.0032	0.0000
CaO	54.2000	59.3600	56.1500	56.8800	56.4300	53.4900	57.2500	57.5600	57.2800	54.6800	56.5600	56.4000	58.1600	57.4200	57.6000	57.4100	57.0800	57.9700	57.6700	57.0400	0.0001	56.8500	43.2600	43.3100	44.2100	43.8800	46.0800	52.7200	54.4600	54.8800	55.9600	55.4900	55.8200	52.2300	55.7100	56.3200	56.3200	44.5700	42.2900	42.6000
FeO	3.2700	0.1369	0.3735	0.4598	0.5223	2.5000	0.5778	0.6130	0.5099	4.9000	0.2694	0.3738	0.3871	0.6475	0.2721	0.3646	0.5125	0.6702	0.5913	0.1353	0.0442	0.0520	0.2255	0.3699	0.4194	0.4707	0.0606	0.0757	0.0456	0.1314	0.2597	0.4467	0.1732	0.3905	0.2165	0.1475	0.1348	1.3300	1.3800	0.3386
SO3	0.0195	0.0064	0.1195	0.1097	0.0355	0.0875	0.2029	0.1514	0.1708	0.0752	0.0837	0.1225	0.2251	0.1386	0.1286	0.1447	0.0259	0.0226	0.0548	0.0226	0.0574	0.0129	0.0263	0.0329	0.0000	0.0000	0.0000	0.0000	0.0162	0.0260	0.0323	0.0356	0.0258	0.0555	0.0551	0.0194	0.0161	0.0000	0.0000	0.0065
As205	0.0000	0.0362	0.0000	0.0201	CBEU.U	0.0000	0.0000	0.0000	0.0000	0.0088	0.0225	0.0266	0.0085	0.0000	0.0000	0.0343	0.0258	0.0119	0.0000	0.0040	0.0000	0.0303	0.0306	0.0100	0.0350	0.0000	0.0000	0.0000	0.0152	0.0000	0.0000	0.0000	0.0000	0.0339	0.0000	0.0000	0.0000	0.0000	0.0025	0.0302
MgO	0.4064	0.5604	0.2644	0.2071	0.2793	0.2143	0.1785	0.1370	0.1807	0.3242	0.1600	0.2352	0.1666	0.1563	0.1283	0.1575	1.5929	0.9940	0.8054	0.0000	0.1228	0.0213	2.1700	2.1400	2.1500	1.8400	1.7000	1.3989	1.7000	1.7100	1.4061	0.9839	1.3810	1.5281	1.5107	1.1456	1.1284	1.7700	1.2359	1.2039
K20	0.0000	0.0000	0.0144	0.0037	0.0000	0.0000	0.0006	0.0023	0.0043	0.0005	0.0039	0.0120	0.0155	0.0278	0.0139	0.0077	0.0022	0.0009	0.0000	0.0000	0.0332	0.0066	0.0000	0.0000	0.0000	0.0013	0.0103	0.0026	0.0078	0.0000	0.0000	0.0076	0.0000	0.0053	0.0108	0.0100	0.0017	0.0061	0.0060	0.0136
MnO	3.1000	1.0970	2.4200	2.1700	2.0800 1.6900	1.8700	0.9053	1.0391	0.9435	2.9300	0.7207	0.5920	0.5466	1.1850	0.6017	0.5097	0.5285	0.3552	0.2079	0.0180	0.0000	0.0133	10.0200	10.1500	9.5400	9.2900	8.6900	4.1000	2.0600	1.4200	0.5765	0.9610	0.4684	0.2377	0.4454	0.2088	0.1421	8.4600	10.5800	11.5300
SrO	0.0636	0.1004	0.0124	0.0250	0.0504	0.0000	0.0000	0.0001	0.0377	0.0128	0.0000	0.1377	0.0000	0.0377	0.0249	0.0000	0.0883	0.0377	0.0251	0.1869	0.1082	0.0000	0.0000	0.0000	0.0258	0.0131	0.0000	0.0000	0.1263	0.1008	0.0882	0.0881	0.0627	0.1256	0.2013	0.0000	0.0000	0.0776	0.2724	0.0258
Ar	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Va2O	0.0484	0.0002	0000.0	0.0032	0.0029 0.0029	0.0214	0000.0	0.0222	0.0545	0000.0	0000.0	0.0226	0.0536	0.0294	0000.0	0000.0	0000.0	0000.0	0.0346	0.0401	0.0842	0.0464	0.0381	0.0263	0.0287	0.0086	).0526	00000	0.0057	0.0165	0.0343	0.0396	0.0302	0.0290	0.0393	0000.0	0.0120	0000.0	0.0393	).0350
Line <sup>1</sup>		-	ე ო	ი ი	ი ო	с С	с С	3	3 (	-	-	-		-	-	-		-	-	-	-		4	4	4	4	4	4	4	4	4	4	4	4	4	4	4 (	5	5 (	5
N° Doint	42	43	4	42 24	40 47	48	49	50	51	52	53	54	55	56	57	58	59	09	61	62	83	25	65	99	67	88	60	20	71	72	73	74	75	76	11	78	79	80	81	82

Total	55.6867	58.9678 58.8426	59.2108	58.7705	58.7026	58.8070	58.5183	56.7067	57.0156	57.0593	58.1424	58.5035	58.3650	57.9571	57.5879	58.3173	57.7321	57.6143	56.1073	57.4059	57.5971	59.0578	58.4490	58.6494	57.5495	57.2256	59.2202	58.9557	58.5792	58.9595	59.7144	57.6006	56.9849	57.6498	57.2158	57.2365	57.8105	57.6067	59.0493
P205	0.0953	0.2854	0.2306	0.2548	0.2062	0.1965	0.2019	0.1372	0.1463	0.1464	0.1907	0.1650	0.1985	0.2432	0.1871	0.2178	0.2006	0.1816	0.1294	0.1344	0.1747	0.2667	0.1957	0.2602	0.1950	0.1944	0.1764	0.2288	0.2084	0.1759	0.2452	0.1281	0.0998	0.1468	0.1605	0.0999	0.1708	0.1010	0.2188
ū	0.0008	0000 0	0.0000	0.0024	0.0098	0.0000	0.0006	0.0044	0.0121	0.0000	0.0036	0.0000	0.0045	0.0010	0.0003	0.0000	0.0064	0.0062	0.0000	0.0029	0.0086	0.0000	0.0002	0.0053	0.0029	0.0155	0.0085	0.0069	0.0151	0.0000	0.0024	0.0143	0.0060	0.0000	0.0000	0.0000	0.0071	0.0000	0.0008
CoO	0.0000	0.0146	0.0694	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0415	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0298	0.0349	0.0488	0.0525	0.0000	0.0000	0.0000	0.0000	0.0620	0.0380	0.0026	0.0047	0.0000	0.0000	0.0000	0.0000	0.0000
Cr203	0.0000	0.0000	0.0074	0.0000	0.0000	0.0000	0.0000	0.0000	0.0143	0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0206	0.0000	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0070	0.0229	0.0000	0.0000	0.0000	0.0080	0.0480	0.0000	0.0397	0.0422	0.0091	0.0000	0.0000	0.0000	0.0362
SiO2	0.0235	0.0117	0.0109	0.0006	0.0273	0.0000	0.0471	0.0251	0.0244	0.0268	0.0289	0.0251	0.0624	0.0194	0.0524	0.0296	0.0121	0.0330	0.0043	0.0245	0.0448	0.0138	0.0044	0.0012	0.1733	0.1620	0.0267	0.0340	0.0026	0.0489	0.0000	0.0276	0.0059	0.0071	0.0366	0.0435	0.0122	0.0168	0.0321
Al203	0.0104	0.0109	0.0000	0.0000	0.0157	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0268	0.0000	0.0000	0.0131	0.0058	0.0000	0.0000	0.0294	0.0000	0.0197	0.0090	0.0000	0.0210	0.0000	0.0250	0.0000	0.0014	0.0096	0.0359	0.0000	0.0000	0:0050	0.0011	0.0000	0.0000	0.0187	0.0182	0.0000
CaO	42.4500	54 9600	55.3100	55.4600	55.7700	55.4000	55.8800	44.7400	45.3100	45.7600	51.5800	54.6100	55.0600	55.0500	55.0600	57.7100	57.0900	57.2700	43.4700	47.5900	48.8800	53.6900	55.7900	55.5100	55.1300	56.4300	56.8500	56.6200	49.0300	50.0600	52.1600	47.8800	45.3600	46.6600	45.2900	44.6900	48.2200	47.4800	50.1700
FeO	0.5643	0.0788	0.1203	0.2481	0.3846	0.5934	0.3961	0.3075	0.3208	0.0323	0.0756	0.1093	0.2987	0.2301	0.1904	0.0452	0.0242	0.0000	0.2955	0.4116	0.0733	0.0797	0.0826	0.3017	0.2146	0.0580	0.8437	0.4043	1.3100	0.3033	0.1201	0.0820	0.0178	0.0183	0.2866	0.6997	0.1375	0.0838	0.0453
SO3	0.0000	0.0098	0.0032	0.0355	0.0258	0.0550	0.0484	0.0000	0.0197	0.0000	0.0000	0.0000	0.0097	0.0000	0.0291	0.0354	0.0000	0.0096	0.0524	0.0359	0.0000	0.0747	0.0194	0.0000	0.0000	0.0097	0.0484	0.0193	0.0000	0.0196	0.0391	0.0000	0.0295	0.0163	0.0263	0.0361	0.0066	0.0033	0.0033
As205	0.0038	0.0762	0.0000	0.0000	0.0000	0.0256	0.0000	0.0000	0.0000	0.0000	0.0394	0.0144	0.0000	0.0000	0.0000	0.0249	0.0000	0.0110	0.0055	0.0000	0.0018	0.0022	0.0000	0.0000	0.0000	0.0199	0.0000	0.0000	0.0015	0.0000	0.0041	0.0032	0.0000	0.0181	0.0000	0.0000	0.0000	0.0745	0.0742
OgM	1.2897	1.3188 1.6900	1.5122	1.2664	1.0980	1.0271	1.1765	2.0200	2.0200	1.8200	1.6380	2.1100	2.0900	1.9100	1.6244	0.0157	0.0000	0.0056	1.2228	1.4176	1.4046	1.4497	1.5940	1.7500	1.3283	0.0112	0.8064	1.0860	1.9600	2.1400	2.1400	1.4253	1.9800	1.8800	2.1200	2.1700	1.5389	1.5375	1.6900
K20	0.0000	0,000,0	0.0000	0.0000	0.0052	0.0085	0.0000	0.0000	0.0000	0.0002	0.0053	0.0000	0:0030	0.0000	0.0043	0.0009	0.0005	0.0064	0.0000	0.0038	0.0000	0.0000	0.0000	0.0104	0.0055	0.0000	0.0000	0.0000	0.0020	0.0000	0.0000	0.0027	0.0012	0.0052	0.0078	0.0054	0.0000	0.0005	0.0020
MnO	11.2100	4.5/00	1.9100	1.4900	1.1330	1.4000	0.7504	9.3500	9.0800	9.2000	4.5300	1.4400	0.5773	0.5022	0.2668	0.0345	0.0518	0.0589	10.8700	7.7700	6.9000	3.3900	0.7329	0.7137	0.4314	0.1098	0.4601	0.5254	6.0400	6.0400	4.8600	7.8200	9.3600	8.8500	9.1500	9.4100	7.6900	8.2700	6.7000
SrO	0.0000	0.0000	0.0000	0.0127	0.0000	0.1009	0.0000	0.1164	0.0644	0.0000	0.0509	0.0000	0.0377	0.0000	0.1509	0.1869	0.2740	0.0000	0.0000	0.0000	0.0896	0.0758	0.0000	0.0377	0.0127	0.1124	0.0000	0.0000	0.0000	0.1279	0.0257	0.1794	0.0774	0.0000	0.0774	0.0648	0.0000	0.0128	0.0766
Ar	0.0000	0.000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Na2O %	0.0389	0.0000	0.0368	0.0000	0.0270	0.0000	0.0173	0.0061	0.0036	0.0221	0.0000	0.0029	0.0232	0.0012	0.0091	0.0106	0.0519	0.0320	0.0275	0.0152	0.0000	0.0062	0.0000	0.0033	0.0000	0.0023	0.0000	0.0296	0.0000	0.0000	0.0078	0.0000	0.0000	0.0000	0.0515	0.0171	0.0087	0.0083	0.0000
Line	ر م	ດທ	- D	2 Q	2 Q	2 Q	2	9	9	9	9	9	9	9	9	9	9	9	2	2	2	2	2	2	2	2	œ	œ	œ	œ	œ	œ	ŝ	œ	ø	ø	80	œ	80
N° point	83	85 85	86	87	88	89	06	91	92	93	94	95	96	97	98	66	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122

°	Line	Na2O	Ar	SrO	MnO	K20	MgO	As205	SO3	FeO	CaO	AI2O3	SiO2	Cr203	C00	Ū	P205	Total
point		%	1				I											
123	8	0.0054	0.0000	0.0000	4.4300	0.0000	2.0300	0.0061	0.0065	0.2025	52.6000	0.0080	0.0207	0.0348	0.0000	0.0000	0.2084	59.5524
124	8	0.0064	0.0000	0.0000	5.5700	0.0000	2.2300	0.0000	0.0000	1.0710	49.6700	0.0236	0.0171	0.0000	0.0607	0.0000	0.1924	58.8412
125	8	0.0151	0.0000	0.0000	1.8400	0.0000	1.0377	0.0447	0.0000	1.0561	55.7200	0.0158	0.0070	0.0000	0.0326	0.0043	0.2502	60.0235
126	ø	0.0073	0.0000	0.1254	0.3677	0.0018	0.7791	0.0000	0.0775	0.5725	57.5800	0.0000	0.0087	0.0028	0.0159	0.0087	0.2390	59.7864
127	ø	0.0000	0.0000	0.2510	0.3431	0.0000	0.8968	0.0000	0.0453	0.7673	57.0800	0.0151	0.0375	0.0079	0.0000	0.0053	0.1781	59.6274
128	8	0.0000	0.0000	0.0000	0.3001	0.0000	0.9662	0.0297	0.0000	0.8867	57.2800	0.0000	0.0310	0.0000	0.0000	0.0066	0.2443	59.7446
129	8	0.0000	0.0000	0.0000	0.1873	0.0021	0.4889	0.0000	0.0032	0.8864	57.6600	0.0000	0.0164	0.0000	0.0098	0.0043	0.1834	59.4418
130		0.0116	0.0000	0.1246	0.0000	0.0000	0.0000	0.0000	0.0161	0.0326	57.7200	0.0079	0.0060	0.0000	0.0000	0.0000	0.1981	58.1169
Minimum		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	55.6867
Maximum		0.3078	0.0000	0.2740	11.5300	0.0999	2.2300	0.0745	0.2258	5.2800	59.3600	3.6000	106.9200	0.0644	0.0764	0.1728	0.5232	110.3040
Average		0.0209	0.0000	0.0551	2.6511	0.0045	0.8859	0600.0	0.0548	0.5225	52.0633	0.0384	3.2591	0.0079	0.0116	0.0071	0.2209	59.8121
Sigma		0.0327	0.0000	0.0716	3.2916	0.0108	0.7263	0.0155	0.0573	0.7939	12.8626	0.3128	16.4957	0.0142	0.0192	0.0162	0.0977	11.3435
Number of	120																	
data	671																	