# GEOCHEMISTRY OF TRAVERTINE DEPOSITS AS A GEOTHERMAL EXPLORATION TOOL: A CASE STUDY AT CAJÓN DEL MAIPO, CENTRAL ANDES, CHILE

Aldo Anselmo[1], Diego Morata[1], Antonio Delgado-Huertas[2], Martin Reich[1] and Linda Daniele[1]

[1]Department of Geology and Andean Geothermal Center of Excellence (CEGA), Faculty of Physics and Mathematical Sciences,
Universidad de Chile, Plaza Ercilla 803, Santiago, Chile

[2] Instituto Andaluz de Ciencias de la Tierra (IACT)(CSIC-UGR), Avda. de las Palmeras, 4, 18100 Armilla, Granada, España

aldo.anselmo@ug.uchile.cl

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## ABSTRACT

Travertine deposits have been widely studied due their relevance in palaeoenvironmental studies. By means of morphological, mineralogical and geochemical studies, it is possible to constrain the physicochemical conditions of the parental fluids from which they formed. In this research, we studied active and fossil travertine deposits near the Baños Colina (2500 m a.s.l., 30-52°C) and Baños Morales (1850 m a.s.l, 14-23 °C) hot springs located in the Andean Cordillera near the city of Santiago (33°S -34°S). Field observations were combined with X-ray diffraction, scanning electron microscopy and isotope ratio mass spectrometry determinations in travertine and water samples from the hot springs. Different field morphologies were recognized including cascades, dams, terraces, and fissure ridges. The mineralogy of the deposits consists of calcite and aragonite on shrubs and fan disposition, respectively. The $\delta^{13}C$(PDB) values of travertine range from -3.06 to 15.48 ‰, while the $\delta^{18}O$(PDB) vary from -19.47 to -6.73 ‰, showing a high correlation between them (R:0.75-0.95 and P>0.05). The $\delta D$ and $\delta^{18}O$ data of the hot spring water plot along the local meteoric water line, and their $\delta^{13}C$(PDB) values range from -4.19 to 8.05 ‰. These data indicate that the studied travertine deposits have a thermometeogenic character. The close spatial relationship of the studied travertines with regional structures suggest that they may have formed due the fault-related infiltration of meteoric fluids. We propose a model where surficial waters mix with deeper fluids followed by $CO_2$ exsolution driven by depressurization, triggering the surface carbonate precipitation. According to this model, the travertine deposits at Cajón del Maipo can be considered as surface expressions of a deeply seated convecting geothermal system.

## 1. INTRODUCTION

Travertine definition is still on debate and for some authors the concept may overlap with tufa. We considered travertine as a chemical-precipitated continental limestone, formed due the transfer of carbon dioxide from or to a groundwater source, independent on the parental fluid temperature and they can be classified as thermogene or meteogene, depending on the $CO_2$ source (Pentecost, 2005). Many travertine deposits have been registered worldwide and have been widely studied on the last years (Asta et al., 2017; De Filippis and Billi, 2012; Kele et al., 2008; Okumura et al., 2011; Özkul et al., 2013; Quade et al., 2017). Their characteristics such as morphology, fabrics, chemistry and mineralogy are controlled on the physicochemical conditions of the parental fluids (Chafetz and Folk, 1984; Gandin and Capezzuoli, 2014; Jones, 2017; Jones and Renaut, 2010). Stable isotope studies on travertine and tufa deposits have been developed on many different sites, due their potential as a paleoclimate proxy (Andrews, 2006; Garnett et al., 2004; Kele et al., 2011; Quade et al., 2017; Valero-Garcés et al., 2001) and for assess the mechanism of the hydrothermal system from which they form (Frery et al., 2017; Mao et al., 2015).

In this work we show results from travertines at Baños Morales and Baños Colina hot springs, located in Cajón del Maipo on the western side of the Andean Cordillera between the 33°S-34°S. The good preservation of fossil deposits and the active carbonate precipitation at the hot springs make this area a suitable place for this research. This works aims to understand the conditions on which the Cajón del Maipos travertine deposits were formed and how they relate with geothermal systems in the area.

## 2. GEOLOGICAL BACKGROUND

Baños Morales and Baños Colina hot springs are located on the Eastern Principal Cordillera (EPC) between the 33°40´S and 34°S (figure 1). This segment represent a transition between a subhorizontal subduction (to the north) and normal subduction (to the south) and it consists of a thick sequence of Mesozoic sedimentary rocks, including limestones and evaporites, characterized by an important deformation into the Aconcagua fold-and-thrust belt (Giambiagi et al., 2015). Volcanic activity occurs in this latitude with the presence of the active San Jose volcano on the north limit of the Southern Volcanic Zone (Stern, 2004).

Previous studies have characterized the springs located on the EPC on this latitude, showing that the chemistry correspond to mature $Na^+$-$Cl^-$, controlled by the interaction of meteoric recharge water with the Mesozoic sequences and the mixing with deep originated compounds such as $CO_2$ (Benavente et al., 2016; Daniele et al., 2016).

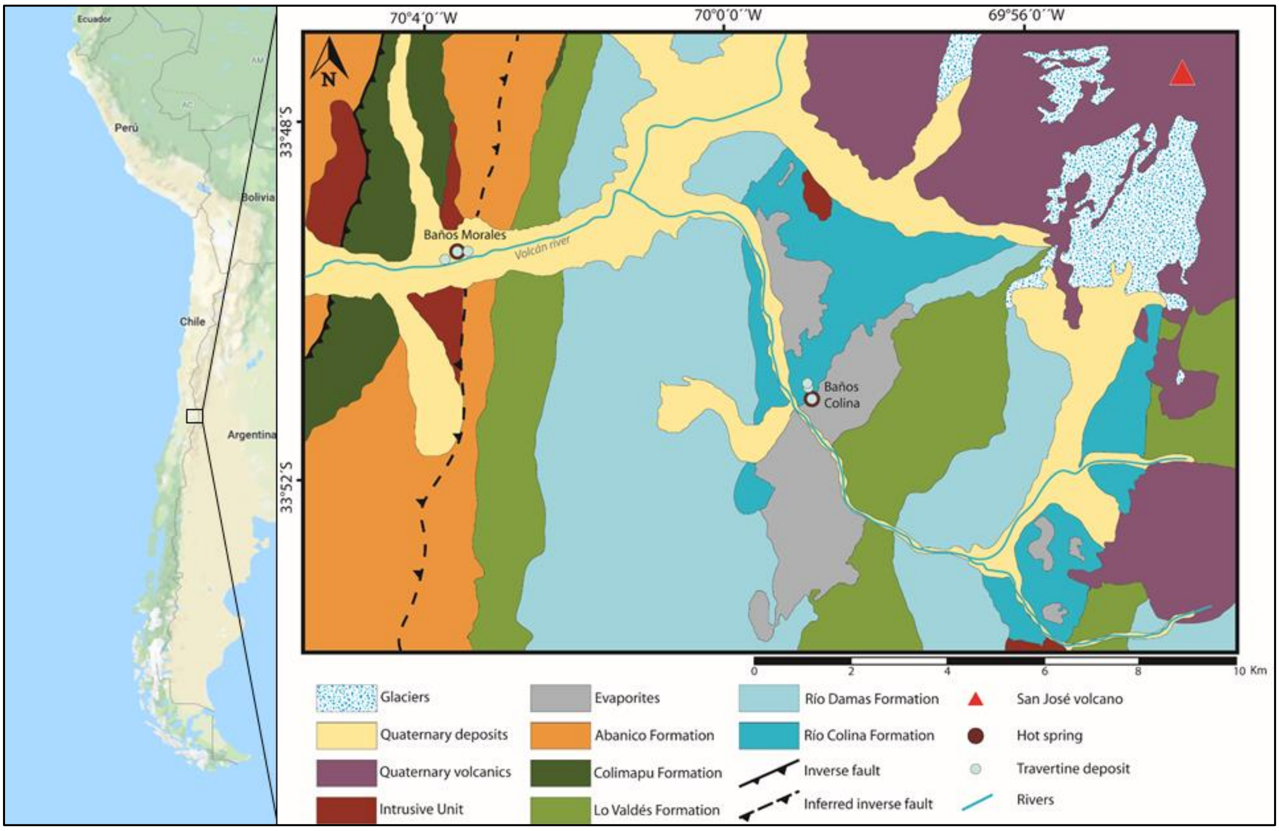

**Figure 1: Location and geologic map of the study zone. Modified and simplified from Thiele (1980).**

## 3. SAMPLING AND METHODS

### 3.1 Sampling description

Two fieldwork campaign were done for travertine and water sampling, one during January 2016 and on august 2017. We sampled 6 main travertine deposits, sampling was done transversal to the lamination on bedded deposits and downhill on slopes. On active deposits we also sampled water from the springs and did in situ measures for pH, temperature, redox potential (Eh) and electrical conductivity (EC). For anions, cations and traces analysis, water samples were filtered using 0.45 µm Milipore filters, for the last two, samples were also acidified with nitric acid. All samples were stored on pre-cleaned polyethylene bottles at 4°C.

### 3.2 Travertine analysis

Raw travertine rock samples were observed on a FEI Quanta 250 scanning electron microscopy (SEM) for mineralogical and textures characterization. At the CEGA SEM laboratory.

For mineralogical and stable isotopes characterization part of the samples were cleaned, with brush and compressed air, and hand grounded on an agate mortar for X-ray diffractometry (XRD) and stable isotope analysis, the samples were not sieved to avoid contamination. The grounded rocks were analyzed by XRD, on a Bruker D8 Advance diffractometer with Cu Kα radiation from the Physics Department of the Faculty of Physics and Mathematical Sciences of the Universidad de Chile.

Carbon and oxygen isotope analysis were run in duplicates. Five milligrams of carbonate powder was positioned in a 12 mL Exetainer vial that was subsequently flushed with helium. After this, acid digestion was carried out with the addition of 0.1 mL of 100% $H_3PO_4$ at 50°C (McCrea, 1950). After 24 hours of reaction the resulting $CO_2$ was analyzed by a Finnigan DeltaPLUS XP isotope ratio mass spectrometer (IRMS). These procedure and analysis was done in the Laboratory of Biogeochemistry of Stable Isotopes of the Andalusian Institute of Earth Sciences (CSIC) in Granada, Spain.

### 3.3 Water analysis

Major, minor and trace elements were analyzed in the Andean Geothermal Center of Excellence (CEGA) laboratories. Atomic Absorption Spectrophotometry (AAS), on a Perkin-Elmer Pinaacle 900F, was used for major cations ($Na^+$,$K^+$, $Ca^{2+}$, $Mg^{2+}$) measurements. Ion Chromatography (IC), with a Dionex ICS 2100, was used for anions ($F^-$, $Cl^-$, $SO_4^{2-}$, $Br^-$ and $NO_3^-$). $HCO_3^-$ concentration were determined by volumetric titration, using a Hanna HI-902C, with the Giggenbach and Goguel (1989) method. Traces elements were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on a Thermo iCAP Q.

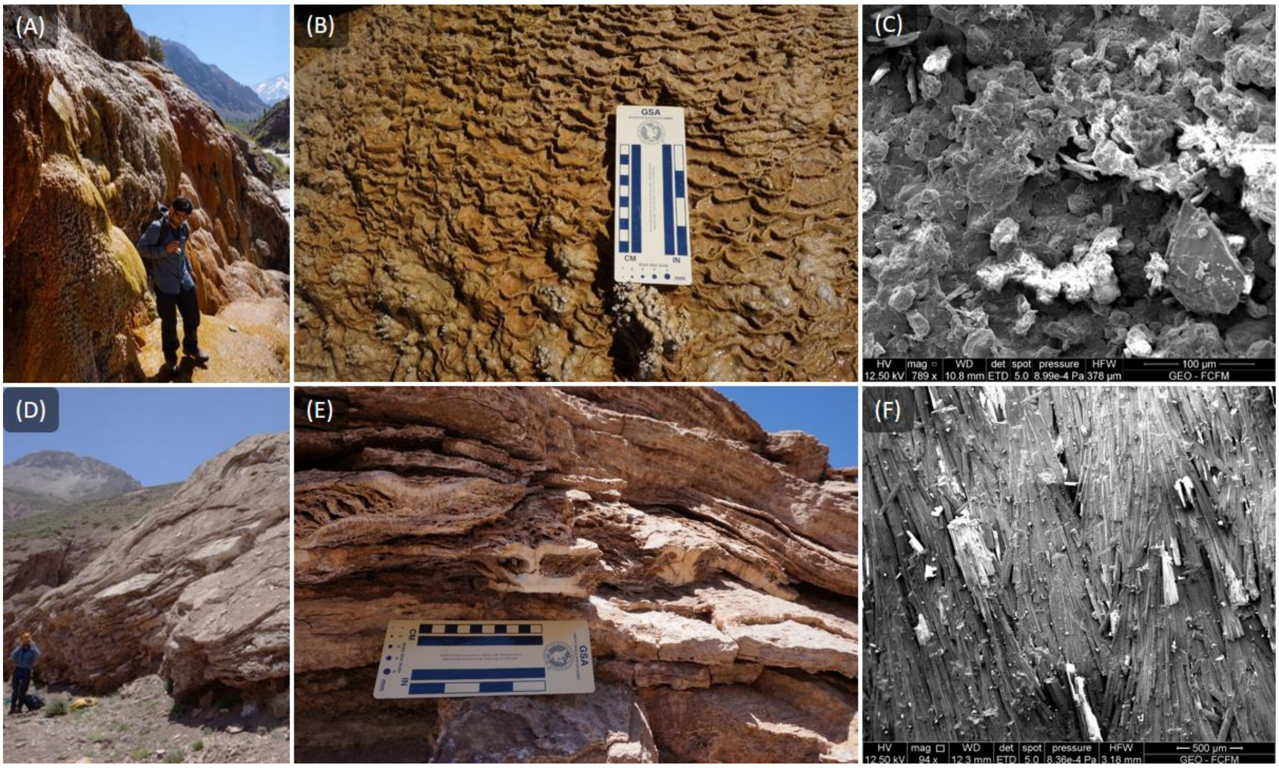

**Figure 2: (A) Cascade deposit near Baños Morales hot springs. (B) Minidams and coraloids at the surface of a slope active deposit. (C) SEM image of calcite and aragonite on a bedded travertine sample. (D) Fissure ridge deposit near Baños Colina hot spring. (E) Bedded and banded travertine on the flank of the fissure ridge from image (D). (F) SEM image of aragonite fans from a banded travertine sample.**

## 4. RESULTS

### 4.1 Travertine morphologies

Six main deposits have been studied, all of them are placed over unconsolidated mass removal deposits in the surroundings of the hot springs. Three of them are still active and carbonate precipitation occurs direct from thermal waters forming mainly dams, slopes and cascades shaped deposits. In the fossil deposits the same morphologies are recognized plus fissure ridges and filled fractures.

Dams are well developed only in Baños Colina hot springs where the water flow is high enough to form terraced mounds, no fossil deposits of this morphology have been founded. Because of their tourism interest these deposits are continuously modified by anthropogenic activity which changes the deep and shape of the pools.

Slope deposits with an E-W orientation occurs covering part of the north shore of El Volcán river near Baños Morales. It consists of a thin layer (<10cm) of about 400 m$^2$ of travertine with coraloids and minidams (figure 2.B) textures on its surface. Springs mounds are recognizable in active and fossil slopes, but in the former biomats are present and carbonates have a reddish-brownish color which changes as it dries to white and gray tones. Downhill, on drastic increase of the slopes accretionary cascades are formed with the same textures and colors on its surface (figure 2.A).

A 12 m height and covering 250 m$^2$ fissure ridge deposit is located near Baños Colina hot springs (figure 2.D). Two kind of carbonate are present: (1) a bedded travertine which is the most of the bulk of the deposit with high porosity and lamination, and (2) a banded travertine with low porosity that is present on the fractures of the fissure ridge (figure 2.E), which is a distinctive characteristic of fissure ridges (De Filippis et al., 2013). The main fissure has a N47W strike which is similar with the orientation of the other deposits in this area. On the north side of the ridge there is a fracture of 3 m of width and at least 10 m of height with a N40W strike filled with a white banded non-porous travertine.

### 4.2 Mineralogy

XRD data show that all of the samples are mainly composed by calcite and aragonite. In most of the cases calcite is the dominant phase (>90%). Aragonite have higher percentage on samples that were taken where biofilms were present, on drop walls of some dams and on fractures banded travertine. No evidence of recrystallisation or dissolution/reprecipitation process have been founded on the microscopy.

SEM-SE observations of the samples match with the XRD results and it shows a massive rhombohedral (figure 2.C) or shrub disposition of the calcite and a ray fan (figure 2.F) or rosette distribution of aragonite crystals. Sparite and micrite alternation is common on the banded and bedded travertine.

### 4.3 Stable isotopes on travertine

Samples from each deposit where analyzed to obtain values for stable carbon and oxygen isotopic composition, $\delta^{13}$C and $\delta^{18}$O respectively. The $\delta^{13}$C(PDB) values of travertine range from -3.06 to 15.48 ‰, while the $\delta^{18}$O(PDB) vary from

-19.47 to -6.73 ‰ (figure 3). There is a high correlation between both isotopes on all the deposits (R:0.75-0.95 and P>0.05). The highest values correspond to samples from the active slope deposits and the lowest values are from banded travertines.

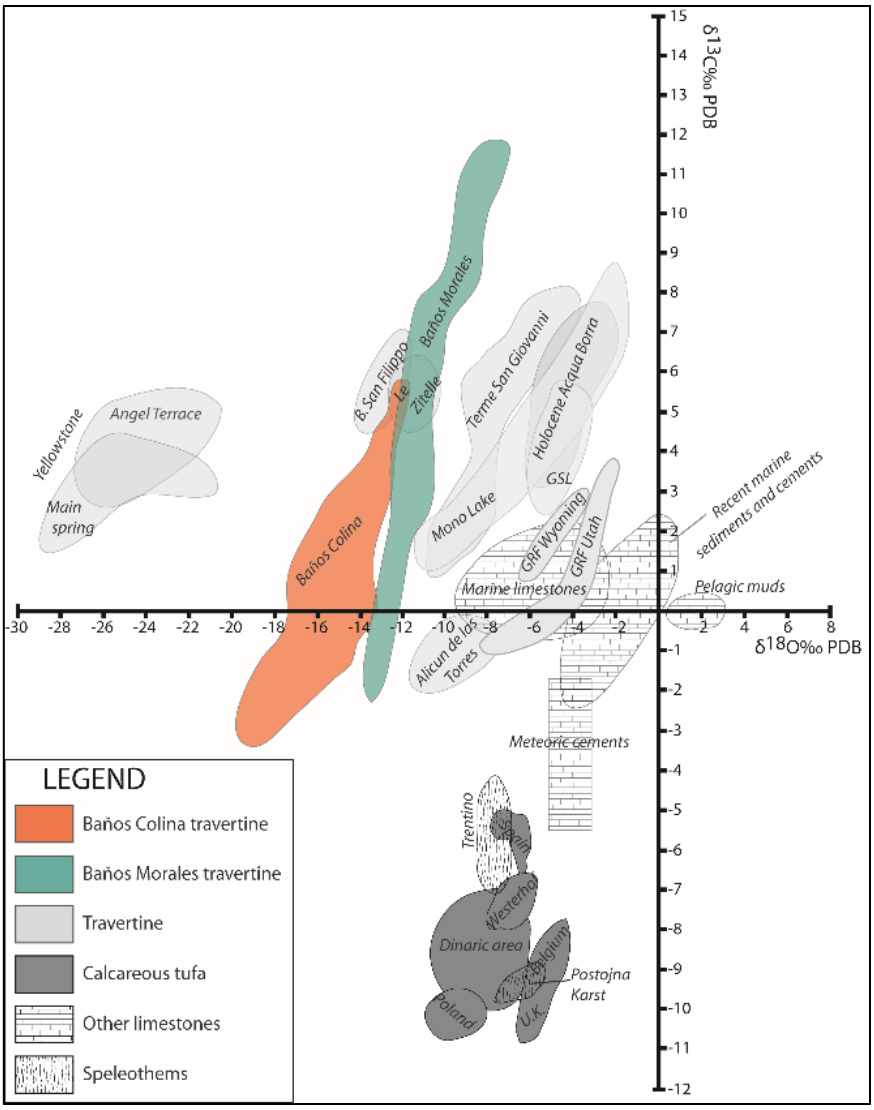

**Figure 3: Plot of $\delta^{18}O$ and $\delta^{13}C$ of the measured deposits and of different places in the world (Gandin and Capezzuoli, 2008; Porta, 2015).**

### 4.4 Water geochemistry

In situ measures shows that the waters at Baños Morales have a temperature between 14-23 °C, a pH of 6.3 and EC of 28.1 µS/cm; on the other hand, Baños Colina waters have a temperature between 30-52°C, a pH of 6.8 and EC of 8.4 µS/cm. The thermal waters analysis shows that all the hot springs correspond to mature $Na^+$-$Cl^-$ waters. δD and $\delta^{18}O$ data of the hot spring waters plot along the local meteoric water line(Hoke et al., 2013), and their $\delta^{13}C$(PDB) values range from -4.19 to 8.05 ‰, the higher values were obtained for Baños Morales samples.

## 5. DISCUSSION

### 5.1 Travertine morphologies

Some authors have considered that hot springs travertine formation is related with active tectonics (Çakir, 1999; Crossey et al., 2006; Hancock et al., 1999). Cascades, dams and slope deposits are formed due to travertine precipitation from a water runoff (Chafetz and Folk, 1984) and indicates the presence of springs with different flows on the past. While fissure ridge genesis is in part related to the tectonics and are usually located on locally extensional regime that allows the formations of structures that transport the fluid to the depth and then back to the surface (Brogi and Capezzuoli, 2009; De Filippis et al., 2013; De Filippis and Billi, 2012). Cajón del Maipo travertine deposits are placed on a zone characterized by a regional compression deformation and there is no previous works about the local structural context, but the presence of this morphologies and orientated deposits, with big fractures filled with carbonates, lead to think about the presence of minor normal faults on an extensional regime.

### 5.2 Mineralogy

Even though the travertine mineralogy has been widely studied and it is constraint mainly to calcite and aragonite, the precipitation control factors of which polymorph will be formed is still not completely understood. The problem lies on the aragonite precipitation on thermodynamics conditions where calcite is stable. Under this conditions aragonite precipitation is controlled by three factors: (1) $CO_2$ content and evasion rate from parental waters, (2) Mg:Ca water ratio and (3) the presence of biofilms (Jones, 2017); other factors such as temperature (Folk, 1994; Kitano, 1962; Zeller and Wray, 1956), pH of the water (Matsumoto et al., 2010; Tai and Chen, 1998) or the presence of divalent cations (Wada et al., 1995) have been also considered by some authors. Aragonite will precipitate on $CO_2$ oversaturated waters and high $CO_2$ exsolution rate, on fluids with low $CO_2$ degassing rate and Mg:Ca rate bigger than 1 and on presence of biofilms due organic activity. Aragonite is also registered on waters with high temperatures, however it is no clear where is the exact limit and it has a wide range between 30-70°C. The dominant precipitation control will change for each flow and even on the same water body may change. To establish which of the factors control the mineralogy, active precipitation is required. On the aragonite samples from Baños Morales and Baños Colina two different causes can be identified. Firstly on Baños Morales samples they are located on quiet water pools or low flows, where $CO_2$ depends on chemical gradients and it is not enhanced by turbulence or mechanics aspects, the Mg:Ca ratio are all under 0.19, with temperatures around 20 °C; then the aragonite presence is explained by the presence of biofilms with cyanobacteria around the vent of the springs. On the other hand, Baños Colinas aragonite bearing samples are present on two different morphologies but with similar conditions: (1) drop walls where water turbulence increase $CO_2$ degassing and temperature can reach 50°C and (2) banded travertine of fossil fissure ridge deposits, in this case water conditions can not be measured, but pressure decrease produce a higher $CO_2$ degassing and the temperature is higher than surface currents.

The constant mineralogy proportions (calcite >90%) and the absence of reprecipitation evidence on slope deposits and bedded travertine suggest that $CO_2$ degassing, Mg:Ca and organic activity have no major differences during the deposits formation.

### 5.3 Stable isotopes on travertines and water

The $\delta^{18}O$ values in carbonates depends of the $\delta^{18}O$ and the temperature of the parental fluid. Once it is proved that the precipitation occurred under isotopic equilibrium they may be used for palaeotemperature calculations (Friedman and O'Neil, 1977; Kim and O'Neil, 1997; McCrea, 1950). However, non-equilibrium conditions have been registered on different natural travertine deposition environments (Asta et al., 2017; Kele et al., 2011, 2008; Özkul et al., 2013).

For travertine samples of one of the Baños Colina hot springs pool (BC-01, 38°C) and one from the vent of a Baños Morales hot spring (MP-01, 13°C) the 1) Friedman and O´Neil (1977) and 2) Kim O´Neil (1997) equations were used to confirm if the precipitation occurs under equilibrium:

1) $$10^3 \ln \alpha_{c\text{-}w} = \frac{2{,}78\cdot 10^6}{T^2} - 2.89$$

2) $$10^3 \ln \alpha_{c\text{-}w} = \frac{18030}{T} - 32.42$$

With $\alpha_{c\text{-}w}$ the fractionation factor of oxygen isotope exchange between calcite and water and T the temperature.

For the BC-01 sample the temperature of the water was underestimated, 32°C and 33°C respectively with each equation. This difference can be explained due the presence of aragonite on this sample what can produce a difference of 5°C in the temperature estimation (Kele et al., 2008), if that the case isotopic equilibrium conditions can be assumed. However, for the sample MP-01 only 2°C and 5°C was calculated, which can not be explained by the presence of aragonite, but the presence of biofilms indicate bacterial activity which can remove isotopically light $CO_2$ (Guo et al., 1996). Near the vent of a spring, $CO_2$ degassing produce an increase of the pH which lead to $HCO_3^-$ dissociation into $CO_3^{2-}$ and $H^+$, oversaturating the solution and then carbonate will precipitate; Kele (2008) proposed that this process occurs so fast that the $\delta^{18}O$ of the carbonate should be very close to that of the parental water $HCO_3^-$. Considering this a different equation can be used for geothermometer purpose (Halas and Wolacewicz, 1982):

3) $$10^3 \ln \alpha_{HCO_3^-\text{-}w} = \frac{2.92\cdot 10^6}{T^2} - 2.66$$

Which gives a 13°C, confirming what Kele (2008) proposed.

From $\delta^{13}C$ of carbonates it is possible to infer the source of the $CO_2$ of the parental fluid. The $\delta^{13}C$ values of Baños Colina and Baños Morales are similar to many thermogene travertine deposits (figure 3), which are higher than meteogene deposits due to non soil-zone carbon sources, such as water rock reactions, thermometamorphic reactions associated with magmatic activity and rapid $CO_2$ degassing (Kele et al., 2011; Özkul et al., 2013).

Water $\delta D$ and $\delta^{18}O$ data show a meteoric origin with thermogene water values for the $\delta^{18}O$ (Pentecost, 2005). The $\delta^{13}C$ in Baños Colina values are similar to other thermal springs also suggesting a magmatic o metamorphic origin (Tiwari et al., 2016), while the higher values of Baños Morales water can be explained by the presence of biofilms that can remove locally isotopically light $CO_2$ (Guo and Riding, 1994). These data indicate that the studied travertine deposits have a thermometeogenic character

## 6. CONCLUSION

The close spatial relationship of the studied travertines with regional structures and the presence of morphologies such as fissure ridges or filled fractures and veins, suggest that they may have formed due the fault-related infiltration of meteoric fluids. Stable isotopic data show a thermometeogenic character of the carbonates with meteoric recharge and non soil-zone $CO_2$ sources. We propose a model where surficial waters mix with deeper fluids followed by $CO_2$ exsolution driven by depressurization, triggering the surface carbonate precipitation. According to this model, the travertine deposits at Cajón del Maipo can be considered as surface expressions of a deeply seated convecting geothermal system.

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