

Evaluation of the Oxygen Isotope Fractionation in Aragonitic Travertines from the Fitero Thermal Springs (Navarra, Spain)

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INTRODUCTION

The Fitero thermal waters are one of the best known in the Navarra province (Spain) and they are located in the Fitero village where two spa resorts use them for balneotherapy practices.

Previous authors have studied and characterised these thermal waters (e.g. Auqué *et al.*, 1988 or Coloma *et al.*, 1997). Despite the valuable information provided by these earlier studies the aragonite precipitates (or travertines, in the terminology proposed by Ford and Pedley, 1996) associated to these springs are poorly studied.

Oxygen isotope composition of aragonitic travertines and speleothems are very useful to reconstruct past paleoclimate and paleoenvironmental conditions (e.g. Fouke *et al.*, 2000; Pentecost, 2005; Kele *et al.*, 2008; 2011; Lachniet, 2015). However, the use of the $\delta^{18}\text{O}$ contents in aragonite can cause some problems in the reconstruction of paleotemperatures. One of these problems is that the isotopic aragonite - water equilibrium during the travertine precipitation in natural systems is not often attained due to the kinetic isotope effects related to CO_2 outgassing and high precipitation rates (Fouke *et al.*, 2000; Kele *et al.*, 2008; 2011; among others). Different experimental and empirical calibration equations for the $\delta^{18}\text{O}$ aragonite - water equilibrium fractionation have been proposed, although it is still unclear how representative they are of the real aragonite - water equilibrium (e.g. Kele *et al.*, 2015 or Lachniet, 2015). Therefore, the study of actively precipitating aragonitic travertines can provide a better understanding of these kinetic effects and help to interpret the

isotope composition in old travertines.

In this context, the aim of this study is to evaluate whether the isotopic signature of the aragonitic travertines developed in the Fitero thermal system is in agreement with some the "equilibrium equations" proposed for the aragonite - water fractionation.

GEOLOGICAL SETTING

The Fitero thermal system is located in the Navarra province (Spain), in the NW part of the Iberian Chain, in the contact between the Cameros Range and the tertiary Ebro Basin (Coloma *et al.*, 1997; Fig 1).

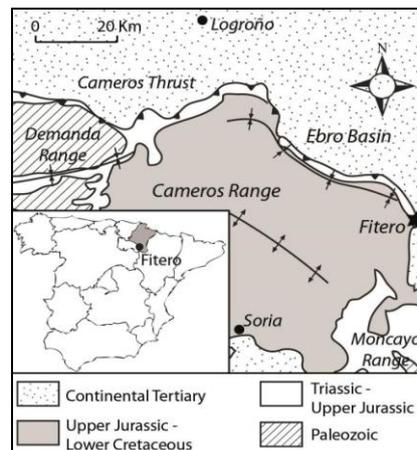


fig 1. Location of the study area (modified from Gil *et al.*, 2002).

The thermal waters aquifer is hosted in the carbonates of the Lower Jurassic (Coloma *et al.*, 1997). The waters ascend to the surface through the Cameros thrust, which puts into contact the Cameros Range and the Ebro Basin. The thermal springs are located in the outcrops of the Lower Jurassic materials in contact with the Keuper Facies (Coloma *et al.*, 1997).

METHODOLOGY

Several samples of the thermal waters and of the travertines precipitating from them were taken and analysed and one representative sample of each was selected for this study. The selected water corresponds to a sample taken in the main spring of the Bécquer spa, and the travertine sample was taken in the exit point of one of the spa drain pipes. The water sample was taken by the standard procedures. Electrical conductivity, temperature and pH were determined *in situ*. Alkalinity was measured by titration, chloride and fluoride by selective electrodes and sulphates by colorimetry. The major cations were analysed by ICP-OES and the stable isotopes by CF-IRMS.

The travertine sample was taken at the end of one of the pipes that drain the thermal water from the spa, specifically from a cooling pool, where the thermal water is cooled down to about 40 °C. This pipe has a diameter of about 30 cm and 30° of inclination with a difference of height close to 20 m from the pool to the exit point. The major and minor elements were measured by absorption spectrometry and the stable isotopes by mass spectrometry. The mineralogy of the sample was determined by X-Ray Diffraction and the petrographical and textural observations were made with a petrographic microscope and a field emission scanning electron microscope (FESEM).

The PHREEQC geochemical code (Parkhurst and Appelo, 2013) and the LLNL database, provided with it, have been used to calculate the saturation state with respect to the mineral phases and the CO_2 partial pressure.

palabras clave: Travertinos, Aragonito, Sistema termal, Isótopos estables

key words: Travertines, Aragonite, Thermal system, Stable isotopes

RESULTS

Main characters of the waters

The waters are chloride – sodium type with a spring temperature of 45.5 °C and pH of 6.68. The main dissolved elements are Cl (1610 ppm), SO₄ (1376 ppm) HCO₃⁻ (174 ppm), Na (981 ppm), Ca (469 ppm) and Mg (92.10 ppm). The isotopic values of δ¹⁸O (-8.7 vs V-SMOW) and δ²H (-63.9 vs V-SMOW) indicate that this thermal water is from a meteoric origin, according to the Spanish Meteoric Water Line (Díaz-Teijeiro et al., 2009).

The calculated saturation states show that calcite is slightly oversaturated (IS = 0.22), aragonite is almost in equilibrium (IS = 0.07) and dolomite is slightly undersaturated (IS = - 0.28). Finally, the pCO₂ is much higher than the atmospheric (log pCO₂ = - 1.58).

Main characters of the travertines

The travertines precipitated in the pipe have a thickness of about 10 cm. They consist of an intercalation of clear and dark bands of less than 1 cm thickness. Each band contains an alternation of thinner layers with a less contrast in their colour but distinguishable in a thin section. The X-Ray Diffraction analyses determined that the dark bands are composed by aragonite and a small amount of goethite and the clear bands are mainly constituted by aragonite although minor amounts of calcite are also present. The texture observed in the petrographic analyses is fibrous aragonite with fan shaped aggregates elongated in the growth direction. Calcite is forming thin layers between the thicker dark and clear aragonitic bands. Fig. 2 shows a detail of the aragonite needles in a FESEM image.

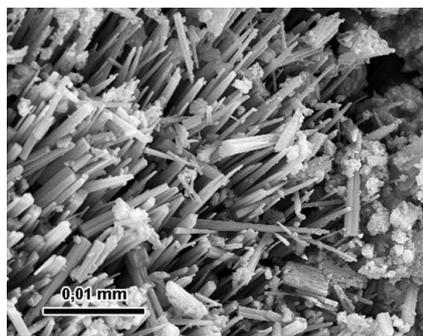


fig 2. FESEM image of the travertine (dark band) in which the aragonite needles can be seen.

The results obtained from the analyses of the clear and dark bands are shown in Table 1. In general, there are not

	Ca	Mg	Na	Sr	Fe	Mn	δ ¹⁸ O
Fit-D1	360300	100	2290	12576	4331	12	17.896
Fit-D2	361200	100	2415	12920	3750	14	17.719
Fit-D3	365100	100	2315	12901	4178	13	17.761
Fit-C1	361300	300	2130	12493	3107	23	17.927
Fit-C2	349400	400	2293	11939	2308	26	17.834
Fit-C3	351700	200	2378	12411	2245	35	17.778

Table 1. Analytical results of the different bands from the travertine sample. The Fit-D are the dark bands and the Fit-C the clear bands. All the elements are in ppm. The δ¹⁸O is in ‰ vs V-SMOW.

significant differences between them. All bands have important contents of Sr, as it is expected for aragonite (Pentecost, 2005). The contents of Mg and Mn are higher in the clear bands, since these contain calcite and these elements substitutes Ca easier in calcite than in aragonite (Dickson, 1990; Pentecost, 2005). The Fe is higher in the dark bands, which is consistent with the presence of goethite in these bands.

Oxygen isotope fractionation

The temperature during the precipitation of the Fitero travertines has been evaluated by using different calibrates proposed by several authors for the equilibrium water – aragonite (Table 2):

- The classical equation of Grossman and Ku (1986), deduced from aragonitic foraminifera, gastropods and scaphods in the range of 2.5 to 26 °C, provides an average temperature of 40.5 °C. The Böhm et al. (2000) equation, also proposed from biogenic aragonites (sponges in the range of 3 to 28 °C) predicts an average temperature of 39.9 °C.
- Kim et al. (2007) established their equation in experiments with inorganic aragonites in the range of 10 to 40 °C. The average temperature obtained with this calibrate is 39.2 °C.

- Finally, Kele et al. (2015) proposed an equation derived from a set of samples constituted by calcitic and aragonitic travertines and tufas and some biogenic calcites. The temperature calculated with this equation is the highest, with an average of 47.4 °C.

Most of the results obtained with the selected equations are around 40 °C, which is the temperature of the waters discharged by the pipe.

DISCUSSION

According to the speciation - solubility calculations, the waters are almost in equilibrium with calcite, and in clear equilibrium with aragonite. As a consequence of this saturation state, the travertine precipitation must be triggered by an intense CO₂ outgassing during the water circulation through the pipe due to a turbulent discharge. This process causes a pH increase of the waters and, consequently, an oversaturation of the carbonate phases.

The precipitation of aragonite would be favoured over the calcite precipitation, most probably, due to the water temperature (about 40 °C). Several authors have pointed out that the main controlling factor in the aragonite precipitation is temperature. Aragonite precipitates when the water temperature is in the range 30 – 60 °C

	Grossman and Ku (1986)	Böhm et al. (2000)	Kim et al. (2007)	Kele et al. (2015)
Fit-D1	40.1	39.5	38.8	47.0
Fit-D2	41.0	40.4	39.7	47.9
Fit-D3	40.8	40.2	39.5	47.7
Fit-C1	39.9	39.3	38.6	46.8
Fit-C2	40.4	39.8	39.1	47.3
Fit-C3	40.7	40.1	39.4	47.6

Table 2. Temperatures obtained with different oxygen isotopic aragonite – water equilibrium equations.

(e.g. Pentecost, 2005 and references therein). Fouke et al. (2000) reported that only aragonite precipitates above 44°C whilst in the range of 30 – 43 °C calcite precipitates with aragonite. Therefore, the presence of calcite in thin bands between the aragonitic thicker bands suggests an alternation in the water temperature. Aragonite would precipitate during the thermal water discharges and calcite between discharges, when the remaining water in the pipe undergoes a progressive cooling.

The temperatures obtained for the travertine precipitation with different fractionation equations (Table 2) are in the range of 38.6 to 47.9 °C, which are close to the temperature of the thermal waters. The differences obtained using different equations may be due to the data used in the calibrations. For example, Grossman and Ku (1986) and Böhm et al. (2000) equations were calibrated from biogenic aragonites, and in spite of this, the results are similar to the temperatures obtained with the Kim et al. (2007) calibrate for inorganic aragonites. Kim et al. (2007) also reported that the biogenic aragonites were within the uncertainty range of their abiogenic aragonite – water equation.

The results obtained with the Kele et al. (2015) equation provide the highest temperature values. This discrepancy could be due to the fact that they used aragonitic and calcitic samples for the calibration. Although in their case the differences between aragonite and calcite were negligible (probably because they used an important number of samples for the calibration), inorganic aragonite is enriched 0.6 ‰ – 0.8 ‰ in $\delta^{18}\text{O}$ with respect to calcite (at 25 °C; Tarutani et al., 1969; Kim et al., 2007).

In any case, the precipitation temperatures obtained for the studied sample using different $\delta^{18}\text{O}$ aragonite – water equilibrium fractionation equations are, in general, in agreement with the temperature of its parental water. This suggests that, despite the high CO_2 outgassing in the pipe, the travertine precipitation took place, at least, close to the oxygen isotope equilibrium represented by the equation of Kim et al. (2007) for inorganic aragonitic precipitates.

CONCLUSION

Some travertines precipitated from the Fitero thermal waters have been studied. These precipitates consist of an alternation of dark and clear bands. The dark ones are composed of aragonite and minor amounts of goethite and the clear ones of aragonite and a small amount of calcite. Aragonite precipitation seems to be favoured over the precipitation of calcite by the temperature of the waters (around 40 °C). Finally, the oxygen isotope values indicate that the travertine precipitation took place close to the equilibrium conditions despite the high CO_2 outgassing process that occurs during the aragonite precipitation.

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