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Application of different geothermometrical techniques to a low enthalpy thermal system

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Abstract

The reservoir temperature of the waters in the low temperature carbonate-evaporitic geothermal system of Arnedillo has been estimated by using two different techniques: 1) chemical geothermometers and 2) geothermometrical modelling. By combining the results of both techniques a reliable range of temperature of 90 ± 20 °C has been proposed for the waters in the reservoir. Despite being a carbonate-evaporitic system, the cationic geothermometers have provided good results, which, together with the geothermometrical modelling, indicate that the waters have reached equilibrium with anhydrite, quartz, calcite, dolomite, albite and K-feldspar in the reservoir.

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1. Introduction

This study aims to determine the reservoir temperature of the low enthalpy Arnedillo thermal system which is hosted in carbonate-evaporitic materials. This has been done by using two different techniques: chemical geothermometers and the geothermometrical modelling.

There are different types of chemical geothermometers. The classical geothermometers are those based on the dissolved silica or cation contents. The cationic geothermometers often present problems when applied to low temperature or carbonate-evaporitic thermal systems as they have been calibrated with waters from high temperature systems and hosted in different materials (e.g. granites)^{1,2}. Other chemical geothermometers, such as Ca-Mg and SO₄-F geothermometers¹, have been specifically calibrated for their use in medium- to low-temperature carbonate-evaporitic systems. All of them have been used in this work.

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The geothermometrical modelling presents some advantages over the chemical geothermometers since it also allows determining 1) which are the minerals in equilibrium with the waters in the reservoir and 2) the presence of secondary processes during the ascent of the thermal waters to the surface³.

These two different approaches are used in this study in order to test their applicability in this kind of systems.

2. Geological setting

The studied thermal springs are in Arnedillo, La Rioja (Spain), in the NW part of the Iberian Range, close to the contact between the Cameros Range (Triassic, Jurassic, and Cretaceous materials) and the Tertiary Ebro Basin⁴ (Fig. 1). The aquifer of the Arnedillo thermal waters is placed in the carbonates of the Lower Jurassic in contact with the Keuper Facies⁴. The springs are characterised by a flow rate of about 22 l/s and nearly 50 °C, and the waters are of chloride-sodium type⁴ with total dissolved solids (TDS) around 7,000 ppm.

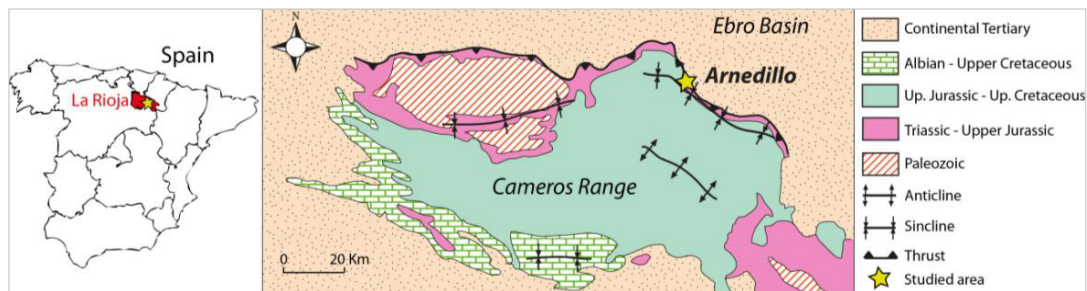


Fig. 1. Geographical and geological location of the studied area.

3. Methodology

Two springs were sampled following the standard procedures of water sampling. Temperature, pH and electrical conductance were measured *in situ*. The major and minor cations were analysed by ICP-OES and ICP-MS, respectively. Alkalinity was determined by titration, chloride and fluoride by selective electrode and sulphates by colorimetry. The reservoir temperature has been calculated by two different techniques: 1) chemical geothermometers; and 2) geothermometrical modelling.

The use of chemical geothermometers consists of determining the temperature of the waters in the reservoir using empiric or experimental calibrates. These calibrates are deduced from temperature-dependent heterogeneous chemical reactions which control the elemental contents of the waters and assume that the contents have not been modified during the ascent of the waters to surface⁵. A great number of chemical geothermometers, with different calibrates, are available in the literature². The ones that have been used in this work are presented in Table 1.

Table 1. Chemical geothermometers and their calibrates used in this study. The results (in °C) obtained for the two samples (AR1 and AR2) are also shown.

Geothermometer	Author of the calibrate	AR1	AR2
SiO ₂ -quartz	Truesdell ⁶	95.15	92.90
	Fournier ⁷	95.01	92.76
	Michard ⁸	96.20	93.95
SiO ₂ -chalcedony	Fournier ⁷	64.60	62.19
	Arnorsson et al. ⁹	66.34	64.08
Na-K	Giggenbach ¹⁰	96.71	104.75
	Fournier ¹¹	75.44	83.61
K-Mg	Giggenbach et al. ¹²	61.02	63.62
Na-K-Ca ($\beta=4/3$)	Fournier et al. ¹³	88.18	90.99
Ca-Mg	Chiodini et al. ¹	108.89	110.22
SO ₄ -F	Chiodini et al. ¹	-8.46	-9.29

Despite the fact that they are usually inappropriate for carbonate-evaporitic systems, the geothermometers based on the cationic content have been considered here because some of their calibrates have provided good results in other similar systems. Additionally, the geothermometers based on the silica contents and some specific geothermometers¹ (Ca-Mg and SO₄-F) calibrated to be used in this type of systems have been tested too (Table 1).

The geothermometrical modelling technique simulates a theoretical increase in the temperature of the waters to find the point in which the saturation states of a set of minerals (assumed to be present in the reservoir) converge simultaneously towards equilibrium. The assumption that the water chemistry does not change during its ascent is also necessary in this approach. The calculations have been done with the PHREEQC geochemical code¹⁴ and the LLNL thermodynamic database provided with it.

4. Results

4.1. Chemical geothermometers

The results obtained by applying the different chemical geothermometers are listed in Table 1. All the calibrates considered for the SiO₂-quartz geothermometer predict a temperature of about 95 °C whilst the temperature obtained with those for the SiO₂-chalcedony geothermometer is lower, about 65 °C. With the Na-K geothermometer the calculated temperature ranges from 80 to 100 °C depending on the calibrate used, and something similar, about 90 °C, is obtained with the Na-K-Ca geothermometer. In contrast, the temperature provided by the K-Mg is considerably lower, around 60 °C. The temperature predicted by the Ca-Mg geothermometers is higher than that predicted by the rest of geothermometers, about 110 °C. Finally, despite the equilibrium of the waters with anhydrite (see below), the geothermometer based on SO₄-F provides incoherent results (- 9 °C) due to the lack of equilibrium with fluorite.

4.2. Geothermometrical modelling

According to the known and expected mineralogy of the aquifer materials, the set of minerals selected for the geothermometrical calculations have been: anhydrite, calcite and dolomite. Quartz, chalcedony, K-feldspar and albite were also included for two main reasons: 1) the carbonate formations contain detrital material and 2) the geothermometers SiO₂-quartz and Na-K used above, have given good results. Other aluminosilicate phases could be in the aquifer, and laumontite has been selected as an example of this group.

The results obtained for the two samples used here are in the same range and, to make the plots more clear, only one of them (AR2) will be presented. Fig. 2a shows that, except for chalcedony, calcite and dolomite, the saturation states of the rest of the minerals converge towards equilibrium at a temperature between 80 – 100 °C.

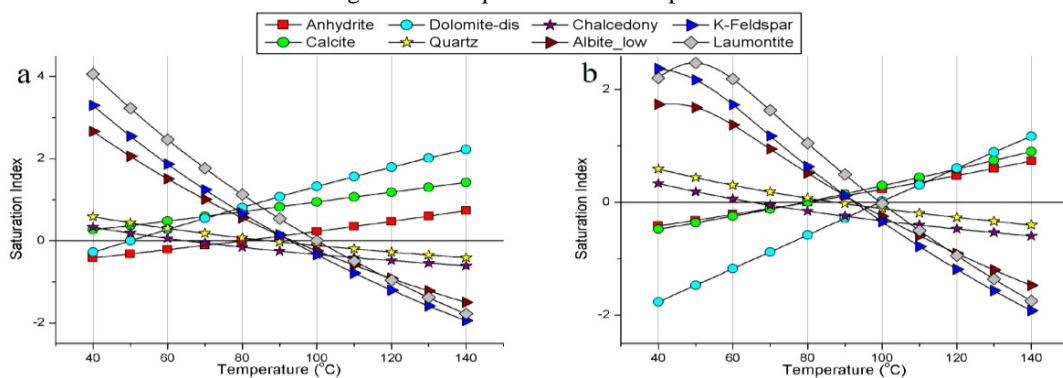


Fig. 2. Graphical representation of the saturation indices of the different minerals considered in equilibrium in the reservoir, with respect to the temperature. (a) and (b) show the results before and after, respectively, assuming an increase of the dissolved inorganic carbon.

There is an agreement in the fact that the SiO₂-chalcedony geothermometer and the chalcedony equilibrium modeling, both predict a lower temperature. This supports that quartz is the silica phase controlling the silica

contents in these groundwaters. The lack of agreement for calcite and dolomite, which presumably are in equilibrium in this carbonate reservoir, could be interpreted as due to the CO₂ outgassing during the groundwaters ascent to surface, since they have a pCO₂ higher than the atmosphere. In order to properly reconstruct the conditions at depth, a theoretical simulation of CO₂ addition was performed. The results indicated that after the addition of a certain amount of CO₂, calcite and dolomite converged to equilibrium at the same range of temperatures (Fig. 2b).

5. Discussion and conclusions

A good agreement has been found between the geothermometrical modelling results and those obtained with most of the geothermometers and calibrates used in this study, including cation geothermometers (Na-K, Na-K-Ca). This is particularly interesting as it is something quite unusual in low temperature systems hosted in carbonate-evaporitic materials.

The lower temperature provided by the K-Mg is probably due to the fact that the K and Mg dissolved contents in the Arnedillo thermal system are not controlled by the phases used to define this geothermometer.

The agreement found with the rest of the chemical geothermometers suggests that the equilibrium with calcite, dolomite, albite, K-feldspar and quartz has been reached in the reservoir. This set of minerals shows the same equilibrium agreement at the same temperature range when used in the geothermometrical modelling.

The almost perfect coincidence to the same temperature for quartz and anhydrite allows establishing an accurate range of temperature (around 85 °C), since these phases are highly reliable in this calculations⁵.

The results of the Ca-Mg geothermometer could be affected by uncertainties due to the disorder degree of dolomite. If these results are excluded, by combing the others a temperature range of 90 ± 15 °C could be proposed. Nonetheless, even if those results are included the range would be 90 ± 20 °C, also acceptable since the uncertainty range usually considered in this calculations is ± 20 °C³. In that case, the groundwaters would be in equilibrium with anhydrite, quartz, calcite, dolomite, albite, K-feldspar and other aluminosilicates, like laumontite.

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References

- Chiodini G, Frondini F, Marini L. Theoretical geothermometers and pCO₂ indicators for aqueous solutions coming from hydrothermal systems of medium-low temperature hosted in carbonate-evaporite rocks. Application to the thermal springs of the Etruscan Swell. Italy. *App Geochem* 1995; **10**: 337–346.
- D'Amore F, Arnórsson S. Geothermometry. In: Arnórsson S, editor. *Isotopic and chemical techniques in geothermal exploration, development and use*. Viena: International Atomic Energy Agency; 2000. p. 152-199.
- Tole MP, Arnannsson H, Pang Z, Arnórsson S. Fluid/mineral equilibrium calculations for geothermal fluids and chemical geothermometry. *Geothermics* 1993; **22**: 17-37.
- Sánchez JA, Coloma P. El agua subterránea en la Rioja. *Zubia* 1998; **10**:11-25.
- Marini L. *Geochemical techniques for the exploration and exploitation of geothermal energy*. Laboratorio di Geochimica, Università degli Studi di Genova, Genova, Italia; 2004.
- Truesdell AH. Geochemical Techniques in Exploration. Summary of Section III. In *Proceedings of the Second United Nations Symposium on the Development and Use of Geothermal Resources*. San Francisco, California, USA; 1975. p. liii-lxxx.
- Fournier RO. Chemical geothermometers and mixing models for geothermal systems. *Geothermics* 1977; **5**: 41–50.
- Michard G. Geothermomètres chimiques. *Bull du BRGM (2nd Ser.)*, section III 1979; **2**, 183-189.
- Arnórsson S, Gunnlaugsson E, Svavarsson H. The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigations. *Geochim et Cosmochim Acta* 1983; **47**: 567-577.
- Giggenbach WF. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim et Cosmochim Acta* 1988; **52**: 2749–2765.
- Fournier RO. A revised equation for the Na-K geothermometer. *Geothermal Resources Council Transactions* 1979; **3**: 221–224.
- Giggenbach W, Gonfiantini R, Jangi BL, Truesdell AH. Isotopic and chemical composition of Parbati valley geothermal discharges, N.W. Himalaya. India. *Geothermics* 1983; **12**: 199-222.
- Fournier RO, Truesdell AH. An empirical Na–K–Ca geothermometer for natural waters. *Geochim et Cosmochim Acta* 1973; **37**: 1255–1275.
- Parkhurst DL, Appelo CAJ. Description of Input and Examples for PHREEQC Version 3. A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. In: U.S. Geological Survey, editor. *Techniques and Methods*, book 6, chap. A43; 2013.