Application of different geothermometrical techniques to a low enthalpy thermal system

Mónica Blasco\textsuperscript{a,1}, Luis F. Auqué\textsuperscript{a}, María J. Gimeno\textsuperscript{a}

\textsuperscript{a}Earth Sciences Department, University of Zaragoza. C/Pedro Cerbuna, 12, Zaragoza 50009, Spain.

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 ºC 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.

Keywords: Geothermal system; Thermal water; Chemical geothermometers; Geothermometrical modelling

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)\textsuperscript{1,2}. Other chemical geothermometers, such as Ca-Mg and SO\textsubscript{4}-F geothermometers\textsuperscript{1}, have been specifically calibrated for their use in medium- to low-temperature carbonate-evaporitic systems. All of them have been used in this work.

* Corresponding author. Tel.: +34-976-761071; fax: +34-976-761106.

E-mail address: monicabc@unizar.es
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 surface.

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 Basin (Fig. 1). The aquifer of the Arnedillo thermal waters is placed in the carbonates of the Lower Jurassic in contact with the Keuper Facies. The springs are characterised by a flow rate of about 22 l/s and nearly 50 °C, and the waters are of chloride-sodium type with total dissolved solids (TDS) around 7,000 ppm.

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 surface. A great number of chemical geothermometers, with different calibrates, are available in the literature. The ones that have been used in this work are presented in Table 1.

<table>
<thead>
<tr>
<th>Geothermometer</th>
<th>Author of the calibrate</th>
<th>AR1</th>
<th>AR2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂-quartz</td>
<td>Truesdell⁶</td>
<td>95.15</td>
<td>92.90</td>
</tr>
<tr>
<td></td>
<td>Fournier⁷</td>
<td>95.01</td>
<td>92.76</td>
</tr>
<tr>
<td></td>
<td>Michard⁸</td>
<td>96.20</td>
<td>93.95</td>
</tr>
<tr>
<td>SiO₂-chalcedony</td>
<td>Fournier⁷</td>
<td>64.60</td>
<td>62.19</td>
</tr>
<tr>
<td></td>
<td>Arnorsson et al.⁹</td>
<td>66.34</td>
<td>64.08</td>
</tr>
<tr>
<td>Na-K</td>
<td>Giggenbach¹⁰</td>
<td>96.71</td>
<td>104.75</td>
</tr>
<tr>
<td></td>
<td>Fournier¹¹</td>
<td>75.44</td>
<td>83.61</td>
</tr>
<tr>
<td>K-Mg</td>
<td>Giggenbach et al.¹²</td>
<td>61.02</td>
<td>63.62</td>
</tr>
<tr>
<td>Na-K-Ca (β=4/3)</td>
<td>Fournier et al.¹³</td>
<td>88.18</td>
<td>90.99</td>
</tr>
<tr>
<td>Ca-Mg</td>
<td>Chiodini et al.¹</td>
<td>108.89</td>
<td>110.22</td>
</tr>
<tr>
<td>SO₄-F</td>
<td>Chiodini et al.¹</td>
<td>-8.46</td>
<td>-9.29</td>
</tr>
</tbody>
</table>
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 geothermometers (Ca-Mg and SO$_4$-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 code$^{14}$ 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 SiO$_2$-quartz geothermometer predict a temperature of about 95 °C whilst the temperature obtained with those for the SiO$_2$-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 SO$_4$-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 detritial material and 2) the geothermometers SiO$_2$-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.

![Figure 2](image_url)

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 SiO$_2$-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 ºC), since these phases are highly reliable in this calculations.

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 ºC could be proposed. Nonetheless, even if those results are included the range would be 90 ± 20 ºC, also acceptable since the uncertainty range usually considered in this calculations is ± 20 ºC. In that case, the groundwaters would be in equilibrium with anhydrite, quartz, calcite, dolomite, albite, K-feldspar and other aluminosilicates, like laumontite.

Acknowledgements

Mónica Blasco has worked on this study thanks to a scholarship from the Ministry of Education, Culture and Sports of Spain, for the Training of University Teachers (ref. FPU14/01523). This study forms part of the activities of the Geochemical Modelling Group (University of Zaragoza and Aragón Government).

References