Science of the Total Environment 615 (2018) 526–539

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Low temperature geothermal systems in carbonate-evaporitic rocks: Mineral equilibria assumptions and geothermometrical calculations. Insights from the Arnedillo thermal waters (Spain)

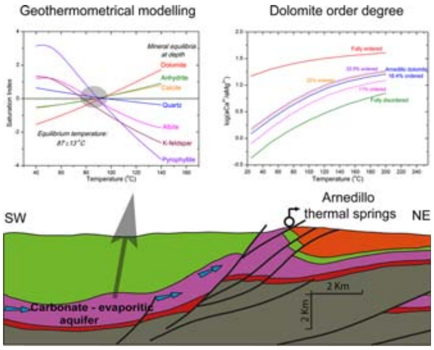
Mónica Blasco *, María J. Gimeno, Luis F. Auqué

Geochemical Modelling Group, Petrology and Geochemistry Area, Earth Sciences Department, University of Zaragoza, Spain C/ Pedro Cerbuna 12, 50009 Zaragoza, Spain

HIGHLIGHTS

- Mineral equilibria in low temperature geothermal systems are discussed.
- Consequences on some geothermometrical methods are addressed.
- The order degree of the dolomite present in the aquifer is calculated.
- A low temperature geothermal system hosted in carbonate rocks is used as an example.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 August 2017
Received in revised form 24 September 2017
Accepted 25 September 2017
Available online xxxx

Editor: D. Barcelo

Keywords:
Low temperature geothermal system
Geochemical modelling
Geothermometry
Mineral equilibria
Dolomite order/disorder degree

ABSTRACT

Geothermometrical calculations in low-medium temperature geothermal systems hosted in carbonate-evaporitic rocks are complicated because 1) some of the classical chemical geothermometers are, usually, inadequate (since they were developed for higher temperature systems with different mineral-water equilibria at depth) and 2) the chemical geothermometers calibrated for these systems (based on the Ca and Mg or SO_4 and F contents) are not free of problems either. The case study of the Arnedillo thermal system, a carbonate-evaporitic system of low temperature, will be used to deal with these problems through the combination of several geothermometrical techniques (chemical and isotopic geothermometers and geochemical modelling).

The reservoir temperature of the Arnedillo geothermal system has been established to be in the range of 87 ± 13 °C being the waters in equilibrium with respect to calcite, dolomite, anhydrite, quartz, albite, K-feldspar and other aluminosilicates. Anhydrite and quartz equilibria are highly reliable to stablish the reservoir temperature. Additionally, the anhydrite equilibrium explains the coherent results obtained with the $\delta^{18}O$ anhydrite – water geothermometer. The equilibrium with respect to feldspars and other aluminosilicates is unusual in carbonate-evaporitic systems and it is probably related to the presence of detrital material in the aquifer.

The identification of the expected equilibria with calcite and dolomite presents an interesting problem associated to dolomite. Variable order degrees of dolomite can be found in natural systems and this fact affects the associated equilibrium temperature in the geothermometrical modelling and also the results from the Ca-Mg geothermometer. To avoid this uncertainty, the order degree of the dolomite present in the Arnedillo reservoir has been determined and the results indicate 18.4% of ordered dolomite and 81.6% of disordered dolomite.

---

* Corresponding author.
E-mail address: monicabc@unizar.es (M. Blasco).

https://doi.org/10.1016/j.scitotenv.2017.09.269

Overall, the results suggest that this multi-technique approach is very useful to solve some of the problems associated to the study of carbonate-evaporitic geothermal systems.

1. Introduction

The study of the chemical and isotopic composition of thermal waters allows identifying the water-rock interaction processes involved in their evolution, determining the possible secondary processes that could affect them during their ascent to surface (e.g. mineral reequilibrium or mixing) and establishing the reservoir temperature by geothermometrical methods. This characterisation is the first step to evaluate the geothermal potential of an area (e.g. D'Amore and Arnórsson, 2000). Nowadays, the use of geothermal energy is diversifying and the technical advances make possible to obtain electrical energy from waters of lower temperature. Additionally, one of the possibilities considered for the CO_2 geological storage is the use of deep saline aquifers, usually hot, hosted in sedimentary rocks (e.g. Auqué et al., 2009, and references therein). These deep storages are inaccessible for their study in an initial stage and, therefore, the information obtained from low to medium temperature thermal systems with similar hydrogeochemical characteristics becomes a suitable and very convenient source of information.

The temperature in the deep reservoirs can be determined by several chemical and isotopic geothermometers and by geothermometrical modelling. However, these techniques present some problems in the case of carbonate-evaporitic aquifers. The classical cationic geothermometers (based on the equilibrium with aluminosilicate phases) are useful in systems with high temperature or with host rocks like granites or basalts in which the waters have reached the equilibrium with various aluminosilicates such as albite or K-feldspar (e.g. Arnòrsson et al., 1983; Asta et al., 2012; Auqué et al., 1997; Buil et al., 2006; Choi et al., 2005; D'Amore et al., 1987; Fouillac and Michard, 1981; Fournier, 1981, 1977; Giggenbach et al., 1983; Giggenbach, 1988; Kharaka and Mariner, 1989; Mariner et al., 2006; Mutlu and Güleç, 1998; Stefánsson and Arnórsson, 2000, among much others). These equilibria are not likely to have been attained in carbonate-evaporitic systems and they may provide erroneous results (Chiodini et al., 1995; Karimi and Moore, 2008; Levet et al., 2002; López-Chicano et al., 2001; Sonney and Vuataz, 2010) although, in some cases, the silica and some cationic geothermometers have provided good results (e.g. Apollaro et al., 2012; Blasco et al., 2017; Fernández et al., 1988; Gökgöz and Tarkan, 2006; Michard and Bastide, 1988; Mohammadi et al., 2010; Pastorelli et al., 1999; Wang et al., 2015).

The more suitable geothermometers are, obviously, those developed for this kind of systems, that is, the Ca-Mg and SO_4-F geothermometers, initially proposed by Marini et al. (1986) and reviewed by Chiodini et al. (1995) afterwards. However, even these might have problems since the former can be affected by the uncertainties in the thermodynamic properties of dolomite (due to non-stoichiometry of order/disorder degree; Chiodini et al., 1995; Frondini, 2008; Helgeson et al., 1978; Marini, 2006; Palandri and Reed, 2001) and the latter will only be suitable if the waters are in equilibrium with anhydrite (or gypsum) and fluorite (Chiodini et al., 1995) which is not always the case.

The isotopic geothermometry is another possible technique although it may also be problematic. For example, the $\delta^{18}O$ exchange between CO_2 and H_2O is easily modified during the ascent of the waters to surface since the kinetics of the exchange reaction is fast and the isotopic reequilibrium takes place even at low temperatures (D'Amore and Arnórsson, 2000). Other common isotopic geothermometer is the $\delta^{18}O$ SO_4-H_2O, but traditionally its calibrations are based in the HSO_4-H_2O exchange, and the HSO_4 is not present in neutral to basic waters (Boschetti, 2013). Some new calibrations have been recently proposed trying to solve this problem, although they are not widely used yet.

Finally, the geothermometrical modelling (or multicomponent solute geothermometry; e.g. Spycher et al., 2014) is very useful since it allows determining the reservoir temperature by studying the saturation states of a vast number of minerals, providing important information about the probable mineral set the waters are in equilibrium with in the reservoir. Additionally it allows evaluating the secondary processes (e.g. mixing, degasification or mineral reequilibrium) that could affect the waters during their ascent to surface (Asta et al., 2010; Auqué et al., 2009; Michard and Fouillac, 1980; Michard and Roekens, 1983; Michard et al., 1986a; Palandri and Reed, 2001; Pang and Reed, 1998; Reed and Spycher, 1984; Tole et al., 1993). Nevertheless, this technique also shows some problems associated to the uncertainties in the mineral solubility of some minerals (Palandri and Reed, 2001).

The study of the low-medium temperature geothermal system of Arnedillo will be used 1) to test all the mentioned geothermometrical techniques, in order to improve their knowledge for their use in further studies; and 2) to characterise hydrogeochemically this natural thermal system for a future exploitation of its geothermal potential.

2. Geological and hydrogeological setting

The Arnedillo thermal waters emerge near the Cidacos River, in the Arnedillo village (La Rioja, Spain). Geologically, they are located in the NW of the Iberian Chain, in the contact between the eastern Cameros Range and the tertiary Ebro Basin (Fig. 1; Coloma et al., 1997; Sánchez and Coloma, 1998).

The Cameros Range, constituted mainly by Mesozoic formations, is bounded by two continental basins and two Palaeozoic reliefs: the Ebro and Duero basins in the north and the south, respectively; and the Demanda and Moncayo Ranges at the east and west (Gil et al., 2002). The Triassic is represented by Buntsandstein (sandstones, siltstones and breccias surrounding the Demanda Range), Muschelkalk (mainly dolostones, although the outcrops in the area are scarce) and Keuper facies (gypsum/anhydrite, marls and clays) which is the detachment level for the tertiary thrusting (Coloma, 1998; Gil et al., 2002).

The marine Jurassic formations (up to Kimmeridgian, Upper Jurassic) are the ones found in the rest of the Iberian Chain (Coloma, 1998; Gil et al., 2002; Goy et al., 1976), consisting of dolostones and limestones with some intercalations of marls: Imon (dolostones), Cortes de Tajuña (dolomitic breccias with anhydrite), Cuevas Labradas (limestones and dolostones), Cerro del Pez (marls), Barahona (bioclastic limestones), Turmiel (marls and limestones), Chelva (limestones), Aldealpozo (black limestones) and Torrecilla (limestones with corals). These formations are mainly constituted by carbonates but some terrigenous deposits are also present (Goy et al., 1976). These Triassic and marine Jurassic formations constitute the pre-rift sequence.

A rifting process took place at the end of the Jurassic and during the Cretaceous, resulting in the formation of the Cameros Basin. The corresponding formations are known as the syn-rift sequence, which is constituted by continental sediments from the Upper Jurassic (Tithonian) to the Lower Cretaceous (Albian) (Coloma, 1998; Gil et al., 2002; Mas et al., 1993). These continental sediments have been traditionally divided into five groups (Tischer, 1965): Tera, Oncala, Urbión (fluvial sediments consisting of lutites and sandstones), Enciso and Oliván (lacustrine sediments constituted by limestones, marls and limolites).

The Upper Cretaceous constitutes the post-rift sequence and consists of carbonates from the Urgon Facies, the Utrillas Sandstones and the carbonate sedimentation at the end of this period (Gil et al., 2002).

During the Tertiary the tectonic inversion resulted in the relief of the Cameros Range and the formation of the tertiary basins, which were