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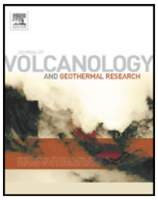

Hydrochemistry and geothermometrical modeling of low-temperature Panticosa geothermal system (Spain)

Maria P. Asta [a,*], Maria J. Gimeno [b], Luis F. Auqué [b], Javier Gómez [b], Patricia Acero [b], Pilar Lapuente [b]

[a] School of Natural Sciences, University of California, Merced, 5200 North Lake Road, Merced, CA 95343, United States
[b] Department of Earth Sciences, University of Zaragoza, Petrology and Geochemistry Area, Pedro Cerbuna, 12, 50009, Zaragoza, Spain

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ABSTRACT

The chemical characteristics of the low-temperature geothermal system of Panticosa (Spain) were investigated in order to determine the water temperature at the reservoir and to identify the main geochemical processes that affect the water composition during the ascent of the thermal waters. In general, the studied waters are similar to other geothermal systems in the Pyrenees, belonging to the group of granite-related alkaline thermal waters (high pH, low total dissolved solids, very low magnesium concentration, and sodium as the dominant cation). According to the alkaline pH of these waters, they have a very low CO_2 partial pressure, bicarbonate is the dominant anion and silica is partially ionized as $H_3SiO_4^-$. The unusually active acid–base pairs (HCO_3^-/CO_3^{2-} and, mainly, $H_4SiO_4/H_3SiO_4^-$) act as homogeneous pH buffers and contribute to the total alkalinity in these alkaline waters. On the basis of the study of the conservative elements, a mixing process between a hot and a cold end-member has been identified. Additionally, in order to determinate the water temperature at the reservoir, several geothermometric techniques have been applied, including both geothermometrical modeling and classical geothermometrical calculations. The geothermometrical modeling seems to indicate that thermal waters re-equilibrate with respect to calcite and kaolinite during their ascent to the surface. Modeling results suggest that these thermal waters would be in equilibrium with respect to albite, K-feldspar, quartz, calcite, kaolinite and zoisite at a similar temperature of 90 ± 20 °C in the reservoir, which is in good agreement with the results obtained by applying the classical geothermometers.

1. Introduction

Alkaline geothermal systems placed in granitic rocks have been widely studied during the last decades with geothermal prospecting aims (Suarez, 1998; Lund and Freeston, 2001; Coolbaugh et al., 2002; Marques et al., 2003; Manning et al., 2007; Majumdar et al., 2009). As it occurs in other types of geothermal systems, the chemical characteristics of geothermal fluids provide useful information on the primary and secondary (hydrothermal) mineralogy in the reservoir and on the existence of secondary processes affecting the thermal waters during their ascent. They also allow estimating the temperature of the thermal waters in the deep reservoir. Therefore, geochemical prospecting of natural thermal systems may provide useful information about the potential of geothermal areas to be used as a possible source of energy.

Geothermometrical methods use the chemical composition of hydrothermal solutions to estimate the reservoir temperature, assuming that the fluid composition does not change remarkably during its ascent to surface conditions. Classical chemical geothermometers are commonly used to estimate the temperatures at depth in geothermal areas, providing very reliable estimations (e.g. Fournier, 1977; Michard, 1979; Fouillac and Michard, 1981; Fournier, 1981; Arnorsson et al., 1983; Giggenbach et al., 1983; D'Amore et al., 1987; Nieva and Nieva, 1987; Giggenbach, 1988; Kharaka and Mariner, 1988; Chiodini et al., 1995; Mutlu and Güleç, 1998; Stefánsson and Arnórsson, 2000; Choi et al., 2005; Mariner et al., 2006; among many others). These geothermometers consist of equations or models based on temperature-dependent chemical reactions from which equilibrium temperatures can be calculated. The results of these classical techniques can be validated by applying geochemical modeling calculations, which provide more information as well as a more generalized approach to the chemical geothermometry and its associated problems. These calculations are focused on the evolution of the saturation indexes of a selected group of minerals, assumed to be present in the reservoir rocks (rock-forming or fracture filling minerals), as the temperature increases. Since it is supposed that thermal waters are in equilibrium with those phases under reservoir conditions, if all mineral equilibria are attained for a similar temperature, this is considered to correspond to the reservoir temperature.

This geochemical modeling approach was initially developed by Michard and co-workers in alkaline thermal waters (Michard and Fouillac, 1980; Michard and Roekens, 1983; Michard et al., 1986) and later by Reed and co-workers (Reed and Spycher, 1984; Pang and Reed, 1998; Palandri and Reed, 2001) for other types of thermal systems.

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[*] Corresponding author. Tel.: +1 209 228 4393.
E-mail address: masta@ucmerced.edu (M.P. Asta).

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Geochemical modeling calculations present important advantages over the classical geothermometers. They provide a more comprehensive view on the mineral equilibrium assemblage and on the chemical characters of thermal waters at depth (e.g. pH values). Additionally, they allow ascertaining the presence of secondary processes and their effects during the ascent of the thermal waters (e.g. mineral reequilibrium processes, mixing with cold waters, etc.; Michard and Fouillac, 1980; Michard and Roekens, 1983; Reed and Spycher, 1984; Michard et al., 1986; Tole et al., 1993; Pang and Reed, 1998; Palandri and Reed, 2001).

With all this background in mind, this work is aimed at studying the hydrochemistry of the spring waters of the Panticosa geothermal system in order to determine the water temperature at the reservoir and to identify and quantify the effects of the main secondary processes during the ascent of the thermal waters. The obtained results allow understanding the behavior of this system and are useful for planning future management of the geothermal resources of the Panticosa geothermal system. Moreover, the usefulness of the applied methodology is tested, which may allow its application to the study of other geothermal systems.

2. Geological setting

The Panticosa geothermal system is located in the Hercynian plutonic complex of Cauterets–Panticosa in the central sector of the Axial Zone of the Pyrenees (NE Spain; Fig. 1). This calc-alkaline and aluminous granitic complex occupies an area of more than 250 km^2 of exposed surface in the western Axial Zone of the Pyrenees (Fig. 1) and it is formed by three plutons: Panticosa, East Cauterets and West Cauterets. These plutons display a concentric compositional zoning (Debon, 1972, 1975; 1980; Leterrier and Debon, 1978) composed by granites and monzogranites with biotite in the core with a gradual transition to granites with biotite, granodiorites and tonalites in the external zone. The plutonic complex intrudes through folded pelite, limestone, quartzite formations and flysch facies (Devonian-Carboniferous age). These rocks are metamorphosed within the chlorite zone of the greenchist facies. A contact metamorphic aureole, superimposed on the regional metamorphism, extends around the whole complex.

An important feature related to the thermal springs is the intense fracture networks, with preferred orientations E–W and N–S, which have enhanced the development of the geothermal system, gathering the main water-conducting flow-paths. These structural features seem to be involved in the development of this thermal circuit at depth, where both fracture systems intersect, favoring water circulation (IGME, 1994; Moreno et al., 1997; Sánchez-Navarro, 2000). A simplified sketch for the studied water system is presented in Fig. 2.

The Panticosa thermal system is located mainly in the slopes of a glacial cirque. The wide extension of the granitic outcrops and relatively high pluviometry (more than 150 mm/year) favor an important and continuous water recharge from high altitude (around 2400 m, as deduced from isotopic data; Auqué, 1993) and create the important hydraulic gradient driving the emergent thermal water fluxes. The hydrothermal circuit is assumed to be U-shaped (Fig. 2; Auqué, 1993; IGME, 1994), as also described for other thermal systems in the Pyrenees (e.g. Luchon, Chevalier-Lemire et al., 1990; Cauterets, Soulé, 1990 and Caldas de Boi, Auqué, 1993; Asta et al., 2010) and in other granitic geothermal systems (e.g. Druschel and Rosenberg, 2001).

3. Materials and methods

3.1. Sampling and analytical methods

A total of 6 thermal springs and the cold waters of the Lake spring (representative of the superficial detritic aquifer in the zone, Figs. 1 and 2) were sampled in June 2003 in the surroundings of the Panticosa Resort (Table 1). Due to accessibility problems, the Tiberio spring, with the highest temperature in the Panticosa system (IGME, 1982, 1994; Auqué, 1993; Auqué et al., 1996, 1997, 1998), was not sampled during this campaign and, therefore, literature data from Alaux-Negrel et al. (1993) and Auqué et al. (1998) were considered in this study. Prior to the use of these reported data, the sampling and analytical methodologies used in those studies were checked to confirm their suitability (e.g. in situ determination of pH and temperature and well documented sampling and analytical methodologies).

Water temperature and pH were determined on site. Water pH was measured in the field using a portable pH-meter (Thermo Orion model 250A) with ORION815600 Ross combination pH electrode with temperature compensation after calibration with standard buffer solutions of pH 7.0 and 10.01. The error associated to pH measurements, including both accuracy and reproducibility, is better than ±0.05 pH units. Temperature was measured with the probe connected to the pH-meter and the measurement error is estimated to be better than ±0.3 °C.

Poly-ethylene bottles of 1000 and 100 mL volume (pre-washed with HCl and subsequently rinsed three times with double-distilled water) were used for each sample for anion and cation analysis, respectively. Samples for anion determination were taken without filtering or adding acid; analysis of those samples was carried out in

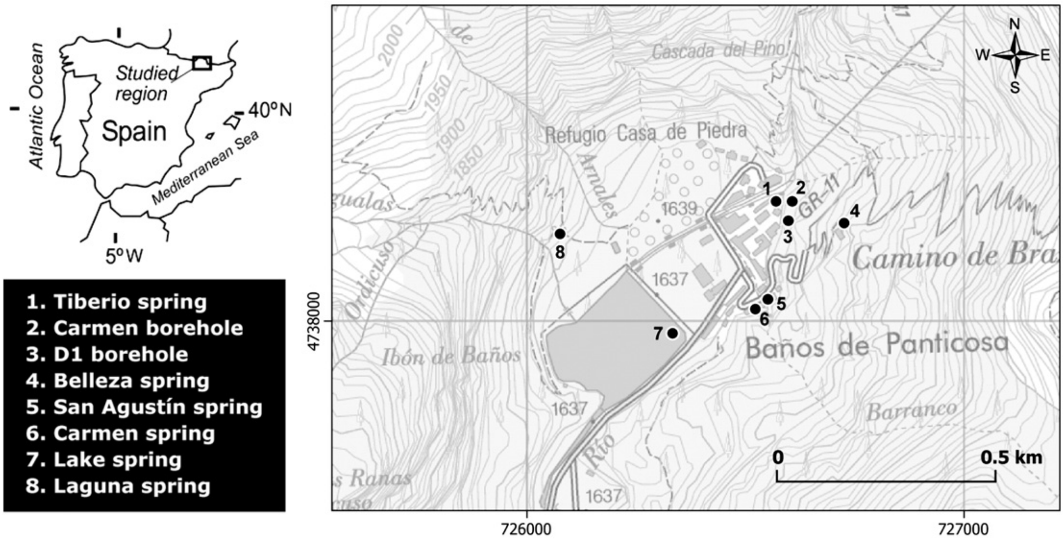

Fig. 1. Location of Panticosa geothermal system and the springs studied in the Panticosa resort.