Study of the Secondary Processes in the Alkaline Geothermal System of Panticosa (NE, Spain)

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INTRODUCTION.

In this work, some of the most important irreversible processes (cooling, mixing and CO_2 exchange) affecting the hydrogeochemistry of alkaline thermal systems developed in crystalline rocks are studied. The effects of those processes have been quantified with the assistance of geochemical modeling applied to the Panticosa geothermal system (central sector of the Axial Zone of the Spanish Pyrenees). The most important feature of this plutonic complex related to the thermal springs is the intense fracture network which has 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 (Fig. 1).
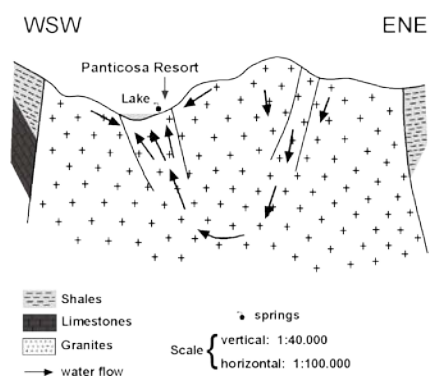

fig 1. Simplified sketch of the Panticosa hydrothermal system (modified from ITGE, 1994).

METHODOLOGY.

A total of 6 springs and the cold waters of the Panticosa lake spring, representative of the superficial detritic aquifer in the zone were sampled in the Panticosa Resort in April 2003. Cations and silicon were analyzed in the Centre de Recherches Petrographiques et Geochimiques (Nancy, France) by ICP-OES. Mg was determined by inductively coupled plasma mass spectrometry (ICP-MS). Total alkalinity was analyzed within 24 hours of sampling by volumetric titration with H_2SO_4 0.02 N and potentiometric determination of final point at pH 4.5. Cl- and F- were determined by ion-selective electrodes and SO_4 concentrations were determined with an spectophotometer using a turbiditic method with Ba.

Moreover, pH, Eh, temperature and conductivity were measured in the field.

Following the hydrochemical modelling methodology successfully used in other works (Auqué, 1993; Asta et al., 2010), speciation-solubility and reaction-path calculations were carried out in order to identify and quantify the main processes controlling the hydrochemical evolution of groundwaters in the Panticosa thermal system. All the simulations presented here were performed with the assistance of the geochemical code PHREEQC (Parkhurst and Appelo, 1999) using the WATEQ4F thermodynamic database (Ball and Nordstrom, 1991).

RESULTS.

The Panticosa geothermal system displays a range of temperatures from 8.3 to 44.1 °C and pH values from 7.4 to 9.2. Sodium is the dominant cation, especially in the hottest waters (up to 30 mg/L), being the concentrations of K, Ca and Mg very low (even below the detection limit of ICP-OES in the case of Mg). Silicon contents are also higher in the hottest waters, reaching values as high as 27.5 mg/L. Alkalinity values (as HCO_3^-) are as high as 53 mg/L. With regard to the anionic contents, they are generally low.

Mixing of solutions with different chemical characters seems to be the main process determining the hydrochemistry of the studied springs. The presence of mixing can be evidenced by a simple analysis of binary correlation between elements of conservative behaviour which, for the studied system, are mainly Na and Si. Figure 2a shows the very good correlation found between these two elements. This result suggests the
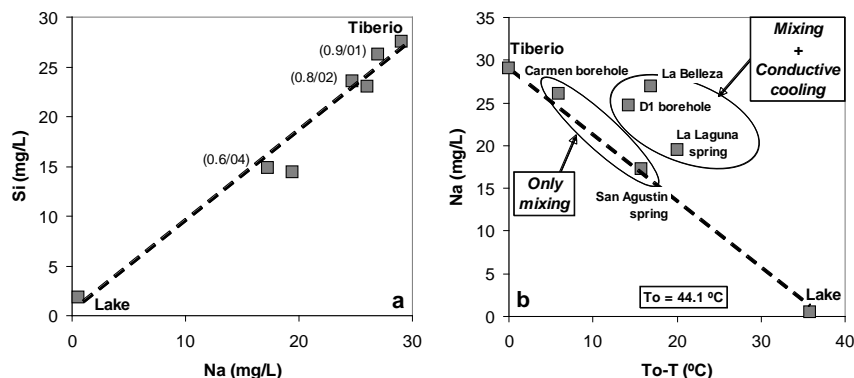

fig 2 Correlation diagram between Na and Si (a). In panel (a) the line represents the theoretical trend of the mixing between the thermal (Tiberio borehole) and the cold end-member (Lake). The numbers beside the points indicate the thermal-non thermal end-member mixing proportion. Relationship between sodium and the cooling process expressed as the difference between the temperature in the thermal end member (To, Tiberio borehole) and the temperature in the rest of the springs (T) (b).

mixing of two end-member waters: a thermal water (similar to the one sampled in the Tiberio borehole) and a cold water (similar to the one sampled in the Lake), with a linear change in concentration with respect to the mixing fraction.

As an additional test for the presence of secondary processes, the evolution of Na concentrations has been compared with the observed temperature and pH evolution. Figure 2b shows the evolution of Na concentration versus the amount of cooling, expressed as the difference between the temperature of the thermal end member (T_0, for the Tiberio borehole) and the measured temperature of each spring (T). The position of the springs affected only by mixing with cold and shallow water (those on the mixing line) and which are affected by an extra cooling that displace them towards the right of the mixing line. This seems to be the result of a conductive cooling along the flow paths.

PHREEQC Simulations and pH Evolution.

In order to obtain the theoretical pH path by mixing the hot (Tiberio) and the cold waters (Lake), a first **PHREEQC** simulation was devised (black solid line between Tiberio and Lake in Fig. 3). According to the results, pH remains almost constant (or slightly increasing) for proportions larger than 50% of the hot end member, which displays an important pH buffer capacity due to its alkaline character and to the active presence of the acid-base pairs

HCO_3^-/CO_3^{2-} and $H_4SiO_4^0/H_3SiO_4^-$ (an important percentage of silica appears as $H_3SiO_4^-$ in alkaline waters). For smaller mixing proportions of hot end member, pH decrease steadily with the increase of cold waters fraction (Fig. 3).

A second PHREEQC simulation was designed to model conductive cooling by means of a progressive decrease of temperature. The results indicate that water conductive cooling generates trends of linear pH increase as temperature decreases (Fig. 3).

As shown in Fig. 3, most of the springs display pH values lower than it would correspond to simple mixing or mixing plus conductive cooling. An explanation would be the input of CO_2 to the waters, which, moreover, seem to be in equilibrium with pCO_2 noticeably lower (log pCO_2 in the range of -4.63 to -4.02) than the atmospheric value (log pCO_2=-3.5). To explore this possibility, different amounts of CO_2 have been simulated to be irreversibly added to the thermal end-member composition (Tiberio). Then, over each solution, a mixing process with different proportions of the cold end member (Lake) has been simulated. As can be observed in Fig. 3, the hypothesis of CO_2 input superimposed to mixing (plus cooling, generally) allows explaining the measured pH values of all the thermal waters.

Finally, since calcite is the only mineral phase whose dissolution-precipitation is fast enough to influence pH in the system, the saturation indices of the Panticosa thermal waters with respect to calcite were calculated, showing to be

close to equilibrium (within a ±0.3 SI units of uncertainty range). As stated above, those waters display CO_2 partial pressures lower than the atmosphere. Therefore, they will tend to incorporate $CO_{2(g)}$ at the springs, which will favour calcite undersaturation. Therefore, only calcite dissolution would be possible if this mineral is present in the system. However, the small differences in the calcium contents of the analysed waters, even assuming that were only promoted by calcite, also suggest that calcite dissolution is not a significant process. So, dissolution of calcite does not seem to play an important role in controlling the pH of these waters.

CONCLUSIONS.

This study has proven, with the assistance of geochemical modeling, that the superposed effects of cooling, mixing and $CO_{2(g)}$ input can explain the pH changes and the geochemical features of the waters of the Panticosa geothermal system. It is also expected that these processes may be altered by the more variable characters in the "superficial system". Therefore, the conductive cooling and mixing intensity affecting different springs would not be constant and may dynamically change with time depending on precipitation, recharge of the superficial aquifers, etc.

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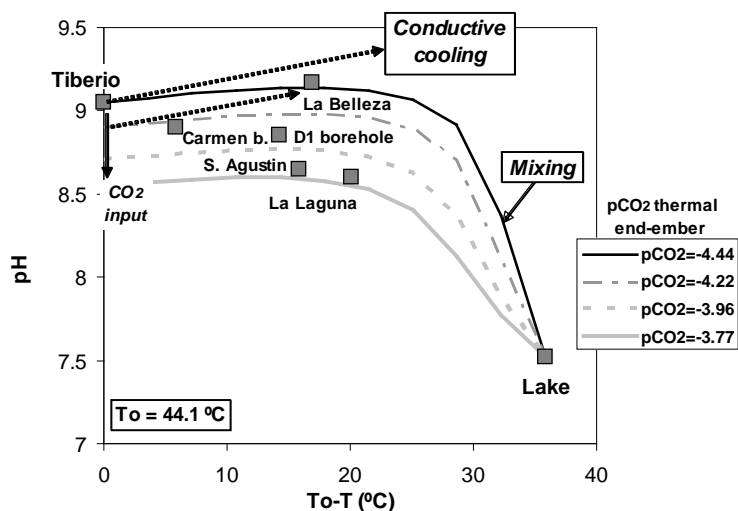
fig 3. Simulation of mixing process between Tiberio and Lake (black solid line) and between CO_2-enriched thermal end members and Lake waters (dashed and solid grey lines). It is also represented the evolution of pH during the conductive cooling of Tiberio (pCO_2= -4.44) and a CO_2-enriched thermal end member with pCO_2=-4.22 (dashed black lines).