Geothermometrical modelling applied to the CO_2-rich thermal waters of the Lanjarón hydrothermal system (Granada, Spain)

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INTRODUCTION

The interest in hydrothermal systems with CO_2-rich waters has raised significantly in the last decades, due to their potential as natural analogues for the geological storage of CO_2, especially with respect to the possible leakage processes during the storage (e.g. Pauwels *et al.*, 2007). The Lanjarón hydrothermal system, one of these CO_2-rich water systems, is located in the Internal Areas of the Baetic System in Sierra Nevada (Granada) and the origin of this CO_2 is mostly endogenous and related to active seismic zones (Cerón and Pulido-Bosch, 1996). The deep reservoir of this carbonic system can be considered a good analogue for studying the conditions and the possible processes in the deep storage of CO_2, and with that aim, a geothermometrical study of this system is presented in this work. Classical geothermometers and geothermometrical modelling have been applied in order to quantify the conditions of temperature, pH and mineral equilibrium in the deep reservoir, as well as the processes that affect these parameters during the ascent of the thermal waters to the springs.

METHODOLOGY

Analytical data of the Lanjarón waters from a 2014 sampling campaign, carried out by the Geochemical Modelling Group from the University of Zaragoza, have been used. Temperature, pH and conductivity were measured in situ. Total alkalinity was determined by titration. Cl^- and F^- were analysed by the specific electrodes of chloride ORION 94-17B and fluoride ORION 94–09, respectively. SO_4^{2-} has been determined by turbidimetry. These anions were analysed in the Geochemistry Laboratory of the Earth Sciences Department of the University of Zaragoza. Ca, Mg, Na, K, Si, Ba, Sr and Li were analysed by atomic emission spectrometry in plasma ICP (ICP-OES) in the central chemical laboratories (SAI) of the same university. The geothermometrical calculations are based on the assumption that the waters in the deep reservoir have reached the equilibrium with the host rocks; in this case, schists, carbonates and, to a lesser extent, evaporites. Thus, the geothermometrical modelling consists of evaluating the evolution of the saturation indices of a group of selected minerals as the water temperature increases, until they reach equilibrium at a certain common temperature value or range. This modelling has been performed with PHREEQC (Parkhurst and Appelo, 2013) and the LLNL thermodynamic database. Additionally, the classical chemical geothermometers Si-quartz and Si-chalcedony, among others not shown here, have been used as they are not affected by CO_2 transfer processes, and therefore they are the most reliable in these systems.

RESULTS AND DISCUSSION

The geothermometrical techniques have been applied to the spring Capuchina, since it is the most representative of the CO_2-rich waters, and the results are shown in Figure 1. In order to reproduce the reservoir equilibrium conditions, the calculations simulate the increase in temperature simultaneously with a process of CO_2 input. The addition of different amounts of CO_2 has been simulated to optimize the convergence towards equilibrium of three minerals, one affected by CO_2 transfer (calcite) and the others unaffected (quartz and anhydrite). Figure 1 shows that by simulating the addition of 1640 mmol/l of CO_2, the convergence of the saturation indices (S.I.) of calcite, quartz and anhydrite was obtained at a temperature of 116 ± 7 ºC. The temperature at which dolomite reaches equilibrium is approximately 123 ºC, which is very similar, indicating a high reliability of the simulation results. On the other side, the pH value calculated at the equilibrium temperature of the reservoir is 4.61, which is significantly lower than the value measured in the spring (pH = 6.07). This is most likely due to the pH increase during the water ascent (conductive cooling) and, mainly, to the CO_2 loss at surface. Other simulations have been successfully carried out with different phases and considering other processes such as re-equilibrium with calcite, but the uncertainties were slightly higher and we only show here the most precise and reliable results obtained.

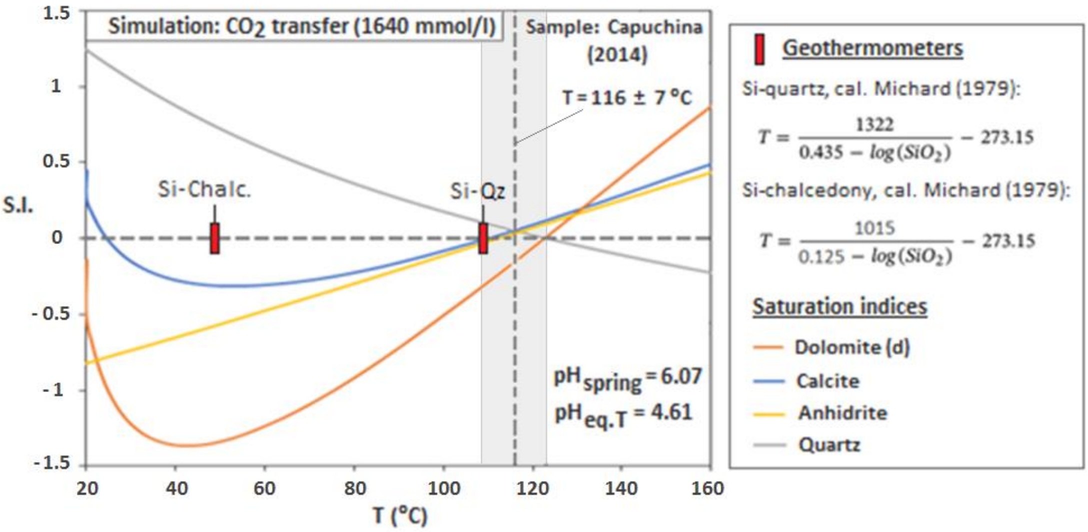

Fig 1. Results of the geothermometrical simulation and classical geothermeters applied to the sample Capuchina (2014), imposing a CO_2 input of 1640 mmol/l. Uncertainty (shaded band) is given as the standard deviation of the equilibrium temperatures. SiO2 concentrations in the geothermometer calibrations are in mol/l.

Regarding the classical geothermometers, the Si-quartz geothermometer predicts a temperature of 108 ºC, similar to that obtained with the geothermometrical simulation (116 ºC). Nonetheless, the Si-chalcedony geothermometer provides a temperature of 48 ºC, which is significantly lower than those obtained with the Si-quartz geothermometer and the simulation. This is probably due to the fact that the silica phase in equilibrium in the reservoir is quartz instead of chalcedony (simultaneous equilibrium with these two phases cannot occur).

CONCLUSIONS

The results of geothermometrical modelling provide a temperature of 116 ± 7 ºC in the deep reservoir and a pH value of 4.6, much lower than the spring value (pH = 6.07), which is probably due to the conductive cooling and, mainly, degassing effects. Indeed, it has been necessary to restore the effect of CO_2 loss in the simulation to optimize the results. In parallel, one of the most reliable classical chemical geothermometer in this system, Si-quartz, predict a reservoir temperature of 108 ºC, similar to that obtained by geothermometrical modelling. Finally, through the highly precise convergence of the S.I. at equilibrium it has been deduced that the thermal waters have probably reached the equilibrium with quartz, anhydrite, calcite and dolomite in the deep reservoir.

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