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Processes releasing arsenic to groundwater in the Caldes de Malavella geothermal area, NE Spain

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ABSTRACT

Arsenic concentrations exceeding the World Health Organization drinking water guideline (10 μg/L) have been measured in thermal and non-thermal groundwaters from the Caldes de Malavella geothermal area (La Selva graben, NE Spain). The CO_2-rich Na-HCO_3 thermal waters (up to 60 °C at the spring) have elevated arsenic concentrations ($[As_T]$ from 50 to 80 μg/L). The non-thermal waters are of Ca-Na-HCO_3-Cl type and have $[As_T]$ between <1 and 200 μg/L, defining a hot-spot distribution. The present-day contribution of As from CO_2-rich thermal waters to non-thermal aquifers is very limited, as shown by the concentration of geothermal tracers such as Li and B. Redox-controlling processes appear to govern the mobility of As in the non-thermal waters. Arsenate is clearly predominant in most oxidizing groundwaters (>85% of As(V) over total As), whereas reducing, high-As groundwater reaches up to 100% in arsenite. The reductive dissolution of Fe(III) oxyhydroxides and the coupled release and reduction of adsorbed As explain the elevated dissolved arsenite (up to 190 μg/L) and Fe (up to 14 mg/L) content in the more reducing non-thermal groundwater. Conversely, the high levels of nitrate (up to 136 mg/L) ensure an oxidizing environment in most non-thermal groundwaters ($[As_T]$ between <1 and 60 μg/L). Under these conditions, Fe(III) oxyhydroxides are stable and As release to groundwater is not related to their dissolution. Instead, dissolved arsenate concentrations up to 60 μg/L are explained by a competition for sorption sites with other species, mainly bicarbonate and silicic acid, while arsenate desorption due to pH increase is not considered a major process.

1. Introduction

Arsenic is a pervasive trace component in geothermal systems worldwide (e.g. Criaud and Fouillac, 1989; Wilkie and Hering, 1998; Schwenzer et al., 2001; Le Guern et al., 2003; Aksoy et al., 2009) and has been found in significant concentrations (up to 200 μg/L) in the low enthalpy geothermal field of Caldes de Malavella, NE Spain (Cama et al., 2008; Piqué et al., 2008; Fig. 1). Since Roman times, the village of Caldes de Malavella is well known for its thermal baths, and since the late 1800s, its CO_2-rich thermal waters (up to 60 °C at the spring) are bottled and commercialized.

Arsenic levels in the CO_2-rich thermal springs of Caldes de Malavella are between 50 and 80 μg/L, while it can reach 200 μg/L in non-thermal groundwaters (Piqué et al., 2008), which is far above the guideline concentration for drinking

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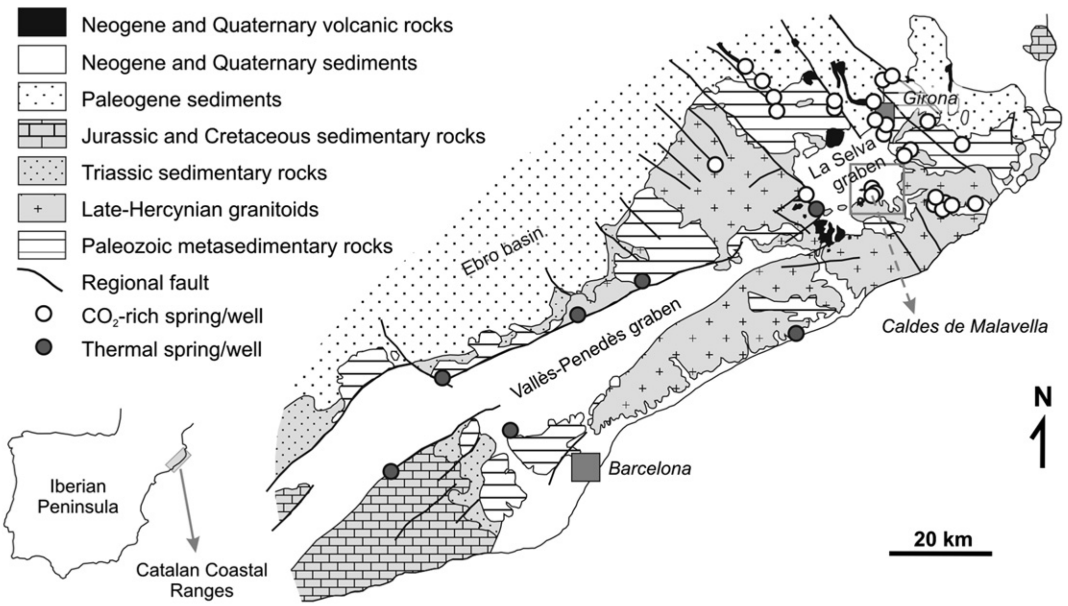

Fig. 1 – Geological map of the northern part of the Catalan Coastal Ranges, with the location of the Caldes de Malavella geothermal field and CO_2-rich and thermal wells and springs. The gray square corresponds to the location of the study area, enlarged in Fig. 2.

water set by the World Health Organization (10 μg/L; WHO, 2006). The wells formerly used to supply drinking water to the village (around 6800 inhabitants) provided high-As non-thermal groundwater, and concentrations of arsenic in tap water reached 150 μg/L in summer 2005, coinciding with a period of high water demand (Cama et al., 2008). New wells were drilled in the area for drinking water supply and extractive operations from the high-As wells ceased in 2006; nevertheless, thermal springs open to the public and groundwater extracted in many private wells have high arsenic concentrations.

The origin, extent and temporal variations of the high arsenic concentrations in the Caldes de Malavella geothermal area are not well known. Preliminary hypotheses suggest that arsenic in non-thermal aquifers could derive from deep geothermal fluids (Cama et al., 2008), though no conclusive evidence has been provided. The main objectives of the present study are: (1) to elucidate the processes controlling arsenic mobility/retention in groundwater from the Caldes de Malavella geothermal field and surrounding area; and (2) to know the role played by the geothermal CO_2-rich fluids on the arsenic concentration in non-thermal, shallower groundwater. The applicability of field sampling techniques to separately collect arsenite [As(III)] and arsenate [As(V)] species is also assessed. The results from this study may contribute to predict future effects of arsenic pollution on As-poor groundwater and to find technical solutions for water treatment.

2. Geological setting

The geothermal field of Caldes de Malavella is located at the southern margin of La Selva graben, in the Catalan Coastal Ranges (Fig. 1). The latter are two ENE-WSW-trending Alpine ranges, ~250 km-long and parallel to the Mediterranean coast, which acquired their present subdivision into horsts and grabens during the late Oligocene-early Miocene opening of the Valencia trough (Roca et al., 1999). The horsts are made up of Hercynian basement materials overlain by Mesozoic and Cenozoic cover rocks, while the grabens are filled with Neogene sediments and, in the northern part of the ranges, also with volcanic rocks (Fig. 1). The massifs surrounding La Selva graben are made up of Paleozoic metasediments intruded by late Hercynian calcalkaline granodiorites and leucogranites. In the northern margin, Paleogene sedimentary units also crop out (Fig. 1).

The La Selva graben (ca. ~200 km^2) is limited by NE–SW and NNW-SSE-trending faults and is subdivided by NE–SW, NNW-SSE and N–S directed faults. The geothermal field under study is located in an area where several faults converge, at the boundary between the crystalline basement and the basin (Fig. 1). The sedimentary filling of the graben mainly consists of Neogene clays, with interbedded levels of arkosic sands, gravels and minor conglomerates, all partially covered by Quaternary alluvial sediments. The sediment thickness varies from tens to more than 300 m, due to faulting and to the possible existence of paleoreliefs (Pous et al., 1990). A number of episodes of Neogene basaltic alkaline volcanism are recorded at the margins of the basin, in close association with faults (Fig. 1). In the study area, the volcanic materials correspond to few outcrops of altered alkaline olivine basalts and to a tuff ring (Camp dels Ninots volcano), which is filled with maar sediments (Fig. 2; Vehí, 2001).

3. Hydrogeological setting

In the area under study, three main hydrogeological units have been differentiated (e.g. Menció, 2005): (1) the Neogene