Science of the Total Environment 429 (2012) 57–75

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

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

Arsenic in volcanic geothermal fluids of Latin America

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ARTICLE INFO

Article history:
Received 18 October 2010
Received in revised form 16 August 2011
Accepted 16 August 2011
Available online 27 January 2012

Keywords:
Arsenic
Geothermal system
Latin America, Volcanic fluids
Geothermal fluids

ABSTRACT

Numerous volcanoes, hot springs, fumaroles, and geothermal wells occur in the Pacific region of Latin America. These systems are characterized by high As concentrations and other typical geothermal elements such as Li and B. This paper presents a review of the available data on As concentrations in geothermal systems and their surficial discharges and As data on volcanic gases of Latin America. Data for geothermal systems in Mexico, Guatemala, Honduras, El Salvador, Nicaragua, Costa Rica, Ecuador, Bolivia, and Chile are presented. Two sources of As can be recognized in the investigated sites: Arsenic partitioned into volcanic gases and emitted in plumes and fumaroles, and arsenic in rocks of volcanic edifices that are leached by groundwaters enriched in volcanic gases. Water containing the most elevated concentrations of As are mature Na–Cl fluids with relatively low sulfate content and As concentrations reaching up to 73.6 mg L^{-1} (Los Humeros geothermal field in Mexico), but more commonly ranging from a few mg L^{-1} to tens of mg L^{-1}. Fluids derived from Na–Cl enriched waters formed through evaporation and condensation at shallower depths have As levels of only a few μg L^{-1}. Mixing of Na–Cl waters with shallower meteoric waters results in low to intermediate As concentrations (up to a few mg L^{-1}). After the waters are discharged at the ground surface, As(III) oxidizes to As(V) and attenuation of As concentration can occur due to sorption and co-precipitation processes with iron minerals and organic matter present in sediments. Understanding the mechanisms of As enrichment in geothermal waters and their fate upon mixing with shallower groundwater and surface waters is important for the protection of water resources in Latin America.

1. Introduction

In Latin America, volcanism and geothermal systems are more common in the Pacific zone (Fig. 1), which is an intensively populated region with a high demand of potable water. The presence of As in geothermal waters and its environmental impact has long been recognized, e.g. Long Valle Caldera, USA (Wilkie and Hering, 1998); Los Azufres, Mexico (Birkle, 1998; Birkle and Merkel, 2000); Los Humeros, Mexico (González et al., 2001). The purpose of this paper is to present a general overview of the state of As contamination arising from geothermal resources in Latin America, and to identify processes that produce high As concentrations and mechanisms that immobilize or release As into the environment.

Geothermal activities are associated with four different settings (Chandrasekharam and Bundschuh, 2002): active volcanoes, continental collision zones, continental rift systems associated with active volcanism, and continental rifts not associated with volcanoes. In the case of Latin America, As-rich geothermal waters are usually associated with areas of active volcanism. Birkle and Bundschuh (2007b) have identified the mixing of As-rich geothermal groundwater with cold aquifers as the main environmental problem in As contamination. However, in some cases, As-rich surface waters are found in rivers and lakes close to spring discharges (e.g. Cumbal et al., 2009), or in lakes filling volcanic calderas (e.g. López et al., 2009).

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0048-9697/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.scitotenv.2011.08.043

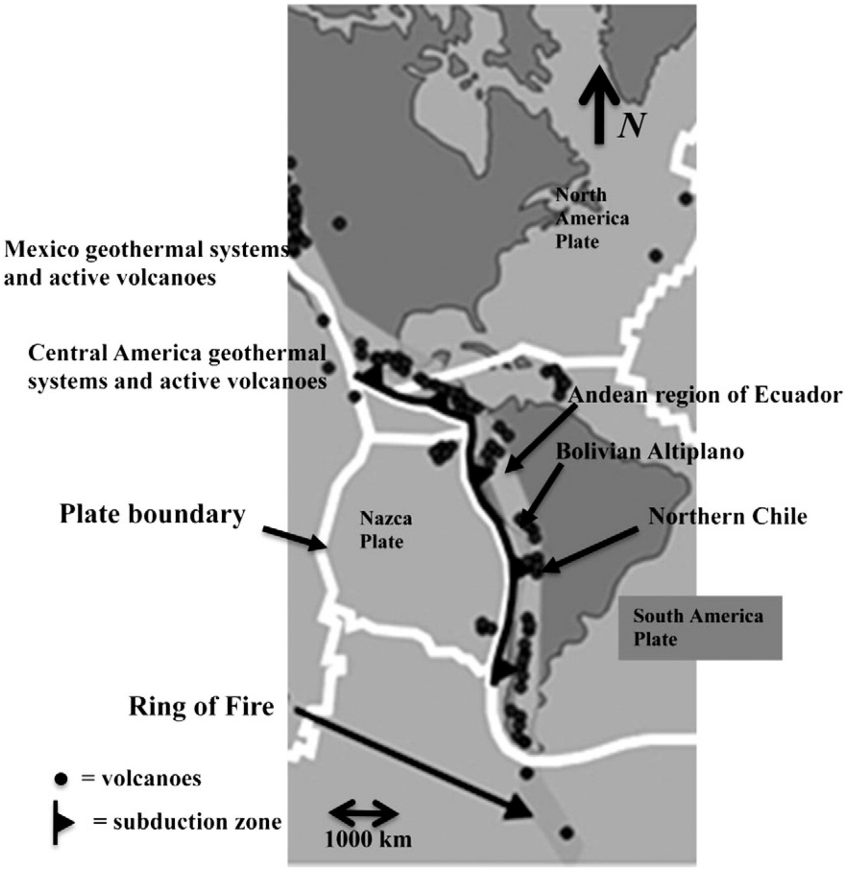

Fig. 1. Location map showing volcanoes, the ring of fire, and plate boundaries.

Even when As is detected in some volcanic emissions (e.g. Signorelli, 1997), it is not common to find reports of As concentrations for volcanic gases (e.g. Gemmel, 1987; Mambo and Yoshida, 1993). The way that As is partitioned between the volcanic fluids and the magma is not well understood due to lack of data in the melt and gas phase. Experimental and theoretical work on the stoichiometry and stability of As gaseous complexes in the system As–H_2O–NaCl–H_2S at temperatures up to 500 °C and pressures up to 6×10^7 Pa (600 bars, Pokrovski et al., 2002b) indicate that $As(OH)_3$(gas) is the predominant As complex in both volcanic gases and boiling hydrothermal systems. This species is proposed as responsible for the preferential partitioning of As into the vapor phase as observed in fluid inclusions from high-temperature magmatic-hydrothermal ore deposits (Pokrovski et al., 2002b).

With respect to As in fumarole gases, studies in Yellowstone (USA) show that toxic inorganic AsH_3 is the most volatile of the inorganic species. Organic methylated species $(CH_3)_2AsCl$ is the most commonly found in the gas phase, followed by $(CH_3)_3As$, $(CH_3)_2AsSCH_3$, and CH_3AsCl_2 (Planer-Friedrich et al., 2006). The degree of toxicity of the methylated forms is unknown.

In comparison, the behavior of sources and fate of As in geothermal systems are better understood (e.g. Arellano et al., 2003; Birkle and Bundschuh, 2007b; Goff et al., 1986a; González et al., 2001). In deep geothermal systems, reducing conditions prevail. Arsenic is present as As(III) and the solution is undersaturated with respect to arsenopyrite and other As minerals (Webster and Nordstrom, 2003). These undersaturated conditions also occur for minerals containing B, F, Li, Hg, Se, and Tl. According to Webster and Nordstrom (2003), arsenopyrite is not a conspicuous mineral in geothermal systems. Birkle et al. (2010) state that the saturation state of geothermal waters with respect to arsenopyrite depends on reservoir temperature. For temperatures between 150 and 250 °C, As occurs as As-bearing pyrite rather than as arsenopyrite, or is associated with iron oxides. At higher temperatures, arsenopyrite (FeAsS) and other As-bearing minerals can be found. Equilibrium between As-bearing pyrite and fluids is responsible for the As concentrations measured in high and moderate temperature hydrothermal systems, with local dissolution of arsenopyrite creating more reducing conditions which are likely to favor the precipitation of gold from hydrothermal solutions (Pokrovski et al., 2002a, 2002b).

Arsenic can be present in geothermal reservoirs as well as in spring discharge and fumarolic gases. However, the highest concentrations of As are found in mature NaCl waters (up to tens of thousands μg/kg) that have been in contact with the rocks for a long period of time (Birkle et al., 2010), suggesting that the increase in As concentration is due to the longer residence time (and leaching) of the waters. Thus, As concentrations are considerably higher in geothermal systems occurring in volcanic rocks than in high and low enthalpy systems in sedimentary rocks. The path of geothermal reservoir waters to the surface can occur in four different ways. (1) If the upflow (for example along a fault zone to the surface) is fast, with a minimal lost of conductive heat to the wallrock, the composition of the discharging water is similar to the reservoir water producing a Na–Cl rich water, with near neutral pH, high silica content due to the long rock–fluid interaction, sulfate concentrations lower than Cl concentrations, and enrichment in CO_2 and H_2S gases. These are the mature Na–Cl waters described by Giggenbach (1988). Consequently, these waters should present As concentrations close to reservoir concentrations. (2) If a vapor phase rich in H_2S separates from the reservoir due to pressure changes, and the vapor condenses at shallower levels, acid sulfate waters low in Cl are formed (Giggenbach, 1988). According to Birkle et al. (2010), these condensed waters are low in As because As is partitioned