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The geochemistry of trace elements in geothermal fluids, Iceland

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ABSTRACT

Trace element geochemistry was studied in geothermal fluids in Iceland. The major and trace element compositions of hot springs, sub-boiling, and two-phase (liquid and vapor) wells from 10 geothermal areas were used to reconstruct the fluid composition in the aquifers at depth. Aquifer fluid temperatures ranged from 4 to 300 °C, pH values between 4.5 and 9.3, and fluids typically contained total dissolved solids <1000 ppm, except in geothermal areas that have seawater and seawater-meteoric water mixtures. Trace alkali elements Li, Rb and Cs are among the most mobile elements in aquifer fluids, with concentrations in the range of <1 ppb to 3.49 ppm Li, <0.01 to 57 ppb Cs, and <1 ppb to 3.77 ppm Rb. Their chemistry is thought to be dominated by rock leaching and partitioning into Na- and K-containing major alteration minerals. Arsenic, Sb, Mo and W are typically present in concentrations in the range of 1–100 ppb. They are relatively mobile, yet Mo may be limited by molybdenite solubility. The alkaline earth elements Ba and Sr are quite immobile with concentrations in the range of <0.1–10 ppb Ba and <1–100 ppb Sr in the dilute fluids, but up to 5.9 ppm Ba and 8.2 ppm Sr in saline fluids. These elements show a systematic relationship with Ca, possibly due to substitution for Ca in Ca-containing major alteration minerals like calcite, epidote and anhydrite. Incorporation into major Ca-minerals may also be important for Mn. Many metals including Fe, Cr, Ni, Zn, Cu, Co, Pb and Ag have low mobility and concentrations, typically <1 ppb for Ag, Cd, Co, Cr, Cu, Ni, and Pb, <10 ppb for Zn and < 100 ppb for Fe, although for some metals higher concentrations are associated with saline fluids. Based on the metals assessed, saturation is approached with respect to many sulfide minerals and in some cases oxide minerals but Cu, Ni and Pb minerals are slightly but systematically undersaturated, and Ag phases significantly undersaturated. Evaluation of mineral-fluid equilibria for these metals is problematic due to their low concentrations, problems associated with assessing the aqueous species distribution by thermodynamic calculations, and uncertainties concerning the exact minerals possibly involved in such reactions. Reaction path calculations, poor comparison of concentrations measured in the samples collected at the wellhead and published downhole data as well as boiling, cooling and mass precipitation calculations suggest removal of many metals due to changes upon depressurization boiling and conductive cooling of the aquifer fluids as they ascend in wells. These results imply that processes such as mass precipitation upon fluid ascent may be highly important and emphasize the importance of considering mass movement in geothermal systems.

1. Introduction

Fluids in active geothermal systems are known to be capable of transporting and depositing metals and these fluids provide a modern analog of ore-depositing hydrothermal environments (e.g., Weissberg et al., 1979; Henley and Ellis, 1983; Clark and Williams-Jones, 1990; Simmons and Brown, 2007). Several metals and metalloids present in geothermal fluids (e.g., Al, As, Pb and Zn) may be harmful to the environment, and are of interest in order to understand the potential environmental impacts of the exploitation of geothermal systems (e.g., Kristmannsdóttir and Ármannsson, 2003).

Metals enter geothermal systems with the source water, as magmatic volatiles and/or via rock dissolution, and are transported as simple ions or complexed with ligands like Cl^-, HS^- and OH^- (e.g., Barnes, 1979; Seward and Barnes, 1997; Aiuppa et al., 2000, 2005). The metal concentrations are typically highest in saline fluids but low in dilute fluids (e.g., Henley and Ellis, 1983; Gallup, 1998). Upon ascent of the aquifer fluids to the surface, depressurization boiling, cooling and mixing with colder water may occur resulting in mineral precipitation as shown by scale formation in wells, their distribution in drill cuttings, comparison of fluid data from samples

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collected from wells at the surface and downhole, as well as studies on hydrothermal ore deposits (Ewers and Keays, 1977; Brown, 1986; Kristmannsdóttir, 1989; Clark and Williams-Jones, 1990; Reyes et al., 2002; Hardardóttir et al., 2009, 2010). In addition, boiling and phase segregation may lead to partitioning of some trace elements such as B, As, Hg and Sb between the vapor and liquid phases (e.g., Glover, 1988; Giroud, 2008; Kaasalainen and Stefánsson, 2012), although metal concentrations in the low density-vapor formed upon low-pressure boiling of geothermal fluids are generally thought to be negligible (Heinrich, 2007).

In Iceland, geothermal activity is widespread and the active geothermal systems have been much studied with respect to their subsurface geology, alteration mineralogy and major element fluid composition. The alteration minerals follow temperature-related depth-zonation and include calcite, pyrite and other metal sulfides, chalcedony, zeolites, smectites, and K-feldspar, as well as anhydrite and garnet in saline geothermal systems, with the appearance of quartz, albite, epidote, chlorite, prehnite and actinolite with increasing temperature (Kristmannsdóttir, 1976, 1979; Steinthórsson and Sveinbjörnsdóttir, 1981; Hreggvidsdóttir, 1987; Larsson et al., 2002). The fluids are meteoric water or seawater by origin, or mixtures thereof, with a pH ranging from ∼2 to ∼10 and total dissolved solids (TDS) in the range of 150 and 40,000 ppm but being typically dilute, with TDS between 200 and 2000 ppm, in the basalt environment in Iceland (Table 1, Björnsson et al., 1972; Arnórsson et al., 1983, 2007; Arnórsson, 1995). The aquifer fluids typically have near-neutral pH values and Na, Cl, SO_4 and Si as the dominant dissolved solids, yet in the fluids in high-temperature systems, CO_2, H_2S and H_2 are sometimes more abundant than the solids on a molal basis. The major element composition is characteristically controlled by close approach to equilibria with secondary minerals, except for elements like Cl and B that are essentially incompatible (Arnórsson et al., 1983; Arnórsson and Gunnlaugsson, 1985; Arnórsson and Andrésdóttir, 1995; Stefánsson and Arnórsson, 2000, 2002). However, other processes may also play an important role in determining fluid compositions, including reaction kinetics, extent of water–rock interactions, fluid and acid supply, and heat and fluid transfer (Helgeson et al., 1970; Stefánsson, 2010; Stefánsson et al., 2011), and the role of microbial reactions at temperatures at temperatures above ca. 100 °C remains to be resolved (Marteinsson et al., 2001).

Trace element chemistry may provide further insights into the various processes affecting the fluid compositions. Previous studies on trace element geochemistry of geothermal fluids in Iceland have primarily focused on the distribution of trace elements in various phases (liquid and vapor) and type of waters as well as quantification of the processes controlling their concentrations (Gunnlaugsson and Arnórsson, 1982; Arnórsson, 1984, 2003; Arnórsson and Ívarsson, 1985; Arnórsson and Andrésdóttir, 1995; Stefánsson and Arnórsson, 2005; Arnórsson and Óskarsson, 2007; Giroud, 2008; Fridriksson et al., 2009; Kaasalainen and Stefánsson, 2012). Studies on for example B, As, and W have indicated high mobility of these elements (Arnórsson and Andrésdóttir, 1995; Arnórsson, 2003; Arnórsson and Óskarsson, 2007), while the concentrations of many trace metals (e.g., Ag, Fe, Cu, Pb, and Zn) are thought to be largely affected by sulfide mineral precipitation, as discussed above (e.g., Brown, 1986; Clark and Williams-Jones, 1990; Simmons and Brown, 2007). Based on these studies and others, it is evident that trace element geochemistry may be assessed using similar approaches as for major elements including thermodynamics and kinetics and distribution patterns between vapor, liquid and solid phases.

This study seeks to evaluate the main processes affecting the geochemistry of trace elements in geothermal aquifer fluids in active geothermal systems in Iceland. For this purpose, samples were collected from hot springs, sub-boiling and high-temperature two-phase (vapor and liquid) well discharges and analyzed for their major and trace element concentrations. Based on these data, the aquifer fluid composition at depth was reconstructed and the geochemical behavior of selected trace elements was assessed. The geochemistry of trace elements in various types of surface geothermal waters and vapor vents was covered in an earlier publication (Kaasalainen and Stefánsson, 2012). This study demonstrates that trace elements may give useful insights into the processes affecting fluid chemistry, and may prove to be useful for evaluation of the environmental impact of geothermal energy exploitation. It highlights some challenges associated with surface sampling of the fluids from high-temperature geothermal systems as well as importance to consider mass movement in geothermal systems.

Table 1
Summary of sampled geothermal systems.[a]

Geothermal area	Host rock	t^{aquifer} (°C)[b]	Cl (ppm)
Krafla and Námafjall	Basalt (dacite)	>350	<100
Hellisheidi	Basalt (rhyolite)	∼300	<200
Nesjavellir	Basalt	>380	<100
Hveragerdi	Basalt	230–250	<200
Reykjanes	Basalt	320	<22,000
Svartsengi	Basalt	240	<15,000
Geysir	Rhyolite (basalt)	∼260	<150
Southern Lowlands	Basalt, rhyolite	<40–180	<10–1200
Torfajökull	Rhyolite	265	<600

[a] References: Björnsson et al. (1972), Arnórsson (1977, 1978, 1985, 1995), Ármannsson et al. (1982, 1987), Ragnarsdóttir et al. (1984), Sveinbjörnsdóttir et al. (1986), Arnórsson et al. (1978, 1987) Lonker et al. (1993), Arnórsson and Andrésdóttir (1995), Geirsson and Arnórsson (1995), Ivarsson (1998), Gudmundsson and Arnórsson (2002, 2005), Stefánsson et al. (2011).

[b] Maximum aquifer temperatures based on well-temperature logging and/or geothermometry temperatures.

2. Materials and methods

2.1. Geothermal fluids database

For the present study, major and trace element compositions of 71 geothermal fluids from 10 geothermal areas collected in 2001–2009 were considered. Based on the chemical data obtained from sub-boiling and two-phase (liquid and vapor) well discharges and hot springs, the geothermal aquifer fluid compositions at depth were reconstructed following the methods described in Sections 2.1.1 and 2.1.2. The geothermal areas sampled for this study include Svartsengi, Reykjanes, Hellisheidi, Nesjavellir, Hveragerdi, Torfajökull, Krafla, Námafjall, Geysir, and Flúdir and other locations in the Southern Lowlands (Fig. 1). The characteristics of the geothermal areas have previously been discussed in the literature, and are summarized in Table 1.

2.1.1. Sampling and analysis

The geothermal fluid samples were collected and analyzed according to methods that have been previously described in detail in Arnórsson et al. (2006), Stefánsson et al. (2007) and Kaasalainen and Stefánsson (2011a), and thus only briefly described here. For hot-springs and sub-boiling wells only the liquid phase was collected, but for two-phase well discharges vapor and liquid samples were collected. The vapor and liquid samples from the two-phase discharges were separated using a Webre separator. Water samples were filtered through a 0.2 μm filter (cellulose acetate) into pre-cleaned bottles (polypropylene or high-density polyethylene). Chloride and F were analyzed by ion chromatography (IC, Dionex IC2000) either in the laboratory or on site. Sulfate concentrations