Chlorine isotope geochemistry of Icelandic thermal fluids: Implications for geothermal system behavior at divergent plate boundaries

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A B S T R A C T

The chlorine isotope composition of thermal fluids from Iceland were measured in order to evaluate the source of chlorine and possible chlorine isotope fractionation in geothermal systems at divergent plate boundaries. The geothermal systems studied have a wide range of reservoir temperatures from 40 to 437 °C and in-situ pH of 6.15 to 7.15. Chlorine concentrations range from 5.2 to 171 ppm and $\delta^{37}Cl$ values are −0.3 to +2.1‰ ($n = 38$). The $\delta^{37}Cl$ values of the thermal fluids are interpreted to reflect the source of the chlorine in the fluids. Geothermal processes such as secondary mineral formation, aqueous and vapor speciation and boiling were found to have minimal effects on the $\delta^{37}Cl$ values. However, further work is needed on incorporation of Cl into secondary minerals and its effect on Cl isotope fractionation. Results of isotope geochemical modeling demonstrate that the range of $\delta^{37}Cl$ values documented in the natural thermal fluids can be explained by leaching of the basaltic rocks by meteoric source water under geothermal conditions. Magmatic gas partitioning may also contribute to the source of Cl in some cases. The range of $\delta^{37}Cl$ values of the fluids result mainly from the large range of $\delta^{37}Cl$ values observed for Icelandic basalts, which range from −0.6 to +1.2‰.

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1. Introduction

Due to its strong hydrophilic nature, chlorine is a powerful tracer for fluid sources and pathways in the Earth's environment. Chlorine stable isotopes have been used to trace fluid sources in the crust and upper mantle, ore deposits, and subduction zones (e.g., Eastoe and Guilbert, 1992; Barnes et al., 2008, 2009; Nahnybida et al., 2009; Selverstone and Sharp, 2011, 2013; Bernal et al., 2014; Chiaradia et al., 2014), but they also provide a means to understand processes such as fluid–rock interactions, volcanic degassing, phase separation, open versus closed system behavior, and diffusion (e.g., Desaulniers et al., 1986; Eggenkamp et al., 1994; Schauble et al., 2003; Sharp et al., 2010; Rizzo et al., 2013; Cullen et al., 2015). These processes are in turn influenced by factors such as temperature, pH and salinity. Understanding the nature of stable isotope fractionation in the chlorine system (^{37}Cl and ^{35}Cl) is still in its infancy, yet linking fractionation to processes and ultimately physical parameters, such as temperature, is profoundly important in deciphering and interpreting fluid, melt and vapor geochemistry in volcanic and geothermal systems.

Most Cl isotope studies on volcanic systems have focused on analyses of gas and/or lava to address questions regarding Cl source and volcanic processes, rather than analyses of thermal waters. Moreover, many of these are limited to data presented solely in abstract or dissertations $\delta^{37}Cl$ values of thermal waters are limited to Indonesia (−0.3 to +0.4‰) (Eggenkamp, 1994), Lesser Antilles (−0.65 to +0.12‰) (Li et al., 2015), Taupo volcanic zone, New Zealand (−0.8 to +0.7‰) (Bernal et al., 2014), Cascades, United States (+0.2 to +1.9‰) (Cullen et al., 2015), Yellowstone (−0.1 to +0.4‰) (Zhang et al., 2004), and the early work on Icelandic fluids (−0.98 to +1.60‰) (Kaufmann and Arnórsson, 1986). Interpretation of these data range from fluid–rock interaction, contribution from degassed Cl from cooling magmas, contribution of slab-derived Cl, and seawater contribution. None of these studies are of geothermal systems at divergent plate boundaries, with the exception of the early data on Icelandic systems, and only one study reports the Cl chemistry of the host volcanic rock in an effort to determine extent of fluid–rock interaction.

Chlorine concentrations in geothermal fluids associated with volcanic and sedimentary rocks vary by several orders of magnitude, from <1 mg/L to >20 g/L (e.g., Michard, 1991; Arnórsson and Andrésdóttir, 1995; Bernal et al., 2014). It is generally accepted that Cl behaves as an incompatible element during formation of alteration minerals (e.g., Michard, 1991; Arnórsson and Andrésdóttir, 1995). Cl concentrations in thermal fluids has been used to ob-

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tain information as to the origin of these waters and to evaluate mixing of thermal and non-thermal water. However, the source of Cl itself in the thermal water remains less understood, with possible sources being seawater, rock leaching, and magma degassing (e.g. Eggenkamp, 1994; Arnórsson and Andrésdóttir, 1995; Bernal et al., 2014; Cullen et al., 2015; Li et al., 2015). Previous work on the source of Cl in thermal fluids have focused on fluids at convergent plate boundaries, where limited data exist for thermal fluids at divergent plate boundaries. Moreover, processes occurring within natural thermal systems possibly affecting Cl concentration and isotope composition, like progressive fluid–rock interaction and boiling and subsequent phase separation, have received limited attention.

In order to further investigate the utility of Cl isotopes as a tracer of source in thermal systems and possible secondary affects due to Cl isotope fractionation, we carried out an empirical study of Icelandic geothermal systems. The chlorine isotope values of geothermal fluids from both boiling and non-boiling springs and wells with a range of Cl concentration and pH has been determined and these values are interpreted by comparing the results with isotope geochemical modeling.

2. Geothermal activity in Iceland

Geothermal activity in Iceland is widespread, and associated with both active volcanic centers and off-axis fractures on the North-American and Eurasian plates. The thermal fluids are of meteoric and seawater origin or mixture thereof, have temperatures of <10 to $>400\,^\circ C$, pH of <2 to >10 and Cl concentration from <1 to $\sim17{,}500$ ppm (e.g. Arnórsson et al., 2007; Kaasalainen and Stefánsson, 2012; Kaasalainen et al., 2015; Stefánsson et al., 2016). The reservoir fluids commonly have close to neutral pH values with Na, Cl, S, C and Si being the dominant dissolved elements, and Cl concentrations of 20–250 ppm (Arnórsson and Andrésdóttir, 1995). Steam-heated waters are also common at the surface of volcanic geothermal systems where they form from vapor condensation into non-thermal water at the surface and subsequent oxidation. These fluids have elevated SO_4 and metal concentrations and low Cl concentration, <10 ppm (Stefánsson, et al., 2016).

The major element composition of geothermal fluids at temperatures above $\sim100\,^\circ C$ is characteristically controlled by close approach to equilibrium with secondary minerals, except for elements like Cl and B that are considered incompatible (Arnórsson et al., 1983; Kaasalainen et al., 2015). The alteration minerals follow a 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 (e.g. Arnórsson et al., 2007).

3. Sampling and analysis

3.1. Major elements

Thermal water samples ($n = 38$) were collected in Iceland from hot springs and well discharges from six geothermal fields: Geysir, Hellisheidi, Nesjavellir, Ölkeld2uháls, Krafla and Flúdir (Fig. 1). For hot springs, only the liquid phase was sampled. From dry vapor well discharges, only the vapor phase was collected. For two-phase well discharges, both the liquid and vapor phases were collected at the wellhead using Webre separator (Arnórsson et al., 2006).

The liquid phase samples were cooled using a stainless steel spiral in-line and then filtered through a 0.2 μm cellulose acetate filter into polypropylene bottles. Samples for major cation analysis were acidified with 0.5 ml concentrated HNO_3 (Suprapur®, Merck)
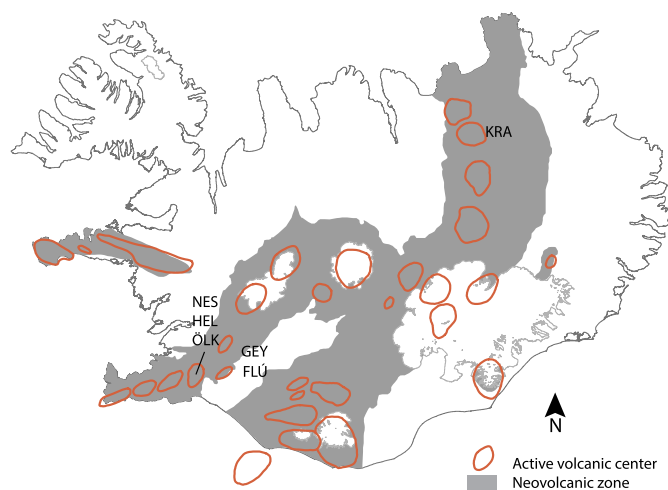

Fig. 1. Geology of Iceland and sample locations. NES: Nesjavellir hydrothermal areas; HEL: Hellisheidi hydrothermal areas; ÖLK: Ölkeldurháls hydrothermal areas; GEY: Geysir hydrothermal area; FLU: Fludir hydrothermal area; KRA: Krafla hydrothermal area.

per 100 ml sample and concentrations were determined using ICP-OES. Two samples for major anion analysis were collected: one, untreated and used for F and Cl concentration determination and another, to which 2% Zn-acetate solution was added to precipitate dissolved sulfide as zinc sulfide leaving dissolved SO_4 in solution for analysis. All anion analysis were carried out using ion chromatography. Samples for determination of CO_2 concentrations were collected into amber glass bottles and analyzed using the modified alkalinity titration method (Stefánsson et al., 2007). Dissolved sulfide concentrations ($\sum S^{-II} = HS^-$ and $H_2S(aq)$) and pH were analyzed on site using titration (Arnórsson et al., 2006) and a combination pH electrode calibrated against commercial buffer solutions, respectively. Vapor samples were collected into evacuated gas bulbs containing 5–10 ml 50% w/v KOH solution. The concentrations of CO_2 and H_2S in the vapor condensate were determined as previously described for liquid samples. The non-condensable gases including H_2, N_2, Ar and CH_4 were analyzed by gas chromatography.

The analytical precision for all major elements based on duplication determination was found to be $<3\%$ at the 95% confidence level and for pH $< \pm0.05$.

3.2. Chlorine stable isotopes

Samples for chlorine isotopes analysis were collected for the liquid phase from hot springs and two-phase well discharges and for the vapor phase from vapor only well discharges. Sample solutions were reacted with 10 ml of 50% HNO_3 and gently heated on a hot plate for 2 h covered with a watch glass containing deionized water to remove the high concentration of sulfur in the samples (Barnes et al., 2009). The samples are then prepared following the methods detailed by Eggenkamp (1994), as modified by Barnes and Sharp (2006). 4 ml of 1 M KNO_3 is added to the sample solution to increase the ionic strength. 1 ml of 0.4 M $AgNO_3$ is then added to precipitate AgCl(s). The AgCl(s) is allowed to precipitate overnight in the dark and then filtered onto quartz filters and reacted with excess CH_3I under vacuum to produce CH_3Cl, the analyte introduced into the ThermoElectron MAT 253 mass spectrometer. $\delta^{37}Cl$ values are reported in standard per mill notation versus Standard Mean Oceanic Chloride (SMOC). Error on each analysis is $\pm0.2‰$, based on the long-average of three seawater standards.