GEOCHEMISTRY OF CO₂-RICH WATERS IN ICELAND

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Abstract

CO₂-rich waters in Iceland from volcanic systems of the Mid-Atlantic Ridge and off-rift volcanic areas of Iceland provide insights into the interactions between CO₂-rich fluids and basaltic crust. These waters, from the Snæfellsnes Peninsula, within the South Iceland Seismic Zone and on the margin of the Torfajökull central volcano, are chemically and isotopically distinct from surface waters, groundwaters and low and high-temperature geothermal fluids in Iceland. Our conceptual model for the evolution of thermal and non-thermal CO₂-rich waters (~4–80 mmol/kg ΣCO₂ (aq); 6.6–192 °C) suggests that lower subsurface temperatures during retrograde alteration and cooling of a geothermal system increase the aqueous solubility of CO₂, which allows anomalously high aqueous CO₂ concentrations. The elevated CO₂ concentrations result in slightly acidic pH (average *in situ* pH of 6.40), which leads to increased dissolution of primary and hydrothermal silicate minerals. Equilibrium with respect to carbonate minerals, calculated using measured solute concentrations, suggests that carbonate mineral reactions control the water compositions in these systems more than in high-temperature systems, and that hydrothermally altered basalts are sufficiently reactive to promote carbonate mineralization during geologic CO₂ sequestration (GCS). Water-rock interaction with previously hydrothermally altered basalts releases trace elements to the aqueous phase to levels above the World Health Organization drinking water limit. The elements of environmental concern include arsenic (<0.01 to 1.08 μmol/kg) and manganese (<0.1 to 184 μmol/kg), highlighting the need for careful site selection during GCS to prevent groundwater contamination.

1. Introduction

Areas with high CO₂ discharge in the form of CO₂-rich gas and CO₂-saturated surface water are globally distributed and occur frequently in seismically active areas (Barnes et al., 1978; Bergfeld et al., 2001a; Chiodini et al., 2001; Crossey et al., 2006; Evans et al., 2008; Evans et al., 2002; Keating et al., 2010; Lewicki et al., 2014). A number of studies have shown that CO₂ degassing in such areas, unassociated with volcanic eruptions, via hydrothermal features, tectonic structures, soil and surface water contributes significantly to regional fluxes and the global flux of volcanic (Aiuppa et al., 2004; Allard et al., 1991; Ármannsson et al., 2005; Burton et al., 2013; Federico et al., 2002; Fridriksson et al., 2006; Viveiros et al., 2010; Werner and Brantley, 2003) and non-volcanic (Chiodini et al., 2000; Girault et al., 2014; Lewicki and

Brantley, 2000; Lewicki et al., 2013, 2003; Newell et al., 2008) CO₂. Because fluid-rock interactions in the subsurface affect the transfer of CO₂ from the lithosphere to the hydrosphere and ultimately to the atmosphere, interpretation of CO₂ discharge from these areas must include assessment of the geochemical reactions that occur in a variety of geologic settings.

In Iceland, CO₂-rich fluids (~4–80 mmol/kg ΣCO₂ (aq)) that circulate through variably hydrothermally altered basalts are present in a variety of settings in geothermal and non-thermal areas (~7–192 °C). These areas are uniquely poised to study the reaction of CO₂ in basaltic reservoirs over long periods (kyr) of time. Although there is no formal definition of a "CO₂-rich fluid," we focus here on waters with more than 4 mmol/kg ΣCO₂ (aq) (ΣCO₂ = [CO₂ + HCO₃⁻ + CO₃²⁻]) and gases containing at least 80% CO₂ by volume, which is consistent with the upper values of ΣCO₂ (aq) in Iceland groundwater (Arnórsson et al., 2010, 2002). The CO₂-basalt systems also serve as natural analogues to assess the efficiency of geologic CO₂ sequestration (GCS) into hydrothermally altered basalts via carbonate mineralization (Goldberg et al., 2008; Matter and Kelemen, 2009; Matter et al., 2016; McGrail et al., 2006; Oelkers et al., 2008; Seifritz, 1990) and the risk of groundwater contamination as a result of leakage (Bickle and Kampman, 2013; Kampman et al., 2016; Keating et al., 2013; Kharaka et al., 2009; Little and Jackson, 2010; Wigley et al., 2013, 2012; Wilkin and Digiulio, 2010) and subsequent dissolution of mineral phases containing trace metals or metalloids (*e.g.*, Ni and As) (Fendorf et al., 1997; Harvey et al., 2012; Larsen and Postma, 1997).

In this study, we expand upon previous work (Arnórsson and Barnes, 1983; Arnórsson et al., 2010) to present a comprehensive review of CO₂-rich fluids in Iceland. We show that hydrothermally altered basalts are reactive to CO₂-rich fluids after multiple stages of hydrothermal alteration and that calcite precipitation is favorable under temperatures, pressures, and CO₂ concentrations relevant to GCS in basalts (Alfredsson et al., 2013; Gislason et al., 2010). In addition, the enhanced dissolution of hydrothermal minerals as a result of the decreased pH imposed by elevated CO₂ fluxes releases trace elements (*e.g.* As, Ba, Mn, Ni) to the aqueous phase at concentrations above World Health Organization (WHO) guidelines for safe drinking water (WHO, 2011). By pairing geochemical analyses of fluids from springs, boreholes and geothermal production wells from the Snæfellsnes Peninsula and the Seydishólar and Torfajökull geothermal areas, which span a range of temperatures and hydrothermal activity (Fig. 1), with a paragenetic study of drill cuttings from corresponding field areas, we have developed a

conceptual model for the formation and evolution of CO₂-rich geothermal and non-thermal waters in Iceland that relates these settings to the typical stages of a magma-hydrothermal system.

2. Geologic background

2.1 Iceland geology

Iceland is located on the Mid-Atlantic Ridge (MAR) at the boundary of the diverging North American and European plates and the underlying Iceland hot spot (Fig. 1). The neovolcanic zone is divided into landward extensions of the MAR and off-rift volcanic zones, including the Snæfellsnes Volcanic Zone in western Iceland and the South Iceland Seismic Zone (Thordarson and Höskuldsson, 2008). Tertiary formations and extinct central volcanoes in southeastern Iceland, northwestern Iceland and on the Snæfellsnes Peninsula indicate that the plate boundary and zone of rifting has migrated east over the past 15 Ma (Martin et al., 2011) (Fig. 1).

As a result of the substantial volcanic activity, Iceland has numerous active and fossil geothermal systems. High-temperature systems, with temperatures ≥ 200 °C at <1 km depth, are largely confined to the neovolcanic zone near active central volcanoes (Arnórsson, 1995a). Low-temperature geothermal activity ≤ 180 °C is widespread in Quaternary and Tertiary formations flanking the MAR and in off-rift volcanic zones (Fig. 1) (Arnórsson et al., 2008; Arnórsson, 1995b). The heat source for the geothermal activity in low-temperature areas is derived from a variety of sources: increased circulation and permeability related to fracturing of young volcanic rocks; or cooling of a high-temperature system due to rift propagation and migration from the main rift (Arnórsson, 1995b). In the high-temperature systems the heat source may be magmatic intrusions or recently consolidated intrusive rock. Alternatively, “non-thermal” surface water and groundwater is not obviously associated with geothermal activity and has temperatures at or below the average ambient temperature (~15 °C). The CO₂-rich fluids of this study are located in the off-rift Snæfellsnes Volcanic Zone and South Iceland Seismic Zone and within the eastern section of the MAR (Fig. 1).

2.2 CO₂ in crustal fluids

CO₂ in crustal fluids may be from a magmatic or mantle source (Ni and Keppler, 2013; Wallace et al., 2015) – carbon exists as a dissolved component in silicate melts, in the exsolved gas phase of a vapor-saturated melt (Jendrzejewski et al., 1997; Matthey, 1991; Pan et al., 1991; Pawley et al., 1992; Stolper and Holloway, 1988), and as structural CO₃²⁻ in basaltic glasses (Brey, 1976; Fine and Stolper, 1986; Stolper et al., 1987). It can also be a product of the breakdown of organic material or can be released during dissolution of carbonate minerals and carbonate rocks undergoing metamorphism (Barnes et al., 1978; Irwin and Barnes, 1980). Worldwide, CO₂ typically comprises more than 90% of the non-steam gas phase in high-temperature (>250 °C) geothermal fluids (Arnórsson et al., 1983). The concentration of CO₂ in geothermal fluids is often found to be in temperature-dependent equilibrium with hydrothermal minerals (Bird and Norton, 1981; Bird and Helgeson, 1981; Freedman et al., 2009; Stefánsson and Arnórsson, 2002), and in cold surface waters with pH >9 by approach to calcite saturation (Arnórsson, unpublished data). In Iceland, fluids with anomalously high CO₂ content (*i.e.* greater than equilibrium with calcite or a mineral assemblage) are found in regions with low-temperature geothermal activity (≤180 °C) outside the main zones of active volcanism and rifting, and on the periphery of active geothermal areas (Fig. 1) (Arnórsson and Barnes, 1983; Arnórsson et al., 2010). One model for the formation of these fluids is the dissolution of CO₂ gas derived from magmatic intrusions into non-thermal or geothermal groundwater and surface water (Arnórsson and Barnes, 1983).

2.3 Study sites: CO₂-rich waters

Snæfellsnes Volcanic Zone

Low-temperature and non-thermal springs with waters rich in CO₂ (6–54 °C; ~5–76 mmol/kg ΣCO₂ (aq)) occur on the Snæfellsnes Peninsula of western Iceland (Fig. 1). Some waters are saturated with respect to CO₂, which degasses upon discharge at the surface or at the wellhead. The peninsula is located along the east-west trending divergent Snæfellsnes Volcanic Zone, an active off-rift volcanic zone with alkali and transitional alkali basalt magmatism (Jakobsson, 1972). From about 15 to 7 Ma, the Snæfellsnes Peninsula was the site of the main rift axis (Fig. 1) (Martin and Sigmarsson, 2010; Sigurdsson, 1970), and drill cuttings from the area reveal fossil greenschist facies hydrothermal alteration from the area (Results 4.1). At present, the tectonics are associated with differential spreading rates of north and south Iceland

(Hardarson et al., 2008). There are no modern surface expressions of high-temperature geothermal activity on the peninsula, such as fumaroles, but craters of the Snæfellsjökull central volcano have erupted as recently as 1,750 years ago (Steinthorsson 1967) and post-glacial volcanic edifices are abundant.

Seydishólar

The Seydishólar area in south Iceland (Fig. 1) is a low-temperature geothermal area that discharges steam-saturated (*i.e.* wet-steam) fluids from ~180 °C aquifers with >30 mmol/kg ΣCO_2 (aq). CO_2 comprises more than ~90% of the total gas by volume. The geothermal fields Hædarendi and Klausturhólar in the Seydishólar area are located within the South Iceland Seismic Zone, which is dominated by transgressive faulting associated with rotation of the Hreppar microplate between the RVZ and EVZ (Einarsson, 2008). Since 1986, a facility at Hædarendi has been producing CO_2 at approximately 2,000 tons annually for greenhouse farming and carbonated beverage bottling in Iceland (Björnsson et al., 2010). Quaternary sub-glacial hyaloclastites, pillow lavas, palagonite breccias, conglomerates and basalts interbedded with interglacial olivine basalts are the oldest rocks of the area (Jakobsson, 1966). The nearby postglacial Grímsnes lavas erupted from at least ten eruptive centers ~8,200–9,700 years ago, mostly from the Seydishólar scoria craters (Sinton et al., 2005), and are composed of tholeiitic olivine basalts and scoria with gabbroic and silicic xenoliths (Jakobsson, 1966).

Torfajökull

The Torfajökull central volcano within the eastern section of the MAR comprises the largest high-temperature geothermal field in Iceland, covering an area of 130–140 km² (Fig. 1) (Gunnarsson et al., 1998; Palmason et al., 1979). Torfajökull forms a caldera massif that is 30 km in the WNW-ESE direction by 18 km in the NE-SW direction (Gunnarsson et al., 1998). Silicic magma production in Iceland is confined to central volcanic complexes, and Torfajökull contains the largest exposure of silicic extrusives in Iceland, with an areal extent of 450 km² (Gunnarsson et al., 1998; Walker, 1966). Basaltic hyaloclastite ridges and intermediate to basaltic lavas 11–70 ka are found on the northern and southern flanks of the volcano and in small patches within the silicic area (Gunnarsson et al., 1998). In postglacial times, there has been mixing of tholeiitic basaltic magma with alkali rhyolite from Torfajökull in the southwest,

outside the caldera rim (Gunnarsson et al., 1998). Geothermal manifestations within the caldera include boiling springs, mud pots and fumaroles 80–110 °C, and there are springs 20–100 °C on and outside the caldera rim (Björke, 2010; Björke et al., 2009; Ólafsson and Bjarnason, 2000). CO₂-rich springs (24–92 °C; ~17–50 mmol/kg ΣCO₂ (aq)) are most frequently observed along the caldera rim, though we did not attempt to map or locate all occurrences for our study.

3. Methods

To characterize ongoing fluid-rock interactions at the study sites, we use petrographic analysis of drill cuttings, field data and geochemical analyses of water and gas samples, stable isotope compositions and thermodynamic equilibrium analysis, the methods for which are described below.

3.1 Solid phase analysis

Drill cuttings from wells on the Snæfellsnes Peninsula and within the Seydishólar area were obtained from the Iceland GeoSurvey (ÍSOR) in 2012. The wells ÖL-05 and ÖL-10 were drilled in 2002 on the farm Ölkelda on the southern coast of the Snæfellsnes Peninsula. They reach depths of 309 m and 66 m and correspond to fluid samples 10ÖL13 and 12ÖL13, respectively. The Hæðarendi and Klausturhólar wells HE-07 and KH-11 are wet-steam wells within the Seydishólar area that were drilled to 900 m and 2504 m deep in 2003 and 2008, respectively. Fluid sample 13HE01 is from well HE-07, and though there is no fluid sample from well KH-11, 13KH02 is within the same field. During drilling, cuttings were collected at 5–10 m intervals for lithologic logging. From these, select samples at 10–15 m intervals were chosen for analysis.

Drill cuttings were analyzed for protolith determination, mineral phase identification, and mineral paragenesis and alteration sequence. Protolith determination was made by inspection with a binocular microscope and by referencing the drilling logs (Marks et al., 2010). Cuttings were embedded in epoxy mounts or made into thin sections for backscattered electron imaging (BSE), textural examination and mineral identification by energy dispersive spectra (EDS) on a scanning electron microscope (SEM) at Stanford University. Bulk rock mineralogical analysis by X-ray diffraction (XRD) was performed at Stanford University.

3.2 Fluid sample collection and analysis

Water and gas samples from 13 springs, 1 stream, and 20 geothermal borehole wells were collected in 2012 and 2013 according to the methods outlined in Arnórsson et al. (2006). This study focuses on the results of 22 samples taken in 2013. Samples were collected into field-rinsed high-density polyethylene (HDPE) or polypropylene (PP) bottles from boreholes and springs using a peristaltic pump and silicone tubing, and from the wet-steam geothermal wells with a small Webre separator to obtain separate water and steam samples. The water samples were filtered onsite through 0.2 μm Millipore cellulose acetate membranes using either a syringe filter or a Teflon filter holder. Samples for major cation and trace element analyses were acidified upon sampling with concentrated Suprapur® HNO_3 and measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), respectively. Samples for anion analyses by ion chromatography (IC) were untreated. Water samples for $\delta^{18}\text{O}$ and δD were unfiltered and collected into airtight bottles with polyvial cone caps to avoid evaporation, and samples taken for pH, total dissolved inorganic carbonate (ΣCO_2) and total dissolved sulfide (H_2S) measurements were collected into bottles with airtight caps to avoid degassing upon temporary sample storage.

Discharge temperature was measured on site at springs and $<100^\circ\text{C}$ boreholes. Aquifer temperatures for wet-steam wells were obtained from drill reports and also estimated from the silica content of the discharged fluid by assuming equilibrium with chalcedony (see Section 3.3). The chalcedony silica geothermometer matches measured subsurface temperatures in low-temperature areas in Iceland from $\sim 110^\circ\text{C}$ (Arnórsson, 1975) up to 180°C (Arnórsson, 1980), and field observations show that the silica content of warm springs is usually nearly equivalent to wells producing fluids from 500–1,000 m. At Seydishólar, the chalcedony equilibrium temperature is within a few degrees of the measured downhole temperature, implying that there is minimal silica precipitation in response to cooling of the fluid. $\Sigma\text{CO}_2(\text{aq})$ was determined usually on site by a modified alkalinity titration within eight hours of sampling, except for 23HS13, 24BK13 and 25JG13, which were titrated within 24 hours after sampling (Arnórsson et al., 2006). The average one standard deviation of duplicate $\Sigma\text{CO}_2(\text{aq})$ measurements was 2.6%. pH was measured on site using a rapid response glass electrode. Dissolved H_2S was determined on site by titration with Hg-acetate with a detection limit of 0.3 $\mu\text{mol/kg}$ (Arnórsson et al., 2006). The ratio of gas to liquid upon discharge was determined at a select number of sites by measuring the volumetric displacement of liquid by the gas phase.

Water samples were analyzed at Stanford University, CA in the Environmental Measurement I: Gas-Solution Analytical Center. Anion analyses (F^- , Cl^- , SO_4^{2-}) by IC had uncertainty between 0.2 and 3.1%, based on the average one standard deviation of standards analyzed throughout the IC runs. Major cation concentrations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Fe^{2+} and Si) determined by ICP-OES and trace element concentrations (Al, As, Ba, Cd, Co, Li, Mn, Ni, Pb, Ti, Zn) measured by ICP-MS had one standard deviation uncertainties between 2.8–8.1% and 2.2–7.5%, respectively, based on triplicate analyses of each sample and standards analyzed throughout the runs. The isotopic compositions of oxygen and hydrogen in the water samples were measured by Isotope Ratio Mass Spectrometry (IRMS) at the Laboratory for Environmental and Sedimentary Isotope Geochemistry at University of California, Berkeley. $^{18}O/^{16}O$ ratios of waters were measured by headspace equilibration after purging with 0.2% CO_2 in helium, and determined by continuous flow (CF) using a Thermo Gas Bench II interfaced to a Thermo Delta Plus XL mass spectrometer. $^2H/H$ ratios of waters were determined by reduction to H_2 (g) using a hot chromium reactor unit (H/Device™) interfaced with a Thermo Delta Plus XL mass spectrometer. The analyses are reported in delta notation and expressed as parts per thousand (‰), in which $\delta^{18}O$ and δ^2H are the ratio between heavy and light isotopes for oxygen and hydrogen, respectively, of an unknown relative to the standard Vienna Standard Mean Ocean Water (V-SMOW) (Craig, 1961). For δ^2H , the total uncertainty ranges from 0.21–1.32‰ (absolute 1 s.d.) and is based on triplicate analyses of each sample. $\delta^{18}O$ analyses were run in duplicate, so the total error is based on the external error determined by repeated analysis of a standard run throughout the analysis and ranges from 0.04–0.06‰ (absolute 1 s.d.).

Gas samples were collected for compositional and carbon isotope analysis. Steam and CO_2 -saturated waters were sampled for gas phase analysis into pre-evacuated Giggenbach-type gas bulbs containing ~10 ml of a 50% KOH solution (Arnórsson et al., 2006). Upon sampling, CO_2 and H_2S gas and, if present, steam dissolve into the basic KOH solution, and non-condensable trace gases concentrate in the bulb headspace. The gas phase was analyzed for Ar, CH_4 , H_2 , N_2 , and O_2 by gas chromatography (GC) at ÍSOR, and the caustic KOH solution was analyzed using wet chemical methods for determination of ΣCO_2 and H_2S (Arnórsson et al., 2006). The ΣCO_2 of the KOH solution of the wet-steam samples, accounting for correction of the blank KOH solution, represents the P_{CO_2} of the gas phase. For samples with a measured gas to liquid ratio (06LH13, 07LH13, 10OL13, and 12OL13), the ΣCO_2 of the “undegassed” aquifer

fluid was calculated by adding the proportional mmol/kg of CO_2 (g), determined by titration of the KOH solution, to the aqueous phase. This ΣCO_2 is referred to here on as ΣCO_2 (tot), and the P_{CO_2} reported is the corresponding equilibrium value. The P_{CO_2} of CO_2 -saturated waters without a gas to liquid ratio and of waters without a gas phase is simply P_{CO_2} in equilibrium with ΣCO_2 (aq).

Gas samples collected into Giggenbach-type glass bulbs without KOH were analyzed for gas phase $\delta^{13}\text{C}$ values and measured by cavity ring-down spectroscopy at the U.S. Geological Survey in Menlo Park, CA. Carbon isotope results are expressed in delta notation as per mil values (‰) relative to PDB (Peedee Belemnite). The standard deviation of the analyses ranges from 0.08–0.77‰. Additional samples were taken for $\delta^{13}\text{C}$ values of the total discharge by collecting water and gas into pre-evacuated glass serum bottles with butyl stoppers. After sampling, the DIC was precipitated as SrCO_3 by adding ammoniacal strontium chloride (Singleton et al., 2012), and the precipitates were removed by filtration, dried and analyzed via the combustion module on the cavity ring-down spectrometer. Based on the variability of analyses of standards run throughout the analysis, the one standard deviation of the combusted samples is 0.92‰.

3.3 Aqueous species distribution and thermodynamic calculations

Aqueous species distribution and pH calculations were performed with the aid of the WATCH computer program (Arnórsson et al., 1982; Bjarnason, 2010), and mineral saturation indices with the multi-component reactive transport code CrunchFlow (Steefel and Lasaga, 1994; Steefel et al., 2015). The WATCH program was used to solve for pH because it computes the composition and pH of an aquifer fluid at depth from data on water and steam samples of wet-steam wells. This is necessary because the separate steam and water samples collected at a wellhead do not always represent the primary composition of the original subsurface geothermal fluid due to effects of phase separation during transport from the reservoir to the wellhead. The wet-steam wells were speciated in WATCH by providing the measured composition of the aqueous and steam phase samples, and the reference temperature was that of the chalcedony geothermometer (Fournier, 1977), which most closely matched borehole log temperatures.

For springs and <100 °C wells that discharge a mixture of water and a gas phase, the aqueous phase was first speciated using the ΣCO_2 (aq) content and the pH measured on-site

to obtain a value for alkalinity. Next, for samples with ΣCO_2 (tot), the pH of the “undegassed” aquifer fluid was calculated iteratively with the WATCH program until the alkalinity value matched that of the degassed sample, since alkalinity is conserved despite degassing. This latter pH and the resulting aqueous species distribution represents the composition of the aquifer fluid at depth. If a gas to liquid ratio, and, subsequently, ΣCO_2 (tot), was not determined, the speciation using the on-site pH measurement and ΣCO_2 (aq) yielded the results of the final and only WATCH run. The temperature used for the speciation calculation at depth was the discharge temperature or based on down-hole measurements when available. For fluids $<100^\circ\text{C}$, neither the Na/K nor the silica geothermometers within the WATCH computer program were used, because studies have shown that the results of such thermometers are not reliable for use with highly reactive CO_2 -rich fluids $<100^\circ\text{C}$ (Aiuppa et al., 2000).

The standard states adopted in this study for the thermodynamic calculations were that of unit activity for pure minerals and H_2O at any temperature and pressure. For aqueous species the standard state was unit activity of the species in a hypothetical 1 mol/kg solution referenced to infinite dilution at any temperature and pressure. For gases, the standard state was unit fugacity of a hypothetical ideal gas at 1 bar of pressure. Gas partial pressures were derived from the calculated gas concentrations in the aqueous phase with the aid of Henry’s Law:

$$\chi_i^{aq} = K_i P_i \quad (1)$$

where χ_i^{aq} is the aqueous mol fraction of the i th gas, K_i is the Henry’s law constant for the i th gas, and P_i is its partial pressure.

Mineral saturation states were calculated with CrunchFlow (Steefel and Lasaga, 1994; Steefel et al., 2015), using the pH from WATCH (Arnórsson et al., 1982; Bjarnason, 2010). Thermodynamic data within the CrunchFlow database is derived from the EQ3/6 database (Wolery et al., 1992). Data for plagioclase feldspar solid solution from Arnórsson and Stefánsson (1999) and aqueous Al-hydroxy complexes from Arnórsson and Andrésdóttir (1999) were also adopted. Mineral saturation states are reported in terms of the logarithm of the reaction quotient, Q , the product of the aqueous species activities of the mineral dissolution reaction, divided by the equilibrium constant, K , computed using the standard Gibbs free energy of formation ($\Delta G_{f,T,P,i}^\circ$), such that $\log K(T, P) = \Delta G_{f,T,P,i}^\circ / 2.303RT$. At equilibrium, $\log(Q/K)$ equals zero, because $K = Q$. When $\log(Q/K) < 0$, the fluid is undersaturated relative to the mineral and

dissolution is favored thermodynamically; when $\log(Q/K) > 0$, the fluid is supersaturated relative to the mineral and precipitation is favored. Dissolution reactions and equilibrium constants ($\log K$) for the minerals considered are given in Table 1. The equilibrium constants for reactions of mineral assemblages relevant to the partial pressure of CO_2 in Icelandic geothermal systems were taken from Stefánsson and Arnórsson (2002) or calculated using data within the CrunchFlow database (Arnórsson and Stefánsson, 1999; Wolery, 1992) and are shown in Table 1 at varying temperatures.

4. Results

Results for optical petrography, XRD and electron microscopy of drill cuttings from the Snæfellsnes Peninsula and Seydishólar areas are described below. Following the lithologic description are the results of the fluid analyses, including the major and minor aqueous cation and anion concentrations, Cl/B relationship, gas compositions and the stable isotopic analyses ($\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$) of the fluids.

4.1. Petrology

Snæfellsnes Peninsula

The lithology underlying the CO_2 springs in the areas of Ölkelda is comprised of hydrothermally altered crystalline and vesicular basalt with abundant chlorite and epidote, similar to the chlorite-epidote zones of basalt alteration described by Franzson et al. (2008), Kristmannsdóttir (1979) and Tómasson and Kristmannsdóttir (1972). As illustrated by backscatter electron images in Figure 2, the matrix of the drill cuttings from wells ÖL-05 and ÖL-10 is comprised of chlorite, laths of albitic plagioclase and/or anorthite (75–100 μm), microcrystalline calcite and quartz. Trace amounts of pyrite ($\sim 100 \mu\text{m}$), and Fe- and Fe-Ti-oxides (ilmenite) occur, as well as relict primary clinopyroxenes (Ca-Fe-Mg). Vesicles are lined by epidote and chlorite and filled with quartz (Fig. 2A) and others are lined with euhedral quartz and Fe-oxides and filled with microcrystalline calcite (Fig. 2B). Within the matrix and in amygdales of calcite and quartz are laths of an Al-Si mineral (75–100 μm) with an EDS spectrum that resembles that of kaolinite (Fig. 2B). Subhedral clinopyroxene within the matrix (10–20 μm) is nearly completely replaced by chlorite. Clinopyroxene phenocrysts (100–200 μm) display zoning with Ca-rich rims and are less altered, with chloritization only along cracks and

grain boundaries. Epidote, which typically forms at temperatures $>260\text{ }^{\circ}\text{C}$ (Bird and Spieler, 2004), is nearly continuous in the cuttings from ~ 20 to 300 m depth and occurs in amygdaloids and also in veins with calcite (Fig. 2C). The current subsurface temperatures are $<60\text{ }^{\circ}\text{C}$, suggesting that the chlorite-epidote alteration occurred during previous hydrothermal events.

Seydishólar

The Seydishólar drill cuttings of HE-07 and KH-11 are composed of vesicular basalt, scoria and distinct zones of silica and carbonate mineralization. The mineral assemblage is composed of albitic plagioclase, K-feldspar, quartz, chlorite, clinopyroxene (Ca-Fe-Mg), calcite and Ca-Fe-Mg carbonate with accessory euhedral pyrite, anhedral Ti-oxides and titanite. The glassy groundmass has altered to quartz, chlorite and calcite (Fig. 3A). Veins of calcite and quartz, and of calcite and chlorite, lined with amorphous silica ($\text{SiO}_{2(\text{am})}$), are present throughout the cuttings. Within HE-07 at depths of 246 m and greater, albitic plagioclase laths ($75\text{--}200\text{ }\mu\text{m}$) are altered and pseudomorphically replaced by calcite (Fig. 3B,C). Clinopyroxene phenocrysts ($\sim 100\text{ }\mu\text{m}$) are often completely replaced by calcite with veins of chlorite, or by chlorite (Fig. 3D). Crystals of kaolinite, identified with XRD and by EDS, are associated with altered feldspar. In two sections of HE-07 from 294–390 m and 609–630 m, the mineral assemblage is comprised nearly exclusively of quartz, ankerite, siderite, and pyrite, and does not appear to replace primary igneous basaltic textures. The drill cuttings of KH-11 contain laumontite from 276 m to about 1060 m. Epidote appears at 482 m and continues with depth, and pyrite is present throughout.

4.2. Aqueous geochemistry

Results of the aqueous geochemical analyses are reported in Tables 2 and 3. The total concentration of aqueous CO_2 ($\Sigma\text{CO}_2(\text{aq})$) in the fluids of this study is plotted as a function of temperature in Figure 4, together with published analyses of Icelandic groundwater (Arnórsson et al., 2002), surface water (Flaathen et al., 2009) and low-temperature geothermal fluids (Arnórsson, 1995; Arnórsson, 1995; Kaasalainen and Stefánsson, 2012; Poreda et al., 1992; Stefánsson and Arnórsson, 2002). Figure 4 shows that the CO_2 -rich fluids of this study contain one to three orders of magnitude more total aqueous CO_2 than Icelandic fluids of the same temperatures (Table 2) (Arnórsson, 1995; Arnórsson et al., 2002; Flaathen et al., 2009). $\Sigma\text{CO}_2(\text{aq})$ ranges from 4.38–76.28 mmol/kg, with $\Sigma\text{CO}_2(\text{tot})$ ranging from 9.68–106.03 mmol/kg in the gaseous water samples and nearly 3,000 mmol/kg for the wet-steam samples from

Seydishólar. All of the spring samples and the drillhole samples 07LH13, 11OL13 and 12OL13 were collected at atmospheric pressure. Table 2 lists the known depths of the drillholes, but we do not have information on screening depths and are therefore not attempting to estimate the pressure of the sample at depth.

Figure 5A presents the aqueous composition of the samples according to the dominant anion, an informal scheme that is used to provide insight into the formation of geothermal fluids (Giggenbach, 1988). Chloride waters with near-neutral pH represent well-equilibrated, deeply circulating fluids from the major up-flow zones. Both sulfate- and bicarbonate-type waters are formed by condensation of geothermal gases into groundwater and surface water and are generally found on the margins of geothermal fields (Giggenbach, 1988). Six samples can be classified as NaCl-type waters, whereas the remaining sixteen are Na-, Ca-, or Mg-HCO₃-type waters (Fig. 5A). Total dissolved solids (TDS) content ranges from ~300–4,000 ppm and increases with increasing $\Sigma\text{CO}_2(\text{aq})$ (Fig. 5B), a trend commonly observed in springs and surface waters with variable P_{CO_2} (Navarre-Sitchler and Thyne, 2007).

The measured pH of the fluids at the surface is reported in Table 2 and ranges from 4.71–8.77 (Fig. 5C). In general, pH decreases with increasing $\Sigma\text{CO}_2(\text{aq})$, and is on average significantly lower than the pH of other Icelandic fluids (Fig. 5C). The samples with the lowest pH are those that visibly appear to have the greatest gas flux. For example, sample 17OV13 is from a cold water pool that dries out periodically and represents dissolution of CO₂ (g) into ponded rain water (Arnórsson et al., 2010).

Dissolved cation concentrations of the CO₂-rich fluids generally increase with increasing $\Sigma\text{CO}_2(\text{aq})$ (Fig. 6A and 7A). Sodium is the dominant cation in most of the samples, with concentrations ranging from ~1–32 mmol/kg, and the second most abundant is Ca, which ranges from 0.04–6.6 mmol/kg (Table 2). The concentration of the divalent cations Ca, Mg and Fe increases with increasing $\Sigma\text{CO}_2(\text{aq})$ (Fig. 6A) and decreases with temperature (Fig. 6B). Sodium and SiO₂ concentrations also increase with $\Sigma\text{CO}_2(\text{aq})$ (Fig. 7A), but do not decrease with increasing temperature and instead slightly increase (Fig. 7B).

CO₂-rich waters of this study contain trace elements (Al, As, Ba, Cd, Co, Li, Mn, Ni, Pb, Ti, Zn) in concentrations equal to or orders of magnitude greater than Iceland groundwater, surface water and geothermal fluids (Fig. 8; Table 3) (Arnórsson et al., 2002; Flaathen et al., 2009; Kaasalainen and Stefánsson, 2012). The concentrations of As and Mn are above World

Health Organization (WHO) guidelines for safe drinking water in several samples from each study area (Fig. 8). The highest concentrations of As, Mn and Ni are in samples with pH between 6.2 and 7.4, which is also the pH range of most samples (Table 3). There are no obvious trends between As and Mn concentrations and ΣCO_2 (aq), but Ni concentrations generally increase with ΣCO_2 (aq) (Fig. 8A). Conversely, there are no overwhelming trends between Ni and temperature, but As concentrations are weakly positively correlated with temperature, and Mn concentrations decrease slightly with increasing temperature (Fig. 8B). Arsenic concentrations increase slightly with increasing SO_4^{2-} , most strongly within the Snæfellsnes samples.

4.3 Chlorine/Boron distribution

Chlorine and boron have often been used as proxies for the extent of rock dissolution because both elements are highly fluid mobile, and the sources of each are well known (Arnórsson and Andrésdóttir, 1995). Both are easily dissolved from volcanic rocks (Ellis and Mahon, 1964, 1967) and are not significantly incorporated into alteration minerals. Therefore, greater concentrations of Cl and B imply more extensive water-rock interaction and basalt dissolution. Figure 9 shows Cl as a function of B in the CO_2 -rich waters relative to ratios of different sources. Seawater, the solid line in Figure 9, has a Cl/B molar ratio of 1330. The dashed line in Figure 9 is the Cl/B molar ratio in alkali basalts from the Snæfellsnes area (27.3); the dotted line is the average ratio in tholeiitic basalts from the MAR (43.2). Both ratios are calculated from the average Cl and B bulk rock concentrations (Arnórsson and Andrésdóttir, 1995). To our knowledge there is no data on Cl and B concentrations of Tertiary tholeiitic basalts of the Snæfellsnes Peninsula.

Three Snæfellsnes samples and the three Seydishólar samples display elevated Cl relative to B, which indicates a seawater component. Seawater likely entered these systems when the ocean transgressed coastal areas at the end of the last glaciation. The presence of seawater in geothermal areas of the Southern Lowlands (Seydishólar) is common, as evidenced by $\delta^{34}\text{S}$ values similar to that of seawater SO_4 (Arnórsson and Andrésdóttir, 1995). Nine samples from Snæfellsnes that do not seem to contain a seawater component fit a trend similar to the ratio of tholeiitic basalts from the MAR more closely than to the Snæfellsnes alkali basalts. This may reflect circulation of the fluids through the Tertiary tholeiitic basalts instead of through younger alkali basalts. The Torfajökull samples do not form a consistent trend. Two have high Cl and B,

and three have elevated B relative to Cl. Boron is released during degassing of magmatic intrusions and has a greater tendency to volatilize relative to Cl, so these samples may reflect the dissolution of steam into groundwater. Because B partitions into low-pressure steam at temperatures greater than ~200 °C (Aggarwal et al., 2000; Giroud, 2008; Glover, 1988), the rising steam may be superheated.

4.4. Gas Composition

The composition of the gas phase of the CO₂-rich fluids is given in Table 4. Gas concentrations are reported as mmol/kg of steam and as volume percent of the gas phase. For simplicity, we are reporting mmol/kg and volume percent CO₂ for only the wet-steam wells and those with a measured gas to liquid discharge ratio (Methods 3.2). Also in Table 4 is the N₂/Ar ratio, which ranges from 47 to 82 for samples in this study. The lower values are consistent with geothermal fluids in Iceland, which have ratios between 40 and 60 (Arnórsson, 1986), and the higher values suggest a variable amount of atmospheric component, which has a ratio of 85. H₂ was detectable in the wet-steam samples 13HE01 (0.34%) and 13KH02 (1.18%) and in samples 06LH13, 10ÖL13 and 19BF13 (0.09 to 0.23%). In the same samples with H₂, CH₄ was detected (0.04 to 2.29%) and was detected in 09LH13 (1.67%) and 22LF13 (0.36%) (Table 4).

4.5. Stable Isotope Composition

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the aqueous phase of the sampled fluids is presented in Table 5. The results are shown in Figure 10 relative to the local meteoric water lines of Iceland as empirically derived in Sveinbjornsdottir et al. (1995). The composition of seawater from the southwest coast of Iceland ($\delta^2\text{H}$: 1.5‰; $\delta^{18}\text{O}$: 0.2‰) (Ólafsson and Riley, 1978) plots off the diagram, as does the range of magmatic water ($\delta^2\text{H}$: ~-80‰ to -40; $\delta^{18}\text{O}$: ~6 to 12‰) (Ellis and Mahon, 1977; Taylor, 1986). Also plotted are the ranges of $\delta^2\text{H}$ compositions, together with corresponding calculated $\delta^{18}\text{O}$ values, of the local meteoric water of each field area based on the deuterium measurements of Árnason (1977). All of the samples from the Snæfellsnes Peninsula and all but one sample from Torfajökull are close to the MWL, but the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ compositions are less than the local recharge by 0.29 to 12.46‰ and 0.18 to 0.97‰, respectively (Fig. 10). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of the Seydishólar waters is less than present-day local meteoric water by ~34‰ and 2.4‰, respectively (Fig. 10).

Carbon isotope composition of the gas phase and of the total fluid of select samples is reported in Table 5 and shown in Figure 11. Because we do not know the relative volume or masses of the aqueous and gas phases in the CO₂-rich waters that were collected into the gas vials for SrCO₃ precipitates, we cannot assess the isotopic values of or equilibrium between the two phases. However, the gas phase has a lower $\delta^{13}\text{C}$ value than the total fluid for two of the three samples measured with both techniques, which is expected (Friedman and O'Neil, 1977). For the third sample, the $\delta^{13}\text{C}$ values of the two types of analyses overlap within error. The $\delta^{13}\text{C}_{\text{CO}_2}$ values range from -19.08 to 1.82‰, and the samples with the most negative $\delta^{13}\text{C}_{\text{CO}_2}$ have the lowest ΣCO_2 (aq) (Fig. 11). Seven of the thirteen samples are within the range of $\delta^{13}\text{C}_{\text{CO}_2}$ of Iceland geothermal fluids from the MAR (-5.3 to 2.9‰) and another is within ten percent of the range (Barry et al., 2014; Poreda et al., 1992; Sano et al., 1985). Five samples have significantly more negative $\delta^{13}\text{C}_{\text{CO}_2}$ values than the range of MAR fluids.

5. Discussion

The CO₂-rich waters of this study are lower in pH and higher in TDS than groundwaters, surface waters and both low- and high-temperature geothermal fluids in Iceland. Figure 5 shows that both pH and TDS co-vary with aqueous CO₂ concentrations, which demonstrates that the increased dissolved CO₂ significantly affects low-temperature metasomatic processes in basaltic aquifers. Figure 12 schematically illustrates a magma-hydrothermal system at two different stages: high-temperature (A), and during cooling (B). As represented by Figure 12A, the Seydishólar fluids most closely represent a primary, NaCl-type geothermal fluid that has undergone depressurization boiling. According to drilling reports, a steam phase forms at ~150 m. We describe below how only the Seydishólar fluids show evidence of high-temperature water-rock interaction. As shown in Figure 12B, in general, as geothermal systems cool, crystallized magmatic intrusions and late stage dikes continue to release CO₂, while at the same time the decreased subsurface temperatures result in increased solubility of aqueous CO₂. This scenario represents systems on the Snæfellsnes Peninsula where subsurface temperatures are <60 °C, though it is unclear whether the CO₂-rich gas is from ancient intrusions (Tertiary) or associated with younger activity (post-glacial). The rising gas dissolves into meteoric water that has infiltrated to varying depths in the subsurface, and higher temperature discharge waters reflect greater depths of circulation (Arnórsson and Barnes, 1983). The CO₂-rich water migrates

towards the surface, exsolving once the total gas pressure, calculated from gas analyses, is greater than the hydrostatic pressure (Fig. 12B), the maximum estimated depth of which is ~4 m at Snæfellsnes. Most of the Torfajökull springs, which are found on the lower temperature margins of the central Torfajökull high-temperature activity can be described as steam-heated waters, which are formed by the condensation of a CO₂-rich steam into non-thermal groundwater or surface water (Arnórsson et al., 2007; Björke et al., 2009; Ellis and Mahon, 1977; Ólafsson and Bjarnason, 2000).

In this section we outline the isotopic and thermodynamic evidence and interpretation used to constrain the hydrodynamic processes associated with the formation and transport of the CO₂-rich fluids in each area. To determine the consequences of the elevated CO₂ concentrations, we combine mineral saturation state indices with relative mobility calculations to identify the mineral dissolution and precipitation reactions that most influence the major aqueous component composition and mobilize elements of environmental concern to the aqueous phase.

5.1. Isotopic signatures of hydrologic processes

As outlined in section 4.5, the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of fluids from each field site indicate that the water is meteorically derived (Fig. 10). Additionally, the $\delta^{13}\text{C}_{\text{CO}_2}$ values of the gas phase and of the total discharge of about half of the analyzed samples correspond generally to magmatic values (Results 4.5, Fig. 11). However, mixing of CO₂ and water from multiple sources, water-rock interaction, phase separation and low-temperature CO₂ degassing during fluid transport have modified the stable isotope composition of the fluids, and the effects of these processes can elucidate the mode of transport and water type in each area.

5.1.1. Source of CO₂ as evidenced by fluid $\delta^{13}\text{C}$ values

In this section, we interpret the $\delta^{13}\text{C}_{\text{CO}_2}$ of the CO₂-rich fluids to determine the source of CO₂ and explore processes that can modify its isotopic signature. Figure 11 shows the $\delta^{13}\text{C}$ values and CO₂ content (ΣCO_2 (aq)) of the possible sources of CO₂ in consideration: (1) magmatic, which includes CO₂ released during the dissolution of hydrothermal carbonate minerals; (2) biogenic soil CO₂; and (3) atmospheric CO₂. The CO₂ in MAR fluids represents an endmember magmatic CO₂ source, the $\delta^{13}\text{C}$ of which ranges from about -5.3 to 2.9‰ (Barry et al., 2014; Poreda et al., 1992) (Fig. 11). The P_{CO_2} of MAR fluids varies from ~0.2–11 bar

(Stefánsson and Arnórsson, 2002), and is shown on Figure 11 with a corresponding equilibrium ΣCO_2 (aq) concentration range of ~20 to 160 mmol/kg. Soil CO_2 resulting from microbial respiration and degradation of organic matter is represented by $\delta^{13}\text{C}$ of -25‰ (Breecker et al., 2009). The concentration of biogenic soil CO_2 is highly variable by location and thus is shown in Figure 11 with a range from <0.1 to 0.35 mmol/kg, which is in equilibrium with 700-10,000 ppm CO_2 (g) (Breecker et al., 2009). Lastly, present-day atmospheric CO_2 has a $\delta^{13}\text{C}$ of -8‰, and the CO_2 (aq) in equilibrium with the P_{CO_2} of the atmosphere ($\sim 4 \times 10^{-4}$ bar) at 25°C is 0.014 mmol/kg (Keeling et al., 2005). Qualitatively, most of the samples fall between the $\delta^{13}\text{C}$ and CO_2 concentration of magmatic and biogenic CO_2 . Indeed, the sample with the most negative $\delta^{13}\text{C}$ also contains measurable CH_4 in the gas phase, which may indicate a biogenic source (Bergfeld et al., 2001b). We conclude that samples with >10 mmol/kg CO_2 and $\delta^{13}\text{C} > -9$ ‰ are associated predominantly with magmatic CO_2 , and those with lower CO_2 concentrations and $\delta^{13}\text{C}$ contain a relatively greater portion of organic CO_2 . This is commonly the case in areas of high CO_2 flux (Bergfeld et al., 2001b; Chiodini et al., 2008; Parks et al., 2013). Previously reported helium isotope ratios ($R = {}^3\text{He}/{}^4\text{He}$) of fluids from the study areas confirm the input of magmatic volatiles. R/R_a values ($R_a = \text{air } {}^3\text{He}/{}^4\text{He}$) range from 18.7 to 21.7 in the Seydishólar area; 9.1 to 9.3 at Lýsuhóll on the Snæfellsnes Peninsula; and 12.8 to 23.7 in the Torfajökull area (Füri et al., 2010; Hilton et al., 1990; Poreda et al., 1992). The values span typical mid-ocean ridge basalt (MORB)-like ratios (8 ± 1) and far exceed them, indicating the presence of mantle He in the fluids.

The $\delta^{13}\text{C}_{\text{CO}_2}$ of a fluid can be used to assess the degree of calcite precipitation and CO_2 degassing during fluid flow (e.g. Evans et al., 2008). At temperatures ≤ 194 °C, ^{13}C is preferentially incorporated into calcite relative to the fluid (i.e., $\alpha_{\text{CO}_2(\text{g})}^{\text{calcite}} > 1$) (Bottinga, 1969). This was invoked by Barry et al. (2013) to explain the observed trend of decreasing $\delta^{13}\text{C}_{\text{CO}_2}$ with decreasing CO_2 concentration of fluids from hydrothermal areas within Tertiary-aged crust in Iceland, implying that calcite precipitation is a dominant process in regulating the CO_2 content of fluids in such low-temperature systems. Though the $\delta^{13}\text{C}_{\text{CO}_2}$ and ΣCO_2 (aq) of the CO_2 -rich fluids of this study follow the expected trend of calcite precipitation, because of the uncertainty associated with assuming calcite saturation during fluid flow and the presence of multiple CO_2 sources, we cannot resolve this model. However, the samples do not conform to a simple binary

mixing model (not shown), which confirms the importance of calcite precipitation. Lastly, at temperatures less than 125 °C, ^{13}C is preferentially retained in the aqueous phase HCO_3^- (aq) relative to CO_2 (g), such that $\delta^{13}\text{C}_{\text{CO}_2}$ (aq) should increase as ΣCO_2 (aq) decreases (Friedman and O'Neil, 1977). This is inconsistent with the observed values of $\delta^{13}\text{C}_{\text{CO}_2}$ at low ΣCO_2 (aq) (Fig. 11) and shows that, though phase separation is certainly occurring in the CO_2 -rich fluids, it does not have a dominant effect on $\delta^{13}\text{C}_{\text{CO}_2}$ values. We thus conclude that the $\delta^{13}\text{C}_{\text{CO}_2}$ of the fluids indicates the CO_2 source.

The CO_2 sourced from a magmatic intrusion and the CO_2 released from the dissolution of previously formed hydrothermal carbonate minerals may have similar $\delta^{13}\text{C}$ values, because the effect of temperature-dependent $\delta^{13}\text{C}$ fractionation during carbonate mineral precipitation and dissolution is negligible within the range of variability of geothermal fluids (Chiodini et al., 2000). Because of this, we consider whether CO_2 sourced from carbonate minerals is enough to account for the high CO_2 content of the CO_2 -rich fluids of this study. The volume of calcite in hydrothermally altered basalts varies from <1 to 20% (Kristmannsdóttir, 1979; Tómasson and Kristmannsdóttir, 1972). Using this range, if all the calcite in a 1 km x 10 m x 10 m flow path of basalt with 6% porosity ($9.4 \times 10^4 \text{ m}^3$ of basalt) dissolved into the water in the pore space, the resulting ΣCO_2 (aq) would be 5.8×10^{-6} to 1.2×10^{-4} mmol/kg. These values are four to six orders of magnitude smaller than the concentrations observed in the CO_2 -rich fluids. As a first order approximation, this calculation shows that carbonate mineral dissolution alone cannot account for the pervasive high CO_2 concentrations, and instead, we conclude that CO_2 is likely from magmatic degassing.

5.1.2. $\delta^2\text{H}$ and $\delta^{18}\text{O}$ as indicators of water source and CO_2 degassing

In this section we use $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values to verify the water source of the CO_2 -rich fluids and interpret the alteration history they record. We discuss the samples from Snæfellsnes and Torfajökull together because of the similar trends in the $\delta^{18}\text{O}$ values, and then we discuss the Seydishólar fluids. The oxygen and hydrogen isotope compositions are reviewed separately because of the specific implications each has regarding fluid mixing, phase separation and fluid-rock interaction.

Snæfellsnes and Torfajökull

Water samples from Snæfellsnes and Torfajökull plot above the local meteoric water line but have $\delta^{18}\text{O}$ values less than the range of values observed in local groundwater by 0.15 to 0.90‰, which is outside the range of error for the $\delta^{18}\text{O}$ measurements (Methods 3.2) (Fig. 10). Such a negative shift in $\delta^{18}\text{O}$ relative to local meteoric water, observed previously in other CO_2 -rich waters, has been attributed to oxygen isotope exchange between CO_2 (g) and H_2O (aq) (Delalande et al., 2011; Kristmannsdóttir and Sveinbjörnsdóttir, 2012; Marques et al., 2006; Matthews et al., 1987; Newell et al., 2008; Pauwels et al., 1997; Siebe et al., 2007; Vuataz and Goff, 1986; Weaver et al., 2006). During exchange, ^{18}O is preferentially incorporated into CO_2 (g) over H_2O (aq) as indicated by the fractionation factor ($\alpha_{\text{H}_2\text{O(aq)}^{\text{CO}_2\text{(g)}} > 1$) (Bottinga, 1968; Friedman and O'Neil, 1977), which leaves the sampled aqueous phase depleted in ^{18}O relative to the gas phase. To quantify the effect of the isotopic exchange, below we model the process by assuming open system, irreversible Rayleigh distillation during shallow, low-temperature degassing. We also consider the effect of mixing of magmatic CO_2 (g) and meteoric H_2O (aq) on the $\delta^{18}\text{O}$ values.

The fractionation factor ($\alpha_{\text{H}_2\text{O(aq)}^{\text{CO}_2\text{(g)}}$) for the exchange reaction between CO_2 (g) and H_2O (aq) is expressed by the equation (Bottinga, 1968; Friedman and O'Neil, 1977)

$$1000\ln\alpha = -0.021(10^6/T^2) + 17.99(10^3/T) - 19.97 \quad (3)$$

where T is temperature in Kelvin. We use the following Rayleigh fractionation equation to determine the extent of isotope exchange and model the $\delta^{18}\text{O}$ composition of the waters from Snæfellsnes and Torfajökull (Sharp, 2006):

$$\delta^{18}\text{O}_{\text{H}_2\text{O(aq)}_{\text{final}}} = (\delta^{18}\text{O}_{\text{H}_2\text{O(aq)}_{\text{mw}}} + 1000) * f^{(\alpha_{\text{H}_2\text{O(aq)}^{\text{CO}_2\text{(g)}} - 1)} - 1000 \quad (4)$$

where $\delta^{18}\text{O}_{\text{H}_2\text{O(aq)}_{\text{final}}}$ is the modeled value of the CO_2 -rich water after degassing, $\delta^{18}\text{O}_{\text{H}_2\text{O(aq)}_{\text{mw}}}$ is the initial local meteoric water prior to isotopic exchange, and f is the fraction of ^{18}O remaining in the H_2O (aq) that has not been irreversibly transferred to CO_2 (g) during degassing.

Equation 4 was solved with varying values of f and with temperatures from 10 to 100 °C using a $\delta^{18}\text{O}_{\text{H}_2\text{O(aq)}_{\text{mw}}}$ representative of either the Snæfellsnes or Torfajökull area (Árnason, 1977). Because each sample presumably had a different initial $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ than measured according to the $\delta^2\text{H}$ values, to calculate the apparent fractionation associated with each CO_2 -rich water, we take the difference between the measured $\delta^{18}\text{O}_{\text{H}_2\text{O(aq)}}$ of the sample and the expected $\delta^{18}\text{O}_{\text{H}_2\text{O(aq)}}$,

where the latter was calculated using the measured $\delta^2\text{H}$ (Table 5) and the local meteoric water line relationships of Sveinbjörnsdóttir et al. (1995), ($\delta^2\text{H} = 6.5 * \delta^{18}\text{O} - 3.5$ for $\delta^2\text{H} \geq -76\text{‰}$; $\delta^2\text{H} = 8 * \delta^{18}\text{O} + 11$ for $\delta^2\text{H} < -76\text{‰}$). We have termed this difference between the $\delta^{18}\text{O}_{\text{H}_2\text{O}(\text{aq})}$ of the initial local meteoric water and of either the measured or the modeled $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ the “shift” in $\delta^{18}\text{O}_{\text{H}_2\text{O}(\text{aq})}$ ($\Delta_{\text{H}_2\text{O}(\text{aq})_{\text{final}} - \text{H}_2\text{O}(\text{aq})_{\text{mw}}}$). Figure 13 shows, for varying temperatures, the shift as a function of the mass fraction of ^{18}O in H_2O (aq) that has been transferred to CO_2 (g), or $(1-f)$ of equation 3. We have plotted the isotopic shift of each sample on the model line that corresponds to its discharge temperature on Figure 13. Comparison of the sample shifts to the model results suggests the transfer of <0.5 to 2.5 percent of ^{18}O in H_2O (aq) to CO_2 (g). This shows that CO_2 degassing can significantly modify the $\delta^{18}\text{O}$ value of low-temperature fluids, and is a process that should be considered when evaluating water-rock interactions in active geothermal systems and as an indicator of past processes (Kristmannsdóttir and Sveinbjörnsdóttir, 2012).

It is thus unlikely that the relatively low $\delta^{18}\text{O}$ values of the CO_2 -rich waters are a result solely of mixing of magmatic CO_2 with meteoric water. Magmatic CO_2 has values of $\delta^{18}\text{O}_{\text{CO}_2}$ from approximately 25 to 35‰ (Marques et al., 2006; Matthews et al., 1987). At any CO_2 (g): H_2O (aq) ratio, the $\delta^{18}\text{O}$ value of the aqueous phase would be shifted in a positive direction relative to its initial composition and therefore relative to the meteoric water line if binary mixing of the two phases were the dominant process affecting $\delta^{18}\text{O}$ values. The positive $\delta^{18}\text{O}$ value of magmatic CO_2 could, however, dampen the effect of isotopic exchange during CO_2 degassing, implying that our values of <0.5 to 2.5% exchange are a minimum.

The $\delta^2\text{H}$ of the water samples from Snæfellsnes and Torfajökull should not be affected by the transformation of aqueous CO_2 to CO_2 (g) during degassing. Compared to local meteoric water $\delta^2\text{H}$ values of -50 to -54‰ (Snæfellsnes) and -66 to -72‰ (Torfajökull), the $\delta^2\text{H}$ values of the samples are lower than expected by up to 12‰ and 19‰, respectively (Fig. 10) (Árnason, 1977). However, Árnason (1977) showed that the $\delta^2\text{H}$ of precipitation can vary monthly by as much as 40‰ and on average deviates from the annual mean deuterium content by 13‰. Therefore, the observed variations in the $\delta^2\text{H}$ could be attributed to seasonal variations in precipitation and recharge by snowmelt, which typically has lower $\delta^2\text{H}$ values (Árnason, 1977).

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the Seydishólar waters plot well below the local MWL and are lower than that of present-day local meteoric water by up to $\sim 2.4\text{‰}$ and 32‰ , respectively (Fig. 10). Precipitation in Iceland during the last ice age (Pre-Holocene, $>10,000$ years ago) had significantly lower hydrogen isotope composition, potentially by as much as -80‰ (Árnason, 1977; Arnórsson, 1995). Ice age water in the subsurface is likely a component of the Seydishólar geothermal fluids, lowering the $\delta^2\text{H}$ value, and this has been shown in other geothermal areas of the Southern Lowlands and on the Reykjanes Peninsula (Arnórsson et al., 1993; Arnórsson, 1995; Pope et al., 2009). Additionally, the $\delta^{18}\text{O}$ values form a positive trend away from the MWL, a feature commonly observed in high-temperature geothermal fields due to oxygen isotope exchange with the surrounding rocks during high-temperature water-rock interaction at depth (Criss and Taylor, 1986). By extending the trend of the samples to the MWL, we have determined an initial isotopic composition, prior to water-rock interaction, of $\delta^2\text{H}$: -92‰ and $\delta^{18}\text{O}$: -13‰ . Using these values, the proportion of ice age water and present-day meteoric water to the Seydishólar fluids can be calculated assuming mixing of the two fluids. If we assign the ice age component $\delta^2\text{H}$: -128‰ and $\delta^{18}\text{O}$: -17‰ and present-day meteoric water $\delta^2\text{H}$: -58‰ and $\delta^{18}\text{O}$: -8.5‰ (Árnason, 1977), then the Seydishólar fluids are composed of 48% ice age water and 52% present-day local meteoric water. As shown in active and fossil systems in Iceland, the low $\delta^2\text{H}$ values of hydrothermal fluids are a result of interaction with hydrous alteration minerals (*e.g.* epidote) that formed from deuterium-poor Pre-Holocene glacial meltwater during the last ice age (Pope et al., 2014, 2009). Epidote is pervasive in the Seydishólar drill cuttings and must have formed during previous hydrothermal alteration as the current subsurface temperature is $<200\text{ °C}$ (Section 4.1). These percentages serve as a maximum ice age component and minimum meteoric water component, because the simple mixing model does not take into account additional inputs, such as water from farther inland and higher elevation, which would have a lower $\delta^2\text{H}$ value than the local meteoric water.

5.2. Mineral dissolution and precipitation

The concentration of all major aqueous components, except Cl^- and SO_4^{2-} , in geothermal fluids $>150\text{ °C}$ is most often determined by constraints of local equilibrium with secondary hydrothermal minerals (Arnórsson et al., 1983; Bird and Helgeson, 1981; Bird and Norton, 1981; Giggenbach, 1981; Gudmundsson and Arnórsson, 2005; Stefánsson and Arnórsson, 2002). The

P_{CO_2} of geothermal fluids in Iceland can be described by equilibrium with a mineral assemblage of Ca-bearing aluminosilicate and carbonate minerals (Arnórsson and Gunnlaugsson, 1985; Freedman et al., 2009; Fridriksson et al., 2006; Stefánsson and Arnórsson, 2002). Conversely, the major solute concentrations of non-thermal surface water and groundwater in Iceland are determined more by primary mineral dissolution than by equilibrium with secondary minerals, despite precipitation of secondary minerals such as kaolinite and other clay minerals (Gíslason and Arnórsson, 1993; Gíslason et al., 1996; Stefánsson and Gíslason, 2001). Below, we use thermodynamic analysis to indicate whether geochemical processes of geothermal or non-thermal systems can describe the CO_2 -rich fluids. We compare the P_{CO_2} of the CO_2 -rich fluids to low and high-temperature geothermal fluids to determine whether there is a mineral assemblage that theoretically buffers P_{CO_2} . The analyses are also relevant to CO_2 sequestration, because they help reveal whether each system attains carbonate mineral saturation.

Mineral saturation indices of selected minerals are presented in Figure 14 as a function of pH and temperature (see Methods 3.3). The pH used for the $\log(Q/K)$ calculations is the calculated *in situ* pH (Table 2; Methods 3.3). Oxygen partial pressure (P_{O_2}) from measured gas compositions was used to constrain O_2 (aq) (mmol/kg) (Results 4.4). Sample 13KH01 was not evaluated, because the lack of a gas phase sample (and corresponding P_{CO_2} and calculated pH) would result in misleading saturation indices. We evaluate minerals that are present in the drill cuttings; typically observed in other Icelandic geothermal systems and non-thermal areas of similar temperature range; and that serve as important reactant or product minerals. Some of the minerals evaluated are discussed but not presented in Figure 14.

Figure 14 shows the mineral saturation indices of high-temperature primary and hydrothermal silicate minerals (Fig. 14A) and secondary minerals (Fig. 14B). Primary igneous minerals plagioclase (An70, 70 mole percent anorthite) and clinopyroxene (diopside) are undersaturated in all samples at all pH, temperatures and CO_2 concentrations (Fig. 14), as is olivine. High-temperature alteration minerals epidote (Al-endmember clinozoisite), chlorite (Mg-endmember clinochlore) (Fig. 14A) and prehnite are also largely undersaturated. Low-temperature Ca-bearing zeolites laumontite, mesolite, mordenite and stilbite are all mostly supersaturated. Na-bearing zeolites analcime and natrolite vary in their saturation more than the Ca-zeolites, but are close to saturation. Calcium and Mg-bearing clays montmorillinite, illite,

celadonite are supersaturated, and smectite (high Fe-Mg) is variably saturated. The hydrated aluminosilicate kaolinite is mostly supersaturated (Fig. 14B), and Al-hydroxide gibbsite is near saturation. Quartz and chalcedony are both supersaturated, and amorphous SiO₂ is near saturation. Calcite and magnesite saturation is correlated most with pH, as opposed to temperature or ΣCO₂ (tot) (Fig. 14B), and the degree of undersaturation decreases with increasing pH until saturation is attained at pH ~6.2. As expected, primary minerals are undersaturated, carbonate minerals are close to saturation, and most clays and hydroxides are supersaturated.

Figure 15 presents an alternate way of reviewing the data by casting it relative to the thermodynamic equilibrium of Ca-silicate and carbonate mineral assemblages (see reactions in Table 1). The P_{CO_2} of the CO₂-rich fluids of this study (Table 2; Methods 3.3), together with Icelandic geothermal fluids (Freedman et al., 2009; Stefánsson and Arnórsson, 2002), are shown relative to the mineral assemblages as a function of temperature and are color-coded according to the calculated *in situ* pH of the undegassed fluid and represented symbolically by water-type. This approach conserves Al in the solid phase, which eliminates uncertainty introduced by thermodynamic data of aqueous Al species (Schecher and Driscoll, 1987). At temperatures >150 °C, the P_{CO_2} of geothermal fluids is constrained by approach to local equilibrium with the assemblage prehnite, clinozoisite (czo), calcite and quartz (Freedman et al., 2009; Stefánsson and Arnórsson, 2002):

This reaction is plotted for a clinozoisite activity of 1.0 and of 0.3 to represent an Fe composition of 0 and 2.1 moles, respectively. Departure from this equilibrium occurs with excessive influx of CO₂ associated with magmatic intrusions and diking events, such as at Krafla during the eruptive events of 1975 to 1984 (Ármannsson et al., 1989). The irreversible reaction of plagioclase with CO₂-rich fluids to form calcite and kaolinite is also shown:

Plagioclase (An₇₀) will not precipitate at temperatures <400 °C (Bowers et al., 1984), and thus the reaction represents the ranges of P_{CO_2} at which anorthite is stable and unstable. Anorthite was modeled with an activity of 0.70 to represent An₇₀. Lastly, calcite equilibrium is shown at pH 6.0, 6.5, 7.0 and 7.5.

The thermodynamic constraints bound the CO₂-rich fluids to a zone in which the precipitation of secondary silicate minerals and calcite is favored (Fig. 15). In agreement with individual mineral saturation indices, Figure 15 shows that equilibrium between hydrothermal silicate minerals clinozoisite, quartz and prehnite (reaction 5) does not constrain the P_{CO_2} of the CO₂-rich fluids.

Mineral saturation states and thermodynamic modeling show that hydrothermal silicate mineral dissolution provides a source of divalent cations for carbonate mineral precipitation. The closer approach to calcite equilibrium with increasing pH (Fig. 14B) reflects enhanced dissolution of primary and hydrothermal silicate minerals and greater extent of water-rock interaction, which is likely a result of longer fluid residence times. Fluids with similar CO₂ concentrations and lower pH do not reach saturation with calcite because there has not been sufficient H⁺ consumption through mineral dissolution, which may be due to fast flow rates and short transport times. An alternative to reaction limitation by fluid residence time is that the system is limited by supply of Ca or Mg-bearing minerals as reactants. However, petrologic observations show that there is abundant Ca-Na plagioclase, Ca-epidote and Mg-bearing chlorite (Fig. 2 and 3), implying that there is sufficient reactant. The destabilization and enhanced dissolution of primary and hydrothermal minerals is fundamental in explaining the high aqueous concentration of not only divalent cations, but also trace elements in the CO₂-rich waters.

5.3. Factors controlling trace element mobility at Snaefellsnes

Relative mobility (RM) describes mass transfer between the solid and aqueous phases by comparing an element's concentration in the source rock material to its concentration in water. RM calculations are employed to investigate chemical weathering in groundwater systems and in river catchments to evaluate metasomatic reactions (Aiuppa et al., 2000; Flaathen et al., 2009; Gíslason et al., 1996). Here each element's mobility is presented relative to Na, because Na is a major element in both basaltic lithology and fluids and is considered the most mobile major element during chemical weathering of basalt in Iceland (Gíslason et al., 1996). The water/rock concentration of the element of interest is normalized to that of Na using the following equation:

$$RM = [X_{\text{water}} / Na_{\text{water}}] / [X_{\text{rock}} / Na_{\text{rock}}] \quad (7)$$

The RM of Na is 1, so that any element with RM >1 is more mobile than Na. Here we present the relative mobility (RM) of elements in the Snaefellsnes fluids relative to the bulk rock

composition of Tertiary tholeiitic lava flows from the Snæfellsnes Peninsula (Hardarson, 1993). Bulk rock arsenic concentrations were obtained from data on hydrothermally altered Tertiary basalts from east Iceland (Olsen et al., 2011). As shown in Figure 16, the order of average element mobility in decreasing order is $Rb \gg As > K > Sr > Mg > Ba > Ca > Mn > Ni > Zn > Pb > Fe \gg Ti > Al$. The minimum and maximum RM for each element are shown by dotted lines bounding the average trend in Figure 16.

Rubidium, the only element with $RM > 1$, commonly substitutes for Na and K in alkali feldspar. Strontium and Ba commonly substitute for Ca, and Ba also for K, within feldspar (Klein and Dutrow, 2008). The high mobility of Rb, Sr and Ba, therefore, reflects the instability of feldspar.

RM of arsenic ranges from 0.005 to 1.43, intermediate between Rb and K. Arsenic, a chalcophile element, is hosted in basaltic rocks as a common impurity in secondary sulfide minerals such as pyrite (O'Day, 2006) and in iron-ore minerals such as magnetite, ilmenite and titanomagnetite (Arnórsson, 2003; Onishi and Sandell, 1955). Experimental results suggest that arsenic is also contained in highly soluble salts deposited from magmatic vapors on mineral grain surfaces (Ellis and Mahon 1964; Onishi and Sandell 1955). There have been few studies of As in Icelandic rocks, but its distribution appears to be controlled by a combination of primary igneous processes and hydrothermal alteration. Arnórsson (2003) showed that the bulk rock As content of basalts and silicic rocks from active areas within the MAR increases with increasing silicic character, which is expected due to the element's incompatible nature during partial melting and fractional crystallization (Baur and Onishi, 1978). However, in a study of As distribution in variably hydrothermally altered rocks from the active systems Reykjanes and Krafla and the fossil system Geitafell, Olsen et al. (2010) did not observe an increase in As with the degree of silicic evolution, suggesting that primary rock-forming processes alone cannot explain bulk rock As content. Instead, the most hydrothermally altered basalts had the highest bulk rock As concentrations, and As and sulfur content were positively correlated in drill cuttings from Reykjanes. Analyses of pyrite grains confirmed that As was hosted within hydrothermal pyrite, demonstrating that As was mobilized during hydrothermal alteration and then sequestered within Fe-sulfide minerals (Olsen et al., 2011). The Snæfellsnes drill cuttings contain abundant hydrothermal pyrite (Fig. 2C), with which As could be associated and released as pyrite dissolves. Though there are no definitive trends between As RM and temperature, ΣCO_2 , H_2S ,

SO₄ or Fe concentration, As concentrations generally increase with temperature (Fig. 8B), which suggests a mineral-solution equilibrium (*i.e.*, pyrite solubility) control consistent with Ballantyne and Moore (1988).

The divalent cations Mg and Ca, and multivalent Mn have similar RM. Within the Snæfellsnes drill cuttings, the major Ca and Mg-bearing phases are clinopyroxene, carbonate, plagioclase (Ca), epidote (Ca) and chlorite (Mg), (Fig. 2). In basalts, Mn²⁺ is hosted as a trace element in primary clinopyroxene and also substitutes for Ca²⁺ and Mg²⁺ in carbonate minerals (Klein and Dutrow, 2008). Of these phases, Ca-Mg bearing silicates are undersaturated (Fig. 14A) and likely sources of Ca²⁺ and Mg²⁺, and the carbonate minerals (calcite, aragonite, dolomite, magnesite) are near saturation (Fig. 14B) and therefore potential sinks. Though not identified in the drill cuttings, retrograde Ca and Mg-bearing zeolites and clays may be additional phases that incorporate Ca²⁺ and Mg²⁺. The Ca RM average of 0.05 is relatively low compared to the RM range of 0.06 to 0.40 for Icelandic basaltic groundwater, surface water, and geothermal fluids studied by Gíslason et al. (1996) and Markússon and Stefánsson (2011) and compared to the RM of ~1 measured in CO₂-rich waters by Flaathen et al. (2009).

The transition metals Ni, Zn and Fe, as well as Pb, range in RM from ~0.001 to 0.1. Pyrite and clinopyroxene are likely sources of Fe²⁺ and Ni²⁺, and epidote is a source of Fe³⁺. All phases are present in the Snæfellsnes drill cuttings (Results 4.1; Fig. 2). Though Ni is a common trace element in olivine (Galoisy et al., 1995), the mineral was not observed in the drill cuttings. Previous studies have shown that the similar mobilities of Ni, Zn, Fe and Pb may reflect their complexation as aqueous bicarbonate and carbonate species in CO₂-rich fluids (Aiuppa et al., 2000). Redox-sensitive elements Fe and Mn have some of the largest variability in RM (Fig. 16). Deposits of Fe-rich (<1–17 wt%) carbonate (calcite and/or aragonite) form at the outlet of certain springs (08LH13, 16CS13, 18BF13, 19BF13, 23HS13) and around some drillholes (07LH13, 10OL13), and Fe(III)-oxyhydroxides form at 12OL13, 21OS13 and 25JG13. XRF analyses show that significant amounts of As (~2–203 ppm), Mn (~92–7,000 ppm), and Ni (~13–40 ppm), as well as Sr, Ba, and Zn, are associated with these deposits. These results are similar to the compositions of other surface deposits and travertines from CO₂ springs in Italy and Greece and to experimental observations of cation adsorption onto and coprecipitation with carbonate and Fe(III)-oxyhydroxides (Aiuppa et al., 2000; Le Guern et al., 2003; Murray, 1975; Winkel et al., 2013). Given these observations, it is likely that redox-sensitive elements are in a soluble

reduced state (Fe^{2+} , As^{3+}) until discharging at the surface, and upon oxidation (Fe^{3+} , As^{5+}) are incorporated via adsorption and/or co-precipitation into the carbonate deposits or associated Fe(III)-oxyhydroxides.

6. Implications

6.1. Implications for geologic CO_2 sequestration (GCS) into basalts

The feasibility of geologic CO_2 sequestration (GCS) in basaltic rocks has been investigated primarily through experimental methods (Peuble et al., 2015; Galeczka et al., 2014; Gysi and Stefánsson, 2012a, 2012b; McGrail et al., 2006; Rosenbauer et al., 2012; Schaef and McGrail, 2009; Schaef et al., 2010) and, to a lesser extent, via natural analogues (Flaathen et al., 2009; Lu et al., 2011) and pilot projects (Alfredsson et al., 2013; Gislason et al., 2010; Matter et al., 2011; McGrail et al., 2011). These studies have focused on the reactivity of CO_2 with fresh, unaltered olivine-rich material, basalt and basaltic glass. Our analysis of CO_2 -rich fluids in Iceland as natural analogues of CO_2 sequestration into basalt demonstrates that, despite the effects of hydrothermal alteration on crystallinity, mineral assemblage, porosity and permeability, which are all aspects that affect reactivity (Gislason and Oelkers, 2003; Neuhoﬀ et al., 1999; Olsen et al., 2011; Rogers et al., 2006; Wolff-Boenisch et al., 2006), the dissolution of hydrothermal silicate minerals is as efficient as fresh basaltic material in supplying divalent cations for carbonate mineral precipitation. Though hydrothermally altered basalts are sufficiently reactive to promote carbonate mineralization, such formations are potentially more likely to release trace elements to solution, because hydrothermal alteration progressively enriches secondary sulfide minerals (pyrite) in trace elements (As, Ni) (Olsen et al., 2011, 2010). Our results suggest that CO_2 -rich fluids promote both the breakdown of hydrothermal sulfide minerals and the transport of released trace metal(loid)s through the aqueous phase (Aiuppa et al., 2000) (Results 4.2). The release of trace metal(loid)s either within an injection reservoir, along the flowpath of migrating CO_2 , or within shallow drinking water aquifers composed of hydrothermally altered basalts would thus depend on the amount of ΣCO_2 (aq), the resulting pH and the presence of secondary Fe(III)-oxyhydroxides and clays that may remove trace metal(loid)s from solution. In Iceland, drinking water aquifers within Quaternary formations often overlie hydrothermally altered basalts, and there are a number of drinking water aquifers within Tertiary formations that have likely undergone hydrothermal alteration (Gunnarsdottir et

al., 2015). Therefore, the degree of hydrothermal alteration, and in particular the modal abundance of hydrothermal sulfides, should be a careful consideration for GCS site selection in basaltic rocks to minimize the risk of groundwater contamination by trace metal(lloid) mobilization.

6.2. *CO₂ discharge and cycling in volcanic areas*

Our field studies are qualitatively consistent with observations from other geologic settings where CO₂ degassing through surface waters is a passive but persistent mode of CO₂ flux throughout the magmatic stages of basaltic geothermal activity in Iceland. The geothermal systems of Seydishólar and Torfajökull and the non-thermal areas of Snæfellsnes display the prevalence and diverse modes of CO₂ degassing from both high and low-temperature settings in Iceland. As described in Section 5.1.2, there is limited to no evidence that a significant steam phase (water vapor >100 °C) is associated with the cold springs of the Snæfellsnes Peninsula. At Torfajökull, the steam condenses at shallow depths. Therefore, the CO₂ in springs and groundwaters was probably locally transported as a separate CO₂-rich gas before dissolving into perched aquifers and shallow surface water (*e.g.* Barnes et al., 1978) (Fig. 12). Multiphase flow modeling has shown that, because of the different thermodynamic properties of water (Keenan et al., 1969) and CO₂ (Altunin, 1975; Duan and Sun, 2003), and water and gas relative permeabilities during multiphase flow (Bertels et al., 2001; Burnside and Naylor, 2014, and references therein), it is not uncommon for water vapor in a geothermal fluid to condense in the subsurface and for CO₂ gas to continue to migrate through permeable pathways (Bergfeld et al., 2001; Chiodini et al., 2005; Lewicki and Oldenburg, 2005; Peiffer et al., 2014).

As discussed in sections 4.2 and 5.2, increased ΣCO₂ (aq) concentration results in both enhanced silicate mineral dissolution and carbonate mineral dissolution/precipitation reactions, dependent on approach to equilibrium. When calcite is undersaturated, calcite that precipitated during prior hydrothermal alteration dissolves, but the Ca released was initially sourced from Ca-bearing silicate minerals. Although some Icelandic rivers show Ca isotopic signatures consistent with calcite dissolution (Jacobson et al., 2015), this reflects the dissolution of an intermediate reservoir of Ca that formed as a result of silicate weathering. Thus, silicate weathering in hydrothermal areas is still relevant for alkalinity and bicarbonate fluxes in rivers.

7. Conclusions

CO₂-rich waters in Iceland are associated with low-temperature geothermal areas in the waning stages of magmatic activity, on the margins of high-temperature systems within the MAR, and in off-rift systems where ΣCO_2 (aq) solubility is increased. Oxygen and hydrogen isotope ratios show that the water in these systems is dominantly meteoric, with a variable component of seawater in systems near the coast and an ice-age water component in systems in the Southern Lowlands. Low-temperature CO₂ degassing results in depletion in ¹⁸O relative to local meteoric water. Carbon isotope ratios indicate that the CO₂ is magmatic in source and is modified by mixing with biogenic CO₂ and calcite precipitation. Increased ΣCO_2 (aq) concentrations result in enhanced mineral dissolution and total dissolved solids. Equilibrium with respect to calcite suggests that carbonate mineral reactions are more important controls on water composition in low-temperature settings (≤ 150 °C) than in high-temperature systems (≥ 200 °C). Trace element concentrations are greater in CO₂-rich waters than in other systems in Iceland as a result of the dissolution of hydrothermal sulfide minerals, which are likely enriched in certain elements (As).

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References

- Aggarwal, J.K., Palmer, M.R., Bullen, T.D., Arnórsson, S., Ragnarsdóttir, K. V., 2000. The boron isotope systematics of Icelandic geothermal waters: 1. Meteoric water charged systems. *Geochim. Cosmochim. Acta* 64, 579–585. doi:10.1016/S0016-7037(99)00300-2
- Aiuppa, A., Allard, P., D'Alessandro, W., Agnes, M., Parello, F., Treuil, M., Valenza, M., 2000. Mobility and fluxes of major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily). *Geochim. Cosmochim. Acta* 64, 1827–1841.
- Aiuppa, A., Caleca, A., Federico, C., Gurrieri, S., Valenza, M., 2004. Diffuse degassing of carbon dioxide at Somma-Vesuvius volcanic complex (Southern Italy) and its relation with regional tectonics. *J. Volcanol. Geotherm. Res.* 133, 55–79. doi:10.1016/S0377-0273(03)00391-3
- Alfredsson, H.A., Oelkers, E.H., Hardarsson, B.S., Franzson, H., Gunnlaugsson, E., Gislason, S.R., 2013. The geology and water chemistry of the Hellisheidi, SW-Iceland carbon storage site. *Int. J. Greenh. Gas Control* 12, 399–418. doi:10.1016/j.ijggc.2012.11.019
- Ármannsson, H., Benjamínsson, J., Jeffrey, A., 1989. Gas changes in the Krafla geothermal system, Iceland. *Chem. Geol.* 76, 175–196.
- Arnason, B., 1977. Hydrothermal systems in Iceland traced by deuterium. *Geothermics* 5, 125–151.
- Arnórsson, S., 1975. Application of the Silica Geothermometer in Low Temperature Hydrothermal Areas in Iceland. *Am. J. Sci.* doi:10.2475/ajs.275.7.763
- Arnórsson, S., 1980. Chemical geothermometers. *Naturufraedingurinn* 50, 121–138. (in Icelandic with English summary)
- Arnórsson, S., 1986. Chemistry of Gases Associated with Geothermal Activity and Volcanism in Iceland: A Review. *J. Geophys. Res.* 91.
- Arnórsson, S., 1995. Geothermal systems in Iceland: Structure and conceptual models—I. High-temperature areas. *Geothermics* 24, 561–602. doi:10.1016/0375-6505(95)00025-9
- Arnórsson, S., 1995. Geothermal systems in Iceland: Structure and conceptual models—II. Low-temperature areas. *Geothermics* 24, 603–629.
- Arnórsson, S., 2003. Arsenic in surface- and up to 90°C ground waters in a basalt area, N-Iceland: processes controlling its mobility. *Appl. Geochemistry* 18, 1297–1312. doi:10.1016/S0883-2927(03)00052-0
- Arnórsson, S., Andréðottir, A., 1995. Processes controlling the distribution of boron and chlorine in natural waters in Iceland. *Geochim. Cosmochim. Acta* 59, 4125–4146.
- Arnórsson, S., Axelsson, G., Sæmundsson, K., 2008. Geothermal systems in Iceland. *Jökull* 58, 269–302.
- Arnórsson, S., Barnes, I., 1983. The nature of carbon dioxide waters in Snæfellsnes, western Iceland. *Geothermics*. doi:10.1016/0375-6505(83)90027-5
- Arnórsson, S., Bjarnason, J.O., Giroud, N., Gunnarsson, I., Stefánsson, A., 2006. Sampling and analysis of geothermal fluids. *Geofluids* 6, 203–216. doi:10.1111/J.1468-8123.2006.00147.X
- Arnórsson, S., Gunnlaugsson, E., 1985. New gas geothermometers for geothermal exploration—

- calibration and application. *Geochim. Cosmochim. Acta* 49, 1307–1325. doi:10.1016/0016-7037(85)90283-2s
- Arnórsson, S., Gunnlaugsson, E., Svavarsson, H., 1983. The chemistry of geothermal waters in Iceland. III. Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta* 47, 567–577.
- Arnórsson, S., Gunnlaugsson, E., Svavarsson, H., 1983. The chemistry of geothermal waters in Iceland. II. Mineral equilibria and independent variables controlling water compositions. *Geochim. Cosmochim. Acta* 47, 547–566.
- Arnórsson, S., Hurtig, N.C., Gysi, A.P., Bird, D.K., O'Day, P., 2010. Carbon dioxide waters in Iceland: A natural analogue to CO₂ sequestration in basaltic aquifers, in: 13th International Symposium on Water-Rock Interaction.
- Arnórsson, S., Sigurdsson, S., Svavarsson, H., 1982. The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0° to 370°C. *Geochim. Cosmochim. Acta* 46, 1513–1532. doi:10.1016/0016-7037(82)90311-8
- Arnórsson, S., Stefánsson, A., 1999. Assessment of feldspar solubility constants in water in the range 0° to 350°C at vapor saturation pressures. *Am. J. Sci.* 299, 173–209.
- Arnórsson, S., Stefánsson, A., Bjarnason, J.Ö., 2007. Fluid-fluid interactions in geothermal systems. *Rev. Mineral. Geochemistry* 65, 259–312. doi:Doi 10.2138/Rmg.2007.65.9
- Arnórsson, S., Sveinbjornsdottir, A.E., Andrésdóttir, A., 1993. Processes influencing $\delta^2\text{H}$, $\delta^{18}\text{O}$, B and Cl distribution in cold and thermal waters in the NW-Peninsula and in the Southern Lowlands, Iceland.
- Arnórsson, S., Gunnarsson, I., Stefánsson, A., Andrésdóttir, A., Sveinbjornsdottir, A.E., 2002. Major element chemistry of surface- and ground waters in basaltic terrain, N-Iceland. I. Primary mineral saturation. *Geochim. Cosmochim. Acta* 66, 4015–4046.
- Ballantyne, J.M., Moore, J.N., 1988. Arsenic geochemistry in geothermal systems. *Geochim. Cosmochim. Acta* 52, 475–483. doi:10.1016/0016-7037(88)90102-0
- Barnes, I., Irwin, W., White, D., 1978. Global distribution of carbon dioxide discharges and major zones of seismicity. *U.S. Geol. Surv., Water-Resour. Invest. Rep.*, pp. 78-39
- Barry, P.H., Hilton, D.R., Furi, E., Halldórsson, S.A., Grönvold, K., 2014. Carbon isotope and abundance systematics of Icelandic geothermal gases, fluids and subglacial basalts with implications for mantle plume-related CO₂ fluxes. *Geochim. Cosmochim. Acta* 134, 74–99. doi:10.1016/j.gca.2014.02.038
- Baur, W.H., Onishi, H., 1978. Arsenic 33, in: Wedepohl, K.H. (Ed.), *Handbook of Geochemistry*. Springer-Verlag.
- Benson, S.M., Cole, D.R., 2008. CO₂ Sequestration in Deep Sedimentary Formations. *Elements* 4, 325–331. doi:10.2113/gselements.4.5.325
- Bergfeld, D., Goff, F., Janik, C.J., 2001. Elevated carbon dioxide flux at the Dixie Valley geothermal field, Nevada; relations between surface phenomena and the geothermal reservoir. *Chem. Geol.* 177, 43–66. doi:10.1016/S0009-2541(00)00381-8
- Bergfeld, D., Goff, F., Janik, C., 2001. Carbon isotope systematics and CO₂ sources in The Geysers-Clear Lake region, northern California, USA. *Geothermics* 30, 303–331.

- Bickle, M., Kampman, N., 2013. Lessons in carbon storage from geological analogues. *Geology* 41, 525–526. doi:10.1130/focus0420132.1
- Bird, D.K., Norton, D.L., 1981. Theoretical prediction of phase relations among aqueous solutions and minerals: Salton Sea geothermal system. *Geochim. Cosmochim. Acta* 45, 1479–1493. doi:10.1016/0016-7037(81)90280-5
- Bird, D.K., Helgeson, H.C., 1981. Chemical interaction of aqueous solutions with epidote-feldspar mineral assemblages in geologic systems. II. Equilibrium constraints in metamorphic/geothermal processes. *Am. J. Sci.* 281, 576–614.
- Bird, D.K., Spieler, A. R., 2004. Epidote in Geothermal Systems. *Rev. Mineral. Geochemistry* 56, 235–300. doi:10.2138/gsrmg.56.1.235
- Bjarnason, J.Ö., 2010. The chemical speciation program WATCH, version 2.4. Reykjavik, Iceland.
- Björke, J., 2010. Fluid-rhyolite interaction in geothermal systems, Torfajökull Iceland-secondary surface mineralogy and fluid chemistry upon phase segregation and fluid mixing. M.Sc. Thesis, University of Iceland.
- Björke, J., Stefánsson, A., Fridriksson, T., 2009. Fluid geochemistry and surface alteration associated with rhyolitic rocks, Torfajökull Iceland. *Goldschmidt Abstracts, Mineralogical Magazine*. pp. 66–180.
- Björnsson, S., Gudmundsdottir, I., Ketilsson, J., 2010. Geothermal Development and Research in Iceland. *Orkustofnun, Reykjavík, Iceland*.
- Bottinga, Y., 1968. Calculation of fractionation factors for carbon and oxygen isotopic exchange in the system calcite-carbon dioxide-water. *J. Phys. Chem.* 72, 800–808.
- Bottinga, Y., 1969. Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite-carbon dioxide-graphite-methane-hydrogen-water vapor. *Geochim. Cosmochim. Acta* 33, 49–64.
- Bowers, T.S., Jackson, K.J., Helgeson, H.C., 1984. *Equilibrium Activity Diagrams for Coexisting Minerals and Aqueous Solutions at Pressures and Temperatures to 5 kb and 600 °C*. Springer- Verlag, Berlin.
- Breecker, D.O., Sharp, Z.D., McFadden, L.D., 2009. Seasonal bias in the formation and stable isotopic composition of pedogenic carbonate in modern soils from central New Mexico, USA. *Bull. Geol. Soc. Am.* 121, 630–640. doi:10.1130/B26413.1
- Brey, G., 1976. CO₂ solubility and solubility mechanisms in silicate melts at high pressures. *Contrib. to Mineral. Petrol.* 57, 215–221. doi:10.1007/BF00405226
- Burnside, N.M., Naylor, M., 2014. Review and implications of relative permeability of CO₂/brine systems and residual trapping of CO₂. *Int. J. Greenh. Gas Control* 23, 1–11. doi:10.1016/j.ijggc.2014.01.013
- Chiodini, G., Caliro, S., Cardellini, C., Avino, R., Granieri, D., Schmidt, A., 2008. Carbon isotopic composition of soil CO₂ efflux, a powerful method to discriminate different sources feeding soil CO₂ degassing in volcanic-hydrothermal areas. *Earth Planet. Sci. Lett.* 274, 372–379. doi:10.1016/j.epsl.2008.07.051
- Chiodini, G., Frondini, F., Cardellini, C., Granieri, D., Marini, L., Ventura, G., 2001. CO₂

- degassing and energy release at Solfatara volcano, Campi Flegrei, Italy. *J. Geophys. Res.* 106, 16213–16221.
- Chiodini, G., Granieri, D., Avino, R., Caliro, S., Costa, A., Werner, C., 2005. Carbon dioxide diffuse degassing and estimation of heat release from volcanic and hydrothermal systems. *J. Geophys. Res.* 110, B08204. doi:10.1029/2004JB003542
- Criss, R.E., Taylor Jr., H.P., 1986. Meteoric-hydrothermal systems. *Rev. Mineral. Geochemistry*, 16, 373–424.
- Crossey, L.J., Fischer, T.P., Patchett, P.J., Karlstrom, K.E., Hilton, D.R., Newell, D.L., Huntoon, P., Reynolds, A.C., de Leeuw, G.A.M., 2006. Dissected hydrologic system at the Grand Canyon: Interaction between deeply derived fluids and plateau aquifer waters in modern springs and travertine. *Geology* 34, 25. doi:10.1130/G22057.1
- Delalande, M., Bergonzini, L., Gherardi, F., Guidi, M., Andre, L., Abdallah, I., Williamson, D., 2011. Fluid geochemistry of natural manifestations from the Southern Poroto–Rungwe hydrothermal system (Tanzania): Preliminary conceptual model. *J. Volcanol. Geotherm. Res.* 199, 127–141. doi:10.1016/j.jvolgeores.2010.11.002
- Duan, Z., Sun, R., 2003. An improved model calculating CO₂ solubility in pure water and aqueous NaCl solutions from 273 to 5333 K and from 0 to 2000 bar. *Chem Geol* 193, 257–271.
- Einarsson, P., 2008. Plate boundaries, rifts and transforms in Iceland. *Jökull* 58, 35–58.
- Ellis, A., Mahon, W.A., 1964. Natural hydrothermal systems and experimental hot-water / rock interactions. *Geochim. Cosmochim. Acta* 28, 1323–1357.
- Ellis, A., Mahon, W.A., 1967. Natural hydrothermal systems and experimental hot water/rock interactions (Part II). *Geochim. Cosmochim. Acta* 31, 519–538.
- Ellis, A., Mahon, W.A., 1977. *Chemistry and Geothermal Systems*. Academic Press, Inc., New York, New York.
- Evans, M.J., Derry, L.A., France-Lanord, C., 2008. Degassing of metamorphic carbon dioxide from the Nepal Himalaya. *Geochemistry, Geophysics, Geosystems* 9 (4), Q04021. doi:10.1029/2007GC001796
- Evans, W.C., Sorey, M.L., Cook, A.C., Kennedy, B.M., Shuster, D.L., Colvard, E.M., White, L.D., Huebner, M.A., 2002. Tracing and quantifying magmatic carbon discharge in cold groundwaters: Lessons learned from Mammoth Mountain, USA. *J. Volcanol. Geotherm. Res.* 114, 291–312. doi:10.1016/S0377-0273(01)00268-2
- Fendorf, S., Eick, M.J., Grossl, P., Sparks, D.L., 1997. Arsenate and Chromate Retention Mechanisms on Goethite. 1. Surface Structure. *Environ. Sci. Technol.* 31, 315–320. doi:10.1021/es950653t
- Fine, G., Stolper, E., 1986. Dissolved carbon dioxide in basaltic glasses: concentrations and speciation. *Earth Planet. Sci. Lett.* 76, 263–278. doi:10.1016/0012-821X(86)90078-6
- Flaathen, T.K., Gislason, S.R., Oelkers, E.H., Sveinbjörnsdóttir, Á.E., 2009. Chemical evolution of the Mt. Hekla, Iceland, groundwaters: A natural analogue for CO₂ sequestration in basaltic rocks. *Appl. Geochemistry* 24, 463–474. doi:10.1016/j.apgeochem.2008.12.031
- Fournier, R., 1977. Chemical geothermometers and mixing models for geothermal systems.

Geothermics 5, 41–50.

- Franzson, H., Zierenberg, R., Schiffman, P., 2008. Chemical transport in geothermal systems in Iceland. *J. Volcanol. Geotherm. Res.* 173, 217–229. doi:10.1016/j.jvolgeores.2008.01.027
- Freedman, A.J.E., Bird, D.K., Arnórsson, S., Fridriksson, T., Elders, W.A., Fridleifsson, G.O., 2009. Hydrothermal minerals record CO₂ partial pressures in the Reykjanes geothermal system, Iceland. *Am. J. Sci.* 309, 788–833. doi:10.2475/09.2009.02
- Fridriksson, T., Kristjánsson, B.R., Ármannsson, H., Margrétardóttir, E., Ólafsdóttir, S., Chiodini, G., 2006. CO₂ emissions and heat flow through soil, fumaroles, and steam heated mud pools at the Reykjanes geothermal area, SW Iceland. *Appl. Geochemistry* 21, 1551–1569. doi:10.1016/j.apgeochem.2006.04.006
- Friedman, I., O’Neil, J.R., 1977. Compilation of stable isotope fractionation factors of geochemical interest, in: Fleischer, M. (Ed.), *Data of Geochemistry*, 6th ed. U.S. Geological Survey Professional Paper. 440-KK. 60 pp.
- Füri, E., Hilton, D.R., Halldórsson, S.A., Barry, P.H., Hahm, D., Fischer, T.P., Grönvold, K., 2010. Apparent decoupling of the He and Ne isotope systematics of the Icelandic mantle: The role of He depletion, melt mixing, degassing fractionation and air interaction. *Geochim. Cosmochim. Acta* 74, 3307–3332. doi:10.1016/j.gca.2010.03.023
- Galeczka, I., Wolff-Boenisch, D., Oelkers, E.H., Gislason, S.R., 2014. An experimental study of basaltic glass–H₂O–CO₂ interaction at 22 and 50°C: Implications for subsurface storage of CO₂. *Geochim. Cosmochim. Acta* 126, 123–145. doi:10.1016/j.gca.2013.10.044
- Galoisy, L., Calas, G., Brown Jr., G.E., 1995. Intracrystalline distribution of Ni in San Carlos olivine: an EXAFS study. *Am. Mineral.* 80, 1089–1092.
- Giggenbach, W., 1981. Geothermal mineral equilibria. *Geochim. Cosmochim. Acta* 45, 393–410.
- Giggenbach, W.F., 1988. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geothermometers. *Geochim. Cosmochim. Acta* 52, 2749–2765. doi:10.1016/0016-7037(88)90143-3
- Giroud, N., 2008. A Chemical Study of Arsenic, Boron and Gases in High-Temperature Geothermal Fluids in Iceland. Ph.D. Thesis, University of Iceland.
- Gíslason, S.R., Arnórsson, S., 1993. Dissolution of primary minerals in basaltic natural waters: saturation state and kinetics. *Chem. Geol.* 105, 117–135. doi:10.1016/S0009-2541(00)00262-X
- Gíslason, S.R., Arnórsson, S.A., Ármannsson, H., 1996. Chemical weathering of basalt in southwest Iceland: effects of runoff, age of rocks and vegetative/glacial cover. *Am. J. Sci.* 296, 836–907.
- Gislason, S., Oelkers, E., 2003. Mechanism, rates, and consequences of basaltic glass dissolution: II. An experimental study of the dissolution rates of basaltic glass as a function of pH and temperature. *Geochim. Cosmochim. Acta* 67, 3817–3832. doi:10.1016/S0016-7037(00)00176-5
- Gislason, S.R., Wolff-Boenisch, D., Stefánsson, A., Oelkers, E.H., Gunnlaugsson, E., Sigurdardóttir, H., Sigfusson, B., Broecker, W.S., Matter, J.M., Stute, M., Axelsson, G.,

- Fridriksson, T., 2010. Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *Int. J. Greenh. Gas Control* 4, 537–545. doi:10.1016/j.ijggc.2009.11.013
- Glover, R.B., 1988. Boron distribution between liquid and vapour in geothermal fluids, in: 10th New Zealand Geothermal Workshop. pp. 223–227. doi:10.1017/CBO9781107415324.004
- Goldberg, D.S., Takahashi, T., Slagle, A.L., 2008. Carbon dioxide sequestration in deep-sea basalt. *Proc. Natl. Acad. Sci.* 105, 9920–5. doi:10.1073/pnas.0804397105
- Gudmundsson, B.T., Arnórsson, S., 2005. Secondary mineral–fluid equilibria in the Krafla and Námafjall geothermal systems, Iceland. *Appl. Geochemistry* 20, 1607–1625. doi:10.1016/j.apgeochem.2005.04.020
- Gunnarsson, B., Marsh, B.D., Taylor Jr., H.P., 1998. Generation of Icelandic rhyolites: silicic lavas from the Torfajökull central volcano. *J. Volcanol. Geotherm. Res.* 83, 1–45. doi:10.1016/S0377-0273(98)00017-1
- Gysi, A.P., Stefánsson, A., 2012a. Experiments and geochemical modeling of CO₂ sequestration during hydrothermal basalt alteration. *Chem. Geol.* 306–307, 10–28. doi:10.1016/j.chemgeo.2012.02.016
- Gysi, A.P., Stefánsson, A., 2012b. CO₂-water–basalt interaction. Low temperature experiments and implications for CO₂ sequestration into basalts. *Geochim. Cosmochim. Acta* 81, 129–152. doi:10.1016/j.gca.2011.12.012
- Hardarson, B.S., 1993. Alkaline Rocks in Iceland with Special Reference to the Snaefellsjökull Volcanic System. Ph.D. Thesis, University of Edinburgh.
- Hardarson, B., Fitton, J., Hjartarson, A., 2008. Tertiary volcanism in Iceland. *Jökull* 58, 161–178.
- Harvey, O., Qafoku, N., Cantrell, K., Lee, G., Amonette, J.E., Brown, C.F., 2012. Geochemical Implications of Gas Leakage associated with Geologic CO₂ Storage—A Qualitative Review. *Environ. Sci. Technol.* 47, 23–36.
- Hilton, D.R., Grönvold, K., O’Nions, R.K., Oxburgh, E.R., 1990. Regional distribution of ³He anomalies in the Icelandic crust. *Chem. Geol.* 88, 53–67.
- Irwin, W.P., Barnes, I., 1980. Tectonic relations of carbon dioxide discharges and earthquakes. *J. Geophys. Res.* 85, 3115. doi:10.1029/JB085iB06p03115
- Jakobsson, S., 1966. The Grimsnés Lavas SW-Iceland. *Acta Nat. Islandica* 2, 6–30.
- Jakobsson, S., 1972. Chemistry and distribution pattern of recent basaltic rocks in Iceland. *Lithos* 5, 365–386.
- Jendzejewski, N., Trull, T.W., Pineau, F., Javoy, M., 1997. Carbon solubility in Mid-Ocean Ridge basaltic melt at low pressures (250–1950 bar). *Chem. Geol.* 138, 81–92. doi:10.1016/S0009-2541(96)00176-3
- Kaasalainen, H., Stefánsson, A., 2012. The chemistry of trace elements in surface geothermal waters and steam, Iceland. *Chem. Geol.* 330–331, 60–85. doi:10.1016/j.chemgeo.2012.08.019
- Keating, E.H., Fessenden, J., Kanjorski, N., Koning, D.J., Pawar, R., 2010. The impact of CO₂ on shallow groundwater chemistry: Observations at a natural analog site and implications

- for carbon sequestration. *Environ. Earth Sci.* 60, 521–536. doi:10.1007/s12665-009-0192-4
- Keating, E.H., Hakala, J.A., Viswanathan, H., Carey, J.W., Pawar, R., Guthrie, G.D., Fessenden-Rahn, J., 2013. CO₂ leakage impacts on shallow groundwater: Field-scale reactive-transport simulations informed by observations at a natural analog site. *Appl. Geochemistry* 30, 136–147. doi:10.1016/j.apgeochem.2012.08.007
- Keeling, C.D., Piper, S.C., Bacastow, R.B., Wahlen, M., Whorf, T.P., Heimann, M., Meijer, H.A., 2005. Atmospheric CO₂ and ¹³CO₂ exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications, in: Ehleringer, J.R., Cerling, T.E., Dearing, M.D. (Eds.), *A History of Atmospheric CO₂ and Its Effects on Plants, Animals, and Ecosystems*. Springer- Verlag, New York, New York, pp. 83–113.
- Keenan, J.H., Hill, P.G., Keyes, F.G., Moore, J.G., 1969. *Steam Tables: thermodynamic properties of water, including vapor, liquid, and solid phases*. John Wiley, Hoboken, NJ.
- Kharaka, Y.K., Thordsen, J.J., Hovorka, S.D., Seay Nance, H., Cole, D.R., Phelps, T.J., Knauss, K.G., 2009. Potential environmental issues of CO₂ storage in deep saline aquifers: Geochemical results from the Frio-I Brine Pilot test, Texas, USA. *Appl. Geochemistry* 24, 1106–1112. doi:10.1016/j.apgeochem.2009.02.010
- Klein, C., Dutrow, B., 2008. *Manual of Mineral Science*, 23rd ed. John Wiley & Sons.
- Kristmannsdóttir, H., 1979. Alteration of Basaltic Rocks by Hydrothermal-Activity at 100–300°C. In: Mortland, M.M., Farmer, V.C. (Eds.), *Developments in Sedimentology*. Elsevier, Amsterdam, pp. 359–367
- Kristmannsdóttir, H., Sveinbjørnsdóttir, Á.E., 2012. An anomalous thermal water from Hofstadir western Iceland: Evidence for past CO₂ flushing. *Appl. Geochemistry* 27, 1146–1152. doi:10.1016/j.apgeochem.2012.02.030
- Larsen, F., Postma, D., 1997. Nickel Mobilization in a Groundwater Well Field: Release by Pyrite Oxidation and Desorption from Manganese Oxides. *Environ. Sci. Technol.* 31, 2589–2595. doi:10.1021/es9610794
- Le Guern, C., Baranger, P., Crouzet, C., Bodéan, F., Conil, P., 2003. Arsenic trapping by iron oxyhydroxides and carbonates at hydrothermal spring outlets. *Appl. Geochemistry* 18, 1313–1323. doi:10.1016/S0883-2927(03)00053-2
- Lewicki, J.L., Hilley, G.E., Shelly, D.R., King, J.C., McGeehin, J.P., Mangan, M., Evans, W.C., 2014. Crustal migration of CO₂-rich magmatic fluids recorded by tree-ring radiocarbon and seismicity at Mammoth Mountain, CA, USA. *Earth Planet. Sci. Lett.* 390, 52–58. doi:10.1016/j.epsl.2013.12.035
- Lewicki, J.L., Oldenburg, C., 2005. Near-Surface CO₂ Monitoring And Analysis To Detect Hidden Geothermal Systems, in: *Thirtieth Workshop on Geothermal Reservoir Engineering*. Stanford, California.
- Little, M.G., Jackson, R.B., 2010. Potential impacts of leakage from deep CO₂ geosequestration on overlying freshwater aquifers. *Environ. Sci. Technol.* 44, 9225–32. doi:10.1021/es102235w
- Lu, H.-Y., Lin, C.-K., Lin, W., Liou, T.-S., Chen, W.F., Chang, P.Y., 2011. A natural analogue for CO₂ mineral sequestration in Miocene basalt in the Kuanhsi-Chutung area, Northwestern Taiwan. *Int. J. Greenh. Gas Control* 5, 1329–1338.

doi:10.1016/j.ijggc.2011.05.037

- Marks, N., Schiffman, P., Zierenberg, R.A., Franzson, H., Fridleifsson, G.Ó., 2010. Hydrothermal alteration in the Reykjanes geothermal system: Insights from Iceland deep drilling program well RN-17. *J. Volcanol. Geotherm. Res.* 189, 172–190. doi:10.1016/j.jvolgeores.2009.10.018
- Markússon, S.H., Stefánsson, A., 2011. Geothermal surface alteration of basalts, Krýsuvík Iceland — Alteration mineralogy, water chemistry and the effects of acid supply on the alteration process 206, 46–59. doi:10.1016/j.jvolgeores.2011.05.007
- Marques, J., Andrade, M., Carreira, P.M., Eggenkamp, H.G.M., Graça, R.C., Aires-Barros, L., Antunes da Silva, M., 2006. Chemical and isotopic signatures of Na/HCO₃/CO₂-rich geofluids, North Portugal. *Geofluids* 6, 273–287. doi:10.1111/j.1468-8123.2006.00144.x
- Martin, E., Paquette, J.L., Bosse, V., Ruffet, G., Tiepolo, M., Sigmarsson, O., 2011. Geodynamics of rift–plume interaction in Iceland as constrained by new ⁴⁰Ar/³⁹Ar and in situ U–Pb zircon ages. *Earth Planet. Sci. Lett.* 311, 28–38. doi:10.1016/j.epsl.2011.08.036
- Martin, E., Sigmarsson, O., 2010. Thirteen million years of silicic magma production in Iceland: Links between petrogenesis and tectonic settings. *Lithos* 116, 129–144. doi:10.1016/j.lithos.2010.01.005
- Matter, J.M., Broecker, W.S., Gislason, S.R., Gunnlaugsson, E., Oelkers, E.H., Stute, M., Sigurdardóttir, H., Stefánsson, A., Alfredsson, H.A., Aradóttir, E.S., Axelsson, G., Sigfússon, B., Wolff-Boenisch, D., 2011. The CarbFix Pilot Project—Storing carbon dioxide in basalt. *Energy Procedia* 4, 5579–5585. doi:10.1016/j.egypro.2011.02.546
- Matter, J.M., Kelemen, P.B., 2009. Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation. *Nat. Geosci.* 2, 837–841. doi:10.1038/ngeo683
- Mattey, D.P., 1991. Carbon dioxide solubility and carbon isotope fractionation in basaltic melt. *Geochim. Cosmochim. Acta* 55, 3467–3473. doi:10.1016/0016-7037(91)90508-3
- Matthews, A., Fouillac, C., Hill, R., O’Nions, R.K., Oxburgh, E.R., 1987. Mantle-derived volatiles in continental crust: the Massif Central of France. *Earth Planet. Sci. Lett.* 85, 117–128.
- McGrail, B.P., Schaef, H.T., Ho, A.M., Chien, Y.-J., Dooley, J.J., Davidson, C.L., 2006. Potential for carbon dioxide sequestration in flood basalts. *J. Geophys. Res.* 111, 1–13. doi:10.1029/2005JB004169
- McGrail, B.P., Spane, F.A., Sullivan, E.C., Bacon, D.H., Hund, G., 2011. The Wallula basalt sequestration pilot project. *Energy Procedia* 4, 5653–5660. doi:10.1016/j.egypro.2011.02.557
- Murray, J., 1975. The interaction of metal ions at the manganese dioxide-solution interface. *Geochim. Cosmochim. Acta* 39, 505–519.
- Navarre-Sitchler, A., Thyne, G., 2007. Effects of carbon dioxide on mineral weathering rates at earth surface conditions. *Chem. Geol.* 243, 53–63. doi:10.1016/j.chemgeo.2007.05.009
- Neuhoff, P., Fridriksson, T., Arnórsson, S., Bird, D.K., 1999. Porosity evolution and mineral paragenesis during low-grade metamorphism of basaltic lavas at Teigarhorn, eastern Iceland. *Am. J. Sci.* 299, 467–501.

- Newell, D.L., Jessup, M.J., Cottle, J.M., Hilton, D.R., Sharp, Z.D., Fischer, T.P., 2008. Aqueous and isotope geochemistry of mineral springs along the southern margin of the Tibetan plateau: Implications for fluid sources and regional degassing of CO₂. *Geochemistry, Geophys. Geosystems* 9 (8), Q08014. doi:10.1029/2008GC002021
- Ni, H., Keppler, H., 2013. Carbon in Silicate Melts. *Rev. Mineral. Geochemistry* 75, 251–287. doi:10.2138/rmg.2013.75.9
- O'Day, P., 2006. Chemistry and mineralogy of arsenic. *Elements* 2, 77–83. doi:10.2113/gselements.2.2.77
- Oelkers, E.H., Cole, D.R., 2008. Carbon Dioxide Sequestration A Solution to a Global Problem. *Elements* 4, 305–310. doi:10.2113/gselements.4.5.305
- Oelkers, E.H., Gislason, S.R., Matter, J., 2008. Mineral Carbonation of CO₂. *Elements* 4, 333–337. doi:10.2113/gselements.4.5.333
- Ólafsson, J., Riley, J., 1978. Geochemical studies on the thermal brine from Reykjanes (Iceland). *Chem. Geol.* 21, 219–237.
- Ólafsson, M., Bjarnason, J.Ö., 2000. Chemistry of fumaroles and hot springs in the Torfajökull geothermal area, South Iceland, in: *Proceedings World Geothermal Congress. Kyushu - Tohoku, Japan*, pp. 1547–1552.
- Olsen, N.J., Bird, D.K., Arnórsson, S., 2011. Arsenic redistribution in Icelandic crust. M.Sc. Thesis, Stanford University.
- Olsen, N.J., Bird, D.K., Arnórsson, S., Fridriksson, T., Fridleifsson, G.Ó., Elders, W.A., 2010. Iceland Deep Drilling Project (IDDP): Arsenic Distribution and Mobility in Active and Fossil Geothermal Systems in Iceland. *Proc. World Geotherm. Congr.*
- Onishi, H., Sandell, E., 1955. Geochemistry of arsenic. *Geochim. Cosmochim. Acta* 7, 1–33.
- Pálmason, G., Arnórsson, S., Fridleifsson, I.B., Kristmannsdóttir, H., Saemundsson, K., Stefánsson, V., Steingrímsson, B., Tómasson, J., 1979. The Iceland crust: Evidence from drillhole data on structure and processes, in: *Maurice Ewing Series*, no. 2. Talwani, M., Harrison, C.G., Hayes, D.E. (Eds.), *Deep Drilling Results in the Atlantic Ocean: Oceanic Crust*. Am Geophys Union, Washington, D.C., pp. 43–65.
- Pan, V., Holloway, J.R., Hervig, R.L., 1991. The pressure and temperature dependence of carbon dioxide solubility in tholeiitic basalt melts. *Geochim. Cosmochim. Acta* 55, 1587–1595. doi:10.1016/0016-7037(91)90130-W
- Parks, M.M., Caliro, S., Chiodini, G., Pyle, D.M., Mather, T.A., Berlo, K., Edmonds, M., Biggs, J., Nomikou, P., Raptakis, C., 2013. Distinguishing contributions to diffuse CO₂ emissions in volcanic areas from magmatic degassing and thermal decarbonation using soil gas ²²²Rn–^δ¹³C systematics: Application to Santorini volcano, Greece. *Earth Planet. Sci. Lett.* 377–378, 180–190. doi:10.1016/j.epsl.2013.06.046
- Pauwels, H., Fouillac, C., Goff, F., Vuataz, F.D., 1997. The isotopic and chemical composition of CO₂-rich thermal waters in the Mont-Dore region (Massif-Central, France). *Appl. Geochemistry* 12, 411–427.
- Pawley, A.R., Holloway, J.R., McMillan, P.F., 1992. The effect of oxygen fugacity on the solubility of carbon-oxygen fluids in basaltic melt. *Earth Planet. Sci. Lett.* 110, 213–225.

doi:10.1016/0012-821X(92)90049-2

- Peiffer, L., Bernard-Romero, R., Mazot, A., Taran, Y.A., Guevara, M., Santoyo, E., 2014. Fluid geochemistry and soil gas fluxes (CO_2 – CH_4 – H_2S) at a promissory Hot Dry Rock Geothermal System: The Acoculco caldera, Mexico. *J. Volcanol. Geotherm. Res.* 284, 122–137. doi:10.1016/j.jvolgeores.2014.07.019
- Peuble, S., Godard, M., Luquot, L., Andreani, M., Martinez, I., Gouze, P., 2015. CO_2 geological storage in olivine rich basaltic aquifers: New insights from reactive-percolation experiments. *Appl. Geochemistry* 52, 174–190. doi:10.1016/j.apgeochem.2014.11.024
- Pope, E.C., Bird, D.K., Arnórsson, S., Fridriksson, T., Elders, W.A., Fridleifsson, G.Ó., 2009. Isotopic constraints on ice age fluids in active geothermal systems: Reykjanes, Iceland. *Geochim. Cosmochim. Acta* 73, 4468–4488. doi:10.1016/j.gca.2009.03.033
- Pope, E.C., Bird, D.K., Arnórsson, S., 2014. Stable isotopes of hydrothermal minerals as tracers for geothermal fluids in Iceland. *Geothermics* 49, 99–110. doi:10.1016/j.geothermics.2013.05.005
- Poreda, R.J., Craig, H., Arnórsson, S., Welhan, J.A., 1992. Helium-Isotopes in Icelandic Geothermal Systems: 1. ^3He , gas chemistry, and ^{13}C relations. *Geochim. Cosmochim. Acta* 56, 4221–4228.
- Rogers, K.L., Neuhoﬀ, P.S., Pedersen, A.K., Bird, D.K., 2006. CO_2 metasomatism in a basalt-hosted petroleum reservoir, Nuussuaq, West Greenland. *Lithos* 92, 55–82. doi:10.1016/j.lithos.2006.04.002
- Rosenbauer, R.J., Thomas, B., Bischoﬀ, J.L., Palandri, J., 2012. Carbon sequestration via reaction with basaltic rocks: Geochemical modeling and experimental results. *Geochim. Cosmochim. Acta* 89, 116–133. doi:10.1016/j.gca.2012.04.042
- Sano, Y., Urabe, A., Wakita, H., Chiba, H., Sakai, H., 1985. Chemical and Isotopic Compositions of Gases in Geothermal Fluids in Iceland. *Geochem. J.* 19, 135–148.
- Schaef, H.T., McGrail, B.P., Owen, A.T., 2010. Carbonate mineralization of volcanic province basalts. *Int. J. Greenh. Gas Control* 4, 249–261. doi:10.1016/j.ijggc.2009.10.009
- Schecher, W.D., Driscoll, C.T., 1987. An evaluation of uncertainty associated with aluminum equilibrium calculations. *Water Resour. Res.* 23, 525–534. doi:10.1029/WR023i004p00525
- Seifritz, W., 1990. CO_2 disposal by means of silicates. *Nature* 345, 486.
- Sharp, Z.D., 2006. *Principles of Stable Isotope Geochemistry*. Prentice-Hall Inc., Upper Saddle River, N.J.
- Siebe, C., Goff, F., Armienta, M.A., Counce, D., Poreda, R., Chipera, S., 2007. Geology and hydrogeochemistry of the Jungapeo CO_2 -rich thermal springs, State of Michoacán, Mexico. *J. Volcanol. Geotherm. Res.* 163, 1–33. doi:10.1016/j.jvolgeores.2007.03.008
- Sigurdsson, H., 1970. Structural origin and plate tectonics of the Snæfellsnes volcanic zone, western Iceland. *Earth Planet. Sci. Lett.* 10, 129–135. doi:10.1016/0012-821x(70)90074-9
- Singleton, G.L., Révész, K., Coplen, T.B., 2012. Determination of the $\delta^{13}\text{C}$ of Dissolved Inorganic Carbon in Water; RSIL Lab Code 1710, in: Révész, K., Coplen, T. (Eds.), *Methods of the Reston Stable Isotope Laboratory: U.S. Geological Survey Techniques and Methods*, Book 10. p. 28.

- Sinton, J., Grönvold, K., Sæmundsson, K., 2005. Postglacial eruptive history of the Western Volcanic Zone, Iceland. *Geochemistry, Geophys. Geosystems* 6, 1–34. doi:10.1029/2005GC001021
- Steefel, C., Lasaga, A., 1994. A coupled model for transport of multiple chemical species and kinetic precipitation/dissolution reactions with application to reactive flow in single phase hydrothermal systems. *Am. J. Sci.*
- Steefel, C.I., Appelo, C.A.J., Arora, B., Jacques, D., Kalbacher, T., Kolditz, O., Lagneau, V., Lichtner, P.C., Mayer, K.U., Meeussen, J.C.L., Molins, S., Moulton, D., Shao, H., Šimůnek, J., Spycher, N., Yabusaki, S.B., Yeh, G.T., 2015. Reactive transport codes for subsurface environmental simulation, *Computational Geosciences*. doi:10.1007/s10596-014-9443-x
- Stefánsson, A., Gíslason, S.R., 2001. Chemical weathering of basalts, southwest Iceland: effect of rock crystallinity and secondary minerals on chemical fluxes to the ocean. *Am. J. Sci.* 301, 513–556.
- Stefánsson, A., Arnórsson, S., 2002. Gas pressures and redox reactions in geothermal fluids in Iceland. *Chem. Geol.* 190, 251–271.
- Stolper, E., Fine, G., Johnson, T., Newman, S., 1987. Solubility of carbon dioxide in albitic melt. *Am. Mineral.* 72, 1071–1085.
- Stolper, E., Holloway, J.R., 1988. Experimental determination of the solubility of carbon dioxide in molten basalt at low pressure. *Earth Planet. Sci. Lett.* 87, 397–408. doi:10.1016/0012-821X(88)90004-0
- Sveinbjörnsdóttir, Á., Johnsen, S., Arnórsson, S., 1995. The use of stable isotopes of oxygen and hydrogen in geothermal studies in Iceland. *Proc. World Geotherm. Congr. Florence, Italy* 1043–1048.
- Taylor, B.E., 1986. Magmatic Volatiles: Isotopic Variation of C, H, and S, in: *Reviews in Mineralogy and Geochemistry*. pp. 185–226.
- Thordarson, T., Höskuldsson, Á., 2008. Postglacial volcanism in Iceland. *Jökull* 197–228.
- Tómasson, J., Kristmannsdóttir, H., 1972. High temperature alteration minerals and thermal brines, Reykjanes, Iceland. *Contrib. to Mineral. Petrol.* 36, 123–134. doi:10.1007/BF00371183
- Vuataz, F.D., Goff, F., 1986. Isotope geochemistry of thermal and nonthermal waters in the Valles Caldera, Jemez Mountains, Northern New Mexico. *J. Geophys. Res.* 91, 1835. doi:10.1029/JB091iB02p01835
- Walker, G., 1966. Acid volcanic rocks in Iceland. *Bull. Volcanol.* 29, 375–402.
- Wallace, P.J., Plank, T., Edmonds, M., Hauri, E.H., 2015. Volatiles in Magmas, in: Sigurdsson, H. (Ed.), *The Encyclopedia of Volcanoes*. Academic Press, Inc., New York, New York, pp. 163–183. doi:10.1016/B978-0-12-385938-9.00007-9
- Weaver, T.R., Cartwright, I., Tweed, S.O., Ahearne, D., Cooper, M., Czapnik, K., Tranter, J., 2006. Controls on chemistry during fracture-hosted flow of cold CO₂-bearing mineral waters, Daylesford, Victoria, Australia: Implications for resource protection. *Appl. Geochemistry* 21, 289–304. doi:10.1016/j.apgeochem.2005.09.011
- WHO, 2011. Guidelines for drinking-water quality.

- Wigley, M., Kampman, N., Chapman, H.J., Dubacq, B., Bickle, M.J., 2013. In situ redeposition of trace metals mobilized by CO₂-charged brines. *Geochemistry, Geophys. Geosystems* 14, 1321–1332. doi:10.1002/ggge.20104
- Wigley, M., Kampman, N., Dubacq, B., Bickle, M., 2012. Fluid-mineral reactions and trace metal mobilization in an exhumed natural CO₂ reservoir, Green River, Utah. *Geology* 40, 555–558. doi:10.1130/G32946.1
- Wilkin, R.T., Digiulio, D.C., 2010. Geochemical impacts to groundwater from geologic carbon sequestration: controls on pH and inorganic carbon concentrations from reaction path and kinetic modeling. *Environ. Sci. Technol.* 44, 4821–7. doi:10.1021/es100559j
- Winkel, L.H.E., Casentini, B., Bardelli, F., Voegelin, A., Nikolaidis, N.P., Charlet, L., 2013. Speciation of arsenic in Greek travertines: Co-precipitation of arsenate with calcite. *Geochim. Cosmochim. Acta* 106, 99–110. doi:10.1016/j.gca.2012.11.049
- Wolery, T.J., 1992. EQ3/6: software package for geochemical modeling of aqueous systems: Package overview and installation guide (version 7.0). Lawrence Livermore National Laboratory Report UCRL-MA-110662 PT I, Livermore, California.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2006. The effect of crystallinity on dissolution rates and CO₂ consumption capacity of silicates. *Geochim. Cosmochim. Acta* 70, 858–870. doi:10.1016/j.gca.2005.10.016

Figure Captions

Figure 1. Generalized geologic map of Iceland showing the neovolcanic zones, active low- and high-temperature geothermal systems, previous location of the MAR and study areas. SISZ: South Iceland Seismic Zone; SVZ: Snæfellsnes Volcanic Zone. Adapted from Martin et al. (2011) and Arnórsson (1995a,b).

Figure 2. Backscatter electron images showing the mineral assemblage of ÖL-05 (Ölkelda, Snæfellsnes) drill cuttings. (A) a vesicle is filled with quartz and rimmed with epidote and chlorite (chl) within a crystalline basalt matrix of albite, chlorite, calcite (cc) and Fe-oxide, 129 m; (B) other vesicles are filled with microcrystalline calcite with euhedral quartz, Fe-oxides, and laths of kaolinite on the walls, 204 m; (C) epidote is present in veins with calcite filling void space and euhedral pyrite (pyr) is present throughout the Ölkelda drill cuttings, 204 m.

Figure 3. Backscatter electron images showing the mineral assemblage of HE-07 drill cuttings (Hæðarendi, SISZ). (A) a matrix of silica, calcite (cc), chlorite (chl) and accessory titanite has replaced basaltic glass, and Ti-oxides rim a vesicle, 381 m; (B) calcite replaces variably albitized (alb) Ca-Na plagioclase feldspar (plag), 426 m; (C) chlorite and calcite replaces albite, 426 m; (D) relict clinopyroxene is replaced nearly completely by calcite with veins of chlorite, K-feldspar (Ksp) partially replaces plagioclase, 381 m.

Figure 4. Aqueous phase ΣCO_2 of Icelandic fluids as a function of temperature. CO₂-rich fluids data from this study; geothermal fluids data from Arnórsson (1995a,b), Kaasalainen and

Stefánsson (2012), Poreda et al. (1992), and Stefánsson and Arnórsson (2002); N. Iceland groundwater data from Arnórsson et al. (2002); high-DIC surface water data from Flaathen et al. (2009).

Figure 5. (A) CO₂-rich waters of this study on a ternary bicarbonate-chloride-sulfate diagram plot in the immature field and are classified as HCO₃ or NaCl type waters. Note that HCO₃/10 is used on the bicarbonate-chloride-sulfate ternary diagram so that the data do not cluster near the bicarbonate apex. (B) Total dissolved solids content as a function of ΣCO₂ (aq) of Icelandic CO₂-rich waters, N. Iceland groundwater, high DIC surface water, and geothermal fluids. (C) pH as a function of ΣCO₂ (aq) of Icelandic fluids; pH of geothermal fluids (Arnórsson, 1995b) and CO₂-rich fluids is the calculated in situ pH, but all other fluids are measured pH. See Fig. 4 caption for references.

Figure 6. Divalent cation concentration as a function of (A) ΣCO₂ (aq) and (B) temperature of Icelandic CO₂-rich waters, N. Iceland groundwater, high DIC surface water, and geothermal fluids. See Fig. 4 for references.

Figure 7. Concentration of SiO₂ and Na as a function of (A) ΣCO₂ (aq) and (B) temperature of Icelandic CO₂-rich waters, N. Iceland groundwater, high DIC surface water, and geothermal fluids. See Fig. 4 for references.

Figure 8. Concentration of As, Mn and Ni as a function of (A) ΣCO₂ (aq) and (B) temperature in CO₂-rich waters, N. Iceland groundwater, high DIC surface water and geothermal fluids. The dashed line indicates the World Health Organization guideline value for safe drinking water (As and Ni) or the health-based value for drinking water (Mn). Data sources are referenced in Fig. 4, with additional data on As in groundwater from Arnórsson (2003).

Figure 9: Chlorine and boron concentrations of the CO₂-rich samples of this study relative to the Cl/B ratio of different sources (Arnórsson and Andrésdóttir, 1995).

Figure 10. δ²H_{H₂O} as a function of δ¹⁸O_{H₂O} composition of the aqueous phase of CO₂-rich fluids in each study area. Data from this study is plotted relative to the empirically derived local meteoric water lines of Iceland (Sveinbjörnsdóttir et al., 1995) and the local meteoric groundwater from each study area (shaded blue sections) as calculated from the deuterium map of Árnason (1977). The values of groundwater from the Snæfellsnes and Seydísþólar areas overlap. Seawater from the southwest coast of Iceland plots off the chart (Ólafsson and Riley, 1978). Magmatic water plots off the chart (δ²H: ~-40 to -80‰; δ¹⁸O: ~6 to 12‰) The error on each sample is smaller than the symbol size.

Figure 11. δ¹³C_{CO₂} of the CO₂-rich fluids of this study, analyzed on either the gas phase or of the total discharge, as a function of ΣCO₂ (aq); data points boxed together are analyses of the same sample with both methods. The samples are plotted relative to the endmember range of magmatic CO₂ from the MAR in Iceland (orange shaded area), biogenic soil CO₂ and atmospheric CO₂. The range of δ¹³C_{CO₂} of geothermal fluids from the volcanic zones of the MAR is -5.3 to 2.9‰ (Barry et al, 2014; Poreda et al., 1992; Sano et al., 1985), whereas the of

$\delta^{13}\text{C}_{\text{CO}_2}$ of geothermal fluids from all volcanic areas in Iceland ranges from -18.8 to 4.6‰ (Barry et al., 2014). See text for discussion of calculation and references.

Figure 12. Schematic cross-section of a volcanic geothermal system during high-temperature activity (A) and during later cooling (B) to describe the overall conceptual model for the different stages of CO_2 -rich fluid formation. The Seydishólar fluids and steam-heated waters of Torfajökull most closely resemble the scenario depicted in (A), whereas the cold springs of the Snæfellsnes Peninsula are depicted in (B), though it is unclear whether the source of CO_2 is from ancient or more recent intrusions. As observed through drill cuttings from the Snæfellsnes Peninsula, retrograde carbonate alteration overprints fossil high-temperature hydrothermal alteration minerals (B). Note the decreased subsurface temperatures that result in increased aqueous CO_2 solubility in (B).

Figure 13. Calculated shift in $\delta^{18}\text{O}_{\text{H}_2\text{O}(\text{aq})}$ from local meteoric water at varying temperature as a function of the fraction of ^{18}O in H_2O (aq) that has been transferred to CO_2 (g) through isotope exchange via Rayleigh distillation (dashed lines). Each sample is plotted by matching the observed shift in $\delta^{18}\text{O}_{\text{H}_2\text{O}(\text{aq})}$ (as calculated from comparing the measured $\delta^{18}\text{O}_{\text{H}_2\text{O}(\text{aq})}$ to the expected $\delta^{18}\text{O}_{\text{H}_2\text{O}(\text{aq})\text{mw}}$) to the model result (dashed lines) that corresponds to its discharge temperature. This allows comparison of the predicted mass fraction of ^{18}O transferred from H_2O (aq) to CO_2 (g) for each sample.

Figure 14. Log (Q/K) of select minerals, where Log (Q/K) = 0 is equilibrium. (A) High-temperature primary and hydrothermal silicate minerals plagioclase (An70), clinocllore, Al-endmember epidote clinozoisite and diopside, and (B) Low-temperature secondary minerals calcite, the hydrated aluminosilicate kaolinite, and magnesite as a function of pH, aqueous Na concentration and temperature.

Figure 15. Log P_{CO_2} in equilibrium with ΣCO_2 (aq) or (tot), if available, as a function of temperature of CO_2 -rich fluids of this study and of Iceland geothermal fluids. The CO_2 -rich fluids are color-coded by pH. The dashed and dotted lines are the P_{CO_2} in equilibrium with the mineral reactions as labeled, czo (clinozoisite; activity = 1.0; 0.3), An70 (anorthite). Calcite equilibrium reactions are calculated using log $[a]$ of $\text{Ca}^{2+} = -2.71$.

Figure 16. Mobility of elements in the aqueous phase of Snæfellsnes samples relative to Na, where Na is 1 (solid line = 0). The dark line is the average of all Snæfellsnes samples, and the dotted lines are the maximum and minimum relative mobilities for that element.

A. Active high-temperature system

B. Retrograde low-temperature system

A. High-temperature primary and hydrothermal silicates

B. Low-temperature secondary minerals

Table 1: Equilibrium constants of mineral reactions for thermodynamic evaluation.

	Equilibrium Constants (LogK)							
	0 °C	25 °C	60 °C	100 °C	150 °C	200 °C	250 °C	300 °C
Dissolution Reactions								
High-temperature primary and hydrothermal silicate minerals								
$\text{Ca}_{0.7}\text{Na}_{0.3}\text{Al}_{1.7}\text{Si}_{2.3}\text{O}_8 = 0.7\text{Ca}^{2+} + 0.3\text{Na}^{+} + 1.7\text{AlO}_2^{-} + 2.3\text{SiO}_2(\text{aq})^{\text{a}}$ <i>An70</i>	-19.1760	-18.4440	-17.5890	-16.8650	-16.3280	-16.1740	-16.3710	-16.9040
$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8 + 16\text{H}^{+} = 5\text{Mg}^{2+} + 2\text{Al}^{3+} + 3\text{SiO}_2(\text{aq}) + 12\text{H}_2\text{O}$ <i>clinochlore</i>	76.7345	67.2391	55.7725	45.1520	34.6423	26.2016	19.0325	12.5384
$\text{Ca}_2\text{Al}_3(\text{Si}_3\text{O}_{12})(\text{OH}) + 13\text{H}^{+} = 2\text{Ca}^{2+} + 3\text{Al}^{3+} + 3\text{SiO}_2(\text{aq}) + 7\text{H}_2\text{O}$ <i>clinozoisite</i>	50.2342	43.2569	34.5540	26.2792	17.8766	10.9486	4.9262	-0.6258
$\text{CaMgSi}_2\text{O}_6 + 4\text{H}^{+} = \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{SiO}_2 + 2\text{H}_2\text{O}$ <i>diopside</i>	22.9006	20.9643	18.3539	15.8250	13.2838	11.2437	9.5226	7.9589
Low-temperature secondary minerals								
$\text{CaCO}_3 + \text{H}^{+} = \text{Ca}^{2+} + \text{HCO}_3^{-}$ <i>calcite</i>	2.2257	1.8487	1.3330	0.7743	0.0999	-0.5838	-1.3262	-2.2154
$\text{MgCO}_3 + \text{H}^{+} = \text{Mg}^{2+} + \text{HCO}_3^{-}$ <i>magnesite</i>	2.9734	2.2936	1.4383	0.5875	-0.3520	-1.2275	-2.1152	-3.1178
$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^{+} = 2\text{Al}^{3+} + 2\text{SiO}_2 + 5\text{H}_2\text{O}$ <i>kaolinite</i>	9.0182	6.8101	3.8468	0.9541	-2.0187	-4.5022	-6.7083	-8.8022
Equilibrium Assemblages								
$2\text{Ca}_2\text{Al}_2(\text{Si}_3\text{O}_{12})(\text{OH}) + 2\text{CaCO}_3 + 3\text{SiO}_2 + 2\text{H}_2\text{O} = 3\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_2 + 2\text{CO}_2(\text{g})^{\text{b}}$ <i>clinozoisite calcite quartz prehnite</i>	9.99	8.10	5.80	3.69	1.70	0.19	-1.01	-1.96
$\text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CO}_2(\text{g}) + 2\text{H}_2\text{O} = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + \text{CaCO}_3$ <i>anorthite kaolinite calcite</i>	11.4402	8.8102	6.2689	4.1180	1.9880	0.2025	-1.3293	-2.5345
$\text{CaCO}_3 + 2\text{H}^{+} = \text{Ca}^{2+} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}^{\text{b}}$ <i>calcite</i>	9.9022	9.6623	9.3857	9.1317	8.8691	8.6327	8.3940	8.1239
^a Árnórsson and Stefánsson (1999)								
^b Stefánsson and Árnórsson (2002)								

Table 2: Major hydrogeochemical features of CO₂-rich fluids (>4 mmol/kg) of this study.

Sample	Area	Location	Site type;	ISOR well #; Depth (m)	Water Type	T (°C)	T (°C)	pH	pH	Gas: liquid	ΣCO ₂ (aq)	ΣCO ₂ (total) ^c	P _{CO₂} ^d	H ₂ S (aq)	F	Cl	SO ₄	Na	K	Mg	Ca	SiO ₂	Al	Fe
						discharge ^a	pH meas.	discharge	in situ ^b		mmol/kg	mmol/kg	bar	μmol/kg	mmol/kg	mmol/kg	mmol/kg	mmol/kg	mmol/kg	mmol/kg	mmol/kg	mmol/kg	μmol/kg	μmol/kg
03CS13	Snæfellsnes	64.83210N 22.31583W	drillhole		Na-Cl	53.7	31.6	7.50	7.43		5.029		0.015	0.62	0.028	3.345	0.628	7.003	0.074	0.040	0.567	5.364	0.175	1.272
04CS13	Snæfellsnes	64.83240N 22.31563W	spring		Na-Cl	40.9	28.1	7.45	7.40		5.080		0.013	0.48	0.022	3.073	0.379	7.021	0.069	0.045	0.568	5.235	0.634	0.963
05OL13	Snæfellsnes	64.83669N 22.97664	drillhole		Na-HCO ₃	9.6	14.7	6.15	6.19		57.880		0.396	0.42	0.031	4.855	1.007	22.217	0.532	1.819	5.062	2.979	0.100	133.548
06LH13	Snæfellsnes	64.84483N 23.21995	drillhole		Na-HCO ₃	40.9	34.1	6.46	6.32	0.04	34.109	35.376	0.465	0.92	0.241	1.855	0.393	17.943	0.879	0.777	2.105	7.452	0.093	31.678
07LH13	Snæfellsnes	64.84271N 23.22246W	drillhole		Na-HCO ₃	30.7	20.7	6.36	6.31	0.04	44.760	46.370	0.493	0.30	0.126	1.933	0.463	18.869	0.676	1.785	3.721	5.759	0.032	63.742
08LH13	Snæfellsnes	64.84421N 23.22140W	spring		Na-HCO ₃	40.9	25.0	6.37	6.31		34.830		0.461	0.24	0.210	1.683	0.424	17.173	0.846	0.781	2.186	7.158	0.235	86.454
09LH13	Snæfellsnes	64.84544N 23.21788W	drillhole		Ca-HCO ₃	12.9	15.0	6.55	6.56		8.940		0.052	0.48	0.034	0.606	0.024	0.859	0.034	0.567	1.400	1.653	0.092	205.086
10OL13	Snæfellsnes	64.84837N 22.98953W	drillhole	ÖL-05; 309	Na-HCO ₃	33.0	33.5	6.28	6.25	0.03	44.470	45.604	0.533	<0.04	0.120	4.320	1.554	26.640	0.966	0.660	3.373	7.162	0.173	33.776
11OL13	Snæfellsnes	64.84873N 22.98863W	drillhole		Ca-HCO ₃	10.5	16.2	7.70	7.74		4.380		0.004	<0.04	0.013	0.406	0.119	0.984	0.060	0.313	0.792	0.696	0.101	8.599
12OL13	Snæfellsnes	64.84792N 22.99237W	drillhole	ÖL-10; 67	Na-HCO ₃	15.7	22.0	6.21	6.24	0.03	36.540	37.008	0.290	0.08	0.054	1.854	0.542	13.214	0.422	1.036	3.650	3.452	0.050	59.979
13HE01	Seydishólar	64.07554N 20.86007W	wet-steam well	HE-07; 900	Na-Cl	179.2	22.0	7.01	6.03		20.774		12.700	27.40	0.086	7.846	1.614	25.897	0.937	0.088	0.039	9.610	2.223	2.800
13KH01	Seydishólar	64.09983N 20.8453V	wet-steam well		Na-Cl	180.0	23.3	7.93	N/A		7.092		0.066	19.00	0.048	3.503	0.979	10.253	0.357	b.d.	0.287	11.609	4.907	1.048
13KH02	Seydishólar	64.08614N 20.84325	wet-steam well		Na-Cl	194.7	22.0	8.77	6.08		5.072		5.160	165.7	0.060	3.333	0.854	9.113	0.382	0.002	0.035	12.362	6.287	0.712
16CS13	Snæfellsnes	64.90147N 22.74783W	spring		Ca-HCO ₃	10.8	13.6	5.97	5.99		18.850		0.149	<0.04	0.003	0.267	0.025	2.243	0.094	1.411	1.872	1.413	1.351	8.636
17OV13	Snæfellsnes	64.88734N 23.68894W	spring		Na-Cl	9.5	10.5	4.71	4.71		33.500		0.310	<0.04	0.002	0.397	0.005	0.663	0.027	0.126	0.112	0.600	3.547	5.066
18BF13	Snæfellsnes	64.84554N 023.39437W	spring		Mg-HCO ₃	6.6	12.6	6.14	6.14		75.520		0.520	<0.04	b.d.	0.759	0.067	8.769	0.259	8.185	6.605	3.114	0.121	250.141
19BF13	Snæfellsnes	64.84657N 23.39571W	spring		Mg-HCO ₃	11.7	14.8	6.19	6.21		76.280		0.540	<0.04	0.004	0.695	0.066	8.882	0.261	8.171	6.518	3.061	0.050	250.025
20SL13	Torfajökull	63.87565N 18.94426W	spring		Na-HCO ₃	69.5	19.2	6.63	6.54		28.590		0.486	0.06	0.449	0.742	0.397	16.840	1.031	0.371	0.697	8.539	0.237	7.070
21OS13	Torfajökull	63.87915N 19.16064W	spring		Na-HCO ₃	23.8	19.9	5.67	5.65		36.610		0.458	0.20	0.002	0.419	0.036	4.066	0.358	0.343	1.058	3.428	143.736	2081.694
22LF13	Torfajökull	63.91950N 19.30914W	spring		Na-HCO ₃	91.8	19.2	6.97	6.94		16.690		0.228	0.08	0.939	2.850	0.316	16.267	0.279	0.051	0.229	3.916	0.848	0.864
23HS13	Torfajökull	63.89650N 19.24377W	spring		Na-HCO ₃	82.0	18.8	7.34	7.27		33.079		0.207	0.72	1.068	5.235	0.282	31.571	0.929	0.019	0.202	4.570	1.152	0.472
24BK13	Torfajökull	63.86407N 19.19532W	spring		Na-HCO ₃	40.0	19.6	6.15	6.08		51.020		0.790	<0.04	0.120	0.326	0.732	18.015	0.857	1.422	2.051	4.756	1.417	106.343

^a10OL13 and 13KH01 are from drilling reports. 13HE01 and 13KH02 are chalcedony reference temperatures.
^bCalculated using the WATCH program (Arnórsson et al., 1982; Bjarnason, 2010).
^cDetermined from the gas: liquid ratio measured on site.
^dP_{CO₂} in equilibrium with either ΣCO₂ (aq) or ΣCO₂ (tot).
b.d. below detection

Table 3: Trace element concentrations of CO₂-rich fluids (>4 mmol/kg) of this study.

	As	B	Ba	Li	Mn	Ni	Pb	Rb	Sr	Ti	Zn
Sample	µmol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg	µmol/kg
Detection Limit	0.001	0.006	<0.001	0.002	0.003	<0.001	0.00004	<0.001	0.001	0.001	0.003
WHO guideline ^{a,b}	0.134		5.980		7.281	1.193	0.0483				45.886
03CS13	0.024	9.058	0.012	3.209	0.279	0.070	0.000597	0.051	0.794	0.107	0.079
04CS13	0.021	8.873	0.010	3.116	0.277	0.047	0.000113	0.048	0.697	0.097	0.032
05OL13	0.066	61.496	0.128	42.488	5.108	0.110	0.000167	0.311	7.813	0.072	0.044
06LH13	0.438	35.769	0.515	66.451	3.482	0.044	0.000077	2.052	4.325	0.152	0.070
07LH13	0.279	40.943	0.119	63.324	5.586	0.300	0.000053	0.959	6.962	0.138	0.168
08LH13	0.428	32.809	0.542	60.797	4.799	0.022	0.000132	1.893	4.019	0.137	0.058
09LH13	0.035	1.227	0.059	1.929	153.519	0.017	b.d.	0.032	1.705	0.040	0.092
10OL13	0.288	88.863	0.884	70.648	2.425	0.039	0.000886	1.207	8.737	0.141	0.295
11OL13	0.004	1.638	0.036	1.002	0.959	0.011	b.d.	0.043	1.339	0.017	0.033
12OL13	0.062	30.179	0.302	29.510	3.850	0.037	0.000262	0.362	6.829	0.076	0.285
13HE01	0.732	78.103	0.455	41.777	0.152	0.209	0.000212	1.355	0.947	0.193	0.045
13KH01	0.033	36.164	0.074	23.569	0.250	0.073	0.000162	0.565	1.177	0.196	0.017
13KH02	0.052	34.403	0.079	22.651	0.063	0.099	0.000090	0.689	0.821	0.182	0.015
16CS13	0.000	2.357	0.031	1.475	1.751	0.086	b.d.	0.008	0.151	0.029	0.052
17OV13	0.001	0.717	0.088	0.043	0.590	0.084	0.000055	0.012	0.228	0.015	0.063
18BF13	0.026	37.699	1.159	10.842	13.703	0.381	0.000137	0.102	10.480	0.088	0.027
19BF13	0.033	37.977	2.410	12.670	13.163	0.321	0.000079	0.180	10.129	0.099	0.046
20SL13	0.735	137.175	0.430	41.374	0.407	0.011	b.d.	1.030	1.895	0.195	0.091
21OS13	0.073	19.973	0.165	12.658	184.140	0.022	b.d.	0.496	1.497	0.071	12.162
22LF13	0.296	65.214	0.367	14.534	0.460	0.008	0.000145	0.446	0.859	0.079	0.051
23HS13	1.081	205.100	0.416	101.455	0.985	0.006	0.000148	1.857	3.944	0.105	0.006
24BK13	0.076	109.148	0.536	50.235	3.196	0.044	b.d.	0.692	4.152	0.123	0.089

^aWHO. (2011). Guidelines for drinking-water quality; (4th ed.).
^bMn value is the WHO informal "health-based value" guideline.
b.d. below detection

Table 4: Composition of the gas phase of CO₂-rich fluids (>4 mmol/kg) of this study.

Sample ^a	Area	Site type	ISOR well #; Depth (m)	Gas: liquid L/L	H ₂ S ^b μmol/kg	H ₂ mmol/kg	CH ₄ mmol/kg	N ₂ mmol/kg	O ₂ mmol/kg	Ar mmol/kg	CO ₂ ^c mmol/kg	N ₂ /Ar	H ₂ Vol. %	CH ₄ Vol. %	N ₂ Vol. %	O ₂ Vol. %	Ar Vol. %	CO ₂ Vol. %	Sum Vol %
03CS13	Snæfellsnes	drillhole				0.000	0.000	0.277	0.010	0.006		47.14	0	0	92.54	3.45	1.96		98.0
04CS13	Snæfellsnes	spring			0.000	0.000	0.000	0.142	0.040	0.003		43.88	0	0	79.07	22.23	1.80		103.1
05OL13	Snæfellsnes	drillhole			1.931	0.000	0.000	0.251	0.019	0.005		53.82	0	0	92.04	6.92	1.71		100.7
06LH13	Snæfellsnes	drillhole		0.04	1.937	0.001	0.005	0.051	0.001	0.001	1.235	59.69	0.09	0.41	3.98	0.06	0.07	95.40	100.0
07LH13	Snæfellsnes	drillhole		0.04		0.000	0.000	0.184	0.020	0.004	2.496	43.19	0	0	6.81	0.74	0.16	92.28	100.0
08LH13	Snæfellsnes	spring			0.000	0.000	0.000	0.215	0.072	0.003		71.52	0	0	76.72	25.74	1.07		103.5
09LH13	Snæfellsnes	drillhole				0.000	0.027	0.871	0.200	0.011		80.42	0	2.40	78.63	18.08	0.98		100.1
10OL13	Snæfellsnes	drillhole	ÖL-05; 309	0.03	0.971	0.006	0.001	0.002	0.000	0.000	2.531	Ar = 0	0.23	0.04	0.09	0.01	0.00	98.62	99.0
11OL13	Snæfellsnes	drillhole			17.245	0.000	0.000	1.086	0.252	0.014		78.73	0	0	80.29	18.64	1.02		100.0
12OL13	Snæfellsnes	drillhole	ÖL-10; 67	0.03	0.000	0.000	0.000	4.477	0.985	0.054	2.592	82.28	0	0	55.63	12.25	0.68	32.20	100.8
13HE01	Seydishólar	wet-steam well	HE-07; 900		<0.794 ^b	0.019	0.058	0.458	0.023	0.008	5.219	57.53	0.34	1.01	7.97	0.41	0.14	90.76	100.6
13KH02	Seydishólar	wet-steam well			55.600 ^b	0.043	0.084	2.912	0.000	0.047	0.651	61.62	1.18	2.29	79.54	0	1.29	17.77	102.1
16CS13	Snæfellsnes	spring			0.214	0.000	0.000	0.066	0.032	0.001		47.22	0	0	62.01	29.65	1.31		93.0
17OV13	Snæfellsnes	spring				0.000	0.000	3.398	0.903	0.041		82.08	0	0	79.48	21.12	0.97		101.6
18BF13	Snæfellsnes	spring				0.000	0.000	0.000	0.000	0.000		Ar = 0	0	0	0	0	0		
19BF13	Snæfellsnes	spring			1.942	0.003	0.014	0.142	0.007	0.002		57.27	1.86	8.09	83.64	4.29	1.46		99.3
20SL13	Torfajökull	spring			0.000	0.000	0.000	0.590	1.411	0.063		9.44	0	0	8.84	21.13	0.94		30.9
22LF13	Torfajökull	spring				0.000	0.000	0.055	0.019	0.001		63.39	0	0.36	72.28	25.48	1.14		99.3
23HS13	Torfajökull	spring			0.000	0.000	0.000	0.377	0.120	0.005		74.59	0	0	78.39	24.84	1.05		104.3
24BK13	Torfajökull	spring			0.042	0.000	0.000	0.168	0.050	0.003		60.19	0	0	79.50	23.59	1.32		104.4

^aWe did not obtain gas samples from 21OS13 and 13KH01.
^bBased on titration of KOH solution.
^cValue from Arnórsson et al. (2010).

Table 5: Stable isotope composition of CO₂-rich fluids (>4 mmol/kg) of this study.

Sample	$\delta^2\text{H}$ (‰ VSMOW)	$\delta^{18}\text{O}$ (‰ VSMOW)	$\delta^{13}\text{C}$ (‰ PDB)	Type of $\delta^{13}\text{C}$ sample*	Type of analysis
03CS13	-66.46	-10.09	-15.08	aq + gas	SrCO ₃ combustion
04CS13	-63.22	-10.10	-12.71	aq + gas	SrCO ₃ combustion
05OL13	-61.23	-9.55	-3.92	aq + gas	SrCO ₃ combustion
06LH13	-58.46	-9.10			
07LH13	-60.29	-9.11	-6.21	aq + gas	SrCO ₃ combustion
			-5.89	gas	gas analysis
08LH13	-59.45	-9.12	-5.07	aq + gas	SrCO ₃ combustion
09LH13	-55.16	-8.30	-17.81	aq + gas	SrCO ₃ combustion
10OL13	-64.01	-10.13	-3.23	aq + gas	SrCO ₃ combustion
			-4.09	gas	gas analysis
11OL13	-57.10	-8.72	-14.48	aq + gas	SrCO ₃ combustion
12OL13	-58.08	-9.14	-7.35	aq + gas	SrCO ₃ combustion
			-8.74	gas	gas analysis
13HE01	-87.72	-9.17			
13KH01	-87.48	-9.91			
13KH02	-89.76	-10.85			
16CS13	-58.08	-9.06	-1.34	aq + gas	SrCO ₃ combustion
17OV13	-57.82	-8.26	1.82	gas	gas analysis
18BF13	-55.60	-8.92	-2.45	gas	gas analysis
19BF13	-56.67	-9.16	-3.07	aq + gas	SrCO ₃ combustion
20SL13	-73.83	-10.64			
21OS13	-74.29	-10.83			
22LF13	-76.13	-11.17			
23HS13	-91.80	-11.88			
24BK13	-77.55	-11.34			
*All $\delta^{13}\text{C}$ analyses were done by cavity ring-down spectroscopy; aq + gas samples were measured by SrCO ₃ combustion; gas samples were measured directly.					