Rare earth element concentrations in geothermal fluids and epidote from the Reykjanes geothermal system, Iceland

Conference Paper · April 2015

2 authors:

Andrew P.G. Fowler
University of Minnesota
41 PUBLICATIONS 459 CITATIONS
SEE PROFILE

Robert A. Zierenberg
University of California, Davis
371 PUBLICATIONS 2,165 CITATIONS
SEE PROFILE

Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

Rare Earth Element Concentrations in Geothermal Fluids and Epidote from the Reykjanes Geothermal System, Iceland

Andrew P.G. Fowler and Robert A. Zierenberg

Department of Earth and Planetary Sciences, One Shields Avenue, Davis, CA 95616, USA

apfowler@ucdavis.edu

Keywords: Iceland Deep Drilling Project, Reykjanes Geothermal System, Rare Earth Elements, Epidote

ABSTRACT

The Reykjanes geothermal system is located on the western tip of the Reykjanes Peninsula, approximately 50 km southwest of Reykjavík, Iceland. The Reykjanes geothermal fluid is seawater, chemically modified through boiling and interaction with basaltic host rock, and bares many similarities to mid ocean ridge (MOR) hydrothermal fluids. The Reykjanes geothermal system is the proposed location of the next Iceland Deep Drilling Project (IDDP) well, IDDP-2. The IDDP-2 effort proposes to return fluid and rock samples from the super-critical reaction zone of a sea-floor style hydrothermal system for the first time. Previous studies of seafloor hydrothermal systems provide an analog for conditions that might be encountered during drilling of IDDP-2, however, to use MOR hydrothermal systems as an analog for Reykjanes (and vice versa) we need to understand the key differences.

We have developed protocols to sample and measure rare earth element (REE) concentrations in high salinity geothermal fluids from Reykjanes. We have also measured REE *in-situ* in epidote precipitated from geothermal fluids in Reykjanes drill cutting and drill core samples using Laser Ablation ICP-MS (LA-ICP-MS). Additionally we present results for REE analysis of wholerock samples from the Reykjanes RN-17B IDDP drillcore. Results indicate that 1) REE in Reykjanes fluid samples are enriched in light REE and have large positive Eu anomalies relative to the basaltic host rock, 2) REE in Reykjanes fluids are approximately two orders of magnitude less enriched in REE than has been observed in a range of seafloor hydrothermal vent fluids, and show relative light REE enrichment 3) The REE content of epidote ranges from the maximum observed for whole rock samples to below the method detection limit, and 4) Chondrite normalized REE concentrations in epidote fall on a spectrum between wholerock REE and seafloor hydrothermal fluid REE, and are dissimilar to Reykjanes fluids sampled at the well head.

Our data suggests that Reykjanes geothermal fluids sampled at the wellhead have undergone significant REE loss, and the chondrite normalized REE pattern of Reykjanes geothermal fluids at depth is better reflected by hydrothermal epidote. We suggest the REE content of Reykjanes fluids at depth are more similar to MOR fluids, and that the REE content of Reykjanes fluids is derived from localized fluid-rock interaction is predominantly controlled by seawater/rock ratio and temperature.

LA-ICP-MS analysis of epidote precipitated in veins sequentially over time may provide a means to identify favorable high water/rock ratio and high temperature zones at depth in the Reykjanes geothermal system. Because of the minimal sample preparation and analytical procedures offered by LA-ICP-MS, we will be able to analyze samples in near real time and inform IDDP of high temperature reaction zones that may be encountered while drilling into the supercritical zone of a hydrothermal system prior to attempting to produce hydrothermal fluids from the well.

1. INTRODUCTION

1.1 Rare Earth Element Mobility in Geothermal Systems

The rare earth elements (REE) for the purposes of this study refer to the 14 lanthanide elements from La through Lu, excluding the radioactive element Pm. Light REE (LREE) refers to the elements La through Sm, and heavy REE (HREE) refers to the elements Eu through La.

Several studies have suggested that REE are immobile during metamorphism or hydrothermal alteration (i.e. Thorpe, 1972; Herrmann et al., 1974; Ferrara et al., 1976; Menzies et al., 1977) unless alteration is extreme and involves very high water-rock ratios (Hanson 1980). Also, the extremely low REE concentrations in hydrothermal fluids have been suggested as evidence that the REE budget of host rocks is unaffected by hydrothermal alteration (i.e. Michard et al., 1983; Michard, 1989). Contrary to this, there is strong evidence suggesting that REE are mobile from rocks during hydrothermal alteration (i.e. Alderton et al., 1980; Taylor and Fryer, 1980; Palacios et al, 1986; Corey and Chatterjee, 1989; Arribas et al, 1995; Fulignati et al., 1999), particularly during seawater-basalt interaction (Frey et al, 1974; Wood et al., 1976; Hellman and Henderson, 1977; Ludden, 1979). Also, REE concentrations in hydrothermal fluids have been shown to range from below detection to chondritic values (Wood, 2002), suggesting that REE are significantly mobilized by hydrothermal processes under certain circumstances. This has lead to the suggestion that REE content of geothermal fluids and precipitated alteration minerals may be used as tracers for geothermal fluids and processes (Lottermoser, 1992, Wood, 2002; Humphris and Bach, 2004).

Collection of REE data for geothermal fluids is non-trivial as most have very low REE concentrations in conjunction with high concentrations of total dissolved solids, resulting in significant analytical interferences that make accurate determination of the REE distribution challenging. This is further complicated by partitioning of REE between fluid and vapor phases during fluid sampling (Möller et al., 2008), as well as the potential of REE to co-precipitate or adsorb onto silica or oxide phases formed during or subsequent to the initial sampling. The REE content of fluids may be further modified by reaction with host rock or precipitation along the flow path. The behavior of REE in fluids as a function of temperature, pH, and salinity are generally understood based on laboratory experiments and thermodynamic calculations (Hass et al., 1995; Migdisov and Jones, 2008: Migdisov et al., 2009).

However current technology and expense precludes collection of multiple fluid samples at multiple depth intervals in active geothermal systems. To evaluate the dynamic behavior of REE over time in geothermal fluids during transport through complex subsurface fracture networks, the analysis of alteration minerals that reflect the REE content of hydrothermal fluids is required (Humphries and Bach, 2004).

Fluid/mineral partition data for REE is sparse for most geothermal minerals at typical geothermal temperature and pressure ranges. Fluid/anhydrite REE partition coefficients have been determined for MOR settings (Mills and Elderfield, 1995; Humphris and Bach, 2004), indicating a strong preference for REE in the mineral phase, with little relative REE fractionation to slightly higher preference of LREE in the fluid phase (Humphries and Bach, 2004). The results were successfully applied to understanding the evolution of fluid in the TAG hydrothermal mound (Humphries and Bach, 2004). Zoisite dissolution REE partition coefficients have been determined under amphibolite and eclogite facies metamorphic conditions (550-900°C and 0.6 to 2 GPa) (Brunsmann et al., 2001; Feineman et al., 2007), and indicate the REE are remarkably unfractionated from each other (Feineman et al., 2007). These results coupled with REE chloride complexation data (Migdisov et al., 2009) suggest the dominate control on REE fractionation between sweater hydrothermal fluids and alteration mineral phases is temperature and chloride content, as observed in MOR hydrothermal anhydrite (Humphries and Bach, 2004). Epidote was selected for this study because it is ubiquitous in Icelandic geothermal systems at a range of temperature and depth intervals, and therefore can provide an excellent fluid REE tracer.

1.2 Study Area

The Reykjanes Peninsula is a subaerial continuation of the submarine Mid Atlantic Ridge. The oblique extensional tectonic system and associated volcanism (Clifton and Kattenhorn, 2006) has resulted in significant geothermal activity along the peninsula, including the Reykjanes geothermal system (Jakobsson et al., 1968; Arnorsson, 1995), which is located at the tip of the peninsula (Figure 1).

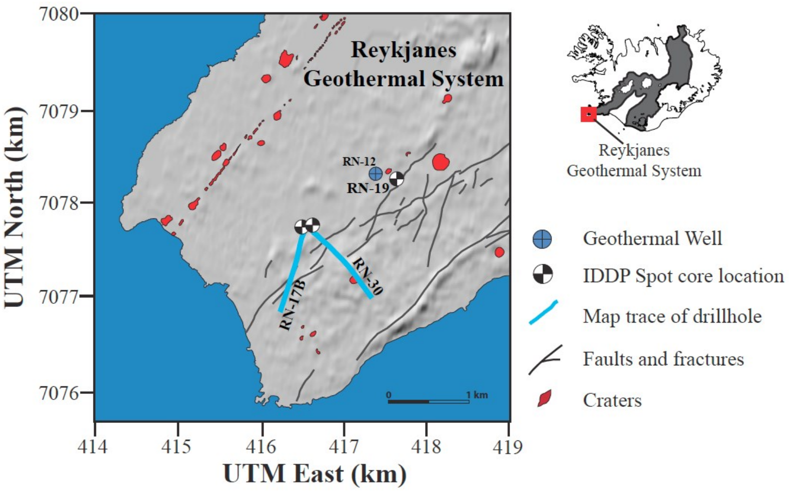

Figure 1: The Reykjanes geothermal system, Iceland.

The Reykjanes geothermal fluid is seawater, chemically modified through boiling and interaction with the basaltic host rock (Arnorsson et al., 1978; Olafsson and Riley, 1978; Sveinbjorndottir, 1986; Arnorsson, 1995). Compared to seawater, Reykjanes geothermal fluids have similar Na and Cl concentrations, increased concentrations of K, Ca, SiO_2, Fe and Al, and decreased concentrations of SO_4 and Mg. Reykjanes geothermal fluids have a reconstructed pH in the range of 5-6 (Arnorsson 1978; Reed and Spycher, 1984; Arnorsson 1995; Hardardottir et al., 2009), significantly more acidic than near neutral pH meteoric water dominated Icelandic geothermal fluids (Arnorsson, 1995).

Despite the similarities of Reykjanes geothermal fluids to those sampled at mid ocean ridges, there are some subtle differences. The deuterium content of fluids and alteration phases are significantly more negative than those sampled at mid ocean ridges (Olafsson and Riley, 1978; Pope et al., 2009). The Reykjanes geothermal system also lacks the pressure head of 2-4 km of cold seawater present at mid ocean ridge systems. As a result, Reykjanes fluids have the potential to flash and precipitate scale minerals at significantly lower temperatures and pressures than those present at MOR hydrothermal vent sites.

The Reykjanes geothermal system is also the location for the Iceland Deep Drilling Project (IDDP) supercritical well (well IDDP-2), targeted for between 4 and 6 km deep (Friðleifsson et al., 2014). The unique suite of samples available thanks to the IDDP effort provides an ideal opportunity to evaluate REE transport under hydrothermal conditions, and to evaluate the utility of REE to inform of potential conditions that may encountered in the subsurface particularly during the drilling of the supercritical IDDP-2 well.

2. METHODS

2.1 Fluid Samples

The Icelandic Geosurvey (ISOR) collected the fluid samples that we analyzed for REE, using their standard well sampling equipment and procedures. Fluid samples were collected in 60 ml HDPE sample containers using a variety of protocols to identify potential contamination sources. Twenty-five samples in total were collected from both RN-12 and RN-19, using both acid washed and non acid washed containers, both filtered and unfiltered samples, and both acidified with ultrapure HNO_3 and not acidified.

Samples were prepared manually using a modified version of the automated pre-concentration method of Zhu et al. (2010). A commercially available brand of syringe driven chelating column (SDCC) was obtained from GL Sciences (InertSEP ME-1) to preconcentrate REE and remove interfering cations from fluids prior to analysis. Reagents included ultra pure grade ammonium hydroxide, acetic acid, double-distilled sub-boiling nitric acid (2M), and Milli-Q water (18.3 MΩ). Ammonium hydroxide (2M) was used to adjust samples to pH 5, verified using a non-contact pH meter (Horriba B-213). Volumes and flow rates into the SDCC were controlled using a syringe pump. Single use, all plastic syringes were used to dispense samples and reagents. All pipette tips, luer fittings, and labware were acid washed in 3M nitric acid for a period of 1 week and rinsed with Milli-Q prior to use. Sample preparation work was completed in a ~1 m^3 acrylic glove box maintained at positive pressure with filtered (0.22 µm) air.

The procedure involved soaking SDCCs overnight in Milli-Q water prior to use. Reagents and samples were introduced to the SDCCs in the following order: 1) SDCCs were cleaned by introducing 5 ml of HNO_3 (2M) at 5 ml min^{-1}, 2) SDCCs were conditioned by introducing 2.5 ml pH 5 ammonium acetate (NH_4Ac) (1M) at 5 ml min^{-1}, 3) 22 ml of sample was loaded to the SDCCs at 5 ml min^{-1}, 4) samples were washed by introducing 2.5 ml Milli-Q at 5 ml min^{-1}, 5) barium was removed from the SDCCs by washing with 2.5 ml of $AcNH_4$ at 5 ml min^{-1}, 5) samples were eluted from the SDCCs by passing 2.2 ml HNO_3 (2M) at 5 ml min^{-1}. Samples were then spiked with an In, Re, and Bi internal standard to correct for instrumental drift.

CASS-4 seawater certified reference material was subjected the same pre-concentration procedure as unknown samples to evaluate the repeatability of the method, utilizing the REE values determined by Lawrence and Kamber, (2007). Acid mine fluid REE reference materials SCREE-1 and PPREE-1 (Verplank et al., 2001) were used to evaluate instrumental stability and the dynamic range of the instrument. SCREE-1 and PPREE-1 standards were not subjected to the preconcentration procedure due to the low pH matrix.

Fluid samples were analyzed at UC Davis using a single collector magnetic sector ICP-MS instrument (ThermoScientific Element XR) (magnetic sector ICP-MS) working in low-resolution mode and equipped with an Apex IR desolating nebulizer for increased sensitivity. Oxide production was evaluated by analyzing single element solutions (10ppb) of REE, and calibrated daily by normalizing to the $^{146}Nd/^{142}Nd^{16}O$ ratio measured from a single element Nd solution. Oxide production was determined to be less than 3% for all single element standards, and values are therefore reported uncorrected. Elemental concentrations of samples and standards were determined using a calibration curve derived from a single element barium solution and a multi-element REE, Sc, and Y solution, diluted to 100ppb, 10ppb, 1 ppb and 0.1ppb.

2.2 Epidote and Wholerock Samples

Epidote drill cutting samples from Reykjanes geothermal wells RN-12 and RN-30 were collected from the ISOR sample library located in Reykjavik, Iceland. Epidote grains from RN-12 drill cutting samples were collected at approximately 100 m intervals, and epidote grains from RN-30 drill cuttings were collected at 50 m intervals. Drill cutting samples were mounted on 1-inch epoxy rounds and polished. Epidote samples from the RN-17B IDDP drill core were prepared as polished 100 µm thick section slides. Samples were analyzed at UC Davis using laser ablation ICP-MS (LA-ICP-MS). Samples were analyzed using an Agilent 7700 quadrupole ICP-MS coupled to a Photon Instruments 193 nm excimer laser. The laser spot size used was 50 µm, with a 10 Hz repetition rate at 50% laser power. NIST 612 and NIST 614 glass were used as a calibration standard and Ca was used as an internal element standard (independently verified using electron microprobe analysis). The detection limit is defined as 3σ baseline recorded prior to and after each ablation pit. Results were processed using the Iolite data reduction software package (Paton et al., 2011).

Whole-rock samples of drill cuttings from various depth and representative samples of the different lithologic intervals in the RN-17B IDDP drill core were analyzed by quadrupole ICP-MS at the Washington State University GeoAnalytical laboratory using the technique described in Marks et al., (2010).

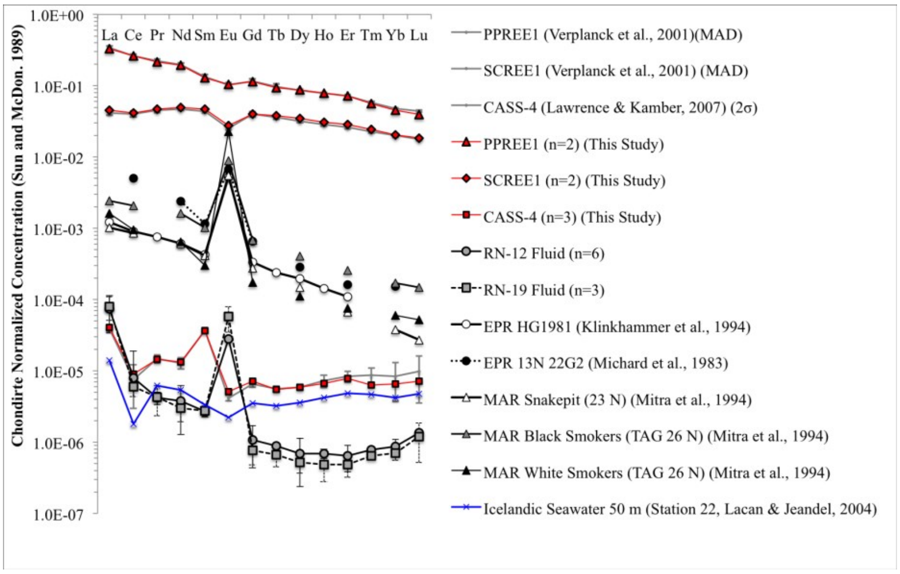

Figure 2: Chondrite normalized REE plot of results for Reykjanes RN-12 and RN-19 fluid samples (1σ error bars) and standards (2σ error bars). A subset of representative REE analyses for MOR fluids and seawater are shown for comparison.

3. RESULTS

Measured REE values for the SCREE-1, PREE-1, and CASS-4 standards fall within acceptable limits and demonstrate the stability and dynamic range of the magnetic sector ICP-MS instrument, and the validity of the fluid preconcentration method (Figure 2). The sampling protocol tests demonstrated that filtering samples or using non-acid washed containers (rinsed with sample fluid prior to collection) had little influence on the analytical results. Acidified samples yielded marginally higher values for REE, but still well within 1σ error determined by repeated CASS-4 standard measurements. The REE values for RN-12 and RN-19 fluids are therefore presented as an average value of multiple measurements of samples collected using the various sampling protocols. The REE concentrations have not been corrected for steam loss during sampling.

The REE contents of fluids sampled at the wellhead from Reykjanes wells RN-12 and RN-19 are identical within 1σ error determined by repeated CASS-4 standard measurements (Figure 2), which for all elements are < 10% RSD. RN-12 and RN-19 fluids are 2 orders of magnitude less enriched in REE than fluids reported from various MOR systems, and are enriched in LREE relative to HREE compared to MOR fluids (Figure 2). Both Reykjanes and MOR fluids have large positive Eu anomalies. Relative to seawater, Reykjanes fluids have a lower REE content with the exception of La, Ce, and Eu.

The analytical precision of LA-ICP-MS epidote analyses was determined through replicate analyses of NIST 612 and NIST 614 standards. The % RSD for all REE in the NIST 612 standard (n=36) was <8%, and the %RSD for all REE in the NIST 614 standard (n=48) was < 4%. The chondrite normalized REE content of epidote in drill cuttings from wells RN-12 and RN-30 range from below detection (0.0035 microgram/kg for La to 0.09 mg/kg for Er; ~ 1.5E-02 to 5.4E-01 on a chondrite normalized plot, respectively) to values consistent with the maximum REE content of unaltered Reykjanes tholeiite (Figure 3). The chondrite normalized La/Sm and La/Yb ratios of epidote from drill cuttings ranges from those of MOR fluids to those of wholerock samples from IDDP cores RN-17B and RN-19. Notably, the La/Sm and La/Yb ratios of epidote do not appear to match the La/Sm and La/Yb ratio of RN-12 and RN-19 fluids sampled at the wellhead (Figure 4). RN-12 and RN-19 fluids sampled at the wellhead have a high La content. Ce/Sm and Ce/Lu ratios were also calculated and also show high values relative to other samples (Figure 4). The chondrite normalized REE content and relative REE slope (La/Sm, Ce/Sm, La/Yb, and Ce/Yb ratios) of epidote in RN-12 and RN-30 do not appear to correlate with depth or REE concentration. Different epidote grains in drill cuttings returned from the same depth interval cover the full spectrum of REE variation observed (Figures 3 and 4).

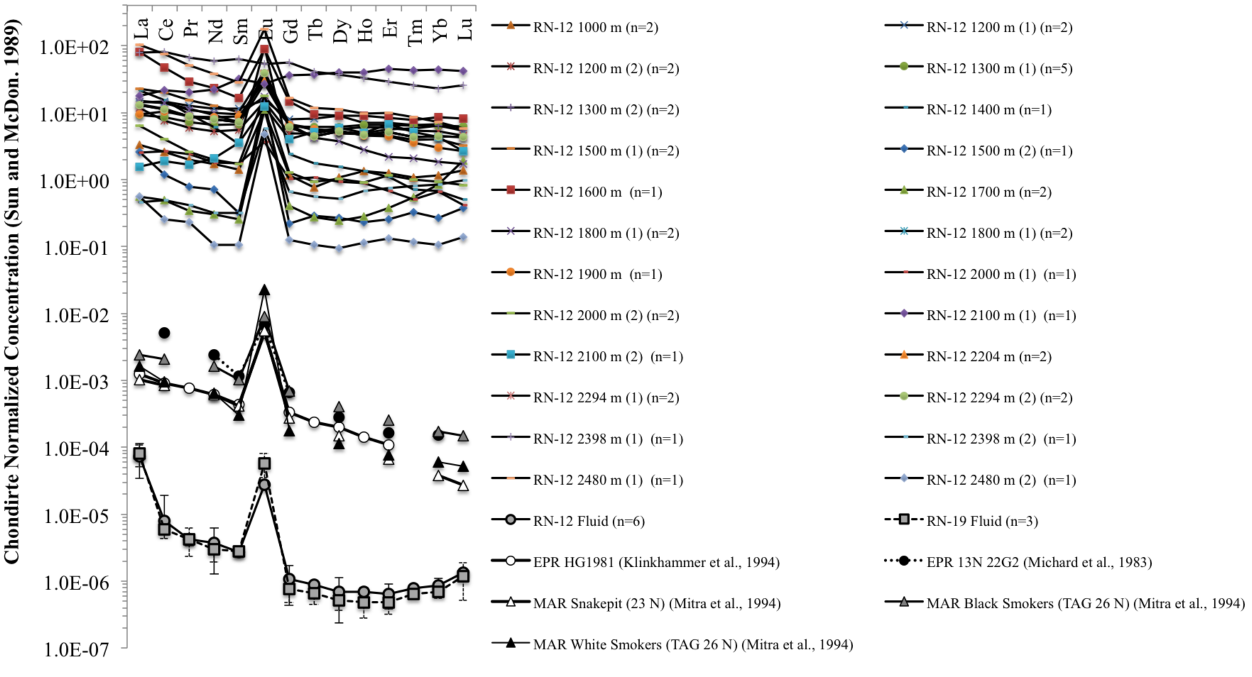

Figure 3: Chondrite normalized REE plot of LA-ICP-MS results for epidote drill cutting samples from Reykjanes well RN-12. RN-12 and RN-19 fluids (this study), and several samples from a range of MOR fluids are shown for comparison.

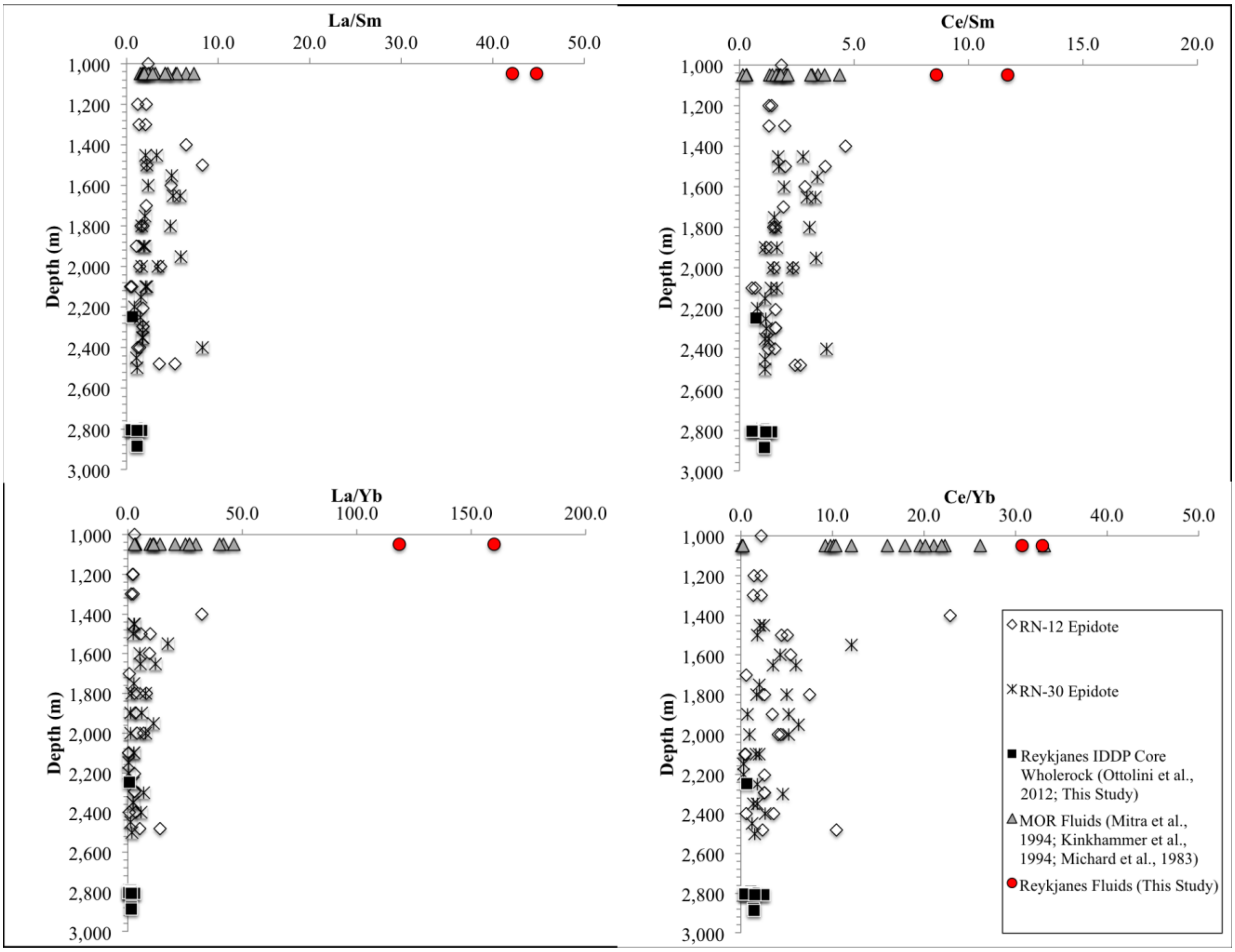

Figure 4: REE ratios for epidote in drill cuttings from Reykjanes wells RN-12 and RN-30. Mid ocean ridge fluids and fluids from this study were arbitrarily plotted at a depth of 1050 m for comparison.

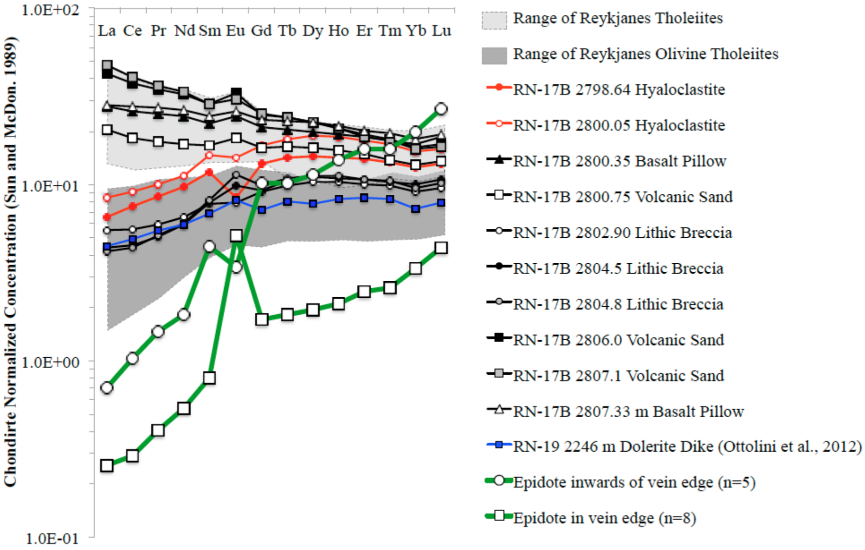

Figure 5: Chondrite normalized REE plot of wholerock samples from the variably hydrothermally altered Reykjanes RN-17B drill core (this study) and unaltered dolerite from the IDDP Reykjanes RN-19 drill core (Ottolini et al., 2012). LA-ICP-MS values for REE in an epidote vein at 2800.05 m are included. Shaded regions for wholerock values of unaltered, subaerially erupted tholeiites and olivine tholeiites for the Reykjanes Peninsula are based on several hundred REE analyses extracted from the GEOROC database (http://georoc.mpch-mainz.gwdg.de).

The REE content of epidote in a vein from 2800.05 m in the IDDP RN-17B drill core varies systematically across the vein. Epidote was measured in the vein edge adjacent to the host rock, inwards of the vein edge, and in the vein center. All epidote in the vein shows LREE depletion, similar to the adjacent host rock. Epidote in the vein edge has a positive Eu anomaly, whereas epidote inwards of the vein edge has a marginally higher REE content and a negative Eu anomaly (Figure 5). The REE content of epidote in the vein center is below the method detection limit (with the exception of Eu) (Figure 6).

Wholerock samples from the RN-17B core (this study) and the RN-19 unaltered dolerite core (Ottolini et al., 2012) fall within the range of unaltered subaerially erupted tholeiite and olivine tholeiite basalts on the Reykjanes Ridge (Figure 5). Wholerock samples of hyaloclastite from the RN-17B core (2798.64 m and 2800.05 m) have anomalous results, with LREE contents in the range of unaltered olivine tholeiites, HREE contents in the range of unaltered tholeiitic basalt, and negative Eu anomalies (Figure 5).

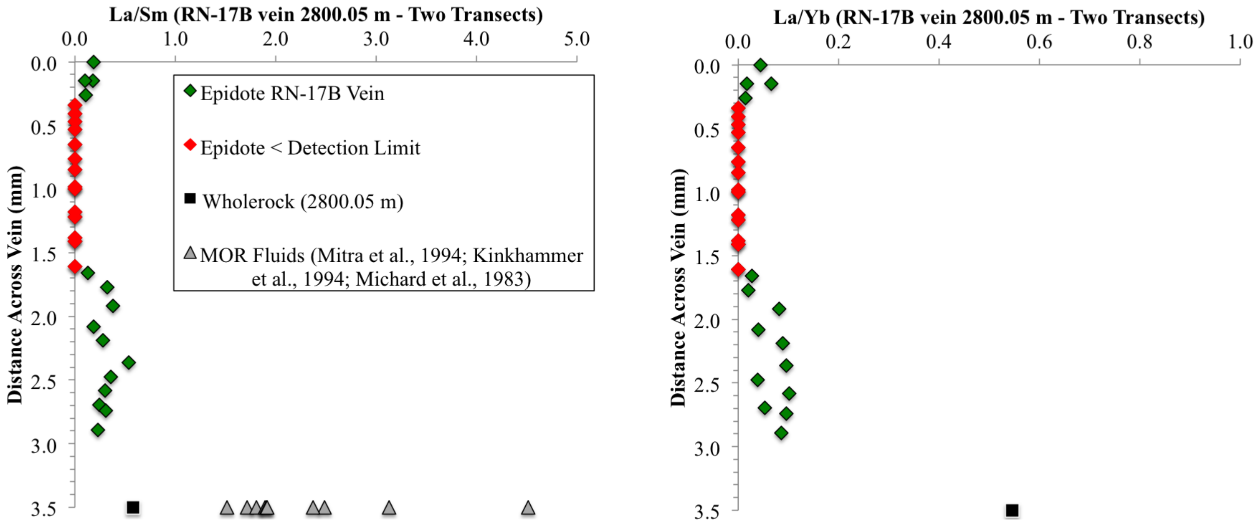

Figure 6: REE ratios for epidote in a single vein from IDDP core RN-17B. REE concentrations for epidote in the vein center are below the detection limit. MOR fluids and fluids from this study were arbitrarily plotted at a vein distance of 3.5 mm for comparison.

4. DISCUSSION

The significantly lower REE in geothermal fluids sampled from the wellheads of Reykjanes wells RN-12 and RN-19 relative to MOR fluids, and REE concentrations generally lower than the seawater-sourced initial fluid (Figure 2) indicate that significant REE loss has occurred prior sampling, presumably by precipitation during fluid boiling due to pH increase. This observation is consistent with the La/Sm, Ce/Sm, La/Yb, and Ce/Yb ratios of hydrothermal epidote in wells RN-12 and RN-30, which suggest fluids at depth in the Reykjanes system have chondrite normalized REE slopes that range from those of MOR fluids to those of unaltered Reykjanes basalts (Figure 4). Scaling is a problem in Reykjanes geothermal production wells, and provides a mechanism for REE loss from fluids to scale minerals in the Reykjanes system that may explain our results. We anticipate measuring REE in Reykjanes fluids from an in-situ downhole sample in the near future to test this hypothesis. The increased stability of LREE chloride complexes in hydrothermal fluids (Migdisov et al., 2009) may explain the LREE enrichment and large La/Sm and Ce/Sm ratios for RN-12 and RN-19 fluids sampled at the wellhead, if chloride complexation in fluids is preferentially fractionating HREE into scale minerals.

The hyaloclastite lithologies at 2798.64 and 2800.05 m in the RN-17B core are pervasively altered to hornblende with extensive albite mineralization, yet perfectly preserve the hyaloclastite texture. Other lithologies in the RN-17B core have crystalline protoliths, and in contrast to the hyaloclastite lithology contain abundant chlorite mineralization (Fowler, 2012 Unpublished MS thesis). Anomalous chondrite normalized wholerock REE patterns for hyaloclastite lithologies compared to crystalline lithologies in the RN-17B core suggest that LREE and Eu have been mobilized from wholerock during seawater-basalt interaction. Previous studies have also reported cases of LREE loss from basalt wholerock during seawater-basalt interaction (Frey et al, 1974; Wood et al., 1976; Hellman and Henderson, 1977). Wholerock REE results for the RN-17B core indicate hyaloclastite lithologies with glass protolith are more susceptible to LREE loss than crystalline lithologies, likely due increased reaction kinetics of glass vs. crystalline protoliths during interaction with hydrothermal seawater (Seyfried and Bischoff, 1981), an observation consistent with altered basaltic crystalline and glass lithologies on the seafloor (Frey et al., 1974). This phenomenon is likely enhanced even further by the larger reaction surface and porosity available in granular hyaloclastite tuffs vs. crystalline lithologies.

Temperature and water/rock ratio are key factors controlling the heavy metal content of hydrothermal fluids (Seyfried and Bischoff, 1981). High temperatures and high water/rock ratios generate lower pH fluids with high heavy metal contents (Seyfried and Bischoff, 1977; Seyfried and Bischoff, 1981; Seyfried and Mottl, 1982) and can result highly modified cation content of the host rock (Zierenberg et al., 1995, Zierenberg et al., 1998). Lower temperatures and lower water/rock ratios generate higher pH fluids with lower transition metal contents (Seyfried and Bischoff, 1977). The predominant control on transition metal transport is water/rock ratio, which influences pH changes due to the metasomatic addition of seawater Mg and Ca ions into basaltic host rock and the associated hydrogen ion release during the formation of hydrous alteration phases (Seyfried and Bischoff, 1981).

The major element composition and low pH of Reykjanes geothermal fluids also results from the metasomatic addition of seawater Mg and Ca ions into basaltic host (Franzson et al., 2008), a process similar to that occurring along MORs (Reed, 1983; Bowers et al., 1985a &1985b, Seyfried and Ding, 1995). REE (particularly LREE) are known to be more mobile in Cl-rich fluids at lower pH and higher temperatures (Migdisov et al., 2009), and likely covary with water/rock ratio and temperature similar to heavy metals in seafloor systems. LREE depletion of the hyaloclastite at 2800.05 m in the RN-17B core may be evidence for alteration at high temperature and high relative water/rock ratio by a chloride-rich fluid.

The systematic variation of REE in LA-ICP-MS transects across an epidote vein at 2800.05 m in the IDDP RN-17B test core (Figure 5) appears to reflect an evolving water rock ratio. If we assume epidote in the vein grew paragentically from the outside inwards over time, the REE slope of the epidote initially matches the adjacent host rock (with the exception of a large positive Eu anomaly), increases slightly in chondrite normalized REE content with a negative Eu anomaly, and REE in subsequent epidote in the vein center is below the method detection limit. Varying water rock ratio and temperature could explain the systematic change in the REE content of the vein epidote. This idea is consistent with results from strontium isotope transects and fluid inclusion measurements across the same vein (Fowler, 2012 unpublished MS thesis) and REE enriched zones in areas of high water/rock rock ratio alteration in the Pindos ophiolite, Greece (Valasami and Cann, 1992).

The REE content of epidote from drill cutting samples also vary from below detection to the maximum REE values observed for unaltered wholerock samples from the Reykjanes Peninsula (>200 wholerock values extracted from the GEOROCK database: http://georoc.mpch-mainz.gwdg.de). In several instances, the REE content of epidote from drill cutting samples varies across this entire range at a single depth interval. Drill cuttings lack the paragenetic context to interpret evolving geothermal conditions, so it is unclear if this relates to real variation or mixing of drill cuttings from different depth intervals during ascent of the drill string. Despite the lack of paragenetic context, the drill cutting results provide valuable information on REE transport. A high REE concentration in drill cutting epidote does correlate with La/Sm and La/Yb ratios of MOR fluids, consistent with experimental evidence for fluid dominated transition metal transport at high water/rock ratios (Seyfried and Bischoff, 1981).

These results highlight the importance of collecting drill core samples during the drilling the supercritical IDDP-2 well to better understand water/rock interaction and geothermal processes as we drill into the supercritical region of a geothermal system for the first time. Evaluation of REE contents of epidote in vein transects has the potential to identify alteration caps that may isolate supercritical fluids from shallower portions of a geothermal system, and aid in the identification of permeability pathways during drilling as samples are returned to the surface.

5. CONCLUSIONS

Reykjanes geothermal fluids sampled at the wellhead are several orders of magnitude less enriched in REE compared to MOR systems, and have a much larger LREE enrichment. In contrast, epidote grains in drill cuttings from RN-12 and RN-30 have La/Sm, Ce/Sm, La/Yb, and Ce/Yb ratios consistent with precipitation from MOR fluids. We speculate that REE in Reykjanes fluids (particularly HREE) are preferentially incorporated into scale minerals on the well casing. An in-situ fluid sample from depth in the Reykjanes system is required to confirm this idea.

The REE content and chondrite-normalized patterns of epidote from Reykjanes drill cuttings appear to have little correlation with depth, likely due the individual epidote grains having no paragenetic context and potential mixing of different depth zones during return of drill cuttings to the surface. It is unclear if the REE variation in drill cutting epidote from specific depth intervals reflects real variation or sample mixing from different depth intervals along with sampling bias during return of drill cuttings to the surface.

In contrast, the REE content of epidote in a vein from 2800.05 m in the RN-17B drill core shows distinct zoning across the vein that covaries with water/rock ratio and temperature, determined by $^{87}Sr/^{86}Sr$ measurements and fluid inclusion measurements, respectively, of the same vein (Fowler, unpublished MS thesis). The REE content of a hyaloclastite wholerock sample from 2800.05 m in the RN-17B core shows anomalous REE patterns compared unaltered Reykjanes basalt and altered crystalline lithologies, yet is consistent with La/Sm and La/Yb ratios observed for the adjacent vein epidote. This suggests the REE in the epidote vein is locally derived from the host rock.

Drill core samples preserve the paragenetic context of vein minerals as opposed to drill cuttings, and are essential for continued evaluation of the REE distribution between host rock, fluids, and alteration mineral phases in active geothermal systems. Continued study of the paragenetic context of the REE content of alteration mineral phases in drill core samples will allow us to evaluate the utility of drill cutting samples for similar types of study. The potential return of drill core from the IDDP-2 effort will allow us to evaluate the REE content of alteration phases in a paragenetic context from the deep reaction zone of an active geothermal system. This information may help identify zones of sealed permeability or active permeability during the IDDP-2 drilling effort.

ACKNOWLEDGEMENTS

This study was made possible thanks to efforts by Guðmundur Ómar Friðleifsson (HS Orka), Þráinn Friðriksson (ISOR), Daði Þorbjörnsson (ISOR), and Hjalti Franzson (ISOR). I would also like to thank the GEORG geothermal research group (Iceland) for their generous support.

REFERENCES

Alderton, D.H.M., J.A. Pearce and P.J. Potts. "Rare Earth Element Mobility During Granite Alteration: Evidence from Southwest England." *Earth and Planetary Science Letters* 49, (1980): 149-165.

Arnórsson, Stefan. "Major Element Chemistry of the Geothermal Sea-Water at Reykjanes and Svartsengi, Iceland." *Mineralogical Society* 42, no. 322 (1978): 209-220.

Arnórsson, Stefan. "Geothermal Systems in Iceland - Structure and Conceptual Models - I. High Temperature Areas." *Geothermics* 24, no. 5/6 (1995): 561-602.

Arribas, Antonio Jr., Charles G. Cunningham, James J. Rytuba, Robert O. Rye, William C. Kelley, Melvin H. Podowysocki, Edwin H. McKee and Richard M. Tosdal. "Geology, Geochronolgy, Fluid Inclusions, and Isotope Geochemistry of the Rodalquilar Gold Alunite Deposit, Spain." *Economic Geology* 90, (1995): 795-822.

Banks, D.A., B.W.D. Yardley, A.R. Campbell and K.E. Jarvis. "Ree Composition of an Aqueous Magmatic Fluid- a Fluid Inclusion Study from the Capitan Pluton, New Mexico, U.S.A." *Chemical Geology* 113, (1994): 259-272.

Bowers, Teresa Suter and Hugh P. Taylor. "An Integrated Chemical and Stable-Isotope Model of the Origin of Midocean Ridge Hot Spring Systems." *Journal of Geophysical Research* 90, no. B14 (1985): 12583-12606.

Bowers, Teresa Suter, K. L. Von Damm and J. M. Edmond. "Chemical Evolution of Mid-Ocean Ridge Hot Springs." *Geochimica et Coemochimica Acta* 49, (1985): 2239-2252.

Brunsmann, Axel, Gerhard Franz and Jorg Erzinger. "Ree Mobilization During Small-Scale High-Pressure Fluid-Rock Interaction and Zoisite:Fluid Partitioning of La to Eu." *Geochimica et Coemochimica Acta* 65, no. 4 (2001): 559-570.

Clifton, Amy E. and Simon A. Kattenhorn. "Structural Architecture of a Highly Oblique Divergent Plate Boundary Segment." *Tectonophysics* 419, no. 1-4 (2006): 27-40.

Corey, Michael C. and A.k. Chatterjee. "Characteristics of Ree and Other Trace Elements in Response to Successive and Superimposed Metasomatism within a Portion of the South Mountain Batholith, Nova Scotia, Canada." *Chemical Geology* 85, (1990): 265-285.

Ferrara, G., F. Innocenti, C.A. Ricci and G. Serri. "Ocean-Floor Affinity of Basalts from North Apennine Ophiolites: Geochemical Evidence." *Chemical Geology* 17, (1976): 101-111.

Franzson, Hjalti, Robert Zierenberg and Peter Schiffman. "Chemical Transport in Geothermal Systems in Iceland. Evidence from Hydrothermal Alteration." *Journal of Volcanology and Geothermal Research* 173, no. 3-4 (2008): 217-229.

Frey, Fred A., Wilfred B. Bryan and Geoffrey Thompson. "Atlantic Ocean Floor: Geochemistry and Petrology of Basalts from Legs 2 and 3 of the Deep-Sea Drilling Project." *Journal of Geophysical Research* 79, no. 35 (1974): 5507.

Friðleifsson, G. Ó, W. A. Elders and A. Albertsson. "The Concept of the Iceland Deep Drilling Project." *Geothermics* 49, (2014): 2-8.

Fulignati, Paolo, Anna Gioncada and Sbrana Alessandro. "Rare-Earth Element (Ree) Behaviour in the Alteration Facies of the Active Magmatic-Hydrothermal System of Vulcano (Aeolian Islands, Italy)." *Journal of Volcanology and Geothermal Research* 88, (1999): 325-342.

Haas, Johnson R., Everett L. Shock and David C. Sassani. "Rare Earth Elements in Hydrothermal Systems: Estimates of Standard Partial Molal Thermodynamic Properties of Aqueous Complexes of the Rare Earth Elements at High Pressures and Temperatures." *Geochimica et Coemochimica Acta* 59, no. 21 (1995): 4329-4350.

Hanson, Gilbert N. "Rare Earth Elements in Petrogenic Studies of Igneous Systems." *Annual Review of Earth and Planetary Sciences* 8, (1980): 371-406.

Hardardottir, V., K. L. Brown, Th Fridriksson, J. W. Hedenquist, M. D. Hannington and S. Thorhallsson. "Metals in Deep Liquid of the Reykjanes Geothermal System, Southwest Iceland: Implications for the Composition of Seafloor Black Smoker Fluids." *Geology* 37, no. 12 (2009): 1103-1106.

Helgadóttir, H.M., S.H. Gunnarsdóttir, Guðfinnsson G.H. and H. Ingólfsson. "Reykjanes – Well Rn-17b, Drilling the Production Part of the Well 933 to 3077 M. Ísor-2009/008, 154 P. & Appendix. (in Icelandic).", (2009).

Hellman, Phillip L. and Paul Henderson. "Are Rare Earth Elements Mobile During Spilitization?" *Nature* 267, (1977): 38-40.

Herrmann, G, Mark J. Potts and Doris Knake. "Geochemistry of the Rare Earth Elements in Spilites from the Oceanic and Continental Crust." *Contributions to Mineralogy and Petrology* 44, no. 1 (1974): 1-16.

Humphris, Susan E. "Rare Earth Element Composition of Anhydrite: Implications for Deposition and Mobility within the Active Tag Hydrothermal Mound." In *PROCEEDINGS-OCEAN DRILLING PROGRAM SCIENTIFIC RESULTS*, 143-162: NATIONAL SCIENCE FOUNDATION, 1998.

Humphris, Susan E. and Wolfgang Bach. "On the Sr Isotope and Ree Compositions of Anhydrites from the Tag Seafloor Hydrothermal System." *Geochimica et Cosmochimica Acta* 69, no. 6 (2004): 1511-1525.

Jakobsson, S.P., J. Jonsson and F. Shido. "Petrology of the Western Reykjanes Peninsula, Iceland." *Journal of Petrology* 19, no. 4 (1978): 669-705.

Lawrence, Michael G. and Balz S. Kamber. "Rare Earth Element Concentrations in the Natural Water Reference Materials (Nrcc) Nass-5, Cass-4 and Slew-3." *Geostandards and Geoanalytical Research* 31, no. 2 (2007): 95-103.

Ludden, John N. and Geoffrey Thompson. "An Evaluation of the Behavior of the Rare Earth Elements During the Weathering of Sea-Floor Basalt." *Earth and Planetary Science Letters* 43, (1979): 85-92.

Marks, Naomi, Peter Schiffman, Robert Zierenberg, Hjalti Franzson and Gudmundur Ó Friðleifsson. "Hydrothermal Alteration in the Reykjanes Geothermal System: Insights from Iceland Deep Drilling Program Well Rn-17." *Journal of Volcanology and Geothermal Research* 189, no. 1-2 (2010): 172-190.

Menzies, Martin, Douglas Blanchard and Jeff Jacobs. "Rare Earth and Trace Element Geochemistry of Metabasalts from the Point Sal Ophiolite, California." *Earth and Planetary Science Letters* 37, no. 2 (1977): 203-215.

Michard, Annie. "Rare Earth Element Systematics in Hydrothermal Fluids." *Geochimica et Cosmochimica Acta* 53, (1989): 745-750.

Michard, Annie, F. Albaréde, G. Michard, J.F. Minster and J.L. Charlou. "Rare-Earth Elements and Uranium in High Temperature Solutions from East Pacific Rise Hydrothermal Vent Field." *Nature* 303, (1983): 795-797.

Migdisov, Art A. and A. E. Williams-Jones. "A Spectrophotometric Study of Nd(Iii), Sm(Iii) and Er(Iii) Complexation in Sulfate-Bearing Solutions at Elevated Temperatures." *Geochimica et Cosmochimica Acta* 72, no. 21 (2008): 5291-5303.

Migdisov, Art A., A. E. Williams-Jones and T. Wagner. "An Experimental Study of the Solubility and Speciation of the Rare Earth Elements (Iii) in Fluoride- and Chloride-Bearing Aqueous Solutions at Temperatures up to 300°C." *Geochimica et Cosmochimica Acta* 73, no. 23 (2009): 7087-7109.

Mills, Rachel A. and Henry Elderfield. "Rare Earth Element Geochemistry of Hydrothermal Deposits from the Active Tag Mound, 26n Mid-Atlantic Ridge." *Geochimica et Coemochimica Acta* 59, no. 17 (1995): 3511-3524.

Möller, Peter, Peter Dulski and Nevzat Özgür. "Partitioning of Rare Earths and Some Major Elements in the Kizildere Geothermal Field, Turkey." *Geothermics* 37, no. 2 (2008): 132-156.

Ólafsson, J. and J.P. Riley. "Geochemical Studies on the Thermal Brine from Reykjanes, Iceland." *Chemical Geology* 21, no. 3-4 (1978): 219-237.

Ottolini, L. P., N. Raffone, G. Ó Fridleifsson, S. Tonarini, M. D'Orazio and G. Gianelli. "A Geochemical Investigation of Trace Elements in Well Rn-17 at Reykjanes Geothermal System, Sw-Iceland." *IOP Conference Series: Materials Science and Engineering* 32, (2012): 012020.

Palacios, C.M., U.F. Hein and P. Dulski. "Behaviour of Rare Earth Elements During Hydrothermal Alteration at the Buena Esperanza Copper-Silver Deposit, Northern Chile." *Earth and Planetary Science Letters* 80, (1986): 208-216.

Paton, Chad, John Hellstrom, Bence Paul, Jon Woodhead and Janet Hergt. "Iolite: Freeware for the Visualisation and Processing of Mass Spectrometric Data." *Journal of Analytical Atomic Spectrometry* 26, no. 12 (2011): 2508.

Pope, Emily C., Dennis K. Bird, Stefán Arnórsson, Thráinn Fridriksson, Wilfred A. Elders and Gudmundur Ó Friðleifsson. "Isotopic Constraints on Ice Age Fluids in Active Geothermal Systems: Reykjanes, Iceland." *Geochimica et Cosmochimica Acta* 73, no. 15 (2009): 4468-4488.

Reed, M. and Nicolas Spycher. "Calculation of Ph and Mineral Equilibria in Hydrothermal Waters with Application to Geothermometry and Studies of Boiling and Dilution." *Geochimica et Coemochimica Acta* 48, (1984): 1479-1492.

Reed, Mark. "Seawater-Basalt Reaction and the Origin of Greenstones and Related Ore Deposits." *Economic Geology* 78, (1983): 466-485.

Seyfried Jr, W. E. and J. L. Bischoff. "Hydrothermal Transport of Heavy Metals by Seawater: The Role of Seawater/Basat Ratio." *Earth and Planetary Science Letters* 34, (1977): 71-77.

Seyfried Jr, W. E. and J. L. Bischoff. "Experimental Seawater-Basalt Interaction at 300 C, 500 Bars, Chemical Exchange, Secondary Mineral Formation and Implications for the Transport of Heavy Metals." *Geochimica et Coemochimica Acta* 45, no. 2 (1981): 135-147.

Seyfried Jr, W. E. and Michael J. Mottl. "Hydrothermal Alteration of Basalt by Seawater under Seawater-Dominated Conditions." *Geochimica et Coemochimica Acta* 46, (1982): 985-1002.

Seyfried, W. E. and Kang Ding. "Phase Equilibria in Subseafloor Hydrothermal Systems: A Review of the Role of Redox, Temperature, Ph and Dissolved Cl on the Chemistry of Hot Spring Fluids at Mid-Ocean Ridges." 91, (1995): 248-272.

Sveinbjörnsdóttir, A. E., Coleman, M. L. and Yardley, B. W. D. "Origin and History of Hydrothermal Fluids of the Reykjanes and Krafla Geothermal Fields, Iceland." *Contributions to Mineralogy and Petrology* 94, no. 1 (1986): 99-109.

Taylor, R.P. and B.J. Fryer. "Multiple Stage Hydrothermal Alteration in Porphyry Copper Systems in Northern Turkey: The Temporal Interplay of Potassic, Propylitic, Phyllic Fluids." *Canadian Journal of Earth Sciences* 17, no. 7 (1980): 901-926.

Thorpe, R.S. "Ocean Floor Basalt Affinity of Precambrian Glaucophane Schist from Anglesey." *Nature Physical Science* 240, no. 103 (1972): 164-166.

Valsami, E. and J. R. Cann. "Mobility of Rare Earth Elements in Zones of Intense Hydrothermal Alteration in the Pindos Ophiolite, Greece." *Geological Society, London, Special Publications* 60, no. 1 (1992): 219-232.

Wood, David A., I.L. Gibson and R.N. Thompson. "Elemental Mobility During Zeolite Facies Metamorphism of the Tertiary Basalts of Eastern Iceland." *Contributions to Mineralogy and Petrology* 55, (1976): 241-254.

Wood, S.A. "Behavior of Rare Earth Elements in Geothermal Systems: A New Exploration Exploitation Tool?" *Final Project Report, DOE Geothermal Reservoir Technology Research 36pp*, (2002).

Zhu, Yanbei, Akihide Itoh, Tomonari Umemura, Hiroki Haraguchi, Kazumi Inagaki and Koichi Chiba. "Determination of Rees in Natural Water by Icp-Ms with the Aid of an Automatic Column Changing System." *Journal of Analytical Atomic Spectrometry* 25, no. 8 (2010): 1253-1258.

Zierenberg, Robert A., Wayne C. Shanks, William E. Seyfried, Randolph A. Koski and Michael D. Strickler. "Mineralization, Alteration, and Hydrothermal Metamorphism of the Ophiolite-Hosted Turner-Albright Sulfide Deposit, Southwestern Oregon." *Journal of Geophysical Research* 93, no. B5 (1988): 4657.

Zierenberg, Robert, P. Schiffman, I.R. Jonasson, R. Tosdal, W. Pickthorn and J. McClain. "Alteration of Basalt Hyaloclastite at the Off-Axis Sea Cliff Hydrothermal Field, Gorda Ridge." *Chemical Geology* 126, (1995): 77-99.