

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

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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 bears 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 whole-rock 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 whole-rock REE and seafloor hydrothermal fluid REE, and are dissimilar to Reykjanes fluids sampled at the wellhead.

Our data suggests that the Reykjanes geothermal fluids sampled at the wellhead have undergone significant REE loss, and the chondrite-normalized REE pattern of the 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 and 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 Lu.

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 limits to chondritic values (Wood, 2002), suggesting that REE are significantly mobilized by hydrothermal processes under certain circumstances. This has led 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 with 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 partitioning data for REE is sparse for most geothermal minerals at typical geothermal temperature and pressure ranges. Fluid/anhydrite REE partitioning coefficients have been determined for MOR settings (Mills and Elderfield, 1995; Humphries 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 partitioning coefficients have been determined under amphibolite and eclogite facies metamorphic conditions (550–900°C and 0.6 to 2 GPa) (Brunsma 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 dominant control on REE fractionation between seawater 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).

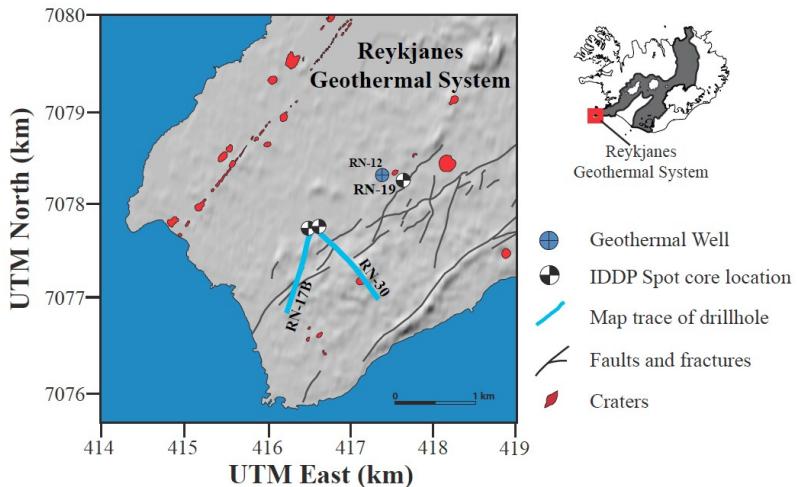


Figure 1: The Reykjanes geothermal system, Iceland.

The Reykjanes geothermal fluid is seawater, chemically modified through boiling and interaction with the basaltic host rock (Arnórsson et al., 1978; Olafsson and Riley, 1978; Sveinbjörnsson, 1986; Arnórsson, 1995). Compared to seawater, Reykjanes geothermal fluids have similar Na and Cl concentrations, increased concentrations of K, Ca, SiO₂, Fe, and Al, and decreased concentrations of SO₄ and Mg. Reykjanes geothermal fluids have a reconstructed pH in the range of 5–6 (Arnórsson, 1978; Reed and Spycher, 1984; Arnórsson, 1995; Hardardóttir et al., 2009), significantly more acidic than near neutral pH meteoric water dominated Icelandic geothermal fluids (Arnórsson, 1995).

Despite the similarities of the 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 utilization of REE to inform about potential conditions that may be 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. A total of twenty-five samples 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 pre-concentrate 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 $\text{M}\Omega$). 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 washed in 3M nitric acid for a period of 1 week and rinsed with Milli-Q water prior to use. Sample preparation work was completed in a $\sim 1 \text{ m}^3$ 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 water 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
- 6) 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 to 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 pre-concentration 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 desolvating nebulizer for increased sensitivity. Oxide production was evaluated by analyzing single element solutions (10 ppb) of REE, and calibrated daily by normalizing to the $^{146}\text{Nd}/^{142}\text{Nd}^{16}\text{O}$ 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 100 ppb, 10 ppb, 1 ppb, and 0.1 ppb.

2.2 Epidote and Whole-rock 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 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 depths 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).

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 pre-concentration 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 as 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.

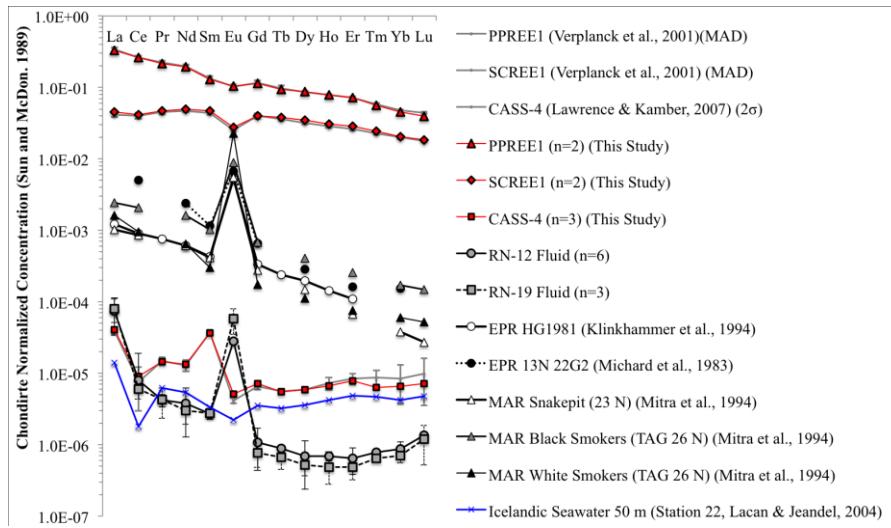


Figure 2: Chondrite-normalized REE plots of Reykjanes RN-12 and RN-19 fluid samples (1 σ error bars) and standards (2 σ error bars). A subset of representative REE analyses for MOR fluids and seawater are shown for comparison.

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 limits (0.0035 microgram/kg for La to 0.09 mg/kg for Er; $\sim 1.5E-02$ to $5.4E-01$ on a chondrite-normalized plot, respectively) to values consistent with the maximum REE content of unaltered Reykjanes tholeite (Figure 3). The chondrite-normalized La/Sm and La/Yb ratios of epidote from drill cuttings range from those of MOR fluids to those of whole-rock 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 ratios of RN-12 and RN-19 fluids sampled at the wellhead (Figure 4). RN-12 and RN-19 fluids sampled at the wellhead have high La contents. 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).

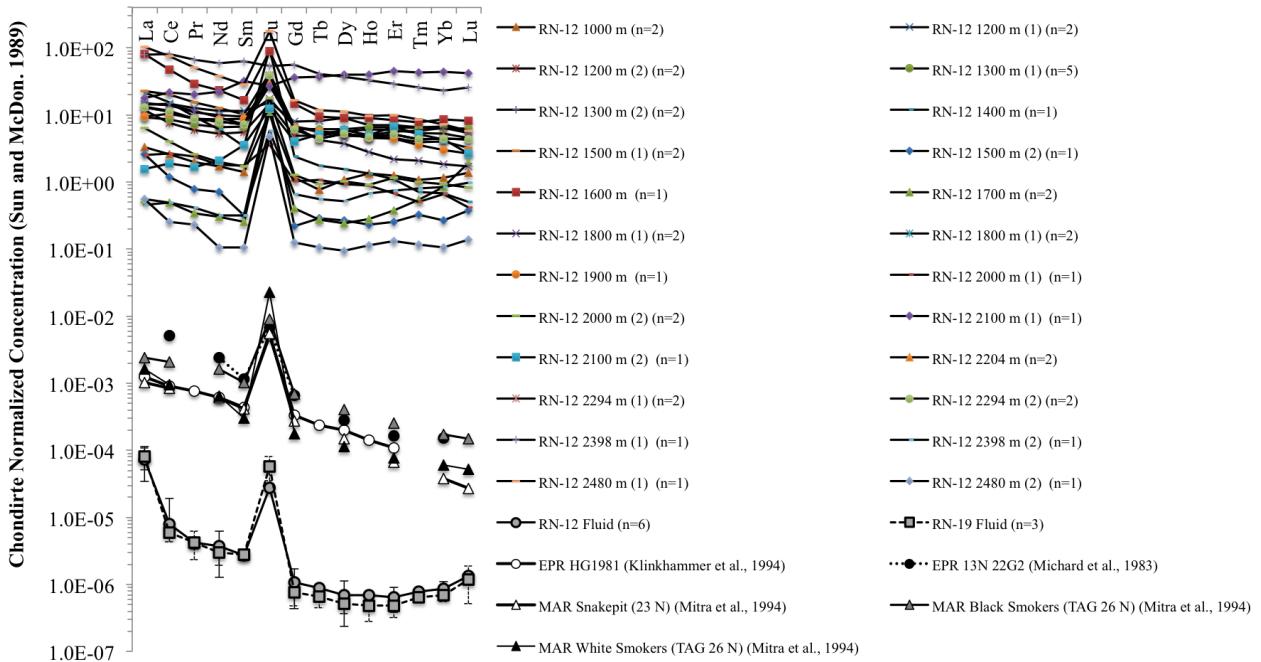


Figure 3: Chondrite-normalized REE plot of LA-ICP-MS results for epidote drill cutting samples from Reykjanes well RN-12, RN-12, and RN-19 fluids (this study), and several samples from a range of MOR fluids are shown for comparison.

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 vein epidotes show

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).

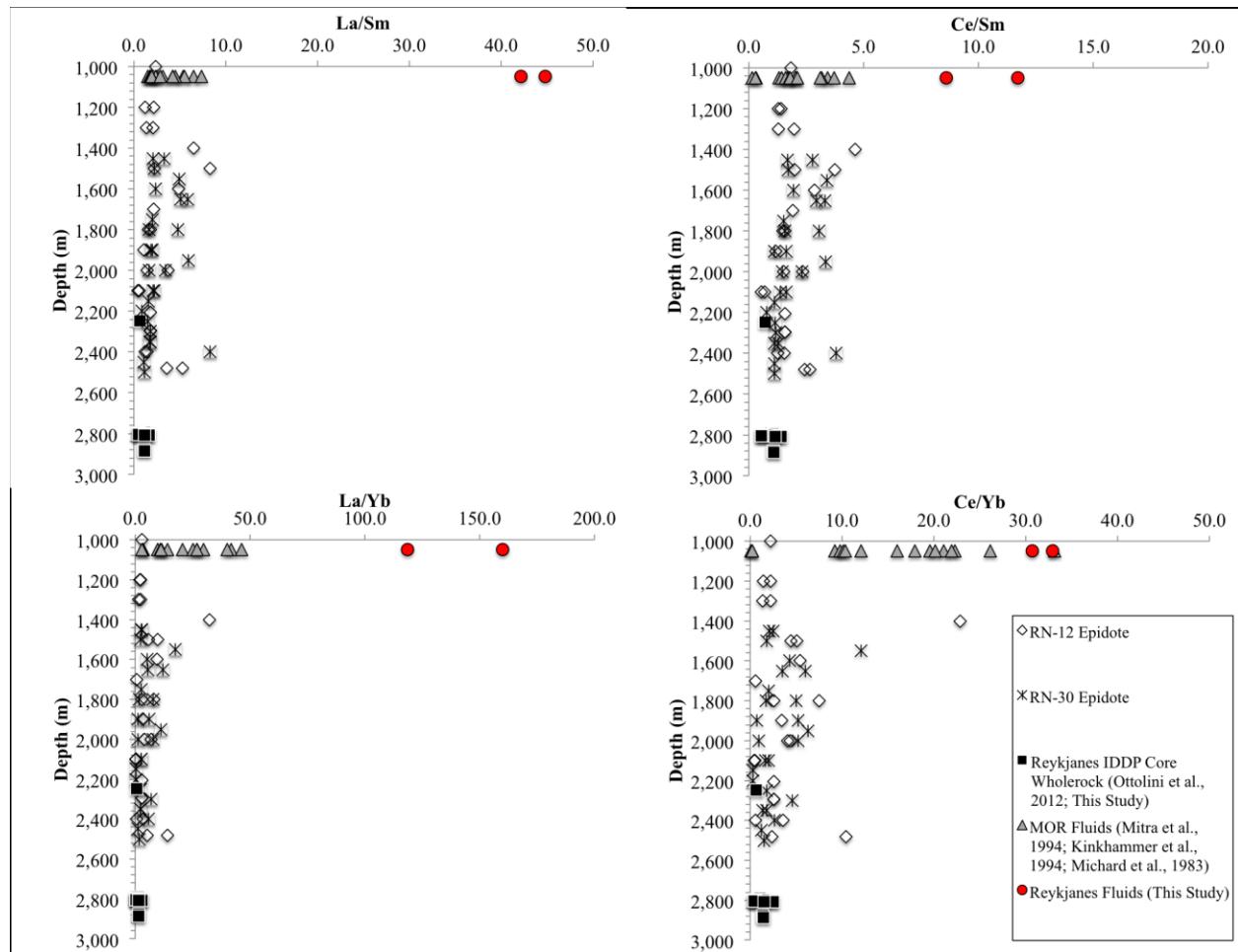


Figure 4: REE ratios for epidote in drill cuttings from Reykjanes wells RN-12 and RN-30. Mid ocean ridge fluids and fluids from this study were arbitrarily plotted at a depth of 1050 m for comparison.

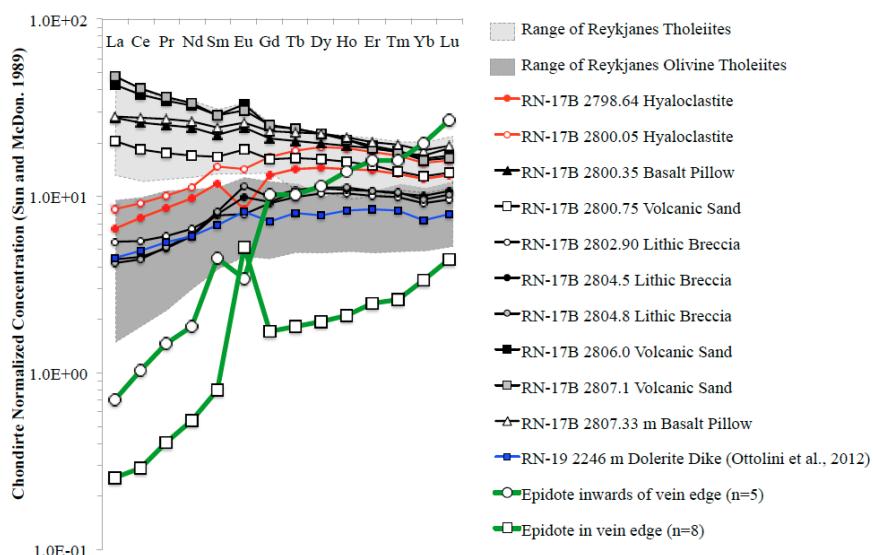


Figure 5: Chondrite-normalized REE plot of whole-rock samples from the variably hydrothermally altered Reykjanes RN-17B drill core (this study) and unaltered dolerite from the IDDP Reykjanes RN-19 drill core (Ottolini et al., 2012). LA-ICP-MS values for REE in an epidote vein at 2800.05 m are included. Shaded regions for whole-rock 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>).

Whole-rock 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). Whole-rock 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).

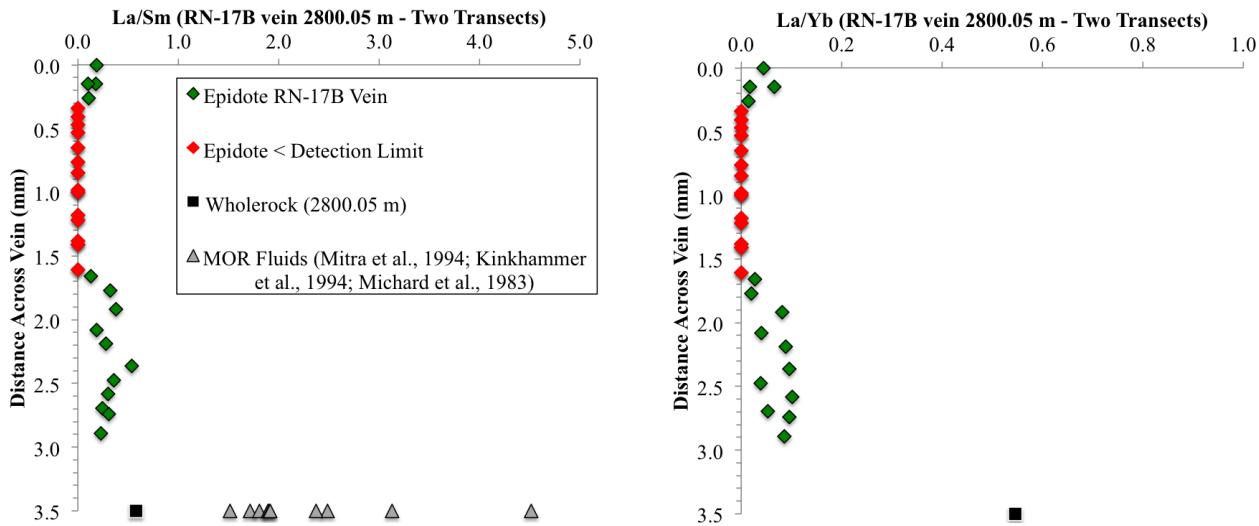


Figure 6: REE ratios for epidote in a single vein from IDDP core RN-17B. REE concentrations for epidote in the vein center are below the detection limit. MOR fluids and fluids from this study were arbitrarily plotted at a vein distance of 3.5 mm for comparison.

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 occurred prior to 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 the 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 high 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 have been pervasively altered to hornblende with extensive albite mineralization, yet they 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 MSc. thesis). Anomalous chondrite-normalized whole-rock REE patterns for hyaloclastite lithologies compared to crystalline lithologies in the RN-17B core suggest that LREE and Eu have been mobilized from the whole-rock during seawater-basalt interaction. Previous studies have also reported cases of LREE loss from basalt whole-rock during seawater-basalt interaction (Frey et al., 1974; Wood et al., 1976; Hellman and Henderson, 1977). Whole-rock REE results for the RN-17B core indicate that 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 contents 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 the water/rock ratio, which influences pH changes due to the metasomatic addition of seawater Mg and Ca ions into the 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 occurs 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 an 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 that the epidote in the vein grew paragenetically 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 MSc. thesis) and REE enriched zones in areas of high water/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 whole-rock samples from the Reykjanes Peninsula (>200 whole-rock 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 a 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 of 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 to 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 $^{87}\text{Sr}/^{86}\text{Sr}$ measurements and fluid inclusion measurements, respectively, of the same vein (Fowler, unpublished MSc. thesis). The REE content of a hyaloclastite whole-rock sample from 2800.05 m in the RN-17B core shows anomalous REE patterns compared to unaltered Reykjanes basalt and altered crystalline lithologies, yet it 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 utilization 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.

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