Sulfide Mineralization in the Reykjanes Geothermal System, Iceland—Potential Applications for Geothermal Exploration

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Keywords

Reykjanes, sulfides, sulfur, mineralization, exploration, seawater, geothermal, hydrothermal, epithermal

ABSTRACT

The nature and distribution of sulfide mineralization in the Reykjanes geothermal field were determined through the study of cuttings and core from wells that intersect different regions of the subsurface hydrothermal system. Samples were evaluated using optical and scanning electron microscopy, major and trace element analysis by in-situ spectroscopic methods, isotopic analyses, and bulk rock chemical analyses. The data suggest that seawater-derived hydrothermal fluids have interacted with primary igneous sulfides present in the host rocks causing alteration and leaching of their base and precious metals. Similar processes have been proposed as a major control of aqueous sulfide production in mid-ocean ridge environments. Hydrothermal sulfide mineralization in the Reykjanes geothermal field is focused around the present-day upflow region, with the most abundant mineralization occurring in the reservoir at a depth of between ~1300 and 2000 m, and at shallow depths above the inferred caprock to the system (<~500 m depth), where mixing with oxidized near-surface waters can be inferred. The downhole distribution of sulfide phases correlates well with the present-day thermal structure of the system.

1. Introduction

Active geothermal systems provide an analog for understanding ancient epithermal metallic mineral deposits. Likewise, the knowledge obtained from the study of ancient epithermal deposits aids in the understanding of processes operating in modern day hydrothermal systems. The steep geothermal gradients present in regions containing these systems activate subsurface convection of hydrothermal fluids, a process that entrains and concentrates available metals. Understanding the processes that control this transport and precipitation of metals not only increases our ability to model extinct environments that may be of economic interest but also provides information that is potentially valuable to the exploration and development of active geothermal resources for electricity and direct use applications. This paper presents the latest results of an ongoing study of sulfide mineralization in the Reykjanes geothermal field, Iceland.

1.1 The Reykjanes Geothermal System

Reykjanes is a basaltic-hosted, seawater-dominated geothermal system situated at the southwest tip of the Reykjanes peninsula. It is one of the smallest high temperature fields in Iceland, covering a surface area of only ~1 km^2. The most recent volcanic eruptions around the Reykjanes geothermal field occurred in the late 12th to early 13th centuries and are thought to have been the result of fissure eruptions that tapped mantle magma reservoirs (Gudmundsson, 2000; Thordarson and Larson, 2007). The subsurface stratigraphy, as determined by analysis of drill cuttings and core, can be divided into two informal units. The uppermost 1 km of the system is dominated by hyaloclastite tuff, breccias, pillow basalts, and tuffaceous and marine sediments. The deeper parts of the system are dominated by basaltic lavas and diabase dikes (Marks *et al*., 2010). Altered and hydrothermally cemented tuffaceous and sedimentary successions from depths of 400 to 1000 m act as a semi-permeable caprock to the hydrothermal system (Friðleifsson *et al.*, 2011). The upwards-stacking stratigraphic sequence of pillow basalts, fossil-bearing hyalo-tuff units, and subaerial basalt flows records a thickening volcanic pile and the emergence of a submarine segment of the Reykjanes Ridge (Franzson *et al.*, 2002). A low resistivity anomaly at 10 km below the surface of the Reykjanes geothermal system has been interpreted as a dense sheeted-dike complex or a large cooling gabbroic intrusion, and likely represents the heat engine of the shallower hydrothermal system (Friðleifsson *et al.*, 2011).

The present-day convecting hydrothermal fluids within the Reykjanes geothermal system represent seawater that has been modified due to basalt-rock interaction at high temperature (Arnórsson, 1978). The total chloride content of the fluid (~3.2 wt.% NaCl) is similar to that of seawater, however, other dissolved components such as K^+, Ca^{2+}, SiO_2, CO_2, and H_2S are significantly enriched relative to seawater. Components, such as SO_4^{2-} and

Mg^{2+} show strong depletions relative to seawater (Björnsson *et al*., 1972; Marks *et al*., 2010; Friðriksson, unpublished data). As a consequence of the fluid salinity, the fluid pH is between 5 and 6, lower than is typically found in other geothermal fields in Iceland (Henley and Ellis, 1983). Fluid inclusions within hydrothermal quartz, calcite, and plagioclase have calculated salinities that range between those of fresh water and seawater (<1,000 and 35,000 ppm NaCl, respectively). These data suggest that glacially-derived freshwater dominated the system at some time during the Pleistocene (Franzson *et al.*, 2002).

Temperatures within the geothermal system follow the boiling point curve below the caprock down to a depth of ~1300 m, below which the system is liquid-dominated and the conditions follow an adiabatic gradient through a freely convecting zone down to a minimum depth of 2.5 km (Franzson *et al.*, 2002). With further increase in depth, temperature is thought to rise conductively (eventually to that of the plutonic body). The highest recorded temperature in the Reykjanes geothermal system is 345°C for production well RN17B at 2.8 km true vertical depth (within the convective region; Friðleifsson *et al.*, 2011).

Sakai *et al*. (1980) determined that the Reykjanes fluid has a residence time of <50 years based on isotopic disequilibrium between sulfate and sulfide. Radium isotopic studies by Kadko *et al*. (2007) suggest an even shorter residence time of <5 years for both the Reykjanes and neighboring Svartsengi systems. Although the Reykjanes geothermal system is fed entirely by seawater, there is a shallow freshwater lens in the upper 30 m due to the penetration of surface waters through the highly faulted and porous rock (Sigurdsson, 1985). The focal point of hydrothermal upwelling in the Reykjanes geothermal field is near the center of the system, around well RN10, as shown by downhole temperature measurements and gas fluxes (Franzson *et al*., 2002; Friðleifsson, pers. comm.; Friðriksson, pers. comm.).

1.2 Sulfur in the Reykjanes Geothermal Field

Present day fluids in the Reykjanes geothermal system contain ~30-80 ppm H_2S and ~10-24 ppm SO_4^{2-} (compared to ~0 and 2700 ppm, respectively for fresh seawater; Friðriksson, unpublished data; Berner and Berner, 1996). Total sulfur concentrations vary from <0.01 to 1.2 wt.% in altered rocks from the Reykjanes geothermal system. The distribution of these concentrations is generally uniform, and is not marked by enrichments at depths where boiling occurs (Padilla *et al*., 2012), as is commonly observed in meteoric water-dominated geothermal systems in Iceland (e.g. Krafla and Námafjall; Gunnlaugsson, 1977). However, above a depth of 400 m at Reykjanes, there is sulfur enrichment due to the interaction of rising steam with colder perched seawater aquifers. This causes anhydrite to precipitate in shallow groundwater due to its retrograde solubility (Padilla *et al*., 2012).

The heavy sulfur isotopic enrichment of sulfide minerals ($\delta^{34}S$ values of +2.9 to +7.9 ‰) in the Reykjanes geothermal system indicates that seawater sulfate makes a large (and perhaps the dominant) contribution to the total sulfur budget of the system. This seawater SO_4^{2-} is likely incorporated into the sulfides through inorganic reduction or isotopic exchange between dissolved sulfate and sulfide in the hydrothermal fluid (Sakai *et al*., 1980).

Deep magmatic degassing and/or basaltic sulfur also likely contributes some H_2S to the convecting fluids. Isotopic analyses of sulfide minerals have shown that mantle-derived sulfur, $\delta^{34}S$ = 0 to +1 ‰, is the main source of sulfur for many meteoric water-dominated geothermal systems in Iceland (Sakai *et al*., 1980). These isotopic values could represent sulfur that has degassed from a mantle-derived magmatic body or sulfur that has been leached from crystallized mantle-derived host rocks. Arnórsson (1995) has argued for the former, concluding that the amount of sulfur needed to account for the sulfide enrichment that we see in upflow zones of Icelandic geothermal systems requires unrealistic volumes of leachable rocks. Fossil analog systems provide further support for this interpretation, with cooled and exposed gabbroic intrusives in altered Tertiary formations in Iceland having lower sulfur content than basaltic glass in eruptive rocks, presumably due to degassing (800 ppm, undegassed; Gunnlaugsson, 1977; Arnórsson, 1995).

1.3 Studies of Sulfide Mineralization in Active Geothermal Systems

Studies of sulfide minerals in active geothermal systems have been undertaken for a limited number of field areas, i.e., the Salton Sea (Skinner *et al*., 1967; McKibben and Elders, 1985; McKibben *et al*., 1987; 1988a), Mataloko (Koseki and Nakashima, 2006), Rotokawa (Krupp and Seward, 1987), and Broadlands (Simmons and Browne, 2000). A greater number of studies have been centered on the study of sulfide scales precipitated within geothermal production pipelines, e.g., at the Salton Sea (Skinner *et al*., 1967), Reykjanes (Hardardottir *et al*., 2010), Ohaaki (Mauk and Brown, 1998), Berlin (Raymond *et al*., 2005), Milos (Andritsos and Karabelas, 1991) and Cerro Prieto (Clark and Williams-Jones, 1990; Thomas *et al*., 1992). Zoned sulfide scalings have also been identified on steam turbine blades at the Reykjanes geothermal power plant (Fridleifsson, pers. comm.), suggesting the possibility of vapor transport and precipitation of these phases.

The most common sulfide phases reported in altered rocks of geothermal systems are pyrite, sphalerite, chalcopyrite, pyrrhotite, and galena (e.g., Simmons and Browne, 2000; Krupp and Seward, 1987; McKibben and Elders, 1985). The mineralization occurs in vugs, veins, and veinlets. Some systems show a zonation from base metal-concentrated at depth, to precious metal-concentrated at shallower levels (Clark and Williams-Jones, 1990; Ewers and Keays, 1977; Buchanan, 1981). The formation of sulfide minerals in geothermal systems is generally attributed to hydrothermal processes, with the notable exception of the Salton Sea, where sulfides are also products of diagenesis and metamorphism (McKibben and Elders, 1985). In the Salton Sea geothermal field, isotopic studies have indicated that sulfide sulfur is derived from the reduction of SO_4^{2-} leached from lacustrine sediments (McKibben *et al*., 1988b). Reduced sulfate, derived from seawater, is thought to be responsible for sulfide mineralization in the Reykjanes geothermal field (Sakai *et al*., 1980). The bulk of the sulfur in dilute, meteoric-water-dominated geothermal systems (e.g. Krafla, Rotokawa, Wairakei, Kawerau) is thought to be derived from magmatic degassing or from aqueous magmatic fluids (Sakai *et al*., 1980; Steiner and Rafter, 1966). A comprehensive, field-wide study relating sulfide occurrences and chemistry to hydrogeological conditions has not yet been conducted for any active geothermal system. This paper presents recent results of such a study for the Reykjanes geothermal field, Iceland.

2. Materials

Sample material from the Reykjanes geothermal field was provided by HS Orka Ltd. Drill cuttings were sampled from 11 geothermal production wells that cover the field (RN03, RN10, RN12, RN13; RN16, RN17B, RN19, RN21, RN27, RN29, RN30). Samples constituting 30 to 40 g of drill cuttings were collected at 100 m intervals from the top to the bottom of each well. Over 250 samples were collected from across the field. Pieces of core were sampled from production wells, RN17B, RN19, and RN30.

Samples of basalt and picritic lava, dikes, and hyaloclastites were taken from outcrops at southwest tip of the Reykjanes Peninsula. These rocks are considered to represent the unaltered host rock of the geothermal system.

3. Methods

Petrographic and hand sample observations were conducted to identify mineral assemblages, determine modal abundances of minerals, establish the timing of mineralization and investigate its genesis. Preliminary optical microscopic mineral identifications were confirmed by Wavelength Dispersive Spectroscopic (WDS) and Electron Dispersive Spectroscopic (EDS) analyses. The distinction between a primary igneous and secondary hydrothermal origin for the sulfides can generally be made from textural examination, e.g., spherical or ovoid shapes of sulfide assemblages in glass or phenocrysts versus post-solidification vug or vein filling. However, where primary textures are only partially preserved this distinction may be difficult to make. In these cases, data on the compositions of the phases and mineral stability data have helped resolve issues of origin. Modal abundances of phases were estimated by image pixel-counting of high-resolution photomicrograph mosaics of selected thin sections.

To evaluate the bulk movement of elements in the Reykjanes geothermal system, estimates of mass gains and losses were made using analyses of bulk rock compositions of drill cuttings and unaltered surface samples analysed with ICP-MS and ICP-ES methods. Analyses of minerals using WDS and Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) provided information on the enrichment and depletion of minerals in a suite of major and trace elements. Total sulfur, sulfide and sulfate concentrations in samples of drill cuttings and core were determined using a combustion-based LECO Sulfur Analyzer. The data on element enrichments and depletions were related to a set of hydrogeological parameters at depths in wells corresponding to those from which the samples were taken. These were used to interpret the physicochemical conditions and controls on the bulk movement of metals in the subsurface. Hand-picked sulfide phases (identified using a Raman microscope) were analyzed for their sulfur isotopic composition using a DELTA^{plus}XP Stable Isotope Ratio Mass Spectrometer at Queen's University, Canada.

4. Results and Discussions

4.1 Mass Transfer Related to Sulfide Mineralization

Pairs of immobile elements analysed in altered and unaltered bulk rock samples produce linear trends on binary plots that do not pass through the origin (Figure 1). This and the fact that both altered and unaltered rocks define the same trends (fractionation) indicate that there was no significant overall volume or mass change during hydrothermal alteration (Cann, 1970, Kranidiotis and MacLean, 1987). As a result, the bulk chemical data can be used directly to interpret element enrichments or depletions in this system, i.e., there is no need to normalize the element concentrations to that of an immobile element (see Grant, 1986).

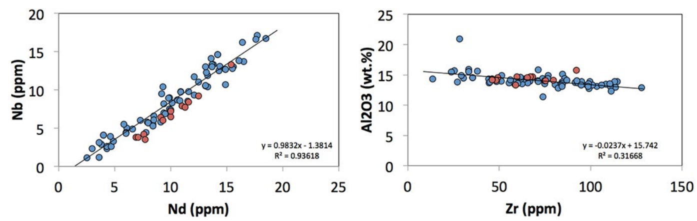

Figure 1. Bivarate plots of probable immobile elements in the Reykjanes Geothermal system. The observation that the altered rocks (blue) help to define the same linear (fractionation) trends as the unaltered rocks (red) indicates that there was no significant volume or overall mass change during alteration.

Bulk rock total sulfide and copper concentrations range from <0.02 to 0.98 wt.% and 40 to 260 ppm, respectively. The range of copper concentrations in unaltered basalts adjacent to the Reykjanes geothermal field is much narrower, i.e., 92 to 146 ppm, with a mean of 135 ppm. This indicates that hydrothermal activity leached and concentrated copper within the system, leaving some areas of the subsurface depleted in copper and other areas enriched.

To aid interpretation of the spatial distribution of the bulk rock chemical data, 3D voxel visualizations (with kriged interpolations)

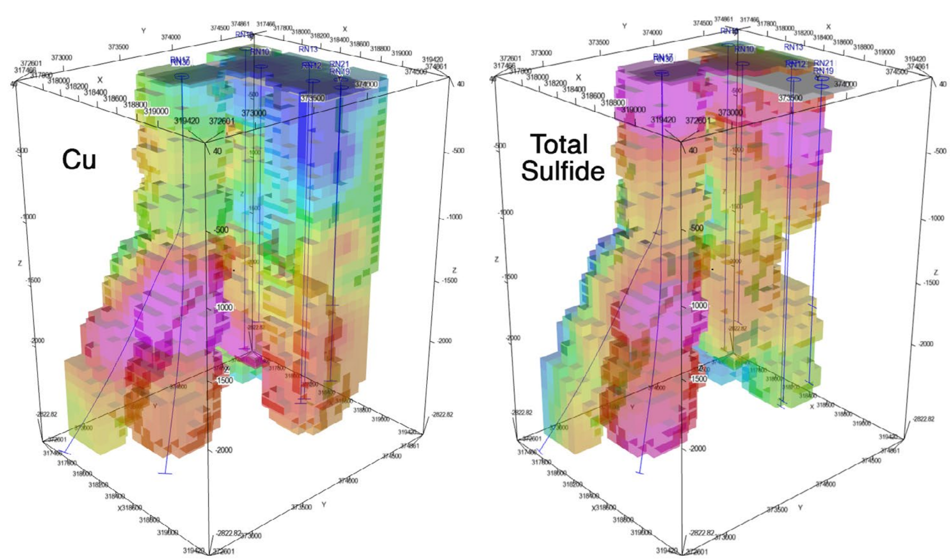

Figure 2. 3D voxel diagrams of bulk rock Cu (left) and total sulfide (right), facing NW. Data interpolations were made using kriging. Well paths are seen as wirelines. Data ranges are from 40 ppm (blue) to 260 ppm (pink) for Cu and 0.01 wt.% (blue) to 0.98 wt.% (pink) for total sulfide.

were constructed using Geosoft Target for ArcGIS. These datasets (Figure 2) identify depth intervals of element enrichment. Copper and sulfide enrichment occurs at a depth of 2000 to ~1300 m, corresponding to regions below and up to the current boiling horizon. Sulfide enrichment also occurred at shallow depths (i.e., <500 m), above the inferred caprock to the system (Fridleifsson *et al.*, 2011). In the latter, mixing of hydrothermal fluids with cool oxidized waters likely promoted sulfide mineralization.

4.2 Sulfide Mineral Petrography

There are four main sulfide phases in the Reykjanes geothermal system. In decreasing order of overall abundance these are: pyrite (py), chalcopyrite (ccp), pyrrhotite (po), and intermediate solid solution (ISS). Trace amounts of sphalerite are also present locally. These sulfides typically constitute <1% of the total rock volume (Figures 3 and 4). There are two distinguishable families of sulfides, a primary igneous assemblage and a hydrothermal assemblage.

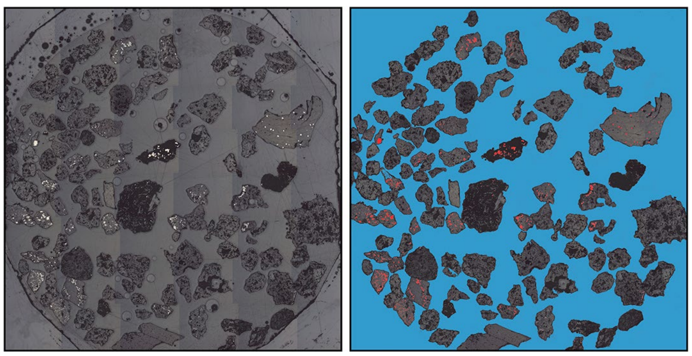

Figure 3. Reflected light mosaic of a polished grain mount from a sulfide-rich sample (RN12, 200 mRF). The highly reflective yellow-white grains are pyrite. The right image has its epoxy background removed and sulfides highlighted in red (used for pixel counting modal analysis). The field of view is 2.5 cm wide.

Primary igneous MSS (now retrograded to pyrrhotite) and ISS are found as irregularly- and droplet-shaped, blebby masses within the downhole basaltic and diabasic units and the unaltered surface samples (Figure 4). The sizes and textures of the MSS and ISS are similar to those of devitrified immiscible sulfide droplets observed from the South Atlantic Ridge (Patten et al., 2012). Partially resorbed pseudomorphs of these igneous sulfides in which MSS was replaced by pyrite are present in regions outside the primary upflow region, including the potential recharge zones in the subsurface of the system. These pyrite grains have a much different color (white versus yellowish-white), shape, texture, and trace element composition to the hydrothermal pyrite found in the altered rocks, and are thought to represent the hydrothermally leached breakdown products of the above-mentioned igneous sulfides.

Neo-formed hydrothermal pyrite and chalcopyrite occur as veins, disseminations, and replacement products. These minerals display sharp grain boundaries, with pyrite commonly exhibiting a characteristic cubic morphology and typical yellowish-white color. Sulfur isotope compositions of hydrothermal sulfides indicate a component of reduced seawater sulfate (Sakai *et al.*, 1980 and this study), providing evidence that these sulfides precipitated from convecting hydrothermal seawater, as discussed below. Hydrothermal pyrrhotite has only been observed at depths between 2513 and 2519 m in core samples from RN30, where it occurs in equilibrium with pyrite, dominantly in fault-controlled veins.

4.3 Sulfide Zonation

The distribution of sulfide minerals in the Reykjanes geothermal system shows a marked zonation corresponding to the present-day upflow zone (centered around RN10; Figure 5). At shallow depth, the only sulfide is hydrothermal pyrite. Chalcopyrite joins pyrite at depths between 152 and 902 m below the surface. The shallowest occurrence of chalcopyrite is in RN10 and the depth of its first occurrence increases progressively with increasing distance of the wells from this zone of high upflow. The deepest documented first occurrence of chalcopyrite is in RN19, one of the lowest-temperature production wells in the Reykjanes geothermal field (Fridleifsson, pers. comm.).

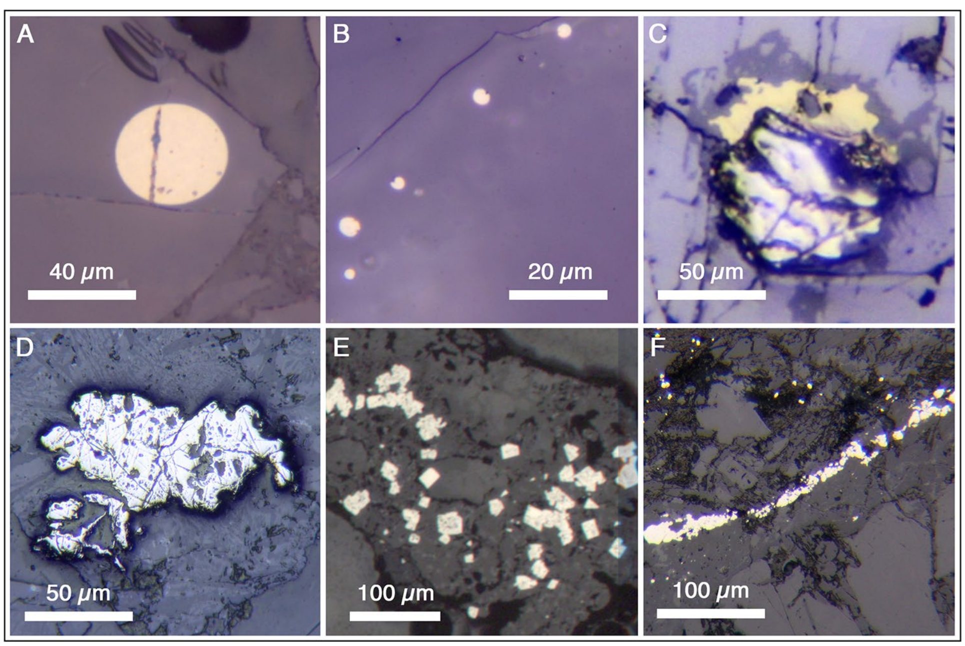

Figure 4. Reflected light photomicrographs of sulfides in the Reykjanes geothermal system. **(a)** and **(b)** Immiscible sulfide blebs in pyroxene phenocrysts from unaltered surface samples. **(c)** Partly resorbed sulfide bleb in which MSS was replaced by pyrite and ISS by chalcopyrite (RN17; 1600 m). **(d)** Partly resorbed igneous sulfide bleb replaced by pyrite (RN17; 2950 m). **(e)** Pyrite cubes (RN12; 200 m). **(f)** Chalcopyrite vein (RN12; 1110 m).

Igneous sulfides occur at depths greater than 1710 m below the surface. The shallowest depth of occurrence of these igneous sulfides correlates negatively with the distribution of temperature in the geothermal system (i.e., the uppermost occurrence of igneous sulfides is deepest in the upflow (high temperature) regions; Figure 5). This negative correlation likely reflects enhanced breakdown of primary igneous sulfides in the regions of upflow due to increased access of the sulfides to hydrothermal fluids.

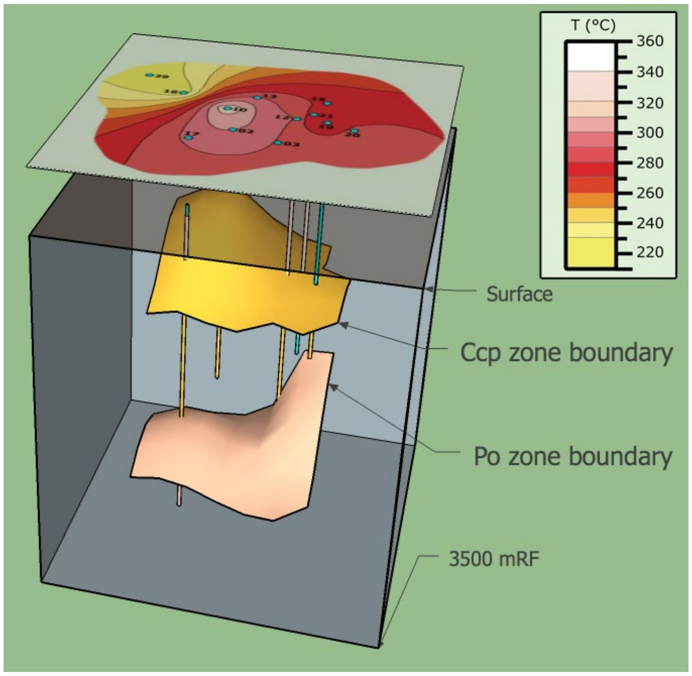

Figure 5. A 3-D block model of sulfide zonation in the Reykjanes geothermal system. Pyrite (Py) dominates above the chalcopyrite (Ccp) zone, the assemblage, Py+Ccp, dominates within the Ccp zone, and Po + ISS + Py ± Ccp occurs beneath the pyrrhotite (Po) zone boundary. The Ccp zone boundary follows the high and low temperature contours provided by Freedman *et al.* (2009).

4.4 Sulfide Trace Element Chemistry

Analyses of the trace element compositions of the sulfide minerals show that they have distinctive precious and base metal (e.g., Cu and Ni) signatures that correlate with the mode of formation of the minerals. The hydrothermal sulfides are strongly enriched in precious metals relative to the igneous sulfides (Figure 6). Chalcopyrite contains the highest concentration of Ag (maximum 260 ppm) and hydrothermal pyrite the highest gold concentration (maximum 4.2 ppm). Significantly, there is a marked depletion of base and precious metals in the pyrite that replaced MSS and corresponding enrichments of base and precious metals in the ISS and Po (formerly MSS), albeit to levels much lower than in the hydrothermal sulfides.

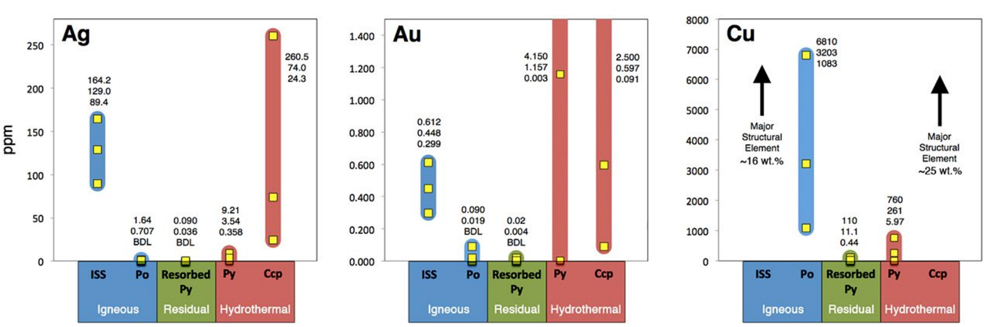

Figure 6. Metal concentrations (LA-ICP-MS and WDS data) in sulfides from the Reykjanes geothermal field. The sulfide minerals are grouped by color according to their interpreted origins (i.e., igneous sulfides, hydrothermal replacement pyrite, and neo-formed hydrothermal sulfides). Numbers on figures indicate the maximum, average, and minimum values.

Element maps produced using LA-ICP-MS analyses reveal that, in segregated immiscible sulfide blebs, Au and Ag are strongly fractionated into ISS and Ni into pyrrhotite/MSS (Figure 7). This is consistent with observations of metal fractionation in igneous sulfide minerals, summarized by Simon and Ripley (2011), who noted that exsolution of sulfide liquids from silicate melts may fractionate precious metals to such an extent that the remaining melt becomes precious-metal depleted. Exsolution of ISS from the sulfide phase further concentrates the precious metals by fractionating them into ISS.

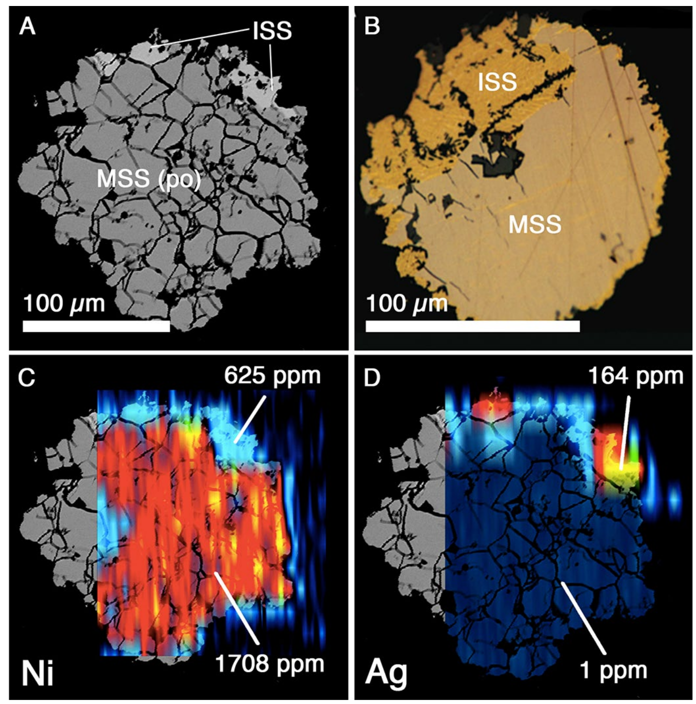

Figure 7. (a) A globule of ISS and pyrrhotite (retrograded from MSS) shown in a backscatter electron image. **(b)** An immiscible sulfide globule from the South Atlantic ridge similar to those found in the Reykjanes geothermal system (Patten et al., 2012). **(c)** and **(d)** LA-ICP-MS maps showing Ni enrichment in pyrrhotite and Ag enrichment in ISS, respectively.

The sulfide trace element data record a history of the hydrothermal mobilization of metals from primary igneous sulfides and their re-concentration in hydrothermal sulfides within the upflow zone of the geothermal system (Figure 8). The proposed model for this process is as follows: (1) precious and base metal enriched primary immiscible sulfide blebs formed during crystallization of the basaltic lava sequence that hosts the Reykjanes geothermal system; (2) seawater- dominated hydrothermal fluids leached metals from these primary sulfides, leaving behind (metal-depleted) resorbed forms that were replaced by pyrite during the leaching; (3) the mobilized metals were concentrated in hydrothermal sulfides that precipitated in the upflow regions

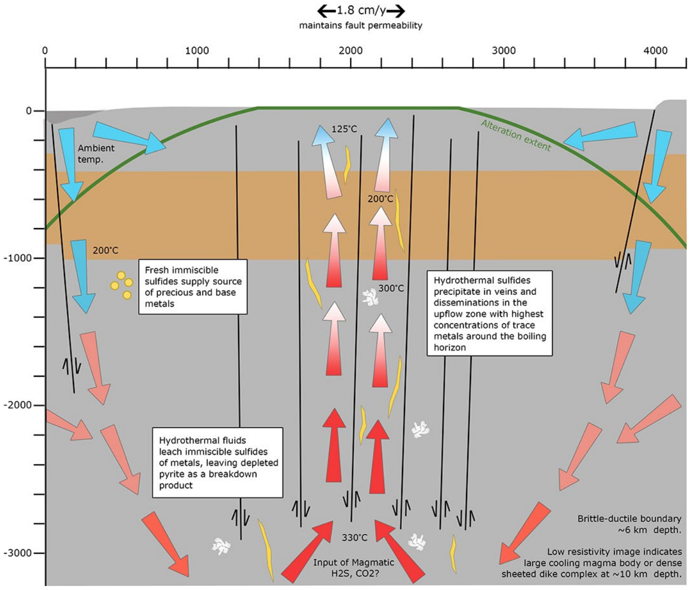

Figure 8. A conceptual model for sulfide mineralization in the Reykjanes geothermal system. The upper grey sequence from 0 – ~400 m depth represents a shallow suite of marine/subaerial lithologies (hyaloclastite, subaerial basaltic flows, minor pillows). The brown layer represents a shallow marine caprock sequence (fossiliferous sedimentary rocks, clastic tuffs, pillow breccia). The lower grey unit represents submarine pillow lavas (basaltic pillows and lava flows at depths below vigorous gas exsolution, crosscutting subvertical sheeted dikes, and minor hyaloclastite).

of the system when they saturated in the fluid due to decreasing temperature (and likely also fluid mixing at depths above the caprock).

The breakdown of primary igneous MSS (or related pyrrhotite) to secondary pyrite involving the reduction of seawater sulfate is thought to be a fundamental process controlling the sulfide production in mid ocean ridge (and corresponding volcanogenic massive sulfide) hydrothermal systems (e.g., Shanks and Seyfried, 1987), and proceeds according to the reaction:

$$8FeS + 10H^+ + SO_4^{2-} = 4FeS_2 + H_2S + 4Fe^{2+} + 4H_2O$$

The results of the present study represent the first detailed documentation of the occurrence of this process in a geothermal system.

4.5 Sulfur Isotope Geochemistry

Sulfide samples analyzed for their sulfur isotopic composition were enriched in ^{34}S, with a narrow range of $\delta^{34}S$ from +4.2 to +6.4 ‰. Modern day seawater sulfate has a $\delta^{34}S$ value of +20.5 ‰, whereas the corresponding value for mantle-derived sulfur is 0 to +1. The greater than +1 $\delta^{34}S$ values of the hydrothermal py and ccp are easily explained by the incorporation of seawater sulfate into the sulfide phases via inorganic reduction or isotopic exchange between dissolved sulfate and sulfide. To understand the S-isotope signature of igneous sulfides in the Reykjanes, in-situ S-isotope analysis is scheduled to be conducted on sulfide phases from cuttings and unaltered surface samples using secondary ion mass spectrometry (SIMS) on a Cameca IMS1280 ion microprobe at the Canadian Centre for Isotopic Microanalysis, Edmonton, Canada.

4.6 Applications of Sulfide Minerals to Geothermal Prospecting

Sulfides are more likely to decompose and re-precipitate elsewhere in response to changing physicochemical conditions (e.g., temperature and pH) in the subsurface than are many of the common hydrothermal silicate minerals present in geothermal systems. This concept can be illustrated by calculating equilibrium constants (log K) for the breakdown reactions between various sulfide phases and comparing them to those for hydrothermal silicate phases (Box 1). These constants show, for example, that the breakdown of ccp to py is thermodynamically favoured relative to the retrograde reaction of epidote to chlorite. The enthalpy data show, moreover, that the breakdown of sulfide minerals is strongly exothermic and leads to the release of sulfuric acid, locally depressing pH and promoting further sulfide dissolution.

Whereas the alteration of common igneous silicate phases such as plagioclase and pyroxene to epidote can occur isochemically in the presence of water, the precipitation of base metal sulfides (e.g., chalcopyrite) generally requires the hydrothermal mobilization and concentration of the dissolved metals and magmatic or seawater-derived sulfur. The fluids carrying these dissolved constituents will naturally be focused along permeable structures that define the upflow regions of a hydrothermal cell. Primary mineralogy is less of a control on disseminated and vein sulfide precipitation than it is on the formation of silicate minerals that more commonly replace primary minerals in the host rock and less commonly form through saturation and precipitation.

The well-developed zonation of hydrothermal sulfides centered on the current highest temperature region in the Reykjanes geothermal system illustrates a potential application of sulfide mineral mapping to geothermal exploration. The preliminary results from this study indicate that by contouring the first downhole occurrence of chalcopyrite it may be possible to identify upflow regions during geothermal exploration (a potentially useful tool to apply during shallow/slimhole drilling campaigns).

a) **Chalcopyrite to Pyrite**

$$CuFeS_2 + H^+ + 2Cl^- + 0.25O_{2(aq)} = 0.5H_2O + FeS_2 + CuCl_2^-$$

Log K @ 50°C	12.1085
Log K @ 100°C	11.0903
Log K @ 300°C	10.9209

b) **Epidote to Chlorite**

$$Ca_2FeAl_2Si_3O_{12}(OH) + 5.5H_2O + Cl^- + 5Mg^{2+}$$
$$= FeCl^+ + 4H^+ + 0.25O_{2(aq)} + 2Ca^{2+} + Mg_5Al_2Si_3O_{10}(OH)_8$$

Log K @ 50°C	-41.7539
Log K @ 100°C	-33.7227
Log K @ 300°C	-14.1133

Box 1. Equilibrium constants for hydrothermal breakdown reactions of **a)** chalcopyrite to pyrite and **b)** epidote to chlorite involving a Cl-H_2O fluid. Note: large log K values indicate that the products are favored.

5. Conclusions

Sulfide minerals in the Reykjanes geothermal system show a pronounced spatial zonation that mimics the present spatial distribution of isotherms. Trace element, bulk chemical, isotopic, and petrographic analyses reveal that metal-enriched primary igneous sulfides were altered by seawater-derived hydrothermal fluids, providing field evidence for a process which is thought to be a fundamental control of aqueous sulfide budgets in mid-ocean ridge environments. Metal-enriched hydrothermal sulfide minerals precipitate in a stratified manner in the upflow region of the system. Sulfide precipitation is pronounced in the convective region of the reservoir and above the caprock, where the mixing of hydrothermal fluids with shallow groundwater is the inferred precipitation mechanism.

Acknowledgements

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