Relating sulfide mineral zonation and trace element chemistry to subsurface processes in the Reykjanes geothermal system, Iceland

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Journal of Volcanology and Geothermal Research, Canada

ARTICLE INFO

ABSTRACT

The nature and distribution of sulfide minerals and their trace element chemistry in the seawater-dominated Reykjanes geothermal system was determined through the study of cuttings and core from wells that intersect different regions of the hydrothermal cell, from the near surface to depths of > 3000 m. The observed sulfide mineral zonation and trace element enrichment correlate well with the present-day thermal structure of the system. Isocubanite and pyrrhotite are confined to the deep, low permeability regions, whereas an assemblage of chalcopyrite and pyrite predominates in the main convective upflow path. The presence of marcasite in the uppermost regions of the system reflects weakly acidic conditions (pH < 5) marginal to the upflow, where outflow and downward percolating fluids have dissolved deeply exsolved CO_2. The presence of "chalcopyrite disease" in sphalerite may be an indication that the system is experiencing a heating trend, following the logic of "zone-refining" in volcanogenic massive sulfide systems. Sulfide sulfur at all analyzed depths in the Reykjanes geothermal system was derived from a mixture of basaltic and reduced seawater sources. Petrographic evidence suggests that seawater-derived hydrothermal fluids have altered primary igneous sulfides in the host rocks, a process that has been proposed as a major control of aqueous sulfide production in mid-ocean ridge environments. Calculations show that igneous sulfides in the host basalts likely account for less than 5% of the total available ore metal budget in the system, however, their contribution to fluid metal budgets is probably significant because of their relatively high solubility. The processes documented by this study are likely analogous to those operating in the feeder and deep reaction zones of mid-ocean ridge seafloor hydrothermal systems. The results show that sulfide mineral zonation and trace element chemistry vary as a function of physicochemical parameters that are relevant to the characterization and exploration of geothermal energy resources.

1. Introduction

Given the high sensitivity of sulfide mineralogy and trace element chemistry to physicochemical parameters such as temperature, fluid sulfidation/oxidation state, and pH, studies of sulfide minerals have the potential to generate valuable information pertaining to the hydrology of geothermal systems. Sulfide minerals occur widely in geothermal systems, and over 95% of all sulfur introduced into the deep regions may be fixed in these minerals upon fluid ascent (Giggenbach, 1977). Studies of sulfide minerals in active geothermal systems have been undertaken in a limited number of field areas, e.g., the Salton Sea (Skinner et al., 1967; McKibben and Elders, 1985; McKibben et al., 1988a, b; Hulen et al., 2004), Rotokawa (Krupp and Seward, 1987), Kirishima (Shoji et al., 1989), Ngawha (Cox and Browne, 1995), Yanaizu-Nishiyama (Shoji et al., 1999), Broadlands-Ohaaki (Simmons and Browne, 2000), Mataloko (Koseki and Kazuo, 2006; Koseki and Nakashima, 2006), and

Joaquina (Libbey et al., 2015). The small datasets and/or limited distribution of samples in the majority of these studies has hindered their application in assessing how sulfide mineral occurrences and chemistry relate to large-scale system hydrology in active geothermal environments. This paper aims to help resolve this issue by providing a detailed system-wide account of sulfide mineralization in the Reykjanes geothermal system, Iceland. Because of its location astride the on-shore expression of the Mid-Atlantic Ridge, the insights gained from the study of the Reykjanes geothermal system are directly applicable to understanding processes that are occurring in the deep sub-seafloor regions of seafloor hydrothermal systems.

A large number of studies have investigated sulfide scales precipitated within geothermal pipelines and wells, e.g., at the Salton Sea (Skinner et al., 1967; Gallup et al., 1990), Milos (Karabelas et al., 1989; Andritsos and Karabelas, 1991), Cerro Prieto (Clark and Williams-Jones, 1990; Thomas et al., 1992; Montalvo et al., 2012), Broadlands-Ohaaki (Mauk and Brown, 1998), Kakkonda (Yanagisawa et al., 2000), Ngawha (Brown and Dorrington, 2001), Berlin (Raymond et al., 2005), and Reykjanes (Hardardóttir et al., 2005, 2010, and 2013). However, the mineralogy of sulfides precipitated within geothermal pipelines and wells cannot be related directly to subsurface assemblages occurring in

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the host stratigraphy, as in the former the fluid is prevented from reacting with the host rock and the resulting chemical buffers for some components (notably, fH_2 and pH) differ from those operating in natural systems.

The most common sulfide minerals reported to occur in the altered rocks of geothermal systems are pyrite, sphalerite, chalcopyrite, pyrrhotite, and galena (e.g., McKibben and Elders, 1985; Krupp and Seward, 1987; Simmons and Browne, 2000). These minerals occur primarily in vugs and veins. Some systems show a zonation from base metal-concentrated at depth, to precious metal-concentrated at shallower levels (Ewers and Keays, 1977; Buchanan, 1981; Clark and Williams-Jones, 1990). 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). Isotopic studies have shown that the sulfide sulfur in the Salton Sea geothermal field is derived from the reduction of SO_4^{2-} leached from lacustrine sediments (McKibben et al., 1988b). Reduced sulfate, derived from seawater, is also partially incorporated into sulfide minerals in the Reykjanes geothermal field (Sakai et al., 1980). The bulk of the sulfur budget in dilute, meteoric-water-dominated geothermal systems (e.g., Krafla, Rotokawa, Wairakei, Kawerau) is thought to originate from host rock leaching or input from magmatic fluids (Steiner and Rafter, 1966; Sakai et al., 1980; Marini et al., 2011; Stefánsson et al., 2015).

2. The Reykjanes geothermal system

2.1. Geologic and geothermal setting

The Reykjanes geothermal system is a basalt-hosted, seawater-dominated active hydrothermal system located at the tip of the Reykjanes peninsula in southwest Iceland. Its presence results from a crustal thermal anomaly associated with the on-shore expression of the Mid-Atlantic Ridge. It is one of the smallest high-temperature fields in Iceland, with surface manifestations and altered ground covering an area of ~1 km^2. The natural heat flow at Reykjanes has been estimated at 130 ± 16 MW_{th} (Friðriksson et al., 2006), which, for an average reservoir temperature of 300 °C (Friðleifsson et al., 2011), equates to 85–109 kg/s of upflowing geothermal fluid. Thirty-seven wells have been drilled into the Reykjanes system, which currently supply 520 kg/s of fluid to the 100 MW Reykjanes Geothermal Power Plant, commissioned in 2006. Reinjection is limited to 140 kg/s through one well (RN20) drilled to the east of the main production area; however, there is a plan to increase this amount (Matthiasdottir et al., 2015).

The upper 1 km of the Reykjanes system is dominated by hyaloclastite tuff, breccias, pillow basalts, and tuffaceous and marine sediments. The deeper parts of the system are composed primarily of basaltic lavas and diabase dikes (Marks et al., 2011). Altered and hydrothermally-cemented tuffaceous and sedimentary successions at depths of 400 to 800 m act as a cap-rock to the hydrothermal system (Friðleifsson et al., 2011; Friðleifsson et al., 2014). A low resistivity anomaly at 10 km below the surface of the Reykjanes geothermal system has been interpreted as a dense, partially molten, sheeted-dike complex or a large cooling gabbroic intrusion, and likely serves as the heat engine that drives the shallower hydrothermal system (Friðleifsson et al., 2011).

The present-day hydrothermal fluid at Reykjanes is heated seawater that has been modified by interaction with basalt at high temperature. Fluid inclusions in hydrothermal minerals have a salinity that ranges between that of fresh water and seawater (<0.1 and 3.5 wt.% NaCl, respectively; Franzson et al., 2002). The range of salinity and the light δD signature of presently circulating fluids (see Pope et al., 2009) suggest that glacially-derived freshwater dominated the system at some time during the Pleistocene (Franzson et al., 2002). There is a shallow freshwater lens in the upper 30 m of the geothermal system due to the penetration of surface waters through the highly faulted, porous rock (Sigurðsson, 1985). As a result of the elevated salinity of the

present-day geothermal fluid, the in-situ pH is about 5.5, lower than is typically the case in other geothermal fields in Iceland (Arnórsson, 1978, Arnórsson et al., 1983; Henley and Ellis, 1983; Darling and Ármannsson, 1989; Arnórsson, 1995; Stefánsson and Arnórsson, 2002; Kaasalainen et al., 2015).

Upflowing geothermal fluids in the Reykjanes geothermal system first boil at a depth of ~1300 m and follow the boiling point with depth curve until they reach the base of the cap rock at roughly 700 m (Franzson et al., 2002; Friðleifsson et al., 2011; Friðleifsson et al., 2014). Deeper in the reservoir, conditions follow an adiabatic gradient through a freely convecting zone down to a minimum depth of 2.5 km for most parts of the field (Franzson et al., 2002). With further increase in depth, temperature rises due to conductive heat transfer (e.g., RN12, RN17B, and RN30; Friðriksson et al., 2015), indicating low permeability in these regions. Measured reservoir temperatures at Reykjanes are commonly in the range of 280 °C to 300 °C, however, temperatures as high as 345 °C and 350 °C have been measured in RN17B and RN30, respectively (Friðleifsson et al., 2011; Friðriksson et al., 2015). These wells were directionally drilled into the south (RN17B) and southeast (RN30) parts of the system. A 3-dimensional visualization of the measured 300 °C isotherm is provided in Fig. 1b.

The Reykjanes geothermal system is centered in a prominent rift-zone graben, however, many of the associated faults are covered by Holocene lavas and not exposed at the surface; this is especially true on the western side of the peninsula where young (<2 ka) lava flows dominate (Sæmundsson, 2011; Friðleifsson et al., 2014; Fig. 1a). Franzson et al. (2002) suggested that there is a primary upflow zone in a volume encompassing RN12, RN21, and the Gunnuhver thermal area, which contains steam vents and acidic steam-heated features (e.g., boiling mud pots and advanced argillic alteration). The orientation of feed zones and the temperature distribution has led to the development of a model that has upflow at Reykjanes controlled by the intersection of a NE–SW trending zone of normal faults and fissures, with a short N–S fracture and an unmapped NW–SE transform fault that cuts through the Gunnuhver thermal area (Sigurðsson, 2010). However, the temperature in RN10 (situated ~600 m to the west of RN12) is 20 °C higher than anywhere else in the reservoir at >1 km depth (the maximum temperature at this depth in RN10 was ~320 °C; Franzson et al., 2002; Björnsson et al., 2004). Moreover, the distribution of measured isotherms relative to the downhole occurrence of actinolite (which crystallizes at a temperature >280 °C) indicates a strong heating trend in this well (with a corresponding cooling trend in RN16; G.Ó. Friðleifsson, Deep Roots Seminar presentation, 2012; Friðleifsson et al., 2014). It is thus likely that the present upflow extends beneath RN10 and RN27. A southwest to northeast migration of the upflow zone was proposed by Pope et al. (2009).

2.2. Sulfur in the Reykjanes geothermal system

Based on reconstructions from analyses of well discharges, reservoir fluids in the Reykjanes geothermal system contain roughly 30 to 80 ppm H_2S (HS^- concentrations are minimal due to the relatively low pH (5.5) of the Reykjanes fluid) and <25 ppm SO_4^{2-}, whereas unmodified seawater contains ~0 ppm H_2S and 2700 ppm SO_4^{2-} (Björnsson et al., 1972; Arnórsson, 1978; Arnórsson et al., 1978; Sakai et al., 1980; Berner and Berner, 2012; Padilla et al., 2012). Total sulfur concentrations in the host rocks vary from below the detection limit (BDL, <0.02 wt.%) to 2.5 wt.% in the altered rocks. Metasomatic enrichments of sulfur are particularly pronounced at depths of <~700 m above the upflow zone intersected by RN10 and RN27 due primarily to sulfide mineral precipitation (Libbey and Williams-Jones, in review-a). At depths of <~300 m, anhydrite also contributes to the sulfur enrichment. There it precipitates (due to its retrograde solubility) as inflowing seawater-derived groundwater mixes and is heated by upwelling boiling fluids (Padilla et al., 2012; Libbey and Williams-Jones, in review-a).