

Composition of Reservoir Liquid and Metals in Pipeline Scale, Reykjanes Geothermal System, SW Iceland

Hardardóttir^{ac}, V., Hedenquist^a, J.W., Hannington^a, M.D., Brown^b, K., Fridriksson^c, TH., and Thorhallsson^c, S.

^aUniversity of Ottawa, Earth Science, 140 Louis Pasteur, Ottawa ON, K1N 6N5 Canada

^bGEOKEM, P.O. Box 95-2210, Swanson, Waitakere 0653, New Zealand

^cIceland Geosurvey, Grensásvegur 9, Reykjavík, 108 Iceland

vigdis.hardardottir@isor.is

Keywords: high-temperature, geothermal system, sulfide, precipitation, seawater, reservoir liquid, base metals, Au, Ag, concentration

ABSTRACT

The Reykjanes high-temperature geothermal system is located in SW Iceland at the toe of the Reykjanes Peninsula, which is the on-land extension of the Mid-Atlantic Ridge. The fluid in the geothermal system is modified seawater, with salinities of 3.2 wt% NaCl, heated to temperatures of between 270 and 315°C at 1.0 to 2.5 km depth, similar to end-member fluids that discharge at black smoker vents on the seafloor. Comparison between the boiling discharge fluid and the pre-boiling reservoir liquid, collected at 1500 m depth in May 2007, demonstrate that the metal concentrations are three to four orders of magnitude higher in the deep liquid; the low concentrations in surface samples is caused by deposition of sulfides during ascent and boiling.

Scales in pipelines from wellhead to the separation station consist of sulfides upstream of the orifice plate; downstream of the orifice plate the scales are mainly amorphous material with minor amounts of sulfides, mainly chalcopyrite, sphalerite, and traces of wurtzite, bornite, digenite, and galena. The concentrations of metals in the scales varies, depending on the location in the pipeline, from trace to maximum values of 31 wt% Cu, 59 wt% Zn, 23 wt% Fe, 17 wt% Pb, 2.3 wt% Ag, and 600 ppm Au; the highest precious metal concentrations are with bornite-rich scales on the orifice plate, where deposit rate is high due to the sharp pressure decrease.

1. INTRODUCTION

The Reykjanes high-temperature geothermal system, SW Iceland, has been utilized for almost 40 years for salt production and fish drying. Since 1999, 17 new wells have been drilled, and from May, 2006, 100 MW of electricity has been produced. The fluid in the Reykjanes geothermal system has a seawater composition and is the only such system developed in Iceland. There are considerable problems faced by the developer company HS Orka HF associated with the utilization of seawater, including sulfide precipitation due to pressure release in the well and surface pipeline, as well as formation of amorphous Fe-silica scales. The sulphides are the first scales to precipitate in Reykjanes pipelines followed by amorphous phases

The metal concentrations in the deep liquid, collected at 1500 m depth, are compared to samples collected at the surface, and also to values for fluids from hydrothermal systems sampled from ocean-floor black smokers. The scales precipitated in surface pipeline provide the opportunity to compare theoretical calculations to these

direct observations at Reykjanes, where temperatures, pressures and fluid composition are well known.

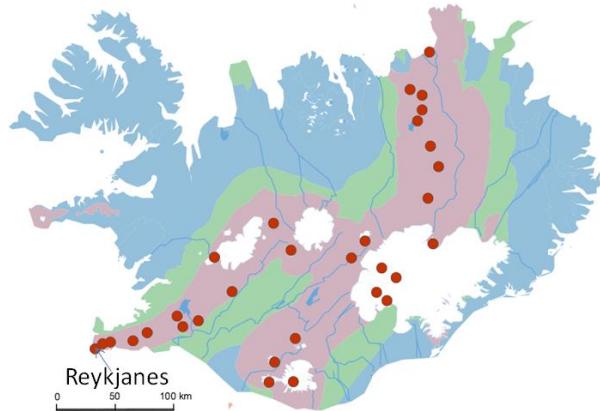


Figure 1: Location of the Reykjanes geothermal area on the Reykjanes peninsula, Iceland (modified from Jakobsson et al., 1978; Saemundsson and Jóhannesson, 2004).

2. REYKJANES GEOTHERMAL SYSTEM

The Reykjanes geothermal system is located at the western tip of the Reykjanes peninsula in southwest Iceland, where the Reykjanes ridge comes on shore; the ridge and peninsula are the northeast continuation of Mid Atlantic Ridge (Fig. 1). The Reykjanes peninsula is only 4 km wide at its narrowest point, surrounded by the ocean on three sides. The surface of the Reykjanes geothermal system is dominated by young basalts erupted since the last glacial period (Saemundsson and Jóhannesson, 2004). The Reykjanes peninsula is composed of rocks of basaltic composition, ranging from few occurrences of small picrite lava shields through olivine-tholeiitic shield volcanoes (2 to 10 kyr) to tholeiitic lavas erupted from fissures (Jakobsson et al., 1978) controlled by NE-SW trending fracture swarms. The deep drilling has revealed that the upper 1000 m consist of sub-aerial lava flows and hyaloclastic tuffs and breccias as well as tuffaceous sediments. Below 1000 m the stratigraphy is dominated by crystalline basalts and pillow lavas, mainly olivine tholeiite in composition (Björnsson et al., 1970, 1972; Franzson et al., 1983, 2002). The area is underlain by a dyke swarm coinciding with the central part of the field (Franzson et al. 2002). Hydrothermal alteration studies by Tómasson and Kristmannsdóttir (1972) and by Franzson et al. (2002) define progressive alteration zonation with increasing depth, from montmorillonite-zeolite-calcite to mixed-layered clay-prehnite and then to chlorite-epidote and epidote-amphibole.

The fluid in the geothermal system is modified seawater, with salinities of 3.2 wt% NaCl. The reservoir temperatures

range from 270° to 315°C at depths of 1000 to 2500 m, and the deep liquid has a pH 4.5 to 5.5, recalculated based on surface sampling of well discharges (Björnsson et al., 1972). Reaction of the seawater as it heats and interacts with the surrounding basalt has resulted in removal of most of the SO_4^{2-} and Mg, by precipitation of anhydrite and formations of clay minerals, whereas the SiO_2 , K and Ca concentrations are elevated compared to seawater (Björnsson et al., 1972; Arnórsson, 1978; Kristmannsdóttir, 1984).

3. SCALES IN SURFACE PIPELINES

Scales collected from wellhead and down to the separations station from a 360 m long pipeline well RN-9 have been grouped by Hardardóttir (2002, 2004) mostly according to their locations and their characteristics. These groups are (1) upstream of the wellhead and to the orifice plate, 15 m long pipeline, less than 1 cm thick scales consisting mostly of sphalerite, chalcopyrite with trace of galena. Other minerals like bornite, pyrrhotite and covellite have been found together with amorphous Fe rich silica. (2) From the orifice plate to the second bend (group 2), pipeline ca 12 m long x 40 cm in diameter nearly clogged by scales consisting mainly of amorphous silica together with alternating layers of sphalerite dendrites and mono-mineral bands of chalcopyrite. Group (3) from bend three to the separation station, little less than 340 m long pipeline with scale thickness from 15 cm at the bottom of the pipe and diminishing down to few millimeter 100 m away. The scales are mainly amorphous silica with trace of sphalerite and chalcopyrite. Further downstream at the lowest point of the pipeline scales consists of fragments of same minerals and as upstream which are cemented together. Group (4) is scales from the separation station and consist also of amorphous silica, sphalerite and chalcopyrite.

The new wells RN-12, 21 and 24 have formed scales on the fluid flow control valve located at the orifice plate. The pressure drops from ~37 bars to 22 bars resulting in scales consisting of sphalerite 45 vol. %, bornite 30 vol. %, 10 digenite vol. %, galena 15 vol. % and traces of amorphous Fe-silica, Ag-sulfides, chalcopyrite, and covellite.

The concentrations of metals in the scales varies, depending on the location in the pipeline, from trace to maximum

values of 31 wt% Cu, 59 wt% Zn, 23 wt% Fe, 17 wt% Pb, 2.3 wt% Ag, and 600 ppm Au; the highest precious metal concentrations are with bornite-rich scales formed on the fluid flow valve at the orifice plate, where deposit rate is high due to the sharp pressure decrease.

Bulk analyses were done on samples from RN-9 pipeline which were collected between wellhead and the separation station and the results are shown in Figure 2. In general the base metals, Cu, Fe, Zn and Pb have their highest concentration upstream of the orifice plate (group 1), up to 90 wt% (60% on average in Fig. 2), but diminish shortly after the pressure drop downstream of the orifice plate, to 30 to 40 wt% (group 2). Thirty meters downstream of the orifice plate the base metals are ~10 wt% (group 3) and <5 wt% at the separation station (group 4). The silica concentration ranges from 5 to 30 wt% upstream of the orifice plate, increasing to 13 to 80 wt% at the orifice plate and the next 30 m downstream. The pressures when these scales formed were from 44 bars to 35 bars at wellhead to the orifice plate and downstream of the orifice plate the pressure was dropped to 11 bars.

4. COMPOSITION OF THE SURFACE FLUID

Liquid and vapor samples from wells drilled into the Reykjanes geothermal area have been collected for over 30 years, but only in the last six years have trace elements such as Cu, Zn, and Pb, as well as Au and Ag, been analysed in liquids sampled at the surface. The composition of the original deep liquid is calculated by restoring the separated vapor to the liquid phase in proportions dictated by the sampling pressure and the deep liquid enthalpy. Reference temperature for each well based on measured temperature and silica concentrations (Fridriksson and Giroud, 2008) are used in the calculation of the deep liquid. Three other assumptions are involved in the calculation of the composition of the deep liquid; first, that the inflow into the well at depth is a single-phase liquid; second, that the ascent of the liquid in the well is adiabatic; and third, that there are no chemical reactions occurring on the way to the surface (other than partitioning of volatile species between the liquid and the vapor phase).

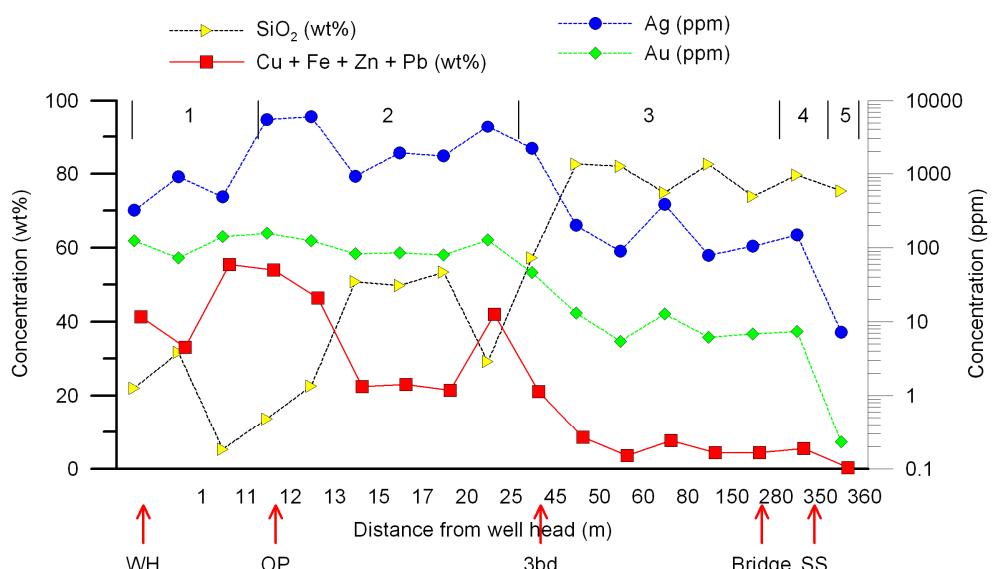


Figure 2: Average summary of the base metals, Cu+Fe+Zn+Pb, SiO_2 , Au and Ag downstream from well-head (WH) to the separation station (SS) from well RN-9. OP, orifice plate; 3bd, third bend; 1-5 are locations groups.

Sulfide scaling in well RN-9 has demonstrated that the last assumption is not valid for the Reykjanes systems, at least not for the metals that form sulfide scales. Table 1 shows the concentrations of Cu, Zn, and Pb, plus other selected trace elements that have been analyzed from samples collected at the surface from RN-19. The concentrations in the surface sample (Table 1) refer to their values after correction for vapor loss, i.e., to reservoir liquid conditions.

Table 1: Fluid compositions Reykjanes; deep liquid (average) and surface fluid, vent fluid from 21°N and sea water.

| | | Deep liquid RN19 (average) ¹ | 21°N OBS ² | Seawater ³ |
|--------------------------|--------------|---|-----------------------|-----------------------|
| Sampling depth | Surface | 1500 m | 2600 m | |
| Temperature °C | 275 | 290 | 350-273 | 2°C |
| pH | 5.99/ 21.9°C | NA | 3.4-3.8 | 7.4-8.5 |
| Cl (mg/kg) | 19608 | NA | 17335 | 19800 |
| Na (mg/kg) | 9812 | 9390 | 9936 | 10800 |
| K (mg/kg) | 1459 | 1582 | 907 | 392 |
| Ca (mg/kg) | 1649 | 1843 | 625 | 411 |
| SiO ₂ (mg/kg) | 635 | 665 | 1082 | 6 |
| Mg (mg/kg) | 0.61 | 5 | 0 | 1290 |
| Al (mg/kg) | 0.10 | 2 | NA | 0.001 |
| Ba (mg/kg) | 9 | 11 | 1 | 0.02 |
| Sr (mg/kg) | NA | 9 | 7 | 8.1 |
| B (mg/kg) | 8 | 8 | 6 | 4.5 |
| Li (mg/kg) | NA | 7 | 6 | 0.18 |
| Br (mg/kg) | 71 | 66 | 64 | 67 |
| I (μg/kg) | na | 649 | NA | 60 |
| Fe (mg/kg) | 0.05 | 58 | 93 | 0.00003 |
| Cu (mg/kg) | 0.0008 | 15 | 2 | 0.0009 |
| Zn (mg/kg) | 0.02 | 15 | 7 | 0.00050 |
| Mn (mg/kg) | 1 | 3 | 55 | 0.0001 |
| Ni (μg/kg) | <0.05 | 307 | NA | 0.48 |
| As (μg/kg) | 0.0001 | 128 | 18.5 | 3.7 |
| Pb (μg/kg) | <0.3 | 234 | 64 | 0.003 |
| Cd (μg/kg) | <0.05 | 125 | 17.4 | 0.1 |
| Cr (μg/kg) | 0.1 | 59 | NA | 0.3 |
| Ag (μg/kg) | na | 57 | 4.1 | 0.002 |
| V (μg/kg) | na | 13 | NA | 2.5 |
| Sb (μg/kg) | na | 31 | NA | 0.24 |
| Mo (μg/kg) | 9 | 21 | NA | 10 |
| Te (μg/kg) | na | 38 | NA | 0.0001 |
| Se (μg/kg) | na | 6 | 5.7 | 0.2 |
| Tl (μg/kg) | na | 12 | NA | 0.01 |
| W (μg/kg) | na | 11 | NA | 0.1 |
| Au (μg/kg) | na | 3 | 0.05-0.2 | 0.004 |
| Sn (μg/kg) | na | 3 | NA | 0.0006 |
| Hg (μg/kg) | <0.002 | 0 | NA | 0.001 |

** Chloride in the down-hole liquid samples was calculated from Na, K, Ca and Mg, as HCl was immediately added after sampling.

¹Hardardóttir et al. (2009); ²Von Damm et al., (1985); ³Lide, (1998).

5. COMPOSITION OF THE DEEP LIQUID

Deep liquid was directly sampled from three wells at 1350 and 1500 m depth in May 2007 (Table 1; Hardardóttir et al., 2009). These deep liquid samples have orders of magnitude higher concentrations of the base metals than do samples collected at the surface (corrected for vapor loss). The Cu

concentration of the deep liquid is similar in the three wells, ~15 mg/kg, as well as the Zn concentration at ~15 mg/kg. Iron concentration has a considerable range but the average composition is ~60 mg/kg, and Pb is ~0.2 mg/kg. Concentrations of other metals are significantly lower than those of Cu, Zn and Fe; Ag and Au, range from 30 to 100 μg/kg and 1 to 6 μg/kg respectively (Hardardóttir et al., 2009). The differences between concentrations of many metals in samples collected at depth are as much as two to four orders of magnitude higher than those in samples collected at the surface. On the other hand, the concentrations of elements that are not incorporated in sulfide scales (e.g., Na, K, Br, B) are very similar in the deep liquid and in the surface samples.

6. DISCUSSION

It is clear that the the high pressure, 45 to 35 bars and/or the temperature 259° to 244°C is the main factor controlling the minerals which precipitated in the pipeline. The main minerals at this pressure range are wurtzite, sphalerite, chalcopyrite, and galena. When the pressure is dropped at the orifice plate down to 22 bars (220°C) from 2006 and to 11 bars (185 °C) from 1988 the main precipitates are amorphous Fe-rich silica together with the sulfides, mainly sphalerite with traces of chalcopyrite, galena, and pyrite.

6.1 Comparison of the Surface Fluid and the Deep Liquid

The major metals Cu, Zn, and Pb in pipeline scales are near detection limits in the fluid sampled at the surface, whereas the downhole-sampled liquid has orders of magnitude higher metal concentration. The concentrations of major elements in the deep liquid, Na, K, Ca, SiO₂, B, Br, and Mg, have similar concentration to those sampled at the surface (Hardardóttir et al., 2009).

These results indicate that the majority of the metals precipitate in the wells prior to reaching the surface sample point, just downstream of the wellhead (Hardardóttir et al., 2009). This is clear based on observation of well RN-9, which was clogged in 1993 after 10 years of discharge, cleaned out, and then blocked again in 2003. Boiling of the liquid in 1983 as it ascended to the surface started at 900 m depth, as indicated by pressure and temperature logging (Steingrímsson and Björnsson 1992), whereas boiling started at 1000 m depth in 2003; in 2009 logging indicates boiling at 1250 m depth in wells, with wellhead pressure of about 35 bars. Wells with much lower pressure (~25 bars) may boil to their bottom at 1800 m, and into the host rock as well.

6.2 Comparison with the Black Smokers

The Reykjanes geothermal system and mid-ocean ridge hydrothermal systems have a similar tectonic setting. Here we compare the Reykjanes deep liquid compositions to those discharged from black smokers on the Mid-Atlantic ridge (TAG) and 21°N of the East Pacific Ridge (generally taken to be typical of high-temperature seafloor fluids). The end-member fluids discharge from black smoker vents at a temperature commonly in the range of 350 to 400°C, whereas the highest temperature measured in the Reykjanes system is 315°C at 1900 m depth. The deep liquids at Reykjanes have similar compositions for most of the major elements to those of the seafloor systems (Kristmannsdóttir, 1984, Hardardóttir et al., 2009). The Fe concentration at Reykjanes is at the lower end of the black smoker range. By contrast, the base metals are considerably lower in most black smoker fluids compared to Reykjanes (Fig. 3a; Hardardóttir et al., 2009); the Zn concentration are similar

to the maximum values found in the black smokers, whereas the Cu and Pb concentrations are an order of magnitude higher in the deep Reykjanes liquid compared to most of the black smoker fluids (Hannington et al., 2005).

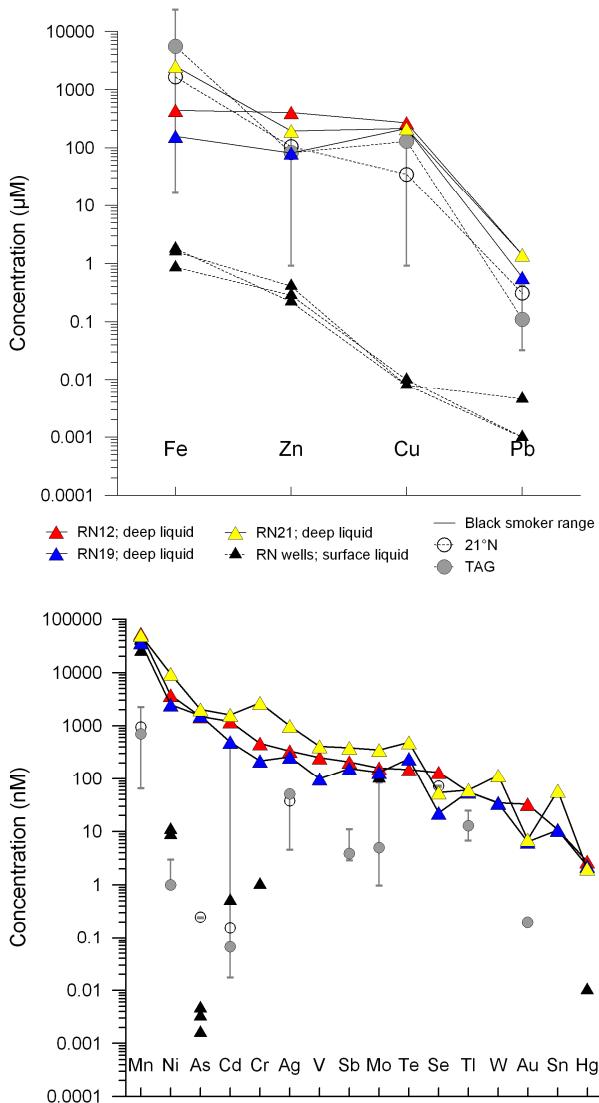


Figure 3: a) Concentrations of Cu, Fe, Zn, and Pb in three downhole liquid samples from Reykjanes, and samples collected from surface, the latter corrected for vapor loss. b) Concentrations of Mn, Ni, As, Cd, Cr, Ag, V, Sb, Mo, Te, Se, Tl, W, Au, Sn, Hg and Co from Reykjanes downhole samples, compared with available data for selected trace elements from 21°N OBS, and TAG, plus the range of other black smoker vent fluids.

The other trace element concentrations in the deep liquid from Reykjanes (Fig. 3b) can be compared with the few data published from black smoker fluids. The concentrations in the Reykjanes deep liquids are typically higher than in black smoker vent fluids (Fig. 3b). For example, the Au, Ag, As, Cd, and Tl concentrations at Reykjanes are all an order of magnitude higher than those in the black smoker fluids, with Sb and Mo concentrations two orders higher. However, concentrations of Se in the Reykjanes deep liquids are similar to black smoker fluids at 21°N, whereas TAG values are an order of magnitude higher in concentration. Nickel concentrations are similar to those in fluids from the ultramafic-hosted Rainbow vent

field, whereas other mid-ocean ridge black smoker fluids are mainly below the detection limit (Douville et al., 2002).

Considering the analogy with the fluids collected at the surface after ascent, depressurization, and boiling at Reykjanes and the overall similarity of the settings of Reykjanes and mid-ocean ridge systems, the low metal composition of the latter leads to the conclusion that most of the black smoker fluids have lost a significant metal content before discharging at the seafloor.

The end-product of the black smoker fluids are the formations of seafloor chimneys which are mainly made up of an outer rim of anhydrite, followed by pyrite and sphalerite and, at higher temperature, an inner rim of chalcopyrite. Pyrrhotite is also abundant in black smokers as well as isocubanite (Hannington et al., 2005). The main mineral difference between Reykjanes and the black smoker chimneys are the precipitation of the anhydrite which due to mixing with the cold surrounding seawater then again at Reykjanes there is no mixing and precipitation of amorphous silica occur.

7. CONCLUSIONS

The surface fluids at Reykjanes are depleted in the metals, Fe, Cu, Zn and Pb as well as the trace metals compared to the deep liquid, indicating that most of the metals have precipitated as the fluids ascend to the surface. Precipitations of sulfides continue in surface pipes, along with amorphous Fe-bearing silica, which causes a large problem in utilizing the geothermal fluid at Reykjanes.

Comparison with mid-ocean ridge black smokers indicates that the tectonic setting as well as the mineralogy is very similar to Reykjanes, but most black smoker fluids have lost a large proportion of their metals prior to discharge at the seafloor, as indicated by the low Cu, Pb and other metal concentrations.

8. ACKNOWLEDGEMENTS

We thank HS Orka HF for the funding and approval that made the deep liquid sampling possible; we are also grateful to the Iceland GeoSurvey for their logistic support. This research was partially funded by a Natural Sciences and Engineering Research of Canada (NSERC) grant to JWH. VH thanks G. Gíslason for discussion, and he and B. Jónsdóttir for assistance with the figures.

REFERENCES

- Arnórsson, S., 1978, Major element chemistry of the geothermal sea-water at Reykjanes and Svartsengi, Iceland: Mineralogical Magazine, v. 42, p. 209-220.
- Björnsson, S., Arnórsson, S., and Tómasson, J., 1970, Exploration of the Reykjanes thermal brine area. Geothermics, Special Issue 2, p.1640-1650.
- Björnsson, S., Arnórsson, S., and Tómasson, J., 1972, Exploration of the Reykjanes thermal brine area: Geothermics Special Issue 2, v. 2, part 2, p 1640-1650.
- Douville, E., Charlot, J.L., Oelkers, E.H., Bienvenu, P., Jove Colon, C.F., Donval, J. P., Fouquet, Y., Prieur, D. and Appriou, P., 2002, The Rainbow vent fluids (36°14'N, MAR): the influence of ultramafic rocks and phase separation on trace metal content in Mid-Atlantic Ridge hydrothermal fluids: Chemical Geology, v. 184, p. 37-48.
- Franzson, H., Gudmundsson, G., Tómasson, J., and Thorsteinsson, Th., 1983, Drilling of well RnG-9,

Reykjanes high-temperature field. National Energy Authority report No. OS-83040/JHD-12B, 31 p.

Franzson, H., Thordarson, S., Björnsson, G., Gudlaugsson, S.Th., Richter, B., Fridleyfsson, G.O., and Thórhallsson, S., 2002, Reykjanes high-temperature field, SW-Iceland. Geology and hydrothermal alteration of well RN-10. Proceedings, Twenty-seventh Workshop on Geothermal Reservoir Engineering. Stanford University, Stanford, California, January 28-30, 2002. SGP-TR-171

Hannington, M.D., de Ronde, C.E.J., and Petersen, S., 2005, Sea-floor tectonics and submarine hydrothermal systems: in Hedenquist, J.W., et al., eds., Economic geology 100th anniversary volume: Denver, Colorado, Society of Economic Geologists, p. 111-141.

Hannington, M.D. and Scott, S.D., 1989, Mineralogy and geochemistry of a hydrothermal silica-sulfide-sulfate spire in the caldera of Axial Seamount, Juan de Fuca Ridge, The Canadian Mineralogist, v. 26, p. 603-625.

Hardardóttir V., 2002, Scales in well 9 Reykjanesi. (in Icelandic). Report OS-2002/011, 48 pages.

Hardardóttir V., 2004, Major and trace elements in scales in pipes from well 9, Reykjanes, Iceland, in Wanty and Seal II eds., 2, Water-Rock Interaction: Taylor and Francis, London, ISBN 90 5809 641 6, p. 1521-1525.

Hardardóttir, V., Brown, K.L., Fridriksson, Th., Hedenquist, J.W., Hannington, M.D. and Thórhallsson, S., 2009, Metals in deep liquid of the Reykjanes geothermal system, southwest Iceland: Implications for the composition of seafloor black smoker fluids. Geology (in review).

Jakobsson, S.P., Jónsson, J., and Shido, F., 1978, Petrology of the Western Reykjanes Peninsula, Iceland. Journal of Petrology, v. 19, part 4, p. 669-705.

Kristmannsdóttir, H., 1984, Chemical evidence from Icelandic geothermal systems as compared to submarine geothermal systems, in Rona, P.A., Bostrom, Laubier, L., and Simith, K. L. Jr., eds., Hydrothermal processes at seafloor spreading centers: Plenum Press, NATO Conference Series, IV Marine Sciences, v. 12, p. 291-320.

Lide, D. R., editor-in-chief, 1998, CRC Handbook of chemistry and physics, 78th edition 1997-1998, CRC Press, Boca Raton New York, p. 14-14.

Saemundsson, K., and Jóhannesson, H., 2004, Geothermal map of Iceland: Iceland GeoSurvey and Icelandic Energy Authority.

Tómasson, J. And Kristmannsdóttir, H., 1972, High temperature alteration minerals and thermal brines, Reykjanes, Iceland. Contributions to Mineralogy and Petrology, v. 36, p. 123-134.

Steingrímsson, B., and Björnsson, G., 1993, Logging of well 9 on Reykjanes in September 1993 (in Icelandic), Orkustofnun, report No. BS/GrB-93/01.

Von Damm, K. L., Edmond, J. M., Grant, B., Measures, C. I., Walden, B., and Weiss R. F., 1985, Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise: Geochimica et Cosmochimica Acta, v. 49, p. 2197-2220.

Von Damm, K.L., 1990, Seafloor hydrothermal activity: Black smoker chemistry and chimneys: Annual Review of Earth Planetary Sciences, v. 18, p. 173-204.

Von Damm, K.L., Edmond, J.M., Grant, B. and Measures, C.I. 1985, Chemistry of submarine hydrothermal solutions at 21 °N, East Pacific Rise: Geochimica et Cosmochimica Acta, v. 49, p. 2197-2220.