



Geothermal surface alteration of basalts, Krýsuvík Iceland—Alteration mineralogy, water chemistry and the effects of acid supply on the alteration process

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ABSTRACT

The geothermal surface alteration of basalts and associated water chemistry at Krýsuvík, SW Iceland were studied. The geothermal area was characterised with zones of intensive surface alteration, steam vents, mud pots and hot springs. The steam-heated geothermal surface waters had pH values between 1.69 and 7.67 and total dissolved solid (TDS) concentrations between 154 and 6660 ppm, with Cl and SO₄ concentration decreasing and increasing with decreasing pH, respectively. Alteration mineral assemblages observed were strongly associated with the surface intensity. In areas of most intensive activity the basaltic rocks were altered to amorphous silica, anatase and pyrite with a crust of native sulphur at the surface. With decreased activity, kaolinite became important, as well as iron oxyhydroxides and oxides. On the flanks of the area montmorillonite was the predominant alteration product. Based on these observations the surface geothermal activity was divided into three groups: (1) *high activity areas* with active steam vents and mud pots and intensive acid leaching, (2) *medium activity areas* where the ground is hot, steam vents and mud pots are uncommon and the surface alteration is less intensive and (3) *low activity areas* on the margins of the surface geothermal activity. The primary factors influencing the steam-heated acid sulphate alteration of basalts included the redox state (oxidation front), supply of acids and pH, and the extent of reaction. The formation of iron- and sulphur-containing minerals and the respective elemental mobility depended on the redox conditions with pyrite formation under reduced conditions and goethite and/or hematite under oxidised conditions. At low pH, Ca, Mg, K and Na were mobile and leached out, whereas Fe, Ti and Al and to a large degree Si were retained in the alteration product. At higher pH values >5 the mobility of Ca, Mg, K and Na was reduced due to the formation of clays.

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1. Introduction

Mud pots, hot springs and steam vents as well as intensive alteration at the surface are common features of many active volcanic geothermal systems. They are produced upon depressurisation boiling of deep aquifer fluids that produce steam rich in volatiles like CO₂, H₂S and H₂ and are neutral to boiled alkaline waters enriched in non-volatiles. Following fluid segregation, the steam rich in volatiles commonly mixes with oxygenated surface waters producing steam-heated acid sulphate waters that readily dissolve the bedrock, thus producing intensive alteration (Arnórsson et al., 2007). Water–rock interaction between steam-heated acid sulphate waters and primary rocks typically produces alteration assemblages characterised by silicic, argillic and advanced argillic alteration (Heald et al., 1987).

The acid–sulphate alteration of active and fossil geothermal systems has been reported in a number of studies (e.g. Klammer, 1997; Mas et al., 2006; Boyce et al., 2007; Karakaya et al., 2007). However, studies of the

alteration mineralogy in geothermal systems in Iceland have mainly focused on sub-surface mineralogy and its application to geothermal exploration. These studies indicate that geothermal aquifer water compositions are controlled by equilibrium between the geothermal minerals and the fluids (Arnórsson et al., 1983; Stefánsson and Arnórsson, 2000; Gudmundsson and Arnórsson, 2005). At low temperatures, the subsurface mineral assemblages are characterised by various smectites and zeolites that are replaced with increasing temperature by chlorite, epidote, prehnite and actinolite. Alkali-feldspars, sulphides, quartz and calcite are found independent of temperature (e.g. Tómasson and Kristmannsdóttir, 1972; Kristmannsdóttir, 1976, 1979; Mehegan et al., 1980; Fridleifsson, 1983; Sveinbjörnsdóttir et al., 1986; Lonker et al., 1993; Franzson et al., 2008). Nevertheless, the surface water chemistry and mineralogy associated with active volcanic geothermal systems in Iceland has received less attention.

Sigvaldason (1959) studied the surface alteration of basalts at Hveragerdi and rhyolites in Torfajökull, Iceland. His study demonstrated that acid surface alteration of basalts was intensive, with montmorillonite, hematite, goethite, anatase, pyrite, kaolinite, opaline silica and elemental sulphur among the secondary minerals and leaching of alkali and alkaline earth metals and to a lesser extent silica,

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iron and aluminium relative to titanium. Arnórsson (1969) observed similar mineralogical alteration at Krýsuvík, Iceland, with the addition that Cu was found to be immobile, whereas many other trace elements like Zn, Ni and Co were found to be mobile relative to Ti. Arnórsson (1969) also reported intensive pyrite and clay formation on the surface of many mud pots which were considered to be formed in situ from the H₂S gas and metals leached from the host rock in these pots. The surface water chemistry as well as the process of water–rock gas interaction producing the intensive leaching and alteration mineralogy, however, has received very limited attention.

The purpose of the present study was to characterise the alteration of basaltic rocks in Iceland associated with steam-heated acid sulphate waters, as well as the water chemistry itself in order to evaluate elemental mobility and the overall gas–water–rock interaction. Samples of alteration products and waters were therefore collected at the Krýsuvík geothermal area, SW Iceland, and analysed, and sets of geochemical model calculations were carried out.

2. The Krýsuvík geothermal area

The Krýsuvík geothermal area is located on the Reykjanes Peninsula, SW Iceland (Fig. 1). The peninsula is an oblique on-shore segment of the Mid-Atlantic ridge and was initiated around 6–7 m.y. ago (Saemundsson, 1979; Clifton and Schliche, 2003). It is made up of basaltic lavas ranging from picrite to tholeiite composition and hyaloclastite ridges formed in subglacial eruptions (Jónsson, 1978). The Krýsuvík field is one of five presently active geothermal fields on the Reykjanes Peninsula.

The geothermal activity at Krýsuvík consists mainly of acid surface alteration and hot ground, steam vents and steam-heated hot springs and mud pots. Distribution of thermal manifestations and geophysical surveys indicate activity of some 40–60 km². The geothermal activity is associated with two hyaloclastic ridges, Sveifluháls and Vesturháls, and a fault running east of Sveifluháls. The main surface activity is confined to the Sveifluháls area, including Austurengjahver and mostly within the

small area of Seltún and Hveradalur. The present study focused on the surface alteration and water chemistry in the Sveifluháls area (Fig. 1).

The Sveifluháls hyaloclastite ridge was formed during the last glaciation (Jónsson, 1978). The stratigraphy is mainly made up of altered tuff with some flows of crystalline basalt, both of originally tholeiitic composition (Immsland, 1973; Gunnlaugsson, 1975).

The surfaces at Krýsuvík are characterised by intensive leaching with montmorillonite, hematite, goethite, anatase, pyrite, kaolinite, opaline silica and elemental sulphur. Copper sulphides and sulphates have also been identified (Arnórsson, 1969). The composition of the associated surface waters, however, is poorly known as well as the alteration mechanism.

3. Methods

3.1. Geothermal waters

Geothermal waters were collected in the Krýsuvík geothermal area, including samples from hot springs, mud pots and runoff (Fig. 1). The water samples were collected and analysed according to standard methods (Arnórsson et al., 2006). The water samples were filtered on-site through 0.2 µm Millipore cellulose acetate filters with a Teflon® filter holder into polypropylene bottles and amber glass bottles. Before sampling, 0.5–1 l of water was pumped through the filtration unit. Samples for determination of major cations were acidified with concentrated nitric acid (Merck Suprapur®), 0.5 ml to 100 ml, whereas samples for determination of trace elements were acidified similarly but with 1.0 ml to 100 ml. Samples for anions were filtered but not further treated. Amber glass bottles were used to collect samples for determination of pH. The pH was determined on-site and/or within a few hours after sampling in the laboratory using a Metrohm pH electrode and meter. The on-site pH and laboratory measurements agreed within allowable uncertainties.

The concentrations of major cations were determined using a Spectro CIROS ICP-AES and Dionex IC-1000 ion chromatograph. The samples were diluted by weight by acidified blank (0.5 ml Merck

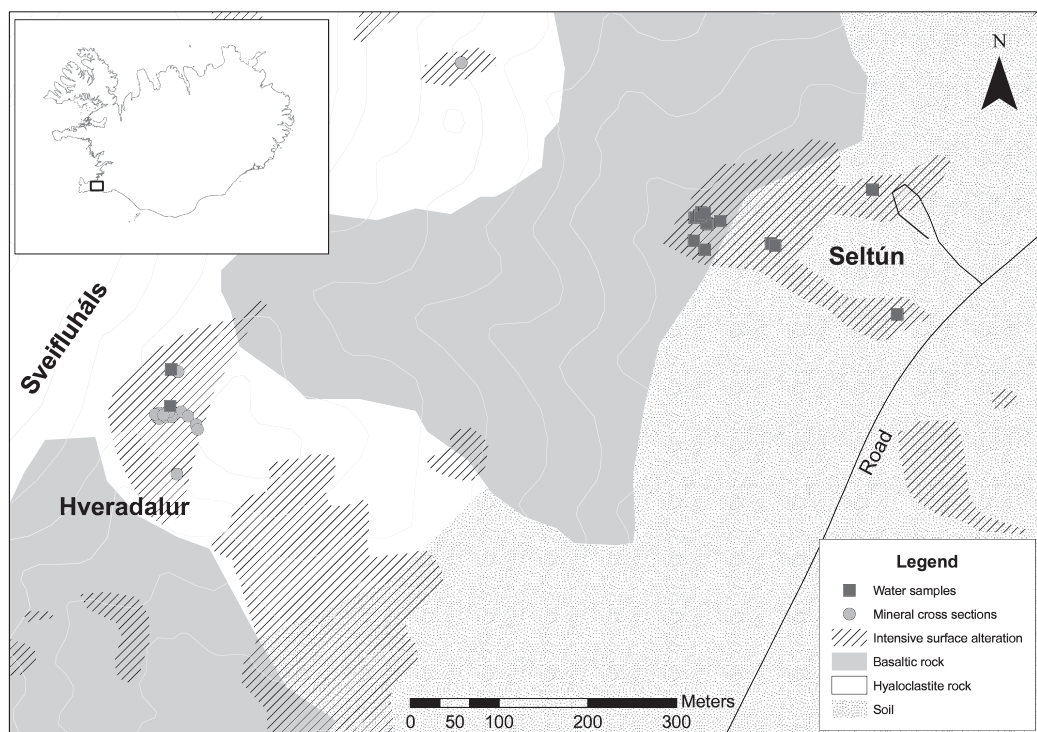


Fig. 1. The Krýsuvík geothermal area.

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