



Chromium geochemistry and speciation in natural waters, Iceland



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ABSTRACT

Natural waters in Iceland were collected and analyzed for chromium concentration and speciation (Cr^{III} , Cr^{VI} and Cr_{TOT}). The water sampled included non-thermal surface and spring water, surface geothermal water, and single and two-phase geothermal well discharges with sampling temperatures of 0–178 °C, pH of 2.0–9.5, and total dissolved solids (TDS) of 35–4030 ppm. The total Cr concentration was between <0.01 and 660 ppb with highest concentrations in waters with the lowest pH. At pH > 4 the measured Cr^{III} concentration was low, generally <1 ppb but with decreasing pH higher Cr^{III} concentrations were observed reaching values of hundreds of ppb. At pH < 6 no measurable Cr^{VI} was detected whereas in neutral to alkaline waters measured Cr^{VI} concentrations were as high as 3 ppb, frequently dominating over Cr^{III} . The Cr chemistry in natural waters associated with mafic rocks in Iceland is largely influenced by the water pH. At low pH Cr-containing minerals are unstable and Cr leaches into the waters as Cr^{III} . Possible oxidation of Cr^{III} to Cr^{VI} is minimized thermodynamically and the mobility of Cr^{VI} is further reduced by surface complexation reactions. At neutral to alkaline pH the primary Cr-containing mineral phases like titanomagnetite and chromite may be stable, limiting Cr-rock leaching. Solubility of secondary Cr^{III} –Fe^{III}-mineral phases may further reduce and/or limit the Cr^{III} availability. In contrast, Cr^{VI} mobility is enhanced at a pH > 8 associated with decreasing importance of mineral surface complexation. Hence, Cr^{VI} becomes an increasingly dominant form of dissolved Cr at pH above 7–8. Many groundwater drinking supplies associated with mafic rocks are characterized by moderately alkaline pH resulting in Cr^{VI} concentrations of a few ppb.

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1. Introduction

Chromium is the 24th most abundant element in Earth's crust with an average concentration of ~100 ppm (Nriagu, 1988; Emsley, 2001). In contrast, the chromium concentrations in natural waters are generally low or <1 ppb (e.g. Richard and Bourg, 1991; Davis et al., 1994). Elevated concentrations of up to several ppm may occur in waters having low pH values, like acid mine drainage (e.g. Accornero et al., 2005). In natural waters chromium occurs in two oxidation states, as Cr^{III} and Cr^{VI} . The two oxidation states are very different in their geochemical and biochemical behavior. Chromium(III) is sparingly soluble in natural waters whereas Cr^{VI} is quite soluble and more mobile. The biological behavior of chromium is also very different with Cr^{III} being an essential nutrient whereas Cr^{VI} is considered to be toxic and a carcinogen (Saner, 1980; Burrows, 1983; Kotas and Stasicka, 2000; ATSDR, 2012).

The concentration of Cr^{III} in aqueous solutions at neutral to alkaline pH is limited by absorption on mineral surfaces and

incorporation into minerals such as chromite, Fe(III) containing mineral, Al hydroxides and clays (Rai et al., 1987, 1989; Sass and Rai, 1987). However, aqueous Cr^{VI} concentrations are affected by adsorption onto Fe oxides and hydroxides at acid to neutral pH conditions as well as having limited thermodynamic redox stability whereas it is more mobile at high pH values. This results in Cr^{III} being the predominant form of aqueous chromium at low pH conditions and Cr^{VI} predominating at high pH conditions (Sass and Rai, 1987). The concentrations of Cr in rocks and minerals are much higher than in natural waters. The average concentration of Cr in ultramafic and mafic rocks is much greater than the average value in the Earth's crust (Nriagu, 1988) possibly resulting in elevated Cr concentrations in surface and ground waters in areas associated with such rock types. For example, in Icelandic basalts the Cr concentration range from 19 to 1342 ppm with a median value of 187 ppm, whereas in silicic rocks the concentrations are much lower, ranging from 0.68 to 46 ppm with a median value of 5 (Kaasalainen and Stefánsson, 2012). The associated total Cr concentrations in natural non-thermal and thermal waters in Iceland range from <0.01 to 660 ppb (Flaathen and Gíslason, 2007; Kaasalainen and Stefánsson, 2012).

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In this study the geochemistry and concentration of Cr in natural waters was investigated. Routine analytical methods were developed to determine dissolved Cr^{III}, Cr^{VI} and total Cr (Cr_{TOT}) concentrations in non-thermal and thermal waters down to concentrations as low as 0.01 ppb. Moreover, based on the results and with the aid of geochemical modeling, the geochemical behavior of Cr^{III} and Cr^{VI} in the natural waters was assessed.

2. Methods

2.1. Sampling and major elemental analysis

Samples of natural waters were collected from several locations in Iceland. The water sampled included non-thermal surface and spring waters, surface geothermal waters, and single and two-phase geothermal well discharges. In addition, data on Cr concentration in natural waters in Iceland partially discussed in Kaasalainen and Stefánsson (2012) were included. The sampled areas include the Southern Lowlands and Geysir geothermal area, Borgarfjörður, Snæfellsnes, Hellisheidi, Krýsuvík, Kverkfjöll, Krafla, Námafjall and Torfajökull (Fig. 1).

The sampling and analytical procedures for major elements have previously been described (Arnórsson et al., 2006; Stefánsson et al., 2007). Water samples were filtered through a 0.2 µm filter (cellulose acetate) into pre-cleaned bottles. Samples for major cation analysis were acidified to 0.5% HNO₃ (Suprapur[®], Merck) and analyzed using ICP-OES. Samples for anion determination were no-further treated and analyzed using IC. Total dissolved sulfide (H₂S) using Hg-titration. The pH and total dissolved carbonate (ΣCO₂) using pH electrode and modified alkalinity titration, respectively (Stefánsson et al., 2007).

The analytical accuracy of all major ions was checked with analyses of known reference samples, including two in-house reference samples, Spói05 and Sel03, as well as the Canadian River Water Standard. The results were always within the analytical precision, based on duplicate analysis. The analytical reproducibility at the 95% confidence level was found to be <5% for all major elements.

2.2. Chromium(III), Cr(VI) and Cr_{TOT} determination

Samples were collected for total Cr concentration. In some cases, additional samples for determination of Cr^{III} and Cr^{VI} concentrations were also collected. Samples for Cr analysis were filtered through 0.2 µm filters (cellulose acetate) in the field into bottles that had been pre-cleaned by soaking in 1 M HCl (>4 h) and rinsing with deionized water prior to sampling. Bottles were then always cleaned with filtered sample water in the field 2–3 times before sampling.

The concentration and speciation of chromium were determined after the appropriated treatment as Cr^{VI} using ion chromatography (IC) followed by complexation with 1,5-diphenylcarbazide (DPC) and detection by UV-Vis spectrophotometry. By this method the concentration of Cr^{VI} was determined as CrO₄²⁻ (Dionex Application Update 144). The total chromium (Cr_{TOT}) concentration was further analyzed as Cr^{VI} after oxidation and Cr^{III} concentration calculated from [Cr^{III}] = [Cr_{TOT}] – [Cr^{VI}]. A summary of the analytical conditions is given in Table 1. A summary of the analytical conditions is given in Table 1. The Cr_{TOT} concentrations reported by Kaasalainen and Stefánsson (2012) and included in this study were analyzed by ICP-MS on acidified samples, 1% HNO₃ (Suprapur[®], Merck).

Most geothermal waters are reduced (e.g. Stefánsson and Arnórsson, 2002; Stefánsson et al., 2005) with Cr^{III} predominating over Cr^{VI} allowing for accurate determination of Cr^{III} by subtracting Cr^{VI} from total Cr_{TOT}. In this case, a 100 ml sample was collected for Cr^{VI} analysis, 2 ml SAP buffer solution (250 mM NH₄SO₄ and 1 M NH₄OH solution) added to the sample and Cr^{VI} concentration analyzed within 24 h using the IC method previously described. For Cr_{TOT} analysis a separate sample was collected, acidified with to 0.1% HCl (Suprapur[®], Merck) and all Cr in the sample oxidized in the laboratory by addition of 0.05-ml 25% H₂O₂ (Suprapur[®], Merck) in a 10 ml sample followed by oxidation in UV-light (Metrohm mercury lamp) for 2 h. After oxidation, 0.2 ml of SAP buffer solution was added to the sample, and Cr_{TOT} analyzed as Cr^{VI} using the IC method previously described. The recovery of Cr^{III} upon oxidation was found to be >97% based on measurements of standard solutions.

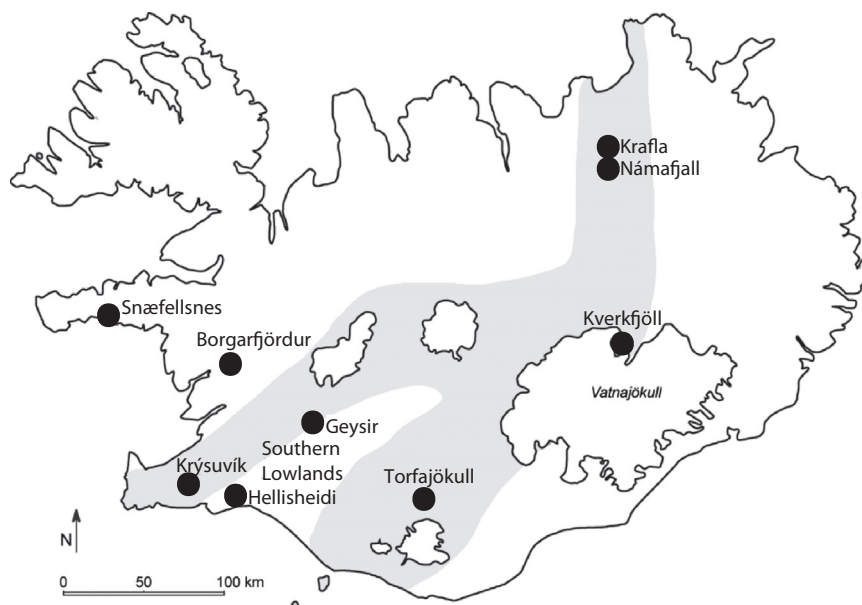


Fig. 1. Location of the sampled geothermal fields. The shaded area shows the active volcanic belt in Iceland.

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