

## Isotopic fractionation between Cr<sup>3+</sup> species in aqueous solutions

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When chromium is oxidized from the 3+ to the 6+ state, the 6+ species displays a  $\delta\text{Cr}_{53-52}$  of up to 7 permil (‰) relative to the 3+ state [1-3]. Here we show that large fractionation predicted by theory [4] within the same oxidation state (3+) can also be evidenced. Cations are present in different species which result from the interaction with the anions present in the solution. Chromium has the property similar to only a few other elements (e.g. Os) that coexisting species do not re-equilibrate immediately when the medium changes (e.g. by dilution or by addition of an acid). In contrast to most cations which interact instantaneously with the aqueous solvent, Cr<sup>3+</sup> requires several days at room temperature in HCl solution for the different species to reach equilibrium.

### Procedure

This property which is usually a drawback for a clean separation of Cr from other elements [5] can be used for identification purposes as described in the following. A chromium III standard solution was made in HCl 6N to produce easily measurable amounts of chlorocomplexes and was left for several days to reach equilibrium. A chromatographic separation [5] was achieved in less than 30mn to avoid significant kinetic isotopic effects. The isotopic ratios of the different hydrated chlorocomplexes as well as the Cl free hydrated  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  cation were measured by high precision MC-ICPMS at medium mass resolution (ca 4000) with a precision of 0.05‰.

### Results and conclusion

The  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  species shows an excess in  $\delta\text{Cr}_{53-52}$  of  $2.37 \pm 0.05$  ‰ relative to the starting Cr solution.  $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}$  displays a deficit in  $\delta\text{Cr}_{53-52}$  of  $-0.03 \pm 0.05$  ‰. The higher complexes  $[\text{CrCl}_x(\text{H}_2\text{O})_{(6-x)}]^{(3-x)+}$   $x > 1$  which have not yet been resolved in the chemical separation display altogether a deficit of  $\delta\text{Cr}_{53-52}$ :  $-0.39 \pm 0.05$  ‰. HBr and H<sub>2</sub>SO<sub>4</sub> media have also been investigated; they yield negative values for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  which are interpreted as being dominated by kinetic effects during the hydrolysis of the anion-chromium complexes.

The results for the HCl media are in a first order agreement with the theoretical estimates of Schauble et al. [1]. Whether the significant fractionation that may occur in solutions within the Cr<sup>3+</sup> oxidation state has an impact in natural samples has to be investigated.

[1] Johnson, Bullen (2004) *Rev. Min. & Geochem.* **55**, 289-319. [2] Ellis et al. (2002) *Science* **295**, 2060-2062. [3] Frei *et al.* (2009) *Nature* **461**, 250-253. [4] Schauble *et al.* (2004) *Chem. Geol.* **205**, 99-114. [5] Strelow (1973) in *Ion exchange and solvent extraction* Marcel Dekker. **5**, 121-206

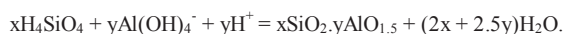
## The solubility of amorphous aluminous silica between 100 - 350°C: Implications for scaling in geothermal power stations

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Scaling is a common problem in geothermal power plants. In particular it occurs from brines where minerals become saturated and precipitate. To prevent scaling, geochemists use thermodynamic modelling to apply treatment methods, such as adjusting temperature or pH. Amorphous aluminous silica scaling has been reported in many geothermal power plants such as in New Zealand, Philippines, Salton Sea, Japan and Iceland [1]. Currently, the sole study on the solubility of amorphous aluminous silica was carried out by Gallup 1998 [2]. These were simple batch experiments in which there was no control on pH or Al concentration. A general reaction can be written for the precipitation of this phase as:



Unlike amorphous silica precipitation, this reaction is pH and Al concentration dependent over a wide region of pH. Unfortunately, there have been no well-controlled experiments to determine thermodynamic data for this reaction.

Preliminary calculations, using the data of Gallup 1998 [2], were used to estimate the solubility of amorphous aluminous silica and compare it with the solubility of pure silica. These show that scaling, caused by amorphous aluminous silica, can occur at temperatures up to 50°C higher than for pure silica, based on the chemistry of a cooling, flashed Ohaaki brine.

Four samples of amorphous aluminous silica scale were collected from Wairakei and Ohaaki geothermal power plants. XRD, XRF and SEM analyses were carried out on the samples and to verify that Al was not present as a distinct Al phase from the amorphous silica. Results from the XRD analyses showed amorphous material with quartz peaks in all samples. XRF results show concentrations of SiO<sub>2</sub> ranging from 73.89-76.70%, Al<sub>2</sub>O<sub>3</sub> from 8.38-10.46%, K<sub>2</sub>O from 2.13-3.05%, Na<sub>2</sub>O from 1.72-2.15%, CaO from 1.08-2.13% and MgO from 0.06-1.99%. Other oxides were less than 1% of the total sample. XRD results and EDX mapping by SEM verified that Al is present within the silica and is not in a distinct phase. Al concentration is zoned and correlates with increases in alkali concentration.

Experiments are planned to investigate the solubility of amorphous aluminous silica in the temperature range 100 - 350°C. These will be conducted at saturated vapor pressure and with varying pH using a continuous flow-through system and batch reactors.

[1] Gallup (1997) *Geothermics* **26**, 483-499. [2] Gallup (1998) *Geothermics* **27**, 485-501.