Experimental study to understand the hydrothermal alteration of iron and chromium hydroxides in a flow-through system

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Chromite is a mineral that has been thought to crystallize under magmatic conditions. However, recent studies [1, 2] suggest that chromite may have also been formed at lower temperatures (e.g., metamorphic or hydrothermal conditions). Chromium that are chemically enriched in ~3.2 Ga banded iron formations (BIFs) are hosted by chromite overgrown by magnetite [1], suggesting that both magnetite and chromite were transformed from primary precipitates: $2(Cr, Fe)(OH)_3 + Fe^{2+} \rightarrow Fe(Fe, Cr)_2O_4 + 2H^+ + 2H_2O$ (1), which is similar to a non-redox transformation between hematite and magnetite [3]. In this study, we experimentally investigated whether the above reaction proceeds at 150°C and 5 MPa using a flow-through type experimental apparatus. The proper control of temperature in the reaction cell was confirmed by measuring the solubility of amorphous silica.

Iron and chromium hydroxides synthesized by mixing sodium chromate and ferrous chloride (1:4 molar ratio) solutions at ambient temperature were reacted with dissolved Fe^{2+} produced by reacting magnetite with an acidic solution (pH=4) at ~150°C in a pre-reaction cell. The pH and dissolved iron concentration in the outflow solution were periodically measured. The chemical analysis of the solutions indicates that the dissolved iron was consumed in the reaction cell with increasing pH, shifting to the experimental condition under which both chromite and magnetite are thermodynamically stable. After 112 hours, the solid samples were recovered from the cell. The XRD spectra and SEM-EDS analyses of the solids indicate the presence of chromium spinel in the reaction products, providing experimental evidence that reaction (1) proceed under the hydrothermal conditions. This new formation model of chromite supports the observation that chromium was chemically enriched in BIFs and is therefore indicative of surface environments on early Earth.

[1] Otake *et al.* (2013) *Min. Mag.* 77, 1901. [2] Arai & Akizawa (2014) *Am. Min.* 99, 28-34. [3] Otake *et al.* (2007) *Earth Plant. Sci. Let.* 257, 60-70.