

Dissolution mechanisms of chromitite: Understanding the release and fate of chromium in the environment

MICHAEL SCHINDLER^{1,*}, AARON J. LUSSIER^{1,3}, EMILIA PRINCIPE^{1,2}, AND NADIA MYKYTCZUK²

¹Department of Earth Sciences, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

²School of the Environment, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

³Canadian Museum of Nature, P.O. Box 3443, Station D, Ottawa, Ontario K1P 6P4, Canada

ABSTRACT

An understanding of the formation of toxic hexavalent chromium (Cr^{6+}) in Cr-containing mine tailings and associated soils and sediments, requires an understanding of the underlying dissolution mechanisms of chromitite, a common chromite-bearing rock in both ophiolites suites and ultramafic intrusions. This study will examine dissolution mechanisms of chromitite in various acidic, neutral, and alkaline solutions containing cultivated bacteria, manganese oxides, sulfates, and phosphates. Dissolution of chromitite is non-stoichiometric under acidic, near-neutral, and alkaline pH conditions and involves the release of chromite nanoparticles and complex dissolution/re-precipitation reactions. Chromitite samples are obtained from the Black Thor chromite deposit in Northern Ontario, Canada; part of the “Ring of Fire” intrusive complex. The examined chromitite is composed of chromite, $(\text{Fe}_{0.5}\text{Mg}_{0.5})(\text{Al}_{0.6}\text{Cr}_{1.4})\text{O}_4$ and clinochlore; $\text{Mg}_3[\text{Si}_4\text{O}_{10}(\text{OH})_2] \cdot [\text{MgAl}_{1.33}(\text{OH})_6]$, the latter phase contains ~3 wt% Cr in the form of chromite nanoparticles. Bulk dissolution data are collected after dissolution experiments with chromitite powders, and the chemical and mineralogical composition of treated chromitite surfaces is characterized with a combination of surface analytical techniques (X-ray photoelectron spectroscopy) and nano- to micro-analytical techniques (scanning electron microscopy, transmission electron microscopy, and focused ion beam technology). In the chromitite systems studied here, the non-stoichiometric dissolution of clinochlore is the dominant reaction, which results in the formation of a hydrous and porous silica precipitate that is depleted in chromite nanoparticles relative to untreated clinochlore. Complete replacement of clinochlore by hydrous silica on the surface of chromitite under acidic conditions promotes the release of chromite nanoparticles and results in higher Cr:Si in solutions and in higher proportions of secondary Cr species on its surface (secondary Cr species are defined as surface terminations that do not occur on an untreated chromite surface, such as $-\text{Cr}^{3+}\text{-OH}_2$ and $-\text{Cr}^{6+}\text{-OH}$). Cultivated bacteria from a sulfide-bearing acid-mine drainage system affect neither the degree of dissolution nor the formation of secondary Cr species, whereas pyrolusite (MnO_2) particles, and adsorbed or precipitated Fe- and Al-bearing hydroxide, -sulfate, and -phosphate species, affect release and re-adsorption of chromite nanoparticles and Cr-bearing species during dissolution of chromitite under acidic, neutral, and alkaline conditions. These results show that weathering of chromitite and the release of Cr into the environment are strongly controlled by factors such as dissolution rates of Cr-bearing silicates and chromite, the release of chromite nanoparticles, re-precipitation of amorphous silica, the presence of particles in solution, and the pH-dependence adsorption (or precipitation) of Fe- and Al-bearing hydroxides and sulfates.

Keywords: Chromite, clinochlore, dissolution, chromate, toxicity, Ring of Fire, X-ray photoelectron spectroscopy, transmission electron microscopy, focused ion beam, bacteria, pyrolusite