Previously unknown mineral-nanomineral relationships with important environmental consequences: The case of chromium release from dissolving silicate minerals

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ABSTRACT

Risk assessments that take into account the formation of environmentally dangerous hexavalent chromium in Cr-containing mine tailings, and associated soils and sediments, require an understanding of the occurrence and speciation of Cr in silicate minerals and glasses. Silicates are more soluble and generally more susceptible to weathering than the refractory mineral chromite, the principal ore mineral of Cr. Studies at the nanoscale using a combination of advanced sample preparation via microtoming and focused ion beam techniques, in combination with state-of-the-art analytical transmission electron microscopy and electron diffraction, reveal the occurrence of chromite nanoparticles held within clinochlore and lizardite grains in chromitite ore (an igneous cumulate consisting primarily of chromite) from the Black Thor Chromium deposit in Northern Ontario, Canada, and the Mistake Mine, Fresno County, California, U.S.A., respectively. Nanoscale examinations of altered chromitite ore samples from the Black Thor deposit after dissolution experiments in sulfuric acid-bearing solutions of pH 2.5 show that clinochlore alters to amorphous silica depleted in chromite nanoparticles. This observation suggests the release of chromite nanoparticles rather than Cr\(^{3+}\) aqueous species during the weathering of chromite-bearing silicate minerals. This will in turn have an impact on the environmental behavior of Cr\(^{3+}\) and its potential oxidation to Cr\(^{6+}\). The formation of Cr\(_{aq}^{6+}\) species in this case will require either the initial dissolution of the nanoparticles or the oxidation of Cr\(^{3+}\) species on the surface of the nanoparticles, either process being a rate limiting step in the formation of Cr\(_{aq}^{6+}\) species.

Keywords: Chromite, nanoparticles, silicates, clinochlore, lizardite, California, Black Thor deposit, Ontario, Nanominerals and Mineral Nanoparticles

INTRODUCTION

Chromium can be potentially harmful in the environment as a result of industrial waste mismanagement, accidental spills, and the presence of Cr-bearing rocks and minerals in aquifers, soils, mines, and mine waste. In ultramafic rocks, Cr is present as Cr\(^{3+}\) which has relatively low toxicity, is a micronutrient, and is relatively insoluble and immobile at neutral to alkaline pH. In contrast, Cr\(^{6+}\) is an environmental toxin and human carcinogen (Fendorf 1995 and references therein) and is highly mobile at neutral to alkaline pH. Cr\(^{3+}\) can be readily oxidized to Cr\(^{6+}\) by naturally occurring Mn\(^{3+/4+}\)-oxides (e.g., Bartlett and James 1979; Eary and Rai 1987; Fendorf 1995; Weaver and Hochella 2003; Oze et al. 2007). Hexavalent Cr can be reduced by organic carbon, bacteria, sulfides, and Fe\(^{2+}\) (e.g., Kamaludeen et al. 2003 and references therein).

Several studies have focused on the Cr chemistry and mineralogy of serpentinite and serpentine-derived soils as Cr-bearing silicates of the serpentine and chlorite-groups are more susceptible to weathering than the refractory mineral chromite (e.g., Fandeur et al. 2009; Hseu and Iizuka 2013; Oze et al. 2004 2007; Morrison et al. 2015). Elevated Cr\(^{3+}\) concentrations in soil pore water and groundwater adjacent to serpentinite have been reported (e.g., Ibickii et al. 2008; Wood et al. 2010). In other locations, spectroscopic studies on the speciation of Cr in serpentine-derived soils indicated the absence of detectable amounts of Cr\(^{6+}\) (Hseu and Iizuka 2013; Fandeur et al. 2009).

Nanoparticles (NPs) are known to adsorb and/or structurally incorporate problematic metallic contaminants, highly actively and efficiently, from their immediate environment and transport them over vast distances via fluvial and alluvial processes (e.g., Hochella et al. 2005; Plathe et al. 2010; Yang et al. 2015). Therefore, it is also likely that, the occurrence of nano-size refractory minerals such as chromite, if present as is the case here (see below), play a significant role in dictating the transport, distribution, bioavailability, and toxicity of Cr in the environment. These phenomena will be particularly critical in areas around mine tailings and chromite-rich soils and sediments down hydrologic gradient. We will show in this study that Cr occurs in the form of chromite NPs that are encapsulated within silicate minerals of the recently discovered large chromite deposits in the McFaulds