

## Release of chromite nanoparticles and their alteration in the presence of Mn-oxides

NEAL W. MCCLENAGHAN<sup>1</sup> AND MICHAEL SCHINDLER<sup>2,\*</sup>

<sup>1</sup>Harquail School of Earth Sciences, Laurentian University, Sudbury, Ontario P3E 2C6, Canada

<sup>2</sup>Department of Earth Sciences, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

### ABSTRACT

The discovery of chromite nanoparticles in silicates of ultramafic rocks may change our approach on the environmental risk assessment of mine waste associated with chromitite mining. This experimental study shows for the first time that the alteration of Cr-rich silicates results in the release of chromite nanoparticles and that their interaction with oxidizing Mn-oxide nanoparticles causes the dissolution of chromite and Mn-oxide nanoparticles and the precipitation of Fe<sup>3+</sup>- and Cr<sup>3+</sup>-hydroxides. Transmission electron microscopy (TEM) in combination with ultra-microtomy, centrifugation, chromatography, ICP-MS, and UV-VIS is used to characterize release and alteration of chromite nanoparticles and the concentrations and speciation of Cr aqueous species. Alteration of clinocllore grains containing chromite nanoparticles results in the release of the nanoparticles and their attachment to Si-bearing Al-hydroxide colloids. Chromite nanoparticles with the end-member composition FeCr<sub>2</sub>O<sub>4</sub> are synthesized, and their interaction with Mn-oxide nanoparticles (hausmannite, Mn<sub>3</sub>O<sub>4</sub>), Fe<sup>2+</sup>-silicates (chamosite, [(Fe<sub>3.9</sub>Mg<sub>0.62</sub>Al<sub>0.48</sub>)Al(Si<sub>3</sub>Al)O<sub>10</sub>(OH)<sub>8</sub>] and organic matter is studied over a period of six to nine months in suspensions of pH = 5. The interaction of chromite and hausmannite nanoparticles is facilitated by the aggregation of the nanoparticles and dissolution-precipitation processes. Processes on the surfaces of the hausmannite nanoparticles include the reductive dissolution of the substrate (reduction of Mn<sup>3+</sup> to Mn<sup>2+</sup> by Fe<sup>2+</sup> species) and its replacement by amorphous or nanocrystalline Cr<sup>3+</sup>-bearing Fe<sup>3+</sup>-hydroxides. Processes on the surfaces of the chromite nanoparticles involve the attachment of hausmannite nanoparticles, the oxidative dissolution of the substrate (oxidation of Fe<sup>2+</sup> and perhaps Cr<sup>3+</sup> by Mn<sup>3+</sup> species), its replacement by an amorphous or nanocrystalline Mn-bearing Cr<sup>3+</sup>-hydroxide matrix and the formation of the Cr<sup>3+</sup>-hydroxides bracewellite and grimaldite within the latter matrix. Analyses of the suspensions indicate only minor amounts of Cr<sup>6+</sup> in the suspensions (<5 µg kg<sup>-1</sup>) suggesting that formation or occurrence of Cr<sup>6+</sup> species can be limited in complex geochemical and mineralogical systems even in the presence of hausmannite nanoparticles.

**Keywords:** Chromite, nanoparticles, alteration, manganese oxide, hexavalent chromium, TEM, colloids, mine waste