High-pressure Cr solubility in chlorites and its implications for clinochlore stability

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Chlorite is an important water carrier which transfers and potentially releases H_2O deep into the Earth´s Mantle. Chlorite stability field does not exceed 760-780°C, at 4 GPa, in a model NCFMASH peridotite, but chlorite was found to extend to more than 850°C, at approx. 3 GPa, in more complex chemical systems [1], in which the addition of Cr_2O_3 stabilizes Cr-chlorite with up to 1.4 wt % Cr_2O_3. To understand the influence of minor components on breakdown reactions, we experimentally investigated chlorite in the Cr_2O_3-MgO-Al_2O_3-SiO_2-H_2O system. Assuming that Cr is substituting for Al in the octahedral site of a clinochlore stoichiometry of $Mg_{10}Al_2(Si_6Al_2)O_{20}(OH)_{16}$ three different bulk compositions A, B and C with Cr/(Cr+Al) = 0.15, 0.5 and 1.0 have been considered. Seeded gels have been used as starting materials and run between 1.5-6.5 GPa, 650-900°C in piston cylinder and multi anvil apparatus. All experiments were fluid saturated. Run products have been inspected by SE/BSE images and were analyzed by EMPA. Synchrotron powder diffraction patterns are available for selected samples. Cr-chlorite was found only in bulk A. It coexists with enstatite up to 3.5 GPa, 800°C; at 5.0 GPa, 750°C it coexists with forsterite, pyrope, and chromite. At 900°C, 3.5 GPa, the anhydrous phase assemblage pyrope, forsterite, spinel has been found. Bulk B and C show chromite, enstatite and forsterite phase assemblage; no pyrope was recovered up to 6.5 GPa, 700°C. Cr-chlorite synchrotron diffraction patterns have been refined by Rietveld method. Results suggest no PT dependence of cell parameters in the range 2.0-5.0 GPa, 750-800°C. ($a=5.3237$ Å, $b= 9.2215$ Å, $c=14.3785$ Å, $\alpha=89.88°$, $\beta= 97.08°$ and $\gamma= 89.99°$). Chromium stronlgy partitions into spinel (XCr=0.8806, followed by orthopyroene (XCr=0.1428), Cr-chlorite (XCr=0.0815) and garnet (XCr= 0.0339). Cr affects the stability of chlorite by shifting its breakdown reactions at slightly higher T, but Cr solubility at high P results to be reduced as compared with low P occurrence.

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Using time-resolved synchrotron XRD and XAS to analyze Mn oxide dissolution in response to biotic and abiotic stimuli

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We used a combination of time-resolved X-ray diffraction (TR-XRD) and X-ray absorption spectroscopy (TR-XAS) to interrogate the mechanisms of manganese oxide dissolution. Manganese oxides are ubiquitous in nature and have been intensively studied as ion exchangers and catalysts because of their high surface areas and open structures. In soils, Mn oxides serve as sinks for contaminants, and by virtue of their redox activity, they control the chemistry and cycling of many elements.

TR-XRD has shown that the dissolution of synthetic sodium birnessite $[Na_{0.5}(Mn^{4+}{}_{1.5},Mn^{3+}{}_{0.5})O_4{\cdot}1.5H_2O]$, a layered manganese oxide, proceeds rapidly in response to direct electron transfer from bacteria with a concomitant structural contraction and precipitation of rhodochrosite ($Mn^{2+}CO_3$). Significantly, electron difference Fourier syntheses revealed no evidence for a redistribution of the interlayer Na cations. In order to document directly the changing states of Mn during this biological reaction, we used TR-XAS to measure the changes in Mn valence and coordination in real time. During these experiments, The Mn absorption edge shifted by -9.7 eV, confirming the reduction of Mn(IV) to Mn(II). Intermediate measurements show absorption edges consistent with mixed Mn valences.

Further birnessite dissolution experiments were carried out using a siderophore as a Mn chelator, and chromium as a Mn reductant. In each case, dissolution was indicated by sharp decreases in XRD peak intensity. However, the structural responses were markedly different from bacterial reduction.