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XANES study of the oxidation state of Cr in lower mantle phases: Periclase and magnesium silicate perovskite

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Abstract

Cr *K*-edge X-ray absorption near-edge structure (XANES) spectra were recorded on Cr:MgO periclase and Cr:(Mg,Fe)O ferropericlase synthesized at different pressures (4 and 12 GPa) and temperatures (1200 to 1400 °C) at reducing oxygen fugacity conditions (~iron-wüstite buffer IW to IW – 2), and on Cr:$MgSiO_3$ perovskite with 0.5 wt% Cr_2O_3. ^{57}Fe Mössbauer spectra were collected on the Fe-containing samples. The aim of the study was to determine the Cr oxidation state in phases found in the Earth's lower mantle, and to examine the possible relationship with the Fe oxidation state in the same materials. To calculate the amount of Cr^{2+}, the intensity of the shoulder at the low-energy side of the edge crest was quantified using the area of the corresponding peak in the derivative XANES spectra (Berry and O'Neill 2004). In Cr:(Mg,Fe)O the relative Cr^{2+} content reached at most 12.5% but results from Mössbauer spectroscopy combined with chemical composition data suggest that some Cr^{2+} oxidized during cooling through the reaction $Cr^{2+} + Fe^{3+} \rightarrow Cr^{3+} + Fe^{2+}$. In iron-free Cr:MgO, the Cr^{2+} content is much higher and reaches ~40%. In Cr:$MgSiO_3$ perovskite with 0.006 Cr pfu (similar to estimated lower mantle abundance), chromium is mainly divalent.

Keywords: XANES, Cr oxidation state, ferropericlase, periclase, Cr:$MgSiO_3$ perovskite