

## Chromium solubility in chlorite and implications on phase relations in the Cr<sub>2</sub>O<sub>3</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O system: an experimental study up to 6.5 GPa, 900°C

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Despite chromium is a minor constituent of the Earth Mantle, it is expected to affect phase equilibria, being incorporated in almost all major mantle phases, i.e. spinels, garnets and pyroxenes. In hydrated ultramafic systems, chlorite, containing 13wt.% of H<sub>2</sub>O, represents a good candidate for transferring water beyond the stability field of antigorite, being stable up to 4-6 GPa, 700-800°C. Chromium solubility on chlorite might further extend its stability and likely influence phase relations.

The goal of this experimental study is to investigate the limit of Cr solubility in chlorite in the context of its thermal stability, extending the analysis of phase relations in H<sub>2</sub>O-saturated Cr-bearing compositions with emphasis on the role of recently newly synthesized crystal structure (phase HAPy, Gemmi et al., 2011) and further constraint Cr partitioning between garnet and spinel at relatively low temperature conditions to be compared with the previously established loop for the spinel to garnet transition (Klemme & O'Neill, 2000).

High pressure experiments have been performed both in end loaded piston cylinder and multi anvil apparatus on chlorite compositions modelled in the system Cr<sub>2</sub>O<sub>3</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. Starting from a clinochlore stoichiometry Mg<sub>5</sub>Si<sub>3</sub>Al<sub>2</sub>(OH)<sub>10</sub> three different Cr/(Cr+Al) ratio have been investigated: bulk A with Cr/(Cr+Al) =0.0075; bulk B with Cr/(Cr+Al)= 0.25 and bulk C with Cr/(Cr+Al) = 0.5. Gels (seeded with 5% natural clinochlore from Val Malenco/Italy) have been used as starting materials and run between 1.5-6.5 GPa, 650-900°C. All experiments were fluid saturated. All run products have been inspected by SE/BSE images and were analyzed by EMPA. Synchrotron powder diffraction patterns are available for most samples.

Cr-chlorite only occurs in bulk A (XCr =0.15). It coexists with enstatite up to 3.5 GPa, 800-850°C, and with forsterite, pyrope and spinel at higher pressure (5.0 GPa, 750°C and 5.5 GPa, 670°C). In agreement with the chlorite terminal reaction the products pyrope, forsterite, spinel form a stable phase assemblage from 3.5 to 5.0 GPa, 800-900°C, beyond the stability field of chlorite+enstatite. Run results at P>5.0 GPa revealed the occurrence of other hydrates; at 5.2, 700°C and 5.4 GPa, 720°C a Cr-bearing phase HAPy was found in assemblage with pyrope, forsterite, and spinel; Mg-sursassite occurred at 6.0 GPa, 650°C with forsterite and spinel. No Cr-chlorite has been found in bulks B and C; the phase assemblage enstatite, forsterite, spinel was found instead from 1.0 to 5.0 GPa and 750-850°C. At higher pressure, at 6.0 GPa, 650°C and 6.5 GPa, 700°C, guyanaite has been found in assemblage with enstatite, forsterite and diaspore.

Cr-chlorite synchrotron diffraction patterns have been refined by Rietveld method. The results show the following cell parameters for the synthesis in the range 2.0-5.0 GPa, 750-800°C. (a=5.3237 Å, b= 9.2215 Å, c=14.3785 Å,  $\alpha=89.88^\circ$ ,  $\beta=97.08^\circ$  and  $\gamma=89.99^\circ$ ).

Chromium strongly partitions into spinel (XCr=0.8806), followed by orthopyroxene (XCr=0.1428), Cr-chlorite (XCr=0.0815) and garnet (XCr= 0.0339). New experimental constraints at relatively low temperature conditions suggest that, for the same bulk Cr/(Cr+Al), the divariant assemblage enstatite, forsterite, spinel and garnet is stable at higher pressure as compared with results reported at higher temperature (1100°C, Webb and Wood, 1986).

Cr affects the stability of chlorite by shifting its breakdown reactions towards higher T and P, but Cr solubility at high P results to be reduced as compared with low P occurrence in hydrothermal environments.

### References

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