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Solving the distribution of Fe^{3+} in chlorite: a XANES study combined with thermodynamic and atomistic modelling

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Among phyllosilicates, chlorite is of particular importance for metamorphic petrology. Found in a wide range of geological environments chlorite is very sensitive to temperature of crystallization through its composition governed by several solid, making chlorite a useful tool for geothermometry (Vidal et al. 2001). Temperature estimations based on thermodynamic modelling or empirical thermometers require knowledge of thermodynamic properties of chlorite end-members and of the actual cation sites populations. However chlorite contains both Fe2+ and Fe3+, thermodynamic models lack ferric end-members or neglect iron speciation, while incorporation of Fe3+ may dramatically impact temperature estimates.

In this context, micro-X-ray Absorption Near-Edge Spectroscopy (μ-XANES) analysis is particularly relevant to study the speciation of Fe in minerals but is complicated by dichroism effects due to beam polarization (Dyar et al. 2001). This study presents in situ, μ-XANES analyses at the Fe K edge ($\sim$ 7100 eV) of a collection of natural and synthetic chlorite, carried out in fluorescence mode at APS (Chicago) and ESRF (Grenoble) with circularly polarized beam, together with other minerals with well-known Fe speciation and/or at equilibrium with chlorite. Use of circular polarization allowed working on zoned crystals and mapping Fe3+/FeTOTAL. Systematic study of Fe speciation has been compared to measurements of Fe content and other major elements via EPMA, SEM and TEM, in order to confidently establish the chlorite structural formula.

Analyses cover the whole range of chemical variations in chlorite reported so far: Fe3+/FeTOTAL varying between 0 and 100%, and Fe always octahedral. μ-XANES mapping shows that Fe speciation varies greatly within a single sample and is not necessarily correlated with variations in Fe content, showing the dynamics of oxygen fugacity equilibration in metamorphic systems where porosity and permeability are very low. Two main substitutions have been identified as principal mechanisms for Fe3+ incorporation in chlorite, partly consistent with previous studies (Trincal & Lanari 2016). Ferric chlorite end-members are defined for each substitution. Combined thermodynamic and atomistic modelling allow prediction of the cation distribution and structure of these ferric end-members, crucial for more reliable thermodynamic temperature estimations.

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