

A XANES and EPMA study of Fe³⁺ in chlorite: Importance of oxychlorite and implications for cation site distribution and thermobarometry

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ABSTRACT

Chlorite is a ubiquitous product of metamorphism, alteration of magmatic rocks and hydrothermal processes owing to its large stability field and wide compositional range. Its composition is governed by several substitutions and has been used as a geothermometer, on the basis of empirical, semi-empirical, and thermodynamic models. As in some other phyllosilicates of petrological interest, the oxidation state of iron in chlorite may differ from the usually assumed divalent state. However, the crystal chemistry of trivalent iron in chlorite remains poorly known, and the thermodynamic properties of ferric chlorite are missing from databases used for petrological modeling. As part of an attempt to fill this gap, we present results from in situ, micrometer-scale measurements of the oxidation state of iron in various chlorite-bearing samples. X-ray absorption near-edge spectroscopy (XANES) was combined with electron probe microanalysis (EPMA) on the same crystals. Results show iron oxidation states varying from ferrous to ferric; iron is in octahedral coordination in all ferromagnesian chlorites but to ~25% tetrahedral in the lithian chlorite cookeite (1.0 wt% Fe₂O_{3(total)}). Absolute amounts of ferric iron cover an unprecedented range (0 to ~30 wt% Fe₂O₃). For highly magnesian, ferric chlorite, Fe concentrations are low and can be accounted for by Al = Fe³⁺ substitution. In Fe-rich samples, Fe³⁺ may exceed 2 atoms per formula unit (pfu, 18 oxygen basis). When structural formulas are normalized to 28 charges corresponding to the standard O₁₀(OH)₈ anionic basis, these measurements define the exchange vector of a di-trioctahedral-type substitution: $3 \text{ } ^{\text{VI}}(\text{Mg}, \text{Fe}^{2+}) = \text{ } ^{\text{VI}}\square + 2 \text{ } ^{\text{VI}}\text{Fe}^{3+}$, as described in earlier studies. However, structural formulas calculated on the basis of the oxygen contents actually measured by EPMA show that this trend is an artifact, due to the neglect of variations in the number of protons in the structure. Our measurements indicate increasing hydrogen deficiency with increasing Fe³⁺ content, up to ~2 H⁺ pfu in the Fe³⁺-rich chlorite samples, corresponding to a net exchange vector of the type $\text{R}^{2+} + \text{H}^+ = \text{Fe}^{3+}$. These results do not support substitutions toward di-trioctahedral ferric end-members, and highlight the need for considering substitution toward an “oxychlorite” (i.e., H-deficient) ferric component, close to tri-trioctahedral, with an O₁₂(OH)₆ anionic basis, even in green, pristine-looking chlorite. The effects of iron oxidation and H deficiency on chlorite geothermometers were explored. They are deterring if H deficiency is ignored but, given the sensitivity of most thermometers to octahedral vacancy, the assumption Fe_{total} = Fe²⁺ is still safer than using high measured Fe³⁺ contents *and* the standard 28 charge basis, which artificially increases vacancies. In such ferric chlorites, EPMA measurement of oxygen allows a fair estimate of H content if Fe³⁺/Fe²⁺ is known; it should be more systematically implemented. For the same reasons, literature data reporting Fe³⁺-rich chlorite with vacancy content along the possibly artificial di-trioctahedral-type substitution should be verified. With the help of constraints from thermodynamic models, charge balance, crystal symmetry, and proton loss, a new cation site distribution is proposed for di-tri- to tri-trioctahedral chlorites in the Fe²⁺-Fe³⁺-Mg-Al-Si-O-H system, allowing a more realistic thermodynamic handling of their solid solutions.

Keywords: Chlorite, oxychlorite, hydrogen deficiency, XANES, EPMA, ferric iron incorporation, geothermometry, solid solution, cation site distribution