Tetrahedral ferric iron in phlogopite: XANES and Mössbauer compared to single-crystal X-ray data

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Abstract: This paper reports the results of a combined methodological study performed on tetraferriphlogopite from the Araxà carbonatite. We compare Mössbauer spectroscopy and X-ray absorption near-edge spectroscopy (XANES) results to previously reported single-crystal X-ray and electron microprobe analysis data (Cruciani & Zanazzi, 1994). The combined techniques provide evidence for the presence of a remarkable amount of tetrahedrally coordinated Fe³⁺ in this sample, and show that high OH content in tetraferriphlogopite is compatible with the large Fe₂O₃/FeO ratio inferred from the chemical and spectroscopic data.

Key-words: tetraferriphlogopite, XANES, Mössbauer, Araxà carbonatite.

Introduction

Tetrahedral sites in micas are normally occupied by Si and Al; however phlogopites from peralkaline rocks such as kimberlites (Neal & Taylor, 1989 and references therein), carbonatites (Faye & Hogarth, 1969; Gaspar & Wyllie, 1987; McCormick & Heathcote, 1987) and lamproites (Foley, 1989) typically have sums of Si and Al less than 4 atoms per formula unit. For most of these micas, Fe³⁺ was assumed to complete the tetrahedral site occupancy ('tetraferriphlogopite'). This assumption is somewhat controversial from a petrological viewpoint and still under debate. Experimental studies on Fe oxidation state found that the Fe³⁺/Fe²⁺ ratio is enhanced in peralkaline melts, where Fe³⁺ behaves preferentially as a tetrahedral species (Dickenson & Hess, 1981). Foley (1989) argued however that the occurrence of Fe³⁺ in the tetrahedra of phlogopites from lamproites would require "prohibitively high" Fe₂O₃/FeO ratios, and suggested that cations other than Fe³⁺ probably fill the Si,Al-deficient tetrahedra.

The occurrence of tetrahedral Fe³⁺ in micas is usually inferred from chemical data alone; however, in the case of incomplete chemical analyses, this indication may be ambiguous. For example, apparent Al-deficiency may arise by neglecting the oxy-substitution and assuming an ideal OH content in formula calculations (Cruciani & Zanazzi, 1994). Less commonly, reverse