Fe\(^{3+}\) distribution in oxidized olivine: A synchrotron micro-XANES study

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**ABSTRACT**

Synchrotron micro-XANES spectroscopy (SmX) is used to examine the amount and distribution of Fe\(^{2+}\) and Fe\(^{3+}\) in five samples of fayalite previously studied by Mössbauer spectroscopy. Rockport fayalite is homogeneous and the Fe in it is completely reduced. Olivine from Qianan is almost completely oxidized, and probably contains finely intergrown silica, laihunite, and hematite with hematite predominating. Pantelleria olivine has an oxidized rim around a reduced core, suggesting either a post-crystallization reaction with fayalite and oxygen going to laihunite and hematite or a change in prevailing oxidation during growth. The texture of olivine from the Mourne Mountains suggests exsolution from a fayalite-laihunite solid solution, based on the substitution of three Fe\(^{3+}\) atoms for two Fe\(^{2+}\) and one vacancy, that was stable at high temperature. Laihunite from the type locality (Lai-He village) shows 1–3 \(\mu\)m mottling between light and dark areas in backscatter images, but these areas cannot correspond to pure fayalite and laihunite exsolution because the bulk Fe\(^{3+}/\Sigma\)Fe of such a combination would not correspond to the SmX value of 67% Fe\(^{3+}\). Rather, the texture observed in backscatter is interpreted to represent alternating areas of magnetite-rich and laihunite-rich compositions with a similar (i.e., 67% Fe\(^{3+}/\Sigma\)Fe) extent of oxidation.

**INTRODUCTION**

In 1934, Nikitin first reported the existence of a Fe\(^{3+}\)-rich olivine, which he called talasskite and later workers (Ginsburg et al. 1962) christened ferrifayalite; however these workers believed that ferrifayalite was a mixture of fayalite, hematite, and quartz. Subsequent discovery of the end-member Fe\(^{3+}\) olivine laihunite (Lai), or Fe\(^{2+}\)Fe\(^{3+}\)\((\text{SiO}_4)\)_2, (Ferrifayalite Research Group 1986; Zhang et al. 1981) was also called ferrifayalite in deference to Ginsburg et al. (1962), but a later single-crystal refinement showed this is a single phase. Recently, the name laihunite was approved by the CNMMN to describe a distorted olivine structure consisting of M2 sites filled by Fe\(^{3+}\), and M1 sites filled by Fe\(^{2+}\) and vacancies in alternate rows parallel to (001). The term “ferrifayalite” is now loosely used to describe samples with compositions representing solid solutions between laihunite and fayalite (although the physical scale of the solid solution is extremely variable), whereas the term “oxidized olivine” usually applies to Fe\(^{3+}\)-bearing olivine with other octahedral cations.

Numerous workers have synthesized (e.g., Ishi et al. 1989a, 1989b; Kondoh et al. 1985; Khisina et al. 1996) and characterized (e.g., Tamada et al. 1983; Shen et al. 1986; Banfield et al. 1990) olivine containing Fe\(^{3+}\). Fe\(^{3+}/\Sigma\)Fe was not directly measured, but it was inferred from vacancy distributions determined by TEM or related techniques. Yet, significant Fe\(^{3+}\) concentrations may occur in olivine but are not revealed by TEM because they are masked by Mg-Fe disorder (Janney and Banfield 1998).

Some oxidized olivine (Ol) has a significantly different structure than laihunite and is actually composed of multiple phases (Banfield et al. 1990; Janney and Banfield 1998). For example, Kitamura et al. (1984) reported interstratifications of OH-mono-layers with olivine (resulting in humite-like layers) in oxidized olivine from mantle kimberlite. TEM on defects in partially oxidized (up to 6% Fe\(^{3+}/\Sigma\)Fe) metastasomatized mantle peridotitic olivine (Banfield et al. 1992) shows intergrowths of olivine and a laihunite-like material. Oxidation of Fa\(_0\) olivine results in formation of “ferriolivine” planes plus magnesioferrite and magnetite (Mgt) (Khisina et al. 1995), whereas olivine oxidized in alkaline environments results in intergrowths of hematite (Hem) and amorphous silica, and oxidation in an acidic environment produces Ol + Hem + Lai (Iishi et al. 1997). These studies confirm the microscale interrelationships between oxides, silica, humite, vacancy-rich zones (laihunite), and vacancy-free zones (fayalite) but do not assess their macroscopic distribution or abundance. Nor have previous studies directly measured the actual Fe\(^{3+}/\Sigma\)Fe content of the phases involved.

To date, the best constraints on these issues come from indirect evidence. Schaefer (1983, 1985) presented results of Mössbauer studies of fayalite with a range of Fe\(^{3+}\) contents from four different localities with variable Fe\(^{3+}/\Sigma\)Fe. Mössbauer spectra and XRD patterns showed the presence of only a single phase with the olivine structure, so the presence of humite, hematite, or magnetite could be ruled out. Schaefer (1983, 1985) also noted that the XRD patterns became increasingly diffuse as the Fe\(^{3+}\) content of the Fa samples increased. Two sets of Mössbauer peaks exist at low temperatures: one octet corresponding to Fe\(^{3+}\) in “normal” olivine and two poorly resolved octets corresponding to Fe\(^{3+}\)-rich olivine. Because the spectra show no evidence of magnetic coupling that would be expected if Fe\(^{3+}\) and Fe\(^{2+}\) shared adjacent octahedra, she concluded that her samples con-