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Iron in kornerupine: A ^{57}Fe Mössbauer spectroscopic study and comparison with single-crystal structure refinement

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Abstract

Iron is an important constituent of kornerupine, $(\square,Mg,Fe)(Al,Mg,Fe)_9(Si,Al,B)_5O_{21}(OH,F)$. We obtained Mössbauer spectra at 300 K on twelve samples with ΣFe = 0.30–1.30 atoms per formula unit (apfu) and $Fe^{3+}/\Sigma Fe$ = 0–0.31; several samples were also run at 77 and 430 K. Models allowing unequivocal refinement of the spectra and determination of site occupancies were developed only when single-crystal refinement (SREF) of six of the samples constrained the number of possibilities. The spectra could then be fitted to three Fe^{2+} doublets and one Fe^{3+} doublet. The Fe^{2+}doublets have nearly identical isomer shifts: δ = 1.14–1.19 mm/s for the octahedral M1 and M2 sites and 1.12–1.20 mm/s for the irregular, eightfold-coordinated X site (relative to α-Fe at 300 K). However, they differ to a variable extent in quadrupole splitting, $\Delta E_Q \approx$ 1.06–1.80, 1.83–2.27, and 2.14–3.41 mm/s, respectively, to the M1, M2, and X sites. The Fe^{3+} doublet corresponds to the M4 site. The Mössbauer and SREF occupancies are in excellent agreement for the six samples.

The M1 doublet is split in B-bearing kornerupine and the proportion of Fe corresponding to each doublet, as well as quadrupole splitting, varies with B content. Similarly, the X doublet is split in F-bearing kornerupine, and quadrupole splitting of the X site increases with increasing F content. In contrast to most silicates, resolution of the spectra improves with increasing temperature. Quadrupole splitting of the X, M1, and M2 sites decreases with temperature, the X site at a lesser rate consistent with its being the most distorted site.

To a first approximation, the $Fe^{3+}/\Sigma Fe$ ratio in kornerupine determined by SREF and Mössbauer spectroscopy increases with increasing Fe_2O_3 and $Fe^{3+}/\Sigma Fe$ ratio of the associated sillimanite, sapphirine, and ilmenite-hematite, i.e., the measured $Fe^{3+}/\Sigma Fe$ ratios are related to the oxygen fugacity at which the kornerupine crystallized.