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Structural properties and heat-induced oxidation-dehydrogenation of manganoan ilvaite from Perda Niedda mine, Sardinia, Italy

PAOLA BONAZZI* AND LUCA BINDI

Dipartimento di Scienze della Terra, Università di Firenze, Via La Pira 4, I-50121, Florence, Italy

ABSTRACT

An unusually Mn-rich ilvaite sample from the Perda Niedda mine in Sardinia, Italy, was studied in order to clarify the Mn^{2+} distribution among the different structural sites, and to observe the structural response of the mineral upon thermally induced oxidation-dehydrogenation. The crystal structure and the chemical composition of one crystal [a = 13.014(5), b = 8.867(3), c = 5.838(4) Å, β = 90.02(4)°] were investigated. X-ray crystal-structure refinement, performed in the *Pnam* space group, and electron microprobe analyses yielded the formula $(Ca_{0.98}Mn^{2+}_{0.02})(Fe^{3+}Fe^{2+})(Mn_{0.72}Fe^{2+}_{0.28})(Si_2O_7)O(OH)$. Crystal chemical details, compared to structural data from literature, led to the assumption that Mn^{2+} replaces Fe^{2+}, mainly at the M2 site. Annealing experiments and structure refinements were performed in the temperature range 400–690 °C. No phase transition was observed over the entire temperature range. Oxidation of Fe^{2+} at the M1 site, with concomitant dehydrogenation, was deduced from examination of the structural adjustments occurring as the temperature was increased. A useful model to evaluate a possible $OH^- \leftrightarrow O^{2-}$ substitution in ilvaite was obtained.