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Synthesis and crystal-chemistry of alkali amphiboles in the system Na$_2$O-MgO-FeO-Fe$_2$O$_3$-SiO$_2$-H$_2$O as a function of f_{O_2}

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ABSTRACT

This paper reports the results of hydrothermal synthesis in the system Na$_2$O-MgO-FeO-Fe$_2$O$_3$-SiO$_2$-H$_2$O. Four samples of stoichiometric magnesioriebeckite composition, ideally $\square Na_2Mg_3Fe^{3+}_2Si_8O_{22}(OH)_2$, were run at 700–800 °C, 0.4 GPa, and redox conditions varying from NNO (Nickel–Nickel Oxide) to NNO + 2.3 log f_{O_2}. Powder XRD and SEM-EDX show a high (>85%) amphibole yield for all samples; however, in no case was the end-member composition attained. EMP analyses show that the amphiboles obtained deviate strongly from nominal stoichiometry toward magnesio-arfvedsonite [$NaNa_2Mg_4Fe^{3+}Si_8O_{22}(OH)_2$]. Powder XRD patterns were indexed in the space group $C2/m$; refined cell-parameters reflect variations in the amphibole composition, and the cell volume is correlated linearly with the A-site occupancy. Mössbauer spectra show that in all samples, Fe^{3+} is completely ordered at M2, whereas Fe^{2+} occurs at the M1, M3, and M4 sites. The Fe^{3+}/Fe^{2+} ratio is a function of f_{O_2}: for increasing oxidation conditions, there is significant increase in ^{M2}Fe^{3+} and decrease in Fe^{2+}, notably in ^{M4}Fe^{2+}. Mössbauer spectra also show significant variation in ^{M1}Fe^{2+} and ^{M3}Fe^{2+} quadrupole splitting as a function of the Fe^{3+} content in the amphibole. IR spectra in the OH-stretching region show a well-resolved quadruplet at frequencies <3680 cm^{-1}, assigned to octahedral $^{M1,3}(Mg, Fe^{2+})$-OH-$^{A}\square$ configurations, and a broad band consisting of four overlapping components related to $^{M1,3}(Mg, Fe^{2+})$ configurations associated with occupied A-sites. Quantitative evaluation of the relative band intensities suggests a linear increase of A-site occupancy with decreasing f_{O_2} of synthesis. The composition of the amphiboles synthesized, can be best described by a combination of the $^{C}(Mg,Fe^{2+})_1$ $^{B}(Mg,Fe^{2+})_1$ $^{C}Fe^{3+}_{-1}$ $^{B}Na_{-1}$ and the $^{A}Na_1$ $^{C}(Mg,Fe^{2+})_1$ $^{A}\square_{-1}$ $^{C}Fe^{3+}_{-1}$ exchange vectors. The experimental trend is in accord with the trend documented for natural amphiboles, and suggests that the amphibole composition can in fact be used to monitor changes in f_{O_2} during crystallization.