Ferric iron and water incorporation in wadsleyite under hydrous and oxidizing conditions: A XANES, Mössbauer, and SIMS study

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Abstract

Wadsleyites with various iron contents were synthesized at ~12–14 GPa and 1400 °C under oxidizing and hydrous conditions in coexistence with enstatite. The samples were studied using micro-X-ray absorption near edge structure (XANES) and micro-Mössbauer spectroscopy to determine the ferric iron contents in polyphasic samples and secondary ion mass spectrometry (SIMS) to determine the water concentrations. XANES and Mössbauer analyses show that ferric iron content increases with increasing total iron content, and reaches a maximum of ~30% Fe^{3+}/Fe_{total}. Two XANES results were cross-checked by Mössbauer analysis and both methods are in reasonable agreement. The use of Fourier transform infrared spectroscopy reveals a new protonation scheme in wadsleyite, with a significant proportion of protons associated with the high-frequency band at 3611 cm^{-1} and a new band located at 3500 cm^{-1}. The intensity of these two bands is higher for Fe^{3+}-rich wadsleyite. SIMS analyses show that water contents in wadsleyite vary from 4500 to 9400 ppm H_2O by weight. Pyroxene water contents range from 790 to 1600 ppm wt H_2O. The concentration of water in both phases decreases with increasing iron content. The partition coefficient of water between wadsleyite and pyroxene varies between 5 and 9 and increases with increasing Fe-number of wadsleyite [i.e., $X_{Fe}/(X_{Fe} + X_{Mg}) \times 100$ ratio]. The divalent cation concentrations (i.e., Mg^{2+} + Fe^{2+}), the Si as well as the H content in wadsleyite decrease with increasing Fe^{3+} content, indicating an incorporation mechanism via substitution into the metal (Me = Mg^{2+} and Fe^{2+}) and Si sites with a ratio of 5/3 for (Fe^{3+}+H^+):Me and of 5/1 for (Fe^{3+}+H^+):Si, similarly as in the dry system. Thus, coupled substitution of Fe^{3+} and H^+ does not affect the incorporation mechanism of Fe^{3+}, but does affect the location of H^+, which is partly incorporated at tetrahedral edges forming $[Fe_{Si}'-(OH)_o^·]^X$ neutral defects substituting for Si. In this model 25% of the ferric iron occupies the tetrahedral sites.

Keywords: Wadsleyite, redox, ferric iron, hydroxyl defects, XANES