Crystal structure of nesquehonite, $MgCO_3 \cdot 3(H,D)_2O$ by neutron diffraction, Raman spectroscopy, and thermal analysis

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Neutron diffraction, Raman spectroscopy, and thermal analysis were performed to investigate the composition, structure, and formation conditions of magnesium carbonate hydrate, nesquehonite. Nesquehonite was prepared from a mixture of $MgCl_2$ and Na_2CO_3 solution at pH 10.9. The crystal structure of deuterated nesquehonite was analyzed by Rietveld refinement of the time-of-flight neutron powder diffraction pattern. The crystal structure possessed monoclinic space group $P2_1/n$ with lattice parameters of a = 7.72100(12), b = 5.37518(7), c = 12.1430(3) Å, β = 90.165(4) °, and V = 503.956(13) Å^3. The refinement with a final crystal structure model of deuterated nesquehonite converged to wRp = 4.22 % and Rp = 3.50 % (Fig. 1). The positions of six deuterium (D) atoms were successfully determined. The result indicated that the D atoms were coordinated to O1, O2, and O6 atoms as water molecules in nesquehonite. It can be therefore considered that nesquehonite obtained in the study had the chemical formula of $MgCO_3 \cdot 3D_2O$. The Raman bands corresponding to the CO_3 bending and stretching vibrations and the OH(OD) stretching vibration agreed substantially with those given by previous studies. The OH stretching vibration at 3555 cm^{-1} was also well consistent with those reported in the literature. It was experimentally impossible to distinguish the difference in chemical formula between $MgCO_3 \cdot 3H_2O$ and $Mg(HCO_3)(OH) \cdot 2H_2O$ by using the powder XRD pattern and the Raman bands of the OH stretching vibrations. The differential thermal analysis (DTA) curve showed three endothermic peaks corresponding to three dehydration reactions, which indicated that three water molecules were released step by step from the $MgCO_3 \cdot 3H_2O$ nesquehonite. There is a distinct difference in dehydration behavior between $MgCO_3 \cdot 3H_2O$ and $Mg(HCO_3)(OH) \cdot 2H_2O$. Therefore, the thermal analysis would be a most useful tool to distinguish the difference in chemical formula of nesquehonite.

Keywords: Nesquehonite, Magnesium carbonate hydrate, Neutron diffraction, Raman spectroscopy, Thermal analysis, Hydrogen bonding network

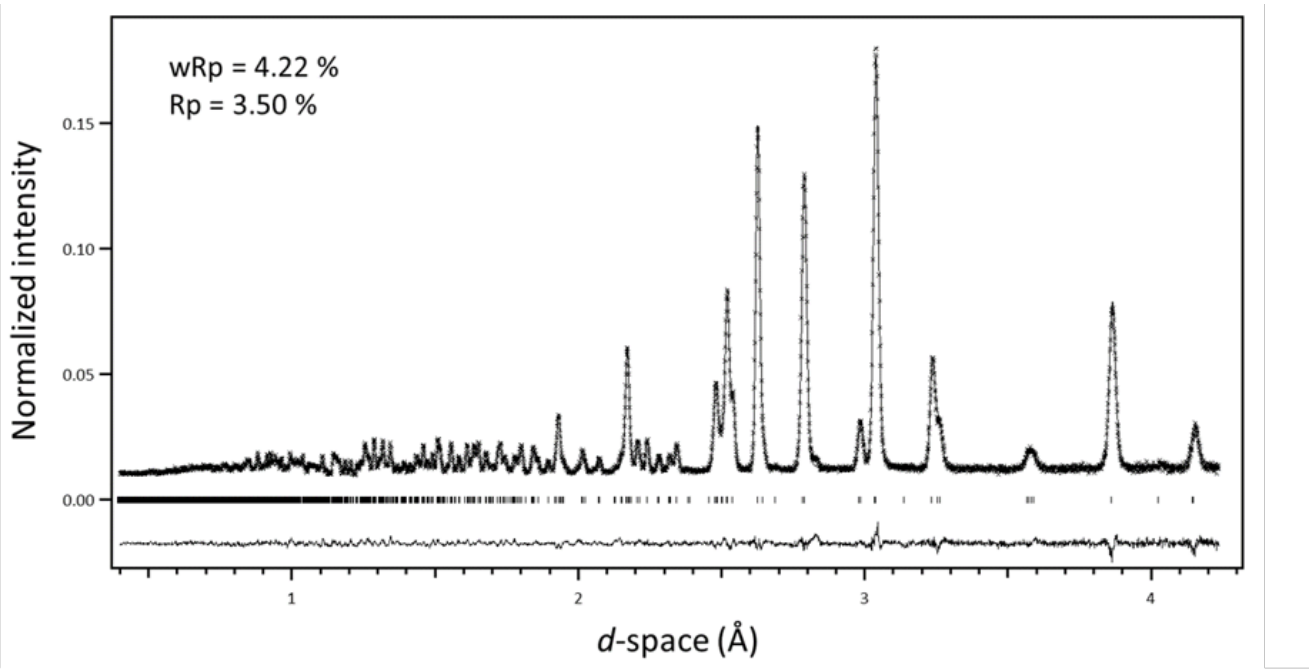

Figure 1 Neutron powder diffraction pattern and the result of fitting by Rietveld refinement for nesquehonite.

