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Applications of Hirshfeld surfaces to mineralogy: An example of alumohydrocalcite, and the classification of the dundasite group minerals

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ABSTRACT

The crystal structure of alumohydrocalcite was determined using synchrotron X-ray radiation. Alumohydrocalcite crystallizes in the triclinic $P\overline{1}$ space group with unit-cell parameters: a = 5.71(5), b = 6.54(4), c = 14.6 (2) Å, α = 81.8(3)°, β = 83.9(3)°, γ = 86.5(7)°, and V = 537(7) Å^3. This mineral has the formula $CaAl_2(CO_3)_2(OH)_4{\cdot}4H_2O$ as opposed to the commonly accepted formula $CaAl_2(CO_3)_2(OH)_4{\cdot}3H_2O$. The fourth water molecule interacts with the strongly bonded polyhedral unit of the structure through hydrogen bonds and connects three adjacent units. This water molecule plays a major role in crystal stability. On heating the sample, this fourth water molecule escapes from the crystal structure as a first one at lower temperature (~105 °C) than the other water molecules in the crystal structure (~128 °C).

Analysis and description of the alumohydrocalcite crystal structure and particularly of the intermolecular interactions, together with a comparison to the crystal structures of other minerals with the analog formula $M^{2+}M^{3+}_2(CO_3)_2(OH)_4{\cdot}nH_2O$, suggests that this mineral is an extension of the dundasite group that should, we propose, be formed for all minerals with the above formula (dundasite, dresserite, strontiodresserite, petterdite, kochsándorite, hydrodresserite, and alumohydrocalcite). They all exhibit very similar patterns on Hirshfeld surfaces. Hirshfeld surfaces appear to be a very useful tool in the analysis of interactions, classification, and validation of mineral crystal structures.

Keywords: Alumohydrocalcite, hydrate, crystal structure, X-ray diffraction, synchrotron radiation