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 P1 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) Å³. This mineral has the formula CaAl2(CO3)2(OH)2·4H2O as opposed to the commonly accepted formula CaAl2(CO3)2(OH)2·3H2O. 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 intramolecular interactions, together with a comparison to the crystal structures of other minerals with the analog formula $\text{M}^2\text{M}^3\text{CO}_3\text{OH}_2\cdot\text{nH}_2\text{O}$, suggests that this mineral is an extension of the dundasite group that should, we propose, form for all minerals with the above formula ( Dundasite, dresserite, strontiodresserite, pettedite, kochsândorite, 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

INTRODUCTION

In this work, we use the alumohydrocalcite structural data as a case study to stress the applications of Hirshfeld surfaces as an excellent tool to characterize intramolecular interactions in minerals in general. Hirshfeld surfaces can be computed for all crystal structures determined up to now. We have applied them to alumohydrocalcite, and to a broader group of minerals with already established crystal structures. The potential similarity of the Hirshfeld surface plots can be used as a base for classification of minerals as we have done for the dundasite group demonstrating that alumohydrocalcite forms an extension of this group. In fact, Hirshfeld surfaces can also be used to validate all known mineral structures because incorrect positions of, for example, hydrogen atoms, lead to contradictions in related, so-called, fingerprint plots.

In this work we also present details of the crystal structure of alumohydrocalcite. It was identified by Bilbin (1926) in samples collected near the village of Poliechino, Western Siberia, Russia, and was named by him after the main components of its chemical composition. Although the mineral is known to occur in a few dozen localities around the world, it can still be considered as a rare and not thoroughly investigated species. As it diffracts X-rays very weakly, there have been no published data on the crystal structure of alumohydrocalcite. This mineral begins a series of studies of known minerals with unknown crystal structures.

Alumohydrocalcite has the generally accepted formula: CaAl2(CO3)2(OH)2·3H2O. It usually forms very tiny needle-like crystals, sporadically exceeding 1 mm in length (Fig. 1). Because of the poor quality and very small size of the crystals, the crystal structure of alumohydrocalcite has not previously been determined. Crystals of alumohydrocalcite are composed of small spherules and radial aggregates, but thin, compact encrustations and powdery, earthy masses are also found. Most alumohydrocalcite aggregates are white or pale-colored, stained by impurities. Chromian varieties are pink to purple. The mineral is very soluble in acids, and is decomposed by boiling water. It crystallizes from low-temperature hydrothermal or carbonated meteoric water acting on argillaceous or carbonate rocks and may be associated with dickite, allophane, gibbsite, calcite, aragonite, siderite, barite, quartz, and other minerals.

Based on alumohydrocalcite from Nowa Ruda (Lower Silesia, Poland), we propose a crystal structure for this mineral deter-

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