

Reexamination of the crystal structure of artinite, $\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$, with two-dimensional disorder

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Artinite is a magnesium carbonate hydrate mineral with the formula $\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$. It is known to possess a disordered structure in which carbonate groups and water molecules alternate statistically along *b*-axis (Akao and Iwai 1977). The Mg atoms are octahedrally coordinated by three hydroxyl groups, two water molecules, and one O(1) atom, and arranged in infinite chains parallel to *b*-axis by sharing edges. In the structure, half of the O(1) atoms is bounded to carbonate groups and the other half is to water molecules. It is therefore possible that in the disordered structure a carbonate group is arrayed at the next of a carbonate group along *b*-axis. However, if a carbonate group is positioned at the next of a carbonate group, the O-O distance between the carbonate groups is 0.894 Å, which is apparently shorter than the van der Waals radius of an O atom (1.40 Å). On the other hand, if the carbonate groups and water molecules strictly alternate along *b*-axis, a periodicity of two unit cell should appear along the *b*-axis. In the study, we reexamined the crystal structure of artinite and reconsidered the disordered configuration of carbonate group and water molecule in the structure.

Naturally occurring artinite (San Benito, USA) was used in the study. Single-crystal X-ray diffraction measurements were performed using Bruker APEXII ULTRA single-crystal diffractometer equipped with a CCD detector, multilayer optics, and graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) generated by a rotating anode. X-ray data were collected at a temperature of -173 °C using a N_2 -gas-flow cryostat. The crystal structure was solved by intrinsic phasing in the APEX2 software package and refined by full-matrix least squares using Shelxl-97 (Sheldrick, 1997). Computational chemistry calculations were performed using Gaussian 09 program (Frisch et al., 2009). Mulliken charges were calculated using Density Functional Theory (DFT) at B3LYP employing 6-31G basis set.

The refined cell parameters are $a = 16.468(8)$ Å, $b = 3.1352(15)$ Å, $c = 6.184(5)$ Å, $\beta = 98.702(5)^\circ$, space group $C2/m$. The unit cell corresponds to the totally disordered configuration of carbonate groups and water molecules on the *b*-lattice. The structure refinement converged to $R1 = 0.0339$, $wR2 = 0.0937$, and $\text{Goof} = 1.013$ for 414 reflections with $F_o > 4s(F_o)$. The bond distances in the MgO_6 octahedron are 2.0345(9) Å (2), 2.0610(13) Å, 2.1641(9) Å (2), and 2.0135(13) Å. Those in the carbonate group are 1.227(3) Å and 1.2920(18) Å (2). When the carbonate group is located at the next to the carbonate group along *b*-axis, the O-O distance between the neighboring O atoms in the carbonate groups is 0.8816(19) Å. The Mulliken charges of the neighboring O atom, O atom on the opposite side, and O atom bounded to Mg atom are -0.378, -0.721, and -0.845, respectively. That of C atom is 1.296.

Crystal structures of magnesium carbonate (hydrate) minerals are always composed of MgO_6 octahedra. Compared with the MgO_6 octahedra constituting hydromagnesite $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, nesquehonite $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, and magnesite MgCO_3 , the MgO_6 octahedron in artinite displays a large quadratic elongation parameter (Robinson et al. 1971). In addition, the carbonate group in artinite can be characterized by highly distorted geometry forming an acute isosceles triangle. The results of crystal structural analysis are in good agreement with those of previous research (Akao and Iwai, 1977).

Furthermore, our study completely supports the conclusion obtained in the early study that every chain running along *b*-axis has two possible positions of carbonate groups and water molecules, thus producing the two-dimensional disorder. The reason why the carbonate groups can be located at an unusual short distance would be explained by the strongly polarized charge distribution within the carbonate groups.

Keywords: Artinite, disordered configuration, single crystal structure analysis, ab initio calculation