Minerals in cement chemistry: A single-crystal neutron diffraction and Raman spectroscopic study of thaumasite, \( \text{Ca}_3\text{Si(OH)}_6\text{(CO}_3\text{)}_3\text{(SO}_4\text{)}_2\cdot12\text{H}_2\text{O} \)

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ABSTRACT

Thaumasite, \( \text{Ca}_3\text{Si(OH)}_6\text{(CO}_3\text{)}_3\text{(SO}_4\text{)}_2\cdot12\text{H}_2\text{O} \), is recognized as a secondary-alteration mineral and indicator of sulfate attack in Portland cement in contact with sulfate-rich groundwater, especially in cold regions. The hydrogen positions in thaumasite have been determined from single-crystal neutron diffraction structure refinements at 300 and 22 K. No phase transitions occur within the temperature range investigated. The structure of thaumasite is largely held together by hydrogen bonding. The major structural units [\( \text{CO}_3 \text{ groups}, \text{SO}_4 \text{ tetrahedra, Si(OH)}_6 \text{ octahedra, and Ca(OH)}_2 \text{(H}_2\text{O)}_2 \text{ polyhedra} \)] are interconnected via 10 distinct hydrogen bonds. Analysis of the difference-Fourier maps of the nuclear density reveals the positions of all 10 hydrogen atoms in the structure, and the hydrogen bonding becomes shorter (stronger) upon decreasing temperature to 22 K. The \( \text{SO}_4 \text{ tetrahedron expands upon decreasing temperature (i.e., negative thermal expansion at the molecular level), driven by shortening of the hydrogen bonding between [CaSi(OH)_6(H_2O)_2]^{4+} columns. Polarized Raman spectra of thaumasite show that the \( \nu_1 \text{ symmetric stretching modes of Si(OH)}_6, \text{SO}_4, \text{ and CO}_3 \text{ occur at \( 658, 983, \text{ and } 1066 \text{ cm}^{-1} \), respectively. In addition, the out-of-plane bending mode (\( \nu_2 \)) \text{ and asymmetric stretching mode (\( \nu_3 \)) \text{ of the carbonate group are tentatively assigned to bands at 887 and 1400 cm}^{-1} \text{, respectively. Bands at 418 and 455 cm}^{-1} \text{ (and possibly at 477 cm}^{-1} \text{) are attributed to the symmetric bending modes (\( \nu_2 \)) \text{ of the sulfate group, and we observe a possible asymmetric stretching mode (\( \nu_3 \)) \text{ of SO}_4 \text{ at 1090–1100 cm}^{-1} \text{. Splitting of some sulfate and carbonate vibrational modes may occur due to hydrogen bonding on all the oxygen sites. At 1685–1710 cm}^{-1} \text{ we observe the H}_2\text{O bending modes (H-O-H), and from 2900–3600 cm}^{-1} \text{ there are 13 distinct bands associated with bending overtones and the O-H stretching vibrations corresponding to H-positions determined in the neutron diffraction study. The effect of the low-temperature stability of thaumasite on the pronounced “thaumasite sulfate attack” of Portland cements observed in cold regions is discussed.} \)

Keywords: Thaumasite, Portland cements, crystal chemistry, single-crystal neutron diffraction, Raman spectroscopy, hydrogen bonding

INTRODUCTION

Thaumasite, \( \text{Ca}_3\text{Si(OH)}_6\text{(CO}_3\text{)}_3\text{(SO}_4\text{)}_2\cdot12\text{H}_2\text{O} \) \( \{a \sim11.030, \ c \sim 10.396 \text{ Å, space group } P6_3, Z = 2\} \), occurs as a low-temperature secondary-alteration phase in mafic igneous and metamorphic rocks. Usually it is associated with zeolites, apophyllite, analcime, calcite, gypsum, and pyrite. Thaumasite forms a solid solution with ettringite, \( \text{Ca}_6[\text{Al(OH)}_6]\text{(SO}_4\text{)}_3\cdot26\text{H}_2\text{O} \) (Moore and Taylor 1970; Barnett et al. 2000), and contains a highly unusual Si site in six-coordination with hydroxyl, \( ^{\text{OH}}\text{Si-OH} \).

Thaumasite and ettringite also form in the porous matrix of aging concrete, especially in contact with sulfate-rich soils or fluids (Crammond 1985) or when limestone is used as a filling material (Hartshorn et al. 1999). Cement hydration products, calcium silicate hydrates—the so-called C-S-H and calcium hydroxide—portlandite Ca(OH)_2, are decomposed as a result of both sulfate attack and of carbonation. Because C-S-H in concrete provides most of the binding strength, thaumasite and ettringite formation leads to weakening and disintegration of the cement matrix especially in concrete structures below ground (e.g., Hartshorn et al. 1999; Bensted 1999; Hobbs and Taylor 2000; Santhanam et al. 2001; Zhang et al. 2009). Degradation of concrete by thaumasite sulfate attack (TSA) has been documented in various environments including an 80-year-old aqueduct in Manitoba, 33-year-old pavement in Ontario, test samples exposed to marine (tidal) conditions, and in laboratory samples exposed to wet–dry cycles in sulfate solution (Thomas et al. 2003). The source of carbonate differs in each of these cases, deriving from de-dolomitization of dolostone aggregates, carbonate ions in the seawater, or atmospheric CO_2 through the process of carbonation. Sulfate attack of Portland cement by thaumasite appears to be greatly accelerated at sub-zero temperatures, as observed from rapid deterioration of reinforced concrete foundations in the Arctic within just two years of construction (Bickley 1999).

The crystal chemistry of thaumasite is unusual: it contains