

Magnesium sulfate trihydrate: an elusive mineral on Earth and Mars?

Fortes, A. D.^{1,2,*}, Lemée-Cailleau, M. –H.³,
Knight, K. S.^{4,5}, & Jura, M.⁴.

¹ Centre for Planetary Sciences at UCL/Birkbeck, Gower Street, London, WC1E 6BT, U.K. ²Department of Earth Sciences, University College London, Gower St. London WC1E 6BT, U.K. ³Institut Laue-Langevin, BP156, 38042 Grenoble cedex 9, France. ⁴ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Chilton, Didcot, Oxfordshire, OX11 0QX, U.K. ⁵ The Natural History Museum, Cromwell Road, London, SW7 5BD, U.K.

*(andrew.fortes@ucl.ac.uk)

Magnesium sulfate trihydrate was, hitherto, one of the last MgSO_4 hydrates with an unknown structure. Amongst the M^{2+}SO_4 hydrates, only two other trihydrates are known, the mineral bonattite ($\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$) and $\text{CrSO}_4 \cdot 3\text{H}_2\text{O}$, which are isostructural in space-group Cc. We have grown large (order 1 mm^3) single crystals, with a flat bladed morphology [forms $\{100\}$, $\{010\}$, $\{102\}$], which are comparatively stable in air at room temperature for periods of at least several days. Our synthesis method suggests to us that MgSO_4 -trihydrate may be formed commonly in low-T hydrothermal systems, but will transform over time to pseudomorphs composed of hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) and/or epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). However, on Mars, the hydration process may be inhibited by the low atmospheric water abundance and the low temperatures.

We report the crystal structure of $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$, determined from neutron single-crystal diffraction measurements made using the VIVALDI diffractometer at the Institut Laue Langevin, and X-ray single-crystal measurements. We also report complementary measurements of the thermal expansion of $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ powder in the range $8 < T < 295 \text{ K}$ made using the High Resolution Powder Diffractometer (HRPD) at the ISIS neutron spallation source, as well as C_p and TGA data. $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ undergoes a first-order phase transition at 245 K from the high-T Pbc_a structure to a low-T monoclinic structure (P2₁/c after permutation of the axes into a standard monoclinic setting); the transition is apparently caused by orientational ordering of the disordered hydrogen bonds in the structure. Unit-cell dimensions are $a = 8.1925(2) \text{ \AA}$, $b = 10.9210(2) \text{ \AA}$, $c = 12.3866(4) \text{ \AA}$ at 295 K, and $a = 12.3616(5) \text{ \AA}$, $b = 8.1414(3) \text{ \AA}$, $c = 10.8324(2) \text{ \AA}$, $\beta = 91.131(3)^\circ$ at 8 K.

The axial thermal expansion is highly anisotropic, being largest along the b -axis (the direction perpendicular to the plane of the h-bonded sheets in the structure) and smallest along the c -axis. The volume thermal expansion at room temperature is comparable to that of hexahydrate, and much larger than that of epsomite, suggesting that MgSO_4 -trihydrate may exert large (i.e., damaging) pore pressures in natural or manmade materials wherever hot aqueous fluids are able to precipitate.

Synthetic $\text{MgSO}_4 \cdot 3\text{D}_2\text{O}$ typically forms small clusters of blades (each shown here is $\sim 1 \text{ mm}$ across the 010 face). These may occur in nature as hexahydrate or epsomite pseudomorphs.

