

IONIC SUBSTITUTION IN MERIDIANIITE ($\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$): SOLID SOLUTIONS AND NOVEL HYDRATES. A. D. Fortes¹, F. Browning¹, and I. G. Wood¹. ¹Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, U.K. (andrew.fortes@ucl.ac.uk)

Introduction: $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$ (MS11) is the most highly hydrated phase in the binary MgSO_4 — H_2O system, having a narrow stability field in contact with aqueous solution [1]. Whilst all of the other known MgSO_4 hydrates (1, 2, $2\frac{1}{2}$, 3, 4, 5, 6, and $7\text{H}_2\text{O}$) have isomorphous or isodimorphous crystalline analogues with alternative cation and oxyanion substituents, MS11 is hitherto unique in occurring solely in the MgSO_4 — H_2O system.

MS11 occurs naturally in periglacial environments on Earth as the mineral meridianiite [2,3]. Moreover, MS11 and other polyhydrated magnesium sulfate minerals may account for the high near-surface hydrogen abundance detected in Martian soils at low latitudes [4]. Apparent crystal moulds have been observed in rocks at Meridiani Planum, Mars, by the ‘*Opportunity*’ Mars Exploration Rover [5], which are believed to have been produced by peritectic melting of MS11 to epsomite (MS7) + brine [6]; Since we may reasonably expect natural martian brines to contain a wide range of dissolved substances, it is important to determine (i) the stability of MS11 in the presence of foreign ions, (ii) the extent to which the structure can accommodate these ions (do end-member 11-hydrates exist with other compositions?) and (iii) to characterize any effect on the structure that could be observable by the miniature X-ray diffractometer aboard the ‘*Curiosity*’ Mars Rover [7].

Experimental Methods 1, Powders: The majority of our work so far has been carried out using powder specimens prepared by rapid quenching of aqueous solutions in liquid nitrogen. The resulting solid blocks consist of one or more hydrates + water ice Ih, which are pulverized, ground to a fine powder under liquid nitrogen and then subjected to crystallographic analysis using either X-rays or neutrons. The X-ray diffraction data were collected using a Panalytical X’Pert Pro powder diffractometer equipped with a bespoke thermoelectrically-cooled cold stage [8]. This device allows us to load pressed powder specimens in our cold room facility (air temperature -12°C), and to make measurements over many hours at temperatures of -10 to -15°C without any icing of the sample. We have collected high quality X-ray diffraction data from specimens doped with Ni^{2+} , Zn^{2+} , Cu^{2+} , Fe^{2+} , Co^{2+} and Mn^{2+} in molar abundances from 0 to 100 % in 10 % increments. Subsequently, we carried out a similar series of measurements on quenched aqueous solutions of MgCrO_4 , MgSeO_4 and MgMoO_4 . At the time of

writing, neutron powder diffraction studies are scheduled for February 2012, to be done using the High Resolution Powder Diffractometer (HRPD) at the ISIS neutron source in the U.K., and we anticipate being able to present some of these data.

Experimental Methods 2, Single Crystals: Guided by the results of our powder studies, we have been able to prepare single crystals of doped meridianiite in aqueous solutions containing up to 50 mol. % Co^{2+} or Mn^{2+} . The Mn-doped crystals are colourless and water-clear, like the pure Mg-bearing variety, but typically exhibit a more slender bladed morphology. The Co-doped crystals have a lucent copper-orange colour (Fig. 1), quite distinct from the opaque dark red of $(\text{Co,Mg})\text{SO}_4 \cdot 7\text{H}_2\text{O}$. The morphology of the Co-doped 11-hydrates closely resembles that of the Mg-bearing variety, though often with a blockier habit.



Figure 1. A crystal of the 11-hydrate (dimensions 13.1 x 6.2 mm) grown from 50 mol. % cobalt doped aqueous MgSO_4 at -3°C . The orange hue deepens with increasing dopant concentration.

Five of these crystals were selected for study using the neutron single-crystal diffractometer (SXD) at the ISIS neutron source. At the time of writing, these measurements were completed, with detailed analysis to follow. Samples of all crystals and residual mother liquor will be subjected to chemical analysis in the near future, by inductively coupled plasma optical emission spectroscopy (ICP-OES), to confirm the partitioning of Co^{2+} or Mn^{2+} into each phase

Results, Cations: We have established that of the seven end-member metal sulfates studied, only MgSO_4 forms an undecahydrate [9]; ZnSO_4 forms an orthorhombic heptahydrate (synthetic goslarite), MnSO_4 , FeSO_4 , and CoSO_4 form monoclinic heptahydrates

(syn. mallardite, melanterite, and bieberite, respectively), and CuSO_4 crystallises as the well-known triclinic pentahydrate (syn. chalcantite). NiSO_4 forms a new hydrate which has been indexed with a triclinic unit cell. The molar volume of this crystal is consistent with it being an octahydrate, $\text{NiSO}_4 \cdot 8\text{H}_2\text{O}$.

Further analysis of doped specimens with mixed cation compositions has shown that synthetic meridianiite is able to accommodate significant quantities of foreign cations in its structure; of the order 50 mol. % Co^{2+} or Mn^{2+} , 20–30 mol. % Ni^{2+} or Zn^{2+} , but less than 10 mol. % of Cu^{2+} or Fe^{2+} . In four of the systems we examined, an ‘intermediate’ phase occurred that differed in hydration state both from the Mg-bearing meridianiite end-member and the pure dopant end-member hydrate. In the case of CuSO_4 , we observed a melanterite-structured heptahydrate at Mg:Cu = 50:50, which corresponds to synthetic alpersite. In the NiSO_4 - and ZnSO_4 -doped systems we identified an entirely new crystalline solid, which exists across a wide range of dopant concentrations; this phase is also seen in the CuSO_4 - and FeSO_4 -doped systems, but over a more limited range, appearing to be metastable with respect to the melanterite-structured heptahydrate. The Ni-doped substance has been indexed with a monoclinic unit-cell. The molar volume is consistent with it being an enneahydrate [i.e., $(\text{Mg}_{0.5}\text{Ni}_{0.5})\text{SO}_4 \cdot 9\text{H}_2\text{O}$].

We find that there is a linear relationship between the rate of change in unit-cell volume as a function of dopant concentration and the ionic radius of the dopant cation [10]; large ions such as Mn^{2+} produce a large inflation of the hydrates’ unit-cell, whereas smaller ions such as Ni^{2+} produce a modest reduction in unit-cell volume (Fig. 2).

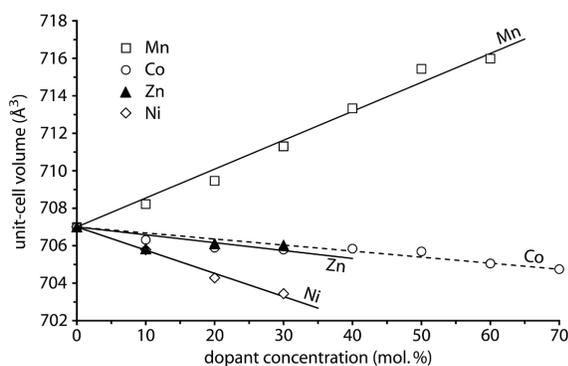


Figure 2. Unit-cell volumes of the cation doped 11-hydrate crystals as a function of dopant concentration, determined from X-ray powder diffraction analysis of nitrogen-quenched polycrystalline samples.

Results, Oxyanions: In marked contrast with the cation-doping studies, we have discovered that it is possible to form end-member 11-hydrates containing

alternative oxyanions. Both $\text{MgCrO}_4 \cdot 11\text{H}_2\text{O}$ and $\text{MgSeO}_4 \cdot 11\text{H}_2\text{O}$ are isostructural with meridianiite and form a complete solution series with the sulfate analogue. The selenate-bearing mixtures form an as-yet unidentified metastable phase on warming from liquid nitrogen temperatures prior to crystallising the meridianiite-structured phase. Thus far, we have obtained only amorphous material or a very poorly crystalline phase from quenched aqueous solutions of MgMoO_4 . The chromate and selenate analogues of meridianiite have substantially inflated and anisotropically strained unit-cells [11]; the magnitude of the strain is comparable to that seen in chromate- or selenate-substituted jarosites [12,13].

Implications: The observation that meridianiite can form in the presence of, and accommodate significant quantities of other ions increases the likelihood that this mineral will occur naturally on Mars – and elsewhere in the outer solar system – in metalliferous brines. Selenium and chromium leached from magmatic sulfide ores or cumulate chromites [14] under strongly oxidising conditions may be readily taken up by meridianiite. We expect inclusion of foreign ions into meridianiite to have a substantial effect of the environmental conditions (and the products) of dehydration to lower hydrates. Our discovery of new hydration states – particularly at dopant concentrations as low as 10 mol. % in Cu^{2+} and Fe^{2+} doped solutions – shows that the mineralogy of evaporites crystallised at low temperatures may be more complex than previously thought. Certainly, additional study of these new 8- and 9-hydrates is necessary in order to accommodate them in geochemical models of martian brine reservoirs [e.g., 15]. X-ray powder diffraction patterns of the new phases and the substantial Bragg peak shifts in doped 11-hydrates [10,11] may aid in characterisation of samples analysed *in situ* by *Curiosity*’s Chemin diffractometer.

References:

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