IONIC SUBSTITUTION IN MERIDIANIITE (MgSO₄·11H₂O): SOLID SOLUTIONS AND NOVEL HYDRATES. A. D. Fortes¹, F. Browning², and I. G. Wood¹. ¹Department of Earth Sciences, University College London, Gower Street, London, WC1E 6BT, U.K. (andrew.fortes@ucl.ac.uk)

Introduction: MgSO₄·11H₂O (MS11) is the most highly hydrated phase in the binary MgSO₄—H₂O system, having a narrow stability field in contact with aqueous solution [1]. Whilst all of the other known MgSO₄ hydrates (1, 2, 2½, 3, 4, 5, 6, and 7H₂O) have isomorphic or isodimorphous crystalline analogues with alternative cation and oxyanion substituents, MS11 is hitherto unique in occurring solely in the MgSO₄—H₂O 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 exists 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 Ni²⁺, Zn²⁺, Cu²⁺, Fe⁴⁺, Co²⁺ and Mn²⁺ in molar abundances from 0 to 100 % in 10 % increments. Subsequently, we carried out a similar series of measurements on quenched aqueous solutions of MgCrO₄, MgSeO₄ and MgMoO₄. 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. % Co²⁺ or Mn²⁺. 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 lustrous copper-orange colour (Fig. 1), quite distinct from the opaque dark red of (Co,Mg)SO₄·7H₂O. The morphology of the Co-doped 11-hydrates closely resembles that of the Mg-bearing variety, though often with a blockier habit.

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Results, Cations: We have established that of the seven end-member metal sulfates studied, only MgSO₄ forms an undecahydrate [9]; ZnSO₄ forms an orthorhombic heptahydrate (synthetic goslarite), MnSO₄, FeSO₄, and CoSO₄ form monoclinic heptahydrates.
(syn. mallardite, melanterite, and bieberite, respectively), and CuSO₄ crystallises as the well-known triclinic pentahydrate (syn. chalcanthite). NiSO₄ 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, NiSO₄·8H₂O.

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. % Co²⁺ or Mn²⁺, 20–30 mol. % Ni²⁺ or Zn²⁺, but less than 10 mol. % of Cu²⁺ or Fe²⁺. 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 CuSO₄, we observed a melanterite-structured heptahydrate at Mg:Cu = 50:50, which corresponds to synthetic alpersite. In the NiSO₄- and ZnSO₄-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 new hydrate crystals as a function of dopant concentration, we have discovered that it is

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 sulphide 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 Cu²⁺ and Fe²⁺ 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 ChemCam diffractometer.

References: