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Acknowledgements This Letter is based on data collected at the Subaru Telescope, which is operated by the National Astronomical Observatory of Japan. We thank C. Koike, I. Yamamura, F. Usui, S. Hasegawa, T. Ootsubo, H. Chihara, T. Nakamoto, H. Tanaka and T. Takeuchi for comments and discussions.

Competing interests statement The authors declare that they have no competing financial interests.

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Magnesium sulphate salts and the history of water on Mars

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Recent reports of ~30 wt% of sulphate within saline sediments on Mars^{1,2}—probably occurring in hydrated form³—suggest a role for sulphates in accounting for equatorial H₂O observed in a global survey by the Odyssey spacecraft⁴. Among salt hydrates likely to be present³, those of the MgSO₄·nH₂O series have many hydration states. Here we report the exposure of several of these phases to varied temperature, pressure and humidity to constrain their possible H₂O contents under martian surface conditions. We found that crystalline structure and H₂O content are dependent on temperature–pressure history, that an amorphous hydrated phase with slow dehydration kinetics forms at <1% relative humidity, and that equilibrium calculations may not reflect the true H₂O-bearing potential of martian soils. Mg sulphate salts can retain sufficient H₂O to explain a portion of the Odyssey observations⁵. Because phases in the MgSO₄·nH₂O system are sensitive to temperature and humidity, they can reveal much about the history of water on Mars. However, their ease of transformation implies that salt hydrates collected on Mars will not be returned to Earth unmodified, and that accurate *in situ* analysis is imperative.

Direct evidence for sulphate salts on Mars dates back to recognition of an Mg–S correlation in X-ray fluorescence data collected by Viking in 1976 at two widely separated landing sites⁶. The Viking data led to the concept of Mg sulphate salt as a widespread cementing agent at ~10 wt% (anhydrous basis) in martian soils⁷, particularly as a shallow ‘duricrust’ within the upper few centimetres of soil. The concept of widespread Mg sulphate salt distribution in soils was reinforced by detection of similar Mg–S

correlations at the Pathfinder landing site in 1997 (refs 8, 9), and by recent determination of comparable Mg–S compositions in soils and within a possible coating of cemented dust on the rock Mazatzal at Gusev crater¹⁰. Global thermal inertia data¹¹ and thermal emission spectroscopy¹² suggest that duricrust may cover vast tracts of land at the martian equator. Widespread distribution of sulphate salt as a cementing agent in soil may be attributed to a relatively young pedogenic process, possibly acidic weathering, that does not require surface water or ground water^{13,14}. A pedogenic origin remains plausible for this particular mode of occurrence, but results from the Mars Exploration Rover Opportunity at Meridiani Planum^{1,2} provide compelling evidence that sediments rich in sulphate salts formed on Mars by evaporation from water.

The Odyssey orbiter has recently provided global maps of water-equivalent hydrogen that reveal surprisingly high abundances of near-surface hydrogen (~9–11 wt% H₂O equivalent⁴) in widespread equatorial regions where water ice is unstable to sublimation¹⁵. The observed H suggests the presence of hydrous silicates or salt hydrates in the upper 1 m of regolith^{16,17}. It has been known since Viking that lesser amounts of Cl and minor amounts of Br are associated with S, and the hydroxylated K–Fe³⁺ sulphate mineral jarosite (20% OH; 11% H₂O equivalent) has been found at Meridiani Planum¹, all of which point to a complex salt assemblage for which many possible mineralogies have been suggested¹⁸. Nevertheless, the widespread Mg–S association observed by Viking, Pathfinder and the MER rovers indicates that some form of MgSO₄·nH₂O is common in soils that are globally distributed on Mars.

The only common, naturally occurring members of the MgSO₄·nH₂O series on Earth are epsomite (MgSO₄·7H₂O, 51 wt% water), hexahydrate (MgSO₄·6H₂O, 47 wt% water) and kieserite (MgSO₄·H₂O, 13 wt% water). These three salts are believed to be the only members that occur on Earth as thermodynamically stable minerals¹⁹. Rare, metastable minerals of the series include pentahydrate (MgSO₄·5H₂O, 43 wt% water), starkeyite (MgSO₄·4H₂O, 37 wt% water) and sanderite (MgSO₄·2H₂O, 23 wt% water). Other hydration states ($n = 12, 3, 1.25$) are not recognized as minerals but can be synthesized. All of these salts consist of SO₄ tetrahedra and Mg(O, H₂O)₆ octahedra; some include extra-polyhedral water (water that is not in octahedral coordination with Mg)²⁰. Epsomite transforms readily to hexahydrate by loss of extra-polyhedral water; this transition is reversible and occurs at ~50–55% relative humidity (RH) at 298 K and at lower temperatures as the activity of water diminishes¹⁹. Kieserite is more stable at lower RH and higher temperature; for example, at moderate heating rates in thermogravimetric analysis the kieserite structure survives to ~670 K, compared with ~450 K for hexahydrate. However, as we show here, kieserite converts to hexahydrate or epsomite as humidity increases, yet these phases do not easily revert to kieserite on desiccation. Metastability, kinetic effects and pathway dependence are important factors in the MgSO₄·nH₂O system.

We have examined formation and transformation of MgSO₄·nH₂O minerals precipitated by evaporation from MgSO₄ solutions or transformed in the solid state under conditions of controlled temperature and humidity. These experiments include formation at conditions of ~1 torr total pressure, which is slightly less than Mars’ atmospheric pressure (~5 torr at most equatorial elevations). Other experiments have been conducted¹⁷ at temperatures from 100 to 298 K, and from 10^{–5} torr to ambient pressure (~580 torr in our laboratory at 2,265 m elevation). In addition, we have used thermogravimetric analysis (TGA) and isothermal controlled-humidity gravimetric analysis to examine water gain and loss from MgSO₄·nH₂O samples. Our most extensive data consist of X-ray diffraction (XRD) analyses collected while samples were held in an environmental cell²¹ at controlled RH and ambient temperature (~298 K) inside the diffractometer.

Results of these experiments show that the reaction path at very low RH ($\leq 0.5\%$) proceeds from precipitation of epsomite through transformation to hexahydrate, but the stable phase, kieserite, does not form. Instead, XRD analysis shows that hexahydrate in crystals of < 1 mm becomes amorphous on timescales of a day (at 1 torr total pressure), a few hours (at 0.02 torr), or minutes (at $\sim 10^{-5}$ torr). This loss of crystal structure can also be observed at 298 K and 0.3–0.4% RH (~ 580 torr total pressure) on a timescale of 40 h (Fig. 1). An unanticipated observation was the retention of original epsomite crystal shapes, even as the crystal structure transformed to hexahydrate and then became amorphous. Desiccation does not lead to disintegration. The amorphous salt resists complete dehydration; after relatively rapid loss of two-thirds of the original 47% water in hexahydrate, the desiccation rate slows markedly. Even after desiccation at 1 torr and 0.5% RH for four months, amorphous salt prepared from centimetre-size hexahydrate crystals retains ~ 22 wt% water, 70% more than the amount of water in kieserite. Under colder conditions on Mars (~ 220 K equatorial average) and at typical Mars surface pressure (~ 5 torr) and diurnal RH ranging from $\sim 1\%$ to 100% (summer equatorial average $\sim 50\%$ RH²²), we expect that the rate of water loss and the kinetics of any transition of the amorphous phase to a crystalline form will be significantly reduced.

When kieserite rather than hexahydrate was exposed to comparable conditions of very low RH, no transition towards an amorphous salt was observed. This indicates that if the salts in soils or sediments on Mars contain kieserite, the kieserite could be stable at the currently dry martian surface but may actually contain less water than if the deposits were initially formed of epsomite/hexahydrate that has since become amorphous. Moreover, although kieserite resists dehydration in vacuum, experiments in the environmental cell show that it is easily hydrated on exposure to elevated humidity

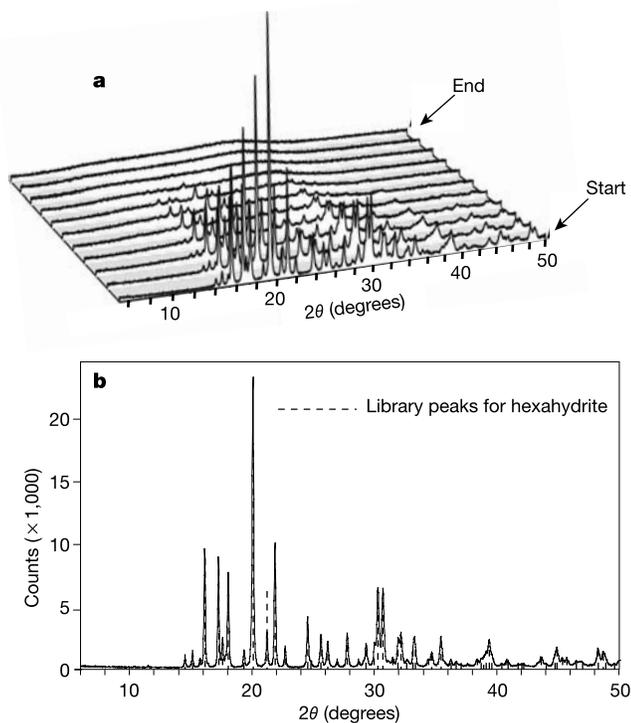


Figure 1 Dehydration experiment in an environmental cell. **a**, Ten sequential X-ray diffraction (XRD) patterns of hexahydrate desiccated at 298 K and 0.3–0.4% RH to produce amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$. The ten XRD patterns represent desiccation over a period of 40 h. **b**, The XRD pattern of the hexahydrate starting material. In Figs 1 and 2, XRD was performed using $\text{CuK}\alpha$ radiation.

($> 55\%$ RH) where it converts to hexahydrate and then epsomite. When desiccated, these minerals become amorphous rather than transforming back to kieserite, indicating that kieserite might not be preserved in deposits that have experienced obliquity-driven cycles of hydration (water-ice stabilization) and desiccation as predicted for the upper 1–2 m of equatorial regolith on timescales of $\sim 10^6$ yr (ref. 15).

We have also examined amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ on re-exposure to humid conditions. Figure 2 illustrates one of these experiments at 298 K and controlled RH of 31%. Within 460 h, amorphous material made from hexahydrate largely recrystallized to form hexahydrate, pentahydrate and starkeyite. Results from several environmental-cell desiccation and hydration experiments at 298 K and a range of RH conditions are summarized in Fig. 3. A significant implication of these experiments is that under conditions of water-ice stability near the martian equator, amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ with diminished water content will not only rehydrate but may recrystallize to minerals that differ from the starting material. Under repeated changes in obliquity and equatorial climate, at the low average surface temperature of 220 K and average RH of $\sim 50\%$ shown in the lower part of Fig. 3, it is difficult to predict what the terminal salt mineral assemblage will be.

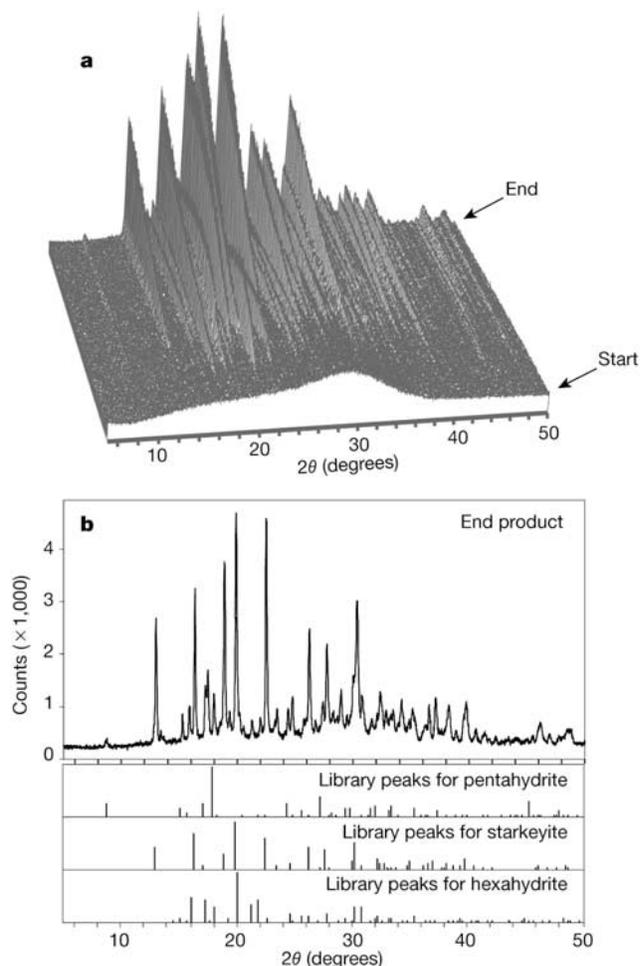


Figure 2 Rehydration experiment in an environmental cell. **a**, 115 sequential XRD patterns of amorphous $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ rehydrated at 298 K and 31% RH over 460 h to form hexahydrate, pentahydrate and starkeyite; there is still some remnant amorphous material at 460 h. **b**, The XRD pattern of the partially recrystallized salts at the end of the experiment, with the library peak positions for the three minerals identified in the sample.

Nevertheless, it is likely that both bedded and soil-cementing salts carry a record of depositional and environmental parameters and thus have the potential to reveal geologic processes on Mars. As just one example, near-surface occurrences of $MgSO_4 \cdot nH_2O$ as soil cement (10 wt% $MgSO_4$ on an anhydrous basis)^{7,8} are likely to account for variable portions of the water contents mapped by the Odyssey spacecraft at low latitudes where water ice is not at present stable⁵. The mineral or amorphous forms of $MgSO_4 \cdot nH_2O$ in martian soils may vary with timing, duration, temperature and geographic distribution of water ice deposits during episodes of greater obliquity. If forms of $MgSO_4 \cdot nH_2O$ also occur as part of the H-bearing mineral assemblage in evaporite sediments, the differences in salt-hydrate mineralogy between sediments and soils will reflect their differing modes of formation and subsequent exposure history.

The data summarized here suggest that studies of martian salts can provide vital information about the hydrogeologic history of Mars. Return of samples to Earth for detailed study will be important for reaching this goal. However, our results also show that mineralogy should be accurately characterized *in situ* before samples are removed from Mars. The ease with which dehydration/rehydration transformations take place in the $MgSO_4 \cdot nH_2O$ system indicates that these and other environmentally sensitive salts collected on Mars probably will not be returned to Earth

unmodified unless exceptional effort is made to preserve martian conditions during sample return and recovery.

Examples from meteorites and the Moon illustrate this problem. Epsomite is observed as a hydrous phase in primitive CI1 chondrites and has been cited as evidence for late-stage oxidation of the CI1 parent body, but a strong case has been made that the epsomite formed after these meteorites were placed in humid terrestrial museums²³. Also, putative occurrences of goethite (FeO(OH)) 'rust' in Apollo 16 rocks have been shown to have formed by hydration-oxidation of primary lawrencite (FeCl₂) (ref. 24) after removal from the Moon. This reaction occurred despite the short travel time and careful protection protocols (for example, storage in dry nitrogen after recovery) for lunar samples. What will we make of martian samples carried on a longer return if they contain unstable salt mixtures about which little is known? Accurate *in situ* mineralogical and chemical analysis is imperative if we are to reach the right conclusions from studies of saline, hydrated martian soils or sediments returned to Earth. □

Received 22 April; accepted 25 August 2004; doi:10.1038/nature02973.

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Figure 3 Results of controlled-humidity XRD experiments at 298 K plotted against stability fields for epsomite, hexahydrate and kieserite, modified from ref. 19. Their study provides accurate constraints on the epsomite to hexahydrate transition (curve 1); their estimate of the hexahydrate to kieserite transition (curve 2) is based on thermodynamic data extrapolated from the experimentally determined solution equilibrium; an alternative estimate of this transition is based solely on thermodynamic data (curve 3). Estimated stability of hexahydrate under martian conditions depends on extrapolation of curves 2 or 3. Stability of the $MgSO_4 \cdot 12H_2O$ phase is poorly constrained. Our experiments show that at RH of ~0.5%, hexahydrate forms from solution but becomes amorphous. Hexahydrate forms and persists at RH values from ~55% down to at least 7%. Amorphous $MgSO_4 \cdot nH_2O$ formed at RH of ~0.5%, and subsequently exposed to RH of 7–55% crystallizes to various hydrates ($n = 1.25$ to 6) dependent on RH; ongoing long-term experiments suggest that crystalline end products vary with RH within the upper shaded region. Above RH of ~55%, both amorphous $MgSO_4 \cdot nH_2O$ and kieserite transform to hexahydrate and then epsomite. At martian conditions below 280 K, the rates and ranges for comparable reactions are not yet determined. The diurnal temperature–RH range shown (lower shaded region) for the Mars surface in summer at the Viking 1 site is from ref. 22. The average diurnal surface temperature of 220 K near the equator varies little despite changes in obliquity¹⁵.

Acknowledgements This research was supported by Los Alamos National Laboratory – Directed Research and Development Funding and by a NASA Mars Fundamental Research Program grant. Comments and suggestions by J. F. Bell and B. C. Clark helped to improve this Letter.

Competing interests statement The authors declare that they have no competing financial interests.

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