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Geochimica et Cosmochimica Acta 71 (2007) 241–250
Geochimica
www.elsevier.com/locate/gca

Experimental stability of magnesium sulfate hydrates that may be present on Mars

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Received 2 February 2006; accepted in revised form 12 July 2006

Abstract

Since the Viking missions in 1976, magnesium sulfates have been predicted to exist on the surface of Mars. Recent orbital measurements suggest that Mg-sulfates are rather ubiquitous on the martian surface. Chemical analyses by landers support the inference that Mg-sulfate hydrates may be one source of the significant quantities of equatorial near-surface hydrogen observed by the neutron and γ-ray spectrometers on the Mars Odyssey spacecraft. The present study was undertaken to examine stability relations among the various Mg-sulfate hydrates. Using saturated salt solutions to control water-vapor pressure at temperatures of 3, 23, 50, 63, and 75 °C, Mg-sulfate phases were allowed to equilibrate from 2 to 3 months to see which hydration states were formed or were stable. Starting materials consisted of hexahydrite ($6H_2O$), starkeyite ($4H_2O$), kieserite ($1H_2O$), a second monohydrate-polymorph available as a chemical reagent, and an anhydrous $MgSO_4$ reagent. Products created in this study included these minerals, along with epsomite ($7H_2O$), sanderite ($2H_2O$), amorphous $MgSO_4$ ($1–2H_2O$), several previously undescribed phases, one of which was quite persistent ($2.4H_2O$), and trace amounts of pentahydrite ($5H_2O$). As expected, Mg-sulfate stability is strongly dependent on water vapor pressure and temperature. Lower temperatures favor the more hydrated Mg-sulfates. However, the $MgSO_4$ system was found to be surprisingly complicated and is strongly dominated by metastability, sluggish kinetics, and reaction pathways. Unexpected results were frequently encountered, in addition to the formation of previously undescribed phases. Several of the hydrates also show significant metastable extensions, such that phase boundaries can only be approximated. For example, kieserite, which has been reported on Mars from OMEGA data, in addition to having a distinct stability region, is resistant to transformation and persists throughout temperature-RH space until very high relative humidities are achieved. Results of this study show that $MgSO_4$ hydrates in addition to epsomite, hexahydrite, and kieserite can persist and should not be overlooked when assessing possible Mg-sulfate minerals that can occur on Mars.
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1. Introduction

Mars has long attracted attention as a possible site for extraterrestrial life (present or past), and as a possible destination for human exploration and habitation. For Mars to support life as we know it, water must be present in some form (e.g., Jakosky and Shock, 1998; NRC, 2003). Of interest in this regard are the neutron spectrometer data collected by the Mars Odyssey spacecraft (Feldman et al., 2004a) showing significant quantities of hydrogen (which they express as water-equivalent hydrogen) in equatorial zones where water-ice is not stable. Bish et al. (2002, 2003) explore the possibility that this hydrogen could be in the form of water or hydroxyl in hydrated minerals such as clays and zeolites. More recently, attention has been given to Mg-sulfate hydrate salts on Mars as they are believed to be a widespread cementing agent in martian soils and a possible contributor to near-equatorial hydrogen (Feldman et al., 2004b). Some of the earliest conclusions concerning Mg-sulfate hydrates, based on results from the Viking landers (Clark et al., 1976; Toulmin et al., 1977), have been strengthened by more recent missions. Results from these later missions support the presence of significant quantities of Mg-sulfates in soils and sediments (e.g., Larsen et al., 2000; Squyres et al., 2004; Bonello et al., 2005; Clark

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0016-7037/$ - see front matter Published by Elsevier Inc.
doi:10.1016/j.gca.2006.07.044

et al., 2005). This evidence for sulfate salt hydrates is now particularly strong, based on a robust and diverse data set of α-proton X-ray Spectroscopy (APXS, Pathfinder and the MER rovers Spirit and Opportunity), and ultraviolet–visible (UV–vis) data from the Mars Express OMEGA spectrometer (e.g., Bibring et al., 2005; Gendrin et al., 2005).

The dominant naturally occurring members of the $MgSO_4 \cdot nH_2O$ series on Earth are epsomite ($MgSO_4 \cdot 7H_2O$), hexahydrite ($MgSO_4 \cdot 6H_2O$), and kieserite ($MgSO_4 \cdot H_2O$). In addition, other magnesium sulfate hydrates (sanderite–$2H_2O$, starkeyite–$4H_2O$, pentahydrite–$5H_2O$) have been identified in evaporites or as efflorescent salts at a few localities, particularity in mines where sulfides alter under humid conditions. Generally, these deposits contain several Mg-sulfate hydrates along with other sulfates such as gypsum, thenardite, konyaite, mirabilite, and bloedite (e.g., Whittig et al., 1982; Last, 1984; Keller et al., 1986; Ducloux et al., 1994; Singer et al., 1999).

Most studies relating to Mg-sulfates examine only the possible occurrences of epsomite, hexahydrite, kieserite, and occasionally an ephemeral 12-hydrate form (e.g., Hogenboom et al., 1995; Archer and Rard, 1998; Chou and Seal, 2003; Feldman et al., 2004b). However, other Mg-sulfates have stability fields (Chipera et al., 2005) and should also be considered when examining the possible species on the surface of Mars. In particular, we have found that starkeyite shows a pronounced stability field located between hexahydrite and kieserite. The objective of this study is to help refine the stability relationships among the various $MgSO_4$ hydrates so that inferences can be made as to which species can exist and how much water they may contain if they are present on the martian surface.

2. Methods

To study the stability relationships among different Mg-sulfate hydrates, various forms of $MgSO_4 \cdot nH_2O$ powders were equilibrated at varying relative humidities controlled using saturated salt solutions at temperatures of 3, 23, 50, 63, and 75 °C. Saturated salt solutions are a well-studied and convenient means of maintaining constant relative humidity (RH). Any salt solution at a constant temperature in a closed system is in equilibrium with a fixed partial vapor pressure of water and thus defines a fixed relative humidity at that temperature (Young, 1967). Saturated salt solutions would be better described as ‘‘slurries’’ composed of liquid and undissolved salt crystals, which by their nature are buffered such that they liberate or adsorb large quantities of water to maintain an equilibrium humidity. Care must be taken in creating the solutions, however, as the solubility changes with temperature and the solutions must be pre-equilibrated at the temperature of interest to ensure that they remain saturated with respect to the salt.

Relative humidity values for the salt solutions used in this study are based on data from Young (1967), Greenspan (1977), Huang and Whetstone (1985), and Foxworthy (1988). Table 1 and Fig. 1 show the salt solutions used for this study along with their %RH values as a function of temperature, using in some cases preferred values as the literature exhibits variability in the reported relative humidity data. Several salts show consistent RH as a function of temperature (e.g., NaCl) but some salts exhibit significant shifts in RH due to variable waters of solvation as a function of changing temperature (e.g., $CaCl_2$). Due to lack of data, some salts were used outside the region of available measured values, requiring that the values be extrapolated from available data (e.g., $Mg(NO_3)_2$) or several data sources be merged (e.g., Greenspan, 1977 and Huang and Whetstone, 1985 for $SrCl_2$). However, for the purposes of determining relative stability fields of the Mg-sulfate phases in this study, minor uncertainties in actual relative humidity for the salt solutions will not cause significant errors in determining the relative positions of stability fields.

To conduct the experiments, saturated salt solutions were placed into Teflon jars (8 cm in diameter, 7 cm tall) covering the bottom to a depth of ~0.5 cm. Into these jars, smaller Teflon vessels containing 0.6 to 1.0 g of the starting Mg-sulfate hydrate powders were placed, with a loose cap to prevent condensation or contaminants from entering, yet allowing air exchange with the relative humidity atmosphere over the saturated salt solution. These powders are dry and are not in contact with the saturated salt solution although water vapor can exchange between the powder and solution. Containers were then placed into ovens (50, 63 and 75 °C), left at ambient room temperature (23 °C) or placed into a refrigerator (3 °C) for equilibration times typically between 2 and 3 months; all temperatures were determined with a thermometer traceable to NIST standards. Initially, short runs (14–20 days) were conducted before the significance of the slow kinetics in the Mg-sulfate hydrate system became apparent. Longer runs were then conducted for most of the experiments in an attempt to attain equilibrium and in several cases to explore reaction kinetics. Run times for the various experiments, both short and long, are listed in Table 1.

Starting materials chosen for this study include anhydrous $MgSO_4$ reagent (Fisher Scientific Certified Anhydrous, CAS 7487-88-9), reagent monohydrate $MgSO_4$ (Aldrich, 97%, CAS 14168-73-1), synthetic kieserite ($1H_2O$), synthetic starkeyite ($4H_2O$), and an ultra-pure reagent that is principally hexahydrite ($6H_2O$) at our laboratory conditions (Alfa Aesar Puratronic 99.997%, CAS 22189-08-8). Starkeyite was synthesized by placing ultrapure reagent hexahydrite over $CaCl_2$ saturated salt solution at 50 °C for times greater than 2 weeks. Kieserite was synthesized in the same fashion but using anhydrous $MgSO_4$ reagent over $SrCl_2$ at 75 °C. Hexahydrite served as a proxy for epsomite as these two phases behave similarly and readily react reversibly to one another across a well defined temperature and relative humidity boundary (Chou and Seal, 2003).

Reaction starting materials and products were analyzed via X-ray powder diffraction (XRD) using a Siemens D500

Table 1
Summary of experimental runs

RH control		Starting Mg-sulfate material				
Salt solution	RH	Hexahydrite	Starkeyite	Kieserite	Reagent monohydrate	Anhydrous $MgSO_4$
3 °C						
NaOH	7	104 d, H(100%)	104 d, S(100%)	104 d, K(100%)	104 d, M(100%)	104 d, A(100%)
LiCl	13	117 d, H(100%)	117 d, S(100%)	117 d, K(100%)	117 d, M(100%)	117 d, A(100%)
$MgCl_2$	34	109 d, E(100%)	109 d, S(100%)	109 d, K(100%)	109 d, M(100%)	109 d, A(60), S(28), H(12)
23 °C						
Vacuum	<1	75 d, Amorph(100%)	75 d, Amorph(100%)	75 d, K(100%)	75 d, M(100%)	75 d, A(100%)
NaOH	7	85 d, S(100%)	85 d, S(100%)	85 d, K(100%)	85 d, M(100%)	85 d, A(100%)
LiCl	11	97 d, S(100%)	97 d, S(100%)	97 d, K(100%)	97 d, M(100%)	97 d, A(100%)
$CaCl_2$	29	83 d, S(93),H(3),P(4)	83 d, S(100%)	83 d, K(100%)	83 d, M(100%)	83 d, A(73),U(27)
$MgCl_2$	33	102 d, S(100%)	102 d, S(100%)	102 d, K(100%)	102 d, M(100%)	102 d, A(66),S(3),U(31)
NaI	38	99 d, H(99),S(1)	99 d, S(100%)	99 d, K(100%)	99 d, M(100%)	99 d, A(36), S(31), U(29), P(4)
$Mg(NO_3)_2$	53	103 d, H(100%)	103 d, H(100%)	103 d, K(84), H(16)	103d,H(61),M(27),K(12)	103 d, H(98), S(2)
$SrCl_2$	71	96 d, E(100%)	96 d, E(100%)	96 d, E(100%)	96 d, E(100%)	96 d, E(100%)
50 °C						
NaOH	6	64 d, S(74), U(26)	64d,S(85),U(7),Sn(3),M(7)	64 d, K(100%)	64 d, M(100%)	64 d, A(100%)
LiCl	11	70 d, S(92), U(8)	70 d, U(87), S(4), M(9)	70 d, K(100%)	70 d, M(100%)	70 d, A(100%)
LiCl		10 d, S(100%)	28 d, S(100%)	—	11 d, M(100%)	10 d, A(100%)
$CaCl_2$	16	73 d, S(100%)	73 d, S(100%)	73 d, K(100%)	73 d, M(100%)	73 d, A(93), Sn(7)
$CaCl_2$		11 d, S(100%)	—	—	11 d, M(100%)	11 d, A(49), U(51)
NaI	30	73 d, S(100%)	73 d, S(100%)	73 d, K(100%)	73 d, M(100%)	73d,A(27),U(27),Sn(28),K(9),M(9)
NaI		12 d, S(100%)	—	—	12 d, M(100%)	12 d, A(42), U(58)
$Mg(NO_3)_2$	45	21 d, S(100%)	21 d, S(100%)	63 d, K(100%)	63 d, M(72), K(28)	21 d, U(71), S(23), A(6)
$SrCl_2$	62	83 d, H(100%)	83 d, H(100%)	62 d, K(99), H(1)	62 d, K(61), M(38), H(1)	83 d, H(99), S(1)
$SrCl_2$		26 d, H(100%)	26 d, H(89), S(11)	—	—	26 d, H(84),S(16)
NaCl	75	83 d, H(100%)	83 d, H(100%)	68 d, H(100%)	68 d, H(100%)	83 d, H(100%)
NaCl		27 d, H(100%)	27 d, H(100%)	—	—	27 d, H(95),S(5)
63 °C						
NaOH	3.5	89 d, M(100%)	89 d, M(100%)	89 d, K(100%)	89 d, M(100%)	89 d, A(81), M(19)
LiCl	11	91 d, M(89), K(8),Sn(3)	91 d, M(100%)	91 d, K(100%)	91 d, M(100%)	91 d, A(96), M(4)
$CaCl_2$	17	91 d, M(75), K(25)	91 d, M(75), K(25)	91 d, K(100%)	91 d, M(100%)	91d, A(45), M(45), K(5), Sn(5)
NaI	25	125 d, K(100%)	125 d, K(100%)	125 d, K(100%)	125 d, M(100%)	125 d, M(66), K(15), A(19)
$MgCl_2$	29	89 d, K(100%)	89 d, K(100%)	89 d, K(100%)	89 d, M(100%)	89 d, M(65), K(24), A(11)
$Mg(NO_3)_2$	42	90 d, S(93), K(7)	90 d, K(100%)	90 d, K(100%)	90 d, M(77), K(23)	90 d, M(41), K(58), A(1)
$SrCl_2$	50	89 d, S(100%)	89 d, S(100%)	89 d, K(100%)	89 d, K(72), M(28)	89 d, K(100%)
$NaNO_3$	67	83 d, H(100%)	83 d, S(100%)	83 d, K(99), H(1)	83 d, K(100%)	83 d, K(99), S(1)
NaCl	74	77 d, H(100%)	77 d, H(100%)	77d, K(90), H(10)	77d, H(69), K(31)	77 d, H(100%)
75 °C						
NaOH	2	70 d, Sn(86), M(14)	70 d, Sn(93), M(7)	70 d, K(100%)	—	—
LiCl	11	68 d, M(100%)	68 d, M(100%)	68 d, K(100%)	68 d, M(100%)	68 d, A(75), M(20), K(5)
LiCl		12d,M(56),Sn(30),U(14)	70 d, M(96), S(4)	—	12 d, M(100%)	13 d, A(100%)
$CaCl_2$	17	66 d, M(70), K(30)	77 d, M(72), K(27)	77 d, K(100%)	66 d, M(100%)	66 d, M(77), A(14), K(9)
$CaCl_2$		14 d, S(74), K(26)	—	—	13 d, M(100%)	14 d, M(56), A(4), K(40)
NaI	23	—	19 d, K(56), M(44)	—	—	—
$MgCl_2$	27	82 d, K(70), M(30)	82 d, K(71), M(29)	—	82 d, M(100%)	82 d, M(65), K(27), A(8)
$Mg(NO_3)_2$	37	69 d, K(100%)	69 d, K(100%)	69 d, K(100%)	69 d, M(77), K(23)	20 d, M(57), K(40), A(3)
$Mg(NO_3)_2$		20 d, S(56), K(44)	20 d, K(85), S(15)	—	—	20 d, K(53), M(45), A(2)
$SrCl_2$	43	67 d, K(100%)	67 d, K(100%)	68 d, K(100%)	68 d, K(100%)	67 d, K(100%)
$SrCl_2$		20 d, S(96), H(4)	20 d, S(100%)	—	—	20 d, K(100%)
$NaNO_3$	65	81 d, S(85), K(15)	81 d, K(100%)	81 d, K(100%)	81 d, K(100%)	81 d, K(100%)
NaCl	74	86 d H(100%)	86d, H(75), S(25)	61 d, K(93), H(7)	61 d, K(100%)	86 d K(100%)
NaCl	74	20 d, H(100%)	19 d, S(98), H(2)	—	—	19 d, K(100%)

Columns provide salt solution used, relative humidity (RH) for that salt solution at the temperature of the experimental runs, and the experimental results for five different starting materials at five different temperatures. For each of the starting materials, the number of days equilibrated are noted as XX d, and quantitative abundances (weight percent) for the products generated in the experiments are listed. Abbreviations for the products are: A, anhydrous; Amorph, amorphous; E, epsomite; H, hexahydrite; K, kieserite; M, reagent monohydrate; P, pentahydrite; Sn, sanderite; S, starkeyite; and U, unknown $MgSO_4$ (2.4hydrate) phase.

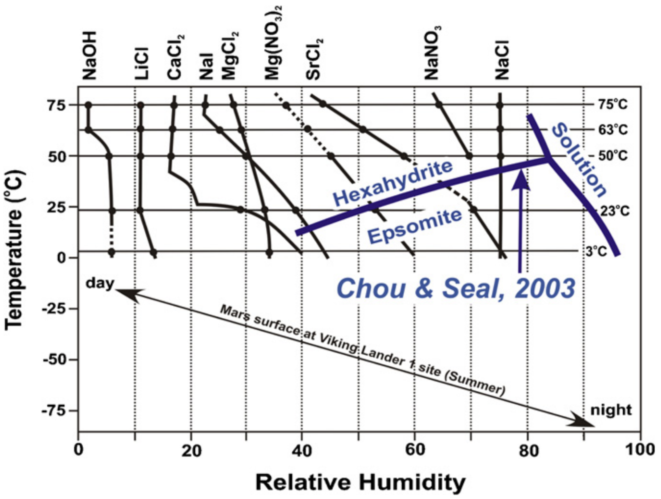

Fig. 1. Saturated salt solutions used in this study plotted as a function of temperature and relative humidity (curves from Young, 1967). Superimposed are the hexahydrite–epsomite–solution data from Chou and Seal (2003) and the late summer day–night temperatures and relative humidities measured at the Viking Lander 1 site (Savijarvi, 1995), to indicate where data need to be extrapolated for Mars-like near-surface conditions.

diffractometer, Cu-Kα radiation, incident beam Soller slits, and a Kevex solid-state PSi detector. Typical runs were conducted from 2° to 70°2θ, using 0.02° steps and counting for at least 2 s/step. Some experiments were conducted at the ambient temperature of the diffractometer (28 °C) under controlled relative humidity generated with an automated humidity-control system (Chipera et al., 1997) that mixes wet and dry N_2 gas using mass-flow controllers, monitored in the sample cell with a Vaisala capacitance film hygrometer for computer automation and control. Repeated XRD scans were collected from 2° to 70°2θ, with 0.02° steps, counting for 4 s/step (each run lasting 4 h) for durations of up to 11 days to determine the changing reaction products and the reaction rates. Reaction products were quantified using full-diffraction-pattern fitting methods. When samples contained phases for which no crystal structure is known (e.g., amorphous $MgSO_4$, sanderite, reagent monohydrate) but for which a pure sample existed to create a standard, the FULLPAT method and software were used (Chipera and Bish, 2002). For samples where crystal structures are available for the component phases (e.g., epsomite, hexahydrite, starkeyite, kieserite), Rietveld refinements were conducted using the whole-pattern-fitting routine included in the Materials Data Inc., JADE version 7 software package. For Rietveld refinements, crystal structures were downloaded from the ICSD database (http://icsdweb.fiz-karlsruhe.de/index.php) using the structures of Calleri et al. (1984) for epsomite, Zalkin et al. (1964) for hexahydrite, Baur (1964) for starkeyite, and Aleksovska et al. (1998) for kieserite.

Some of the low-RH experiments were conducted in a VWR 1410D vacuum oven, maintained at room temperature and roughing-pump vacuum conditions of ~0.5–1.0 torr. Thermogravimetric analyses (TGA) were conducted using a DuPont 951 thermogravimetric analyzer on the amorphous $MgSO_4$ and unknown phases to determine the amounts of water that they contained. Run conditions were from ambient to 600 °C at a rate of 10 °C/min and using 50 cc dry N_2 as a purge gas.

3. Results

Table 1 and Fig. 2 show the experimental results using the above listed starting materials equilibrated at various relative humidities and temperatures. Superimposed on Fig. 2 are the hexahydrite–epsomite experimental data from Chou and Seal (2003). Their very careful experimental work is used as the datum in this paper for the hexahydrite–epsomite–solution stability fields. Real-time X-ray diffraction analyses under controlled humidity at the ambient temperature of the diffractometer (~28 °C) were conducted to reversibly react hexahydrite and epsomite, as an independent confirmation of the Chou and Seal data at 28 °C (Chipera et al., 2005). Also plotted on Fig. 2A are the late summer day–night temperatures and relative humidities measured at the Viking Lander 1 site (Savijarvi, 1995), to indicate where data need to be extrapolated for Mars-like conditions at the equatorial surface. Reaction products formed in these experiments include not only the initial starting materials but also epsomite ($7H_2O$), sanderite ($2H_2O$), limited pentahydrite ($5H_2O$), the amorphous $MgSO_4$ phase described by Vaniman et al. (2004), and several previously undescribed phases that are not listed in the International Centre for Diffraction Data (ICDD) database. One phase in particular forms repeatedly throughout the experiments, contains $2.4H_2O$, and has been given the label of “unknown phase” in this paper.

3.1. Reactions

Some distinct patterns can be observed in the experimental results shown in Fig. 2. In most cases, lower humidity results in a lower hydration state of the reaction products. Likewise, elevated temperature also results in lower hydration state of the $MgSO_4$-hydrates. An exception to this, for sanderite, is discussed below. When analyzing hexahydrite as a starting material (Fig. 2A), decreasing relative humidity or increasing temperature out of the stability field of hexahydrite first produced starkeyite. Further decreases of humidity at ambient temperature resulted in the formation of amorphous $MgSO_4$ as described by Vaniman et al. (2004). Further increases of temperature at moderate humidity resulted in the formation of kieserite. Increases of temperature at lower humidity produced sanderite ($2H_2O$), a monohydrate akin to the starting reagent monohydrate material, and the unknown phase with $2.4H_2O$ whose structure is not in the ICDD database but which is a recurring phase formed in various experiments. Starkeyite showed reaction patterns very similar to hexahydrite (Fig. 2B).

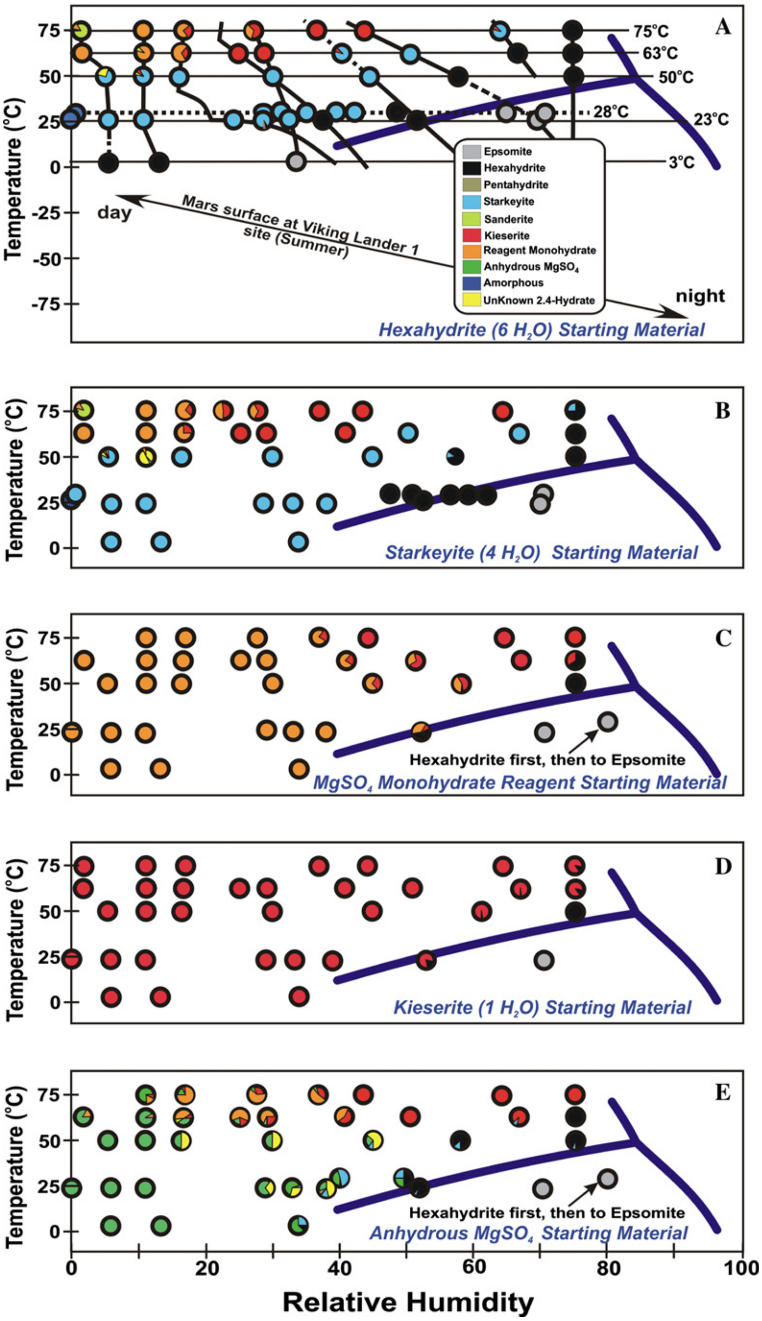

Fig. 2. Experimental results for the equilibration of five Mg-sulfates at different temperatures and relative humidities (see Table 1). The 28 °C data for (A) hexahydrite and (B) starkeyite are from real-time XRD analyses at controlled RH (Chipera et al., 2005, 2006). Superimposed are the hexahydrite–epsomite–solution data from Chou and Seal (2003) and the late summer day–night temperatures and relative humidities measured at the Viking Lander 1 site (Savijarvi, 1995).

For experiments using reagent monohydrate as the starting material (Fig. 2C), the monohydrate is stable over the entire low RH region at all temperatures studied. With increasing RH, the reagent monohydrate reacts to form kieserite. These two polymorphs of $MgSO_4$ monohydrate (kieserite and the reagent monohydrate) were both observed as products and used as starting materials in this study. It is not certain at this time whether the reagent monohydrate is a distinct polymorph or if it is a disordered form of kieserite. When RH is substantially increased, to well into the hexahydrite stability field, the monohydrates react to form hexahydrite. When placed at RH conditions where epsomite is stable, the monohydrates first react to form hexahydrite before they pick up the last water to transform to epsomite. This demonstrates a distinct rehydration reaction path in the Mg-sulfate system where epsomite apparently only forms from a hexahydrite precursor.

From the experiments using kieserite as the starting material (Fig. 2D), it appears that kieserite persists over much of the reaction space studied and extends beyond its thermodynamic stability into other regions, probably due to a large activation energy required for transformation. For example, although starkeyite and hexahydrite react readily to produce kieserite, reversing the reaction with kieserite as a starting material did not result in the formation of starkeyite and only formed hexahydrite when the RH and T conditions were well within the hexahydrite or epsomite stability regions. This phenomenon is commonly observed in the Mg-sulfate system, where phases persist beyond their thermodynamic stability until they can overcome an activation energy barrier (e.g., Hogenboom et al., 1995). The lack of readily reversible reactions between kieserite and either hexahydrite or starkeyite suggests that kieserite has metastable extensions to its stability. Likewise, the reagent monohydrate can be formed from dehydration of starkeyite or hexahydrite (suggesting that it is a stable phase) and it will react to form kieserite. However, the reverse transition from kieserite to the reagent monohydrate structure does not occur. It appears that once kieserite is formed, it not only has its own stability region, but will persist into T-RH space where it may not be the thermodynamically stable phase, but is resistant to change.

When anhydrous $MgSO_4$ is used as a starting material (Fig. 2E), a slightly different trend is seen than when the experiments are conducted from hydrated starting materials. With increasing RH at low temperatures (50 °C and less), the first product to form is the commonly recurring unknown $MgSO_4 \cdot 2.4H_2O$ structure. With further increases in RH, starkeyite forms and then hexahydrite. Once again, when placed in the epsomite field, the anhydrous $MgSO_4$ first reacts to form hexahydrite before it continues to transform to epsomite. At elevated temperature and with increasing RH, anhydrous $MgSO_4$ first forms the reagent monohydrate, and with further increases in RH, kieserite.

When looking at the trends from hexahydrite and starkeyite starting material data, an unexpected and poorly understood result is seen in the location of the regions where the 2-hydrate was found to form (Fig. 2A and B). It appears to violate the expected hydration trend where reduced-water hydrates form with decreasing RH and increasing temperature, (i.e., we observe $7H_2O \rightarrow 6 \rightarrow 4 \rightarrow 1H_2O$, then the 2-hydrate forms). It is currently believed that this out-of-place sanderite is a metastable intermediate form.

Vaniman et al. (2004) and this study found that subjecting hexahydrite to low RH (<1% RH) causes transformation to an amorphous phase within ~32 h at 28 °C. When starkeyite was subjected to low RH (<0.4% RH) for 9 days at 28 °C, it showed no evidence of any transformation to the amorphous Mg-sulfate phase even though it did transform when placed under vacuum. The monohydrates did not form the amorphous phase, even under vacuum. The amorphous phase is probably a metastable product resulting from rapid dehydration of the more-hydrous Mg-sulfate salts. Depending on factors affecting kinetics (e.g., time, temperature, particle size), the amorphous phase may react to a more stable phase or remain amorphous (Vaniman and Chipera, 2006). The amorphous phase is observed via thermogravimetric analyses (TGA) to contain variable water content (between 1 and $2H_2O$), and even more water might be retained in the amorphous form at low temperatures. In all cases, it was more hydrous than the two monohydrate structures.

In addition to the products listed above, we were able to form several $MgSO_4$-hydrates during our studies whose identities in X-ray diffraction analysis are uncertain, as there were no matching phases in the International Centre for Diffraction Data database. One phase in particular was especially recurrent. As there are 0, 1, 2, 4, 5, 6, and 7 hydrates of $MgSO_4$ observed in the natural and synthetic systems, the first inclination based on its position in RH-T space was to suspect that this could be the missing 3-hydrate phase in the sequence. Thermogravimetric analysis data for this "unknown" phase shows it to contain 2.4 waters, which is a bit unusual as the other Mg-sulfate hydrates tend to have near integral values. It is uncertain if the unknown product is a single phase, or polyphase, although it is assumed to be a single phase as its formation was repeated in many of the experiments, producing identical X-ray diffraction patterns.

3.2. Reaction rates, path dependence, and metastability

In Section 2 of this paper, it was noted that the early experiments were conducted for 2–3 weeks (shorter time entries in Table 1). Subsequently, it was decided to run the experiments from 2 to 4 months to better attain equilibrium. The shorter runs in many cases showed a mixture of phases in the product, indicating that transformations have not gone to completion in the relatively short times allowed (Table 1). Indeed, longer runs at the same conditions produced more complete reactions. Interestingly, some of the longer (>66 day) experiments also are polyphase mixtures, indicating that they too may not have gone to completion. In addition, some data suggest that there is a path dependence to the reaction series. To confirm this, experiments were conducted to monitor the reaction progress of hexahydrite at 75 °C over 3 low-RH salt solutions (NaOH–2%RH; LiCl–11%RH; and $CaCl_2$–17%RH) as a function of time (Fig. 3). In all cases, the hexahydrite ($6H_2O$) was gone by the time the samples were analyzed after 24 h of reaction, and the products were dominated by starkeyite ($4H_2O$). The starkeyite product in turn was gone within an additional 24 h in the 11% and 17% RH experiments, although it persisted a bit longer in the 2% RH experiment. The products of the starkeyite reaction were typically the "unknown phase" ($2.4H_2O$) or sanderite ($2H_2O$). With additional time (1–2 weeks) the "unknown phase" completely reacted to form the reagent monohydrate structure and, at more elevated RH, some kieserite. In similar studies, Paulik et al. (1981) and Emons et al. (1990) examine the dehydration of Mg-sulfate-hydrates (using a novel

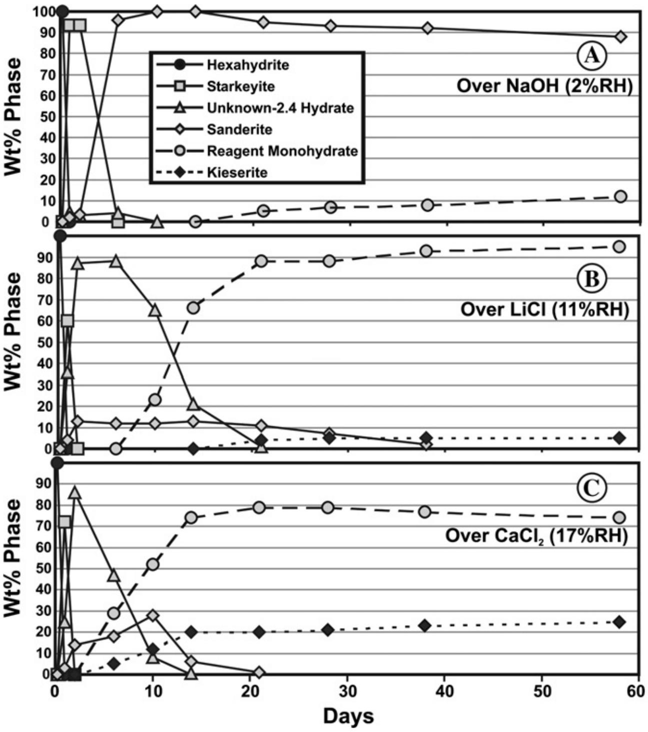

Fig. 3. Reaction progress of hexahydrite placed at 75 °C over three different low- relative humidity salt solutions (A, NaOH–2%RH; B, LiCl – 11%RH; and C, $CaCl_2$–17%RH) as a function of time.

thermogravimetric analysis system) and also monitored weight loss as distinct steps, observing the formation of what they believe to be a 3-hydrate, which with further heating formed a 2-hydrate and then the monohydrate.

As determined from this study, both temperature and time have significant effects on reaction kinetics; experimental reaction times had to be extended from several weeks to several months in an attempt to attain equilibrium, even at elevated temperatures. Reaction times to attain equilibrium at the colder temperatures of the martian surface could be extremely long. The amorphous $MgSO_4$ phase is probably a metastable product induced by rapid dehydration, as kinetics may be too slow to form a more stable crystalline phase. Like other $MgSO_4$ hydrates, the amorphous phase may also require a certain activation energy before it transforms to another phase.

3.3. General stability

The data obtained in this study show that the preponderance of transformations occurring within the Mg-sulfate hydrate system are characterized by metastability, sluggish kinetics, and path dependence, such that stability relationships among the various $MgSO_4$ hydrates can in many cases only be inferred. Fig. 4 depicts approximate stability fields for the various $MgSO_4$ hydrates encountered in this study. Hexahydrite and epsomite are common hydrates on the Earth's surface that occur at ambient temperatures and moderate to elevated RH. However, in our

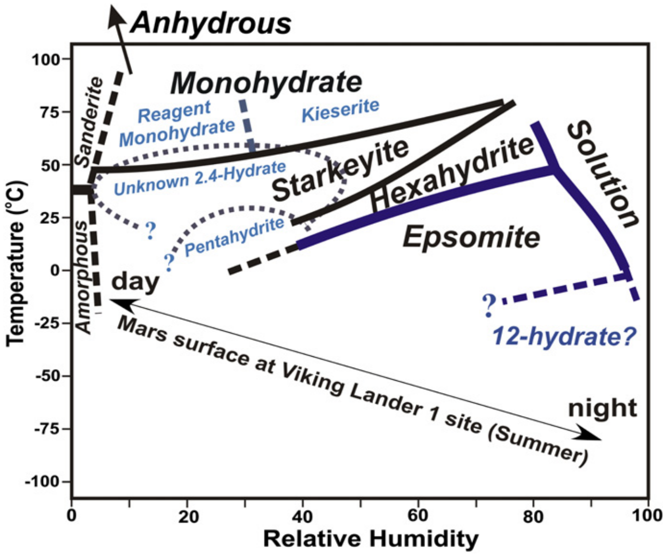

Fig. 4. General stability diagram based on our results and all available data, allowing for complications of metastability and reaction kinetics seen in the Mg-sulfate system. Superimposed are the hexahydrite–epsomite-solution data from Chou and Seal (2003) and the late summer day–night temperatures and relative humidities measured at the Viking Lander 1 site (Savijarvi, 1995). The approximate location for a 12-hydrate phase at elevated relative humidity is also plotted (Himawan et al., 2002).

study, significant stability fields were determined for starkeyite at lower relative humidities. Distinct stability fields were also determined at elevated temperatures for the two monohydrate polymorphs (“reagent monohydrate” and kieserite). The reagent monohydrate will react to form distinct kieserite, but once kieserite is formed, irregardless of the precursor Mg-sulfate hydrate, it tends to persist over much of the experimental RH-T space beyond its own stability region due to extreme metastable extensions. Although sanderite formed in several experiments at low RH and elevated temperature, its occurrence is inconsistent with systematic trends in H_2O content and it appears to be a transient, metastable phase. A transient, metastable region was also observed for the “unknown $MgSO_4$ phase”, with $\sim 2.4H_2O$, situated between sanderite and starkeyite. To date, we were only able to form pentahydrite in any appreciable quantity during rehydration of amorphous $MgSO_4$ hydrate in the controlled-humidity experiments and consequently have little knowledge of where it's stability region might exist. However, a large crystal of epsomite that we grew and then allowed to sit out on the counter to transform to hexahydrite was analyzed three months later and found to have transformed completely to pentahydrite. Also plotted on Fig. 4 is an approximate location of a 12-hydrate Mg-sulfate whose eutectic point has been measured at −3.9 °C (Himawan et al., 2002; Pillay et al., 2005).

Extrapolation to Mars conditions for some of the Mg-sulfate phases is a bit problematic. A limitation of using saturated salt solutions is that experiments can not be conducted at temperatures too much below the freezing point of pure water. In addition, the time required to achieve equilibrium or to even get the reactions to occur are beyond reasonable expectations, as evident from the lack of reaction/equilibration attained in the 3 °C experiments conducted for 3 months presented in this paper (Fig. 2). Vaniman et al. (2006) and Vaniman and Chipera (2006), conducted rehydration experiments placing amorphous $MgSO_4$ (~1.4 waters of hydration) and kieserite at −30 °C with the relative humidity at 100% over water–ice for a period of almost 1 year. Although the rehydration occurred slowly, the end product was epsomite. Interestingly, the reaction product to first crystallize was hexahydrite which then reacted to epsomite, bypassing all the intermediate hydrates. This is in contrast to the dehydration experiments presented in this paper, where stepwise dehydration produced progressively less-hydrated forms of Mg-sulfates until the final monohydrate forms were produced. Vaniman et al. (2006) conducted similar experiments at −80 °C, however, no rehydration was shown to occur, even after 250 days. Dehydration experiments have not yet been conducted at these low temperatures due to the difficulties of obtaining and maintaining extremely low, but constant water vapor pressures over long periods of time.

There has been some confusion in the literature as to whether starkeyite is a stable phase (e.g., Archibald and Gale, 1924; Balarew et al., 2001) but reactions between starkeyite and hexahydrite have been reversed (Chipera et al., 2005; Chou et al., 2005) suggesting that there is a definite thermodynamic stability field for starkeyite. Balarew et al. (2001) conducted an interesting study where they precipitated Mg-sulfate hydrates from various solutions of $MgCl_2$–$MgSO_4$. They found reaction products of 1, 4, 6, and 7 hydrates of which they assumed the tetrahydrate to be metastable, citing a paper by Butchkareva (1973). Balarew et al. (2001) conducted their experiments at 50 and 75 °C and provide a comprehensive listing of results for the various $MgCl_2$–$MgSO_4$ solutions. When their data are compared with Fig. 2 of this paper, using the solution ratio of $MgCl_2$ to $MgSO_4$ to calculate the equivalent relative humidity, the phases formed by Balerew et al. match extremely well with the observed stability fields for hexahydrite, starkeyite, and kieserite presented in this paper. The hypothesis that starkeyite is only a metastable phase may arise from experiments where researchers examined the solid $MgSO_4$ phase in contact with water saturated with respect to $MgSO_4$ at variable temperature (e.g., Archer and Rard, 1998). In these cases, the starkeyite stability field may not intersect the solid–liquid curve, or may have a very short path along this curve as suggested by Archer and Rard, who cite a paper by Polo et al. (1971). In the Balarew et al. (2001) study, their use of $MgCl_2$ has the effect of reducing the activity of water away from the solid $MgSO_4$–liquid water curve, to a region where starkeyite is stable.

With the exception of hexahydrite–epsomite, transformations between the various species involve more than simple removal of water, requiring significant crystal structure rearrangement and overcoming activation energy barriers. Close to stability field boundaries, the reactions are extremely sluggish. As conditions move further from stability boundaries, the reaction driving force can overcome the activation energy barrier with the consequence that an entire phase stability field may be bypassed before a reaction occurs (e.g., kieserite forming hexahydrite directly, bypassing the starkeyite stability field).

Sluggish reactions in the less hydrous Mg-sulfates forms are due at least in part to increasing rigidity of the crystal structures with decreasing water content. A good description of the known crystal structures in the Mg-Sulfate hydrate system can be found in Hawthorne et al. (2000). Although structures are not known for all the phases presented in this paper, a general trend is seen from those that are known that relate to observed Mg-sulfate hydrate stability. For epsomite, the SO_4 tetrahedra are linked to the $Mg(H_2O)_6$ octahedra through hydrogen bonding. Epsomite transforms readily to hexahydrite by loss of the one water molecule per formula unit that is not octahedrally coordinated with Mg. With progressive dehydration, the structures become more tightly cross-linked. For example, the structure of starkeyite is composed of 4-member rings consisting of two SO_4 tetrahedra and two $Mg(O, H_2O)_6$ octahedra. With further dehydration, kieserite forms. Kieserite is unique in the Mg-sulfate system, as it consists of a three-dimensional infinite framework in which the tetrahedral–octahedral chains of SO_4 and $Mg(O, H_2O)_6$ are cross-linked by shared corners between the octahedra and tetrahedra of adjacent chains. This configuration is much more stable and thus it is more resistant to recrystallization than other Mg-sulfate minerals. Recrystallization of kieserite requires significant energy input to overcome activation energy, resulting in significant metastable extensions to its stability range.

The identification of kieserite on the martian surface (e.g., Gendrin et al., 2005) is somewhat inconsistent with the data presented in this paper. It is possible, however, that with sufficient time, the amorphous Mg-sulfate phases, which contain between 1 and $2H_2O$, recrystallize to corresponding $MgSO_4$ phases such as kieserite and sanderite.

4. Conclusions

Results of this study show that $MgSO_4$ hydrates other than epsomite, hexahydrite, and kieserite can persist and may have their own stability fields (especially starkeyite). As expected, Mg-sulfate stability is strongly dependent on water vapor pressure and temperature, albeit with frequent unexpected results (e.g., sanderite [2-hydrate] formation at lower RH than the monohydrates and formation of previously undescribed phases). The $MgSO_4$–H_2O system is surprisingly complicated, and appears to be strongly dominated by sluggish kinetics and path dependence. At lower temperatures, extensive fields of metastability are evident for several phases, in particular the monohydrates, such that phase boundaries can only be approximated. Unlike the well-defined hexahydrite/epsomite transition, occurrences of the other $MgSO_4$-hydrates show considerable overlap, probably indicative of both metastability and kinetic limitations.

Starkeyite has a pronounced stability field in the Mg-sulfate system and should not be overlooked when assessing possible Mg-sulfate minerals that can occur on Mars. It is interesting that given the extent of the starkeyite stability field, especially when forming from hexahydrite, starkeyite is not more prevalent on Earth. However, with natural terrestrial precipitation cycles, it is likely that starkeyite, when it does form, would readily dissolve in even brief rainfall events to reprecipitate from solution as epsomite that may then transform to hexahydrite at typical terrestrial surface conditions. In arid surface areas prone to little precipitation and heated by direct sunlight, kieserite can readily form from hexahydrite or starkeyite and will persist for long periods of time due to the extensive metastable extension of its stability. Geotherm heating with modest burial in low water/rock systems can produce the same result. Upon wetting or exposure to increased humidity, kieserite will readily go back into solution or hydrate to hexahydrite or epsomite, whereupon the cycle may start over again.

Given the trends observed in these experiments and those presented by Vaniman and Chipera (2006), it is likely that $MgSO_4$ would occur on the surface of Mars as one of the more hydrated forms at the higher latitudes, or form the amorphous $MgSO_4$ phase under low RH conditions closer to the equator. At the colder temperatures that prevail at the near-surface, epsomite is a likely product, but with even modest burial, volcanic heating, or impact heating of water-starved salts, other hydrates of $MgSO_4$ may be formed. Work is currently being conducted to determine the rates of reaction of the hydrated forms to the amorphous form and back to see which form is kinetically favored (e.g., Vaniman et al., 2005; Vaniman and Chipera, 2006). If initially formed as an epsomite precipitate from solution, epsomite, hexahydrite, starkeyite, or the amorphous $MgSO_4$ phase would be likely candidates on the martian surface. This does not preclude other formation mechanisms, however, such as from an acid fog (e.g., Singer et al., 1999; Tosca et al., 2004). Likewise, given the fact that several unknown $MgSO_4$ phases were created in this study, other hydrates that are yet unknown could exist on the martian surface where a wide range of low water vapor pressures and low temperatures, not common to Earth, can be found.

Acknowledgment

This work was performed under the auspices of the U.S. Department of Energy (DOE) under contract W-7405-ENG-36 with the University of California. The research project was supported by Los Alamos National Laboratory Directed Research and Development funding. We are grateful to Bill Carey, I-Ming Chou, Gregg Swayze, and an anonymous reviewer for their thoughtful comments which greatly improved the manuscript.

Associate editor: Jeffrey C. Alt

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