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### The preservation of subsurface sulfates with mid-to-high degree of hydration in equatorial regions on Mars



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#### ABSTRACT

At low temperature (*T*), sulfates with high degree of hydration (epsomite and ferricopiapite) have the enlarged stability fields toward low relative humidity (*RH*). They are capable of maintaining high *RH* in a closed environment and keeping an aqueous film at their grain surfaces. More importantly, their dehydration processes are much slower than  $H_2O$  ice sublimation. Using the activation energy (*Ea*) of epsomite dehydration, derived experimentally at Mars relevant atmospheric pressure (*P*) and partial pressure of  $H_2O$  ( $P_{H2O}$ ), we estimated the half-life ( $t_{1/2}$ ) of epsomite dehydration within a model predicted *T* range of subsurface sulfate-rich layer at Mars equator. We found that subsurface hydrous sulfates formed during past high obliquity periods (>45°) have a high probability to maintain mid-to-high degrees of hydration even until the present epoch. This prediction based on experiments is consistent with an observation made by the Spirit rover at Gusev on Mars, and with a field observation at a hyperarid site on Tibet Plateau. Our study supports the hypothesis that subsurface hydrated sulfates are the major host for the high water-equivalent-hydrogen (WEH) values observed at two equatorial regions on Mars.

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#### 1. Introduction

The global distribution of water-equivalent-hydrogen (WEH) down to <1 m depth on Mars was derived from the observations made by the neutron spectrometer (NS) on Mars Odyssey Orbiter (ODY). High WEH values were found at two large regions near the equator (max ~15 wt%, Feldman et al., 2004a; Maurice et al., 2011), with an apparent zonal wave-number-two global distribution (Jakosky et al., 2005). In addition, buried deposits of WEH have been found at concentrations (~50 wt%) larger than can be accommodated by open pore-space volumes within a large region in Arcadia Planitea between 30° and 45° latitude (Feldman et al., 2011).

Three candidates have been proposed for hosting high levels of WEH in equatorial regions on Mars (Feldman et al., 2004b; Jakosky et al., 2005). They are ground ice, adsorbed H<sub>2</sub>O by mineral grains, and hydrous minerals. Ground ice in steady-state is unstable at the current surface and shallow subsurface (<1 m) in equatorial region

on Mars (Leighton and Murray, 1966; Zent et al., 1986). Studies have proposed that ground ice of transient state may exist at some specific locations on Mars, with apparent high albedo and low thermal inertia (Paige, 1992; Bandfield, 2007; Feldman et al., 2011), or in dynamic equilibrium with deep ground water or ground ice (Mellon et al., 1997).

The amount of adsorbed H<sub>2</sub>O within the interstitial spaces among mineral grains depends on the type of minerals, e.g., <1 wt% in basaltic regolith but can be tens of wt% in clay-rich regolith on Earth (Jakosky et al., 2005). CRISM (Compact Reconnaissance Imaging Spectrometer for Mars on the Mars Reconnaissance Orbiter) data analysis suggests that the H<sub>2</sub>O adsorbed by Mars surface dust (shown as a spectral feature near 3  $\mu$ m) exist everywhere (Jouglet et al., 2007; Milliken et al., 2007). The presence of adsorbed H<sub>2</sub>O at Mars surface, however, cannot explain the zonal wave-number-two global distribution of WEH.

Hydrous salts (especially sulfates), phyllosilicates, and zeolites have been proposed as mineral hosts for H<sub>2</sub>O/OH on Mars (Bish et al., 2003; Feldman et al., 2004b; Fialips et al., 2005; Jakosky et al., 2005). Among these minerals, the maximum abundance of structural H<sub>2</sub>O/OH in phyllosilicates and zeolites are in the range of 5–21 wt%, thus they would need to be unrealistically abundances (>50 wt%, Fialips et al., 2005) in near-surface (<1 m) rocks or regolith within equatorial regions in order to account for the high WEH level seen by ODY-NS. In comparison, the maximum



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abundance of structural  $H_2O/OH$  in sulfates is much higher, in the range of 21–62 wt%, thus a lower abundances of sulfates in nearsurface (<1 m) rocks or regolith would be required to match the observed WEH. Therefore, several studies have proposed that hydrous sulfates are the major contributors for the high WEH values found at two equatorial regions on Mars (Feldman et al., 2004b; Jakosky et al., 2005; Fialips et al., 2005).

Hydrous minerals, mainly hydrous sulfates and phyllosilicates, were found by OMEGA (Observatoire pour la Minéralogie, l'Eau, les Glaces et l'Activité) on the Mars Express orbiter (Bibring et al., 2006) and CRISM on the Mars Reconnaissance orbiter (Murchie et al., 2009) at the surface in widely distributed areas on Mars. The regions with high abundance of surface hydrous minerals do not simply overlap with the two equatorial regions with high levels of WEH (Feldman et al., 2004a; McLennan et al., 2010; King and McLennan, 2010). Results from two Mars Exploration Rovers (Gusev crater and Meridiani Planum are within the two high-WEH regions) provide a better ground truth, however, because the rovers studied subsurface materials. For example, the outcrop on the wall of impact craters (tens of meters) (Clark et al., 2005; Squyres et al., 2004, 2006, 2009) and the subsurface regolith (tens of centimeters) in trenches were investigated by the rovers (Arvidson et al., 2006a,b, 2008, 2010; Haskin et al., 2005; Wang et al., 2006a, 2008). Hydrous minerals, such as Fe<sup>3+</sup>-, Mg-, Ca-sulfates, and phyllosilicates, were found (Clark et al., 2007; Haskin et al., 2005; Johnson et al., 2007; Ming et al., 2006, 2008; Morris et al., 2006, 2008; Wang et al., 2006a,b, 2008; Wang and Ling, 2011; Yen et al., 2008).

This manuscript describes the development of a quantitative relationship between the two cycles, the cycle of hydration degree of subsurface Mg-sulfate that follows the cycle of Mars obliquity. This development started from an analysis on the range of hydration degrees of sulfates in the Meridiani outcrop and Gusev subsurface regolith based on two sets of mission data (Section 2); then to address the environmental conditions of the salt-rich subsurface based on a thermal model (Section 3); the knowledge accumulated through the systematic experiments on the thermodynamic and kinetic properties of hydrous sulfates was used (Section 4) in combination with the extraction of the activation energy *Ea* of dehydration process of epsomite under Mars relevant pressure (Section 5), and finally (Section 6) using the derived half-life

 $(t_{1/2})$  of epsomite dehydration under Mars relevant conditions at low temperature, we coupled the dehydration and rehydration of Mg-sulfates with the cycle of Mars obliquity in a period from 6 myr ago to present day. The conclusion from this study, i.e., subsurface hydrous sulfates are the major host of the high WEH levels in two large equatorial regions of Mars, is consistent with the suggestions given by Feldman et al. (2004b), Jakosky et al. (2005), and Fialips et al. (2005), and is supported by two field observations, one on Mars (Section 7) and the other one on Earth (Section 8).

#### 2. The range of hydration degrees of sulfates in MER targets

The MER rovers were not equipped to provide detailed information on the degree of hydration of the minerals; the definitive identification of jarosite (Klingelhofer et al., 2004) is an exception. Nevertheless, the possible range of  $H_2O$  abundance in these subsurface targets can be estimated by using the lowest and the highest stoichiometric degrees of hydration for hydrous minerals as dry and wet end-members. When comparing these possible ranges of  $H_2O$  abundance in Gusev and Meridiani targets with the regional WEH abundances derived from ODY-NS data, a constraint on the degrees of hydration of these sulfates can be established.

Orbital observation indicated that the Meridiani outcrop extends over several hundred kilometers in the region and has a depth of several hundred meters (Arvidson et al., 2006b). Investigations made by the Opportunity rover revealed negligible variations of major element abundances in the upper few meters of this outcrop (Clark et al., 2005; Squyres et al., 2009). Therefore the hydrous minerals of Meridiani outcrop should account for the WEH value seen by ODY-NS (<1 m depth) at Meridiani region. A range of 5.0–16.7 wt% H<sub>2</sub>O was estimated for the Meridiani outcrop (Table 1). Therefore in order to produce WEH of  $\sim$ 12.2 wt% obtained from the newest ODY-NS data analysis (Maurice et al., 2011), it requires the Mg- and Ca-sulfates in Meridiani outcrop to have mid-to-high degrees of hydration.

At Gusev crater, the *in situ* measurements (Alpha particle X-ray spectrometer, APXS, and Mössbauer Spectrometer, MB) that suggested the existences of hydrous sulfates and phyllosilicates were made at discrete locations along the traverse route of the Spirit rover that was geologically highly heterogeneous (Arvidson et al., 2006a, 2008, 2010). We have only limited knowledge of either

#### Table 1

The calculated low and high limits of  $H_2O$  wt% of Meridiani outcrop and of some Gusev targets were based on the wt% of Mg-, Fe-, Ca-sulfates derived using normative calculation on the basis of APXS and MB measurements (Clark et al., 2005; Wang et al., 2006a; Yen et al., 2008), then added  $H_2O$  wt% (=mass of  $H_2O$ /mass of molecule) from two sets of Mg-, Fe-, Ca-sulfates with low and high degrees of hydration, and finally renormalized. For Meridiani outcrop, kieserite (MgSO<sub>4</sub>·H<sub>2</sub>O), jarosite (KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>), and bassinette (CaSO<sub>4</sub>·1/2H<sub>2</sub>O) were used as dry-endmembers, and epsomite (MgSO<sub>4</sub>·7H<sub>2</sub>O), jarosite, and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) were used as wet-endmembers in above calculations. For Gusev targets, kieserite (MgSO<sub>4</sub>·H<sub>2</sub>O), rhomboclase (FeH(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O), and bassanite (CaSO<sub>4</sub>·1/2H<sub>2</sub>O) were used as dry-endmembers and epsomite (MgSO<sub>4</sub>·7H<sub>2</sub>O), ferricopiapite (Fe<sub>4.67</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>·20H<sub>2</sub>O), and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) were used as wet-endmembers in based on the MER observation (jarosite identified by Klingelhofer et al. (2004), ferric sulfates suggested by Johnson et al. (2007)) and the stability field studies of these Ca- and Mg-sulfates (Wang et al., 2009a,b, 2012; Vaniman et al., 2009; RobertSon and Bish, 2012).

Meridiani Planum	Dry mode based on APXS and MB (Clark et al., 2005)				Min-H <sub>2</sub> O-wt% 1w, jaro, bass	Max-H <sub>2</sub> O-wt% 7w, jaro, gyp
	Basaltic, SiO <sub>2</sub> , halides	Mg-sulfates	Fe-sulfates	Ca-sulfates	After re-normalizat	ion
Meridiani outcrop H <sub>2</sub> O (wt%) WEH (wt%)	65% Maurice et al. (2011)	17%	10%	9%	5.6% 12.2%	18.6%
Gusev crater The Boroughs_wall H2O (wt%)	Dry mode based on APXS and MB (Wang et al., 2006a,b,c; Yen et al., 2008) 78.8% 21.2%				1w, rhom, bass	7w, ferri, gyp
Dead Sea_Hula H <sub>2</sub> O (wt%)	33.0%	26.0%	33.0%	8.0%	12.4%	30.3%
Hyrone_white H <sub>2</sub> O (wt%) WEH (wt%)	58.0% Maurice et al. (2011)	9.0%	18.0%	15.0%	7.1% 13.1%	17.4%

*Note*: names of endmember sulfate hydrates:  $1w = MgSO_4 \cdot H_2O$ ,  $4w = MgSO_4 \cdot 4H_2O$ ,  $7w = MgSO_4 \cdot 7H_2O$ , jaro =  $KFe_3(SO_4)_2(OH)_6$ , rhom =  $FeH(SO_4)_2 \cdot 4H_2O$ , ferri =  $Fe_{4,67}(SO_4)_6$  (OH)<sub>2</sub>·20H<sub>2</sub>O, bass =  $CaSO_4 \cdot 1/2H_2O$ , gyp =  $CaSO_4 \cdot 2H_2O$ .

the spatial distribution of these hydrous species at Gusev or their burial depths beyond the floors of trenches made by Spirit. The estimates in Table 1 have a wide range of  $H_2O$  content, 3.1-30.3 wt%, in these regolith targets, a range that includes the WEH  $\sim 13.1$  wt% value obtained at the vicinity of Gusev from the newest ODY-NS data analysis (Maurice et al., 2011). There are two possible ways to match the WEH value. The first is to assume that large quantities of hydrated phases are buried within the shallow subsurface in a broad area in the vicinity of Gusev, which was denied by the fact that the Spirit rover only observed subsurface hydrous salts at discrete spots (e.g., Paso Robles, Dead Sea, and Tyrone). The second is to assume that subsurface hydrous Mg-, Ca-, Fe-sulfates maintain mid-to-high degrees of hydrations, similar as required for Meridiani outcrop based on early analysis.

Hydrous sulfates can experience dehydration and rehydration when environmental conditions change. The major question stimulated by the above MER data analyses is: would the coupling of the two cycles, the cycle of hydration degree of hydrous sulfates that follows the cycle of Mars obliquity, allow the preservation of subsurface hydrous sulfates in equatorial regions on Mars until today?

#### 3. The environmental conditions of the salt-rich subsurface

Two aspects need to be considered in order to answer above question: the environmental conditions of the salt-rich subsurface and the thermodynamic and kinetic properties of hydrous sulfates under those conditions.

Mellon et al. (2004) presented a thermal model of the temperature profile as function of depth for a two-layer regolith on Mars, in which an ice-rich subsurface regolith (with high thermal inertia, 2290 J  $m^{-2}\,\text{K}^{-1}\,\text{s}^{-1/2})$  is covered by a layer of dry surface soil (with low thermal inertia,  $250 \text{ Jm}^{-2} \text{ K}^{-1} \text{ s}^{-1/2}$ ). The model calculation suggests that the large temperature variations at Mars surface during diurnal and seasonal cycles would be isolated by the top dry soil layer and therefore would have little or no influence on the temperature profile of the ice-rich regolith beneath. For example (Fig. 1 of Mellon et al. (2004)), with a surface temperature swing from 150 K to 240 K ( $\Delta T \sim 90$  K), the temperature of an ice-rich subsurface at 0.5 m depth would be maintained in the range of 175–185 K ( $\Delta T \sim 10$  K). This model suggests that the temperature profile of a subsurface layer filled with high thermal inertia material has (1) a lower maximum temperature  $T_{max}$  (e.g., 185 K instead of 240 K) and (2) a smaller temperature variation  $\Delta T$  (e.g., 10 K instead of 90 K). Under a known atmospheric partial H<sub>2</sub>O pressure  $P_{\rm H2O}$ , lower  $T_{\rm max}$  and smaller  $\Delta T$  translate to a higher relative humidity (*RH*) and a smaller  $\Delta RH$ .

The validity of Mellon's model was proven by the depth and stability of Mars ground ice observed at the Phoenix landing site (Mellon et al., 2009) and by the ground ice exposed by recent impact events at mid-latitudes on Mars (Byrne et al., 2009). This thermal model can be extrapolated to the cases of a salt-rich subsurface environment, because most salts have high thermal inertia comparable with H<sub>2</sub>O ice (2218 J m<sup>-2</sup> K<sup>-1</sup> s<sup>-1/2</sup> of gypsum and 3326 J m<sup>-2</sup> K<sup>-1</sup> s<sup>-1/2</sup> of NaCl, Mellon et al., 2008). Thus a similar temperature profile, a low  $T_{\text{max}}$ , a high *RH*, and small  $\Delta T$  and  $\Delta RH$ , within the sulfate-rich subsurface would be anticipated.

## 4. Relevant observations from previous systematic laboratory investigations

Thermodynamic and kinetic properties of Mars relevant hydrous sulfates have been the subjects of many laboratory investigations (Bish et al., 2003; Chou et al., 2002; Chou and Seal, 2003, 2007; Chipera and Vaniman, 2007; Grevel and Majzlan, 2009; Kong et al., 2011a,b; Ling and Wang, 2010; Peterson and Wang, 2006; Majzlan et al., 2004, 2005, 2006; Majzlan and Michallik, 2007; Steiger et al., 2011; Tosca et al., 2007; Vaniman et al., 2004, 2009; Vaniman and Chipera, 2006; Wang et al., 2006c, 2009a, 2011, 2012; Xu et al., 2009). Specifically, the knowledge gained on the stability fields of hydrous sulfates, their phase transition pathways, and their dehydration/rehydration rates under Mars-relevant temperatures (*T*), pressure (*P*), and partial pressure of H<sub>2</sub>O ( $P_{H2O}$ ) can be used to constrain the degrees of hydration of these sulfates that would be stable or metastable on Mars, and further shed light into the subsurface mineral hosts of WEH at two equatorial regions on Mars. Furthermore for the purpose of understanding the past and present habitability on Mars, an environment with certain levels of H<sub>2</sub>O activity could be life-friendly.

We have done two sets of laboratory experiments to study the stability fields and phase-transition pathways of hydrous Mg- and Fe<sup>3+</sup>-sulfates. The experimental details are presented in seven papers (Wang et al., 2006c, 2009a, 2011, 2012; Ling and Wang, 2010; Kong et al., 2011a,b). In this section, we review a few observations that are relevant to the current study.

### 4.1. At low T, highly hydrated sulfates have an enlarged stability field toward low RH

During the dehydration/rehydration experiments of six common Mg-sulfates (MgSO<sub>4</sub>·H<sub>2</sub>O, amorphous-MgSO<sub>4</sub>·2H<sub>2</sub>O, MgSO<sub>4</sub>·4H<sub>2</sub>O, MgSO<sub>4</sub>·7H<sub>2</sub>O, MgSO<sub>4</sub>·11H<sub>2</sub>O, and MgSO<sub>4</sub>, details in Wang et al. (2006c, 2009a, 2011)) at temperature 50 °C, 21 °C, 5 °C, and -10 °C, we noted that the low *RH*-end of the stability field of epsomite MgSO<sub>4</sub>·7H<sub>2</sub>O is 50% *RH* at 21 °C, 40% *RH* at 5 °C, and 13% *RH* at -10 °C, i.e., a decrease of *RH* with decreasing temperature, indicating the enlargement of the stability field of a hydrous Mg-sulfate (with the second highest degree of hydration) towards low *RH* at low *T*.

A similar phenomenon was observed during the dehydration/ rehydration experiments of some common Fe<sup>3+</sup>-sulfates (FeH(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O, amorphous and crystalline Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O, Fe<sub>4.67</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>·20H<sub>2</sub>O, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O, (K, Na, H<sub>3</sub>O)Fe<sub>3</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>, and FeOHSO<sub>4</sub>, details are given in Ling and Wang (2010), Kong et al. (2011a,b), Wang et al. (2012), Liu and Wang (2012), and Lu and Wang (2013)) at temperatures of 95 °C, 50 °C, 21 °C, 5 °C, and -10 °C. We found that the ferric sulfates with high degrees of hydration, i.e., ferricopiapite Fe<sub>4.67</sub>(SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> ·20H<sub>2</sub>O and paraconquimbite Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·9H<sub>2</sub>O are more stable at lower temperature (5 °C to -10 °C) than those with lower degrees of hydration (pentahydrate Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·5H<sub>2</sub>O and kornelite Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O, Lu and Wang, 2013).

In summary, Mg- and  $Fe^{3+}$ -sulfates with high degrees of hydration are more stable at low *RH* and at low temperature.

# 4.2. Hydrous Mg-sulfates have the lowest thermal stability among hydrous Mg-, $Fe^{3+}$ -, $Fe^{2+}$ -, and Al-sulfates

The discussion in Section 3 of this paper will be mainly based on the experimental data from Mg-sulfates. We would, however, emphasize here that hydrous Mg-sulfates have the lowest thermal stability when compared with hydrous  $Fe^{2+}$  and  $Fe^{3+}$ -sulfates, Al-sulfates, and Ca-sulfates.

For example, when comparing the dehydration rates of Mg- and Fe<sup>3+</sup>-sulfates with the highest degree of hydration, epsomite and ferricopiapite, under the same conditions (e.g., 5 °C, 7% *RH*), we found that the dehydration of epsomite (to hexahydrite, MgSO<sub>4</sub>·6H<sub>2</sub>O, then to starkeyite, MgSO<sub>4</sub>·4H<sub>2</sub>O) started at 107 h and 3044 h (4.5 days and 127 days) into the reaction respectively (Wang et al., 2009a). In contrast, the dehydration of ferricopiapite under the same *T* and *RH* (5 °C, 7% *RH*) only started after 1452 days

(3.97 year) into the reaction (to a slightly dehydrated phase named as UK#9 with 19-14 structural H<sub>2</sub>O whose structural and spectral details were described in Wang et al. (2012)). In addition, when comparing the dehydration products of epsomite, melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O), and alunogen (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·17H<sub>2</sub>O) (samples with similar grain size were used) under Mars relevant pressure ( $P_{Mars}$ ) and partial H<sub>2</sub>O pressure ( $P_{H2O}$ ), we found that after ~4 h dehydration at 25 °C, about 70% structural H<sub>2</sub>O was lost from epsomite, but only 40% structural H<sub>2</sub>O was lost from melanterite, and only 25% from alunogen (details in Zhou and Wang (2013)). A study on dehydration of gypsum (Robertson and Bish, 2012) and a comparison between the dehydrations of gypsum and epsomite (Vaniman and Chipera, 2006) both confirmed that the gypsum dehydration is much slower than that of the other hydrous minerals. In conclusion, these experiments demonstrated that hydrous Mg-sulfates have higher rate of dehvdration than Fe<sup>3+</sup>- Fe<sup>2+</sup>-. Al-. and Ca-sulfates under similar environmental conditions.

# 4.3. Hydrous sulfates are capable of maintaining aqueous films at grain surfaces

A fundamental property of hydrous sulfates that may contribute to their stability at low temperature is that they can apparently absorb an aqueous film at grain surfaces, especially at low temperature. Ferricopiapite presents the best example, shown in Figs. 4-6 of Wang et al. (2012). At 5 °C and 73% RH and 64% RH, ferricopiapite samples gradually gained mass and stabilized (duration >4 years) at 32.5 and 26.8 H<sub>2</sub>O molecules per ferricopiapite formula unit (calculated based on the gravimetric measurements of the starting sample and the ending experimental product), while keeping the characteristic Raman spectral pattern of ferricopiapite (which is very different from that of Fe<sup>3+</sup>-SO<sub>4</sub>-H<sub>2</sub>O brine when deliquescence has happened). These data indicate extra 12.5 and 6.8 H<sub>2</sub>O molecules per ferricopiapite formula unit being added into these samples without inducing deliquescence. A similar phenomenon was observed in two experiments at 21 °C at 70% RH and 75% RH, where less extra (10.9 and 6.4) H<sub>2</sub>O molecules per ferricopiapite formula unit were observed. The extra H<sub>2</sub>O molecules in a powder ferricopiapite sample would form aqueous films with considerable thickness at the mineral grain surfaces.

The addition of extra  $H_2O$  molecules into powdered hydrous Mg- and Fe<sup>3+</sup>-sulfates is a general phenomenon observed in our experiments. For example, extra 0.5–1 H<sub>2</sub>O per epsomite formula unit (Wang et al., 2009a) and extra 6–7 H<sub>2</sub>O per jarosite formula unit (Lu and Wang, 2013) were observed. In the latter case, dissolution of jarosite in the initial adsorbed H<sub>2</sub>O at grain surface would reduce the pH of liquid surrounding jarosite grains (Madden et al., 2012). Subsequently in this acidic solution, the dissolution rate of jarosite would increase and lower the pH of solution even further. The low vapor pressure of this aqueous solution would facilitate a continuous transfer of H<sub>2</sub>O from the vapor phase to the sample, as indicated by the increase of extra H<sub>2</sub>O within the samples.

## 4.4. Sulfates with high degrees of hydration within an enclosure can maintain high RH

Furthermore in an enclosure, hydrous sulfates with high degree of hydrations are capable of maintaining a very high relative humidity (*RH*), especially at low temperature. The observations were made using two sealed glass jars, one half-filled with epsomite [MgSO<sub>4</sub>·7H<sub>2</sub>O], and one half-filled with ferricopiapite [Fe<sub>4.67</sub> (SO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>·20H<sub>2</sub>O]. Two *RH* sensors were inserted into the jars with tight sealing. Both jars (containing sulfates and *RH* sensors) were placed in a freezer which maintained a temperature range of  $-10 \pm 1$  °C. For each jar, we conducted a 3-day continuous *RH* measurement. We found that the jar half-filled with epsomite maintained a *RH* range of 96–97% in its head space, and the jar half-filled with ferricopiapite maintained a *RH* range of 75–79%.

These experiments suggest that the environmental conditions (*T* and *RH*) in a subsurface layer filled with hydrous sulfates can be determined by two factors: (1) low  $T_{\text{max}}$  and small  $\Delta T$  suggested by Mellon's thermal model as isolated from the large temperature variations at Mars surface; (2) high *RH* maintained by hydrous sulfates themselves and small  $\Delta RH$  due to small  $\Delta T$ .

# 5. Dehydration/rehydration of Mg-sulfates under Mars relevant *T-P* conditions

To know only the stability field of hydrous sulfates is not enough to understand their potential presence on Mars. The kinetics of dehydration and rehydration cycles, especially the coupling of this cycle with the cycle of Mars obliquity, holds the key.

# 5.1. Dehydration/rehydration of sulfates as influence by the cycles of Mars obliquity and the deposition/sublimation of water ice

Mars is a dynamic system. Its obliquity changes quasi-periodically. Laskar et al. (2004) provided a good solution for the evolution of Mars' spin (and Mars obliquity values) tracing back to 21 million years (myr), using the data from the rotational rate of Mars and numerical integration of the Solar System. Their solution shows that the obliquity of Mars cycled between 15° and 35° (with a mean of 26°) from 5 myr to now, and cycled between 45° and 25° (with a mean >35°) from 21 myr to 5 myr.

These cycles of obliquity would control the cycles of H<sub>2</sub>O ice deposition and sublimation at various regions on Mars. During a high obliquity period, the increased  $P_{H2O}$  and reduced T at and near equatorial regions would induce the deposition of H<sub>2</sub>O ice. When obliquity decreases, most H<sub>2</sub>O ice at low latitude would disappear through sublimation. Quantitatively, climate models predict that when obliquity exceeds 30°, H<sub>2</sub>O ice is stable in shallow subsurface at mid-latitude (Mellon and Jakosky, 1995). When obliquity exceeds 45°, the ice sublimation rate at Polar Regions is very high and H<sub>2</sub>O ice is predicted to persist at the equator (Richardson and Wilson, 2002). A study of Mars surface topography using MOLA (Mars Orbiter Laser Altimeter on Mars Global Surveyor) data by Head et al. (2003) revealed the smoothing at sub-kilometer scales above 30° latitudes in both hemispheres on Mars, and they attributed these phenomena to the H<sub>2</sub>O ice-rich mantling deposits forming during a recent "ice age" on Mars 2.1–0.4 myr ago when obliquity reached >30° periodically.

Affected by the global climate change during the obliquity cycle and the accumulation of  $H_2O$  ice in equatorial region on Mars, the hydration degree of hydrous sulfates in these regions (at the surface and within the subsurface) would follow the same cycle. However, it would follow a lower rate than the rates of  $H_2O$  ice deposition and sublimation, because the dehydration/rehydration process of hydrous sulfates is fundamentally different. Ice is a homogenous bulk material. The sublimation of ice removes  $H_2O$ molecules only at the surface, one layer after another. The rate of this process depends on the environmental conditions (*T*, *P*,  $P_{H2O}$ ), but is not affected by the remaining number of  $H_2O$  molecules in the ice matrix. Thus the ice sublimation (and deposition) process follows zero order kinetics.

In contrast,  $H_2O$  molecules in hydrous sulfates locate within an inhomogeneous matrix and the dehydration of a hydrous sulfate would normally go through steps which involve the hydrates with different degrees of hydration (e.g., MgSO<sub>4</sub>·xH<sub>2</sub>O, x = 11 to 0) and different crystal structures. Effects of cations are also important, found in the dehydration comparison experiments of Mg-, Fe-,

Al-sulfates with similar grain sizes and under the same experimental conditions, (Zhou and Wang, 2013).

Although the dehydration and rehydration processes of a hydrous sulfate will be affected by the structures of intermediate hydrates, a simple model can be used for dehydration process of epsomite under Mars relevant pressure (Fig. 18 in Wang et al. (2009a), Fig. 1, Vaniman et al. (2004)) where amorphous Mg-sulfates were formed. In these experiments, the water content of amorphous Mg-sulfates reduces continuously (MgSO<sub>4</sub>·*x*H<sub>2</sub>O, where *x* changes from 6.5 to 1.8, Fig. 18 in Wang et al. (2009a)); no step-wised structural changes were observed after the starting of amorphous phase formation.

This simple model of H<sub>2</sub>O diffusion was first described by McCord et al. (2001) in a paper that presents their experimental study on dehydrations of MgSO<sub>4</sub>·7H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, and Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O in an ultra-high vacuum chamber  $(1.33 \times 10^{-7} \text{ Pa})$ . In this model, the diffusion rate of H<sub>2</sub>O molecules through the matrix would limit the dehydration rate, i.e., the H<sub>2</sub>O molecules moving from the interior of a grain towards the grain surface could be captured multiple times by vacancy sites (and weak potential energy fields) on the way. Obviously, the more H<sub>2</sub>O a grain of Mg-sulfate (with amorphous structure for this simple model) has lost and the more vacancy sites that are left in the lattice, the harder it will be for the remaining  $H_2O$  to escape. The purpose of employ this simplified model is only to emphasize the difference between the dehydration of a hydrous salt and that of the sublimation of H<sub>2</sub>O ice. It means, compared with the "surface" character of ice sublimation (one layer after another), the dehydration of a hydrous sulfate has a "volume" character, thus it would be much slower. In other word, hydrous sulfates would be thermally more stable than H<sub>2</sub>O ice.

This simple model could not cover many other pathways that the dehydrations of hydrous salts might take under difference conditions. A comparison based on experimental observations (Wang et al. (2009a) for crystalline and amorphous Mg-sulfates; Wang et al. (2012) for crystalline and amorphous  $Fe^{3+}$ -sulfates) suggested that when dehydration went through various crystalline phases, the rate is lower than when it went through amorphous phases with same chemistry. It means that crystalline hydrous sulfates would be thermally even more stable than  $H_2O$  ice.

# 5.2. A rate comparison of dehydration and rehydration of Mg-sulfates at 1 atm and differ T

The cycles of H<sub>2</sub>O ice deposition and sublimation at equatorial region induced by the cycles of Mars obliquity would stimulate the rehydration and dehydration of Mg-sulfates at the surface and within the subsurface. The hydration degree of Mg-sulfates at the surface would be strongly affected by atmospheric conditions; while those within the subsurface would be controlled by subsurface environmental conditions and by their thermodynamic and kinetic properties, among which the temperature dependences of these properties would have the largest effect.

A comparison of the dehydration and rehydration processes of Mg-sulfates, especially their temperature dependences, can be obtained using the data from stability field and phase transition pathway experiments of six common Mg-sulfates at different temperatures (Wang et al., 2006, 2009a, 2011). All of these experiments were conducted at Earth atmospheric pressure ( $P_{Earth} = 1.013 \times 10^5$  Pa), thus the absolute rate values are not suitable to evaluate quantitatively the processes on Mars. Because it is not feasible to accomplish a rehydration experiment under Mars relevant atmospheric pressure within a reasonable time duration (e.g., a few years), we will use the data from the experiments at 1 atm to gain a scheme of rate ratio between the dehydration and rehydration processes as the dependents of temperature.

Fig. 1 compares the temperature dependences of the dehydration and rehydration processes of Mg-sulfates under Earth atmospheric conditions (methodology details in Wang et al. (2011)). It demonstrates that the dehydration process has much stronger temperature dependence than rehydration processes (compare the colored triangles with the black squares). Because the temperature affects the thermal vibration<del>s</del> frequencies of atoms or ionic groups in a crystal structure, which in turn affects the escape rate of H<sub>2</sub>O molecules and the formation rates of new crystal structure(s) of different hydrates during a dehydration process. On the other hand, the progress of rehydration is more affected by the environmental H<sub>2</sub>O fugacity,  $f(H_2O)$ , or partial H<sub>2</sub>O pressure,  $P_{H2O}$ , because it determines the availability of H<sub>2</sub>O molecules in an environment where the rehydration happens.

It is unrealistic to accomplish (within reasonable time duration) a set of laboratory experiments within the model predicted *T* range (e.g., 170–190 K, based on Mellon et al. (2004)). Nevertheless through extrapolation, we can reach a very rough estimation of the trends of the rate ratios as a function of *T*. For example (Fig. 10 and Table 4 of Wang et al. (2011)), the rate of epsomite dehydration at 180 K would be  $10^{-30}$  times the rate of the same process at 294 K. While the rehydration rate of monohydrated Mg-sulfate at 180 K would be only  $10^{-2}$  times the rate of the same process at 294 K. Thus in general at low *T*, the dehydration of epsomite would slow down greatly, while the rehydration of monohydrate

We want to emphasize that only this general understanding on the temperature dependence, not the experimental data under terrestrial atmospheric pressure (Fig. 1), will be used in Section 6 when discussing the dehydration–rehydration cycle of Mg-sulfates on Mars following Mars obliquity cycle.



**Fig. 1.** A comparison of temperature dependences of dehydration and rehydration processes of Mg-sulfates under Earth atmospheric conditions (data from Wang et al. (2009a, 2011)). It demonstrates that the dehydration process is a much stronger temperature dependent than rehydration processes. We would emphasize that only the general understanding from this comparison of *T*-dependence of rates, but none of these data, are used in the discussion of Section 6. In this plot, *t* is the time needed for a total phase conversion at a temperature (*T*) (methodology details in Wang et al. (2011)). A linear regression line with corresponding color was derived from each set of experiments conducted at three temperatures. Tw = epsomite, 6w = hexahydrite, 4w = starkeyite, 1w = kieserite,  $Am = amorphous MgSO_4.2H_2O$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

#### 5.3. Dehydration process of epsomite under Mars relevant pressure

In addition to T and  $P_{H2O}$ , atmospheric pressure is another factor that would influence the rate of the dehydration and rehydration processes of hydrous salts. During a dehydration process under Earth atmospheric conditions, an H<sub>2</sub>O molecule escaped from a salt grain would have the possibility to collide with many gas molecules and other escaped H<sub>2</sub>O molecules. The probability of colliding is a function of their moving speeds (i.e., the temperature T) and the density of surrounding molecules (i.e. the atmospheric pressure  $P_{\text{Earth}}$ ). After the collisions, this H<sub>2</sub>O molecule would have the possibility to hit the surface of a salt grain and to be re-captured. The probability of its re-capture is a function of the potential field at microscopic scale at the grain surface caused mainly by broken chemical bonds. Rehydration of salt grains can happen due to the re-capture of H<sub>2</sub>O molecules. Therefore, the experimentally observed rate of a dehydration process (Fig. 1) is actually a net rate of dehydration minus rehydration under a specific P, T condition; very similar to the process that happens during H<sub>2</sub>O ice sublimation (Bryson et al., 1974; Nelson, 1998; Sack and Baragiola, 1993). This means that in a terrestrial laboratory  $(P_{\text{Earth}} = 1.013 \times 10^5 \text{ Pa})$ , the collisions of escaped H<sub>2</sub>O molecules with atmospheric molecules and their re-capture by salt grains would slow-down the dehydration of a hydrous salt. In contrast, in ultra-high vacuum or in an environment with much lower atmospheric pressure (i.e.,  $P_{Mars}$ ), the rate of net-dehydration would be higher. Consequently, the Ea of net-dehydration derived from any experiment is a function of *P* of the experiments.

The dehydration experiments shown in Fig. 1 were conducted under Earth atmospheric pressure ( $P_{Earth} = 1.013 \times 10^5$  Pa). The activation energy *Ea* and pre-exponential factor (*A*) in the Arrhenius equation were derived, e.g., *Ea* = 1.15 eV for the epsomite (7w) to starkeyite (4w) dehydration (Wang et al., 2011). In comparison, McCord et al. (2001) studied the dehydration of epsomite in an ultra-high vacuum chamber ( $1.33 \times 10^{-7}$  Pa) using a 35-step



Raman Shift (cm<sup>-1</sup>)

**Fig. 2.** Raman peaks of (a) stretching vibrational mode and (b) bending vibrational mode of structural H<sub>2</sub>O in epsomite MgSO<sub>4</sub>·7H<sub>2</sub>O, taken under *P* and *T* conditions relevant to Earth ambient environment and to Mars salt/ice-rich subsurface layers. They demonstrate that the effects of *P* and *T* on the central positions (3350 cm<sup>-1</sup> and 1670 cm<sup>-1</sup>) of these peaks are negligible. Two *v* values  $(5.01 \times 10^{13} \text{ S}^{-1} \text{ and } 1.01 \times 10^{14} \text{ S}^{-1})$  are derived from the peak centers of two modes and used in calculation for Fig. 3 and Table 2.

temperature programmed dehydration (TPD) experiment monitored by a quadruple mass spectrometer. From their experiments, an activation energy, *Ea* value, of  $0.9 \pm 0.10$  eV for epsomite dehydration was extracted. The difference between these two *Ea* values (0.9 eV and 1.15 eV) of the same process at *P*<sub>Earth</sub> and in ultra-high vacuum demonstrates the effect of the environmental pressure (*P*).

In order to make a quantitative evaluation of the dehydration rate of epsomite at Mars relevant conditions, we need to have *Ea* values under Mars relevant atmospheric pressure. This was done by using the data from a set of epsomite dehydration experiments conducted earlier at *P* and  $P_{H2O}$  relevant to Mars. These experiments were first reported in Section 3.4 of Wang et al. (2009) for the purpose of studying the formation of amorphous Mg-sulfates. Now we make a new analysis of the same experimental data, in order to derive a Mars-relevant *Ea* for epsomite dehydration.

In these experiments (Section 3.4 and Appendix in Wang et al. (2009a)), the dehydration of epsomite was conducted in a vacuumed desiccator in which  $P \le 100$  Pa and 0.05 Pa  $\le P_{H20} \le 0.34$  Pa were maintained. These pressures approached the average atmospheric conditions in equatorial regions on Mars, 400 Pa < P < 870 -Pa and  $P_{\rm H2O} \sim 0.04-0.15$  Pa (Smith, 2002). In one of the three sets experiments, eight epsomite samples were placed in a vacuumed desiccator that was maintained approximately at a fixed temperature  $(294 \pm 1 \text{ K}, \text{ or } 273 \pm 0.5 \text{ K}, \text{ or } 265 \pm 3 \text{ K})$ . They were then taken out one by one at predetermined time intervals (20, 40, 60 ... min) from the vacuumed desiccator during the dehydration experiment. Gravimetric measurements were made on each sample to determine the loss of H<sub>2</sub>O per epsomite molecule at each step. Non-invasive Raman spectroscopic measurements were conducted to make phase identification. The formation of amorphous MgSO<sub>4</sub>·xH<sub>2</sub>O (x decreases from 6.5 to 1.8) was observed in all three sets of experiments.

Using their experimental data, McCord et al. (2001) determined that the dehydration process of epsomite (in ultra-high vacuum) fits well with a first order kinetics. We adapt that conclusion and assume the dehydration process of epsomite in low-vacuum (in our experiments and on Mars) follows the first order kinetics too. Similar to McCord et al. (2001), we use the following equation to describe the epsomite dehydration process when applied to the number density of H<sub>2</sub>O molecules in the sample n(t):

$$n(t) = n(0)e^{-\alpha t} \tag{1}$$

with

$$\alpha = v e^{-Ea/kT} \tag{2}$$

Here n(0) is the initial number density of structural H<sub>2</sub>O in epsomite, n(t) is the same value at time t, v is the effective "escape-attempt" frequency (defined by McCord et al. (2001)) that is typically of the order of the vibrational frequency (s<sup>-1</sup>) of the molecular constituents of the mineral, *Ea* is the activation energy (eV), k is Boltzmann's constant (eV K<sup>-1</sup>), and T is absolute temperature (K). Furthermore, Fig. 2 shows that the vibrational frequency of structural H<sub>2</sub>O in epsomite does not change within the range of T and P from laboratory ambient conditions to Mars subsurface conditions. Thus we used a v value ( $5.01 \times 10^{13}$  S<sup>-1</sup>) from the bending vibration mode of epsomite in the following calculations, which is very similar to the v value ( $3.2 \times 10^{13}$  S<sup>-1</sup>) obtained by McCord et al. (2001) from the data analysis of their experiment at ultra-high vacuum.

We derived a Mars relevant *Ea* for epsomite dehydration by minimizing the square of the difference between the calculated and measured n(t)/n(0), determined by fitting Eq. (1) to the data from gravimetric measurements of dehydration products of our experiments at three temperatures (Fig. 3b–d). We used  $\Delta^2 = (Y_{calc} - Y_{meas})^2$  to evaluate the goodness of fit, where  $Y_{meas}$  is

the values of n(t)/n(0) derived from gravimetric data,  $Y_{calc}$  is the value of n(t)/n(0) calculated from Eq. (1) using different *Ea* values. When varying the *Ea* value in a range from 0.9 to 1.15 eV (determined by experiments in ultra-high vacuum  $P = 1.33 \times 10^{-7}$  Pa and  $P_{Earth} = 1.013 \times 10^5$  Pa, McCord et al. (2001) and Wang et al. (2011)), we look for the smallest  $\Sigma(\Delta^2)$  to determine the *Ea* value for the epsomite dehydration at Mars relevant *P* and  $P_{H2O}$  of our experiments. It is very interesting to notice that for all three sets of experiments, the smallest  $\Sigma(\Delta^2)$  values were found for almost equal *Ea* values, 1.031 eV for 294 K and 273 K and 1.032 eV for 265 K (Fig. 3a). Specifically, all experiments conducted at Mars relevant *P* and  $P_{H2O}$ , yield an *Ea* value right in between the *Ea* values found from experiments at ultra-high vacuum and at  $P_{Earth}$ .

In the foregoing calculations, we did not require the calculated n(t)/n(0) to match the last experimental data point in Fig. 3b and the last three points in Fig. 3c for several reasons. The major reason is that all ten Mg-sulfate hydrates (from having 11 structural H<sub>2</sub>O per molecule to anhydrous MgSO<sub>4</sub>, and their polymorphs) have very different crystal structures. The different H<sub>2</sub>O sites in those structures with different bonding energies cause complicated dehydration processes. A very simplified assumption was used in Eq. (1), i.e., H<sub>2</sub>O molecules are removed from epsomite, hexahydrate, pentahydrate, etc., until the formation of anhydrous MgSO<sub>4</sub> by the same mechanism with the same *Ea* value. This assumption is not entirely true especially at the last stage of dehydration, e.g.,

monohydrate MgSO<sub>4</sub>·H<sub>2</sub>O (not MgSO<sub>4</sub>) is the end product of epsomite dehydration in the laboratory under Mars relevant conditions, which is the main reason to not seek the best fit of the last (or last few) experiment data points. In addition, our gravimetric measurements have an uncertainty of ±1 mg (the precision of the balance, Mettler PM480 DeltaRange), thus a larger uncertainty in calculated n(t)/n(0) would occur for the experiment product with low degrees of hydration (lower total mass). At 265 K (Fig. 3d), the experiments ended for other reasons, while the four data points at early stages of dehydration still provide a good enough fit to Eq. (1). This degree of simplification should be acceptable for the following discussion that only looks for trends in the hydration/dehydration process.

For epsomite dehydration that follows first order kinetics (Eq. (1), McCord et al., 2001), the half-life  $t_{1/2}$  is defined as the time required for the number density of structural H<sub>2</sub>O, n(t), to fall to half its original value, n(0). Thus  $t_{1/2} = 0.693/\alpha$ . For example, the calculated  $t_{1/2}$  for the dehydration of epsomite at 294 K at  $P_{\text{Earth}}$  (*Ea* = 1.15 eV) is 197 h, and those at Mars relevant *P* and  $P_{\text{H2O}}$  (*Ea* = 1.031 eV), and at ultra-high vacuum (*Ea* = 0.9 eV) are respectively 106 min and 57 s. They are in good agreement with the values observed in the experiments (McCord et al., 2001; Wang et al., 2009a).

Table 2 shows the calculated  $t_{1/2}$  for epsomite dehydration in a wide temperature range using the new *Ea* value (1.031 eV) and v





determined under Mars relevant  $P_{env}$  and  $P_{H2O}$ . Knowing the uncertainties in the above experiments, we only consider rough trend estimates of  $t_{1/2}$  in the following discussion. The upper three rows are calculated  $t_{1/2}$  values at 294 K, 273 K, and 265 K. The last five rows (190–170 K) are calculated  $t_{1/2}$  values for a T range that is slightly larger than the model predicted T range for a salt-rich subsurface layer on Mars (based on Mellon et al. (2004)). Notice between 190 K and 170 K, the  $t_{1/2}$  of epsomite dehydration would vary from 0.96 myr to  $1.6 \times 10^3$  myr. It means that a reduction of temperature by 10 K in this T range will lengthen the  $t_{1/2}$  value by 35-50 times, which is in general agreement with the conclusion of Section 5.2, i.e., a strong temperature dependence of Mg-sulfate dehydration. For the purpose of being conservative in the following discussion, we would first use the maximum temperature  $T_{\rm max}$   $\sim$  190 K in a 170–190 K T range to estimate the lowest limit of remnant H<sub>2</sub>O in dehydrated sulfates, using the  $t_{1/2}$  value in Table 2.

# 6. Coupling the cycle of Mg-sulfate dehydration/rehydration with the cycle of Mars obliquity

In order to gain a realistic understanding of the current hydration degree of hydrous sulfates within the subsurface of Mars, we need to build a quantitative relationship between the cycles of Mars obliquity (using the data of Laskar et al. (2004)) and the cycle of hydration degree of Mg-sulfate (using the derived  $t_{1/2}$  values in Table 2).

For the purpose of being simple and conservative, we would consider the Mg-sulfates within the equatorial region of Mars only; the warmest, thus the most unlikely location for hydrous sulfates preservation where  $H_2O$  ice would only form and stay when obliquity >45° (Richardson and Wilson, 2002). Based on Laskar et al. (2004), the most recent few periods with obliquity >45° happened between 5.8 myr and 5.4 myr before the present in Mars history, with durations of 0.019, 0.028, 0.026, and 0.008 myr.

Fig. 4 shows a quantitative relationship between the Mars obliquity cycle and the residual structural H<sub>2</sub>O as n(t)/n(0) in Mg-sulfates at Mars equator. During the four periods from 5.8 to 5.4 myr before the present in Mars' history when obliquity >45° (green zones in Fig. 4a), H<sub>2</sub>O ice would persist at Mars equator. The Mg-sulfates co-existing with H<sub>2</sub>O ice would get fully rehydrated, reaching epsomite (7w) or meridianiite (11w), no matter in what temperature zone they occurred because of three reasons: (1) the rehydration rate depends more on  $P_{H2O}$  than on T (Section 5.2), thus the persistence of  $H_2O$  ice at Mars equator would raise  $P_{H2O}$  (*RH* = 100%) and stimulate the rehydration of Mg-sulfates at surface and within the subsurface; (2) the rehydration rates of Mg-sulfates are much less dependent on temperature (Section 5.2, Fig. 1), thus the rehydration (especially  $1w \rightarrow 7w$ ) would be maintained at a moderate rate even at extremely low temperature; (3) the stability field of Mg-sulfates with high hydration degree at low temperature is large (Section 4.1).

In later periods when the obliquity was <45°, surface ice disappears through sublimation at equatorial regions and hydrous sulfates start to dehydrate with a dehydration rate that is heavily depended on *T* (Section 5.2, Fig. 1), but much smaller that ice sublimation rate (Section 5.1). In addition, this dehydration process would be very different at the surface and within the subsurface: the Mg-sulfates at the surface would dehydrate quickly to form either starkeyite (4w) or monohydrate (1w) depending on local chemistry (Wang et al., 2009a); while the Mg-sulfates buried within the subsurface would dehydrate at a very low rate, because of the low  $T_{max}$  (extrapolation from Mellon's model, Mellon et al., 2004, Section 3) and high *RH* maintained in the subsurface salt layer (Sections 4.3 and 4.4) and of the strong *T* dependence of  $t_{1/2}$  of epsomite dehydration (Section 5.3, Table 2).

#### Table 2

Calculated half-life  $t_{1/2}$  (columns 3, 4) of epsomite dehydration under Mars relevant *P* and  $P_{H2O}$ , using Ea = 1.031 eV and  $\nu = 5.01 \times 10^{13}$  S<sup>-1</sup>. This  $\nu$  value (corresponding a Raman peak centered at 1670 cm<sup>-1</sup>, Fig. 4) was chosen to use for general discussion because it approaches the  $\nu$  value ( $3.2 \times 10^{13}$  S<sup>-1</sup>) used by McCord et al. (2001) for epsomite dehydration in ultra-vacuum. The top three rows show a good match with of experimentally observed  $t_{1/2}$ . The bottom five rows provide the estimations (in the order of magnitude) of  $t_{1/2}$  for temperatures in a *T* range (170–190 K) that is slightly larger (to be conservative) than the model predicted *T* range (175–185 K) of subsurface ice-rich layer on Mars (Mellon et al., 2004). Column 5 lists the  $t_{1/2}$  values calculated using a slightly different  $\nu$  value ( $1.01 \times 10^{14}$  S<sup>-1</sup>, corresponding a Raman peak centered at 3350 cm<sup>-1</sup>, Fig. 4) to be compared with column 4. Please note that the change of  $\nu$  value does not change the order of magnitudes of  $t_{1/2}$  values, thus would not affect the discussion in Section 6.

T (K)	Calculated v	v/v = 5.01E13	Calc. $w/v = 1.01E14$	
	α	$t_{1/2}$ (h)	<i>t</i> <sub>1/2</sub> (myr)	$t_{1/2}$ (myr)
294	1.1E-04	1.8E+00		
273	4.7E-06	4.1E+01		
265	1.3E-06	1.5E+02		
255	2.1E-07	9.0E+02		
250	8.4E-08	2.3E+03		
240	1.1E-08	1.7E+04	1.9E-06	2.3E-06
230	1.3E-09	1.5E+05	1.7E-05	2.1E-05
220	1.2E-10	1.6E+06	1.8E-04	2.3E-04
210	9.2E-12	2.1E+07	2.4E-03	3.2E-03
200	5.3E-13	3.6E+08	4.1E-02	5.8E-02
190	2.3E-14	8.4E+09	9.6E-01	1.4E+00
185	4.2E-15	4.6E+10	5.2E+00	8.0E+00
180	7.0E-16	2.8E+11	3.2E+01	5.0E+01
175	1.0E-16	1.8E+12	2.1E+02	3.5E+02
170	1.4E-17	1.4E+13	1.6E+03	2.7E+03

For example, from the last period when obliquity >45°  $(\sim 5.4 \text{ myr ago})$  to 5 myr, epsomite in a subsurface layer at Mars equator with T<sub>max</sub> = 190 K would lose a maximum of 26% structural H<sub>2</sub>O (Fig. 4a) (calculated from Eq. (1) and the  $t_{1/2}$  value in Table 2). From 5 myr ago to the present, the dehydration of subsurface Mgsulfates at Mars equator would continue because no H<sub>2</sub>O ice deposition would happen within a period of obliquity <45° (Fig. 4b). The actual temperature variation range  $\Delta T$  and  $T_{max}$  in a subsurface environment is a function of latitude, the amount of buried salts and H<sub>2</sub>O ice, and their burial depth. In a model predicted T range (170-190 K), Fig. 4b and c show at least 2%, 49%, 88%, 98%, and 99.7% of structural H<sub>2</sub>O in subsurface epsomite would remain until today at Mars equator in the zones with  $T_{\rm max}$   $\sim$  190 K, 185 K, 180 K, 175 K, and 170 K. The large differences among the remained structural H<sub>2</sub>O are induced by a 35–50 times increase of  $t_{1/2}$  per 10 K temperature decrease (Table 2).

Furthermore, the n(t)/n(0) in Fig. 4 was calculated for the warmest place on Mars, e.g., Mars equator. In other low latitude regions on Mars where a large amount of H<sub>2</sub>O ice can form and stay when  $30^{\circ}$  < obliquity <  $45^{\circ}$ , the full rehydration of Mg-sulfates would occur in many recent periods from 5 myr to the present (yellow zone in Fig. 4b, the most recent period happened ~0.37 myr ago). Due to a much shorter dehydration period (from 0.37 myr to present), we anticipate more structural H<sub>2</sub>O in epsomite to remain until today in the subsurface of low latitude regions. In addition, based on Section 4.2, the dehydration processes of Fe<sup>3+</sup>-, Fe<sup>2+</sup>-, Ca-, Al-sulfates would be even slower than Mg-sulfates under the same conditions. Thus if these sulfates formed during high obliquity periods, high % of structural H<sub>2</sub>O would remain in them until today.

There are two ways to validate the foregoing calculation: (1) to directly observe sulfates with high hydration degree in the subsurface; (2) to observe the reduction in hydration degrees after subsurface sulfates being exposed to surface atmospheric conditions. We achieve the first one through an observation in a Mars analog site on Earth (a hyper arid region on Tibet Plateau); we achieve the second one through an observation at Gusev crater on Mars.



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**Fig. 4.** A quantitative relationship between the cycle of hydration degree of Mg-sulfates in the salt-rich subsurface at Mars equator calculated using the  $t_{1/2}$  values for different  $T_{max}$  from Table 2 and the cycle of Mars obliquity (Laskar et al., 2004). (a) As a most conservative example, cycle of obliquity (red colored curve) is compared with the cycle of hydration degree of Mg-sulfates (blue colored curves) within a salt-rich subsurface with  $T_{max} = 190$  K at Mars equator in the period from 6 myr to 5 myr ago. Green colored zones mark the four periods with obliquity >45° when the full rehydration to meridianniite (11w)/epsomite (7w) would be reached, as stimulated by the persistence of H<sub>2</sub>O ice at equator. Blue curves indicate the loss (%) of structural H<sub>2</sub>O in epsomite as n(t)/n(0) as the function of time and at  $T_{max} \sim 190$  K (the high limit of a model predicted *T* range, Mellon et al., 2004, for this conservative example). (b) Comparison of two cycles from 5 myr ago to present at Mars equator. The n(t)/n(0) ratios within salt-rich subsurface at different  $T_{max}$  were expressed in different colors, e.g., 99%, 98%, 49%, and 2% structural H<sub>2</sub>O can be retained in epsomite at a subsurface  $T_{max} \sim 170$  K, 180 K, 185 K, and 190 K. Yellow colored periods mark H<sub>2</sub>O ice would form and persist at many low latitude locations on Mars when obliquity >30°, where the full rehydration of Mg-sulfates to 11w and 7w would be reached in much recent epochs, the nearest one was ~0.37 myr ago. At those locations, 11w or 7w would experience a much shorter duration of dehydration, thus higher degrees of hydration would remain in subsurface Mg-sulfates until today (not shown). (c) Zoomed into 97–100% of n(t)/n(0) of (b).

# 7. Subsurface sulfates with high hydration degree found at Gusev on Mars

The comparisons between the detected WEH levels (ODY\_NS) at Gusev crater and Meridiani Planum with the estimated ranges of  $H_2O$  wt% in the MER targets (Table 1) suggest mid-to-high hydration degrees were retained in those sulfates. Furthermore, due to the large difference in environmental conditions of the surface and salt-rich subsurface of Mars, a subsurface target enriched with hydrous sulfates would experience a change in hydration degree after being excavated and exposed to the current atmospheric conditions at Mars surface.

The existence of Mg-sulfates in two trenches at a flat plan between Bonneville Crater and Columbia Hill made by Spirit rover was implied by a tight MgO vs. SO<sub>3</sub> correlation in APXS data (Haskin et al., 2005; Wang et al., 2006a). Unfortunately, the payload of Spirit cannot determine either the hydration degree or the change in hydration degree for Mg-sulfates. However, the color change of some ferric sulfates can reflect the change of their hydration degrees, thus can be observed using the panoramic multicolor imager (Pancam) carried by the Spirit and Opportunity rover. An example was found at Tyrone site near Home Plate during the exploration made by the Spirit rover.

At the Tyrone site, Spirit rover excavated a large amount of subsurface salty regolith (Fig. 5a). Beneath a layer of basaltic surface soils, two layers of sulfate-rich soils were found: the upper layer was white in color and rich in Ca-sulfates; the lower layer was yellow in color and rich in Fe<sup>3+</sup>-sulfates. After the first excavation of Tyrone subsurface sulfate-rich regolith on sol 784, a set of seven systematic Pancam observations were made on the excavated regolith from sol 864 to sol 1062 by the Spirit rover (from the same location where Spirit passed its 2nd winter on Mars, at almost the same local solar time, under similar atmospheric opacities), in which a color change of Fe<sup>3+</sup>-sulfate-rich yellowish regolith was observed (Wang et al., 2008). Fig. 5b shows a histogram of all data points from Pancam CCD 1024 × 1024 pixels through a filter centered at 753 nm (L2) vs. those through a filter centered at 434 nm (L7). In this histogram, the data from salty regolith occur as two distinct data branches in the upper-right section: the upper data branch represents Tyrone yellowish Fe<sup>3+</sup>-sulfate-rich regolith from deeper depth, the lower data branch represents Tyrone whitish Ca-sulfate-rich regolith from a shallower depth. Comparing the histogram of sol 959 (Fig. 5c) with that of sol 922 (Fig. 5b), the most obvious change is the reduction of distance between the two data branches (marked by two blue arrows) of salty regolith. The Vis-NIR spectra extracted from multicolor Pancam image cubes show this change is caused by an albedo reduction at 673 nm and 753 nm in the later spectra of yellowish Fe<sup>3+</sup>-sulfate-rich regolith (Fig. 9 of Wang and Ling (2011)). A spectral deconvolution analysis (Johnson et al., 2007) suggested that five ferric sulfates make up  $\sim$ 50% of a typical Tyrone yellowish regolith, among them ferricopiapite is the major component ( $\sim$ 27%). On the basis of a systematic experimental investigation on dehydration/rehydration of ferricopiapite under different T and RH conditions (Wang et al., 2012), it was concluded that the change in spectral slope from 434 nm to 753 nm (shown as the reduction of distance between the two data branches in Fig. 5b and c) is consistent with what would be caused by the dehydration of ferricopiapite (Wang and Ling, 2011).

The implied dehydration of ferricopiapite in Tyrone yellowish regolith (excavated from tens' cm depth of the subsurface) suggests that its original environment must have the suitable *T* and *RH* conditions that have prevented (or at least slowed-down) the dehydration of a highly hydrated ferric sulfate (ferricopiapite). It is, therefore, consistent with the conclusion of Section 6.

# 8. Subsurface salts with high hydration degree found in a hyper arid region on Earth

Another evidence to support the conclusion of Section 6 is the direct observation of Mg-sulfates and MgK-chloride with high



**Fig. 5.** Temporal color change observed from Tyrone salty soils (Gusev, Mars) after being exposed to current surface atmospheric conditions, suggesting dehydration of ferricopispite. (a) Pancam false color image of Tyrone salty soils. The yellowish salt soils were dogged out from a deeper depth by the non-function right-front wheel of the Spirit rover. (b and c) A comparison of L2–L7 histograms of multicolor Pancam images (from two of the seven consecutive Pancam observations made from sol 864 to sol 1062) by the Spirit rover. Data points encircled by red squares are from salty soils, upper branch Y = yellowish Fe-sulfate-rich soils, lower branch W = whitish Ca-sulfate-rich soils. The reduction in the separation between two data branches (from sol 922 to sol 959) is indicated by two arrows in blue color, which is caused by the decrease of spectral slope from 434 nm to 753 nm of yellowish salty soils (detailed analysis in Wang and Ling (2011)). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hydration degrees within the subsurface of a hyper arid region on Qinghai-Tibet (QT) Plateau. QT Plateau has the highest average elevation (>4500 m) on Earth. Its atmospheric pressure is ~50–60% of that at sea-level, with low average temperatures, large diurnal and seasonal temperature variations, and high levels of UV radiation. The Himalaya mountain chain (average height >6100 m) south of the QT Plateau largely blocks humid air from the Indian Ocean, and produces a hyper arid region at the north edge of the QT Plateau, the Qaidam basin (N36–39°, E88–100°,  $T_{ave} \sim -4$ °C,  $\Delta T \sim 80$ °C, Aridity Index AI ~ 0.04–0.008, Fig. 6a) (Zheng, 1997; Zheng et al., 2009). Climatically, the low *P*, *T*, large  $\Delta T$ , high aridity, and high UV radiation all make the Qaidam basin to be one of the most similar places on Earth to Mars.

We conducted a field investigation at Da Lang Tan (DLT) saline playa (Fig. 6b) in the Qaidam basin (Wang et al., 2009b), with combined remote sensing (ASTER: Terra satellite, Mayer et al., 2009), in situ sensing (portable WIR-II with a spectral range of 1.25-2.5 µm, Sobron et al., 2009), and laboratory analyses of the samples collected from the field (Laser Raman and Vis-NIR spectroscopy, and XRD, Wang et al., 2009b). One of the preliminary results from this expedition (Wang et al., 2010) is the finding of Mg-sulfates with mid-to-high degrees of hydration, hexahydrite MgSO<sub>4</sub>·6H<sub>2</sub>O, pentahydrate MgSO<sub>4</sub>·5H<sub>2</sub>O, starkeyite MgSO<sub>4</sub>·4H<sub>2</sub>O, and a chloride hydrate, carnalite KMgCl<sub>3</sub>·6H<sub>2</sub>O, within the subsurface salt layers (Fig. 6c). In the laboratory, MgSO<sub>4</sub>·6H<sub>2</sub>O and MgSO<sub>4</sub>·5H<sub>2</sub>O would dehydrate in a few days at relative humidity (*RH*)  $\leq$  33% and a temperature range from 5 °C to 25 °C (Wang et al., 2009a). Finding these highly hydrated salts in the subsurface of a hyper arid region  $(AI \sim 0.01)$  indicates that a salt-rich subsurface layer can indeed maintain an environment that has prevented (or slowed-down) the dehydrations of these hydrous salts.

### 9. Distributions of WEH and sulfur on Mars

The quantitative relationship between the cycles of Mars obliquity and the remaining structural  $H_2O$  in Mg-sulfates within the subsurface at the equator (Fig. 4), the findings of subsurface sulfates with mid-to-high degrees of hydration in an equatorial region on Mars (Fig. 5) and in a hyper arid region on Earth (Fig. 6) all support the hypothesis of structural  $H_2O$  in subsurface sulfates being the major contributor for the high WEH values found at two equatorial regions on Mars (Feldman et al., 2004b; Jakosky et al., 2005; Fialips et al., 2005). Notice that the WEH-map does not show a one-to-one correlation with the Sulfur-map derived from the data of the Gamma Ray Spectrometer on Mars Odyssey (McLennan et al., 2010; King and McLennan, 2010). We believe that it is not the distribution of sulfates, but *the distribution of highly hydrated sulfates within the subsurface*, that plays a major controlling role for the distribution of WEH on the basis of following reasons.

The global distribution of sulfur on Mars would be built by the past and present sulfur related processes, including volcanic, weathering (e.g., hydrothermal, sedimentary, diagenetic, hydrologic), and in addition, atmospheric-surface interactions. Hydrous sulfates would form when large amount of liquid water was available, e.g., in the "theiikian" period (Bibring et al., 2006). Hydrous sulfates can also form during high obliquity periods at the locations where  $H_2O$  ice is present, through atmospheric-surface interactions. At the surface, hydrous sulfates are subject to dehydration under atmospheric conditions in mid-low obliquity periods. In addition, the surface sulfates (and sulfur) can be redistributed through eolian processes. The sulfates (and other S-bearing phases) at the surface would contribute to the global Sulfur-map, but NOT to the global WEH-map.

In contrast, the status and the cycle of hydration degrees of sulfates in the subsurface on Mars would be controlled by the high  $P_{\rm H2O}$  during high obliquity periods and by the low temperature (T<sub>max</sub> in salt-rich subsurface, based on Mellon's model, Mellon et al., 2004) during periods of mid-low obliquity. The former (high  $P_{\rm H2O}$ ) induced rapid rehydration, and the later (low T) induced slow dehydration during the past few million years. In addition during high obliquity periods, the surface H<sub>2</sub>O ice distribution and actual  $P_{\rm H2O}$  at non-polar regions would be controlled by the global atmospheric circulation pattern (Jakosky et al., 2005), which would be affected by ground topography that had changed very little in the past few tens of million years. Therefore the global distribution of surface H<sub>2</sub>O ice during high obliquity periods in the recent few millions years would probably have a relatively persistent pattern. Controlled by this pattern of ice distribution, the global distribution pattern of subsurface sulfates during recent few periods of high obliquity would be persistent too. We believe it is very possible that the global distribution of subsurface sulfates (that maintain mid-high degrees of hydration) produces the observed map of WEH, e.g., a zonal wave-number-two global distribution with high values at two large equatorial regions.

A subsurface environment filled with hydrous sulfates and protected by dry surface soils from the atmosphere would have high



**Fig. 6.** (a) Aridity map of Tibet Plateau, China. A red circle marks the location of Da Lang Tan (DLT) saline playa in Qaidam basin, which has the highest aridity (AI ~ 0.04–0.008) on Tibet Plateau. (b) Subsurface hydrous salts (light toned) in a vertical cross section at DLT, from which the samples for laboratory investigation were collected. (c) Characteristic Raman spectral peaks of MgSO<sub>4</sub>·BH<sub>2</sub>O (6w), MgSO<sub>4</sub>·5H<sub>2</sub>O (5w), MgSO<sub>4</sub>·4H<sub>2</sub>O (4w), MgSO<sub>4</sub>·2H<sub>2</sub>O (2w), MgSO<sub>4</sub>·H<sub>2</sub>O (1w), and KMgCl<sub>3</sub>·6H<sub>2</sub>O obtained from the measurements of the light-toned subsurface salts, taken from the location marked by blue arrows in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

*RH* levels maintained by hydrated sulfates and by adsorbed aqueous films at grain surfaces. In general, an environment with local high *RH* and aqueous films on salt grains could be life-supporting for halophiles, as evidenced by the finding of halophiles under the salt crust at Atacama Desert (Wierzchos et al., 2006) and by a similar discovery of different chains of halophiles within the DLT salt crust at Qaidam basin on Tibet Plateau (Kong et al., 2009, 2010).

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