Stability and spectroscopy of Mg sulfate minerals.

Role of hydration on sulfur isotope partitioning

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ABSTRACT

We study hydrated magnesium sulfate minerals from first-principles calculations based on density-functional theory. We determine the heat of hydration for MgSO₄.nH₂O, compute the Raman and infrared spectra for several phases and calculate the S isotope partitioning as a function of hydration. We find that epsomite and meridianiite, with respectively n=7 and n=11 water molecules per MgSO₄ unit, are particularly stable with respect to other individual or combinations of hydration states. The Raman spectra of all phases present clear SO₄ features that are easily identifiable. We use this to show one can use the vibrational spectroscopic information as an identification tool in a remote environment, like the martian surface. We discuss the character and atomic displacement pattern of all vibration modes and compute the $^{34}$S/$^{32}$S partitioning; this work shows that hydration favors enrichment in the lighter S isotope $^{32}$S with respect to the heavier $^{34}$S, which is accumulated in the less hydrous structures. We show for the first time that the signature of $^{34}$S/$^{32}$S partitioning could be observed by in situ spectroscopy on the surface of Mars. Moreover this can be related to the diurnal cycle of hydration and dehydration and hence it can improve the modeling of the water circulation on Mars.
INTRODUCTION

The presence of monohydrate and multiply-hydrated sulfate minerals at the surface of Mars as major water-bearing minerals is now a well-established fact [e.g. Gendrin et al., 2005, Wray et al., 2009, Flahaut et al., 2010, Noe Dobrea et al., 2012]. Magnesium sulfates play a major role amongst these minerals, but sulfates of other cations have been also proven to exist, like gypsum, jarosite, etc. [Blaney and McCord, 1995, Aubrey et al., 2006, Roach et al., 2009, Horgan et al., 2009, Murchie et al., 2009].

Magnesium sulfates are compounds exhibiting an amazingly large number of hydration states. Apart from two anhydrous phases it can contain almost anything between 1 and 7 water molecules per formula unit, with even up to 11 water molecules for each MgSO₄ unit. The anhydrous phases do not exist as minerals. Their affinity for water is so large that they are currently used as a desiccant. The family of related minerals are, in order of increasing hydration: the monohydrate, MgSO₄·H₂O, also known as the mineral kiesierite [Hawthorne et al., 1987], sanderite, MgSO₄·2H₂O [Ma et al., 2009a], MgSO₄·2.5H₂O [Ma et al., 2009b], starkeyite [Baur, 1964a] and cranswickite [Peterson, 2011], both with MgSO₄·4H₂O formula, pentahydrite, MgSO₄·5H₂O, hexahydrite, MgSO₄·6H₂O [Zalkin et al., 1964], epsomite, MgSO₄·7H₂O [Baur, 1964b], and finally, meridianiite, MgSO₄·11H₂O [Fortes et al., 2008]. Additional minerals are formed in binary and ternary diagrams with other halogenide and/or sulfate systems [Steiger et al., 2011]. The minerals of this group have been traditionally studied in the context of evaporitic deposits, or of alteration products of sulfide minerals. More recently, with the exploration of the Martian surface and of the icy moons from the outer solar system, the planetological importance of these minerals has been fully appreciated.

The relative stability of these phases is conditioned not only by pressure and temperature but also by the partial pressure of water vapor [Hogenboom et
al., 1995, Feldman, et al., 2004, Chou et al., 2013]. Some of these phases can be easily transformed from one to another, but not all such transitions are reversible [Steiger et al., 2011]. The presence of other specific minerals like hydrous silicates [Wilson and Bish, 2012] or organic matter [Aubrey et al., 2006], may affect the stability field of the hydrated MgSO$_4$ phases by changing and/or preserving humidity conditions locally.

Experiments on the phase diagram of the MgSO$_4$ – H$_2$O system reveal that the surface conditions on the planet Mars, and more precisely the day/night cycle, span the static stability field of the mono-, di-, tetra-, hepta- and hendecahydrates. However, as mentioned above, the precise mineralogy may depend on kinetics of reactions and on the thermodynamical path [Vaniman et al., 2004, Wang et al., 2011, Chou et al., 2013].

Here we use first-principles calculations to compute the energies of hydration to help interpret the water cycle on Mars, and to determine the effect of hydration on the Raman spectra and on the isotope partitioning.

**METHODOLOGY**

We perform first-principles calculations using standard density-functional theory (Kohn and Sham 1965; Payne et al. 1992; Martin 2003) in the VASP (ref) and ABINIT (Gonze et al. 2002, 2009) implementations, both based on planewaves and pseudopotentials.

The crystal structures, the heat of formation, and the hydration energies are obtained using VASP simulations, with planar-augmented wavefunction (PAW) (Blochl, 1991) pseudopotentials and the Perdew-Burke-Erzernhof formulation of the Generalized Gradient Approximation (Perdew et al., 1996). The energy cutoffs for the planewaves on respectively the standard grid and the augmented grid are 800 eV and 850 eV kinetic, ensuring an accuracy of the energy better than $\pm$ 0.2 meV. The sampling of the electron density in the reciprocal space is
performed on special k points (Mokhorst and Pack, 1976) with varying density from one structure to the other. With these values we achieve energy convergence on the order of the meV/formula unit. We start from the experimental structures from the references mentioned above, and we fully relax them, i.e. we minimize both the theoretical stresses on the unit cell and the forces on the atoms.

Then we use ABINIT to compute the lattice dynamical properties (Baroni et al., 2001, Gonze et al., 2005), including the Raman spectra with both peak position and intensities (Veithen et al., 2005) on four selected phases: the two anhydrous compounds, kiesierite, and starkeyite. These calculations are performed using the Local Density Approximation for the exchange-correlation, and Troullier-Martins norm-conserving pseudopotentials. We store all the Raman spectra on the WURM website (http://www.wurm.info). For more details of the Raman calculations, choice of parameters, pseudopotentials, etc. see Caracas and Bobocioiu (2011).

Finally the reduced partition function ratios (RPFR) for sulfur isotopes are obtained from comparing the phonon frequencies obtained for various S masses in the zone-center of the Brillouin zone. The procedure has been successfully applied to a variety of minerals (Balan et al., 2009, Reynard and Caracas, 2009).

RESULTS AND DISCUSSION

Energies of hydration

The basic thermodynamic parameters of the hydrated sulfate minerals have been recently measured (Grevel and Majzlan, 2009). The heat of formation for the hydrous phases was reported both from elements and from ionic groups and water molecules, and it was shown that the relative humidity, i.e. the partial water vapor pressure, plays a critical role in the phase diagrams and the relative stability of various phases.

Here, we study and compute the heat of hydration for all the hydrated phases of MgSO₄, based on our calculations at 0K. The results are summarized
in Table 1, where the enthalpy difference between the mechanical mixture of less hydrated phase plus water molecule(s) and the more hydrated phase is computed as follows:

\[
\Delta H_{\text{hydration}} = H_{\text{MgSO}_4\cdot m\text{H}_2\text{O}} - \left[ H_{\text{MgSO}_4\cdot n\text{H}_2\text{O}} + (m-n) H_{\text{H}_2\text{O}} \right], \text{ with } m > n \ (1)
\]

Negative values favor hydration and positive values favor dehydration. In the limit of thermodynamical equilibrium, which applies to our calculations, the hexahydrite turns out to be metastable with respect to any other type of mixture. This is coherent with the experimental phase diagram of the MgSO$_4$ – H$_2$O system, where hexahydrite is metastable at temperatures below freezing [Vaniman et al., 2004, Wang et al., 2006, 2011]. Except for hexahydrite all the other phases are more stable with respect to water vapor and the correspondingly less-hydrated phase.

Heats of reactions between two hydrated phases resulting in a third hydrated phase are listed in Table 2. As expected from the results shown in Table 1, hexahydrite is metastable with respect to the other hydrated sulfates, and epsomite is one of the most stable phases. Reactions between the other sulfates, not involving hexahydrite are easily reversible.

**Raman spectra**

We calculate the Raman spectra of the two anhydrous phases, as well as of kieserite, MgSO$_4$·H$_2$O, starkeyite, MgSO$_4$·4H$_2$O, and epsomite, MgSO$_4$·7H$_2$O, with both peak positions and intensities. The spectra are represented in Figure 1. The results are fully reported on the WURM website, where the reader can find as well the crystal structures, the dielectric properties, and animations with the vibration pattern for each phonon mode in the zone center.

The spectra present similarities between the various phases. Strong signatures of the SO$_4$ groups are clearly distinguishable in all phases, corresponding to the asymmetric stretching and breathing modes. They can be
used as identification criteria for this class of minerals. The vibration modes of
the water molecules lay at high frequency.

Below 700 cm$^{-1}$ the peaks are dominated by lattice modes, where SO$_4$
anionic groups and, for the two hydrated minerals, H$_2$O molecules, vibrate
against each other or against the Mg sublattice as rigid units. These modes have
relatively low intensity.

The modes in the 900-1200 cm$^{-1}$ range correspond to vibrations of the SO$_4$
tetrahedra. In the anhydrous phases the highest-intensity peaks of the spectra
are the breathing modes of the SO$_4$ tetrahedra, at 998 and 1006 cm$^{-1}$ in the
respectively alpha and beta phases. The second most intense mode is the
asymmetric stretching of the tetrahedra, respectively at 1146 and 1128 cm$^{-1}$. In
the hydrated phases, the corresponding breathing modes are at 1004, 985, and
952 cm$^{-1}$ in respectively kieserite, starkeyite, and epsomite, and the strongest
asymmetric stretching at 1120 cm$^{-1}$ in kieserite. The asymmetric stretching
modes are degenerate into several modes with similar intensity over the 1047-
1185 cm$^{-1}$ range in starkeyite and over the 1001-1142 cm$^{-1}$ in epsomite. The
water molecules show a small participation to these modes, probably due to
some dipole-dipole or higher-order dielectric couplings. These modes appear as
small peaks in the same frequency interval in experiments.

In the hydrated phases, the bending water modes form a distinct group, at
1527 and 1543 cm$^{-1}$ in kieserite, in the 1515-1660 cm$^{-1}$ in starkeyite, and in
1560-1655 cm$^{-1}$ range in epsomite.

Above 2900 cm$^{-1}$ the peaks correspond to pure water vibrations and are
found only in the hydrated phases. One can observe symmetric and asymmetric
stretching, signatures that would appear in Raman or infrared. Experimentally the
water vibration peaks are convoluted into large asymmetric wide bands around
3300-3500 cm$^{-1}$.

Our theoretical results are in relatively good agreement with the
experimental measurements [Wang et al., 2006]. The characteristic breathing
modes of the SO$_4$ tetrahedra in the anhydrous phases are at about 20-30 cm$^{-1}$
lower than the experimental values, typical for vibrational calculations (Baroni et
al., 2001, Caracas and Bobocioiu, 2011). For the hydrated phases, this departure is increased to 40 cm\(^{-1}\) for kieserite, but only 15 cm\(^{-1}\) for starkeyite. Globally the inverse correlation between the position of the breathing mode and the hydration state is less pronounced in calculations (about 5 cm\(^{-1}\)/water molecule) than in experiments (about 10 cm\(^{-1}\)/water molecule). Differences can also be seen in the water peaks. In experiments the water peaks are less resolved than in calculations, due to the inherent H disorder present in the samples at finite temperature. The measured vibrational frequencies of water molecules are also higher than in calculations.

These various discrepancies can be attributed to inherent DFT approximations, temperature and anharmonic effects neglected in the calculations, and differences in specific volume between experiment and calculations.

**Isotope partitioning**

The difference in mass associated with various isotopes induces changes in the phonon frequencies, which in turn have an effect on the free energy. The structure with lighter isotopes will see the frequency of the phonon modes increased with respect to the structure with heavier isotopes. The higher the participation of that particular exchanged isotope to one particular mode, the higher is the effect on its frequency. Thus the calculations of the Raman and infrared spectra can be used to determine the effect of hydration on the fractionation of sulfur isotopes.

The reduced partition function ratios, \(\beta^{34S}/^{32S}\) for anhydrous \(\beta\)-MgSO\(_4\), kieserite, starkeyite, and epsomite are listed in Table 3 as a function of temperature for a range relevant for the surface of Mars. We obtain the \(^{34S}/^{32S}\) partitioning functions between any two sulfate phases as the ratios of the corresponding \(\beta\) functions. The results are plotted in Figure 2. The largest values are for the \(\beta\)-MgSO\(_4\) and epsomite pair, considerably larger than for the \(\beta\)-MgSO\(_4\) and any other hydrated sulfate. Hydrating kieserite and starkeyite yields an intermediate value, as expected. Even if temperature reduces the partitioning
effect, this still occurs at the maximum temperatures characteristic for Mars’
surface.

**IMPLICATIONS**

We compute the hydration energies of hydrous and anhydrous phases of
magnesium sulfate minerals. We predict that hydration of anhydrous phases,
mono-, tri- and tetra- hydrates is particularly easy to achieve. Reactions between
sulfates, not involving hexahydrate, are close to equilibrium and thus easily
reversible. Hence both meridianiite and epsomite should be found in large
amounts on the surface of Mars, as they are remarkably stable with respect to
dehydration; we anticipate to see much less hexahydrate, as this phase is
metastable with respect to the other hydrated sulfates.

The simulated Raman spectra show clear and distinctive peaks of the SO$_4^{2-}$
groups and of the H$_2$O molecules, which can help in identification of this group of
minerals. The theoretical results are in good agreement with the existent
experimental measurements and provide a nice complement thereof. The
[http://www.wurm.info](http://www.wurm.info) website provides all details of the spectra.

Finally, our calculations show that the $^{34}$S/$^{32}$S partitioning increases with
increasing difference in hydration. This is consistent with having the less
hydrated species enriched in the heavier isotope, S$^{34}$. Or alternatively, this can
be viewed as hydration increasing the amount of light isotope, S$^{32}$.

This suggests that the signature of the diurnal hydration/dehydration cycles
on Mars should become visible over geological time in the isotopic composition
of the various hydrous magnesium sulfates. The light isotopes would accumulate
in the more hydrated phases, and the heavy isotopes in the more anhydrous
phases. This trend could be captured by in situ spectroscopic measurements. If
kinetic data are available, the amount of partitioning could be even correlated to
the duration of that particular deposit.
Acknowledgement

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References


Wilson, S. A., and Bish, D. L. (2012), Stability of Mg-sulfate minerals in the presence of smectites: Possible mineralogical controls on H2O cycling and
biomarker preservation on Mars, Geochimica et Cosmochimica Acta 96, 120-133.


FIGURE 1. Theoretical Raman spectra of anhydrous $\alpha$-MgSO$_4$, $\beta$-MgSO$_4$, kieserite MgSO$_4$.H$_2$O, starkeyite MgSO$_4$.4H$_2$O, and epsomite MgSO$_4$.7H$_2$O.

FIGURE 2. Theoretical $S^{34}/S^{32}$ partitioning as a function of temperature between $\beta$-MgSO$_4$, kieserite MgSO$_4$.H$_2$O, starkeyite MgSO$_4$.4H$_2$O, and epsomite MgSO$_4$.7H$_2$O. The results suggest that hydration favors enrichment in lighter isotopes. This feature should be visible by in situ measurements on the surface of Mars and could be related to interpret the diurnal cycle of hydration/hydration. $m$ and $n$ denote the number of molecules per MgSO$_4$ unit in the two phases between which the partitioning is plotted.
Table 1.
Heat of hydration for the various magnesium sulfate phases considered in this study. The hydrate with $m$ water molecules needs the amount of energy listed in the table to add $(n-m)$ water molecules/MgSO$_4$ group unit to form a hydrate with $n$ water molecules. $m=n=0$ is for $\beta$-MgSO$_4$. Units are kJ/mol. Negative numbers favor the hydrated phase, positive numbers favor dehydration. In general higher hydrated states are preferred, especially epsomite. Hexahydrite is the only metastable phase at 0K.

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Table 2.
Heat of reaction between sulfates with various hydration states: \( \Delta H_{\text{hydration}} = H_{\text{MgSO}_4.m\text{H}_2\text{O}} + H_{\text{MgSO}_4.n\text{H}_2\text{O}} - 2 H_{\text{MgSO}_4.(m-n)/2\text{H}_2\text{O}} \). Except for the formation of hexahydrite, the other transformations are easily reversible. Epsomite is particularly stable with respect to other hydrated sulfates.

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Table 3.
Reduced partition function ratios (the $\beta_S^{34}/S^{32}$) for $\beta$-MgSO$_4$, kieserite, starkeyite, and epsomite in the temperature range relevant to Mars’s surface.

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<th>Kieserite, MgSO$_4$.H$_2$O</th>
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