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## REVISION 3

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### Stability and spectroscopy of Mg sulfate minerals.

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### Role of hydration on sulfur isotope partitioning

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#### ABSTRACT

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15 We study hydrated magnesium sulfate minerals from first-principles calculations  
16 based on density-functional theory. We determine the heat of hydration for  
17  $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$ , compute the Raman and infrared spectra for several phases and  
18 calculate the S isotope partitioning as a function of hydration. We find that  
19 epsomite and meridianiite, with respectively  $n=7$  and  $n=11$  water molecules per  
20  $\text{MgSO}_4$  unit, are particularly stable with respect to other individual or  
21 combinations of hydration states. The Raman spectra of all phases present clear  
22  $\text{SO}_4$  features that are easily identifiable. We use this to show one can use the  
23 vibrational spectroscopic information as an identification tool in a remote  
24 environment, like the martian surface. We discuss the character and atomic  
25 displacement pattern of all vibration modes and compute the  $^{34}\text{S}/^{32}\text{S}$  partitioning;  
26 this work shows that hydration favors enrichment in the lighter S isotope  $^{32}\text{S}$  with  
27 respect to the heavier  $^{34}\text{S}$ , which is accumulated in the less hydrous structures.  
28 We show for the first time that the signature of  $^{34}\text{S}/^{32}\text{S}$  partitioning could be  
29 observed by in situ spectroscopy on the surface of Mars. Moreover this can be  
30 related to the diurnal cycle of hydration and dehydration and hence it can  
31 improve the modeling of the water circulation on Mars.

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## INTRODUCTION

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

43 Magnesium sulfates are compounds exhibiting an amazingly large number  
44 of hydration states. Apart from two anhydrous phases it can contain almost  
45 anything between 1 and 7 water molecules per formula unit, with even up to 11  
46 water molecules for each  $\text{MgSO}_4$  unit. The anhydrous phases do not exist as  
47 minerals. Their affinity for water is so large that they are currently used as a  
48 desiccant. The family of related minerals are, in order of increasing hydration: the  
49 monohydrate,  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ , also known as the mineral kiesierite [Hawthorne et  
50 al., 1987], sanderite,  $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$  [Ma et al., 2009a],  $\text{MgSO}_4 \cdot 2.5\text{H}_2\text{O}$  [Ma et al.,  
51 2009b], starkeyite [Baur, 1964a] and cranswickite [Peterson, 2011], both with  
52  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  formula, pentahydrate,  $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$ , hexahydrate,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$   
53 [Zalkin et al., 1964], epsomite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  [Baur, 1964b], and finally,  
54 meridianiite,  $\text{MgSO}_4 \cdot 11\text{H}_2\text{O}$  [Fortes et al., 2008]. Additional minerals are formed  
55 in binary and ternary diagrams with other halogenide and/or sulfate systems  
56 [Steiger et al., 2011]. The minerals of this group have been traditionally studied in  
57 the context of evaporitic deposits, or of alteration products of sulfide minerals.  
58 More recently, with the exploration of the Martian surface and of the icy moons  
59 from the outer solar system, the planetological importance of these minerals has  
60 been fully appreciated.

61 The relative stability of these phases is conditioned not only by pressure  
62 and temperature but also by the partial pressure of water vapor [Hogenboom et

63 al., 1995, Feldman, et al., 2004, Chou et al., 2013]. Some of these phases can  
64 be easily transformed from one to another, but not all such transitions are  
65 reversible [Steiger et al., 2011]. The presence of other specific minerals like  
66 hydrous silicates [Wilson and Bish, 2012] or organic matter [Aubrey et al., 2006],  
67 may affect the stability field of the hydrated  $\text{MgSO}_4$  phases by changing and/or  
68 preserving humidity conditions locally.

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

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

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## 80 **METHODOLOGY**

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

86 The crystal structures, the heat of formation, and the hydration energies are  
87 obtained using VASP simulations, with planar-augmented wavefunction (PAW)  
88 (Blochl, 1991) pseudopotentials and the Perdew-Burke-Erzenhof formulation of  
89 the Generalized Gradient Approximation (Perdew et al., 1996). The energy  
90 cutoffs for the planewaves on respectively the standard grid and the augmented  
91 grid are 800 eV and 850 eV kinetic, ensuring an accuracy of the energy better  
92 than  $\pm 0.2$  meV. The sampling of the electron density in the reciprocal space is

93 performed on special k points (Mokhorst and Pack, 1976) with varying density  
94 from one structure to the other. With these values we achieve energy  
95 convergence on the order of the meV/formula unit. We start from the  
96 experimental structures from the references mentioned above, and we fully relax  
97 them, i.e. we minimize both the theoretical stresses on the unit cell and the  
98 forces on the atoms.

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

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

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## RESULTS AND DISCUSSION

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### Energies of hydration

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

121

122 Here, we study and compute the heat of hydration for all the hydrated  
phases of  $\text{MgSO}_4$ , based on our calculations at 0K. The results are summarized

123 in Table 1, where the enthalpy difference between the mechanical mixture of less  
124 hydrated phase plus water molecule(s) and the more hydrated phase is  
125 computed as follows:

126

$$127 \quad \Delta H_{\text{hydration}} = H_{\text{MgSO}_4 \cdot m\text{H}_2\text{O}} - [H_{\text{MgSO}_4 \cdot n\text{H}_2\text{O}} + (m-n) H_{\text{H}_2\text{O}}], \text{ with } m > n \text{ (1)}$$

128

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

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

142

### 143 **Raman spectra**

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

150 The spectra present similarities between the various phases. Strong  
151 signatures of the  $\text{SO}_4$  groups are clearly distinguishable in all phases,  
152 corresponding to the asymmetric stretching and breathing modes. They can be

153 used as identification criteria for this class of minerals. The vibration modes of  
154 the water molecules lay at high frequency.

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

159 The modes in the  $900\text{-}1200\text{ cm}^{-1}$  range correspond to vibrations of the  $\text{SO}_4$   
160 tetrahedra. In the anhydrous phases the highest-intensity peaks of the spectra  
161 are the breathing modes of the  $\text{SO}_4$  tetrahedra, at  $998$  and  $1006\text{ cm}^{-1}$  in the  
162 respectively alpha and beta phases. The second most intense mode is the  
163 asymmetric stretching of the tetrahedra, respectively at  $1146$  and  $1128\text{ cm}^{-1}$ . In  
164 the hydrated phases, the corresponding breathing modes are at  $1004$ ,  $985$ , and  
165  $952\text{ cm}^{-1}$  in respectively kieserite, starkeyite, and epsomite, and the strongest  
166 asymmetric stretching at  $1120\text{ cm}^{-1}$  in kieserite. The asymmetric stretching  
167 modes are degenerate into several modes with similar intensity over the  $1047\text{-}$   
168  $1185\text{ cm}^{-1}$  range in starkeyite and over the  $1001\text{-}1142\text{ cm}^{-1}$  in epsomite. The  
169 water molecules show a small participation to these modes, probably due to  
170 some dipole-dipole or higher-order dielectric couplings. These modes appear as  
171 small peaks in the same frequency interval in experiments.

172 In the hydrated phases, the bending water modes form a distinct group, at  
173  $1527$  and  $1543\text{ cm}^{-1}$  in kieserite, in the  $1515\text{-}1660\text{ cm}^{-1}$  in starkeyite, and in  
174  $1560\text{-}1655\text{ cm}^{-1}$  range in epsomite.

175 Above  $2900\text{ cm}^{-1}$  the peaks correspond to pure water vibrations and are  
176 found only in the hydrated phases. One can observe symmetric and asymmetric  
177 stretching, signatures that would appear in Raman or infrared. Experimentally the  
178 water vibration peaks are convoluted into large asymmetric wide bands around  
179  $3300\text{-}3500\text{ cm}^{-1}$ .

180 Our theoretical results are in relatively good agreement with the  
181 experimental measurements [Wang et al., 2006]. The characteristic breathing  
182 modes of the  $\text{SO}_4$  tetrahedra in the anhydrous phases are at about  $20\text{-}30\text{ cm}^{-1}$   
183 lower than the experimental values, typical for vibrational calculations (Baroni et

184 al., 2001, Caracas and Bobocioiu, 2011). For the hydrated phases, this departure  
185 is increased to  $40 \text{ cm}^{-1}$  for kieserite, but only  $15 \text{ cm}^{-1}$  for starkeyite. Globally the  
186 inverse correlation between the position of the breathing mode and the hydration  
187 state is less pronounced in calculations (about  $5 \text{ cm}^{-1}$ /water molecule) than in  
188 experiments (about  $10 \text{ cm}^{-1}$ /water molecule). Differences can also be seen in the  
189 water peaks. In experiments the water peaks are less resolved than in  
190 calculations, due to the inherent H disorder present in the samples at finite  
191 temperature. The measured vibrational frequencies of water molecules are also  
192 higher than in calculations.

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

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### Isotope partitioning

199

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

207

208 The reduced partition function ratios,  $\beta^{34}\text{S}/\beta^{32}\text{S}$  for anhydrous  $\beta\text{-MgSO}_4$ ,  
209 kieserite, starkeyite, and epsomite are listed in Table 3 as a function of  
210 temperature for a range relevant for the surface of Mars. We obtain the  $^{34}\text{S}/^{32}\text{S}$   
211 partitioning functions between any two sulfate phases as the ratios of the  
212 corresponding  $\beta$  functions. The results are plotted in Figure 2. The largest values  
213 are for the  $\beta\text{-MgSO}_4$  and epsomite pair, considerably larger than for the  $\beta\text{-MgSO}_4$   
214 and any other hydrated sulfate. Hydrating kieserite and starkeyite yields an  
intermediate value, as expected. Even if temperature reduces the partitioning

215 effect, this still occurs at the maximum temperatures characteristic for Mars'  
216 surface.  
217

## 218 IMPLICATIONS

219  
220 We compute the hydration energies of hydrous and anhydrous phases of  
221 magnesium sulfate minerals. We predict that hydration of anhydrous phases,  
222 mono-, tri- and tetra- hydrates is particularly easy to achieve. Reactions between  
223 sulfates, not involving hexahydrate, are close to equilibrium and thus easily  
224 reversible. Hence both meridianiite and epsomite should be found in large  
225 amounts on the surface of Mars, as they are remarkably stable with respect to  
226 dehydration; we anticipate to see much less hexahydrate, as this phase is  
227 metastable with respect to the other hydrated sulfates.

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

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

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

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249 calculations were done on the jade machine of CINES, under DARI grant  
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252 useful discussions about the isotope partitioning.

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## References

258

259 Aubrey, A., Cleaves, H. J., Chalmers, J. H., Skelley, A. M., Mathies, R. A.,  
260 Grunthaner, F. J., Ehrenfreund, P., Bada, J. L., (2006), Sulfate minerals and  
261 organic compounds on Mars, *Geology* 34, 357-360.

262

263 Balan, E., Cartigny, P., Blanchard, M., Cabaret, D., Lazzeri, M., Mauri, F. (2009)  
264 Theoretical investigation of the anomalous equilibrium fractionation of multiple  
265 sulfur isotopes during adsorption, *Earth and Planetary Science Letters* 284, 88-  
266 93.

267

268 Baroni, S., de Gironcoli, S., Dal Corso, A., and Giannozzi, P. (2001) Phonons  
269 and related crystal properties from density-functional perturbation theory.  
270 *Reviews in Modern Physics*, 73, 515–562.

271

272 Baur, W.H. (1964a) On the crystal chemistry of salt hydrates; Part 2, A neutron  
273 diffraction study of  $MgSO_4 \cdot 4H_2O$ . *Acta Crystallographica*, 17, 863–869.

274

275 Baur, W.H. (1964b) On the crystal chemistry of salt hydrates; Part 4, The  
276 refinement of the crystal structure of  $MgSO_4 \cdot 7H_2O$  (epsomite). *Acta*  
277 *Crystallographica*, 17, 1361–1369.

278

279 Blaney, D. L., and McCord, T. B. (1995), Indications of sulfate minerals in the  
280 Martian soil from Earth-based spectroscopy, *Journal of Geophysical Research*  
281 100, 14433-14441.

282

283 Blochl, P., (1994). Projector augmented-wave method. *Physical Review B* 50,  
284 17953-17979.

285

- 286 Caracas, R., and Bobocioiu, E. (2011). The WURM project – a freely available  
287 web-based repository of computed physical data for minerals. American  
288 Mineralogist, 96, 437-444.  
289
- 290 Chou, I-M., Seal II, R. R., and Wang, A. (2013), The stability of sulfate and  
291 hydrated sulfate minerals near ambient conditions and their significance in  
292 environmental and planetary sciences, Journal of Asian Earth Sciences 62, 734-  
293 758.  
294
- 295 Feldman, W. C., Mellon, M. T., Maurice, S., Prettyman, T. H., Carey, J. W.,  
296 Vaniman, D. T., Bish, D. L., Fialips, C. I., Chipera, S. J., Kargel, J. S., Elphic, R.  
297 C., Funsten, H. O., Lawrence, D. J., and Tokar, R. L., (2004), Hydrated states of  
298 MgSO<sub>4</sub> at equatorial latitudes on Mars, Geophysical Research Letters, 31,  
299 L16702.  
300
- 301 Flahaut, J., Quantin, C., Allemand, P., Thomas, P., and Le Deit, L. (2010),  
302 Identification, distribution and possible origins of sulfates in Capri Chasma  
303 (Mars), inferred from CRISM data, Journal of Geophysical Research, 115,  
304 E11007.  
305
- 306 Gendrin A., Mangold, N., Bibring, J.-P., Langevin, Y., Gondet, B., Poulet, F.,  
307 Bonello, G., Quantin, C., Mustard, J., Arvidson, R., and LeMouelic, S. (2005)  
308 Sulfates in Martian layered terrains: the OMEGA/Mars Express view. Science  
309 307, 1587–1591.  
310
- 311 Gonze, X., Beuken, J.-M., Caracas, R., Detraux, F., Fuchs, M., Rignanese, G.-  
312 M., Sindic, L., Verstraete, M., Zerah, G., Jollet, F., Torrent, M., Roy, A., Mikami,  
313 M., Ghosez, Ph., Raty, J.-Y., and Allan, D. C. (2002) First-principle computation  
314 of material properties the ABINIT software project. Computational Materials  
315 Science, 25, 478–492. [<http://www.abinit.org>]  
316
- 317 Gonze, X., Rignanese, G.-M., and Caracas, R. (2005) First-principles studies of  
318 the lattice dynamics of crystals, and related properties. Zeitschrift für  
319 Kristallographie, 220, 458–472.  
320
- 321 Gonze, X., Amadon, B., Anglade, P.-M., Beuken, J.-M., Bottin, F., Boulanger, P.,  
322 Bruneval, F., Caliste, D., Caracas, R., Côté, M., Deutsch, T., Genovesi, L.,  
323 Ghosez, Ph., Giantomassi, M., Goedecker, S., Hamann, D.R., Hermet, P., Jollet,  
324 F., Jomard, G., Leroux, S., Mancini, M., Mazevet, S., Oliveira, M.J.T., Onida, G.,  
325 Pouillon, Y., Rangel, T., Rignanese, G.-M., Sangalli, D., Shaltaf, R., Torrent, M.,  
326 Verstraete, M.J., Zerah G., and Zwanziger, J.W. (2009) ABINIT: First-principles  
327 approach to material and nanosystem properties. Computer Physics  
328 Communications, 180, 2582-2615.  
329

- 330 Grevel, K.-D., and Majzlan, J. (2009) Internally consistent thermodynamic data  
331 for magnesium sulfate hydrates. *Geochimica et Cosmochimica Acta* 73, 6805-  
332 6815.  
333  
334 Hawthorne, F.C., Groat, L.A., Raudsepp, M., and Ercit, T.S. (1987) Kieserite,  
335  $\text{Mg}(\text{SO}_4)\cdot\text{H}_2\text{O}$ , a titanite-group mineral. *Neues Jahrbuch für Mineralogie*,  
336 *Abhandlungen*, 157, 121–132.  
337  
338 Hogenboom, D. L., Kargel, J. S., Ganasan, J. P., and Lee, L. (1995), Magnesium  
339 Sulfate-Water to 400 Mpa Using a Novel Piezometer - Densities, Phase-  
340 Equilibria, and Planetological Implications, *Icarus* 115, 258-277.  
341  
342 Horgan, B. H., J. F. Bell III, E. Z. Noe Dobrea, E. A. Cloutis, D. T. Bailey, M. A.  
343 Craig, L. H. Roach, and J. F. Mustard (2009), Distribution of hydrated minerals  
344 in the north polar region of Mars, *Journal of Geophysical Research*, 114, E01005  
345  
346 Kohn, W. and Sham, L. J. (1965) Self-consistent equations including exchange  
347 and correlation effects. *Physical Review*, 140, A1133–A1138.  
348  
349 Ma, H., Bish, D.L., Wang, H.-W., and Chipera, S. (2009a) Determination of the  
350 crystal structure of sanderite,  $\text{MgSO}_4\cdot 2\text{H}_2\text{O}$ , by X-ray powder diffraction and the  
351 charge flipping method. *American Mineralogist*, 94, 622–625.  
352  
353 Ma, H. Bish, D. L., Wang, H.-W., and Chipera, S. J.(2009b) Structure  
354 determination of the 2.5 hydrate  $\text{MgSO}_4$  phase by simulated annealing.  
355 *American Mineralogist*, 94, 1071–1074.  
356  
357 Martin, R.M. (2003) *Electronic structure. Basic theory and practical methods.*  
358 Cambridge University Press. 596 pp.  
359  
360 Monkhorst, H.J. and J.D. Pack (1976) Special points for Brillouin-zone  
361 integrations. *Physical Review B*, 13, 5188-5192.  
362  
363 Murchie, S., Arvidson, R., Bedini, P., Beisser, K., Bibring, J.-P., Bishop, J., Boldt,  
364 J., Cavender, P., Choo, T., Clancy, R.T. and others. (2009) Compact Recon-  
365 naissance Imaging Spectrometer for Mars investigation and data set from the  
366 Mars Reconnaissance Orbiter's primary science phase. *Journal of Geophysical*  
367 *Research*, 114, E00D07.  
368  
369 Noe Dobrea, E. Z., Wray, J. J., Calef III, F. J., Parker, T. J., and Murchie, S. L.  
370 (2012), Hydrated minerals on Endeavour Crater's rim and interior, and  
371 surrounding plains: New insights from CRISM data., *Geophysical Research*  
372 *Letters*, 39, L23201  
373

- 374 Payne, M.C., M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos (1992)  
375 Iterative minimization techniques for ab initio total-energy calculations: molecular  
376 dynamics and conjugate gradients. *Reviews of Modern Physics*, 64, 1045-1097.  
377
- 378 Perdew, J., Burke, K., Ernzerhof, M., 1996. Generalized gradient approximation  
379 made simple. *Physical Review Letters* 77, 3865-3868.  
380
- 381 Peterson, R.C., Nelson, W., Madu, B. and Shurvell, H.F. (2007) Meridianiite: a  
382 new mineral species observed on Earth and predicted to exist on Mars. *American*  
383 *Mineralogist*, 92, 1756–1759.  
384
- 385 Peterson, R. C. (2011) Cranswickite  $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ , a new mineral from  
386 Calingasta, Argentina. *American Mineralogist* 96, 869-877.  
387
- 388 Reynard, B., and Caracas, R. (2009) H/D isotopic fractionation of brucite  
389  $\text{Mg}(\text{OH})_2$  with water from vibrational spectroscopy and ab initio modeling,  
390 *Chemical Geology* 262, 159-168.  
391
- 392 Roach, L. H., J. F. Mustard, S. L. Murchie, J.-P. Bibring, F. Forget, K. W. Lewis,  
393 O. Aharonson, M. Vincendon, and J. L. Bishop (2009), Testing evidence of  
394 recent hydration state change in sulfates on Mars, *Journal of Geophysical*  
395 *Research*, 114, E00D02.  
396
- 397 Steiger, M., Linnow, K., Ehrhardt, D. and Rohde, M. (2011), Decomposition  
398 reactions of magnesium sulfate hydrates and phase equilibria in the  $\text{MgSO}_4$ -  
399  $\text{H}_2\text{O}$  and  $\text{Na}^+ - \text{Mg}^{2+} - \text{Cl}^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$  systems with implications for Mars,  
400 *Geochimica et Cosmochimica Acta* 75, 3600-3626.  
401
- 402 Vaniman, D. T., Bish, D. L., Chipera S. J., Fialips C. I., Carey, J. W., and  
403 Feldman, W. C. (2004) Magnesium sulphate salts and the history of water on  
404 Mars, *Nature*, 431 663-665.  
405
- 406 Veithen, M., Gonze, X., and Ghosez, Ph. (2005), Non-linear optical  
407 susceptibilities, Raman efficiencies and electrooptic tensors from first-principles  
408 density functional perturbation theory. *Physical Review B*, 71, 125107.  
409
- 410 Wang, A., Freeman, J. J., Jolliff B. L., and Chou, I-M. (2006), Sulfates on Mars: A  
411 systematic Raman spectroscopic study of hydration states of magnesium  
412 sulfates, *Geochimica et Cosmochimica Acta*, 70, 6118–6135.  
413
- 414 Wang, A., Freeman, J.J., Chou, I.-M., Jolliff, B.L., 2011. Stability of Mg-sulfates at  
415  $-10^\circ\text{C}$  and the rates of dehydration/rehydration processes under Mars relevant  
416 conditions. *Journal of Geophysical Research* 116, E12006.  
417
- 418 Wilson, S. A., and Bish, D. L. (2012), Stability of Mg-sulfate minerals in the  
419 presence of smectites: Possible mineralogical controls on  $\text{H}_2\text{O}$  cycling and

420 biomarker preservation on Mars, *Geochimica et Cosmochimica Acta* 96, 120-  
421 133.  
422  
423 Wray, J. J., Noe Dobrea, E. Z., Arvidson, R. E., Wiseman, S. M., Squyres, S. W.,  
424 McEwen, A. S., Mustard, J. F., and Murchie, S. L. (2009), Phyllosilicates and  
425 sulfates at Endeavour Crater, Meridiani Planum, Mars, *Geophysical Research*  
426 *Letters*, 36, L21201  
427  
428 Zalkin, A., Ruben, H., and Templeton, D.H. (1964) The crystal structure and hy-  
429 drogen bonding of magnesium sulfate hexahydrate. *Acta Crystallographica*, 17,  
430 235–240.  
431  
432  
433  
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## FIGURE CAPTIONS

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440 FIGURE 1. Theoretical Raman spectra of anhydrous  $\alpha$ -MgSO<sub>4</sub>,  $\beta$ -MgSO<sub>4</sub>,  
441 kieserite MgSO<sub>4</sub>·H<sub>2</sub>O, starkeyite MgSO<sub>4</sub>·4H<sub>2</sub>O, and epsomite MgSO<sub>4</sub>·7H<sub>2</sub>O.

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445 FIGURE 2. Theoretical S<sup>34</sup>/S<sup>32</sup> partitioning as a function of temperature between  
446  $\beta$ -MgSO<sub>4</sub>, kieserite MgSO<sub>4</sub>·H<sub>2</sub>O, starkeyite MgSO<sub>4</sub>·4H<sub>2</sub>O, and epsomite  
447 MgSO<sub>4</sub>·7H<sub>2</sub>O. The results suggest that hydration favors enrichment in lighter  
448 isotopes. This feature should be visible by in situ measurements on the surface  
449 of Mars and could be related to interpret the diurnal cycle of hydration/dehydration.  
450 **m** and **n** denote the number of molecules per MgSO<sub>4</sub> unit in the two phases  
451 between which the partitioning is plotted.

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## TABLES

458

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460 Table 1.

461 Heat of hydration for the various magnesium sulfate phases considered in this  
462 study. The hydrate with  $m$  water molecules needs the amount of energy listed in  
463 the table to add  $(n-m)$  water molecules/MgSO<sub>4</sub> group unit to form a hydrate with  
464  $n$  water molecules.  $m=n=0$  is for  $\beta$ -MgSO<sub>4</sub>. Units are kJ/mol. Negative numbers  
465 favor the hydrated phase, positive numbers favor dehydration. In general higher  
466 hydrated states are preferred, especially epsomite. Hexahydrate is the only  
467 metastable phase at 0K.

468

$m$	$n$	0	1	3	4	5	6	7	11
0			-86.92	-185.98	-245.75	-307.86	130.11	-447.32	-685.31
1				-99.07	-158.83	-220.95	217.03	-360.41	-598.40
3					-59.77	-121.88	316.09	-261.34	-499.33
4						-62.11	375.86	-201.57	-439.56
5							437.97	-139.46	-377.45
6								-577.43	-815.42
7									-237.99
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473 Table 2.

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

478

m	n	(m+n)/2	$\Delta H_{\text{min}}$ (kJ/mol)
1	5	3	-0.24
1	7	4	-0.44
1	11	6	-10.70
3	5	4	-0.02
3	7	5	-0.18
3	11	7	0.24
5	7	6	-10.52

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482 Table 3.  
483 Reduced partition function ratios (the  $\beta_s^{34/32}$ ) for  $\beta$ -MgSO<sub>4</sub>, kieserite, starkeyite,  
484 and epsomite in the temperature range relevant to Mars's surface.  
485

Temperature (K)	$\beta$ -MgSO <sub>4</sub>	Kieserite, MgSO <sub>4</sub> ·H <sub>2</sub> O	Starkeyite, MgSO <sub>4</sub> ·4H <sub>2</sub> O	Epsomite, MgSO <sub>4</sub> ·7H <sub>2</sub> O
100	1.4402	1.4338	1.4265	1.4161
120	1.3396	1.3351	1.3295	1.3219
140	1.2726	1.2692	1.2647	1.2588
160	1.2249	1.2223	1.2186	1.2138
180	1.1894	1.1873	1.1842	1.1802
200	1.1621	1.1603	1.1576	1.1542
220	1.1404	1.1389	1.1366	1.1336
240	1.1229	1.1216	1.1196	1.1169
260	1.1085	1.1073	1.1056	1.1032
280	1.0965	1.0955	1.0939	1.0917
300	1.0863	1.0855	1.0840	1.0821
320	1.0777	1.0769	1.0756	1.0738
340	1.0703	1.0696	1.0684	1.0668
360	1.0639	1.0633	1.0622	1.0606
380	1.0583	1.0577	1.0567	1.0553
400	1.0534	1.0529	1.0519	1.0506

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