

Unravelling the true nature of Martian 'lh'-kieserite

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The confirmed presence of hydrous sulfates on celestial bodies in our solar system such as Mars or the icy moons of Jupiter and Saturn has been a hotly debated topic for several decades (recently e.g., Clark et al. 2005; Bishop et al. 2009; Noel et al. 2010). Especially Mg-sulfate hydrates, with the ability to change their hydration state based on local humidity and temperature, are regarded as one of the key components governing the water budget at equatorial latitudes on Mars (Milliken et al. 2007).

Furthermore, these and other sulfate compounds are supposed to play an important role on the icy moons of Jupiter and Saturn, where their presence, possibly along with pressure-induced structural changes (e.g., Meusburger et al. 2020), influences thermodynamic equilibria leading to the presence of subsurface oceans, potentially even supporting life (Solomonidou et al. 2009).

Especially kieserite, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, given its broad field of stability compared to the other hydrates, is also believed to form on the surface of the icy moons via decomposition of higher Mg-sulfate hydrates by cosmic rays and UV radiation, with the stability of the sulfate monohydrate strongly enhanced by the surrounding vacuum (Zolotov & Shock 2001).

A still unsolved enigma is the structural and spectroscopic character of the so-called 'lh'-kieserite polytype (where 'lh' stands for 'low-humidity'), which, according to dehydration experiments under simulated Martian conditions performed by Wang et al. (2009), is presumed to be the dominant variant of monoclinic kieserite on the surface of Mars. Until now, however, no thorough investigation of this new 'polytype' has been conducted.

Comparing the powder patterns of 'lh'-kieserite as documented by Wang et al. (2009) to other sulfate species, we observed a striking resemblance between this enigmatic compound and the tetragonal Mg-hydroxide sulfate hydrate ('MHS') mineral caminite. To date, the latter was found on Earth in an entirely different environment compared to that on the surface of Mars – namely in black smokers on oceanic rift zones, reflecting its experimentally confirmed reverse solubility (e.g., Hochella et al. 1983). An entire range of such MHS compounds is anticipated, where the cell metrics are dictated by variable occupancy of the Mg and H sites.

Taking the reverse solubility of the MHS mineral group into account, we designed a novel autoclave prototype, allowing venting of the aqueous solvent at maximum temperature, preventing re-dissolution of the high-temperature phase assemblage upon cooling. Indeed, we were already able to synthesize several representatives of the said tetragonal compounds as single crystals with the expected variability in the Mg- and H-site occupancy, proving the existence of an (at least partial) MHS solid solution series, with tetragonal 'MHS' (Mg-hydroxide sulfate, $c = 12.885 \text{ \AA}$; Fleet & Knipe 1997) and monoclinic kieserite ($2d_{001} = 13.499 \text{ \AA}$; Bechtold & Wildner 2016) as theoretical endmembers. As the Mg-site occupancy decreases in favour of the H content, the tetragonal c -lattice parameter lengthens, conversely to the a axis.

The comparison of powder patterns of 'lh'-kieserite and MSHH shown in Fig. 1 (using CuK α radiation) is quite conclusive: the prominent reflection doublet at 26.5 and 28° 2 θ , along with the characteristic pair at ~55° 2 θ present in both phases, strongly indicates that both compounds are indeed one and the same substance.

This leaves the question as to why the MSHH group has not been previously considered as 'lh'-kieserite. Firstly, naturally occurring minerals belonging to this series are scarce, with only the aforementioned caminite found in nature to date. Secondly, both IR and Raman spectra of kieserite and MSHH bear striking resemblance (Fig. 2), making a spectroscopic discrimination rather ambiguous, more so taking into account the limited signal-to-noise ratio of remote measurements from orbiter instruments.

Our contribution aims to corroborate the existence and properties of the MSHH mineral group, which seems, in light of the newest findings, to represent an important constituent of sulfate assemblages present on celestial bodies in our solar system.

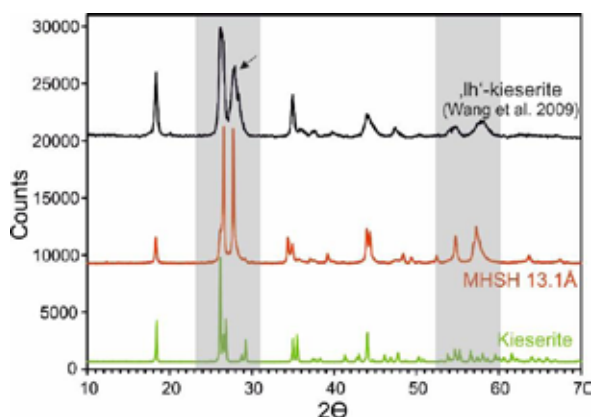


Figure 1. Comparison of the powder pattern of 'lh'-kieserite, MSHH and kieserite. Note the close match between Bragg reflections in 'lh'-kieserite and the MSHH variant with the *c*-cell parameter equal to 13.1 Å (highlighted in grey).

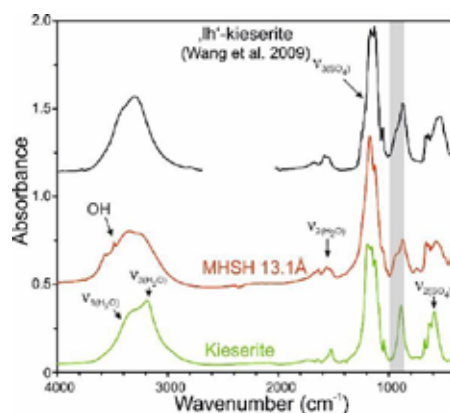


Figure 2. Close resemblance between IR spectra of 'lh'-kieserite, MSHH and kieserite. Apart from a shoulder at ~950 cm⁻¹, diagnostic for MSHH, the spectral envelopes are quite similar.

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- Bechtold A, Wildner M (2016): Crystal chemistry of the kieserite–cobaltkieserite solid solution, Mg_{1-x}Co_x(SO₄)·H₂O: well behaved oddities. - *Eur J Miner* 28, 43-52
- Bishop JL, Parente M, Weitz CM, Noe Dobrea EZ, Roach LH, Murchie LS, McGuire PC, McKeown NK, Rossi CM, Brown AJ, Calvin WM, Milliken R, Mustard JF(2009): Mineralogy of Juventae Chasma: Sulfates in the light-toned mounds, mafic minerals in the bedrock, and hydrated silica and hydroxylated ferric sulfate on the plateau. - *J Geophys Res* 114, E00D09
- Clark BC, Morris RV, McLennan SM, Gellert R, Jolliff B, Knoll AH, Squyres SW, Lowenstein TK, Ming DW, Tosca NJ, Yen A, Christensen PR, Gorevan S, Brückner J, Calvin W, Dreibus G, Farrand W, Klingelhofer G, Waenke H, Zipfel J, Bell III JF, Grotzinger J, McSween, HY, Rieder R (2005): Chemistry and mineralogy of outcrops at Meridiani Planum. - *Earth Planet Sci Lett* 240, 73-94
- Fleet ME, Knipe SW (1997): Structure of magnesium hydroxide sulfate, [2MgSO₄·Mg(OH)₂] and solid solution in magnesium hydroxide sulfate hydrate and caminite. - *Acta Cryst B* 53, 358-363

- Hochella MF, Keefer KD, deJong BHWS (1983): The crystal chemistry of a naturally occurring magnesium hydroxide sulfate hydrate, a precipitate of heated seawater. - *Geochim Cosmochim Acta* 47, 2053-2058
- Meusburger JM, Ende M, Matzinger P, Talla D, Miletich R, Wildner M (2020): Polymorphism of monohydrate sulfate kieserite under pressure and its occurrence on giant icy Jovian satellites. - *Icarus* 336, 113459
- Milliken RE, Mustard JF, Poulet F, Jouglet D, Bibring J-P, Gondet B, Langevin Y (2007): Hydration state of the Martian surface as seen by Mars Express OMEGA: 2. H₂O content of the surface. - *J Geophys Res* 112, E08S07
- Noel A, Bishop JL, Al-Samir M, Gross C, Flahaut J, McGuire PC, Weitz CM, Seelos F, Murchie S (2015): Mineralogy, morphology and stratigraphy of the light-toned interior layered deposits at Juventae Chasma. - *Icarus* 251, 315-331
- Solomonidou A, Coustenis A, Bampasidis G, Kyriakopoulos K, Moussas X, Bratsolis E, Hirtzig M (2011): Water oceans of Europa and other moons: implications for life in other solar systems. - *J Cosmol* 13, 4191-4211
- Wang A, Freeman JJ, Jolliff BL (2009): Phase transition pathways of the hydrates of magnesium sulfate in the temperature range 50°C to 5°C: Implication for sulfates on Mars. - *J Geophys Res* 114, E04010
- Zolotov MY, Shock EL (2001): Composition and stability of salts on the surface of Europa and their oceanic origin. - *J Geophys Res* 106, 32815-32827