Oral presentation

Structural and spectroscopic details of 'magnesium hydroxide sulfate hydrate' (MHSH), representing the enigmatic 'low-humidity'- kieserite on Mars

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The confirmed presence of hydrous sulfates on the surface of Mars has been a hotly debated topic for several decades (recently e.g., [1-3]). 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 minerals governing the water budget at equatorial latitudes on the 'red planet'[4]. Under laboratory conditions, an Mg-sulfate phase with vibrational spectra and a powder pattern very similar to that of kieserite ($MgSO_4 \cdot H_2O$), the so-called 'lh'-kieserite ('lh' meaning low-humidity) was obtained [5]. Until now, it was presumed to be the dominant variant of 'kieserite' on the surface of Mars.

In our studies however, we noticed a striking resemblance between this enigmatic 'lh'-kieserite and the tetragonal Mg-sulfate caminite ($MgSO_4 \cdot \frac{1}{3}Mg(OH)_2 \cdot \frac{1}{3}H_2O$) [6]. Indeed, after successful synthesis of said tetragonal phase using its reverse solubility [6] in custom-made autoclaves, we could confirm that both phases crystallize in the very same structure type with space group $I4_1/amd$. It is built from chains of partially occupied, face-sharing MgO_6 octahedra, alternatively running along [100] and [010], and stacked along the *c*-axis to a three-dimensional framework. This arrangement implies that kieserite-like, corner-sharing octahedral chains are running along the space diagonals of the tetragonal cell, explaining the above-mentioned similarity. In succession, we were able to prepare many further samples in this system, proving to be isostructural but covering a wider range of lattice parameters, varying (to date) from 5.252 to 5.194 Å and from 12.973 to 13.196 Å for the negatively correlated tetragonal *a*- and *c*-axis lenghts, respectively. The changes are due to variable occupancies of the Mg and H sites (with $2H^+$ substituting for Mg^{2+}). Hence, members of this 'MHSH' ('Mg-Hydroxide Sulfate Hydrate') group form a solid solution with theoretical endmembers kieserite (monoclinic, $C2/c$, $a_{red} = 5.149$, $2d_{001} = 13.499$ Å) and 'MHS' [7] ('Mg-Hydroxide Sulfate', $2MgSO_4 \cdot Mg(OH)_2$, tetragonal, $P4_32_12$, $d_{110} = 5.271$, $c = 12.885$ Å).

Contrary to kieserite, MHSH members apparently do not incorporate cosmochemically relevant divalent transition metal cations, such as Fe, Ni, Mn or Co. The sole exception seems to be Zn^{2+}, with an atomic radius close to that of Mg^{2+}, and probably due to the amphoteric nature of ZnO and thus its better solubility: MgO/ZnO was used to provide the necessary excess of divalent cations in the starting batches. As with MHSH, the 'ZnHSH' compounds show a similar yet less pronounced lattice parameter variation governed by changes in the Zn and H site occupancies.

FTIR and Raman spectra as well as powder X-ray patterns of MHSH and ZnHSH are indeed similar to those of kieserite, 'lh'-kieserite [5], and caminite [6], the latter being the only member of the MHSH group found in nature to date. Best matches of both vibrational spectra and powder X-ray data can be seen between 'lh'-kieserite and MHSH compounds with an elevated *c* lattice parameter (~13.15 Å and above). Band positions in vibrational spectra change systematically along the MHSH series: with increase of the *c* lattice parameter from ~13.1 to ~13.2 Å, bands related to vibrations of the sulfate group shift to lower wavenumbers (by several cm^{-1} at most); the band corresponding to the symmetric stretching mode of the H_2O molecule moves to lower wavenumbers as well (from 3260 to 3220 cm^{-1}), whereas the wavenumber of the OH stretching fundamental significantly increases from 3260 to 3537 cm^{-1}. Concerning the ZnHSH-analogues with c ~13.1 Å, most spectral features are shifted to lower wavenumbers in respect to MHSH, by 15-30 cm^{-1} for sulfate-related bands, by 100 cm^{-1} for the $\nu_{1(H_2O)}$ vibration, whereas the OH absorption band is found at a much higher wavenumber of 3472 cm^{-1} (compared to 3332 cm^{-1}), despite being less pronounced.

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