

**Gamma-CaSO<sub>4</sub> with Abnormally High Stability from Hyperarid Region on Earth and from Mars** Erbin Shi<sup>1,2</sup>, Alian Wang<sup>1</sup>, Huafang Li<sup>3</sup>, Ryan Ogliore<sup>4</sup>, Zongcheng Ling<sup>1</sup>, Shandong Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, School of Space Science and Physics, Institute of Space Sciences, Shandong University, Weihai, Shandong, 264209, China. <sup>2</sup>Department of Earth & Planetary Sciences and McDonnell Center for the Space Sciences Washington University in St. Louis, MO, 63130, USA; <sup>3</sup>The Institute of Materials Science & Engineering, Washington University in St. Louis, MO, 63130, USA. <sup>4</sup>Department of Physics and McDonnell Center for the Space Sciences Washington University in St. Louis, MO, 63130, USA; (shierbin1990@gmail.com)

**Introduction:** The ordinary gamma phase of anhydrous calcium sulfate ( $\gamma$ -CaSO<sub>4</sub>) is not stable in the laboratory, even at low relative humidity (RH). When being exposed to air, it absorbs atmospheric H<sub>2</sub>O immediately and converts to bassanite (CaSO<sub>4</sub>·0.5H<sub>2</sub>O) within a few seconds [1-4]. The structure of  $\gamma$ -CaSO<sub>4</sub> is very similar to that of bassanite, both have continuous tunnels along the c-axis ([001]). The cross-sections of their tunnels, evaluated by the distances between the corner oxygens of (SO<sub>4</sub>) tetrahedra and (CaO<sub>6</sub>) octahedra that form the wall of a tunnel, are between 4 to 5.5 Å in both structures. The only difference is that the tunnels in bassanite are partially filled with H<sub>2</sub>O, while the tunnels in  $\gamma$ -CaSO<sub>4</sub> are empty. Because of their structural similarity, it is very difficult to distinguish them using XRD technology, but quite straightforward using Raman spectroscopy, by H<sub>2</sub>O peak of bassanite (at 3555 cm<sup>-1</sup>), and by  $\nu_1$  peak positions (1026 cm<sup>-1</sup> vs. 1015 cm<sup>-1</sup>).

However,  $\gamma$ -CaSO<sub>4</sub> was found stable in the soil or salt samples from Atacama Desert (Chile), White Sands (US), Da Langtan of Qinghai-Tibet Plateau (China), and in Martian meteorite MIL03346, even after those samples were kept in ambient lab-conditions for years [5-8].

*Why  $\gamma$ -CaSO<sub>4</sub> from hyperarid regions on Earth or Mars show unusual stability?* Two issues need to be understood: (1) what is the reason that caused this unusual stability, structural or chemical? (2) is there a relationship between these structural or chemical characters to the hyperarid environment?

To answer these questions, we re-examined an Atacama soil that contains about 20% of  $\gamma$ -CaSO<sub>4</sub> and the  $\gamma$ -CaSO<sub>4</sub> in Martian meteorite MIL03346,168 using multiple micro-analysis technologies.

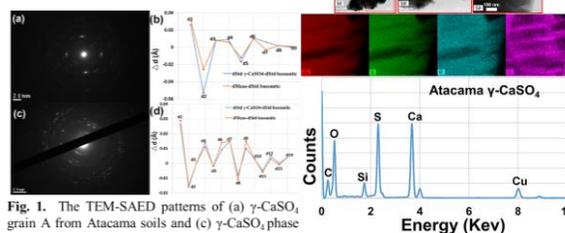
**Experiments:** Three grains of  $\gamma$ -CaSO<sub>4</sub> were picked from Atacama soil using its unique Raman  $\nu_1$  peak at 1026 cm<sup>-1</sup>. Then these single grains were ground, placed on a copper grid, and coated with carbon. These grains were measured firstly using transmission electron microscope-energy dispersive spectrometer (TEM-EDX) for their chemical characters, then using transmission electron microscope-selected area electron diffraction (TEM-

SAED) system for their structural characters. For the  $\gamma$ -CaSO<sub>4</sub> in Martian meteorite MIL03346,168 (found in veins), we first cut off a few micro-pieces using Focus Ion Beam technology (FIB), and then run the same measurements as on Atacama  $\gamma$ -CaSO<sub>4</sub>, electron energy loss spectroscopy (EELS) in TEM/STEM, and nanoscale secondary ion mass spectrometry (NanoSIMS). All instruments used in this study are at Washington University in St. Louis.

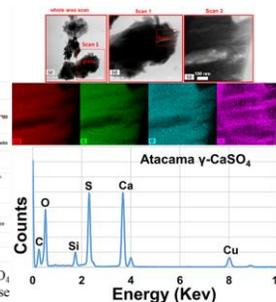
**Results and discussion:** Fig. 1a shows the SAED pattern from a grain of Atacama  $\gamma$ -CaSO<sub>4</sub>, and in Fig. 1c shows the SAED from a  $\gamma$ -CaSO<sub>4</sub> phase in a FIB-cut micro-pieces of MIL03346, 168. The d spacings in the structures of two samples were calculated based on the measurements of 1/2d or 1/d in these patterns. The overall uncertainty for this type of measurements and calculations is 2%. We selected to show the differences between d spacings of two phases, i.e., to compare the  $\square d_{\text{meas}} = (d_{\text{meas-}\gamma\text{-CaSO}_4} - d_{\text{std-bassanite}})$  and the  $d_{\text{std}} = (d_{\text{std-}\gamma\text{-CaSO}_4} - d_{\text{std-bassanite}})$ , which were plotted as an orange line and a blue line respectively in Fig. 1b and 1d.

As shown in Fig. 1b, the orange line has a trend of variation very similar to that of the blue line, which indicates that the measured Atacama  $\gamma$ -CaSO<sub>4</sub> sample (grain A) has a structure very similar to that of standard  $\gamma$ -CaSO<sub>4</sub>. In addition, another two grains of Atacama  $\gamma$ -CaSO<sub>4</sub> have same results as grain A. It means all three grains of Atacama  $\gamma$ -CaSO<sub>4</sub> have structures similar to that of standard  $\gamma$ -CaSO<sub>4</sub>. The TEM-SAED pattern from the Martian  $\gamma$ -CaSO<sub>4</sub> phase in a FIB-cut micro-pieces from a vein in MIL03346, 168 was shown in Fig. 1c. The measurements and calculations similar to Fig. 1a, 1b were used. Obviously, the trend of variation in orange line is very similar to that of blue line. It suggests that the Martian  $\gamma$ -CaSO<sub>4</sub> phase in FIB-cut micro-piece has a structure similar to that of standard  $\gamma$ -CaSO<sub>4</sub>. Moreover, after the FIB and TEM-SAED measurements, the FIB-cut micro-piece was re-checked using Raman spectroscopy, the characteristic Raman peak 1026 cm<sup>-1</sup> of  $\gamma$ -CaSO<sub>4</sub> was found, thus confirmed the finding of TEM-SAED.

From that, the TEM-SAED results on Atacama  $\gamma$ -CaSO<sub>4</sub> and Martian  $\gamma$ -CaSO<sub>4</sub> support that they all have structure very similar to that



**Fig. 1.** The TEM-SAED patterns of (a)  $\gamma$ -CaSO<sub>4</sub> grain A from Atacama soils and (c)  $\gamma$ -CaSO<sub>4</sub> phase in a FIB-cut micro-pieces from a vein in MIL03346, 168. (b) Atacama  $\gamma$ -CaSO<sub>4</sub> grain A, and (d) Martian  $\gamma$ -CaSO<sub>4</sub> phase in a FIB-cut micro-pieces.



**Fig. 2.** Top row: Three-step "zone-in" EDX mapping on Atacama  $\gamma$ -CaSO<sub>4</sub> (Grain A), from Whole Area Scan, to Scan 1, to Scan 2. Bottom row: EDS spectra of  $\gamma$ -CaSO<sub>4</sub> from Atacama soil sample corresponding the element mapping of Scan 2 (grain A);

of standard  $\gamma$ -CaSO<sub>4</sub>. It means that the major reason for the abnormal stability of these  $\gamma$ -CaSO<sub>4</sub> is not the structural changes. At least, their structural changes are not large enough to be detectable by TEM-SAED technology.

TEM-EDS mapping and EDS spectra obtained from the three grains (A, B, C) of Atacama  $\gamma$ -CaSO<sub>4</sub> show that they are not pure  $\gamma$ -CaSO<sub>4</sub>. For example, a three-step “zoom-in” EDS elementary mapping was made on the grain A of Atacama  $\gamma$ -CaSO<sub>4</sub>. Further zoomed into Scan 2 (Fig 2), Si is the only impurity in Atacama  $\gamma$ -CaSO<sub>4</sub>. The EDS mapping revealed that Si is quasi-homogeneously distributed in the matrix of Atacama  $\gamma$ -CaSO<sub>4</sub>, co-existing with Ca, S, and O.

The TEM-EDS mapping and EDS spectra of  $\gamma$ -CaSO<sub>4</sub> phase in FIB-cut micro-pieces also revealed a different chemical feature (Fig. 3). In addition to Si, this Martian  $\gamma$ -CaSO<sub>4</sub> also contains P as an impurity. Both Si and P are quasi-homogeneously distributed in the matrix, co-exist with Ca, S, and O. Using EELS and NanoSIMS analysis, the existences of Si and P within the Martian  $\gamma$ -CaSO<sub>4</sub> were furtherly confirmed.

The Raman spectra of Atacama  $\gamma$ -CaSO<sub>4</sub> and Martian  $\gamma$ -CaSO<sub>4</sub> in Fig. 4 (a, b) revealed many additional peaks in the range of 100-600 cm<sup>-1</sup> that do not belong to  $\gamma$ -CaSO<sub>4</sub> or any sulfates. Many of them are in the spectral region of Si-O<sub>b</sub> vibrations. The positions of additional peaks in Fig. 4a and 4b do not match with any crystalline SiO<sub>2</sub> or other known silicates. Being the only chemical impurity in Atacama  $\gamma$ -CaSO<sub>4</sub>, Si atoms could only bond with oxygen atoms in SO<sub>4</sub> tetrahedra or in CaO<sub>6</sub> octahedra, to form Si-O<sub>b</sub>-S or Si-O<sub>b</sub>-Ca bonds.

To combine the fact the  $\gamma$ -CaSO<sub>4</sub> originated from the hyperacid region on Earth and on Mars can maintain an extraordinary stability in humid environment with the finding of quasi-homogeneous distribution of Si in Atacama  $\gamma$ -CaSO<sub>4</sub> (Si & P in Martian  $\gamma$ -CaSO<sub>4</sub>) and Si-O<sub>b</sub>-(S or Ca) bonding suggested by Raman spectroscopy, we would suggest that the tunnels in these  $\gamma$ -CaSO<sub>4</sub> phases were filled-up by impurities (Si and P), which have prevented the entrance of atmospheric H<sub>2</sub>O from humid air afterward.

A synthesized calcium sulfate, hemimethanolate CaSO<sub>4</sub>·0.5CH<sub>3</sub>OH, is a great example, in which the methanol molecule CH<sub>3</sub>OH enter the structural tunnels [4]. In addition, this CH<sub>3</sub>OH to H<sub>2</sub>O substitution changed the crystal morphology, from a hexagon column (of bassanite) to a shape of cauliflower (of CaSO<sub>4</sub>·0.5CH<sub>3</sub>OH), but interestingly did not change much of its structure parameters from a standard

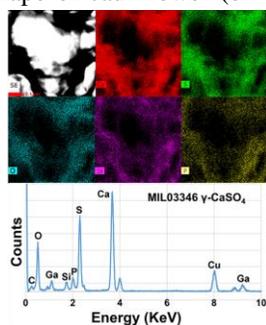


Fig. 3. SE image, EDS mapping, and EDS spectrum of a  $1 \times 1 \mu\text{m}$  area of  $\gamma$ -CaSO<sub>4</sub> phase in FIB-cut micro-pieces.

$\gamma$ -CaSO<sub>4</sub> structure [4]. Similarly, in the two studied impure  $\gamma$ -CaSO<sub>4</sub> samples formed at hyperarid region on Earth and Mars, we observed the crystal morphology change, almost non-detectable structural changes, enriched Si impurity (Si & P in Martian  $\gamma$ -CaSO<sub>4</sub>), and Si-O<sub>b</sub> vibrational peaks.

Moreover, in the Raman spectra of  $\gamma$ -CaSO<sub>4</sub> from MIL03346,168 (Fig. 4b), a weak but sharp peak appeared at 980 cm<sup>-1</sup> (at the left-wing of 1026 cm<sup>-1</sup> peak), which does not exist in the spectrum of Atacama  $\gamma$ -CaSO<sub>4</sub> (Fig. 4a). This peak position is suggestive of a P-O vibrational peak, near the  $\nu_1$  peak (961 cm<sup>-1</sup>) in apatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH, Cl, F)). Similar to the cases of Si atoms or Si-O bonds or CH<sub>3</sub>OH molecules, the structural tunnels in  $\gamma$ -CaSO<sub>4</sub> structure also would be able to tolerant the entrance of P atoms or bonded P-O.

**Conclusions:** In this study, we used multiple microanalysis to characterize the chemical and structural properties of two such  $\gamma$ -CaSO<sub>4</sub>: from an Atacama soil and from veins in Martian meteorite MIL03346,168. We found the abnormally high stability of those  $\gamma$ -CaSO<sub>4</sub> from hyperarid environments was due to the chemical impurities, with non-detectable structural distortion. Silicon was determined quasi-homogeneously distributed in Atacama  $\gamma$ -CaSO<sub>4</sub>, and silicon plus phosphorus in martian  $\gamma$ -CaSO<sub>4</sub>. These impurities filled the structural tunnels, blocked the entrance of atmospheric H<sub>2</sub>O, and thus maintained the abnormally high stability of these  $\gamma$ -CaSO<sub>4</sub>. In future, the geological process of the impurities enters the  $\gamma$ -CaSO<sub>4</sub> will be discussed and advance to know the geology history of Mars.

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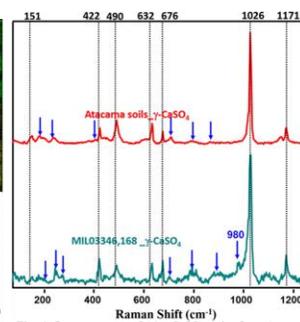


Fig. 4. Raman spectra of (a)  $\gamma$ -CaSO<sub>4</sub> grains from Atacama soil, and (b) from a spot in the  $\gamma$ -CaSO<sub>4</sub> phase in a FIB-cut micro-piece of Martian meteorite MIL03346,168.