

**MARTIAN SULFATES: GYPSUM CRYSTAL CHEMISTRY AND CHARACTERIZATION OF TWO TERRESTRIAL ANALOGS.** J.J. Papike, ([jpapike@unm.edu](mailto:jpapike@unm.edu)), P.V. Burger, J.M. Karner, and C.K. Shearer, Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico 87131

**INTRODUCTION:** Gypsum, along with kieserite and jarosite, are the most positively identified sulfates on Mars. Large gypsum sand dunes exist near the north pole of Mars (Fishbaugh et al. [1]) and bear similarities to the gypsum sand dunes near White Sands, New Mexico (Langford [2]). We use a sample from White Sands as a terrestrial analog of evaporitic gypsum and gypsum samples from the precious metal deposit at Goldfield, Nevada (Vikre et al. [3]; Papike et al. [4]) as a terrestrial analog of hydrothermal gypsum. We will review gypsum crystal chemistry and present new EMP and SIMS analyses for the two terrestrial gypsum suites.

**CRYSTAL CHEMISTRY:** The crystal structure information is derived from a neutron diffraction refinement by Cole and Lancucki [5]. We present the crystal structure illustrations (Figure 1a,b) in space group C2/c with cell dimensions  $a = 5.67$ ,  $b = 15.20$ , and  $c = 6.53$  Å. The beta angle is 118.6 degrees. The formula units  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  per unit cell,  $Z = 4$ . Thus there are 4 Ca, 4 S, 16 O, and 8  $\text{H}_2\text{O}$  groups per unit cell. Figure 1a (projection down the c-axis) shows the C-centered nature of the unit cell and all symmetrically distinct atoms. There are three symmetrically independent oxygen atoms O(I), O(II), and O(W) and two symmetrically independent hydrogen atoms H(I) and H(II). The Ca and S atoms are in special positions and sit on 2-fold axes (Figure 1b). The important 8-coordinated Ca-site has 8 ligands, 6 oxygen atoms and 2 oxygen atoms in  $\text{H}_2\text{O}$  groups. The mineral Churchite,  $\text{REE}^{3+}\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , is isostructural with gypsum and may suggest a charge-balancing mechanism for the incorporation of REEs and Y, namely REE-P for Ca-S. Although most gypsum is of nearly stoichiometric end-member composition there can be significant Sr substitution. The partition coefficient for Sr gypsum/fluid is  $\sim 0.5$  (Kushnir [6]) but has a range of values from 0.2 - 0.7. **EMP ANALYSES:** Analyses presented in Table 1 were performed on a JEOL 8200 EMP at the Department of Earth and Planetary Sciences/Institute of Meteoritics, University of New Mexico. The EMP is equipped with five wavelength dispersive (WD) X-ray spectrometers and an ultrathin-window energy dispersive spectrometer. Heating under the electron beam and resulting volatilization of  $\text{H}_2\text{O}$  and S are a major concern during analysis of gypsum. Optimum conditions for WD analysis of major and minor elements were determined to be a 1 nA beam current and a 30  $\mu\text{m}$  spot size at 15kV. We normalized the data to 6 oxygens per formula. We cannot analyze

for H with the electron microprobe, but the stoichiometry we determine for these samples argues for 2  $\text{H}_2\text{O}$  groups.

**SIMS ANALYSES:** SIMS analyses were conducted using an oxygen beam with a 10 kV primary accelerating voltage, 20 nA beam current, and a -75 volt offset in order to minimize isobaric interferences. Ion yield was calibrated using  $^{44}\text{Ca}$ ; Ca concentration had been independently determined using the EMP. Elements were individually calibrated using two in-house apatite standards, Durango and ORNL. Barium analyses are based solely on the NIST 610 synthetic glass standard. The SIMS data are presented in Table 2 and illustrated (chondrite normalized) in Figures 2a, b. Although the REEs are in low concentration, mainly below one times chondrite, the pattern shapes are remarkably similar. Figure 2a shows the REE patterns for 5 different White Sands gypsum grains and Figure 2b compares the average REEs for White Sands grains with the REEs for the two Goldfield samples. These REE concentrations are significantly lower than those measured in gypsum from martian meteorite Nakhla by Bridges and Grady [7] who found REE concentrations up to 100 times chondrite. The Ba concentration are also low, below 2 ppm. Strontium concentrations are higher and variable, Goldfield 200-300 ppm and White Sands 1000-3000 ppm. If we assume a  $D_{\text{Sr}}$  of 0.5 then the solutions that precipitated the gypsum, now found in the White Sand dunes, contained 2000 to 6000 ppm or between 0.2 and 0.6 wt.% Sr. These variations likely reflect different stratigraphic positions in the Permian evaporitic Yeso source formation located in the San Andres Mountains located in SW New Mexico [2]. **ACKNOWLEDGEMENTS:** We thank Laura Crossey, UNM, for the White Sands sample and Peter Vikre, USGS, for the Goldfield samples. This research was supported by a NASA Cosmochemistry grant to JJP.

**REFERENCES:** [1] Fishbaugh et al. (2007) JGR, 112, EO7002. [2] Langford (2003) Quaternary International, 104, 31-39. [3] Vikre et al. (2005) USGS Open-File Report 2005-1258. [4] Papike et al. (2006) Am. Min., 91, 1197-1200. [5] Cole and Lancucki (1973) Acta Cryst. B30, 921-929. [6] Kushnir (1982) GCA, 46, 433-446. [7] Bridges and Grady (2000) EPSL, 176, 267-279.

Figure 1 a.

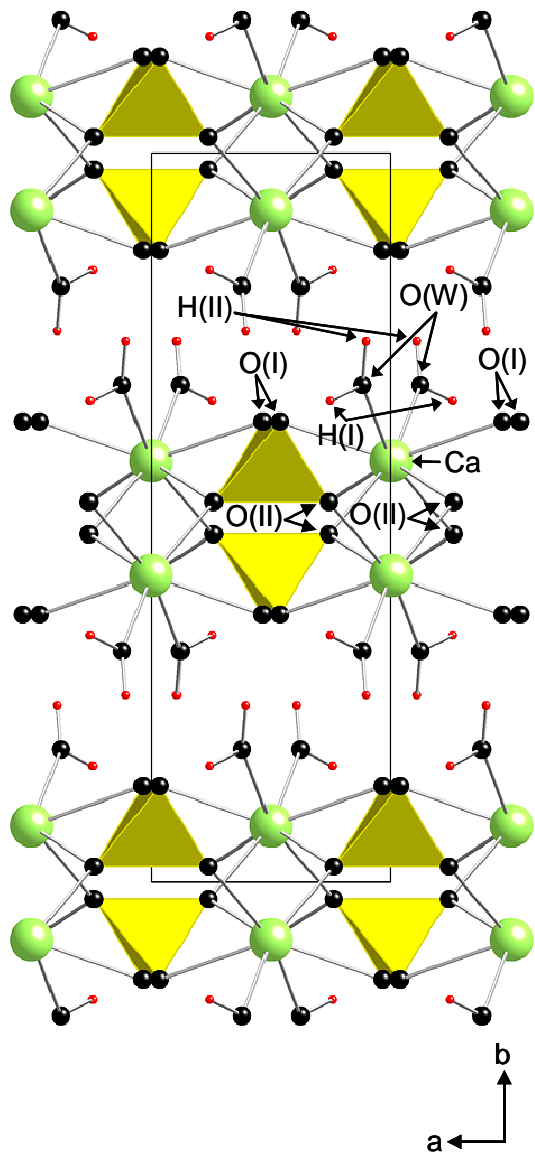


Figure 1 b.

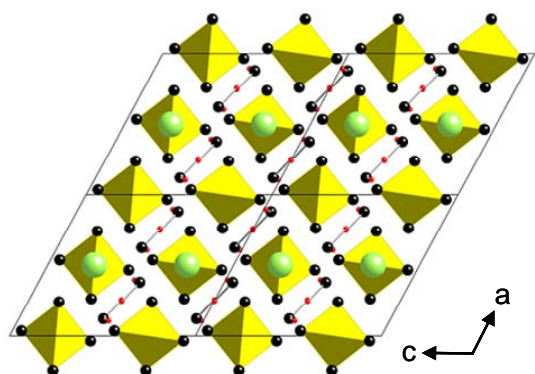


Figure 2a, b. REE patterns for gypsum.

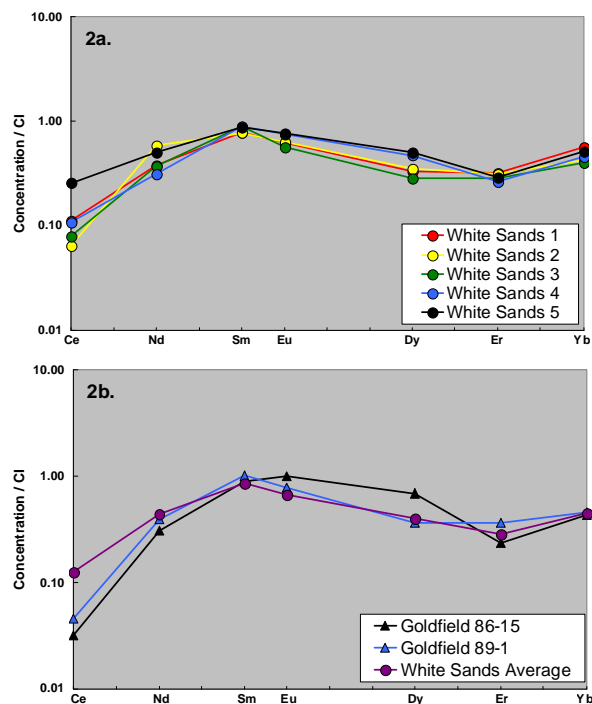


Table 1. EMP analyses of gypsum

Probe point	ws-12	ws-15	ws-18	ws-20	89-1,2	89-1,10	89-1,14	89-1,19	86-15,7	86-15,14
SrO	0.19	b.d.	0.18	0.16	b.d.	b.d.	0.07	b.d.	0.08	0.09
SO <sub>2</sub>	44.69	45.0	45.3	46.0	46.6	46.1	46.2	46.5	45.6	44.8
Na <sub>2</sub> O	0.03	b.d.	0.07	b.d.	b.d.	0.06	0.06	b.d.	b.d.	b.d.
Fe <sub>2</sub> O <sub>3</sub>	b.d.	b.d.	0.22	0.10	b.d.	0.06	b.d.	0.05	b.d.	b.d.
CaO	34.12	33.8	33.7	33.3	32.6	32.7	32.8	32.4	33.2	33.6
MgO	0.11	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.09	0.07
K <sub>2</sub> O	0.03	0.05	b.d.	b.d.	b.d.	0.04	0.04	b.d.	b.d.	b.d.
Al <sub>2</sub> O <sub>3</sub>	0.29	b.d.	b.d.	b.d.	b.d.	b.d.	0.08	b.d.	b.d.	0.06
BaO	b.d.	b.d.	0.03	b.d.	b.d.	b.d.	0.08	b.d.	0.12	0.13
(H <sub>2</sub> O)*	20.54	21.2	20.5	20.4	20.8	21.0	20.7	21.1	20.9	21.2
(Total)	100	100	100	100	100	100	100	100	100	100
Cations based on 6 oxygens										
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.97	0.97	0.99	1.00	1.00	0.99	1.00	1.00	0.99	0.97
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe <sup>3+</sup>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	1.06	1.04	1.05	1.03	1.00	1.01	1.01	0.99	1.03	1.04
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H	3.98	4.07	3.96	3.94	3.98	4.02	3.97	4.02	4.02	4.09
Total	6.04	6.09	6.01	5.97	5.98	6.02	5.99	6.02	6.04	6.10

b.d. = below detection  
 \*Calculated by difference from assumed 100% sum

Table 2. SIMS analyses of gypsum.

Sample	Sr ppm	Ba ppm	Ce ppm	Nd ppm	Sm ppm	Eu ppm	Dy ppm	Er ppm	Yb ppm
WS Avg.	1597.47	0.91	0.14	0.36	0.22	0.06	0.15	0.07	0.12
GF 86-15	219.78	0.06	0.04	0.25	0.23	0.10	0.27	0.06	0.11
GF 89-1	290.01	0.08	0.05	0.33	0.26	0.08	0.14	0.09	0.11