

SPECIATION OF SULFUR IN CARBONATES IN A 4.1-BILLION-YEAR-OLD MARTIAN METEORITE.

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Introduction: Previous Mars explorations showed that liquid water existed on the Martian surface [1]. A 4.1-billion-year-old (Ga) Martian meteorite, Allan Hills (ALH) 84001 [2], contains carbonate minerals that are interpreted to have crystallized from the surface water of ~3.9–4.0 Ga on Mars [3, 4]. Sulfur, a redox sensitive element, is a promising tracer for constraining the oxidation process. Speciation analysis on S in carbonate provides information on the depositional environment of the carbonate [5]. In order to determine the S speciation, X-ray Absorption Near Edge Structure (XANES) analysis was performed. This study reports the presence of trace amounts of S in the ALH carbonates as carbonate associated sulfate (CAS).

Method: A thin section of ALH 84001, 81 was allocated from the NASA Johnson Space Center in Houston, Texas. We obtained the back scattered electron (BSE) and X-ray images with SEM-EDS at ELSI and ISAS. Major element compositions of the carbonates were determined with EPMA at ELSI and ISAS (15 kV, 20 nA, beam size: 1 μm in diameter). The peak and background measurement times were 20 s and 10 s, respectively. Four separated areas (~500 μm square) with the characteristic carbonate aggregates were observed.

Prior to the XANES analysis, X-ray fluorescence (XRF) maps (scanned in 20 μm step) were obtained to determine analytical spots with referring to the BSE and X-ray images (Fig. 1). The S K-edge (2472 eV) XANES spectra were measured at BL27SU of the SPring-8 synchrotron radiation facility. The X-ray beam was focused using a K-B mirror to a final spot size of 15 (H)

$\mu\text{m} \times 15$ (V) μm . The X-ray energy was calibrated with the peak top of the sulfate (gypsum) at 2480 eV.

Results: We classified the carbonates in our sample into 3 types following the petrographic definition [6]: rosette, slab carbonate, post-slab magnesite. The grain size of characteristic carbonates, which are called "Rosette", varies from approximately 50 to 100 μm (Fig. 1). The quantitative analysis determines that the ALH carbonates in the thin section have a compositional range of MgO (14–41 wt.%), FeO (3–25 wt.%), CaO (3–26 wt.%), and MnO (< 4 wt.%). The XANES spectra showed a diagnostic signature of oxidized S [S(VI) (2480 eV)] in all of the analytical points (N = 30, 27 carbonates and 3 maskelynites) (Fig. 2). X-ray absorption peaks corresponding to S(–II) (2468 eV), and S(IV) (2476 eV) were observed in 9, and 29 analytical spots, respectively. The spectra obtained in 5 analytical spots present a broad peak at around 2472 eV which corresponds to the organic S species except for organosulfate. The number of peaks observed for each chemical species according to carbonate classification is summarized in Table 1.

Discussion:

S(VI). There are two possible explanations for the presence of S(VI) in the ALH carbonates: i) coprecipitation of sulfate minerals with carbonates, or

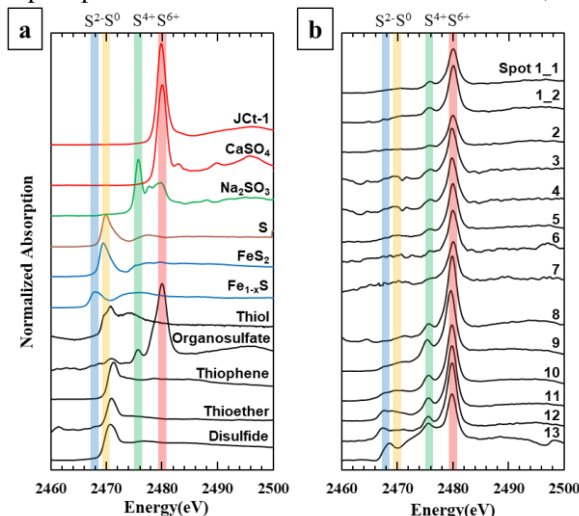


Fig. 2. Sulfur K-edge XANES spectra. a, Spectra of reference samples. b, Spectra of ALH carbonates. The red (2480 eV), green (2476 eV), yellow (2472 eV), and blue (2468 eV) lines indicate the absorption peaks of S (VI), S(IV), S(0), S(–II), respectively.

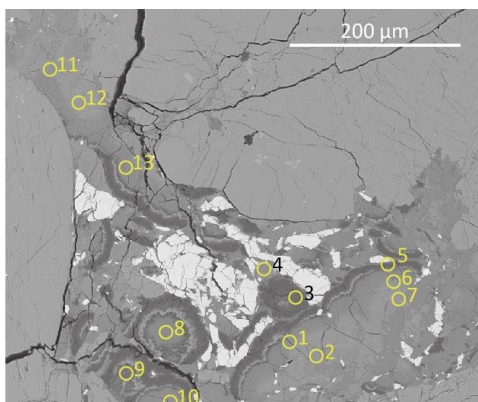


Fig. 1. A BSE image of the ALH carbonates (yellow circle, data are in Fig. 2b).

	N	S(VI)	S(IV)	S(-II)	Organic S
RC	12	12	12	4	1
Slab	14	14	14	4	4
PSM	1	1	1	0	0
Msk	3	3	2	1	0
Sum.	30	30	29	9	5

Table 1. The number of peaks observed for each chemical species according to carbonate classification. N is the total number of analytical spots. Abbreviation: RC, rosette carbonate; Slab, slab carbonate; PSM, post-slab carbonate; Msk, maskelynite.

ii) substitution of sulfate ion (SO_4^{2-}) for carbonate ion (CO_3^{2-}) during precipitation of carbonates (CAS). Our XANES spectra of the ALH carbonates did not show oscillations in the energy region of 2485–2500 eV, indicating the presence of CAS. We performed thermodynamic calculations using Geochemist's Workbench (GWB) to estimate Eh-pH condition in the fluid system of H^+ - e^- - H_2O - SO_4^{2-} - Fe^{2+} - HCO_3^- - Al^{3+} - $\text{SiO}_2(\text{aq})$ - Mg^{2+} - Mn^{2+} - K^+ under 0.1 bar at 293 K [7]. Thermodynamic calculations further indicated that S mainly occurred as sulfate ion in the water at Eh-pH conditions where the ALH carbonate precipitated (Fig. 3). These results suggest that the observed S(VI) species could have occurred as CAS in the ALH carbonates under the fluid conditions of $\text{pH} > 6.6$ and $-0.71 < \text{Eh}(\text{V}) < 0.85$.

Organic S. A linear combination fitting (LCF) showed that the XANES spectra at around 2470–2475 eV are better reproduced when organic S was included. The XANES-LCF suggested the presence of the organic S in 5 analytical spots of the ALH carbonates. Assuming that the organic S is of Martian origin, S would have played an important role in organic chemical reaction on Mars ~4 billion years ago.

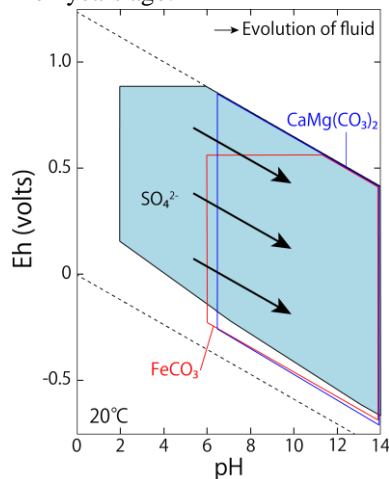


Fig. 3. Eh-pH conditions for sulfur in the aqueous solution coexisting with the ALH carbonates at ~4.0 Ga.

Models. Our XANES analysis indicates the presence of CAS in the ALH 84001 carbonates. The possible source of the CAS-forming fluid in ancient Mars is (Case-1) groundwater [8] or (Case-2) surface water [1] (Fig. 4). The source water interacted with the parent rock (ultramafic cumulate) of ALH 84001. The water-rock interaction could have progressively increased pH of the CAS-forming fluid (Fig. 3), precipitating the ALH 84001 carbonates. The microcrystals of iron-sulfide might have mechanically mixed into the carbonates during the carbonate formation [9].

Conclusion: We analyzed S species in the ALH 84001 carbonates using XANES. The S(VI) signature was detected from all the analytical spots, whereas the possible presence of S(IV) and S(-II) was suggested in some analytical spots. The origins of S(VI) in the ALH carbonates could represent CAS. The XANES-LCF suggested the presence of the organic S in the ALH carbonates. We proposed the model that explained the incorporation of S into ALH carbonates underground.

References: [1] Carr M. H. (2007) *Cambridge University Press*. [2] Lapen T. J. et al. (2010) *Science*, 328(5976), 347-351. [3] Halevy, I. et al. (2011) *Proceedings of the National Academy of Sciences*, 108(41), 16895-16899. [4] Borg L. E. et al. (1999) *Science*, 286(5437), 90-94. [5] Busenberg E. and Plummer L. N. (1985) *Geochimica et Cosmochimica Acta*, 49(3), 713-725. [6] Corrigan C. M. and Harvey R. P. (2004) *Meteoritics & Planet. Sci.*, 39(1), 17-30. [7] Melwani Daswani M. et al. (2016) *Meteoritics & Planetary Sci.*, 51(11), 2154-2174. [8] Michalski, J. R. et al. (2013) *Nature Geoscience*, 6(2), 133. [9] Thomas-Keprta K. L. et al. (2009) *Geochimica et Cosmochimica Acta*, 73(21), 6631-6677.

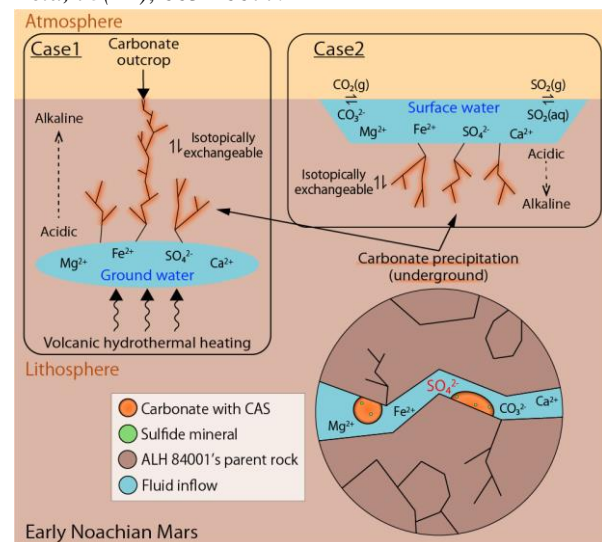


Fig. 4. Proposed models that explain the incorporation of sulfur into carbonates of ALH 84001.