

Sulfur species in carbonates of a 4.1-billion-year old Martian meteorite constraining conditions of water on ancient Mars

*Kajitani Iori^{1,2}, Ryoichi Nakada³, Mizuho Koike¹, Gaku Tanabe⁴, Tomohiro Usui^{1,5}, Tetsuya Yokoyama⁴, Keisuke Fukushi⁶

1. Institute of Space and Astronautical Science, 2. The University of Tokyo, 3. Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 4. Tokyo Institute of Technology, 5. Earth-Life Science Institute, Tokyo Institute of Technology, 6. Kanazawa University

Introduction

Geological and geomorphological evidence suggests the presence of liquid water on the Martian surface in the past [1]. A 4.1-billion-year old (Ga) Martian meteorite, Allan Hills (ALH) 84001 [2], has trace amounts of carbonates (ALH carbonates) that are interpreted to have formed from Martian near-surface fluids at ~3.9–4.0 Ga [3, 4]. Carbonates on Earth can contain trace amounts of sulfur [5]. Sulfur, a redox-sensitive element, is a promising tracer for constraining the oxidation process. In this study, we conducted sulfur K-edge X-ray absorption near edge structure (μ -XANES) analyses to estimate a possible redox condition of the aqueous fluids in the 4 Ga Martian near-surface system.

Methods

Sulfur K-edge XANES spectra were measured at BL27SU of SPring-8. The X-ray beam was focused to a final spot size of 15 (H) \times 15 (V) μm^2 . Thermodynamic calculations were performed to estimate Eh-pH conditions of the relevant aqueous and mineral species at 293K [6].

Results and Discussion

The μ -XANES spectra showed a diagnostic signature of oxidized sulfur [S(VI)] in all of the analytical points (N = 30). X-ray absorption peaks corresponding to S(–II) and S(IV) were observed in 2 and 26 analytical spots, respectively. XANES spectra indicated that a possible explanation for the presence of S(VI) in the carbonates is a substitution of sulfate ion (SO_4^{2-}) for carbonate ion (CO_3^{2-}) during precipitation of carbonates (i.e., carbonate associated sulfate: CAS) [5]. Results of the thermodynamic calculations suggested that conditions of the fluid that formed ALH carbonates range from approximately 9 to 11 for pH and –0.5 to 0.8 for Eh (V). The S(IV) signature may be either i) the analytical artifact (e.g., photoreduction of sulfate), or ii) an endogenous sulfite phase in the carbonates. The S(–II) signature is explained by the presence of iron-sulfide microcrystals [7].

An incorporation mechanism of sulfur into the ALH carbonates was proposed based on the results of our μ -XANES analyses and the thermodynamic calculations. The water-rock reaction with the parent rock of ALH 84001 gradually increased the pH of the fluid and precipitated CAS-bearing ALH carbonates. The microcrystals of iron-sulfide were mixed into the ALH carbonates during the formation. The possible source of the CAS-forming fluid in ancient Mars is either groundwater [8] or surface water [1]. In either case, this water source should have been isotopically exchangeable to the atmosphere [9].

The virtue of our model is that it would provide a plausible explanation about the missing carbon sink proposed by atmospheric escape models [10,11]. The source water should have had originally an acidic

to neutral pH condition under which any carbonates are unstable. The original acidic/neutral pH condition suggests that the carbonate formation should have taken place underground in ancient Mars, implying the existence of subsurface carbonate storage as a dominant carbon sink even in the present Mars.

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