Finding of oxidized sulfur species in carbonates from a Martian meteorite Allan Hills 84001 using μ-XANES

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The widespread evidence of liquid water on Mars has led to detailed studies of Martian habitable surface environments [1]. Among them is the geochemical study of carbonate in the 4-billion-year old meteorite Allan Hills (ALH) 84001 because the carbonate is interpreted to have formed from fluids in the early stage of Mars history (~4 Ga) [2]. This study examined speciation of sulfur in carbonates of ALH 84001 as a proxy to trace the chemical evolution of fluids that formed the ALH 84001 carbonates.

We conducted sulfur K-edge (2472 eV) micro X-ray absorption near edge structure (μ-XANES) analysis at BL27SU at SPring-8. X-ray beam was focused using a K-B mirror to a final spot size of 15 (H) ×15 (V) μm^2. Prior to the μ-XANES analysis, X-ray fluorescence mapping which was scanned in 20 μm step was obtained to determine the analytical spot with referring to the petrological observation and backscattered electron images using electron prove micro analyzer (EPMA).

A diagnostic signature of oxidized sulfur [S(VI)] was observed in all the analytical points, whereas X-ray absorption peaks corresponding to S(-II) and an organic sulfur (Di-n-octadecyl disulfide) were observed in some analytical spots. We propose two possible processes for the incorporation of S(VI) species in the carbonate grains of ALH 84001 on the Martian surface: (co-)precipitation of sulfate minerals with the carbonate or substitution of sulfate ion for carbonate ion (carbonate associated sulfate: CAS). The incorporation of trace amount of sulfate minerals is consistent with the widespread distribution of sulfate-bearing deposits in Noachian terranes [3]. However, any type of sulfate minerals has not been observed in the carbonate grains of ALH 84001 even using the transmission electron microscope observations [4]. On the other hand, the CAS-bearing carbonates are common on Earth, though the concentration of CAS in carbonate is typically low (~100s-1,000s ppm) [5]. We conducted thermodynamic calculations under conditions proposed to explain the ALH 84001 carbonates [6, 7]. The thermodynamic calculations indicated that sulfur mainly occurred as sulfate ion in water at Eh-pH conditions where the ALH 84001 carbonate precipitated. This result suggests a possibility that the observed S(VI) species could have occurred as CAS in the ALH 84001 carbonates under the fluid conditions ranging from 6 to 9 for pH and -0.25 to 0 for Eh (V).

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