MINERALOGY AND SULFUR X-RAY ABSORPTION NEAR-EDGE STRUCTURE (S-XANES) ANALYSIS OF BOCKFJORD VOLCANIC COMPLEX CARBONATES, A POTENTIAL MARTIAN ANALOG.

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Introduction: Martian surface environment during the Noachian period is of high astrobiological interest because it was potentially habitable [1]. Carbonates formed on ancient Mars provide a valuable window into it as records of the nature of aqueous environments in which they formed [2]. However, a problem faced by the study of Martian carbonates is that only a single sample of Noachian Martian carbonate-bearing material – Allan Hills (ALH) 84001 – is available on the Earth. Terrestrial analog materials can provide a larger sample size and known geological context to allow better understanding of findings from ALH 84001.

Sample: Bockfjord Volcanic Complex (BVC) carbonates from the Spitsbergen Island, Svalbard, Norway, are known as a potential terrestrial analog for Martian carbonates because of similarities in petrology and mineralogy between some BVC carbonates and those in ALH 84001 [3]. The basaltic host rock of the BVC, formed from subglacial eruption at ca. 1 Ma [4], contains carbonate cement and globules like those in ALH 84001 [5]. The formation mechanism of these carbonates is still debated, with the two major hypotheses being hydrothermal alteration [3] and cryogenic degassing [5]. In order to reconstruct the formation environment and process of the BVC carbonates, more detailed studies of both the mineralogy (unaltered host rock, carbonates, and associated alteration products) and fluid condition (pH and Eh) are needed. In this study, a sample of carbonate-bearing basaltic breccia from the Sverrefjell Volcano in the BVC, SVB 1-5 (Fig. 1), is analyzed to obtain a complete picture of the minerology and data for calculating the fluid condition.

Methods: Mineralogy was analyzed with a scanning electron microscope (SEM) and its coupled energy-dispersive X-ray spectroscopy (EDS) function.

As the first step to reveal the fluid condition, sulfur X-ray absorption near-edge structure (S-XANES) measurements were conducted on 12 areas in SVB 1-5, selected based on the SEM-EDS observation to cover the entire range of carbonate compositions and petrological settings. Sulfur is a good proxy for tracking the redox condition of fluids because of its redox sensitivity [6]. The S K-edge XANES were measured at the SPring-8 synchrotron radiation facility in Hyogo, Japan.
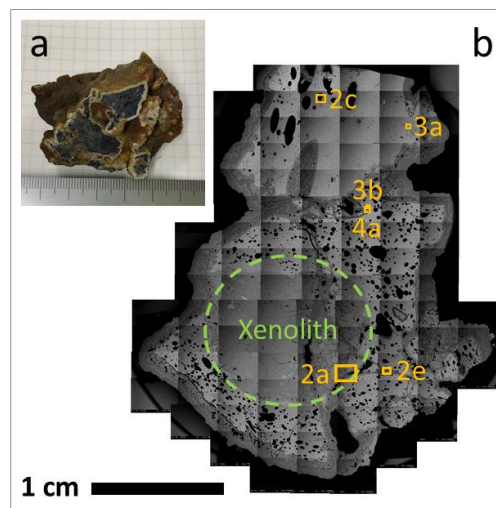

Fig. 1: (a) SVB 1-5. (b) Backscattered electron (BSE) image of the thick section used in this study. The xenolith is outlined by the dotted line, and yellow boxes indicate the fields of view of BSE images in subsequent figures.

Results:

Mineralogy. Main constituents of the basaltic host rock of SVB 1-5 are clinopyroxene crystals, a feldspathic mesostasis, and magnetite grains. Larger crystals of olivine and orthopyroxene are scattered in the host rock. A mantle xenolith is present (Fig. 1b), containing olivine, orthopyroxene, clinopyroxene, and spinel. Carbonates in SVB 1-5 mostly exist as single or connected globular forms with sharp radial changes in cation composition. They can be categorized into three types: Fe-poor, Fe-rich, and intermediate (Fig. 2). An Fe-rich layer exists on the rim of most of the globules, regardless of the type. Silicate alteration products are associated with the carbonates, including talc, a silica phase, and zeolite (Fig. 3).
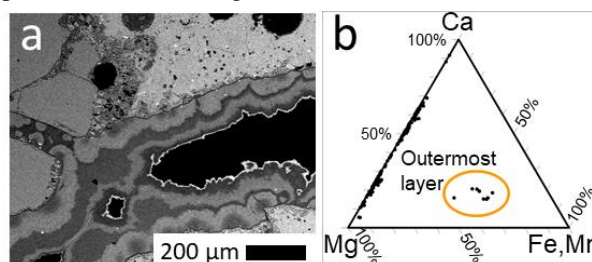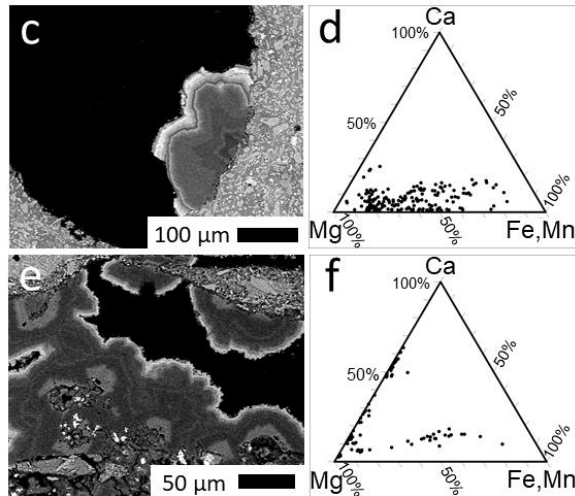
Fig. 2: BSE images (examples) and cation compositions (all measurements) of carbonate globules in SVB 1-5. (a)(b) Fe-poor globules, (c)(d) Fe-rich globules, (e)(f) intermediate globules.
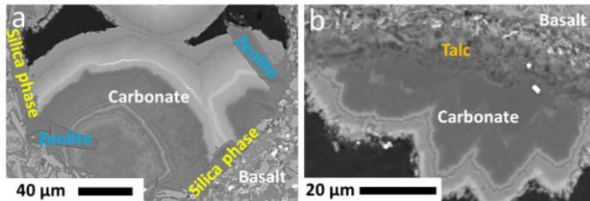

Fig. 3: Silicate alteration products associated with carbonate globules in SVB 1-5.

S-XANES. Most of the spectra of carbonates show a prominent peak at around 2480 eV, corresponding to S^{6+} species. The post-edge regions are mostly smooth without apparent oscillation, suggesting the presence of S^{6+} as carbonate-associated sulfates (CAS) [7]. Reduced sulfide peaks (~2470 eV) are commonly present. Comparison of the peak energies to those of standard reference materials (Fig. 4b) suggests the presence of native S or inorganic sulfides like pyrrhotite or pyrite in some analytical spots and organic sulfides mostly in the outermost, Fe-rich layer of the globules (e.g., Spot 4, Fig. 4). Distinct sulfite peaks (around 2475.7 eV) are clearly observed in spectra from Fe-rich globules and the outermost, Fe-rich parts of some other globules (e.g., Spot 4, Fig. 4). In most other spectra, while a low peak or "shoulder" usually exists, no clearly separate sulfite peak from the sulfate peak is present.
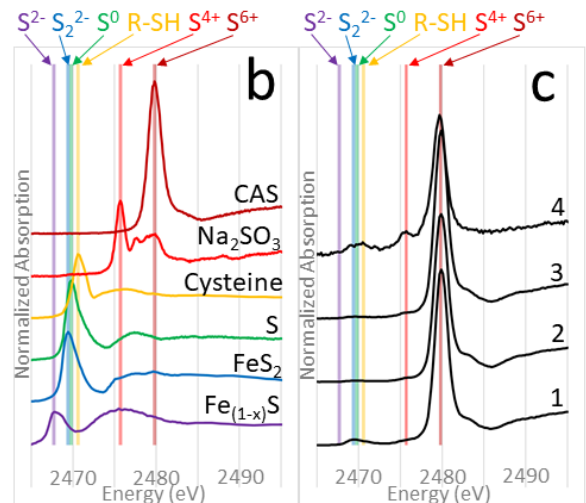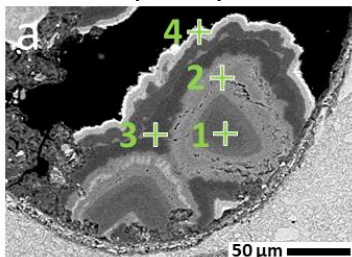

Fig. 4: (a) BSE image of an intermediate carbonate globule in SVB 1-5. (b) S-XANES spectra of reference materials. (c) S-XANES spectra of spots labelled in (a).

Discussion: Compared to carbonate globules in ALH 84001 [8], the zoning patterns of the BVC carbonates are different (usually Mg-rich cores to Fe-rich rims or alternating layers instead of Fe, Ca-rich cores to Mg-rich rims). Unlike ALH 84001, SVB 1-5 contains silicate byproducts associated with carbonates, providing a complete record of the carbonate formation process.

The presence of CAS as the main S species in the carbonates is consistent with S-XANES results for ALH 84001 carbonates [6]. This suggest that BVC carbonates and ALH 84001 carbonates may have formed under similar fluid conditions.

The S-XANES spectra obtained from the Fe-rich outermost layer of carbonate globules (e.g., Spot 4, Fig. 4) indicate the presence of organic sulfide, while those from most other carbonates do not. This suggests that organic sulfides concentrate in the outermost layers of the globules. Since these layers are also enriched in Fe, they may contain magnetite-macromolecular carbon assemblages similar to those found in the ALH 84001 carbonates [9].

References:

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