

## Analysis of secondary minerals found in basalt rock samples collected at South Pacific Gyre by $\mu$ -XAFS and EPMA

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### 1 Introduction

The aim of our study is to examine whether weathering of basalt can be induced by biotic process at site U1365 in South Pacific Gyre (SPG). For this purpose, we analyzed secondary minerals observed in basalt samples collected at sediment-basement interface at South Pacific Gyre by microscale analytical techniques (EPMA and  $\mu$ -XAFS) to find any biogenic signatures left in the samples.

### 2 Experiment

Red-colored altered part was found in the basalt sample and coated the basalt rock piece with a thickness of 200-300  $\mu$ m (Fig. 1). Bacterial community of the altered part was obtained by PCR-based 16S rRNA gene sequence analysis. Additionally, in order to analyze the alteration part in situ, the basalt rock sample was thin-sectioned with thickness of ca. 50  $\mu$ m. EPMA and SEM analyses were performed to obtain chemical maps and morphology at microscale.  $\mu$ -XAFS analysis for Fe was conducted at BL4A, KEK-PF, to obtain directly mineralogical information on the alteration part.

### 3 Results and Discussion

In 16S rRNA-DNA analysis, the majority of clones in the altered part (~50%) was similar to those found in negative controls such as surface and bottom seawater samples. In addition, cell number estimated by SYBR Green-I staining was also small in the altered part, which indicates that present microbial activity was low at altered part. Based on SEM analysis, the altered solids were partially composed of fibriform aggregates. The major chemical component in the part was dominantly Fe and the concentration of Fe ranged from 30 to 50 wt% (Fig. 2). Abundance of dissolved oxygen in the interface of site U1365 was around 60-80  $\mu$ M and moderate oxidizing condition was formed there. This implies that chemical species of Fe in the altered part is thermodynamically stable Fe(III) (hydr)oxides such as ferrihydrite, goethite, and hematite. Fig. 3 shows the Fe  $\mu$ -XANES spectra for the Fe-rich altered part. Fe  $\mu$ -XANES features of the spots in the altered part (spots 1-6) are similar to those of Fe(III) hydroxides and significantly differ from other Fe species including Fe(II) (Fig. 3B). Fitting results show that the spots 1-6 contain 60-80% hematite and 20-40% goethite and that no ferrihydrite (amorphous Fe oxyhydroxides) was observed, indicating that hematite dominates as the Fe phase in the altered parts as expected in thermodynamically calculation. Fe mineralogy had no specific relationship with depth in altered part.

Several previous studies have documented that biogenic Fe(III) hydroxides are often nanosized particles and composed of short-ordered Fe-O<sub>6</sub> linkage (Toner et al., 2009), which is not common in inorganically synthesized Fe (hydr)oxides. They noted that the Fe local structure and morphology in Fe (hydr)oxides can be used for signature of biogenically formed Fe(III) (hydr)oxides. Thus, we're planning to examine the chemical speciation of the altered parts by EXAFS as a future work, which leads to better understanding of biogenic signature of the Fe-rich secondary minerals in detail.

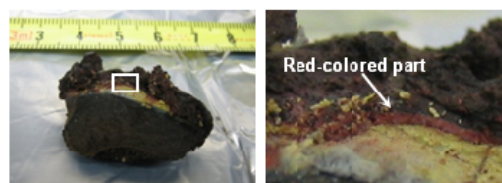


Fig. 1: Pictures of basalt rock piece collected at sediment-basalt interface at SPG.

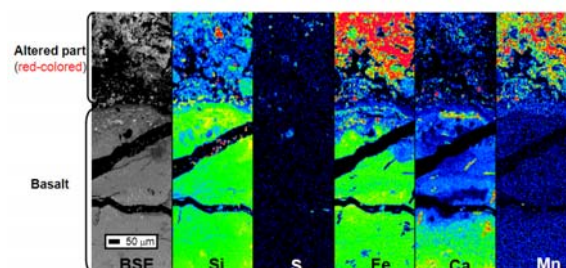


Fig. 2: Backscattered electron photograph (BSE) and elemental distribution maps for Si, S, Fe, Ca, and Mn.

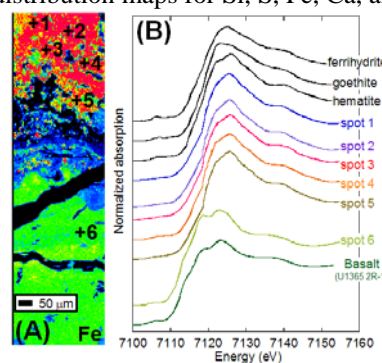


Fig. 3: (A) Analyzed spots in Fe elemental map. (B) Fe K-edge  $\mu$ -XANES spectra of standards and spots 1-6.

### References

[1] B. Toner *et al.*, *Geochim. Cosmochim. Acta* **73**, 388 (2009).

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