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Alteration of submarine basaltic glass from the Ontong Java Plateau: A STXM and TEM study

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Abstract

Frequent observations of tubular to vermicular microchannels in altered basalt glass have led to increasing appreciation of a possible significant role of microbes in the low-temperature alteration of seafloor basalt. We have examined such microchannel alteration features at the nanoscale in basalt glass shards from the Ontong Java Plateau using a combination of focused ion beam milling, transmission electron microscopy and scanning transmission X-ray microscopy. Three types of materials were found in ultrathin cross-sections cut through the microchannels by FIB milling: fresh basalt glass, amorphous Si-rich rims surrounding the microchannels, and palagonite within the microchannels. X-ray absorption spectroscopy at the C K-edge and Fe $L_{2,3}$-edges showed the presence of organic carbon in association with carbonates within the microchannels and partial oxidation of iron in palagonite compared with basalt glass. Although these observations alone cannot discriminate between a biotic or abiotic origin for the microchannels, they provide new information on their mineralogical and chemical composition and thus better constrain the physical and chemical conditions prevailing during the alteration process.

Keywords: basalt; glass alteration; palagonite; TEM; bacteria

1. Introduction

The alteration of ocean basalts partly controls the composition of seawater and of the oceanic crust (*e.g.*, Edmond et al., 1979; Hart and Staudigel, 1982), which in turn influence the Earth's mantle geochemistry and dynamics (*e.g.*, Hofmann and White, 1982; Bach et al., 2003) and the O_2 content of the atmosphere (*e.g.*, Lecuyer and Ricard, 1999). Alteration of oceanic basalts may also have a significant impact on Earth's climate on geological timescale by providing a sink for atmospheric CO_2 through carbonatization of oceanic basalts (*e.g.*, Staudigel et al., 1989; Caldeira, 1995; Brady and

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Gislason, 1997; Sleep and Zahnle, 2001). Understanding the dominant mechanisms of oceanic crust alteration at low temperatures is thus critical for assessing the rate-controlling steps of chemical exchange and improving existing models of Earth's geodynamic evolution throughout geological time.

A vast literature exists about low-temperature alteration of seafloor basaltic glass (*e.g.* Staudigel and Hart, 1983; Zhou and Fyfe, 1989; Crovisier et al., 2003; Schramm et al., 2005). Over the two last decades, an increasing number of studies have proposed that microbes mediate alteration of volcanic material in the oceanic crust leading to the inference that an extensive subsurface biosphere exists within the basaltic basement of the uppermost ocean crust (*e.g.* Thorseth et al., 1992, 1995a; Staudigel et al., 1998; Furnes et al., 2001a; Banerjee and Muehlenbachs, 2003). This idea is based on textural, chemical, and microbiological observations. For example, spherules of varying sizes (0.3–10 µm) within fresh glass as well as tubes or vermicular channels (1–10 µm wide by up to 100 µm long) have been interpreted as resulting from microbes dissolving and tunnelling into the glass. The altered glass areas have elevated levels of C, N, P and K which have been attributed to the presence of microbial cells (*e.g.*, Torsvik et al., 1998; Banerjee and Muehlenbachs, 2003). The lower δ^{13}C values of carbonates disseminated in altered basalt compared to those of fresh crystalline basalt have been interpreted as resulting from oxidation of organic carbon (Furnes et al., 2001b; Banerjee and Muehlenbachs, 2003). Microbial-like forms have been observed by SEM in association with the channels (Banerjee and Muehlenbachs, 2003) and a diverse community of Bacteria and Achaea has been characterized based on 16S rRNA gene amplification of DNA in altered basalts (Thorseth et al., 2001; Lysnes et al., 2004). Positive staining by ethidium bromide, acridine orange or DAPI (4′, 6-diamidino-2-phenylindole) in the microchannels has been interpreted as evidence for the presence of nucleic acids (*e.g.*, Thorseth et al., 1995a; Banerjee and Muehlenbachs, 2003). Finally, it has been reported that these alteration features only develop in a very specific depth and temperature window that is compatible with life (Furnes et al., 2001a; Walton and Schiffman, 2003; Staudigel et al., 2006).

Despite the reports of some etch pits produced by microbes in laboratory experiments with basaltic glass (Callot et al., 1987; Staudigel et al., 1995, Thorseth et al., 1995b), the microchannel texture has not been reproduced so far either in biotic or abiotic laboratory experiments (Thorseth et al., 1995b). A consistent biochemical mechanism has, however, been suggested for localized dissolution of glass along microchannels, which are thought to result from colonizing bacteria that produce acidic substances which locally change the pH and hence dramatically enhance dissolution of the glass (*e.g.*, Staudigel et al., 2006). This texture and associated geochemical features have been used as a signature of former biological activity. One example is the use of such a texture and features to infer the existence of ~ 3.5 Ga old traces of life in weathered basalts from Archean greenstone belts (Furnes et al., 2004; Banerjee et al., 2006; Staudigel et al., 2006).

A further detailed study of such alteration textures in modern basaltic glass, in particular the speciation of carbon and characterization of associated nanophases, may provide additional constraints on the conditions of alteration. Here we present the results of a nanoscale study of microchannel features in basalt glass shards from the Ontong Java Plateau using a combination of Focused Ion Beam (FIB) milling, Transmission Electron Microscopy (TEM) and Scanning Transmission X-ray Microscopy (STXM), which is a transmission microscopy based on synchrotron radiation. These techniques provide an unprecedented insight into the compositional variations and mineralogy of the purported microbial microchannels at the nanoscale.

2. Experimental methods

2.1. Samples

The samples for this study were recovered during Leg 192 of the Ocean Drilling Project (ODP) from Hole 1184A located at depth of 1661.1 m on the eastern lobe of the Ontong Java Plateau. We studied samples from Unit 2 which are volcaniclastic rocks consisting of ash- to lapilli-sized lithic clasts and vitric shards, accretionary lapilli, armoured lapilli, and crystal fragments (plagioclase and pyroxene) in a matrix of fine grained vitric and lithic ash, clay and other alteration minerals cemented by smectite, analcime, calcite, rare celadonite, and several zeolites. Preliminary analyses of glass shards throughout the volcaniclastic unit suggest they are restricted to a narrow range of basaltic compositions and eruption of the volcaniclastic units was likely penecomtemporaneous with the main plateau magmatic event at 122 Ma (Banerjee and Muehlenbachs, 2003). We re-observed one of the thin sections prepared by Banerjee and Muehlenbachs (2003) that contained variably altered glass shards in which textures of possible microbial origin had been observed. This thin section was gold coated before Focused Ion Beam milling.