Earth and Planetary Science Letters 374 (2013) 239–250

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Geochemical characterization of tubular alteration features in subseafloor basalt glass

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ARTICLE INFO

Article history:
Received 24 August 2012
Received in revised form
2 May 2013
Accepted 6 May 2013
Editor: G. Henderson
Available online 3 July 2013

Keywords:
tubular alteration
subseafloor
synchrotron
element map
XANES
FIB

ABSTRACT

There are numerous indications that subseafloor basalts may currently host a huge quantity of active microbial cells and contain biosignatures of ancient life in the form of physical and chemical basalt glass alteration. Unfortunately, technological challenges prevent us from observing the formation and mineralization of these alteration features *in situ*, or reproducing tubular basalt alteration processes in the laboratory. Therefore, comprehensive analysis of the physical and chemical traces retained in mineralized tubules is currently the best approach for deciphering a record of glass alteration. We have used a number of high-resolution spectroscopic and microscopic methods to probe the geochemical and mineralogical characteristics of tubular alteration features in basalt glasses obtained from a suite of subseafloor drill cores that covers a range of different collection locations and ages. By combining three different synchrotron-based X-ray measurements – X-ray fluorescence microprobe mapping, XANES spectroscopy, and μ-XRD – with focused ion beam milling and transmission electron microscopy, we have spatially resolved the major and trace element distributions, as well as the oxidation state of Fe, determined the coordination chemistry of Fe, Mn and Ti at the micron-scale, and constrained the secondary minerals within these features. The tubular alteration features are characterized by strong losses of Fe^{2+}, Mn^{2+}, and Ca^{2+} compared to fresh glass, oxidation of the residual Fe, and the accumulation of Ti and Cu. The predominant phases infilling the alteration regions are Fe^{3+}-bearing silicates dominated by 2:1 clays, with secondary Fe- and Ti-oxides, and a partially oxidized Mn-silicate phase. These geochemical patterns observed within the tubular alteration features are comparable across a diverse suite of samples formed over the past 5–100 Ma, which shows that the microscale mineralization processes are common and consistent throughout the ocean basins and throughout time. The distributions of Ti and Cu are distinct between tubular mineralization and the crack-filling minerals and thus delineate sequential stages of fluid–rock interaction. The preserved chemistry of clay and oxide mineralization in the tubular alteration then represents a common precursor state (e.g. Ti accumulation), that has not yet undergone recrystallization (e.g. titanite formation) as observed in many older, metamorphosed examples of tubular alteration.

1. Introduction

Within the past few years it has become widely accepted that the oceanic subsurface harbors significant biomass and microbial diversity, including whole new clades of microorganisms (e.g. Mason et al., 2009; Santelli et al., 2008, 2009; Edwards et al., 2011, 2012; Orcutt et al., 2011). There are also clues that the subseafloor may have been inhabited throughout the history of life on Earth in the form of mineralized tubules in altered basalt glasses that appear to be biological in origin (Staudigel et al., 1995, 2008; Torsvik et al., 1998; Fisk et al., 1998; Furnes et al., 2001a, 2001b, 2004; Benzerara et al., 2007; Walton, 2008; McLoughlin et al., 2009; Fliegel et al., 2010b, 2011). Tubular alteration features are abundant in relatively young subseafloor glasses, and similar features have been found in ancient volcanic rocks, including the Pilbara Craton (~3.35 Ga) in western Australia (Staudigel et al., 2006; Banerjee et al., 2007), and the Barberton Greenstone Belt (~3.45 Ga) in South Africa (Furnes et al., 2004; Banerjee et al., 2006; Fliegel et al., 2010a). The tubules in the Archean rocks have been directly dated to be nearly as old as the eruptive age of the rocks themselves, and thus they might in fact represent some of the oldest biosignatures on Earth (Furnes et al., 2004; Staudigel et al., 2006; Banerjee et al., 2006, 2007; Fliegel et al., 2010a; McLoughlin et al., 2012). In addition, it is likely that if there were

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Abbreviations: μ-XANES, micro X-ray absorption near-edge structure; XRF, X-ray fluorescence; μ-XRD, micro X-ray diffraction; STXM, scanning transmission X-ray microscopy; FIB, focused ion beam; TEM, transmission electron microscopy; EDX, energy-dispersive X-ray spectroscopy; DSDP, Deep Sea Drilling Project; ODP, Ocean Drilling Program; mivb, meters into volcanic basement

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http://dx.doi.org/10.1016/j.epsl.2013.05.012

past life on Mars it would have occupied the endolithic niche at some point in its evolution, or possibly even originated there (Fisk and Giovannoni, 1999; Wierzchos and Ascaso, 2002; Banerjee et al., 2004; Fisk et al., 2006; McLoughlin et al., 2007). Thus, the potential of tubular alteration features in subseafloor basalt glasses and ophiolites as biosignatures is important in both understanding the history of life on Earth and the search for extraterrestrial life in our solar system.

There are a number of different pieces of evidence that have been cited in support of the biogenicity of tubular alteration features; these studies have been extensively reviewed elsewhere (e.g. Furnes et al., 2001b; Staudigel et al., 2008, and references therein). However, there are still many questions surrounding the mechanisms of formation and mineralization of the tubules. Efforts to reproduce subseafloor conditions in the lab and induce the formation of tubules, or even identify the organisms responsible, have been unproductive (e.g. Santelli et al., 2010). It has been difficult to constrain the conditions under which the potential biological mechanisms producing these alteration features operate, and it is possible that they work on such long time scales that we may never be able reproduce the processes experimentally. This means that for now we are left with interpreting the clues preserved within the tubules. A better understanding of the geochemical characteristics of these alteration features will help to elucidate the mechanisms of their formation, mineralization, and preservation.

The tubular features are up to a few microns in diameter, thus, it is on this scale that the features must be analyzed. There have been a handful of previous studies that have used high-resolution techniques to show the nanoscale structures and chemical distributions within putative bioalteration features in subseafloor basalt glass (Alt and Mata, 2000; Benzerara et al., 2007; Staudigel et al., 2008; Fliegel et al., 2010b, 2011, 2012; McLoughlin et al., 2011; Knowles et al., 2012). However, no previous studies have examined the micron-scale changes in redox chemistry, trace element distributions, and specific mineralogies associated with tubular alteration. In the current study, we used three different synchrotron-based X-ray techniques, combined with focused ion beam (FIB) milling, and transmission electron microscopy (TEM) in order to probe the geochemical characteristics of tubular alteration features and surrounding alteration zones in young samples that have not undergone metamorphism.

2. Methods

2.1. Samples

Table 1 shows the name, location, age, and depth of the samples used in this study. All of the samples were originally obtained from drill cores from the Deep Sea Drilling Project (DSDP) and Ocean Drilling Program (ODP). Sample 896A-11R1, from the Costa Rica Rift, was drilled during leg ODP 148 (Alt et al., 1993). Hole 396B, from the mid-Atlantic, was drilled during DSDP leg 46 (Dmitriev et al., 1978), and Hole 418A, in the southwestern Atlantic, was drilled during DSDP leg 52 (Robinson et al, 1979). For more information on the sample sites and core descriptions see Furnes et al. (2001b) and references therein.

Table 1
Sample details.

Sample	Location	Age (Ma)	Depth (mivb)[a]
896A-11R1	Costa Rica Rift	5.9	90
46-396B-16	Mid-Atlantic	10	140
46-396B-20	Mid-Atlantic	10	140
418A-56-5	Southwest Atlantic	110	312
418A-49-2	Southwest Atlantic	110	147
418A-43-1	Southwest Atlantic	110	100

[a] Meters into volcanic basement.

2.2. X-ray fluorescence (XRF) microprobe mapping and micro-X-ray absorption near-edge structure (μ-XANES) spectroscopy

X-ray microprobe and microspectroscopy analyses were conducted on the insertion device beamline 13-IDC at the Advanced Photon Source (APS) at Argonne National Laboratory, Chicago. The incident energy was selected using a Si 111 monochromator and the beam was focused to $\sim 2.5 \times 2.5\ \mu m^2$ using Kirkpatrick–Baez mirrors, resulting in a flux of $\sim 10^{11}$ photons/s. For X-ray microprobe element mapping, the beam was rastered across the area of interest with a stepsize of 1.0 μm, and full fluorescence spectra were collected using a four-element vortex silicon drift detector (SDD). Each region of interest was mapped at 7120, 7126, and 7133 eV for Ca, Mn, Ti, respectively and Fe fluorescence yield, and was re-mapped at 10 keV for trace element distributions. The windowed total fluorescence counts for each element were deadtime corrected and normalized to the incident count rate at the ion chamber upstream of the sample to give net fluorescent counts per pixel. The proportions of Fe^{2+} *versus* Fe^{3+} in any given pixel were determined using a matrix of normalized XANES fluorescence values from three different standards: Zabargad Olivine (100% Fe^{2+}), Dyar Hematite (100% Fe^{3+}), and National Museum of Natural History Magnetite (66.7% Fe^{3+}). The maps were plotted and analyzed using Sam's Microprobe Analyses Kit (http://smak.sams-xrays.com/). The oxidation state maps were generated by simultaneously fitting the fluorescence yield values for each pixel of each map using the normalized fluorescence values of three different Fe standards analyzed by Fe K-edge XANES spectroscopy (Mayhew et al., 2011).

For the μ-XANES analyses the detector was calibrated using the absorption edges of an Fe^0 foil (7112.0 eV) and a Ti foil (4966.0 eV). All scans were collected from 80 eV below to 150 eV above the absorption edge of the element of interest. XANES spectra were normalized using Athena, part of the IFEFFIT software package (http://cars9.uchicago.edu/ifeffit/).

2.3. Fe and Ti μ-XANES linear combination fitting

Normalized Fe and Ti μ-XANES spectra were fit to model compound databases using the least squares fitting module of Sam's Interface for XAS Package, or SIXPack (http://sixpack.sams-xrays.com/). The Fe model compound database was compiled and narrowed down to relevant end-member compounds from each mineral group as described elsewhere (Mayhew et al., 2011). The Ti model compound database was compiled from a mix of spectra collected as part of the current study, as well as obtained from previous studies (Berry et al., 2007; Pearce et al., 2012). All model compounds were calibrated in energy to the relevant Fe or Ti foil edge. The SIXPack least squares fitting module has several different options for fitting algorithms, for this study we used the CycleFit routine. This algorithm works by iteratively fitting the spectrum for each model compound to the experimental spectrum and computing an *R*-value for the fit. This process is cyclic, each time adding in the component from the previous cycle that gave a fit with the lowest *R*-value. The cycles were terminated when no additional component improved the total *R*-value by at least 10%. For most of the experimental spectra the number of components necessary to complete the fitting process was between 2 and 5. The fit range used for the Fe XANES