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Abiotic and candidate biotic micro-alteration textures in subseafloor basaltic glass: A high-resolution in-situ textural and geochemical investigation

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ABSTRACT

The oceanic crust provides one of the largest habitats for subsurface microbial life on earth, where lithoautotrophs utilize redox gradients between reduced elements in volcanic rocks and oxygenated seawater to form the basis of a deep microbial biosphere. Progressive alteration of the oceanic crust is argued to be "in part" microbially mediated, but identifying robust textural and geochemical biosignatures with good fossilization potential is challenging.

This study investigates pillow basalts from the Antarctic Australian Discordance (AAD) at the South East Indian Ridge (SEIR) containing candidate textural biosignatures in alteration products of the glassy margins (Thorseth et al., 2003). Samples include 2.5 Ma dredged seafloor basalts, and 18–28 Ma drill core samples from the Ocean Drilling Program (ODP) Leg 187. The focused ion beam (FIB) technique was used to prepare electron transparent foils across spherical microtextures in zeolite filled fractures and altered glass (palagonite), and across microtunnels at the interface of fresh and altered glass. Transmission electron microscopy (TEM) was used to map chemical and ultrastructural variations and to evaluate both biotic and abiotic origins of the candidate textural biosignatures in the FIB prepared foils.

Three foils were cut from zeolite hosted, hollow microspheres, which comprise purely Fe-oxyhydroxides, or mixed Mn–Mg, and Fe–Mn oxyhydroxides. The microspheres are 1 to 4 μm across, with a radiating ultrastructure, and have a denser inner surface and a more porous outer surface, suggesting outwards growth from a spherical initial surface. Amorphous organic carbon is associated with some of the microtextures both on the inner and outer walls. These microtextures are interpreted as mineral encrusted microbial cells. A FIB-foil was also cut from palagonite-hosted microspheres, which are more irregular in shape and partially infilled by palagonite. Amorphous organic carbon is abundant in the vicinity of the microtextures but is spatially unrelated, and may be derived from several sources. The results indicate that maturation of the palagonite, involving dehydration and recrystallization, overprints and destroys potential biosignatures in this alteration phase. In contrast, the zeolite-hosted microtextures appear to have a higher preservation potential. Tubular microtextures in the glass at the alteration front comparable to argued "bioalteration" textures are also abundant in the AAD basalts. However, their angular cross-sectional shape and lack of "bio-elements" in the palagonite infill, mean that an abiotic origin cannot be excluded.

In summary, FIB-TEM provides multiple high-resolution lines of information to characterize alteration textures in ocean floor basalts. Comparing the evidence obtained from glass hosted microtunnels, zeolite and palagonite hosted microspheres we conclude that the zeolite hosted microtextures are the strongest candidate biosignature. The combination of the size, rim ultrastructure, and elemental composition is consistent with an origin as cell encrustations, resulting from the biologically induced mineralization of microbial cells that inhabited fractures in pillow lavas both at the seafloor and the subseafloor stage.

1. Introduction

The volcanic part of the oceanic crust represents the world's largest saline aquifer, where on-axis hydrothermal activity and off-axis seawater circulation causes extensive seawater–rock interaction. This provides a wide range of temperatures and geochemical gradients where microorganisms can employ chemosynthetic metabolism, which is the foundation of the deep-biosphere (e.g. Gold, 1992; Deming and Baross, 1993; Thorseth et al., 1995aFisk et al., 1998; Bach et al., 2006). In these subsurface environments, geological and biological processes are closely linked. The volcanic, physical, and chemical

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interactions in the young crust fundamentally control the microbial communities that are present (e.g. Edwards et al., 2005; Einen et al., 2008; Santelli et al., 2008). At the same time, microorganisms are argued to partly mediate the alteration of the oceanic crust and thus may change the composition of the circulating fluids as a consequence of their metabolic activity (e.g. Rouxel et al., 2008). Palagonite, which is the first alteration product of volcanic glass, is a heterogeneous, amorphous material that age towards a more crystalline state containing a mixture of palagonite and smectite, until it is entirely recrystallized to smectite (e.g. Stroncik and Schmincke, 2002). It is in these alteration products that candidate textural signatures of microbial activity have been proposed (e.g. Alt and Mata, 2000; Thorseth et al., 2001). In this study we aim to test the biogenicity of microtextural evidence preserved in different basaltic alteration products using FIB-TEM (focused ion beam, transmission electron microscopy).

Significant advances have been made in the last two decades in documenting the extent, identity, and the metabolic activity of the microbial communities in the oceanic crust, in large part due to technological advances in seafloor drilling and also microbiological techniques (e.g. Edwards et al., 2011). In young (<100 Ka) unsedimented seafloor lavas, estimates of prokaryotic cell densities range between $1 * 10^6$ and $1 * 10^9$ cells/g, several orders of magnitude larger than the overlying deep seawater, and there is little difference between samples of different depth and age (e.g. Einen et al., 2008; Santelli et al., 2008). Phylogenetic studies have revealed high biodiversity with bacteria being the dominating branch, typically 88%–99.9% (Einen et al., 2008; Santelli et al., 2008). Iron and manganese oxidation are in theory a considerable source of metabolic energy for lithoautotrophs in the oceanic crust (Edwards et al., 2005). Both elements occur in reduced form (Fe^{2+} and Mn^{2+}) in basaltic glass, which makes them one of the primary sources of energy for the deep biosphere (Edwards et al., 2005). Iron oxidizing and reducing bacteria from seafloor samples have been cultured on different media, including pyrite (FeS_2), siderite ($FeCO_3$), basaltic rock and glass under both anaerobic and aerobic conditions by several different workers, and these studies have confirmed that there is an active Fe-cycle within seafloor microbial communities (e.g. Edwards et al., 2003; Lysnes et al., 2004).

To investigate possible microbial life in the ancient rock record and other planetary objects it is necessary to establish positive evidence for microbial activity, in the form of textural, chemical and isotopic signatures. One of the first putative microbial biosignatures was pitting at the alteration front, with or without microbial cells, in volcanic glass from Iceland (Thorseth et al., 1992). This was taken to suggest that the microbes are changing their micro-environment (e.g. pH), thus enhancing dissolution of the volcanic glass around them (Thorseth et al., 1992, 1995a). This had far reaching implications for the later interpretation of tubular and granular microtextures observed at the interface between fresh and altered volcanic glass from the in-situ oceanic crust, which were also interpreted as an expression of this microbially mediated pitting process (Thorseth et al., 1995b; Furnes et al., 1996; Fisk et al., 1998). Further substantiating evidence was argued to come from nucleic acids detected within the textures by DNA staining and fluorescence *in situ* hybridization (FISH), indicating the presence of microbial cells responsible for these textures (Thorseth et al., 1995a; Furnes et al., 1996; Giovannoni et al., 1996; Torsvik et al., 1998; Banerjee and Muehlenbachs, 2003). Since this early work there have been numerous discoveries of microtextures in altered volcanic glass from the modern oceanic crust widely referred to as "bioalteration textures" (e.g. Furnes and Staudigel, 1999; Furnes et al., 2001a, Banerjee and Muehlenbachs, 2003), as well as from ophiolites (Furnes, 2001b), and greenstone belts (Furnes et al., 2004; Banerjee et al., 2006). However, care must be taken when connecting tubular and granular microtextures in volcanic glass directly to microbial activity as there are several abiotic processes that can conceivably produce similar textures (e.g. McLoughlin et al, 2010; Lepot et al., 2011; Fisk et al, 2013), and several of these will be discussed below.

A further type of biosignature for microbial activity in seafloor and subseafloor environments comes from cell-shaped textures in authigenic minerals in fractures and vesicles in altered volcanic glass. For example, sub-spherical textures of Mn and Fe oxyhydroxides have been observed on zeolite crystals in dredged samples from the Australian-Antarctic Discordance (AAD) at the Southeast Indian Ridge (SEIR) (Thorseth et al., 2003). They occur in clusters or as individuals on zeolite crystal faces, and are often associated with pits in the zeolite. Cell-shaped textures have also been reported in fracture filling minerals in pillow lavas from the Emperor Seamount Chain by Ivarsson et al. (2008) and in palagonite from the Arctic Mid-Ocean Ridge (AMOR) (Thorseth et al., 2001; Kruber et al., 2008), the AAD of the SEIR (Thorseth et al., 2003) and the Mid-Atlantic Ridge (MAR) (Cockell et al., 2010). The cell-like textures within the fracture filling minerals observed by Ivarsson et al. (2008) are at the interface between zeolite (phillipsite) and carbonate (aragonite) and are interpreted to be filamentous, spherical microbial cells, and biofilms on the basis of their morphology, early paragenesis, high carbon content, and fluorescent DNA staining. In the AMOR samples the microbial cells leave cavities within the palagonite, and the cavities contain carbon and nitrogen with manganese rich rims, suggesting that the cells were encrusted in manganese before being encapsulated by the palagonite (McLoughlin et al., 2011).

The contribution of abiotic processes leading to glass dissolution and secondary mineral precipitation in seafloor environments need to be carefully considered when investigating putative biosignatures. For example, filled spherical to hemi-spherical alteration textures formed by abiotic chemical exchange between freshwater or seawater and volcanic glass have been reported by several workers and need to be carefully distinguished from argued biotic microtextures (Trichet, 1970; Thorseth et al., 2003; Kruber et al., 2008; Cockell et al., 2010). Also the syngenicity, namely the relative timing, and the endogenicity, namely the spatial connection between geochemical evidence and textural remains needs to be established. Thus, organic molecules and negative $\delta^{13}C$ values found in both tubular and granular microtextures are not necessarily related to the tunneling or pitting process, but might have been transported by seawater from sources elsewhere and might therefore be unconnected to the microtextural evidence (e.g. Wacey et al., 2014). In the case of ancient metavolcanic glass the number and complexity of such events can be numerous, and for example, the age of titanite growth forming filamentous microtextures in Archean metavolcanic glass from the Barberton greenstone belt (Furnes et al., 2004) has recently been disputed by Grosch and Mcloughlin (2014).

In laboratory experiments it is difficult to recreate both abiotic and biotic corrosions of volcanic glass over long time spans under conditions comparable to the in-situ oceanic crust, and this may explain why it has not been possible to generate tubular "bioalteration" textures in laboratory culture experiment. The inability to generate such microtextures remains a major challenge to their inferred biogenicity. At the same time, we also need to appreciate that there are several abiotic processes that can conceivably control the formation of tubular microtextures in volcanic glass. For example, phase separation in melts due to liquid–liquid immiscibility can cause the melt to separate into two (or more) phases that are interconnected and this is known as spinodal decomposition (Mauro et al., 2013 and references therein). When the melt quenches it will form glass that consists of these different compositional phases, which could lead to differential rates of dissolution of the glass, thus forming tubular microtextures (Veksler et al., 2007). Another known abiotic mechanism for forming tubular microtextuTres is ambient inclusion trails (AIT), where mineral grains migrate through a substrate by pressure solution and/or chemical dissolution (Mcloughlin et al., 2010 and references therein). In a recent abiotic dissolution experiment using 1% hydrofluoric acid (HF) on volcanic glass Fisk et al. (2013) produced both pits and microchannels that were argued to show similar distribution and sizes to putative biotic pits and tubular textures. In summary, these experiments clearly demonstrate that pits and