ANCIENT MICROBIAL ALTERATION OF OCEANIC CRUST ON TWO EARLY ARCHEAN CRATONS AND THE SEARCH FOR EXTRATERRESTRIAL LIFE. N. R. Banerjee[1,2,3], H. Furnes[3], A. Simonetti[4], K. Muehlenbachs[4] H. Staudigel[5], M. de Wit[6], M. Van Kranendonk[7], [1]Integrated Ocean Drilling Program, College Station, TX 77845, USA (neil.banerjee@gmail.com), [2]Department of Earth and Atmospheric Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada, [3]Department of Earth Science, University of Bergen, Allegt. 41, 5007 Bergen, Norway, [4]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada, [5]Scripps Institution of Oceanography, University of California, La Jolla, CA 92093-0225, USA, [6]AEON and Department of Geological Sciences, University of Cape Town, Rondebosch 7701, South Africa, [7]Geological Survey of Western Australia, 100 Plain St., East Perth, Western Australia 6004, Australia.

Introduction: Recently discovered biosignatures in the formerly glassy rims of ~3.2 to ~3.5 billion-year-old pillow lavas from both the Barberton Greenstone Belt [1,2], South Africa (BGB) and the Pilbara craton, W. Australia (PWA) suggest they were colonized by microbes early in Earth's history. These subaqueous volcanic rocks represent a new geological setting in the search for early life on Earth. This is not entirely surprising since microbial alteration of basaltic glass in pillow lavas and volcaniclastic rocks is well documented from recent oceanic crust and well-preserved ophiolites [3-8].

Here we review the evidence for microbial alteration of basaltic glass from modern oceanic crust and present data from two early Archean greenstone belts. We describe the use of petrological and geochemical methods for the detection of microbial activity and show how this combination of methods can be used to convincingly demonstrate its presence. We further suggest that these techniques could be used to prospect for evidence of past life in extraterrestrial basaltic rocks.

Modern Oceanic Crust: Petrographic analysis of basaltic glass preserved as pillow rims or within volcaniclastic rocks invariably reveals the presence of microbial alteration textures produced by etching of glass during microbial colonization. Two textural types of microbial alteration are commonly observed: tubular and granular. Tubular textures are the most visually striking and are characterized by micron-scale, tubular to vermicular features and branching bodies. These tubes are commonly highly convoluted, ramose, and/or twisted. Granular textures appear as solid bands, semicircles or irregular patches of individual and/or coalesced spherical bodies with irregular protrusions into fresh glass. Both textures are observed to extend away from fractures and glass shard boundaries, along which liquid water was once present, into unaltered glass.

Detailed SEM imaging of the microbial alteration textures reveal the presence of delicate filament-like structures and material resembling desiccated biofilm. The filaments are commonly attached to tube walls and display complex morphologies including hollow, filled, and segmented varieties. The filaments are primarily composed of clay minerals similar in composition to palagonite formed during abiotic alteration of basaltic glass. However, these morphologies do not resemble diagenetic clay minerals or inorganic dissolution features but are suggestive of a biogenic origin.

X-ray element maps collected by electron microprobe show elevated levels of C, N, P, and K associated with the microbial alteration features. These enrichments are highly restricted to the immediate area of microbial attack and quickly diminish away from these areas. The intensity of these signals varies between samples but is present in all cases where microbial alteration textures exist.

Disseminated carbonate in pillow-rim basalt glasses from *in situ* oceanic crust show differences in C isotope ratios from those of the adjacent crystalline cores that likely relate to microbial activity during alteration. Bulk-rock carbon isotope ratios of carbonates in samples of microbially altered volcanic glass are variably depleted by as much as –20‰. Crystalline basalt commonly has values bracketed between normal marine carbonate (0‰) and mantle values (–5 to –7‰). The generally low $\delta^{13}C$ values of carbonates in microbially-altered basaltic glass are attributed to metabolic by-products of *Bacteria* oxidizing dissolved organic matter from pore waters.

Early Archean Oceanic Crust: Ophiolites and greenstone belts provide an opportunity to prospect for evidence of microbial alteration in oceanic basalts of much greater age than found in the modern oceans. The BGB contains exceptionally well-preserved mafic to ultramafic pillow lavas, sheet flows, and intrusions interpreted to represent ~3.48 to ~3.22 billion-year-old (Ga) oceanic crust and island arc assemblages [9,10]. The 5 – 8 km thick Euro Basalt of the ~3.35 to ~3.31 Ga Kelly Group (PWA) also contains exceptionally well preserved pillow lavas and is interpreted to represent the eruptive products of a mantle plume [11,12]. In both the BGB and Euro Basalt, the outermost 10-20 mm of most pillows is defined by a dark zone that represents the chilled, originally glassy rim. In many cases part of the glassy margin spalled off during pillow growth and formed interpillow hyaloclastite. Due to the pervasive greenschist-facies metamorphic overprint in both of these localities, these rims now consist of extremely fine-grained chlorite with scattered grains of quartz, epidote, and amphibole.

Interpillow hyaloclastites from the BGB show very little evidence of deformation and preserve original jigsaw breccia textures with outlines of individual glass shards clearly visible in thin section. Original glass shards are completely replaced by greenschist-facies minerals and the interstial spaces are filled with quartz and calcite.

Micron-sized tubular structures mineralized by titanite are present in the formerly glassy rims and interpillow hyaloclastites of the BGB and PWA pillow lavas. Based on their similarity to textures observed in recent glassy pillow basalts, we interpret these structures to represent ancient mineralized traces of microbial activity formed during biogenic etching of the originally glassy pillow rims and hyaloclastites as microbes colonized the glass surface. We propose the glassy rims of both the BGB and PWA pillow lavas hosted similar microbial communities that left behind biomarkers ~3.2 to ~3.5 billion-years-ago.

Individual glass shards in interpillow hyaloclastites from the BGB also preserve fractures along which incipient alteration is observed. Areas of quartz along these fractures contain irregular patches of individual and/or coalesced spherical bodies mineralized by titanite that protrude away from the filled fracture. The individual spherical bodies or patches are commonly 1 – 4 µm in diameter. Both the tubular and granular textures are remarkably similar to microbial alteration patterns at the interface between fresh glass and microbial alteration fronts observed in pillow basalts from *in-situ* oceanic crust.

Since volcanic glass is scarce throughout the rock record, evidence for bioalteration in greenstone belts is more commonly observed as geochemical fingerprints left behind by microbial activity in the form of elevated levels of typical biologically important elements. X-ray mapping reveals carbon (not bound as carbonate), and to a lesser extent nitrogen, along the margins of the tubular structures in both BGB and PWA as in the modern ones interpreted as residual organic material.

Disseminated carbonates within the microbially altered BGB pillow rims have C-isotope values depleted by as much as –16‰ , which is consistent with microbial oxidation of organic matter. In contrast, the crystalline pillow interiors exhibit C isotope values bracketed between Archean marine carbonate (~0‰) and mantle CO_2 (–5 to –7‰). The low ^{13}C of the BGB carbonates suggest that oxidative metabolic pathways may have been utilized by microbes colonizing the early Archean seafloor. In contrast, all of the PWA samples analyzed have values bracketed between Archean marine carbonate and mantle CO_2.

Petrography, overlapping metamorphic and magmatic ages from the pillow lavas, as well as direct dating of the titanite within microbial tubules by in situ laser ablation multi-collector-ICP-MS all demonstrate that the titanite is of Archean age and implies the microbial alteration process occurred soon after eruption. We suggest microbial alteration proceeded immediately after pillow formation, in a similar fashion to what invariably can be observed in pillow lavas of modern ocean crust. We regard these features as evidence of biological activity and that the volcanic glass-microbe interaction was a process already established in the early Archean oceans.

Application to Extraterrestrial Material: These techniques could be easily applied to samples returned from Mars and other extraterrestrial bodies where liquid water and conditions suitable for life may have existed. Since basalts are likely to be returned by any extra-terrestrial sample return mission they should be assessed for their potential in recording and preserving biological traces of life.

References: [1] Furnes, H. et al. (2004) *Science*, *304*, 578–581. [2] Banerjee, N. et al. (in press) *EPSL*, doi:10.1016/j.epsl.2005.11.011. [3] Thorseth, I. H. et al. (1992) *GCA*, *56*, 845-850. [4] Staudigel, H. (1995) *Chem. Geol., 126*, 119-135. [5] Torsvik, T. et al. (1998) *EPSL, 194*, 165-176. [6] Furnes, H. and Staudigel, H. (1999) *EPSL, 166*, 97-103. [7] Furnes et al. (2001) *Geochem. Geophys. Geosyst., 2*, 2000GC000150. [8] Banerjee, N. R. and Muehlenbachs, K. (2003) *Geochem. Geophys. Geosyst., 4*, 2002GC000470. [9] de Wit, M. et al. (1987) *J. Afr. Earth Sci., 6*, 681-730. [10] de Wit, M. (2004) *Dev. Precamb. Geol., 13*, 549-614. [11] van Kranendonk, M. et al. (2002) *Econ. Geol., 97*, 695-732. [12] van Kranendonk, M. and Pirajno, F. (2004) *Geochem.: Explor., Environ., Anal., 4*, 253-278.

Acknowledgements: This study was supported by grants from the Norwegian Research Council, the National Sciences and Engineering Research Council of Canada, the US National Science Foundation, the Agouron Institute, and the National Research Foundation of South Africa.