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Evaluating the extent of microbial mediation in volcanic glass alteration by NanoSIMS: Insights from recent and Archean metabasaltic pillow lavas

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The alteration of subseafloor volcanic glass provides potential habitats and energy sources that may sustain deep microbial ecosystems. Yet, the extent to which low-temperature glass alteration is mediated by microorganisms remains poorly constrained, in part because robust textural and geochemical signatures that can be used to evaluate microbial involvement are yet to be agreed. Here we employ high-spatial-resolution elemental mapping and in-situ isotopic measurements by NanoSIMS (nanoscale secondary ion microprobe) to evaluate candidate traces of life in altered volcanic glass. Two case studies are presented: (1) incipient alteration of recent $<$100,000 yr-old seafloor lavas from the Norwegian-Greenland Sea and (2) alteration textures in Paleoarchean meta-volcanic glass of the Barberton Greenstone Belt, South Africa.

The alteration of basaltic glass to palagonite in lavas from the Arctic Mohns Ridge has been characterized by scanning electron microscopy and bulk geochemical analyses (Kruber et al. 2008). Here TEM-EDS and NanoSIMS are combined to investigate rounded to elongated pores 0.5-2 μm across embedded in compact palagonite with sizes and shapes comparable to microbial cells (McLoughlin et al. 2011). In-situ elemental mapping revealed that the micropore rims are similar in composition to the bulk palagonite, but significantly, some rims are enriched in manganese accompanied by elevated concentrations of carbon and nitrogen within the micropores. Hence these structures are interpreted as fossilized bacteriomorphs of endolithic microbes that inhabited fractures in the basaltic glass. The preferential accumulation of Mn in some of the cell-encrustations suggests the mineralization of Mn-oxidizing bacteria. In summary, we illustrate that sub-micron scale elemental mapping particularly of Mn is a promising biosignature in altered volcanic glasses.

On the early Earth it has been proposed that septate clusters of titanite microtextures found in pillow lava rims are the remains of microbes that tunneled into Archean subseafloor volcanic glass (Furnes et al. 2004). Here we use NanoSIMS to investigate microtextures in $\sim$3.45 Ga pillow lavas of Hooggenoeg Formation, South Africa (McLoughlin et al. 2012). Extensive elemental mapping was undertaken to test reports of enrichments in carbon (possibly also nitrogen) along the margins of the microtextures previously interpreted as decayed cellular remains. No $^{12}C^-$ or $^{26}CN^-$ was found along the margins of the microtextures thus excluding a key line of evidence used to support the biogenicity of the microtextures. On the other hand, sulfide inclusions in the microtextures record strongly negative sulfur isotope fractionations $\delta^{34}S_{VCDT}$ -39.8 to -3.2‰. The magnitude, range and spatial heterogeneity of these fractionations are consistent with an early microbial origin and thus we propose that the sulfides formed during early fluid-rock-microbe interaction involving sulfur-processing microbes. In summary, in-situ sulfur isotope analysis of basalt-hosted sulfides provides alternative evidence for an Archean sub-seafloor biosphere that is independent of previous textural arguments.

In conclusion, the study of modern to ancient volcanic glass by NanoSIMS allows us to investigate the extent to which microbes participate in glass alteration. Combined elemental mapping and in-situ isotopic analysis enables us to evaluate candidate textural and geochemical biosignatures and investigate potential microbial metabolisms involved in glass alteration through geological time.