Thermophile inhabitants of the Archean seafloor basalts

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Temperature constraints on Archean sub seafloor, glass etching microbial communities, Barberton Mt. Land, SA, may be inferred from their basalt host's alteration and silicification history. Microbial etching of basaltic glass in pillow rims and hyalloclastites produces conspicuous petrographic textures of micron-sized cavities and tunnels. Simultaneously, or subsequent to the generation of these textures, the originally empty space is filled with authigenic and/or metamorphic titanite. The glass is hydrated, converting to chlorite without noticeably changing its $\delta^{18}O$ from its primary value of 6‰ (SMOW) in sharp contrast to 8 to 10‰ in the adjacent pillow cores, implying no regional metamorphic homogenization. Also implied, as is seen in modern pillows, that access by fluids was restricted to the glassy margins but not in the pillow cores. $\delta^{13}C$ contrasts of putative metabolic low-^{13}C disseminated carbonate in the bioaltered rims *vs.* marine carbonate in the cores also support the suggestion that the ichnofossils are part of a locally closed system.

The pillow pile as a whole was altered in an open system possibly by differing mechanisms. One, a passive alteration by SiO_2 laden seawater and the other by a more focused hydrothermal flow. Basalts which host the ichnofossils underlie by ~100 m, high-^{18}O cherts (~20‰) and are proportionately higher -^{18}O than those near the lower-^{18}O hydrothermal cherts (~15‰). In both, $\delta^{18}O$ is correlated with SiO_2 but the slopes are different, 2% addition of SiO_2 per ‰ for basalts beneath high-^{18}O chert *vs.* 7% SiO_2 per ‰ of ^{18}O enrichment in barren basalts associated with hydrothermal cherts. The data is best explained by -1‰ seawater depositing cherts and silicifying the basalts at the top of the section at ~80°C. We suggest that the Archean glass altering microbes were thermophilic, living at ~80°C.

Molecular-level control of oxide dissolution: Insights from NMR and computational chemistry

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Dissolution rates at the oxide/water interface depend on a variety of physical and chemical factors, including the so-called *reactive surface area*, which can change as a reaction proceeds or as it approaches equilibrium. We have investigated the problem of quantifying reactive surface area for acid-mediated dissolution through the study of *reactive surface hydroxyl groups,* and have found their number to be proportional to reaction rate for a suite of aluminosilicate glasses [1]. The number of these species also changes as a function of reaction time in both the laboratory and the field. We measure reactive hydroxyls on low surface area materials, which are relevant to geochemical studies, using a recently developed ^{19}F magic angle spinning nuclear magnetic resonance (NMR) approach where we covalently attach a ^{19}F containing monochlorosilane probe molecule to hydroxyl moieties on the oxide surface [2]. By analogy to the known reactions of monochlorosilanes on silica surfaces, where they bond to lone (*i.e.,* non-hydrogen-bonded) Q^3 species, we propose a model where these sites are implicated in the control of dissolution processes. One hypothesis that is consistent with our findings as well as published modelling, laboratory, and field observations is that over short timescales, dissolution is controlled by fast-dissolving sites, while over long timescales, dissolution is controlled by slower-dissolving sites. It follows then that the surface density of these slower-dissolving sites is proportional to the number of silane-reactive Q^3 sites. However, at the molecular level a number of questions related to the mechanism of dissolution remain, and will be addressed here through presentation of NMR and computational results. We propose that one important factor for predicting dissolution rates is that the silane-reactive sites are not part of a hydrogen-bonded network on the surface of the glasses, and therefore represent a fraction of the surface more accessible for chemical reactions. By providing computational chemists with an understanding of our methods, observations, and models, these results should provide further testable hypotheses for mechanisms of proton-promoted dissolution.

[1] Washton *et al.* (2008), *Geochim. Cosomochim. Acta* **72**, 5949-5961. [2] Fry *et al.* (2003), *J. Am. Chem. Soc.* **125**, 2378-2379.