

Energetics of catabolic reactions in diffuse hydrothermal fluids – Clues to subseafloor microbial metabolism

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The hot spots of life in the deep sea are associated with hydrothermal vent systems, where reduced, metal- and sulfide-rich fluids are generated by water-rock-reactions. When these fluids mix with oxygenated seawater, large redox disequilibria develop that can support chemolithoautotrophic microorganisms. Besides hydrothermal plumes and sulfide chimney walls, a likely habitat for microorganisms is the subseafloor, where upwelling vent fluids and cold seawater mix and form low-temperature hydrothermal fluids that slowly seep out of the seafloor (diffuse fluids). Indeed, microbiological [1,2] and geochemical [3,4] investigations provide strong support for microbial activity within this subseafloor mixing zone.

Here we use geochemical mixing models and free energy calculations to identify which catabolic pathways are energetically feasible. The approach mixes high temperature vent fluid with seawater until either enthalpy or silica concentrations match the values of diffuse fluids. The difference between predicted and observed concentrations of non-conservative species in the diffuse fluids reveal which chemical species were consumed or produced by microbial metabolism. Further, discrepancies between free energies predicted from the mixing model and those calculated for the diffuse fluid compositions provide insights into the kinds of redox (i.e., potential catabolic) reactions taking place in the system. From 1991 to 2000, the diffuse fluids at 9°N on the East Pacific Rise [3] evolved from supporting predominantly sulfide and hydrogen oxidation, shifting to iron oxidation, and then back to hydrogen oxidation. Diffuse fluids from the Mid-Atlantic Ridge at 5°S [2] indicate that methanogenesis and sulfate reduction are efficiently utilized such that the free energies are lowered to -10 to -20 kJ/mol electron acceptor.

[1] Huber *et al.* (2003) *FEMS Microbiol. Ecol.* **43**, 393-409.

[2] Perner *et al.* *Environ. Microbiol.*, submitted. [3] von Damm & Lilley (2004) *Geophys. Monogr.* **133**, 245-268.

[4] Proskurowski *et al.* (2008) *GCA* **72**, 2005-2023.

Volatility in BABB: Implications for Nb/Ta in the mantle source region

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New trace element data have been acquired for glass rinds and corresponding whole-rock samples of back-arc basin basalts from the Havre Trough in the SW Pacific. For most elements the match in compositions between glass and whole-rock pairs is very close, if not identical. In other cases, small variations exist that can be explained by the lack of olivine (for example) phenocrysts in digests of the handpicked glass.

Another suite of more volatile elements also show marked differences that we attribute to outgassing of the magmas during vesiculation and eruption. The levels of W and Mo, for example, are invariably enriched in the data for glass samples relative to the corresponding fine-grained rocks. Closer investigation, employing laser ablation techniques, reveals that there is no element enrichment in the glass *per se*; rather, the elevated volatile element contents can be attributed to the occurrence of trace minerals lining some of the vesicle walls.

One entirely unexpected outcome of this work is the observation that enrichment in W in the bulk-glass digests correlates positively with Nb/Ta indicating that the exotic minerals in vesicles have highly fractionated Nb/Ta ratios. In contrast, the crystalline whole-rock data for each sample suite cluster in both W content and Nb/Ta value. Nevertheless, this observation has a number of important implications 1) we may not have been measuring what we thought when analysing apparently pristine handpicked glass, requiring a re-think of possible correction and/or sample preparation protocols 2) it is less clear that Nb/Ta determinations of BABB (and other vesicular rocks?) genuinely reflect those of the magma and may simply be recording the extent to which the magma has been outgassed prior to or during eruption and 3) petrogenetic models in which the (apparent?) Nb/Ta of the magma is employed to constrain the composition of the underlying mantle source may need to be revisited in the light of this work.