

Chemical reactivity of aqueous aluminum nanoclusters

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Introduction

Dissolved Al(III) forms strong hydroxo complexes such as $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}(\text{aq})$ (Keggin Al_{13}) and the even larger $(\text{AlO}_4)_2\text{Al}_{28}(\text{OH})_{56}(\text{H}_2\text{O})_{24}^{18+}(\text{aq})$ (Al_{30}). The aqueous chemistry of the two polynuclear aluminum compounds is of great interest in relation to chemical weathering of minerals, acidification of soils and surface waters, toxicity of dissolved aluminum and the formation of secondary minerals. Lately, these nanoclusters have also found applications in catalysis, food chemistry, cosmetic products and paper production.

Acid-Base Chemistry

The two aluminum nanoclusters are stable in slightly acidic aqueous solution due to their high positive charge. While the positive charge of $7+$ of Al_{13} is preserved at $\text{pH} < 6$, it is lost almost completely between $\text{pH} 6$ and 7 (Furrer et al., 1992). Upon titration into the alkaline region, the Al_{13} units tend to aggregate, especially at high concentrations and at extended experimental duration. The larger Al_{30} is less symmetric and probably deprotonates over a wider pH range than the Al_{13} nanocluster.

Decomposition Kinetics

The rate law for the proton-promoted decomposition of the Al_{13} molecule has been experimentally determined by Wehrli et al. (1990), Furrer et al. (1999) and Amirbahman et al. (2000), but no data exist yet for Al_{30} . At $\text{pH} > 2.5$, the decomposition kinetics of Al_{13} is first-order with respect to the dissolved proton concentration. At $\text{pH} < 2.5$, an additional pathway, which is second-order, becomes effective. The decomposition rate of Al_{30} in acidic solutions is considerably slower compared to Al_{13} and probably could be further inhibited in presence of anionic ligands such as phosphate (PO_4^{3-}) or vanadate (HVO_4^{3-}).

References

- Amirbahman A, Gfeller M. and Furrer G., (2000), *Geochim. Cosmochim. Acta* **64**, 911-919.
Furrer G., Gfeller M. and Wehrli B., (1999), *Geochim. Cosmochim. Acta* **63**, 3069-3076.
Furrer G., Ludwig C. and Schindler P.W., (1992), *J. Colloid Interface Sci.* **149**, 56-67.
Wehrli B., Wieland E. and Furrer G., (1990), *Aquatic Sci.* **52**, 3-13.

Bioalteration in a subseafloor tuff – the link between rocks and sediments

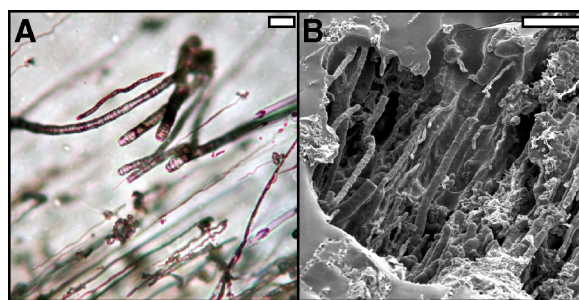
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We report microscopic textural, geochemical, isotopic, and biomolecular evidence for microbial alteration of glass shards in a 337.7 m thick sequence of possibly middle Eocene poorly sorted vitric and lithic tuffs, lapilli tuffs, and lapillistones. The samples are from Ocean Drilling Program Hole 1184A drilled at a water depth of 1661.1 m on the eastern salient of the Ontong Java Plateau during Leg 192.

Petrographic analysis has revealed an astounding density and variety of alteration textures. Micron-scale, tubular to vermicular, channel-like features with both smooth and scalloped walls commonly extend from the interface of a clay alteration rim into unaltered glass (Fig. 1A). SEM images indicate these channels are highly convoluted and also reveal the presence of filaments and thin films (likely biogenic) in channels near the clay alteration – glass boundary (Fig. 1B).

Figure 1: Transmitted light photomicrograph (A) and SEM image (B) of biogenic features. Scale bar ~20µm.



X-ray element maps show elevated levels of carbon, nitrogen, phosphorous, and potassium associated with the microbial alteration features. X-ray maps also indicate the presence of micron-sized grains of iron sulphides (most likely pyrite) at the margin of some channels and granular alteration features. These may have formed from reduction of sulphate by microbes, possibly as an energy source. Bulk-rock carbon isotope ratios of carbonates in glassy tuffs are depleted (less than -8 per mil), suggesting biologic fractionation. Nucleic acid stains that specifically bind to double-stranded DNA and RNA have confirmed the presence of cellular material in the channels. The biogenic features may, therefore, be relatively recent and the microbes may be currently active.

Glass shards in these tuffs were likely exposed to much higher water-rock ratios than the glassy rims on basaltic pillow lavas. Also, the tuffs are overlain by 201.1 m of Miocene calcareous sediment that may be a source of nutrients. These two factors may explain the higher proportion of bioalteration features relative to glassy basalts. We suggest that marine tuffs may host a previously overlooked and still unquantified flourishing deep biosphere that contributes significantly to global geochemical fluxes.