Chemical exchange between volcanic ash in seawater: abiotic versus biotic, warm *vs* cold

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Volcanic glass is probably chemically the most reactive material that is deposited in the oceans, as aerosol, as suspended river load from volcanic terrain, or as part of the extrusive layer of the oceanic crust. The total volume of this material is large, probably on the order of about 10^{16}g/a, providing the potential of very large chemical fluxes. Recent studies have shown that microbial activity plays an important role in the dissolution of glass in the marine environment, through mediation of the dissolution process, and, presumably, utilization of components of the glass freed up during this process (e.g. Thorseth *et al.*, 1995; Furnes *et al.*, 1996, Giovannoni *et al.*, 1996; Staudigel *et al.*, 1995). The interaction between biota and volcanic glass is likely an influence on local ecology as well as on the chemical mass balance between biosphere, hydrosphere and lithosphere.

We carried out a series of experiments to explore further the role of colonizing microorganisms on the dissolution of glass. All experiments were done with natural populations of microbes from surface sea water at two temperatures, under the ambient light intensity in the laboratory and in the dark. Open system experiments were done with a constant supply of fresh seawater. The closed system apparatus included 50l seawater reservoirs and a FEP Teflon column setup with approximately 150 g of glass (Staudigel *et al.*, 1997). A closed system with autoclaved components and seawater served as an abiotic control. More recent continuous flow experiments include approximately 300 g of glass and a continuous flow of 20 l of fresh sand-filtered seawater per day. We carried out an experiment at 60° C and compared this to an experiment at 16°C. Run products were analysed for major and trace elements and for changes in glass surface structure and in microbial colonization by SEM. Microbial populations were characterized with a variety of metabolic tests.

Closed-system sterile control experiments remained sterile for periods exceeding 450 days showing that these experimental conditions do not allow for microbial contamination. Biologically active experiments display a diverse population of microbes, including a series of algae including Si utilizers (diatoms) and algae with aragonitic exosceletons (halimeda). In cold experiments we identified several chemolithotrophs including a rod-shaped motile sulphur-oxidizer, probably Thiobacillus sp., and two strains of rod-shaped non-motile ammonia-oxidizers. Photoautotrophs, all cyanobacteria, include Spirulina, Phormidium, Anacystis, and a sheathed, filamentous strain that is probably either Anabaena or Nostoc. 6O°C experiments displayed no significant thermophile activity for the first two months of its duration. However, after about 8 months we could identify a diverse population of thermophilic microorganisms, including heterotrophs, sulphur-oxidizers, nitrite-oxidizers and ammonia-oxidizers. These results suggest that surface seawater has the means to transport thermophilic microbial life, even though in our experiments it took between two to eight months for them to appear. Overall these results suggests that surface seawater contains a sufficiently diverse environmental microbial population that can adjust to a wide range of conditions, and newly developed hydrothermal systems do not remain abiotic for a long time after initiation. Such processes are expected to occur not only in the mixing zone of

high temperature hydrothermal effluents, but also in their downwelling portions.

Abiotic and biotic dissolution of glass differ fundamentally in terms of reaction rates and in their ability to retain chemical components in the form of an authigenic locally deposited sediment, or mobilize specific chemical elements into solutions. Overall, biotic glass dissolution is accompanied by increased formation of authigenic minerals, approximately at twice the rate of abiotic experiments. $^{87}Sr/^{86}Sr$ data suggest that uptake of seawater Sr into glass is enhanced by a factor of about 3-4, and mobilization of basaltic Sr by a factor of at least 30. Some aragonitic carbonate contains more basaltic Sr than the surrounding solution, indicating non-equilibrium uptake, possibly due to development of a boundary layer within a biofilm.

Abiotic dissolution mobilizes Si, and Ca, while fixing Mg to an authigenic sediment deposited between glass fragments. Formation of algae in all portions of the experiments but in particular in the authigenic reactor sediment, result in effective local fixation of Si and Ca. The authigenic Si is almost entirely derived from glass dissolution, while most of the Ca comes from seawater. In terms of net transport, biologically active experiments tend to stabilize Si, while they clearly remove Ca from seawater into the authigenic sediment deposited in the pore space between the glass. This fixation of Si and Ca may be somewhat reduced when an experiment is placed into darkness, but Si utilization continues. The abundance of diatoms in all portions of the flow-through experiments, and the commonly observed interlayering of siliceous oozes with volcaniclastics suggests that at least some silica deposition in the oceans may be linked to the deposition and biologically mediated dissolution of volcanic ash.

Overall, our experiments show that glass dissolution is strongly influenced by microbial activity that is found to colonize glass surfaces very rapidly, under a wide range of temperatures, at least to about 60°C. Thus, most low temperature alteration processes are probably mediated by microbial activity, and there is a strong possibility that chemical exchange between volcanic materials and seawater may be influenced by the biological evolution of the earth. Pre-biotic exchange almost certainly displayed quite different reactions than a biotic earth. In particular microbial fixation of specific chemical elements would be critically linked to its first appearance datum. These processes are very likely to influence the chemical evolution of seawater and the recycling of seawater-derived components into the mantle.

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