Influence of water - rock interaction on the chemistry of surface water in volcanic areas

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Natural water
River and spring water samples were collected from an andesitic volcano, Norikura, central Japan and a region covered in “Shirasu” ignimbrite on Kyushu Island. The statistical analysis showed that the water chemistry of those areas is only slightly influenced by hot springs or anthropogenic pollution, but is highly controlled by weathering of silicate rocks or ignimbrite. On the basis of the thermodynamic and stoichiometric calculation based on water–rock interaction, the water chemistry was successfully demonstrated by the following simple theoretical equation: 

\[ [\text{Si}] = 2[\text{Na}^+] + (2[\text{K}^+]) + [\text{Mg}^{2+}] \]

Experiment of water-rock interaction
Rock dissolution experiments in a batch system were performed on andesite and “Shirasu” ignimbrite. The reactors were filled with 100 gram of rock powder and 2L of water, of which pH were adjusted with sulfuric acid and were left for over one year. The experimental results successfully demonstrated the above relations between silicon and cations.

![Graph of measured and estimated silicon concentrations](image)

Figure 1: Measured and estimated silicon concentrations. [Si] estimated is given by \((2[\text{Na}^+]+[\text{Mg}^{2+}])\). Open circles are the river water samples taken from Shirasu ignimbrite region, and solid squares are the experimental water samples of batch system.

A whiff of oxygen before the Great Oxidation Event?

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Many lines of evidence point to a rapid rise of atmospheric \(\text{O}_2 (P_{\text{O}_2})\) between 2.45 - 2.22 Ga, a transition often referred to as the Great Oxidation Event (GOE). Before this time non-mass-dependent S isotope data (NMD-S) indicate that \(P_{\text{O}_2}\) was ≤\(10^{-5}\) times the present atmospheric level (PAL). The cause of the GOE is unknown. It could have been an immediate consequence of the evolution of oxygenic photosynthesis. Alternatively, \(P_{\text{O}_2}\) may have been controlled by a balance between oxidants and reductants at the Earth’s surface that crossed a critical threshold at that time. In the latter case, oxygenic photosynthesis could have evolved long before the GOE. This debate can be addressed by looking for evidence of trace \(\text{O}_2\) in the geologic record before 2.45 Ga.

The abundances of some redox-sensitive transition elements, such as Mo and Re, in ancient sediments can help address this problem because their weathering fluxes and global ocean budgets are sensitive to the availability of \(\text{O}_2\). The rates of weathering of sulfide minerals which are major carriers of these elements in igneous rocks are geologically rapid even when \(P_{\text{O}_2} \sim 10^{-5} \text{PAL}\).

High-resolution chemostratigraphy in a newly-obtained late-Archean drill core reveals an episode of enrichment of these elements in the late Archean Mt. McRae Shale, Western Australia. Mo and Re concentrations in a pyritic black shale unit reach ~ 40 ppm and ~ 35 ppb, respectively. These enrichments are superimposed on a background of < 5 ppm and < 10 ppb, respectively, in underlying pyritic black shales. Re-Os geochronology demonstrates that the enrichment is a primary sedimentary feature dating to 2501 ± 8 Ma. Correlations with organic carbon indicate these metals were derived from contemporaneous seawater, providing convincing evidence that these metals were dissolved in late Archean oceans. The enrichment episode may record a change in local or global ocean Mo and Re inventories in response to changing \(P_{\text{O}_2}\). These findings point to the presence of small amounts of \(\text{O}_2\) in the environment > 50 Ma before the start of the GOE.

References