Don't Neglect Serpentinization

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Why did atmospheric O_2 only increase at 2.45 Ga when various indirect indicators suggest that oxygenic photosynthesis had already evolved by 2.7 Ga or earlier? This question has perplexed geologists for the past decade or more. Suggested hypotheses include: 1) Oxygenic photosynthesis was not actually invented until 2.45 Ga; 2) O_2 could not rise until the dissolved ferrous iron in the ocean was titrated out; 3) The mantle became more oxidized with time so that volcanic gases also became more oxidized; 4) The continents became more oxidized with time so that metamorphic gases became more oxidized; 5) The ratio of C and S relative to H in volcanic gases increased with time because of more active recycling of carbon and sulfur; and 6) A gradual switch from submarine to subaerial volcanic outgassing caused volcanic gases to become more oxidized with time. This last hypothesis has at least two variants, presented, respectively, by Kump and coauthors [1,2] and Gaillard et al. [3]. These variants differ with respect to the temperature at which submarine volcanic gases last equilibrate with basalts before being vented into the ocean. Here, I suggest that hypothesis (6) is indeed correct, but that the interaction of hydrothermal fluids with seafloor rocks is not well accounted for by any of the existing models [1-3]. Warm (~350°C) water can react with ultramafic rocks, generating hydrogen, by the process of serpentinization. This process happens only in restricted environments today, e.g., in deep fracture zones around the Mid-Atlantic ridge. However, on the early Earth, a hotter mantle may have generated thicker, more ultramafic oceanic crust, along with widespread hydrothermal activity. Gradual cooling of the mantle led to a change in tectonic styles, reflected by the Archean-Proterozoic geologic boundary, and also to a reduction in production of hydrogen from serpentinization. Thus, this hypothesis is closely related to the Kump and Gaillard models, but it includes additional types of water-rock interactions.

References: [1] Kump LR, Seyfried WE. 2005. *Earth Planet. Sci. Lett.* 235: 654-662. [2] Kump LR, Barley ME. 2007. *Nature* 448: 1033-1036. [3] Gaillard F, Scaillet B, Arndt NT. 2011. *Nature* 478: 229-232.

Experimental and field studies of Li cycling in subduction zones

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Li is one of the most prominent tracers that provides insights on fluid-rock diagenetic or metamorphic reactions, hence, on the subsurface hydrology in subduction zones. Like the other alkali elements it strongly partitions into the fluid-phase, in particular at moderate to elevated temperatures; the magnitude of the partition is strongly temperature dependent. Li and its isotopes have been used for tracing fluid reactions and cycling at plate boundaries. In subduction zones the nature of the subducted material has a strong influence on the observed variations in Li isotopes. Data from two subduction zones, Costa Rica, and Nankai Trough, will be presented.

Recent hydrothermal experiments by Wei Wei on MORB-seawater and smectite-seawater, 35-350 °C at 25 °C steps, and 600 bars, greatly expanded the data-base and insights on the behavior of Li. The results indicate that Li is released into the fluid-phase throughout the temperature range of the experiments, with a strong threshold of significant release at ~250 °C; indeed, Li concentrations increase in fluids with depth in subdution zones. Accordingly, because clay-rich sediments and altered oceanic crust are enriched in Li and the Li isotope values are lower than seawater value; the fluids that migrate up-dip from a deeper source into the ocean should have a lower isotope signature, eventually approaching the source material, as observed in the pore fluids of the décollement zones at the Costa Rica and Nankai Trough subduction zones. The experiments show a linear trend starting at seawater and decreasing with temperature (δ^7Li versus T), and can facilitate estimation of the fluid source temperature if the mineralogy of the subducting material is known.

The formation fluids recently recovered at two sites at the Costa Rica subduction zone provide, for the first time, two-year records on temporal variations (1) on the chemistry of the incoming plate upper basement formation fluid, (2) on the décollement fluid at 0.6 km arcward of the deformation front, and (3) on the relations of chemistry, tectonic events, and flow rates. The formation fluid Li concentrations and isotope data at the ODP reference Site 1253 support mixing between seawater and a deep-sourced fluid in the forearc of the Costa Rica subduction zone, implying that the uppermost permeable basement serves as pathway of fluid expulsion from the forearc. At the Nankai Trough décollement the Li concentrations are significantly higher and the δ^7Li value is lower than at Costa Rica, reflecting the different sediment inputs and geothermal gradients at these two subduction zones.