

Primary hematite formation in an oxygenated deep sea 3.46 billion years ago

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The 3.46 Ga Marble Bar Chert/Jasper unit (MBC) in the Pilbara Craton, Western Australia is a 50-200 m-thick and ~30 km-long body, precipitated at depths >200m in a submarine caldera. Using a variety of techniques (SEM, TEM, EPMA, XRD, etc), we have investigated the mineralogical characteristics of the principal Fe-bearing minerals in more than 100 jasper samples from a MBC core, which was recovered by the Archean Biosphere Drilling Project. We have found that each hematite particle in the MBC is a nano-sized (100–600 nm), single, clean, euhedral crystal, whereas both magnetite and siderite crystals are much larger and often contain inclusions of nano-sized hematite crystals. These features indicate the hematite particles are primary. They directly nucleated as single hematite crystals at $T > \sim 60^\circ\text{C}$ during rapid mixing of Fe^{2+} -rich (~1 mM) hydrothermal fluids ($T = 100\text{-}200^\circ\text{C}$) with O_2 -rich (>10 μM) local seawater at depths >200 m; the hematite did not form through transformation of ferrihydrite and/or goethite that formed by UV photolysis of Fe^{2+} -rich solution in the photic zone. In contrast, the magnetite and siderite crystals most likely formed during the early diagenesis of the MBC where an anoxic environment was created by the decay of organic matter. Our findings imply that oxygenic photoautotrophs had evolved, resulting in the oxygenation of at least some intermediate and deep ocean regions ~3.46 Ga ago.

Adsorption of HCl onto volcanic ash

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HCl molecules emitted from volcanoes breakdown to form chlorine free radicals via heterogeneous chemical reactions and photolysis, which act as catalysts to the breakdown of ozone in the stratosphere. Ozone depletion of up to 2-7% was estimated following the Pinatubo 1991 eruption [1]. However, only stratospheric HCl is dangerous to ozone, and the amount of HCl that reaches these levels is often lower than expected [2]. This suggests that HCl is removed from the eruption column at tropospheric levels. Previously suggested mechanisms include inclusion of HCl into supercooled droplets or ice crystals [3].

In order to investigate the removal of HCl from the atmosphere by adsorption onto ash in volcanic plumes, glass with the composition of the Pinatubo 1991 dacite [4] was synthesised and ground to ash-sized particles using a planetary mill. The ash was then placed in a simple volumetric vacuum device, which was purged with HCl gas to a desired pressure. The ash was connected to the system and the adsorption of HCl onto the ash surface recorded by the resulting pressure drop until an equilibrium pressure was reached.

Preliminary results from experimental runs beginning with an HCl gas pressure of 31 mbar, 100 mbar, 250 mbar, 504 mbar and 975 mbar indicate that adsorption on the order of 0.5 mgm^{-2} occurs even at low partial pressures of HCl.

- [1] Robock (2000) *Rev. Geophys.* **38**, 191-219.
[2] Oppenheimer (2003) In *Treatise on Geochemistry*. [3] Textor *et al.* (2003) *Geol Soc Lon Spec Pub* **213**, 307-328. [4] Scaillet & Evans (1999) *J. Petr.* **40**, 381-411.