

A record of paleoproterozoic surface ocean redox from iodine-to-calcium ratios

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Despite geochemical inferences of surface ocean and atmospheric oxygen accumulation prior to and at the Great Oxygenation Event (GOE) at 2.4 Gyr ago, a record of oxygen accumulation in the shallow ocean has yet to be demonstrated. Iodine-to-calcium ratios (I/Ca) in carbonates have recently been revealed as a paleoredox indicator, as iodate (IO₃⁻) is restricted to oxic waters and is the exclusive iodine species associated with carbonate precipitation¹. With a similar pE to that of O₂/H₂O, the presence/absence of IO₃⁻ is a more sensitive indicator of deoxygenation than other redox-dependent elements such as manganese and nitrogen, making I/Ca ideal for evaluating *in situ* redox in the early shallow ocean. Analysis of I/Ca in a series of Archean and Proterozoic dolomites show that the initial shift in I/Ca began at the GOE with a further increase following this at the Lomagundi carbon isotope excursion (LE). A tentative threshold for surface water oxygen accumulation of > 1 μM at the GOE is inferred from the shift in I/Ca from observations at modern oxygen minimum zones². A second order control on I/Ca ratios is the total iodine reservoir size, which is largely controlled by the burial and remineralization of organic matter. The LE is widely accepted to have resulted from an intense relative increase in organic carbon burial rates. The increase in I/Ca at the LE, despite likely reduction in the total iodine reservoir size due to organic burial, suggests expanded oxygenation, potentially into deeper water settings. Increasing I/Ca from a stratigraphic section of the Mcheka Formation, representing the later stage of the LE, may reflect increasing total iodine reservoir size, as organic carbon remineralization begins to outpace burial as carbon isotopes begin to retreat from > 10 ‰ to near 6 ‰. More generally, these data highlight the potential strength of the I/Ca proxy even in Precambrian samples.

[1] Lu, Jenkyns & Rickaby (2010), *Geology* 38, 1107-1110.

[2] Rue, Smith, Cutter & Bruland (1997), *Deep-Sea Research* 44, 113-134

Dark organic matter in permanently shadowed craters on Mercury

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Data from instruments aboard the MESSENGER spacecraft have confirmed that radar bright regions in permanently shadowed craters, with temperatures less than 100 K, in the north polar region of Mercury are water ice [1-3]. In areas with temperatures up to 350 K, the Mercury Laser Altimeter observed radar-dark regions which are most likely an amorphous carbon-rich organic layer with a distribution peaking around 160 K, covering and in some cases extending beyond near-surface water ice deposits [1,2].

Simple organic molecules and water are delivered to Mercury by cometary impacts. A portion of these molecules could migrate to the polar regions of Mercury and become cold-trapped in permanently shadowed craters [4,5]. The magnetic field lines of Mercury create a cusp where solar wind plasma is transferred to the planet's surface in the north polar region with a peak proton flux of 1.9 x 10⁸ cm²/s [6].

Ion radiation processes organic molecules to species with greater molecular weights and greater C/H ratios as hydrogen ions escape. This process can continue until the organics become amorphous carbonaceous material or even graphite or other forms of elemental carbon which have low albedos similar to those of the dark material observed in permanently shadowed craters. Based on estimated proton and electron fluxes to the north polar region of Mercury, 3.35 x 10²⁷ molecules/cm² of polycyclic aromatic hydrocarbons can be created from processing methane over the lifetime of the solar system. Due to the ion radiation and source of organic molecules, it is likely that the radar-dark material is highly processed carbonaceous organic material.

[1] Paige *et al* (2013) *Science* 339, 300-303. [2] Neumann *et al* (2013) *Science* 339, 296-300. [3] Lawrence *et al* (2013) *Science* 339, 292-296. [4] Zhang & Piage (2009) *GRL* 36, L16203. [5] Zhang & Paige (2010) *GRL* 37, L03203. [6] Mouawad *et al* (2011) 211, 21-36.