What caused the 2.4 Ga rise of oxygen?

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The Great Oxidiation Event (GOE) was an increase in O_2 levels from <1 ppm to 0.2-2% at ~2.45-2.22 Ga. How it happened is still debatable. One idea is that the GOE ensued when oxygenic photosynthesis originated [1]. But evidence suggests that oxygenic photosynthesis considerably predates the GOE, e.g., from redox-sensitive metals, stromatolites, organic carbon derived from methanotrophs, and biomarkers [2]. Instead, reductants plausibly cleared the late Archean air of O_2. Most hypotheses explain the delay by suggesting that O_2 sources took time to overwhelm O_2 sinks.

The O_2 source, organic carbon (C_{org}) burial, may have slowly increased to cause the GOE [3]. But the noisy $\delta^{13}C$ record may not allow for such a change [4], while the decomposition of C_{org} in the $\sim 10^8$ yr geologic cycle destroys O_2 gains from C_{org} burial. Also, inventories show that continents have excess oxygen, not excess C_{org} [5]. An alternative is that O_2 could have risen if the sink from volcanic reducing gases declined. Many ideas have focused on a shift in mantle or seafloor reductant fluxes [4], including appeals to changes in subaerial vs. submarine gases [6, 7]. But for this idea to work, the surface still has to export net reductant to the mantle, which is itself initially reduced.

Oxidation of *other* planetary or satellite surfaces is universally attributed to the escape of hydrogen. This accounts for Mars' redness and tenuous O_2 atmospheres on Europa, Ganymede, and Rhea. Earth's pre-GOE atmosphere was enriched in CH_4 and H_2 and prone to hydrogen escape at rates that must have produced large irreversible oxidation. If continents grew until ~3-2 Ga, they would have accumulated excess oxygen in minerals. Atmospheric O_2 would have become more stable by application of Le Chatelier's principle to the surface environment of the whole Earth.

Conclusions: Overall, rapid escape of hydrogen to space from the pre-GOE atmosphere should have gradually oxidized the Earth, accompanied by falling atmospheric CH_4 levels. The disappearance of S isotope mass independent fractionation at 2.4 Ga is best explained by the collapse of CH_4 as marine sulfate levels grew and methanotrophy kicked in [8]. The "tipping point" for flooding the atmosphere with O_2 was when the flux of O_2 from the burial of organic carbon exceeded O_2 losses. Glaciations during 2.45-2.22 Ga suggest oscillations in atmospheric composition until a new O_2 balance with oxidative weathering was established.

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Reconstructing impact basins from *ex situ* shocked zircon

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Meteorite impacts have played a critical role in the evolution of Earth and the terrestrial planets. Large impacts cause profound geomorphic changes of the crust, the concentration of economic metals, and have been correlated to climate change and biological extinctions. Despite the importance of impact cratering to a variety of disciplines, the terrestrial impact record is poorly known. On Earth, most impact structures have been removed by erosion or burial; only 180 impact structures have been confirmed, and none from the Archean when impact rates were higher. To locate Earth's missing impact record, and to build a tool for extraterrestrial impact chronology, we present a method to identify evidence of eroded impact craters through the identification of detrital (*ex situ*) shocked minerals.

We describe a detrital shocked zircon collected in modern sediment in the Vaal River basin at the Vredefort Dome in South Africa, one of Earth's largest known impact structures. Detailed isotopic, elemental (U-Th-Pb, $\delta^{18}O$, REE), and microstructural (CL, BSE, EBSD) analysis reveals that the detrital grain comprises a single mineral record of the giant impact basin. Multiple shock microstructures, including planar fractures (PFs) and granular texture, occur in different domains distinguished by CL zoning and U-Pb age, and allow the determination of the age of the source terrain and timing of impact. EBSD analysis documents the presence of shock-induced microtwins in one PF orientation. Oxygen isotopes ($\delta^{18}O$) and trace elements (REE, Th, U, Pb) record the variable response of an evolved granitoid zircon to extreme conditions during and after impact.

Modeling the source of this zircon yields the following impact basin reconstruction. The target rocks were comprised of 3161±71 Ma felsic granitoid; the impact crater thus formed on an Archean craton. U-Pb ages of granules record a Proterozoic impact at 1974±74 Ma. The impact created a >5 km diameter complex crater, as evidenced by the presence of PFs. PFs and microtwins require pressures >20 GPa; granular texture requires higher pressure, ~50 GPa. The two billion year time lag indicated by the presence of a detrital shocked zircon from a ca. 2 Gyr old impact in modern sediments suggests either that the impact structure may have been considerably larger than 5 km and eroded, or that the structure escaped early erosion due to burial and was later exposed. Thus with the exception of original crater size, many significant aspects of the Vredefort impact are accurately recorded in this grain. This method of impact basin reconstruction from single grains is well-suited for studies of lunar impacts, and also for other sample return missions where the quantity of sample is limited.