Off-axis oxidation of oceanic crust as a record of marine O_2 concentrations

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Today, off-axis circulation of seawater through oceanic crust transfers O_2 from the ocean/atmosphere to the solid earth and results in the oxidation of iron in igneous minerals. This oxidation is apparent in the top 500 m of deep-sea cores of Phanerozoic oceanic crust, which typically have elevated average Fe(III)/Fe(II+III) values (~0.4-0.6) relative to initial values (0.1-0.3) [Bach & Edwards, 2003, *GCA*]. The deep ocean is thought to have become oxygenated sometime between the Neoproterozoic and Paleozoic, but the timing is uncertain. Thus, Fe(III)/Fe(II+III) values of preserved oceanic crust vs. time could reflect the timing of deep-ocean oxygenation. We compiled records of Fe(III)/Fe(II+III) from preserved volcanic sequences of oceanic crust (pillow basalts and massive basalt flows) over the past 3.5 billion years (1104 measurements from 67 formations) to test this idea.

Cenozoic to Mesozoic samples yield average Fe(III)/Fe(II+III) values of 0.53 ± 0.08 (1 s.e.) similar to values (0.4-0.6) of altered oceanic crust of similar ages recovered from deep-sea drill cores. Paleozoic samples yield values of 0.39 ± 0.05. Neoproterozoic and Mesoproterozoic-Archean samples yield values of 0.25 ± 0.02 and 0.24 ± 0.02 respectively.

These temporal changes (i.e., the increase in Fe(III)/Fe(II+III) in Phanerozoic vs. Precambrian samples) could reflect shifts in marine O_2 concentrations or later alteration. Later alteration is a concern as Precambrian vs. Phanerozoic samples are frequently more metamorphosed. For example, if metamorphism drives reduction of Fe(III) to Fe(II), the record could be aliased. We tested for this using a compilation of Fe(III)/Fe(II+III) ratios of intrusive and extrusive continental igneous rocks [Keller et al., 2015, *Nature*]. Intrusive rocks show no significant change in Fe(III)/Fe(II+III) with time. Extrusive rocks, in contrast, increase in Fe(III)/Fe(II+III) from 2.4-1.25 Ga, likely due to the oxygenation of the atmosphere at 2.4 Ga and then are stable to the present. Thus, metamorphism of subaerially oxidized, extrusive Proterozoic rocks does not obviously alter Fe(III)/Fe(II+III) ratios.

Consequently, we interpret the temporal evolution of preserved oceanic crust Fe(III)/Fe(II+III) values to indicate that deep ocean O_2 concentrations rose to sufficient levels to measurably oxidize oceanic crust during the Paleozoic Era. We will discuss the implications of this record for the history of atmospheric and marine O_2 concentrations.