

Tracing the redox-state of Earth's upper mantle in the Archaean

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The redox state of the upper mantle in the Archaean through to the Proterozoic is a key parameter as it would have buffered atmospheric composition and interacted with the ocean-atmosphere system. There have been multiple approaches using geochemical proxies, such as V-Sc and redox-sensitive stable isotopes (e.g., Fe) applied to mantle-derived rocks to investigate this problem. As whole-rock samples are prone to overprinting (alteration, metamorphism) and as mafic rocks are particularly difficult to date, a technique using a robust U-bearing accessory mineral might allow better and more trustworthy temporal constraints to be measured. Recent work developing an oxybarometer based on S in apatite using μ -XANES has shown great promise as apatite can seamlessly incorporate reduced and oxidised S species and directly reflect the fugacity of host magmas. To overcome common secondary processes affecting matrix apatite such as alteration and recrystallisation, apatite inclusions trapped in zircon during magmatic crystallisation have been proven to be robust. This method has the advantage that the enclosing zircon can be dated and the mantle source traced via Lu-Hf and O isotopes analyses in zircon. To demonstrate that this approach works, we have studied 2.35 Ga TTGs and 2.13 Ga sanukitoids from the Mineiro Belt, Brazil. These rocks temporally straddle the Great Oxidation Event (GOE) and represent a tipping point of geodynamical change, marked by a transition from flat to steep subduction in the presence of a mantle wedge. Apatite inclusions in zircons from this TTG-sanukitoid transitional magmatic record reveal a change from reduced to more oxidised conditions from pre- to post-GOE. This change is interpreted as the result of recycling of atmospherically-altered sediments into the mantle. As the Archaean is marked by subtle but important atmospheric events, such as the oxygenation 'whiffs', we analysed apatite inclusions in zircon grains of sanukitoids from Pilbara and Kaapvaal cratons that crystallised from 3.4 Ga to 2.7 Ga to trace surface-mantle interactions in the early Earth. Remarkably, our dataset shows relatively oxidising conditions for all measurable inclusions (i.e., with S above limit of detection), suggesting a dynamic recycling mechanism in the early Earth potentially powered through oxygenation episodes.