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Melting sediment and subducting bacteria: exploring the connection between the Great Oxidation Event and the rise of $\delta^{18}O$ in zircon.

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Zircon is a ubiquitous and robust mineral that survives multiple sedimentary cycles with little modification to its isotopic composition. This feature makes zircon the perfect archive for recording changes in crustal processes over deep time. In particular, oxygen isotopes in zircon inform on the degree to which a magmatic system has incorporated supracrustal material. That is because oxygen isotopes are highly fractionated by near surface processes, resulting in sedimentary rocks becoming strongly enriched in ^{18}O especially during the formation of clays [1, 2]. When these sediments are assimilated into magmatic systems the $\delta^{18}O$ composition of the magma also becomes isotopically heavy with the $\delta^{18}O$ VSMOW of sedimentary rocks typically from 6-40‰ [3]. In contrast the $\delta^{18}O$ signature of mantle is narrowly constrained between 4.7‰ and 6.0‰ [4]. Thus, any significant increase from the mantle value in zircons with concordant U-Pb ages has been interpreted to result from incorporation of supracrustal material [5].

Work over the past decade has shown that the maximum $\delta^{18}O$ value of zircons has increased through geologic time, indicating progressive reworking of supracrustal material in Earth's magmatic systems [5, 6]. During the Archean, $\delta^{18}O$ values in zircon remain relatively subdued with maximum values ~8‰ [5, 7] then, between 2.5 and 2.1 Ga, the maximum values rise to ~14‰ and remain relatively constant to the present [6]. The rise has been interpreted as either representing a shift in sediment composition through time [5] or a shift in the magnitude of supracrustal reworking via tectonic processes [6]. Furthermore, it is conspicuous that the rise in atmospheric oxygenation, known as the Great Oxidation Event [8], appears to coincide with the rise of $\delta^{18}O$. We present a suite of zircon $\delta^{18}O$ analyses from southwestern Australia that provide better constraint on the timing of $\delta^{18}O$ rise in zircon. These data show a step change in $\delta^{18}O$ with a ~50 Ma time lag from the disappearance of mass-independent fractionation of sulphur isotopes and enhanced deposition of marine sulphate which are generally associated with the onset of the Great Oxidation Event. We argue that the formation and subsequent subduction of marine sulphate which carries a significant enrichment of ^{18}O is responsible for the strong shift in $\delta^{18}O$ values in zircon. This implies a direct link between the composition of the continental crust, atmospheric chemistry, and evolution of Earth's biosphere.

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