Micro-scale (SIMS) sulphur isotope evidence for late Archean rise in shallow oceanic free oxygen.

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Biological innovation involving iron and sulphur significantly predated the increase of free oxygen in Earth's atmosphere 2.3 billion years ago. The reasons for this delay in free oxygen build-up remain unclear. Sulphur isotopes facilitate investigation of this question because sulphur metabolising bacteria from deep branches of the Tree of Life can impart characteristic mass dependent fractionation. Biological effects are superimposed on mass independent fractionation signatures that are unique to the ancient anoxic atmosphere [1]. Although distinctive isotope effects have previously been shown from rocks older than 2.3 billion years [2], the extent of isotopic fractionation and its significance have remained elusive. Here we report *in situ*, high spatial resolution secondary ion mass spectrometer (SIMS, [3]) measurements of 2.52 billion year old sedimentary sulphides that reveal variability in sulphur isotope composition within specimens on unprecedentedly fine scale (<25 microns). The results indicate the operation of bacterial sulphur isotope fractionation, as well as implying that its extent depended on sedimentary facies and was, in some depositional settings limited by available sulphate. Correlated mass dependent and independent fractionation arrays provide a novel method for quantifying the degree of fractionation to nearly double that of previous estimates, provided that marine sulphate had a relative ^{33}S deficit. By 2.52 billion years, microbial sulphate reduction, elemental sulphur and sulphide oxidation as well as water column sulphate reduction were all operating, albeit only in the uppermost layer of the stratified ocean.

References

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