LETTERS

Oxidation of the Ediacaran Ocean

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Oxygenation of the Earth's surface is increasingly thought to have occurred in two steps. The first step, which occurred ~2,300 million years (Myr) ago, involved a significant increase in atmospheric oxygen concentrations and oxygenation of the surface ocean[1,2]. A further increase in atmospheric oxygen appears to have taken place during the late Neoproterozoic period[3,4] (~800–542 Myr ago). This increase may have stimulated the evolution of macroscopic multicellular animals and the subsequent radiation of calcified invertebrates[4,5], and may have led to oxygenation of the deep ocean[6]. However, the nature and timing of Neoproterozoic oxidation remain uncertain. Here we present high-resolution carbon isotope and sulphur isotope records from the Huqf Supergroup, Sultanate of Oman, that cover most of the Ediacaran period (~635 to ~548 Myr ago). These records indicate that the ocean became increasingly oxygenated after the end of the Marinoan glaciation, and they allow us to identify three distinct stages of oxidation. When considered in the context of other records from this period[7–15], our data indicate that certain groups of eukaryotic organisms appeared and diversified during the second and third stages of oxygenation. The second stage corresponds with the Shuram excursion in the carbon isotope record[16] and seems to have involved the oxidation of a large reservoir of organic carbon suspended in the deep ocean[6], indicating that this event may have had a key role in the evolution of eukaryotic organisms. Our data thus provide new insights into the oxygenation of the Ediacaran ocean and the stepwise restructuring of the carbon[6,16,17] and sulphur cycles[3,18,19] that occurred during this significant period of Earth's history.

The Huqf Supergroup provides one of the best-preserved, most continuous sections of Ediacaran-age strata[20] (Fig. 1). The Abu Mahara Group contains Marinoan-equivalent (~635-Myr-old) glacial deposits (Fiq Formation and associated Hadash cap carbonate) that overlie ~800-Myr-old crystalline basement[7]. Nafun Group sediments were deposited in a regionally extensive sag basin under open, shallow marine conditions, and each formation can be traced laterally for several hundred kilometres[21]. Nafun strata (see Supplementary Information for a detailed discussion of lithostratigraphy) comprise two clastic-to-carbonate shallowing-upward successions (Masirah Bay Formation–Khufai Formation; Shuram Formation–Buah Formation) with an unconformity across the Khufai–Shuram boundary that probably includes the interval of Gaskiers glaciation ~580 Myr ago (ref. 22). Global correlation of $\delta^{13}C_{carb}$ (carbonate, see Supplementary Information for carbon and sulphur isotope nomenclature) anomalies provides two age constraints for the Buah Formation (Fig. 1): ~550 Myr for the mid-Buah (correlation with Doushantuo Formation, China[7,9]), and ~548 Myr for the upper Buah (correlation with Nama Group, Namibia[7,8]). These correlations are supported by multiple ages[7] spanning 541–547 Myr ago obtained from the overlying Ara Group.

Here we present carbon and sulphur isotope data from the Huqf Supergroup (Fig. 1; see Supplementary Information for detailed discussion of the data). All data were collected from cuttings in the Miqrat-1 well (Supplementary Fig. S1), previously established as one of the most representative subsurface sections of Huqf strata[16]. The Shuram Formation preserves a >15‰ negative excursion in $\delta^{13}C_{carb}$, reaching a minimum of about −12‰. The excursion spans ~500 m of stratigraphic section[16] and is the largest known perturbation to the global carbon cycle in Earth history.

The Shuram excursion is fundamentally different from all known $\delta^{13}C_{carb}$ excursions (for example the Marinoan cap carbonate, the Ediacaran/Cambrian boundary and the Permian/Triassic boundary), in that $\delta^{13}C_{carb}$ reaches well below the mantle value of about −6‰. Because $\delta^{13}C_{carb}$ values below −6‰ cannot readily be explained by changes in organic carbon burial or isotope fractionation during carbon fixation[4], the Shuram excursion was initially attributed to diagenetic alteration of the $\delta^{13}C_{carb}$ signal[16,21]. However, standard methods of assessing diagenesis (see Supplementary Fig. S2a, b, and discussion in Supplementary Information) indicate that these samples retain primary $\delta^{13}C_{carb}$ values. Furthermore, the Shuram excursion is now documented in more than 30 sections in Oman, covering a region in excess of 10^5 km^2 with little variation in either magnitude or duration[16,21,23]. Additionally, potentially correlative excursions have been found across the globe: the Doushantuo Formation, China[9]; the Wonoka Formation, Australia[13]; the Johnnie Formation, USA[14]; and the Nama Group, Namibia[15] (Fig. 2). Taken together, they indicate strongly that the Shuram excursion is a primary record of an unprecedented perturbation to the global carbon cycle.

Unlike younger carbon isotopic anomalies that are expressed by $\delta^{13}C_{carb}$ in carbonate sections and $\delta^{13}C_{org}$ (organic carbon) in siliciclastic sections, the Shuram excursion has been identified only in carbonate sections[9,13–16,24]. Given the absence of covariation in $\delta^{13}C_{org}$ with $\delta^{13}C_{carb}$ during the Shuram excursion reported here and from the Wonoka Formation in Australia[13], the excursion would be undetectable in Shuram-equivalent siliciclastic strata, which require $\delta^{13}C_{org}$ for chemostratigraphy. This may explain why the Shuram excursion has not been found in more Ediacaran sections (for example siliciclastic-dominated sections such as the Windermere Supergroup, Canada).

The data presented here indicate progressive oxidation of the Ediacaran ocean in three stages after the end of Marinoan glaciation. These successive stages occur well after the last of the extreme Neoproterozoic glaciations[9] and before the extinction and subsequent evolutionary radiation across the Ediacaran/Cambrian boundary[20]. The first stage of oxidation occurs in the Khufai and Masirah Bay formations above the Marinoan-equivalent Hadash cap carbonate. In the Hadash cap, $\Delta\delta^{34}S$, the difference between coeval $\delta^{34}S_{SO_4}$ (carbonate-associated sulphate) and $\delta^{34}S_{pyr}$ (pyrite)

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(Fig. 1e), ranges from 1‰ to 12‰. These low values, consistent with those found above the coeval Marinoan diamictite in Namibia[19], indicate marine sulphate concentrations ($[SO_4]$) of less than 200 μM (ref. 25), which prevents the expression of significant isotopic fractionation during bacterial sulphate reduction (BSR). Throughout the Masirah Bay and Khufai formations above the cap carbonate, $\Delta\delta^{34}S$ increases gradually to ~35‰, recording an increase to $[SO_4] > 200$ μM and unlimited expression of BSR fractionation. Although it is difficult to gauge the magnitude of the increase in $[SO_4]$, reports[18,19] of Ediacaran and early Cambrian enrichment and variability in $\delta^{34}S_{SO_4}$ suggest that $[SO_4]$ did not exceed ~5 mM (ref. 26), which is appreciably lower than the modern value of 28 mM. Two key fluxes for regulating $[SO_4]$ are riverine sulphate derived from pyrite oxidation (source) and marine reduction of sulphate to sulphide (sink). Because these fluxes both depend directly on oxygen concentrations, increased $[SO_4]$ probably correlates with increased oxygen availability. It is likely that the increase in $[SO_4]$ above the cap carbonate is in part the recovery from a glacially induced drawdown of sulphate concentrations[19]. However, on the basis of ~610-Myr-old detrital zircons in the upper Khufai[7,27] the minimum time represented by the increase in $\Delta\delta^{34}S$ in stage I strata overlying the ~635-Myr-old Marinoan cap carbonate is ~25 Myr and therefore probably records an increase in atmospheric oxygen in addition to any effects associated with deglaciation. This increase in $\Delta\delta^{34}S$ constitutes the first stage (Fig. 1, stage I) of Ediacaran oxidation observed in the Huqf sediments. Throughout stage I strata, $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ were not coupled.

The second stage (Fig. 1, stage II) of Ediacaran oxidation corresponds to the duration of the Shuram excursion and encompasses the Shuram and lower Buah formations. Although these strata lie immediately above the Khufai, the likely presence of a significant unconformity prevents meaningful comparison between data from the base of the Shuram and those from the top of the Khufai. The absence of a parallel negative excursion in $\delta^{13}C_{org}$ suggests that pools of organic carbon and dissolved inorganic carbon in the Ediacaran ocean were effectively decoupled, such that excursions in $\delta^{13}C_{carb}$, which reflects the dissolved inorganic carbon pool—the source for carbon fixation of coeval organic matter—were not recorded in $\delta^{13}C_{org}$ of syndepositional sediments[6]. Our trends agree with the observation[6] of an overall absence of covariation between $\delta^{13}C_{org}$ and $\delta^{13}C_{carb}$ in a global compilation of Neoproterozoic data from ~730 to 555 Myr ago. With decoupled carbon reservoirs, negative excursions in $\delta^{13}C_{carb}$ can result from the oxidation of part of a much larger DOC reservoir represented by the deep ocean, and their amplitude is limited by $\delta^{13}C_{org}$ (about −30‰) rather than mantle composition (about −6‰) as in a steady-state model. (Here and throughout the text, the term DOC is used to refer to a large reservoir of organic carbon (not the result of coeval primary production) suspended in the deep ocean; use of the term DOC is not intended to distinguish between truly 'dissolved' organic carbon and suspended colloidal or fine particulate organic carbon.) This vast organic reservoir would effectively buffer coexisting $\delta^{13}C_{org}$ through adsorption on siliciclastic particles and/or during carbonate precipitation in significant excess of the influx of detritus from primary production. At the initiation of the Shuram excursion, this adsorption would have to contribute ≥90% of TOC to mask the signal of $\delta^{13}C$-depleted primary organic matter. However, because the organic reservoir is depleted through progressive oxidation, the relative contribution of coeval $\delta^{13}C$-depleted primary production to $\delta^{13}C_{org}$ increases; this is observed (Fig. 1b) in the upper portion of stage II as $\delta^{13}C_{org}$ decreases from about −26‰ to about −31‰. As the organic reservoir is finally oxidized, the onset of covariation in

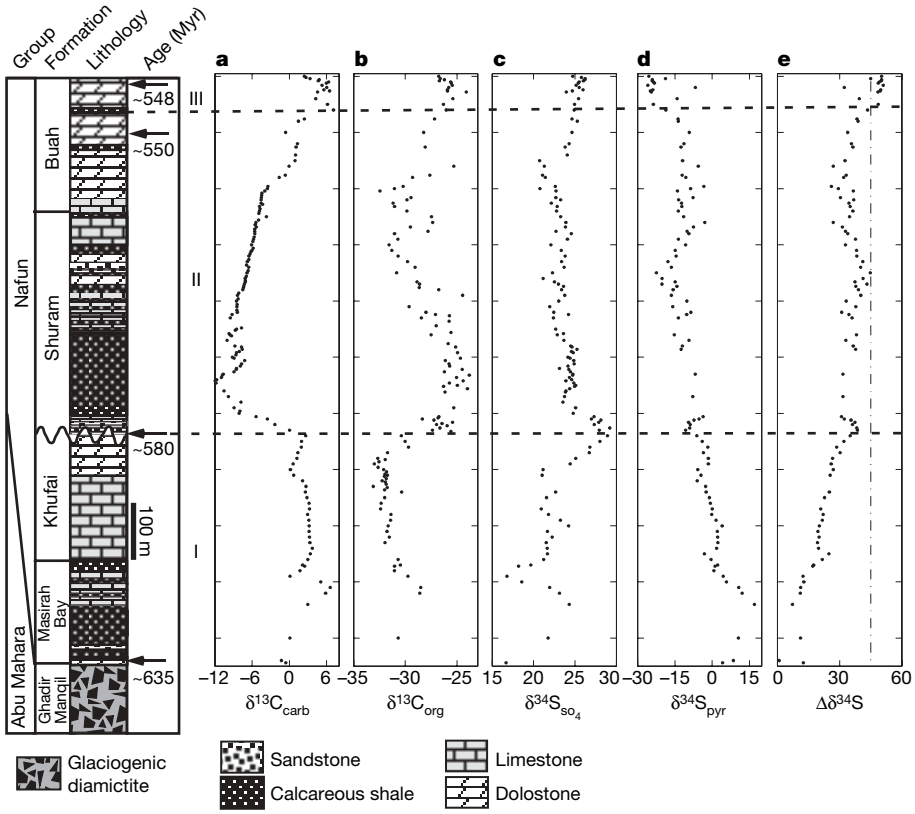

Figure 1 | Huqf Supergroup showing geochronological, palaeobiological and chemostratigraphic contraints. The Hadash cap carbonate lies immediately above the Ghadir Manqil glacial diamictite and conformably below the Masirah Bay Formation. Geochronological constraints are from correlation to other sections containing U–Pb zircon ages on ash beds[8,9,22]. Data plotted are $\delta^{13}C_{carb}$ (**a**), $\delta^{13}C_{org}$ (TOC) (**b**), $\delta^{34}S_{SO_4}$ (**c**), $\delta^{34}S_{pyr}$ (**d**) and $\Delta\delta^{34}S = \delta^{34}S_{SO_4} - \delta^{34}S_{pyr}$ (**e**). The dashed line at 46‰ indicates the maximum fractionation associated with BSR. The 2σ error bars for isotopic measurements, based on replicate analyses of standards and samples, are $\delta^{13}C_{carb}$ and $\delta^{34}S_{SO_4} \leq 0.15$‰; $\delta^{13}C_{org}$ and $\delta^{34}S_{pyr} \leq 0.4$‰.

$\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ ($r^2 = 0.72$ for the upper ~200 m of section) becomes apparent. Further evidence supporting oxidation during stage II is given in Supplementary Information.

The constancy of $\Delta\delta^{34}S$ during the Shuram excursion indicates that, despite these changes, BSR under sulphate-replete conditions remained the dominant pathway for sulphur cycling in the ocean. However, in the upper Buah, an increase in $\Delta\delta^{34}S$ to ~50‰ indicates a change in the metabolisms involved in marine sulphur cycling. The maximum fractionation observed[3] in both laboratory and field studies during BSR is 46‰; typical fractionations are often much smaller[28]. However, communities characterized by BSR coupled with bacterial sulphur disproportionation (BSD), a pathway[3] in which intermediate-valence sulphur species (for example S^0 and $S_2O_3^{2-}$) are split into ^{34}S-enriched sulphate and ^{34}S-depleted hydrogen sulphide, have fractionations that can approach 70‰. There is evidence from paired $\delta^{33}S$–$\delta^{34}S$ data for the evolution of BSD as early as the Mesoproterozoic[29]; however, there have been no reports of a coeval $\Delta\delta^{34}S$ of more than 46‰ in any Proterozoic sample[30]. Because BSD requires the presence of intermediate-valence sulphur species, the oxidative sulphur cycle must have been active. Evidence for BSD therefore demonstrates additional oxidation of the Ediacaran ocean immediately after the Shuram recovery and constitutes the third stage (Fig. 1, stage III) of Ediacaran oxidation preserved in the Huqf sediments.

The data presented in this paper provide a record of multistage oxidation of Earth's surficial environment during Ediacaran time. We now place this record into a global palaeobiological context by integrating coeval records of both plankton (acanthomorph acritarchs) and benthic Ediacaran soft-bodied animals into our chemostratigraphic context (Fig. 2). Well-characterized palynological assemblages that record the evolution of the acanthomorph acritarchs[10] are preserved in two chemostratigraphically constrained sections (China and Australia) potentially correlative to the Shuram excursion (Fig. 2). In Australia, the appearance of acanthomorph acritarchs coincides approximately with the onset of the Shuram excursion (our stage II oxidation) in the Wonoka Formation, Adelaide Rift Complex[10,13]. The Acraman impact event has previously been postulated as the stimulus for the acanthomorph acritarch radiation[10]. However, impact ejecta occur ~140 m below strata marking both the radiation and the initiation of the Shuram excursion. We therefore propose alternatively that the acritarch radiation is temporally correlated with the increased oxidation of the ocean and subsequent ecological changes that occurred during the Shuram excursion. The most diverse assemblage of acritarchs occurs in the Julie Formation, Amadeus Basin[10], during an excursion in $\delta^{13}C_{carb}$ of up to +5‰ (Fig. 2), which we interpret as equivalent to the stage III oxidation event based on $\delta^{13}C_{carb}$ correlation to the upper Buah Formation in Oman and the lower Nama Group of Namibia, where the age of the correlative positive $\delta^{13}C_{carb}$ isotopic excursion is constrained to ~548 Myr (ref. 8). Although neither the carbonates of the Nama Group nor those of the Buah Formation have yielded well-preserved acritarch populations, acanthomorph acritarchs in the shale-rich Doushantuo Formation of China[10] appear at about the same stratigraphic position as the reported Shuram excursion[9]. The coincidence of the latter two stages of oxidation with the first appearance and subsequent diversification of acanthomorph acritarchs suggests that the oxidation of the ocean had a major role in the evolution of these planktic photosynthetic organisms.

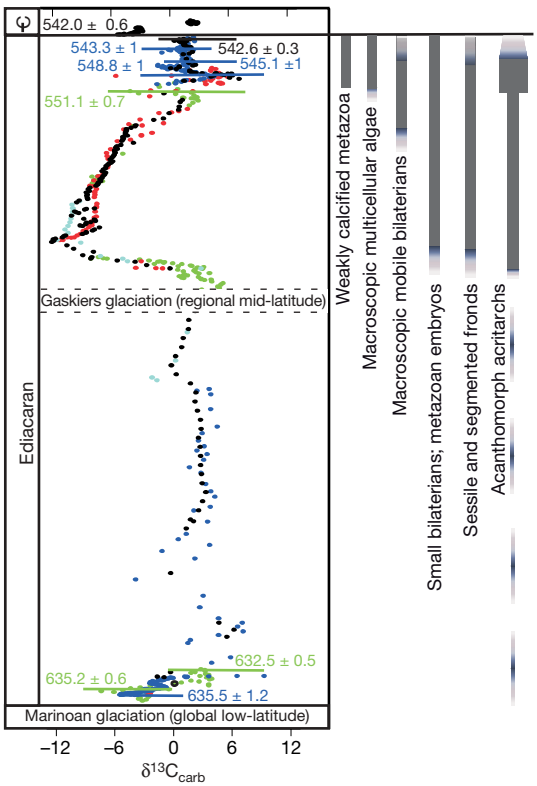

Figure 2 | Compilation of Ediacaran $\delta^{13}C_{carb}$ from sections known to contain the Shuram excursion. The vertical axis is approximate time, with known geochronological constraints plotted. On the right are plotted the known range of acanthomorph acritarchs and Ediacaran biota (shading indicates uncertainty relative to $\delta^{13}C$ chemostratigraphy). Points are coloured as follows: black, Oman; dark blue, Namibia; green, China; red, Australia; cyan, Death Valley. Full references for data, U/Pb zircon ages, biostratigraphic range, and the method for correlating sections are provided in Supplementary Information.

It is not possible to determine confidently whether the first known appearance of the Ediacaran biota at ~575 Myr ago (ref. 12) predates or postdates the onset of the Shuram excursion, because of a lack of overlapping biostratigraphic and chemostratigraphic data. However, both the Shuram excursion and the first appearance of Ediacaran organisms are believed to postdate the Gaskiers glacial event ~580 Myr ago (see Supplementary Information), yet predate the positive $\delta^{13}C_{carb}$ excursion ~548 Myr ago. It is therefore possible that the second stage of oxygenation helped to stimulate the radiation of the first Ediacaran organisms, which are interpreted to have been sessile frond-like animals (such as *Charnia*); although these organisms seem to have inhabited a variety of different palaeoenvironments[11,12], all evidence indicates that they were probably confined to the oxygenated mixed layer of the ocean. However, it is not until ~555 Myr ago (ref. 11), as the Shuram excursion drew to a close, that we see the appearance of the first motile, bilaterian organisms (for example, *Kimberella*) in a wider range of depositional facies. Finally, the first calcifying metazoa *Cloudina* and *Namacalathus*, well documented in both Oman and Namibia, appeared ~548 Myr ago, after the strong BSD signal. The coincidence of the latter two stages of oxidation identified in this study with the appearance of motile and calcifying Ediacarans, respectively, suggests that the events observed in Oman were global and affected the evolution of early metazoa.

Examination of the Huqf Supergroup, Sultanate of Oman, reveals a three-stage oxidation of the Ediacaran ocean. The first stage corresponds to an increase in sulphate concentrations (>200 μM) after the Marinoan glaciation, due in part to an increase in atmospheric oxygen. The second stage consists of the Shuram excursion and the oxidation of a deep-ocean DOC reservoir, probably the last major redox barrier to ocean oxygenation. This stage is coincident with the appearance of complex acanthomorph acritarchs and motile metazoa. The final stage of Ediacaran oxidation is characterized by strong signals of BSD and covariation in $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$, coincident with an increase in the diversity of acanthomorph acritarchs and the first appearance of the calcifying metazoa *Namacalthus* and *Cloudina*. Taken together, these data record the progressive oxygenation of the Ediacaran ocean, stimulating the evolution of both planktic and benthic groups of organisms.

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