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# Isotopic Evidence for Massive Oxidation of Organic Matter Following the Great Oxidation Event

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The stable isotope record of marine carbon indicates that the Proterozoic Eon began and ended with extreme fluctuations in the carbon cycle. In both the Paleoproterozoic [2500 to 1600 million years ago (Ma)] and Neoproterozoic (1000 to 542 Ma), extended intervals of anomalously high carbon isotope ratios ( $\delta^{13}\text{C}$ ) indicate high rates of organic matter burial and release of oxygen to the atmosphere; in the Neoproterozoic, the high  $\delta^{13}\text{C}$  interval was punctuated by abrupt swings to low  $\delta^{13}\text{C}$ , indicating massive oxidation of organic matter. We report a Paleoproterozoic negative  $\delta^{13}\text{C}$  excursion that is similar in magnitude and apparent duration to the Neoproterozoic anomaly. This Shunga-Francevillian anomaly may reflect intense oxidative weathering of rocks as the result of the initial establishment of an oxygen-rich atmosphere.

The generally high values of carbon isotope ratio ( $\delta^{13}\text{C}$ ) [ $\sim +10$  per mil (‰)] during the Paleoproterozoic Lomagundi-Jatuli (LJ) event [2200 to 2060 million years ago (Ma) (1–3)] indicate that rates of organic matter deposition exceeded that of oxidative weathering, reflecting high rates of net oxygen production during what has come to be known as the Great Oxidation Event [GOE (4, 5)]. The swings to markedly low  $\delta^{13}\text{C}$  values in the Neoproterozoic indicate excess organic matter oxidation over burial in sediments and atmospheric  $\text{O}_2$  depletion. The most notable of these, the globally distributed Shuram-Wonoka anomaly (6), is characterized by a negative shift in  $\delta^{13}\text{C}$  of sedimentary carbonates of between  $-8$  to  $-18$ ‰. However, covariation between oxygen isotope ratio ( $\delta^{18}\text{O}$ ) and  $\delta^{13}\text{C}$  in many Shuram-Wonoka carbonate sections, together with the absence of a parallel  $\delta^{13}\text{C}$  excursion in contemporaneous organic matter, has led some to conclude that the Shuram-Wonoka anomaly is an artifact of interaction with fluids in the subsurface, either in a subaerial weathering environment where groundwaters have low  $\delta^{18}\text{O}$  values typical of rainfall and are enriched in  $^{12}\text{C}$  through the decomposition of organic matter in soils or in a deep burial diagenetic environment at elevated temperatures (7, 8). There has been no

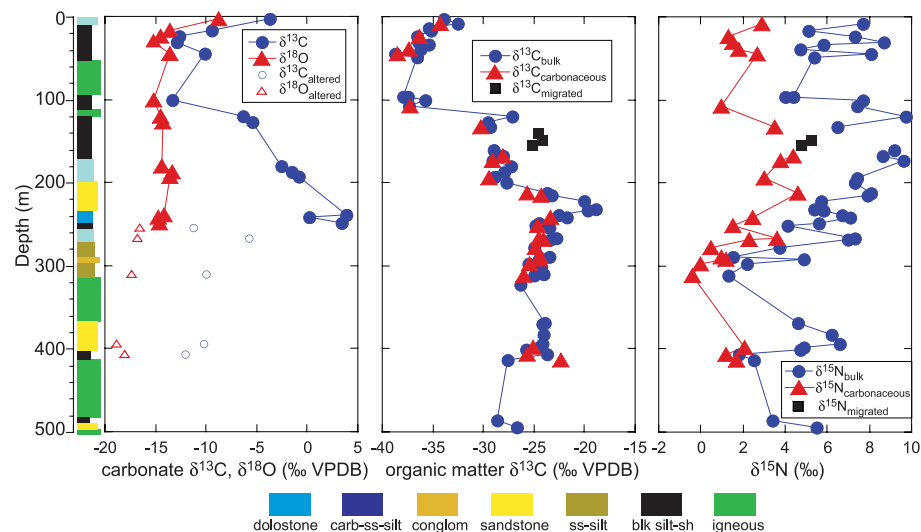
evidence of a large negative  $\delta^{13}\text{C}$  anomaly in the Paleoproterozoic (9), but sampling of this earlier interval has been relatively limited.

We sampled carbonate rocks and organic-carbon-bearing shales from the Zaonega Formation (ZF) in FAR-DEEP (Fennoscandia Arctic Russia–Drilling Early Earth Project) drill cores 12A and 12B from the Paleoproterozoic Onega Basin on the southeastern margin of the Fennoscandian Shield (10). FAR-DEEP recovered more than 3500 m of volcanic and sedimentary rocks from the Paleoproterozoic Era of the Kola Peninsula and Karelian regions of northwestern Russia. The Onega Basin sedimentary and volcanic rocks accumulated in a marine basin within a rifted active continental margin. This

succession includes shungite deposits, a noncrystalline and nongraphitized form of carbon representing petrified oil (11), as well as enigmatic organosiliceous rocks and petrified oil fields with up to 99 weight % (wt. %) C. Overlying and underlying formations constrain the age of the ZF between  $1980 \pm 27$  Ma (mean  $\pm 1$  SD) and  $2090 \pm 70$  Ma (12–14).

In the lower part of the succession (below 250 m), the  $\delta^{13}\text{C}$  of organic matter has values typical of Proterozoic shales ( $\sim -25$ ‰), whereas the concretionary and vein calcites in the rhythmically bedded, turbiditic graywacke-siltstone-mudstone that dominates the sedimentary rocks of this part of the ZF have very low  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, likely reflecting diagenetic and metamorphic rather than seawater conditions (Fig. 1). This interpretation is supported by the relatively small isotopic difference between carbonate and organic matter ( $\Delta^{13}\text{C}_{\text{carb-org}}$ ), averaging  $13.8 \pm 2.1$ ‰ (mean  $\pm 1$  SD) for carbonates below 250 m compared with  $25.3 \pm 2.7$ ‰ for carbonates above 250 m in the section [supporting online material (SOM) text].

A prominent, two-step negative  $\delta^{13}\text{C}$  excursion of about  $-14$ ‰ occurs from 220 to 100 m core depth in carbonates, bulk organic matter, and HF/HCl insoluble organic matter (carbonaceous material including kerogen and pyrobitumen). The first step is smaller, about  $-4$ ‰, and occurs over 20 m of core (from 220 to 200 m). The second is larger,  $\sim -10$ ‰, again over about 20 to 30 m of section (from 130 to 100 m). Near the top of the core interval, there is a return to somewhat less negative  $\delta^{13}\text{C}$  in both carbonates and organic matter.  $\delta^{18}\text{O}$  varies over a relatively small range ( $\pm 1$ ‰) within the interval of the



**Fig. 1.** (Left to right) Lithostratigraphy; carbon and oxygen isotope compositions of carbonates (including samples inferred to have been affected by diagenesis, designated as altered); carbon isotope composition of organic matter, including bulk, acid-insoluble (carbonaceous), and migrated fractions; and nitrogen isotopic composition of both combined mineral and carbonaceous (bulk) and acid-insoluble carbonaceous materials from FAR-DEEP cores 12A and 12B. Samples that are clearly migrated pyrobitumens are indicated with black symbols in the third and fourth panels. VPDB, Vienna Pee Dee belemnite.

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negative anomaly in  $\delta^{13}\text{C}$  and with no trend up section.  $\delta^{18}\text{O}$  values are at the lower envelope of the Proterozoic range of values (15), indicating substantial diagenetic or metamorphic alteration of the oxygen isotope composition of the carbonates. This alteration apparently did not significantly affect the carbon isotope composition of the carbonates.

Nitrogen isotope values ( $\delta^{15}\text{N}$ ) of bulk sediment are low (2 to 6‰) below 300 m core depth and even lower in the acid insoluble (carbonaceous) fraction, ranging between 0 and 2‰. From 300 to 215 m, the  $\delta^{15}\text{N}$  of the bulk sediment and carbonaceous material  $\delta^{15}\text{N}$  increases markedly to ~10 and 5‰, respectively. Bulk sediment  $\delta^{15}\text{N}$  remains generally elevated, but, at ~130 m, carbonaceous material returns to near pre-excursion values (1 to 3‰). The isotopic difference between bulk rock and carbonaceous  $\delta^{15}\text{N}$  is likely the result of a combination of primary environmental signals recorded in the carbonaceous material and the incorporation of isotopically heavy diagenetic and metamorphic ammonium into clays (16) (SOM text).

In contrast to the Shuram-Wonoka anomaly, the ZF reveals parallel  $\delta^{13}\text{C}$  excursions in carbonates and organic matter but no change in carbonate  $\delta^{18}\text{O}$ , suggesting it is not primarily a result of diagenetic alteration. We interpret the carbon isotope anomaly to reflect the geologically rapid oxidation of a massive amount of ancient organic matter. The source of organic matter could have been sedimentary material deposited during the preceding LJ interval of elevated  $\delta^{13}\text{C}$  (1–3). Subsequent exposure and oxidation may have occurred during uplift and rifting associated with the breakup of a Paleoproterozoic supercontinent (17). Oxygen-rich groundwaters would have interacted with kerogen in shales, driving massive oxidation and

release of  $\text{CO}_2$  and generating negative  $\delta^{13}\text{C}$  excursions, just as they apparently led to supergene iron-ore enrichment worldwide (17). Alternatively, oxidation of global anoxic or euxinic basins (18) enriched in dissolved organic matter (19) could explain the excursions in both the N and C isotopes, especially if the event proves to be considerably shorter than the 110-million-year maximum duration for deposition of the ZF (12–14) and thus required a proportionately smaller transfer of  $^{13}\text{C}$ -depleted organic carbon to the inorganic pool.

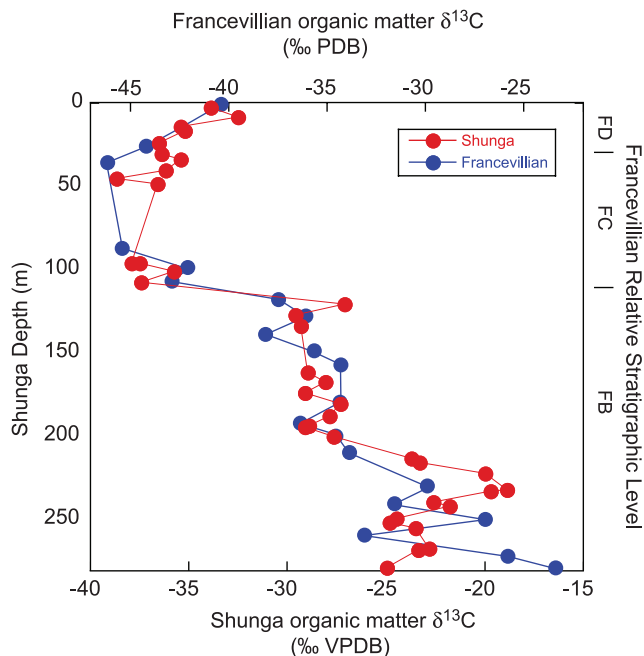
The dynamic response of the nitrogen cycle in the ZF is consistent with increased availability of  $\text{O}_2$  and oxidation of reduced N-species ( $\text{NH}_4^+$  and organic N) in the Onega Basin water column and is similar to the response documented in Archean sequences (16, 20) during apparent transient oxygenation events. Carbonaceous-matter  $\delta^{15}\text{N}$  values are initially low, likely reflecting a biological  $\text{N}_2$ -fixation source for nutrient nitrogen. Transition from a largely anoxic Onega Basin water column to one that is oxidized in surface waters would have allowed for enhanced microbial conversion of ammonium to nitrite and nitrate (nitrification), and nitrate reduction and anaerobic ammonium oxidation at depth. The coupled processes of nitrification and nitrate reduction fractionate N isotopes, with  $^{14}\text{N}$  preferentially incorporated into  $\text{N}_2$  or  $\text{N}_2\text{O}$ , leading to  $^{15}\text{N}$ -enrichment of the residual dissolved inorganic nitrogen pool (21). Thus, the observed  $\delta^{15}\text{N}$  increase of 5‰ from 300 to 215 m core depth in carbonaceous material reflects an expansion of the redox cycling of nitrogen. The ~3‰ decrease in  $\delta^{15}\text{N}$  values above 130 m may have been a consequence of  $\text{O}_2$  consumption during organic matter oxidation resulting in the crossing of basal redox thresholds and limitation of nitrogen redox cycling. Additionally, the

drop in  $\delta^{15}\text{N}$  could also, in part, reflect an intensification of nitrogen fixation in response to fixed-nitrogen deficits.

The apparently correlative, organic-C-rich shales of the  $2083 \pm 6$  to  $2050 \pm 30$  Ma Francevillian Series of Gabon (22, 23) display a negative  $\delta^{13}\text{C}$  excursion that, after accounting for basinal differences in productivity or thermal maturity leading to a several permil offset, is strikingly similar in overall magnitude and detailed stratigraphic trend to that of the ZF rocks analyzed here (Fig. 2). Moreover, a recent analysis of the carbonate rocks from the Francevillian documents an 8 to 10‰ negative excursion in  $\delta^{13}\text{C}$  (24) that corresponds to the second phase of decline in  $\delta^{13}\text{C}$  of the organic matter. We therefore suggest that this “Shunga-Francevillian” excursion was global in extent.

The Shunga-Francevillian anomaly may represent the oxidative recycling of a fraction of the organic matter sequestered during the preceding LJ high- $\delta^{13}\text{C}$  interval, triggered by the attainment of atmospheric and groundwater oxygen levels sufficient [~1% of modern (25)] to mobilize uranium (leading to the Oklo natural fission reactors in the Francevillian), generate supergene iron ores (17), and oxidize fossil organic matter during weathering. The well-established cessation of mass-independent fractionation of sulfur isotopes (S-MIF) ~2400 Ma has led to the notion that the GOE was an abrupt event occurring in the early Paleoproterozoic (26). A recent quantitative reanalysis of oxygen indicators preserved in Paleoproterozoic paleosols (27) indicates instead that oxygen levels rose gradually in the early Paleoproterozoic but more rapidly between 2100 and 2000 Ma, achieving a value that was ~1% of modern. Evidence presented here supports the conclusion that the GOE played out over hundreds of millions of years, gradually crossing the low atmospheric  $\text{O}_2$  threshold for pyrite oxidation [ $10^{-8}$  to  $10^{-5}$  of the present atmospheric level [PAL (28, 29)] by ~2500 Ma and the loss of S-MIF [~ $10^{-5}$  PAL (30)] by ~2400 Ma and then increasing at an ever-increasing rate through the Paleoproterozoic, achieving levels ~1% PAL by 2000 Ma (27).

**Fig. 2.** Comparison of bulk organic matter  $\delta^{13}\text{C}$  values from the Onega Basin (Shunga) of Fennoscandia (FAR-DEEP cores 12A and 12B) and the Francevillian Basin of Gabon (22). The depth axis for the Shunga samples is as in Fig. 1. The Francevillian depth axis is in relative stratigraphic position, as reported by Gauthier-Lafaye and Weber (22), and aligned with the Shunga profile by matching the two prominent steps in  $\delta^{13}\text{C}$ . FB, FC, and FD are recognized stratigraphic units in the Francevillian Formation.



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#### Supporting Online Material

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Materials and Methods

SOM Text

Figs. S1 to S4

Tables S1 and S2

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# Fossilized Nuclei and Germination Structures Identify Ediacaran “Animal Embryos” as Encysting Protists

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Globular fossils showing palintomic cell cleavage in the Ediacaran Doushantuo Formation, China, are widely regarded as embryos of early metazoans, although metazoan synapomorphies, tissue differentiation, and associated juveniles or adults are lacking. We demonstrate using synchrotron-based x-ray tomographic microscopy that the fossils have features incompatible with multicellular metazoan embryos. The developmental pattern is comparable with nonmetazoan holozoans, including germination stages that preclude postcleavage embryology characteristic of metazoans. We conclude that these fossils are neither animals nor embryos. They belong outside crown-group Metazoa, within total-group Holozoa (the sister clade to Fungi that includes Metazoa, Choanoflagellata, and Mesomycetozoea) or perhaps on even more distant branches in the eukaryote tree. They represent an evolutionary grade in which palintomic cleavage served the function of producing propagules for dispersal.

The ~570-million-year-old phosphorites of the Ediacaran Doushantuo Formation in southern China contain globular fossils showing palintomic cleavage (cell division not accompanied by cytoplasmic growth). These have been interpreted as embryos of some of the earliest animals (1–8) and alternatively as giant bacteria (9). Preservation of internal cellular structures, such as nuclei, within Doushantuo fossils (5, 8, 10) may provide further clues to their biological nature. Such structures, however,

are frequently discounted as features of taphonomic degradation (9, 11, 12).

To resolve the issue, we investigated ~450 Doushantuo embryo-like fossils using synchrotron-radiation x-ray tomographic microscopy (srXTM), a nondestructive technique for three-dimensional imaging internal structure at micrometer resolution (13). Fourteen specimens preserve a distinct class of subcellular bodies—one per cell—that are potentially identifiable as preserving evidence of nuclei (Figs. 1 and 2 and figs. S1 to S4). The specimens are referable to *Tianzhushania* [senior synonym of *Megasphaera*, *Parapandorina*, and *Megaclonophycus* (3, 6, 14)] and *Spirallicellula* (15). The nucleus-like bodies fulfill relevant criteria for biogenicity: Their occurrence is consistent and repeated (12 of the 14 specimens have one such body in each cell); they are regularly positioned in the cells within any single individual (central to the cells in four of the specimens, peripherally in the others); they have a consistently globular shape; and the volumetric ratio between bodies and cells corresponds to that of nuclei and cells in eukaryotes (fig. S6

and table S1). Furthermore, one specimen (Fig. 2 and fig. S1, D to H) has two elongated and one dumbbell-shaped nucleus-like body, suggesting that they are in the process of division.

The cell content surrounding the nucleus-like bodies is generally homogenous but sometimes with a finely granular fabric of dispersed less-dense objects about 1 to 3 μm in size (for example, dark spots in the peripheries of Fig. 1, F to I). This fabric may reflect the bacterial replacement of cytoplasm seen in taphonomic experiments with modern embryos (10). The outer parts of the nucleus-like bodies are preserved as a fabric of euhedral apatite crystals (Fig. 1C), a few micrometers in size, or of botryoidal void-filling growth (Fig. 1G). Internally, there is usually a spheroidal body, about 20 to 50 μm in diameter (Fig. 1, B and C, and figs. S1H and S4, C and L). In most cases, this body is positioned eccentrically, so that it appears to merge with the surrounding matrix, which has a similar fabric (Fig. 1C). The fossilized fabric is similar to that of the cytoplasm, although it may differ slightly in x-ray attenuation. The spherical bodies resemble nucleoli (8), but given the void-filling character of the surrounding fabric, they are more likely to represent shrunken nucleoplasm.

The nucleus-like bodies meet the criteria for structures present in the living organism. They are unlikely to be taphonomic artifacts, and we therefore identify them as nuclei. The nuclear envelope is not fossilized (the eukaryote nuclear envelope consists of two lipid bilayers only a few nanometers thick, with miniscule fossilization potential), but evidence of the presence of a nucleus is preserved by the mold of its external morphology. This interpretation is inconsistent with a proposed hypothesis that the microfossils are giant bacteria (6, 9, 14, 16, 17). It is consistent with a eukaryote affinity, but this does not necessarily imply that the Doushantuo fossils represent embryos of animals. None of the putative metazoan characters identified in the cellularly preserved Doushantuo fossils (1, 4, 5, 8) are metazoan synapomorphies [supporting online material (SOM) text]. Some are taphonomic artifacts, but the rest are holozoan sympleisomorphies or

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