

The late Precambrian greening of the Earth

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Many aspects of the carbon cycle can be assessed from temporal changes in the $^{13}\text{C}/^{12}\text{C}$ ratio of oceanic bicarbonate. $^{13}\text{C}/^{12}\text{C}$ can temporarily rise when large amounts of ^{13}C -depleted photosynthetic organic matter are buried at enhanced rates¹, and can decrease if phytomass is rapidly oxidized² or if low ^{13}C is rapidly released from methane clathrates³. Assuming that variations of the marine $^{13}\text{C}/^{12}\text{C}$ ratio are directly recorded in carbonate rocks, thousands of carbon isotope analyses of late Precambrian examples have been published to correlate these otherwise undatable strata and to document perturbations to the carbon cycle just before the great expansion of metazoan life. Low $^{13}\text{C}/^{12}\text{C}$ in some Neoproterozoic carbonates is considered evidence of carbon cycle perturbations unique to the Precambrian. These include complete oxidation of all organic matter in the ocean² and complete productivity collapse such that low- $^{13}\text{C}/^{12}\text{C}$ hydrothermal CO_2 becomes the main input of carbon⁴. Here we compile all published oxygen and carbon isotope data for Neoproterozoic marine carbonates, and consider them in terms of processes known to alter the isotopic composition during transformation of the initial precipitate into limestone/dolostone. We show that the combined oxygen and carbon isotope systematics are identical to those of well-understood Phanerozoic examples that lithified in coastal pore fluids, receiving a large groundwater influx of photosynthetic carbon from terrestrial phytomass. Rather than being perturbations to the carbon cycle, widely reported decreases in $^{13}\text{C}/^{12}\text{C}$ in Neoproterozoic carbonates are more easily interpreted in the same way as is done for Phanerozoic examples. This influx of terrestrial carbon is not apparent in carbonates older than ~ 850 Myr, so we infer an explosion of photosynthesizing communities on late Precambrian land surfaces. As a result, biotically enhanced weathering generated carbon-bearing soils on a large scale and their detrital sedimentation sequestered carbon⁵. This facilitated a rise in O_2 necessary for the expansion of multicellular life.

Carbonate is initially precipitated in the ocean as metastable calcite and/or aragonite, and is subsequently transformed into stable interlocking crystals of low-Mg calcite and/or dolomite. In this 'lithification' process, the originally precipitated phases undergo dissolution, reprecipitation, and isotopic re-equilibration with ambient pore fluids⁶. With the exception of rare, relatively well-preserved Phanerozoic shells, this happens to all carbonates. Precambrian carbonates are limestone or dolostone rocks; there are no preserved initial Precambrian marine precipitates.

On the basis of studies of Cenozoic deposits, lithification is most rapid in sediments in coastal areas where meteoric ground waters mix with marine pore fluids⁶. The process yields a roughly co-variant relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in which $\delta^{13}\text{C}$ decreases as $\delta^{18}\text{O}$ decreases^{7–9} (Fig. 1a). The trend documents phases that formed in mixed meteoric/marine pore fluids. Meteoric waters are depleted in ^{18}O relative to ocean water, so $\delta^{18}\text{O}$ decreases with increasing proportions of meteoric water. Photosynthesizing communities living in coastal recharge areas preferentially fix ^{12}C , such that the biomass is

typically over 20‰ depleted in ^{13}C relative to the marine inorganic C reservoir. This ^{13}C -depleted C is incorporated into the meteoric water

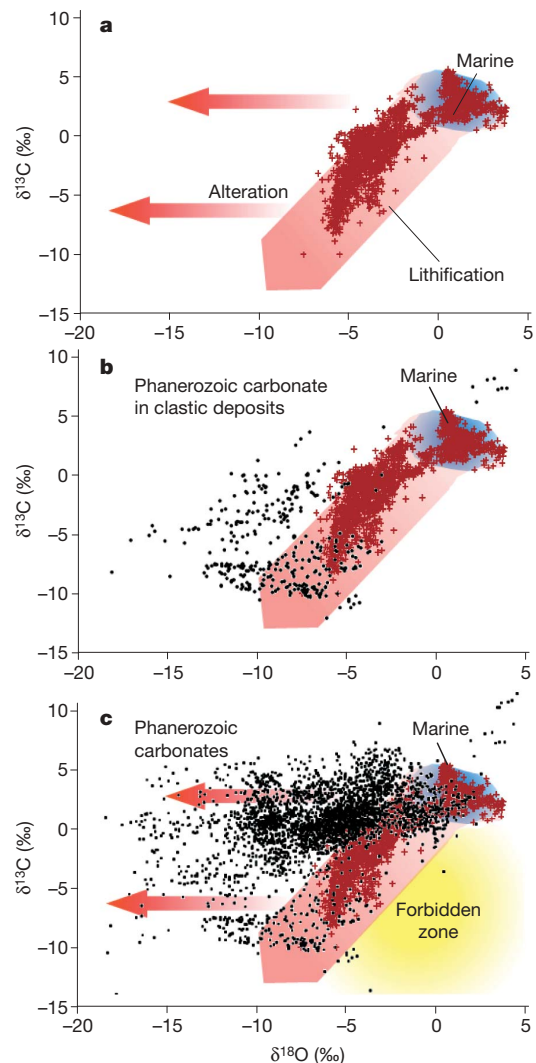


Figure 1 | Stable isotopes in Phanerozoic carbonates. **a**, Cenozoic limestones/dolostones form by way of solution/reprecipitation of primary marine precipitates. Blue area is dominantly marine pore fluids, red area contains significant meteoric water component. Both areas define the 'lithification' zone. Later deep burial and/or metamorphic alteration yield data to the left of the lithification domain, as shown by the arrows. **b**, Carbonate cements, lenses and beds in dominantly clastic successions. The lithification domain from **a** is shown in this and all subsequent figure panels for reference. **c**, Phanerozoic carbonates plot in or to the left of the lithification zone and avoid the forbidden zone. Data for this and all other figures are available in Supplementary Information.

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pore fluids through decomposition of the constantly renewing biomass and becomes incorporated into limestone/dolostone during lithification. A co-variation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ arises because low $\delta^{18}\text{O}$ signifies more meteoric water and thus a greater introduction of photosynthetically depleted ^{13}C from the subaerial recharge area. Pervasive intrusion of meteoric waters during sea-level fall is common on carbonate platforms. Pleistocene examples yield negative $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ over stratigraphic thicknesses $>100\text{ m}$ (ref. 7). $\delta^{13}\text{C}$ systematically decreases upward in the stratigraphic succession, like patterns widely reported for Neoproterozoic strata. The stratigraphic trend develops during lithification and is unrelated to any change in the global oceanic $\delta^{13}\text{C}$.

Carbonate rocks are susceptible to later recrystallization during deep burial, and can isotopically re-equilibrate with higher-temperature fluids depending upon the water/rock (W/R) ratios and the isotopic composition of the fluids. The W/R ratio of metamorphic fluids is typically high with respect to O and low with respect to C, so carbonate $\delta^{18}\text{O}$ is driven to lower values through higher-temperature equilibration while $\delta^{13}\text{C}$ undergoes little change¹⁰ (Fig. 1a). Ancient carbonates that form in coastal pore fluids and undergo later alteration

therefore display values that plot in, or to the left of, the lithification domain (Fig. 1a). Whereas $\delta^{13}\text{C}$ values as low as -10‰ can occur, most are greater than -5‰ . Low $\delta^{18}\text{O}$ of an ancient rock may have been set during the initial lithification event or during a much later metamorphic event. For example, a rock sample in the lithification domain (Fig. 1a) with $\delta^{18}\text{O} = -4\text{‰}$, $\delta^{13}\text{C} = -3\text{‰}$ does not represent the value of the initially precipitated marine sediment but does represent the initial, 'unaltered' value of the limestone or dolostone that formed during lithification. In Cenozoic rocks, its position in the crossplot would indicate that meteoric waters rich in coastal photosynthetic C were a component of the pore fluids during lithification. Neoproterozoic carbonate rocks should first be evaluated in this manner, which is well understood for Cenozoic limestone/dolostone formation.

Many published Neoproterozoic C isotope data are for dominantly clastic sections with relatively thin carbonate beds, cements and accumulations. Phanerozoic examples of carbonate in dominantly clastic sequences also display wide variations in $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ (Fig. 1b). In some successions, the isotopic signal is set during lithification in isotopically evolving pore fluids, as discussed above.

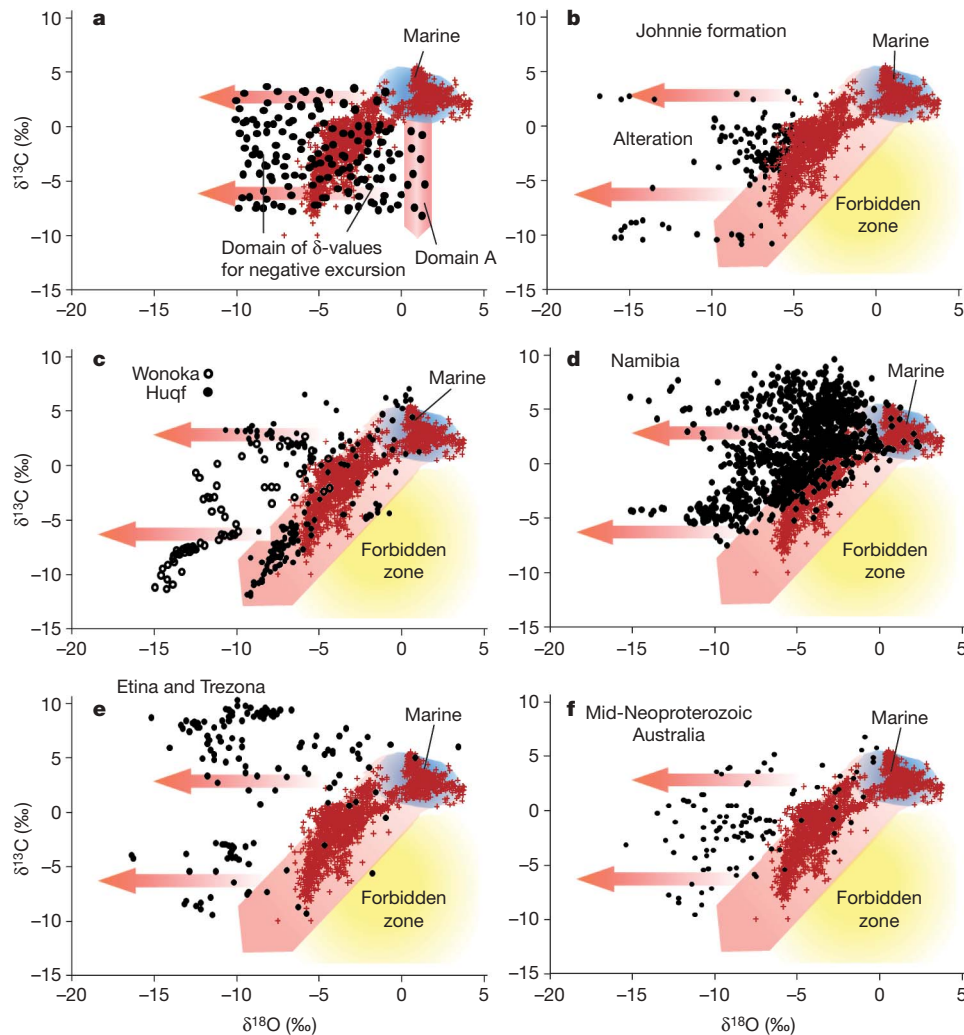


Figure 2 | Neoproterozoic carbonates. **a**, Data pattern expected for marine carbonates during a negative excursion of the global marine inorganic C reservoir. $\delta^{18}\text{O}$ of sea water is unaffected, so initial precipitates have marine $\delta^{18}\text{O}$ and progressively lower $\delta^{13}\text{C}$ depending upon the magnitude of the negative excursion (domain A). Subsequent alteration shifts the values to

lower $\delta^{18}\text{O}$. No forbidden zone occurs. **b–f**, Data for claimed negative C excursions all plot in or to the left of the forbidden zone. **b**, Johnnie Formation, USA; **c**, Wonoka Formation (Australia) and Huqf Group (Oman); **d**, Namibia (Africa); **e**, Etina and Trezona Formations (Australia); and **f**, Mid-Neoproterozoic (Australia).

For example, low $\delta^{18}\text{O}$ in carbonate-cemented shelf sands and silts results from meteoric waters in phreatic lenses, and low $\delta^{13}\text{C}$ is contributed from the terrestrial phytomass¹¹. More commonly, circulating deep basinal fluids produce late carbonate cements and lenses during burial. These have low $\delta^{18}\text{O}$ from equilibration with pore fluids at elevated temperatures, and $\delta^{13}\text{C}$ typically less than -5‰ from thermal decarboxylation of buried organic matter encountered along the fluid flow path^{12,13}. In all cases, the data plot near or to the left of the lithification reference domain (Fig. 1b).

In clastic-dominated sequences, the pore fluid W/R ratio for C is much larger than in limestone/dolostone sections. Any initial carbonate precipitates are therefore more susceptible to alteration of the C isotope ratio. Modern phreatic lenses over 100 m thick occur today in clastic sequences out to 100 km offshore¹⁴. Submarine groundwater flux rates through these lenses even exceed river runoff¹⁵. Such lenses migrate as a band across the shelf that tracks sea-level variation and exposes the vast majority of clastic shelf sediment to meteoric waters at some point during burial^{11,16}. Shelf sediments dominate past successions preserved in the stratigraphic record, so thick clastic sequences with low- $\delta^{18}\text{O}$, low- $\delta^{13}\text{C}$ carbonate are expected.

The pattern of lithification followed by possible later metamorphism results in a forbidden zone, which contains little data, located to the right of the lithification zone on the isotopic crossplot. Thousands of published analyses of Phanerozoic carbonates clearly avoid the forbidden zone (Fig. 1c). The majority of these data are for carbonate-dominated systems and thus have $\delta^{13}\text{C} > -5\text{‰}$.

Thousands of $\delta^{13}\text{C}$ analyses have now been published for Neoproterozoic carbonates to possibly correlate strata and explore for perturbations to the global C cycle. As observed in the Pleistocene⁷, thick intervals of negative $\delta^{13}\text{C}$ values occur in the Neoproterozoic but are considered to record profound perturbations to the global marine carbon cycle unique to the Neoproterozoic rather than being considered in terms of normal mixed meteoric/marine lithification or decarboxylation. In some cases, stratigraphic relations require these excursions to be sustained for millions of years at values even below the mantle average of -5‰ , the minimum value for a steady state C isotope mass balance in the Phanerozoic ocean¹⁷.

The relationship between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ provides a useful means of distinguishing meteoric and burial lithification from marine excursions. Putative changes in the $\delta^{13}\text{C}$ of the ocean relate only to the well-mixed dissolved inorganic C reservoir, and show no relationship to $\delta^{18}\text{O}$ because the $\delta^{18}\text{O}$ of sea water is affected by totally different processes. A perturbation to the global C cycle that lowers the $\delta^{13}\text{C}$ of the surface ocean's dissolved inorganic C reservoir by claimed values of 5–12‰ (for example, ref. 2) therefore yields a negative excursion with values that would plot in the forbidden zone. Indeed, such excursions would define a vertical band for the precipitated carbonate as the excursion progressed down from the normal marine carbonate values (Fig. 2a). If the $\delta^{13}\text{C}$ of the precipitate is inviolate as currently assumed, later alteration drives $\delta^{18}\text{O}$ to lower values and a 'box-like' data array results, bounded to the right by the vertical excursion trajectory (Fig. 2a, domain A). This array is therefore expected, in contrast with that observed for the Phanerozoic.

Five classic examples of successions claiming to represent marine negative C isotope excursions do not show the expected crossplot for such excursions (Fig. 2b–f). Instead, they are bounded by the Cenozoic lithification domain to the right, and stream off to lower $\delta^{18}\text{O}$ values that are readily attributable to later metamorphic alteration. In all cases, the lower $\delta^{13}\text{C}$ values are associated with lower $\delta^{18}\text{O}$ values.

These data are incompatible with the excursion scenario unless (1) carbonates deposited during a negative $\delta^{13}\text{C}$ excursion are more susceptible to later $\delta^{18}\text{O}$ metamorphic alteration in proportion to their negative $\delta^{13}\text{C}$ value, or (2) $\delta^{18}\text{O}$ of sea water decreases as $\delta^{13}\text{C}$ of sea water decreases to produce an array that fortuitously resembles the Cenozoic lithification domain (Fig. 1a). There is no known geological mechanism compatible with the first scenario, and the second

would require synchronous changes of $>8\text{‰}$ in the $\delta^{18}\text{O}$ of sea water during the time of the putative C isotope excursions. No mechanisms that synchronously change oceanic $\delta^{18}\text{O}$ are known or have been proposed. The alternative explanation—that the Neoproterozoic carbonates underwent the same processes of lithification and metamorphism observed in Phanerozoic carbonates—is a simpler explanation for these data, and does not require extraordinary and anomalous behaviour of the C cycle specific to the Neoproterozoic.

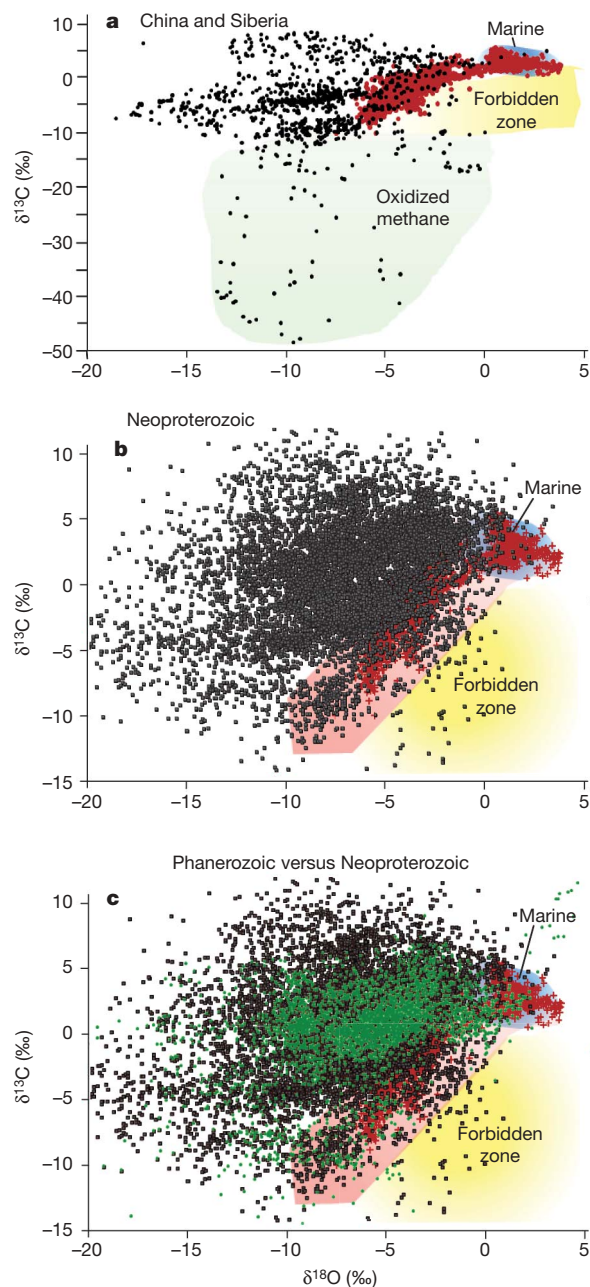


Figure 3 | All Neoproterozoic and Phanerozoic carbonates. **a**, Extreme ^{13}C depletions associated with oxidation of methane in samples from China and Siberia. Note expanded vertical scale. **b**, All published Neoproterozoic data. Nearly all plot in or to the left of the lithification reference domain. Most of the few values plotting in the forbidden zone probably represent unusual examples involving oxidation of methane, as documented for the China and Siberia forbidden zone samples. **c**, Comparison of Phanerozoic carbonates (green points) with Neoproterozoic carbonates. The data are isotopically indistinguishable.

Some Neoproterozoic carbonates with $\delta^{13}\text{C}$ as low as -40‰ do plot in the forbidden zone (Fig. 3a), but most of these have been attributed to local oxidation of methane^{3,18}. All unfiltered, published Neoproterozoic data (over 8,000 samples; references in Supplementary Information) yield very few samples in the forbidden zone (Fig. 3b). Several of those that do are thin horizons in otherwise low- ^{13}C intervals, and several are for claimed glaciomarine concretions¹⁹. The Neoproterozoic data are essentially indistinguishable from the Phanerozoic data (Fig. 3c). Similar to their Phanerozoic counterparts, carbonate sequences have $\delta^{13}\text{C} > -5\text{‰}$, whereas clastic sequences yield $\delta^{13}\text{C}$ as low as -10‰ . Rather than indicating C isotope excursions, the Neoproterozoic data seem to represent normal isotope variations that occur during lithification and metamorphism. Apparent correlations of low $\delta^{13}\text{C}$ between widely separated sections may relate simply to eustatic sea-level drops where phreatic lenses intrude simultaneously during lithification.

Consequences of this interpretation include: (1) $\delta^{18}\text{O}$ values of Neoproterozoic sea water were similar to that of the Cenozoic, consistent with the Muehlenbachs model²⁰; (2) a terrestrial phytomass existed that was large enough to inject enough photosynthetic C into coastal ground waters to produce identical C isotope depletions in marine carbonate to those observed in the Phanerozoic. The nature of the photosynthesizers is obscured by the absence of preserved terrestrial surfaces, although molecular and other evidence suggest the expansion of a primitive land biota starting at least by 1 Gyr ago^{5,21–23}. It was probably composed of protists, mosses, fungi and liverworts with evidence of lichen by 600 Myr ago^{5,24}. (3) Marine $\delta^{13}\text{C}$ may have varied in the Neoproterozoic, but this could only be deduced following careful consideration of large isotopic changes that occur during lithification and later alteration. The most positive $\delta^{13}\text{C}$ in a co-variant data array is the best minimum estimate of the marine $\delta^{13}\text{C}$ of the local marine depositional environment. This approach was used in one early study²⁵, and similar analysis is now warranted for all other Neoproterozoic sections.

If the first expansion of photosynthesizing communities on the land surface occurred in the Neoproterozoic, then carbonates deposited before 850 Myr ago should not show significant negative $\delta^{13}\text{C}$ values. Indeed, they cluster around $\delta^{13}\text{C} = 0 \pm 2\text{‰}$ (Fig. 4). Any earlier coastal phytomass was apparently not significant enough to produce strongly negative $\delta^{13}\text{C}$ in carbonates during the stabilization process.

The contrasting isotope data between 850 Myr ago and the Neoproterozoic suggest that the terrestrial expansion of photosynthesizing communities preceded the significant climate perturbations of

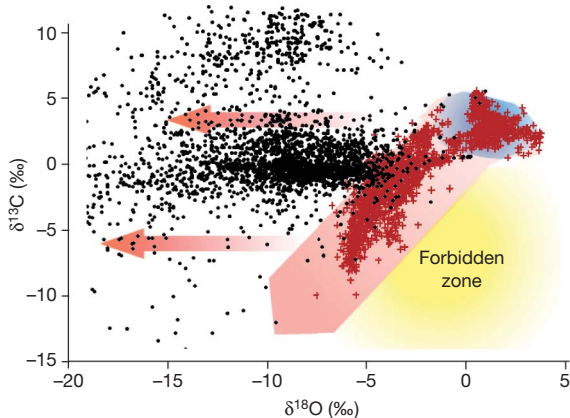


Figure 4 | Pre-850 Myr ago marine calcite and dolomite. These data do not display the ^{13}C depletions associated with lithification as observed for younger carbonates. Low ^{13}C was not being introduced during lithification, indicating minimal photosynthesizing communities on land in coastal areas. Being much older, these have undergone significantly more metamorphism to lower $\delta^{18}\text{O}$ values. Most of the very low $\delta^{13}\text{C}$ values are for vein-rich samples or high-grade metamorphic rocks.

the late Precambrian glaciations, and was followed by a rise of O_2 (ref. 26) and a secular change in terrestrial sediment composition⁵. The onset of significant biotically enhanced terrestrial weathering would have increased the flux of lithophile nutrient elements and clay minerals to continental margins. This would have increased production and burial preservation of organic C towards modern values^{5,27,28} and consequently facilitated the stepwise rise in atmospheric O_2 necessary to support multicellularity. The terrestrial expansion of an extensive, simple land biota indicated by the isotope data may thus have been a critical step in the transition from the Precambrian to the Phanerozoic world.

METHODS SUMMARY

All data plotted in the figures were extracted entirely from the published literature and online databases. All known Neoproterozoic data published as of 2008 were compiled without filtering or exclusion. The accompanying Excel file (Supplementary Information) lists all data and references for convenient reconstruction of the figures.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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Author Contributions Both authors shared equally in interpretations and implications of the data. L.P.K. compiled the data, wrote the initial draft, and managed revisions.

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