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Stable isotopic evidence for increased terrestrial productivity through geological time

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Marine life on Earth is known back to the Archean Eon, when life on land is assumed to have been less pervasive than now. Precambrian life on land can now be tested with stable isotopes because living soil CO_2 is isotopically distinct for both carbon and oxygen from both marine and volcanic CO_2. Our novel compilation of previously published oxygen and carbon isotopic compositions of pedogenic and paleokarst carbonate can be compared with the coeval marine record. Long-term enrichment (to heavier isotopic composition) of oxygen, but no significant trend in carbon through time, long apparent from marine carbonate, is now demonstrated also for pedogenic and paleokarst carbonate. Oxygen isotopic enrichment is not due to changing global temperature or hypsometry, but to increased evapotranspiration and photosynthesis on larger continents. Differences in isotopic composition between land and sea have increased in an episodic fashion, peaking at times of major evolutionary innovations for life on land, and also at times of ice ages. The $\delta^{13}C$ and $\delta^{18}O$ divergences between land and sea correspond to terrestrial productivity spikes including evolution of Neoproterozoic (635 Ma) lichens, middle Ordovician (470 Ma) non-vascular land plants, middle Devonian (385 Ma) forests, early Cretaceous (125 Ma) angiosperms, and middle Miocene (20 Ma) sod grasslands.

Keywords Oxygen isotopes, Carbon isotopes, Land productivity, Ice ages

The biological carbon cycle of reduction to organic matter and oxidation to CO_2 has been critical to life and paleoclimate on Earth, and its 3.6 Ga record in stable isotopic composition of marine carbonates and organic matter has been known for some time[1]. Stable isotopic records of pedogenic carbonate in paleosols have proven important proxies for past precipitation, temperature, and atmospheric CO_2 greenhouse control of climate[2], and this study examines their role in deep time. Living soils of Earth are biological reactors that not only support and supply life, but create new materials such as clay and carbonate, and filter air and water with planetary effects[2–4]. Paleosols and paleokarsts are less well known than marine carbonates, and their differences are outlined in Fig. 1 and Table 1. The influence of soil on isotopic composition of surficial systems can be traced because of the generally more negative isotopic composition of CO_2 in soil compared with air and sea (Fig. 2). Other isotopic differences between land and sea are the correlated $\delta^{13}C$ and $\delta^{18}O$ not found in marine or lacustrine carbonate[4]. The higher oxygen isotope ratio in air compared with the sea, or Dole effect, has been attributed to photosynthesis, respiration, and evapotranspiration, and used to examine terrestrial productivity differences between glacial-interglacial cycles of the Pleistocene[3]. Here we examine for the first time stable isotopic changes on land over the past 3600 million years.

Soil CO_2 is central to these differences, because it is derived by microbial decay of organic matter from plant and other photosynthesis fractionated from air by an enormous −29‰ $\delta^{13}C$ through the photosynthetic enzyme rubisco into organic matter, then passed with little isotopic fractionation by bacterial decay to soil CO_2[4]. Both carbon and oxygen are affected because rubisco selects light isotopologues[4] of gaseous CO_2. Soil CO_2 is concentrated by 2–4 orders of magnitude (to 2,000-100,000 ppm) over concentrations in the atmosphere (200–400 ppm) because of microbial respiration in tight spaces[2]. Soil CO_2 in soil water thus produces unusually effective carbonic acid for incongruent dissolution of feldspars and other minerals to soil clays[5], consuming carbon while recording O and C isotopic compositions within hydrated, adsorptive soil clays[6]. In semiarid climates soil CO_2 is incorporated in carbonate such as calcite and dolomite, preserving soil CO_2 isotopic compositions[2]. Thus, pedogenic carbonate and clayey sediments are potential archives of paleoenvironments and life on land.

This study to examine differences in isotopic composition of different reservoirs of carbon and oxygen in deep time is based on a large compilation of marine, lacustrine, paleokarst, and pedogenic carbonate isotopic analyses, in modern environments as well as in deep time. Paleoenvironmental interpretations of each of the

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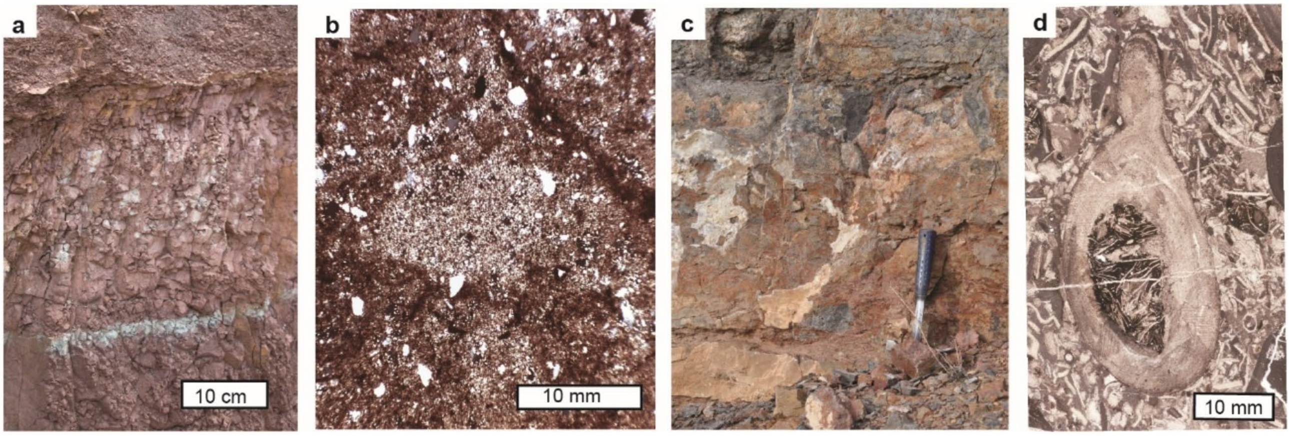

Fig. 1. Paleosol (**a**-**b**) and paleokarst (**c**-**d**) in outcrop (**a**, **c**) and petrographic thin sections oriented vertical to bedding (**b**, **d**). The paleosol has sharp surface above another sharp surface of underlying paleosol, and a central (Bk) horizon of white calcareous nodules. The paleokarst has ferruginized solution planes emanating from the upper surface and staining seashell fragments, unlike overlying and underlying gray marine limestones. (**a**-**b**) Sekawa silty clay loam paleosol in Tonian (758 Ma), Carbon Canyon Member of Galeros Formation, in Nankoweep Creek, Arizona[7]: (**b**-**c**) Pakuitah profile in Early Cambrian (513 Ma), Chambless Limestone, near Cadiz, California[5].

Pedogenic	Paleokarst	Aquatic carbonate
Fossil land animals and root traces	Fossil marine or lake shells	Fossil marine or lake shells
Unbedded nodular	Bedded to massive	Bedded to massive
Diffuse zone of nodules in claystone	Thick sequence red stained	Thick sequence grey coloured
Highly correlated δ^{13}C‰ and δ^{18}O‰	Poorly correlated δ^{13}C‰ and δ^{18}O‰	Uncorrelated δ^{13}C‰ and δ^{18}O‰
Mainly Negative δ^{13}C‰ and δ^{18}O‰	Mainly Negative δ^{13}C‰ and δ^{18}O‰	Mainly positive δ^{13}C‰ and δ^{18}O‰
Displacive and replacive cements	Cavity fill sparry cements	Cavity fill sparry cements

Table 1. Differences between pedogenic, paleokarst, and aquatic carbonate.

carbonates was taken from cited literature. Pedogenic carbonate is generally found in replacive and displacive micritic calcite or dolomite nodules within red beds[7] (Fig. 1a,b). Marine and lacustrine carbonate is generally sparry to granular, with well preserved molluscs and other aquatic fossils. Paleokarsts are marine or lacustrine carbonate, altered from an irregular surface by red discoloration and divided by dissolution planes filled with red clay[5] (Fig. 1c,d).

Materials and methods

Data compilations

This study is based on two original compilations and one published compilation. Marine carbonate isotopic data from 9,748 analyses of little-altered shells, limestones and dolostones is from an independent previously published compilation with high standards of data quality[8]. The first original compilation is 33,322 carbon and oxygen isotopic compositions of a variety of modern earth materials, including carbonates (Fig. 2: Supplementary Information Online Table 1; available online here https://blogs.uoregon.edu/gregr/detailed-webpage/downloadable-data/). Second is a compilation of 7,175 oxygen and carbon isotopic analyses of paleosol carbonate, and 2,152 analyses of paleokarsts from published literature (Fig. 3: Supplementary Information Online Tables S2-S3. Many of the Precambrian analyses were made using a Finnegan MAT 253 mass spectrometer in the Department of Earth Sciences, University of Oregon. Carbon and oxygen isotopic values are both reported here versus the VPDB standard, for ease of comparison (Fig. 2) with other carbonates, in addition to the separate standard for oxygen of SMOW. Delta notation for oxygen is by comparison with these standards as follows $\delta^{18}O=(\delta^{18}Osample/\delta^{18}Ostandard-1).1000$. Where values were originally reported in SMOW (‰), they were converted to PDB using this equation [$\delta^{18}O_{VPDB}=(0.97001.\delta^{18}O_{SMOW})-29.99$]. Δ^{17}O is reported as deviation from a reference fractionation line[9] of $\delta^{17}O=0.5305.\delta^{18}O$, by the formula $\Delta^{17}O=\delta^{17}O-0.5305.\delta^{18}O$.

Bins for data were chosen *apriori* to reflect major events in the evolution of life on land as established not only by the fossil record, but by the study of fossils soils. The bins include major ice ages: Cryogenian[7], Hirnantian[10], PermoCarboniferous[11], early Cretaceous[12], and Pleistocene[13] represented by periglacial paleosols such as ice wedges and sand wedges[7,11,12]. Also included were major events such as advent of lichens and other megascopic microbial consortia[14] on land, non-vascular land plants[10], trees[15], and grasses[13], evident from fossil roots and other traces in paleosols[10,13,15]. Bins also include major mass extinctions which also affected soil productivity,

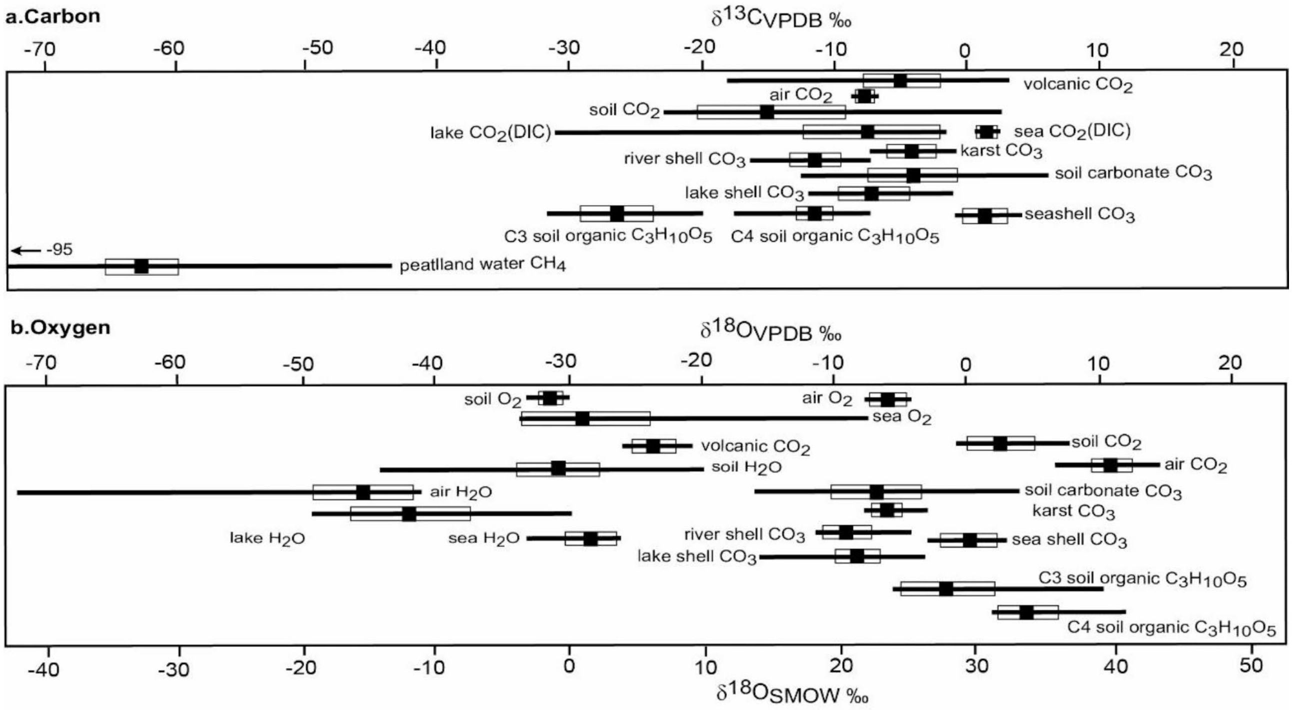

Fig. 2. Carbon (**a**) and oxygen (**b**) isotopic composition of different earth materials. Black box is mean, open box is one standard deviation of mean and whiskers are total range of compiled data (for sources see Supplementary Information Table S1).

such as the mid-Ediacaran[16], Hirnantian[10], Frasnian-Famennian[17], Late Permian[18], Late Jurassic[19] and Late Cretaceous[20]. All data were conformed to the 2020 Geological Time Scale[21]. Choosing bins in this way, from the same fossil soils used to evaluate major events, was designed not to discover divergences, but to test the effects of major events on stable isotopic composition on land and sea.

Data quality

A concern with similar compilations of marine isotopic data has long been that dispersion of results was due to burial alteration and secondary recrystallization. Marine limestone exposed in paleokarst, for example, is diagenetically replaced by isotopically lighter oxygen of meteoric water[22]. Reddening and karst fissuring were used to identify paleokarst in our compilation (Fig. 1c,d), as well as geological studies revealing major disconformities, with cave breccia, red cave earth, and speleothems documented in the sources cited[14,16]. Low temperature recrystallization of carbonate does not alter stable isotopic composition, but at temperatures in excess of 400°C, isotopic exchange with graphite can enrich carbon isotopic composition of calcite[23]. None of the samples in our compilation were metamorphically altered to this extent of recrystallization. For these reasons, compilations of stable isotopic composition of marine carbonate were focused on materials with demonstrable original skeletal structure, such as prismatic microstructure of brachiopod shells[8]. Our compilation similarly chose nodular pedogenic carbonate with replacive micrite like that of unaltered soils documented in thin section (Fig. 1b).

The quality of our data is also revealed by dispersion for different time bins, not significantly greater than for highly vetted marine data for oxygen[8], and less dispersed than for carbon (Figs. 3 and 4). Probability from an F test that variances are not equal between marine and paleosol carbonate is highly unlikely for both carbon (10^{-14}) and oxygen (10^{-5}). Probability from an F test that variances are not equal between marine and paleokarst carbonate are significant for carbon (0.02), but barely significant for oxygen (0.19), presumably because of variable karstification of marine carbonate.

Results

Modern stable isotopic variation

Different modern carbonate, waters and gases show dramatic variation in stable isotopic composition: from -75 to $+11$‰ for $\delta^{18}O$ and -95 to $+5$‰ $\delta^{13}C$ vs. PDB (Fig. 2). The lowest oxygen isotopic composition is in water vapor of air at high latitudes[24], and the highest oxygen isotopic composition is C4 organic matter[25]. The lowest carbon isotopic composition is in methane of peatland water[26], and the highest carbon isotopic composition is within soil carbonate[27].

The difference between air and marine O_2 isotopic composition, or Dole effect, remains profound as an average, but there are intermediate connecting values (Fig. 2). Another big difference is carbon isotopic composition of peatland methane[26] and that of C3 and C4 plants[28]. Variation in isotopic composition of some

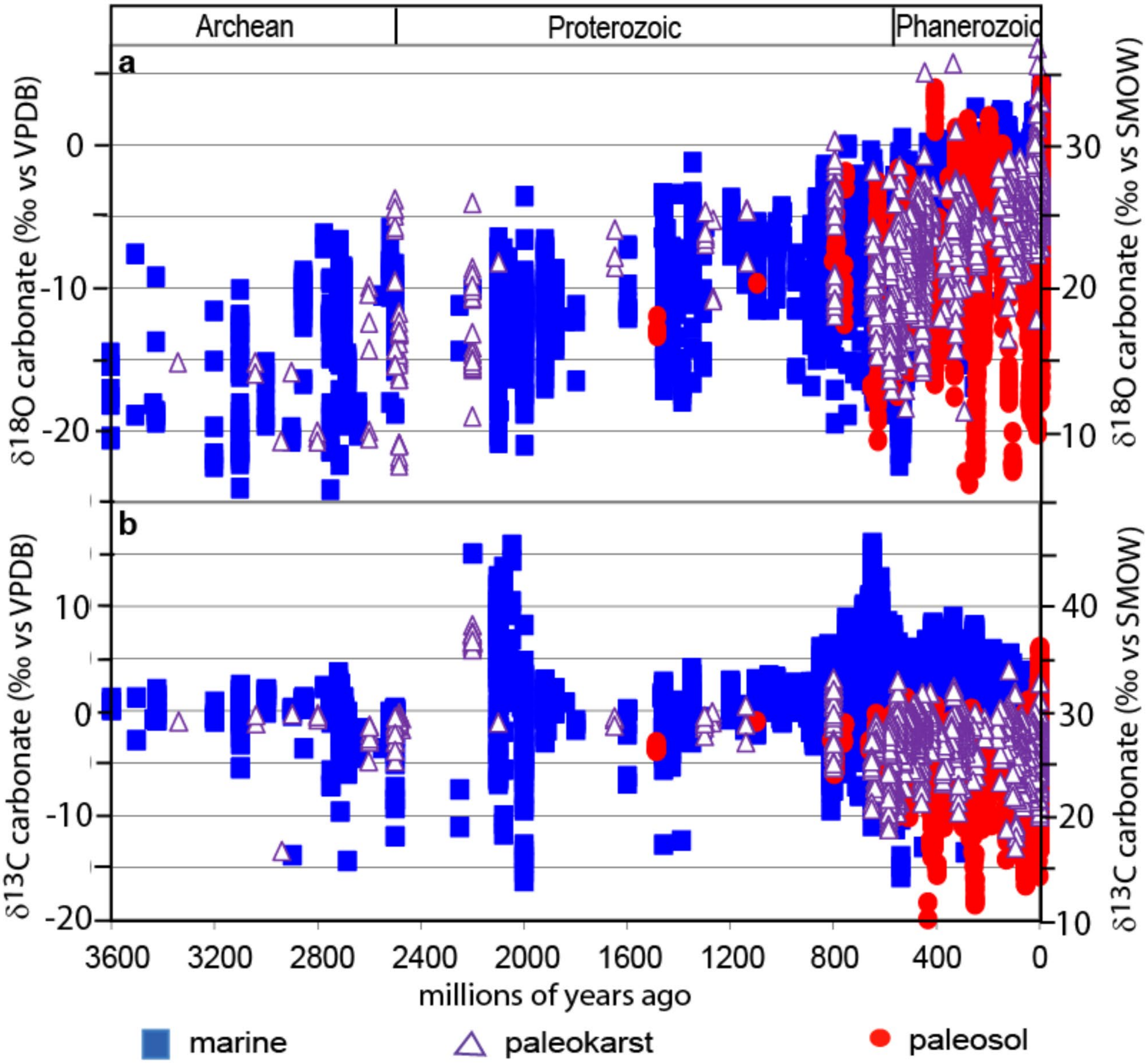

Fig. 3. Stable isotopic composition of marine, paleokarst and paleosol carbonate through time. (**a**) Oxygen. (**b**) Carbon (for data see Supplementary information Tables S2-S3).

reservoirs is large, but impressively narrow isotopic variation was found in dissolved inorganic carbon in the sea, and in oxygen in soil and the sea (Fig. 2).

Past stable isotopic variation

The most intriguing secular trends observed were long-term enrichment (to heavier isotopic composition) of oxygen[8,28], but no significant trend in carbon through time (Fig. 3). Both trends have long been apparent from marine carbonate[1,8], but we here demonstrate that they also are found in pedogenic and paleokarst carbonate. The overlap between marine and non-marine data is substantial for oxygen, but carbonate carbon values of paleosols and paleokarst are generally lower than the marine values (Fig. 3).

Because of overlapping values we binned data to examine averages and standard deviations for different time intervals of known major evolutionary and paleoclimatic events to reveal differences between land and sea. Numbers of analyses within each bin are substantial, with tens of analyses for Precambrian, but hundreds for each bin in the Phanerozoic (Fig. 4c). In general, marine isotopic values for both oxygen and carbon are heavier than paleosol values, with paleokarst values in between (Fig. 4a-b).

The difference between paleosol and paleokarst isotopic composition (Fig. 5c-d) also reveals that paleosols are isotopically more divergent from marine than paleokarst, which is mostly meteorically weathered marine limestone. Furthermore, the divergence between land and sea carbonate stable isotopic composition generally increased over time.

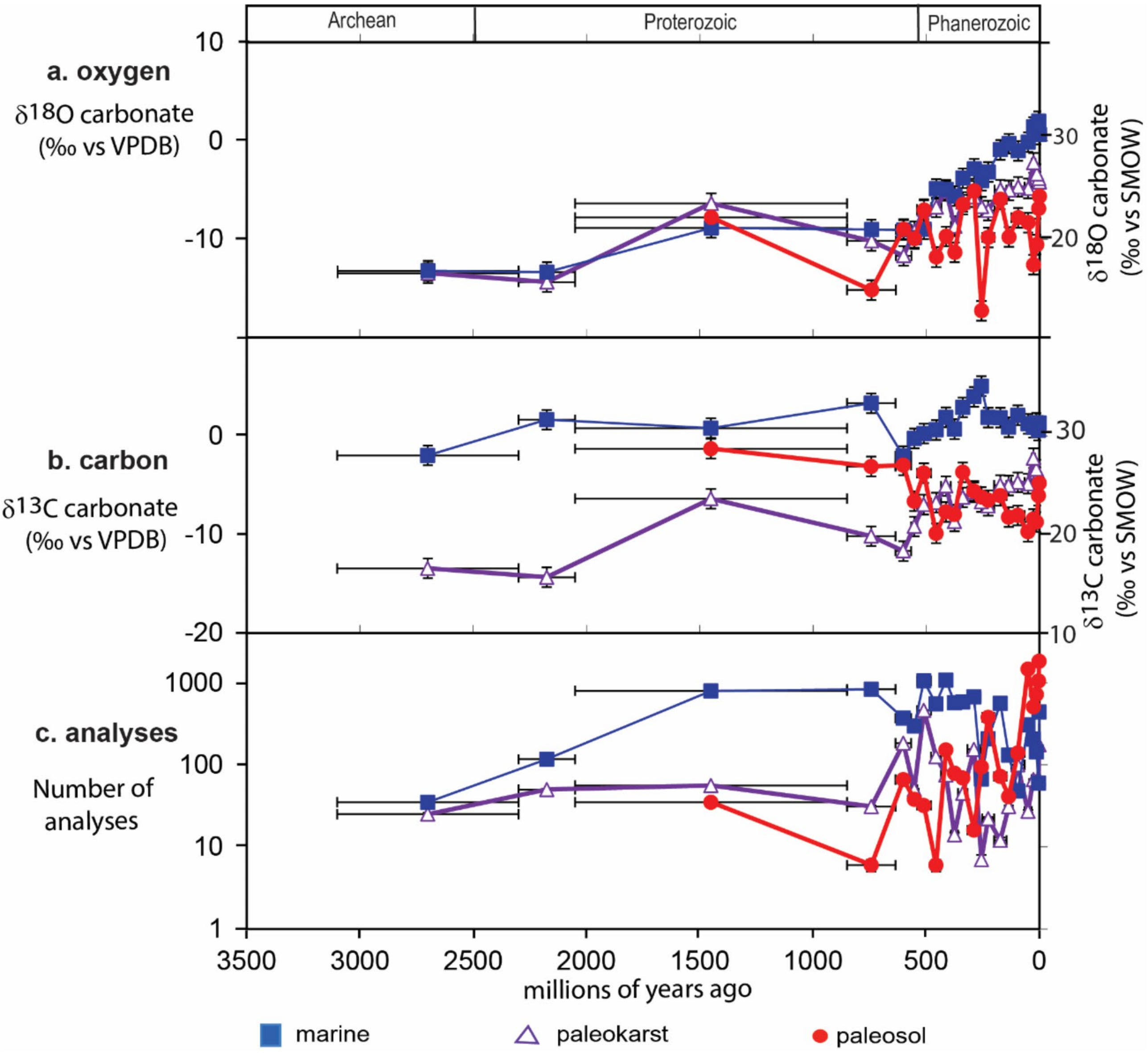

Fig. 4. Variation in stable isotopic composition of paleosol, paleokarst and marine carbonate in deep time. (**a**) Oxygen; (**b**) carbon; (**c**) number of analyses for each plotted point. Based on 7175 calcareous paleosols, 2175 paleokarsts and meteorically altered marine carbonates, and 9478 little-altered marine carbonates. Error bars in isotope analyses are 2 standard errors (For data see Supplementary Information Tables S4-S5).

Our binning of these data also show that long-term isotopic divergence between marine and non-marine carbonate has proceeded episodically: times of large divergence alternated with times of less divergence (Fig. 5c-d). The times of greatest divergence were times of major biotic innovations, such as multicellularity, land plants, forests, and grasslands (Fig. 5a). Divergence extremes were also close to times of major glacial episodes, including Neoproterozoic Snowball Earth (Fig. 5b). Biotic and climatic global change events were recorded by strong land-sea isotopic differences.

Interpretations of modern stable isotopic variation

In modern environments the largest isotopic fractionations for carbon are biological and for oxygen are physical. Extremely depleted (negative) oxygen isotopic composition is created by atmospheric fractionation of water vapor by rainout of isotopically heavier water during movement of air masses to high latitudes and altitudes[24]. This is revealed by our data showing that oxygen in air is less varied isotopically, and much heavier than oxygen in atmospheric water vapor (Fig. 2). These isotopic fractionations are also related to global temperature and ice volume to the extent that these have regulated circulation of water vapour in the atmosphere during the Quaternary[29].

Extremely depleted (negative) carbon isotopic composition is created by methanogens and methanotrophs, but C3 plants produce significantly depleted organic matter, and C4 plants less significant carbon isotopic deviation[16]

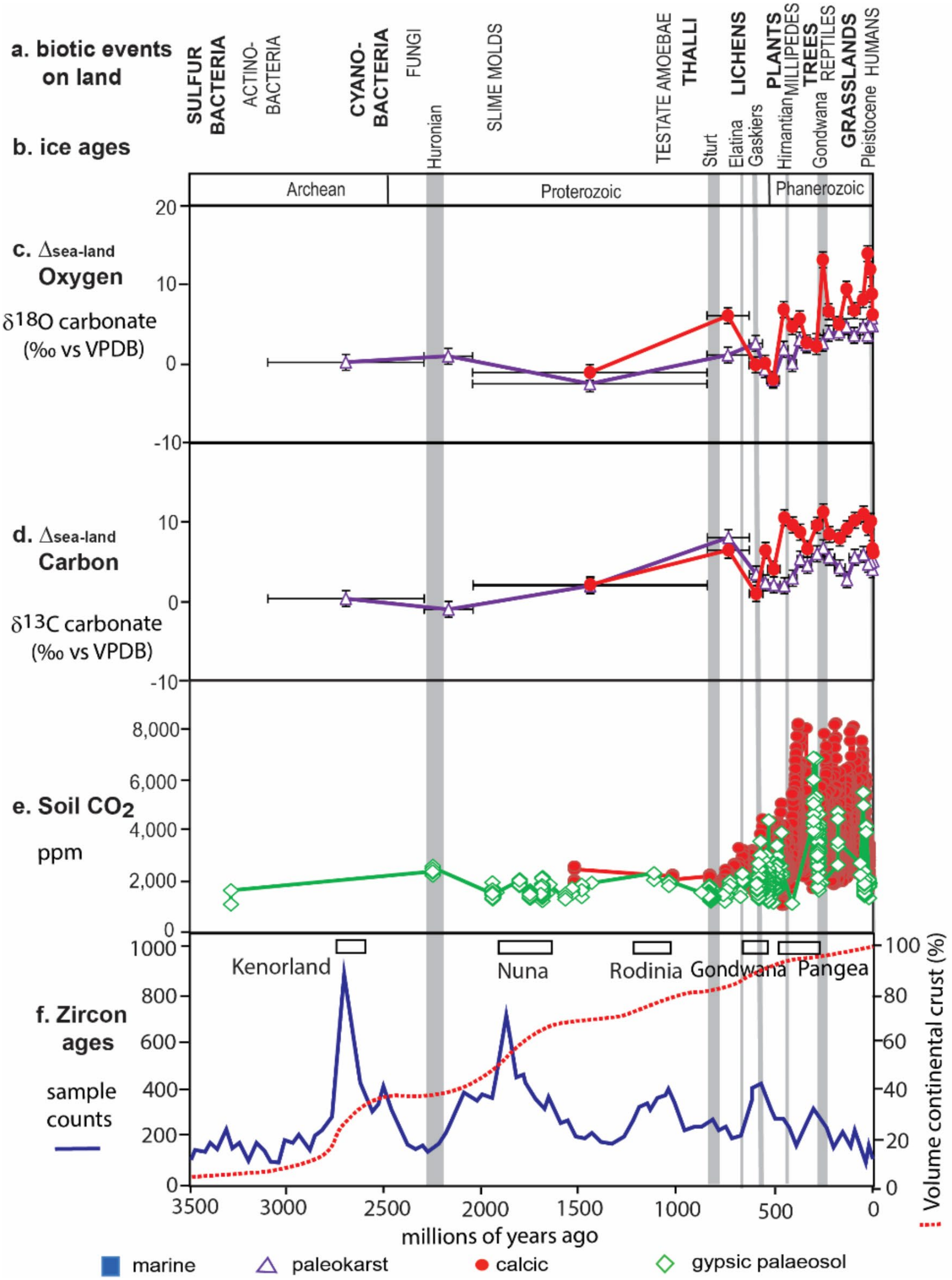

Fig. 5. Difference between paleokarst and paleosol stable isotopic composition and the isotopic composition of marine carbonate in deep time, as a metric of terrestrial productivity compared with depth to salts in paleosols, (**a**) biotic events, (**b**) ice ages, (**c**) oxygen isotopic composition difference between sea and land, (**d**) carbon isotopic composition difference between sea and land, (**e**) secondary soil productivity as ppm CO_2 inferred from compaction-corrected depth to gypsum and calcite in paleosols[1], (**f**) zircon ages, supercontinents and continental growth as a proxy for tectonic activity[38,48]. (For data see Supplementary Information Tables S4-S5).

from atmospheric CO_2. The enzyme responsible for extreme isotopic discrimination of methanogenesis is methanofuran[30]. The enzymes for methanotrophy, methane monooxidases, are less discriminatory[31]. Such extremely depleted carbon isotopic values are rare. and restricted to local anoxic parts of the modern world.

The enzyme responsible for carbon isotopic fractionation in plants and cyanobacteria, is rubisco, which selects for light isotopologues of CO_2. Rubisco cannot discriminate whether CO_2 is light for oxygen or carbon[4] but selects for light isotopologues of CO_2, and so creates cellulose and pedogenic carbon with diagnostic high correlation[32] between isotopic composition of $\delta^{13}C$ and $\delta^{18}O$. Thus, oxygen as well as carbon in organic matter and pedogenic carbonate is also to some extent, enzymatically lightened. This photosynthetic linkage may explain why oxygen in soil O_2 and CO_2, and in both paleosol and paleokarst carbonate, are all isotopically lighter than oxygen in atmospheric O_2 and CO_2 (Fig. 2). Unlike methanogenesis, photosynthesis with plant and bacterial rubisco is a dominant process for stable isotopic discrimination in the modern oxygenated world and has been for the past 3600 Ma[1].

Alternative interpretations for past stable isotopic variation

Changing temperature?

The explanation offered most frequently for the higher (heavier) isotopic composition of oxygen through time is that surface temperatures were much higher in the past than now[7]. Following this logic, the temperature of Cambrian oceans by the current temperature-related fractionation of oxygen would have been as high as 60ºC, probably beyond the viable range for trilobites[8]. Similar calculations for marine carbonates older than 2500 Ma give an occasionally boiling ocean, again unlikely for Archean fossils[33]. Extensive ice ages in deep time back to 2400 Ma are evidence against such warmth[34]. A hot Precambrian is also contrary to what is known about stellar evolution of our Sun, which would have been about 30% dimmer at 4500 Ma, and 20% dimmer by 2500 Ma[35]. Although temperature effects may locally have created isotopically heavier oxygen in deep time, temperature does not explain all these data.

There also are difficulties with the idea that this secular trend reflects burial paleotemperatures affecting older rocks more than younger rocks. The Phanerozoic increase in the trend is from marine brachiopods with well-preserved shell microstructure as evidence against such diagenetic recrystallization[8]. Only micritic paleosol nodules were included in this compilation (Fig. 1a,b), not associated sparry calcite found even in modern soils[2,32], including micritic nodules from paleosols altered by greenschist facies metamorphism[10,36]. Furthermore, the distinctive isotopic composition of paleosol and paleokarst carbonate is due to early diagenesis, between deposition and burial[32], because original correlations between $\delta^{13}C$ and $\delta^{18}O$ in pedogenic carbonate are not reset by burial diagenesis, or lower greenschist facies metamorphism[10].

Changing hypsometry?

Another possibility is that the secular change reflects long term change in altitude, partial pressure of oxygen, or total atmospheric pressure, because each of these variables declines with altitude, and temperature-corrected oxygen isotopic composition of precipitation and ground water also declines with altitude[37]. Such an interpretation would imply that paleoaltitude, oxygen partial pressure, or total atmospheric pressure has declined though time, contrary to other indications. Reconstructed global hypsometry with continental growth back 3500 million years shows at least a doubling of continental topographic relief[38], rather than a decline. Growth of continental relief though time is also apparent from evolving triple oxygen isotopic composition of shales[6], and increased sediment flux[39]. Oxygen levels in the atmosphere have increased by several orders of magnitude since the Archean, judging from paleosol oxidation[40], mass independent fractionation of sulfur[41], marine redox proxies[42], and global isotopic mass-balance models[43]. Studies of the diameter of late Archean (2700 Ma) raindrop prints show that total atmospheric pressure has not changed significantly[44]. Observed isotopic enrichment of oxygen through time proceeded despite these opposing trends. Declining continental relief, atmospheric oxygenation and pressure, may explain some locally heavy oxygen isotopic values, but again not the whole of these data.

Changing atmosphere?

A likely explanation is that, rather than changes in paleoenvironment, the isotopic composition of oxygen in water of the sea, air and soil was lighter by as much as -4 to -12‰ during the Precambrian (3800 – 500 Ma), compared with today (Fig. 3). Such isotopically lighter ocean oxygen is allowed by extrapolation back from the secular variation of $\Delta^{17}O$ and $\delta^{18}O$ of granites and shales[6,9], and by comparison of iron oxide isotopic composition with other oxides[45].

What mechanism would make such a difference over such a long time? One idea is that changing isotopic composition reflects seawater alteration of basalt by hydrothermal circulation within mid-ocean ridges, with ^{18}O exchange from sea water to altered basalt declining with greater hydrothermal temperature[45]. Thus, observed ^{18}O enrichment of sea water could be created by declining sequestration of ^{18}O in basalt due to a greater abundance of deeper (> 2.5 km) and hotter (> 350ºC) mid-ocean ridge alteration forward through time[46]. Such long-term changes are not supported by reconstructed deepening of oceans through time[38]. Mid-ocean ridge hydrothermal isotope exchange can be reconsidered from new evidence of $\Delta^{17}O$ analyses, which are seldom positive or near zero in oceanic basalts[9]. This evidence against trends in deep and hot oceanic basalt alteration negates a globally important role for marine hydrothermal alteration in ^{18}O enrichment through time[9].

Another plausible explanation for long term ^{18}O enrichment not favoured by our data, is photosynthetic fractionation by the land plant enzyme rubisco and stomatal diffusion, which select light isotopologues[4] of CO_2 to give strong correlation of $\delta^{13}C$ and $\delta^{18}O$ in both plant organic matter and pedogenic carbonate[32]. This must be a minor effect globally because both isotopes are only a little lighter on land than in the sea (Fig. 2), and increasingly heavy oxygen through time is not matched by carbon, which remains remarkably steady (Fig. 3).

The interpretation favoured here is that mass-dependent evapotranspiration from increasingly large continents[38] and more elaborate vegetation[7,13–18] explains the isotopic enrichment of carbonate oxygen through time. Isotopic enrichment of $\delta^{18}O$ and depletion of $\Delta^{17}O$ through time[9] is a soil and leaf residue from preferential evaporation of light (^{16}O-rich) isotopologues of photosynthetic O_2 and H_2O from soils and plant stomata[3]. Enrichment of $\delta^{18}O$ and depletion of $\Delta^{17}O$ has been modelled with increasing soil weathering quantified by chemical index of alteration[6]. This difference for soils and sediments of low latitudes and altitudes dominating the sedimentary record was enhanced by depletion of $\delta^{18}O$ and enrichment of $\Delta^{17}O$ due to Raleigh distillation of water vapor at high latitudes and altitudes[9,24]. Furthermore, chemical weathering was promoted through time by evolution of more substantial and effective organisms on land creating higher soil respiration and carbonic acid in soils[5]. This had the effect of delivering more cations to the ocean to promote siliceous plankton and marine reverse weathering[5]. Evapotranspiration was enhanced by evolution of elaborate fractal structure in lichens[7,14] and early land plants[10], but much more evaporation was promoted by transpiration from stomata supplied by secondary xylem of trees[15,17], which evolved during the Middle Devonian (387 Ma). Transpiration now contributes to the atmosphere twice the amount of water as ground evaporation[47]. On land now, enrichment of $\delta^{18}O$ by photosynthetically produced O_2 is $+6.5 \pm 2.1‰$, by respiratory fractionation is $+17.7 \pm 1.0‰$, and by evaporation from leaves is $+0.75 \pm 0.05‰$, for a total enrichment of $+23.5 \pm 2.3‰$, or the Dole effect[3].

Biotic enhancement events

The carbon and oxygen isotopic difference between land and sea increased through time, as continental land area and relief increased[6,38,39], but times of strong divergence alternated with time of less divergence (Fig. 5c-d). Short term isotopic differences between land and sea through geological time are obscured by noise in raw plots (Figs. 3 and 4), but are significant for both carbon and oxygen when data are binned for comparable time intervals (Fig. 5c-d). Multimillion year fluctuations on the general trend do not match tectonic pulses for mountain building and supercontinent amalgamation inferred from zircon ages of granites. The continental growth curve from zircon and other geological data shown in Fig. 5f, takes a middle path between curves with modern land area by 4000 Ma at one extreme, and only 75% by 500 Ma at the other extreme[48]. Successive supercontinents were Kenorland (2700 Ma), Nuna (1870 Ma), Rodinia (1000 Ma), Gondwana (600 Ma), and Pangea (300 Ma), and these do not match observed inflexions of isotopic land-sea differences (Fig. 5c,d). Initial Archean assembly of Kenorland enriched $\delta^{18}O$ and depleted $\Delta^{17}O$ of shales[6], but is largely before the carbonate record assembled here, which does not show large divergences at times of supercontinent assembly.

Instead, differences from the general trend are largest at times of major evolutionary increases in biological productivity on land, including evolutionary appearance of late Tonian (800 Ma) amoebozoa and fungi[7], Ediacaran (635 Ma) lichens[14], middle Ordovician (470 Ma) non-vascular land plants[10], middle Devonian (385 Ma) forests[15], early Cretaceous (125 Ma) angiosperms[12], and Miocene (20 Ma) sod grasslands[13]. While these major events are poorly dated by the fossil record of microbes and plants alone, they are accurately dated by root traces and other fossils in paleosols of this compilation (Figs. 4 and 5). These differences also correspond with times of more productive paleosols on land as indicated by depth to salts[36]. The depth to soil salts today has been calibrated to soil CO_2 concentration at the end of the growing season for both calcite and gypsum nodules[2]. Compaction-corrected depths can be used to derive fluctuations in productivity of aridland soils through time (Fig. 5e).

Major advances in terrestrial plant productivity and terrestrial carbon sequestration also correspond with ice ages, which has been labelled the Proserpina Principle[49], including the Sturt and Elatina glaciations of Neoproterozoic Snowball Earth[7]. The Elatina glaciation may be better known as Marinoan, but that name is technically incorrect[7]. The record of pedogenic carbonate extends only back as far as 2400 Ma, and the oldest pedogenic carbonate isotopic data in our compilation is 1460 Ma[40]. There are no known Archean pedogenic carbonates, but a few known Archaean paleokarsts show a continuation of oxygen isotopic enrichment and steady carbon isotopic composition through time (Fig. 3a,b). Archean soil salts were not carbonates, but sulfates of possible biogenic origin back 3700 million years[50], as in paleosols of comparable geological age on Mars[51]. Stable isotopic discrimination by soil microbiomes extended at least that far back in geological time, and left a legacy of isotopic differences between land and sea.

Conclusions

The increasingly profound influence of life on land through geological time demonstrated here, played a role in maintaining planetary habitability. Over billions of years, warming due to an increasingly bright sun due to stellar evolution was offset by cooling due to increased carbon consumption on land[5]. The Devonian advent of trees by evolution of secondary xylem for structural support[15] increased local evapotranspiration, carbon consumption, and deep soil weathering by an order of magnitude[5]. Later trees were able to expand their geographic range to drier climates through biological innovations such as seeds[15]. The global reach of terrestrial isotopic fractionations was, like the Ancient Rome, achieved by local innovations, and then imperial conquest[13]. Other comparable advances were Neoproterozoic advent of lichens on land[14], the Ordovician rise of non-vascular land plants[10], the evolution of rapidly reproducing flowering plants[12], and grass-grazer coevolution[13]. Isotopic enrichment of carbonate oxygen through time on land and at sea is best explained by mass-dependent fractionation during evapotranspiration from increasingly large continents[38] and more elaborate vegetation[7,13–15].

Increasingly effective life on land also played a role in restoring equilibrium in the carbon cycle, and carbonate isotopic composition of carbon, after short term runaway greenhouse spikes on millennial and million-year time scales[5]. Short-term geographic expansion of productive forests and grasslands followed CO_2 pollution events from large igneous province basaltic eruptions and from large asteroid impacts, thus mitigating global greenhouse crises[52]. Variations in solar insolation due to Milankovitch orbital variations also promoted photosynthetic cooling by expansion of productive tropical forest and grassland ecosystems, and their enhanced carbon sequestration and chemical weathering. The other side of this Milankovitch scale, soil thermostat was expansion of unproductive desert soils (Aridisols) and frozen soils (Gelisols) during ice ages, diminishing terrestrial carbon consumption to levels eventually overwhelmed by continued volcanic degassing[52]. The chilling effect of silicate-weathering and biomass sequestration of CO_2 thus offset volcanic and impact releases of CO_2 to mitigate lethal global warmings[52]. Soils and their ecosystems have proven a global thermostat on both long and short time scales.

Data availability

All data generated and analysed during this study are included in the published article and supplementary material, which is a large compilation of published data. Data in Excel are available online here https://blogs.uoregon.edu/gregr/detailed-webpage/downloadable-data/.

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Author contributions

GJR collected samples, assembled the database from new and published materials, and created first draft and figures. INB provided isotopic analyses and aided revision of figures and text.

Declarations

Competing interests

The authors declare no competing interests.

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