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Continental Magmatism and Uplift as the Primary Driver for First- Order Oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ Variability with Implications for Global Climate and Atmospheric Oxygenation



Continental Magmatism and Uplift as the Primary Driver for First-Order Oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ Variability with Implications for Global Climate and Atmospheric Oxygenation

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ABSTRACT

Oceans cover 70% of Earth's surface, setting it apart from the other terrestrial planets in the solar system, but the mechanisms driving oceanic chemical evolution through time remain an important unresolved problem. Imbalance in the strontium cycle, introduced, for example, by increases in continental weathering associated with mountain building, has been inferred from shifts in marine carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. There are, however, uncertainties about the spatial and temporal patterns of crustal evolution in Earth's past, particularly for the period leading up to the Cambrian explosion of life. Here we show that U-Pb age and trace element data from a global compilation of detrital zircons are consistent with marine carbonate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, suggesting changes in radiogenic continental input into Earth's oceans over time. Increases in riverine Sr input were related to the break-up and dispersal of continents, with increased weathering and erosion of a higher proportion of radiogenic rocks and high-elevation continental crust. Tectonic processes exert a strong influence on the chemical evolution of the planet's oceans over geologic time scales and may have been a key driver for concomitant increases in atmosphere-ocean oxygenation and global climate cooling.

INTRODUCTION

Planetary differentiation has led to two fundamental types of crust on Earth: (1) continental, which tend to survive over long periods acquiring ancient rock records and evolved compositions; and (2) oceanic, which tend to be juvenile and rapidly recycled by subduction (Campbell and Taylor,

1983). According to standard models, continental crust is primarily formed by fluid flux melting in the mantle wedge above subducting hydrated oceanic plates as they are recycled into the mantle. This is then followed by fractional crystallization of mantle-derived magmas and/or partial melting of preexisting crustal lithologies (Hawkesworth and Kemp, 2006; Moyen et al., 2021). Collectively, these "distillation" processes have led to the development of a more felsic crust with a significant enrichment of incompatible elements, such as rubidium and strontium, with respect to the mantle as Earth has aged (Veizer, 1989; McDermott and Hawkesworth, 1990). However, the questions of how the continental crust has evolved chemically over time and how it has influenced Earth's oceans and atmosphere remain as fundamental unresolved problems.

Earth's present oceans have a uniform Sr isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$) that primarily reflects the balance between radiogenic Sr input from weathering of the continents and unradiogenic Sr input from hydrothermal alteration of oceanic crust (Veizer and Mackenzie, 2014). Although $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in marine carbonates are better documented for Phanerozoic versus Precambrian marine limestones, oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios appear to have departed from mantle values as early as ca. 2.8 Ga (Shields and Veizer, 2002) (Fig. 1A). This transition has been interpreted to mark a change from mantle- to river-buffered oceans as the continents rose and hydrothermal circulation of oceanic crust decreased as heat dissipated from Earth with time (Veizer and Mackenzie, 2014). $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have

subsequently risen in association with the differentiation of the crust, with rapid increases during two principal intervals in the Precambrian, namely in the Paleoproterozoic and Neoproterozoic (Shields and Veizer, 2002) (Fig. 1A). Identifying potential drivers for these shifts in marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios during the Precambrian is of widespread interest because of possible links to major perturbations in the global carbon cycle and hypothetical connections to changes in tectonism, climate, and atmospheric-oceanic oxygenation (Shields, 2007; Campbell and Allen, 2008; Sobolev and Brown, 2019).

The average Sr isotopic composition of the present oceanic crust is relatively uniform (~ 0.703), but the Sr isotopic composition of today's continental crust (~ 0.73 on average) is spatially highly variable (~ 0.703 to >0.73) due to a heterogeneous rock record that includes juvenile and ancient, evolved crustal components (Veizer and Mackenzie, 2014). The average Sr isotopic composition of today's rivers (~ 0.711) reflects a balance of the weathering of such sources on a global scale (Veizer and Mackenzie, 2014), but the dynamic nature of the solid Earth has likely led to changes in the proportion of radiogenic rocks being weathered on Earth's surface over time. This notion is supported by recent analyses of a global detrital zircon database, which have led to the conclusion that, at least for the past 1.0 Ga, increases in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios recorded in marine limestones generally coincide with decreases in the ϵ_{Hf} composition of zircons produced by increased magmatic reworking of preexisting radiogenic crust (Bataille et al., 2017). Decreases in zircon

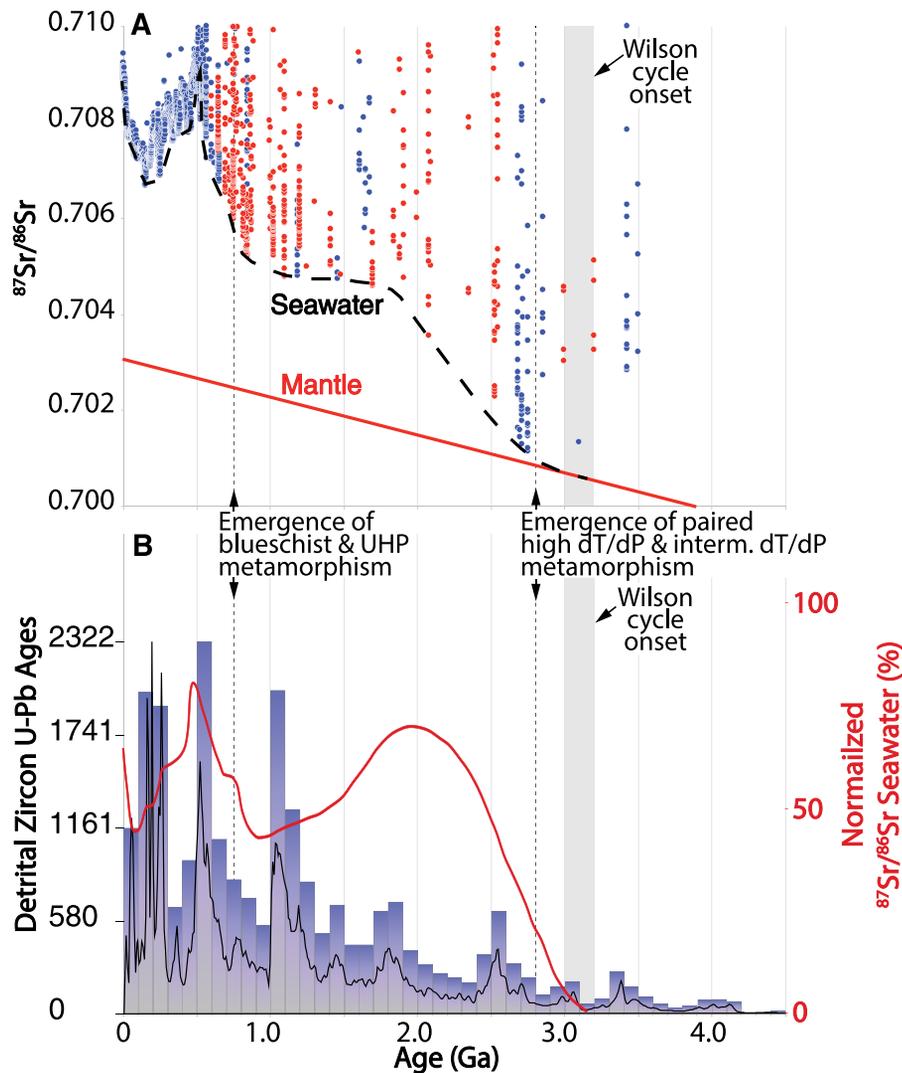


Figure 1. (A) $^{87}\text{Sr}/^{86}\text{Sr}$ evolution of seawater from marine limestones and fossils with respect to the mantle contribution (Shields and Veizer, 2002). Red data points are poorly constrained in age (greater than ± 50 Ma). (B) Normalized marine $^{87}\text{Sr}/^{86}\text{Sr}$ evolution from Shields (2007) with respect to kernel density estimate plot and histogram (Vermeesch, 2012) of cumulative U-Pb age data ($n = 24,190$) for the global compilation of detrital zircons analyzed in this study. Emergence of paired high dT/dP-intermediate dT/dP metamorphism and widespread ultrahigh-pressure (UHP) and blueschist metamorphism (cold subduction) from Brown and Johnson (2018), and Wilson cycle onset from Shirey and Richardson (2011).

ϵHf have been found to correlate with increases in whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Bataille et al., 2017). Increases in oceanic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios have, therefore, been linked to the production, and weathering, of extensive felsic igneous rocks along convergent margins involving subduction or collisions (Bataille et al., 2017). A plausible causal link exists because such rocks tend to be eroded rapidly due to their high elevations above sea level in proximity to oceans (Milliman and Syvitski, 1992).

Increases in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios recorded in marine limestones have recently been

shown to correlate with changes in zircon trace element ratios indicative of increased crustal reworking and thickness recorded in Neoproterozoic to Triassic sandstones from Antarctica (Paulsen et al., 2020). Increases in crustal thickness lead to increases in continental elevation (mountain building), which has in turn been associated with increased Sr runoff into Earth's oceans (Edmond, 1992; Richter et al., 1992; Raymo and Ruddiman, 1992; Shields, 2007). Therefore, the record of increases in crustal assimilation and thickness from Antarctica may point to significant, punctuated releases

of Sr from the continental reservoir. This represents a potentially important suite of coupled processes operating outside of the steady-state, and hence warrants investigation on a global scale.

This study integrates detrital zircon U-Pb age and trace element proxies for an exceptionally large global detrital zircon data set ($n = 24,206$) from samples derived from Earth's major continental landmasses to develop a better understanding of the petrotectonic evolution of continental crust through time and its potential link to the $^{87}\text{Sr}/^{86}\text{Sr}$ evolution of Earth's oceans (see Supplemental Material¹ for data, sources, and methods). The cumulative zircon age distribution binned in 0.1-Gyr age intervals in Figure 1B shows a series of age peaks similar to other global U-Pb detrital zircon age data sets (Campbell and Allen, 2008). The majority of zircons in this data set ($\text{Th}/\text{U} > 0.1$) are expected to be derived from felsic igneous rocks formed along convergent margins, which represent the primary source for zircons within the geologic record (Lee and Bachmann, 2014).

PATTERNS OF CRUSTAL REWORKING

Thorium is an incompatible element that becomes enriched relative to other elements as continental crust matures (McLennan and Taylor, 1980). Therefore, increases in Th/Yb ratios in zircon should correlate with increases in the production of evolved felsic rocks associated with magmatic recycling of older radiogenic crust (Barth et al., 2013). Monte Carlo bootstrap resampling of the trace element record (to minimize the effect of sampling bias presented by zircon age peaks) shows that increased Th/Yb ratios are generally associated with two principal periods in the Precambrian since 3.0 Ga (Fig. 2A). The results suggest a higher proportion of magmas characterized by increased assimilation of radiogenic crust at 2.5–1.9 Ga and 0.7–0.5 Ga. Igneous zircon Th contents may be influenced by the presence of rare accessory phases (e.g., allanite) that compete to incorporate Th during crystallization (Kirkland et al., 2015). However, this pattern is also recognized on a global scale in the zircon Hf isotope record, the isotopic value of which is primarily controlled by the amount of crustal recycling in magmas. ϵHf -age values from a separate

¹Supplemental Material. Table S1 (detrital zircon U-Pb age and trace element ratio global compilation, sample location maps, methods, and data sources). Go to <https://doi.org/10.1130/GSAT.S.16942894> to access the supplemental material; contact editing@geosociety.org with any questions.

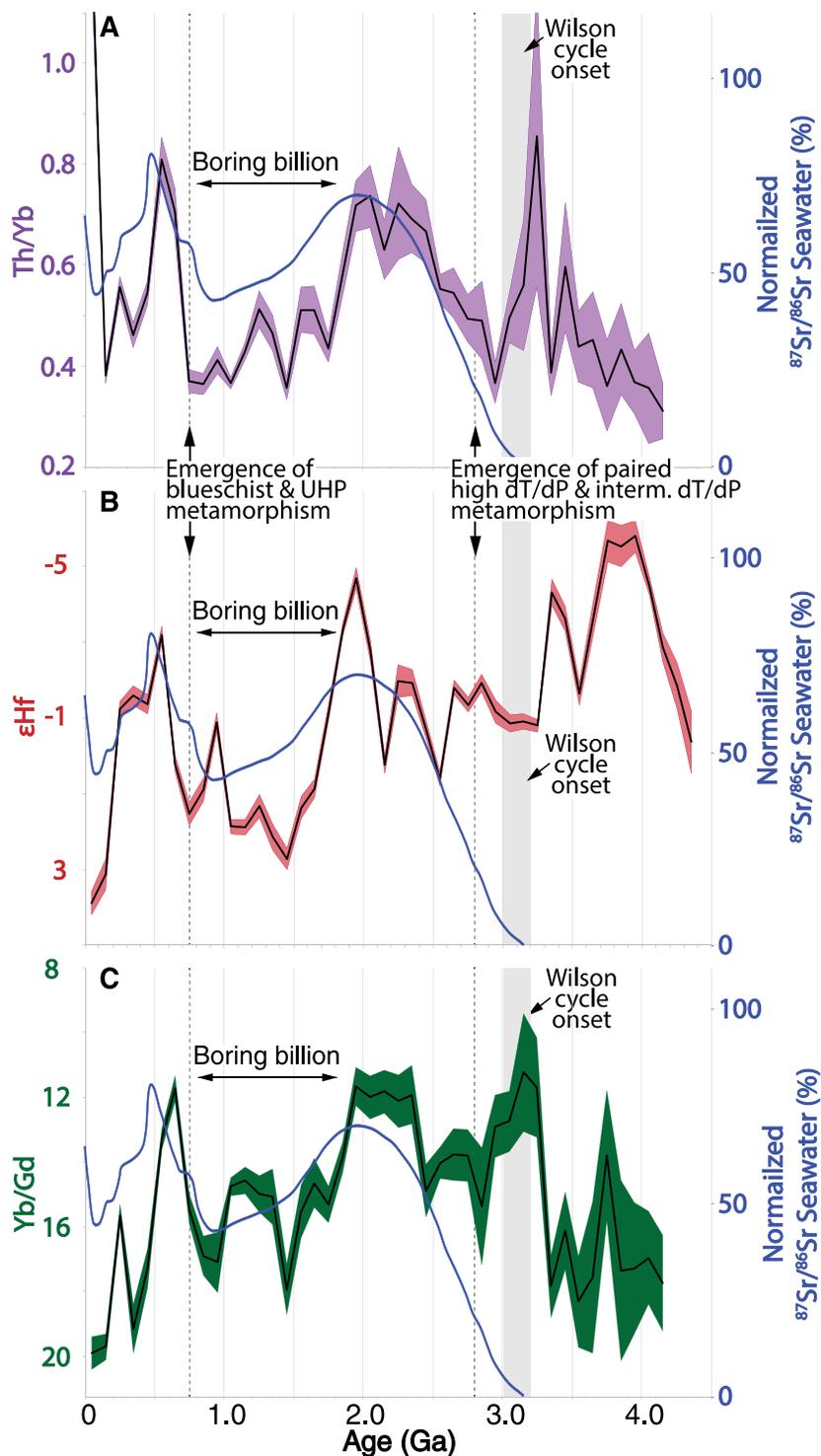


Figure 2. (A) Average Th/Yb (crustal input proxy); (B) ϵ Hf (crustal input proxy; note axis reversal); and (C) Yb/Gd (crustal thickness proxy) with their 95% confidence envelopes determined by Monte Carlo bootstrap resampling of zircons in 0.1-Gyr time brackets compared to normalized marine $^{87}\text{Sr}/^{86}\text{Sr}$ evolution. ϵ Hf data from Puetz and Condie (2019). Age of “boring billion” from Holland (2006). UHP—ultrahigh-pressure.

large detrital zircon data set ($n = 70,656$) show that significant negative deviations of ϵ Hf values correlate with these Th/Yb peaks (Fig. 2B). The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope curve shown in Figures 2A–2B, which is

normalized to model $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the global river and mantle inputs, shows increases that post-date the peaks in crustal assimilation indicated by zircon Th/Yb and ϵ Hf values—a time lag that may in part

reflect processes such as weathering and erosion. The zircon trace element data are, therefore, consistent with the hypothesis that increases in the proportion of evolved magmas along convergent margins have had an important influence on radiogenic Sr input into Earth’s oceans during these time intervals.

PATTERNS OF CRUSTAL THICKENING

Increases in magmatic reworking of pre-existing radiogenic crust should occur associated with thermal maximums as the crust thickens (DeCelles et al., 2009). Garnet is a mineral found in crustal magmas that is highly sensitive to pressure and incorporates heavy rare earth element (HREE)+Yb relative to other trace elements (Ducea et al., 2015). Therefore, changes in Yb/Gd ratios in zircon, for example, are thought to correlate with changes in the crustal thickness during magmatism (Barth et al., 2013). The trace element record retained within the zircon data shows that the lowest Yb/Gd ratios in the data set (Fig. 2C) correlate well with the Paleoproterozoic and Neoproterozoic Th/Yb and ϵ Hf peaks. These crustal thickness patterns are similar to those presented recently based on La/Yb ratios for a global compilation of 5587 detrital zircons (Balica et al., 2020). In particular, both analyses show Paleoproterozoic and Neoproterozoic peaks in crustal thickness that are separated by an intervening interval from ca. 1.8 Ga to 0.8 Ga during a period of environmental stasis known as the “boring billion” (Holland, 2006). The trace element data are therefore consistent with increased assimilation of radiogenic crust during periods of increased crustal thickness along convergent margins. Increases in crustal thickness are in turn associated with mountain building driven by tectonic shortening along Earth’s major convergent plate boundaries involving advancing states of subduction and collisions. Thus, the patterns in the zircon trace element data are also consistent with the hypothesis that increases in the proportion of radiogenic rocks (e.g., older basement) uplifted and exposed along convergent margins have had an important influence on radiogenic Sr input into Earth’s oceans (Richter et al., 1992).

CRUSTAL THICKNESS AND Sr FLUX

Geologists have long recognized that the widespread generation of continental topographic relief, which increases the overall

surface area and potential energy, should correlate with increases in sedimentary flux into Earth's oceans. Analysis of Phanerozoic sedimentary rock records suggests that increasing sedimentary flux correlates with increases in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in marine limestones (Hay et al., 2001). Detrital zircon age peaks have been attributed to increases in sedimentary flux associated with widespread continental collisions and convergent margin magmatism (Campbell and Allen, 2008; McKenzie et al., 2016). However, other authors have favored increases in preservation for these age peaks (Hawkesworth et al., 2009), and zircon abundance does not always correlate with increases in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Earth's oceans over time (Fig. 1B).

Increases in sedimentary flux derived from weathering of a greater proportion of elevated continental crust should, however, occur associated with an increase in flysch deposition. Flysch successions include interbedded graywackes and shales rich in quartz and feldspars, which, when water-saturated, are fertile sources for the generation of S-type granites (Collins and Richards, 2008; Zhu et al., 2020). Thus, S-type granite production may serve as a proxy for previous intervals of increased flysch deposition. We identified zircons that are likely to have been derived from S-type granite using the trace element discrimination procedure of Zhu et al. (2020), wherein S-type granites typically have elevated phosphorus concentrations relative to I-type granites because apatite [$\text{Ca}_5(\text{PO}_4)_3(\text{OH},\text{F},\text{Cl})$] crystallization is suppressed in the S-type magmas. To test the hypothesis that the peaks in crustal thickness were associated with an increase in S-type granites, we integrated S-type zircons identified within our data set with those found through an examination of zircons from 52 of Earth's major rivers (Zhu et al., 2020). Peaks in S-type zircon percentages overlap or even postdate the latter stage of increases in crustal thickness identified here (Fig. 3A). Thus, increasing radiogenic Sr input into Earth's oceans appears to be related to (1) the weathering of a greater proportion of radiogenic rocks produced and exposed as the crust thickened during the Paleoproterozoic and Neoproterozoic time intervals, and (2) concomitant increases in continental weathering and sedimentary flux into the oceans.

The results reviewed above provide important confirmation that increases in Sr recorded in marine carbonates correlate with first-order changes in convergent margin tectonism over time (Bataille et al.,

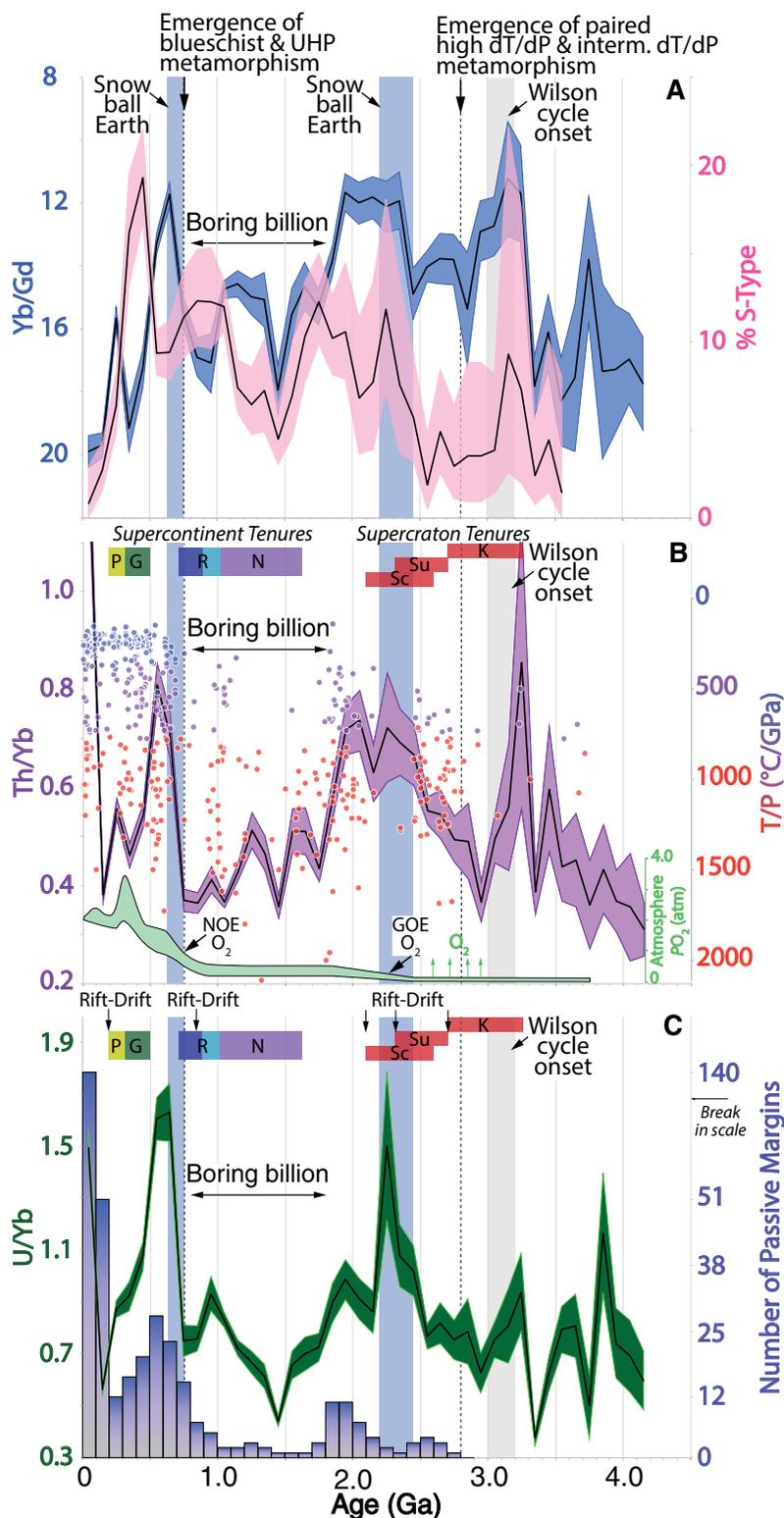


Figure 3. (A) Average Yb/Gd (crustal thickness proxy) compared to the percentage of S-type zircons with its 95% confidence envelope. (B) Th/Yb (crustal input proxy) compared to a global compilation of ages versus temperature/pressure (T/P) (°C/GPa) of high dT/dP (granulite–ultrahigh temperature [UHP]) (red); intermediate dT/dP (eclogite–high-pressure granulite) (purple); and low dT/dP (high-pressure–UHP) metamorphism (blue) from Brown and Johnson (2018). (C) U/Yb (crustal input and fluid input proxy) compared to a global compilation of passive margin abundance from Bradley (2008). Tenure of supercontinent/cratons from Bradley (2011), increases in atmospheric oxygen, early “whiffs” of oxygen (green arrows) and intervening boring billion from Holland (2006) and Lyons et al. (2014), and snowball Earth glaciations adapted from Sobolev and Brown (2019). Supercontinent/craton abbreviations: K—Kenor; Su—Superia; Sc—Sclavia; N—Nuna; R—Rodina; G—Gondwana; P—Pangea. NOE—Neoproterozoic oxygenation event; GOE—Great oxygenation event.

2017; Gernon et al., 2021). Increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Cenozoic marine limestones have been associated with decreases in unradiogenic Sr flux related to lower seafloor spreading rates (Van Der Meer et al., 2014) and cooler ocean temperatures (Coogan and Dosso, 2015), suggesting that the cause of increased $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the oceans may be multifactorial. The ancient ocean crust record is in large part lost due to subduction (Scholl and von Huene, 2009), but our results suggest that increases in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in oceans have been strongly influenced by a continental component. If the increases in the proportion of radiogenic sources and sedimentary flux represent a coupled suite of processes as we contend, then they raise the question as to why convergent margin tectonism changed during these time periods. Insight into this issue comes from an examination of modeling and other proxy data sets to which we now turn.

SUPERCONTINENT PATTERNS AND SR FLUX

Modeling studies suggest that supercontinent tenures should be marked by elevated temperatures in the underlying subcontinental mantle with convergent margins in retreating states with arcs on thinner crust in outboard locations with respect to the continents (Lenardic et al., 2011; Lee et al., 2013; Lenardic, 2016). Temporal considerations based on multiple proxy data sets suggest that the lows in crustal recycling and thickness identified in the zircon proxy data overlap with the tenure of supercontinents over Earth's history (Figs. 3A–3B) (Bradley, 2011). For example, the low in crustal recycling and thickness during the boring billion correlates with the tenure of Nuna during a period dominated by high dT/dP metamorphism (Fig. 3B) and higher thermal gradients (Brown and Johnson, 2018). This pattern may reflect supercontinent insulation of the mantle (Brown and Johnson, 2018) associated with the development of hot back-arc environments (Hyndman et al., 2005) and a greater proportion of convergent margins in retreating states with arcs on thinner crust in outboard localities (Roberts, 2013; Paulsen et al., 2020; Tang et al., 2021).

Supercontinent break-up, by contrast, should lead to a release of potential energy stored in the underlying mantle (Lenardic, 2016). Thermal release of the mantle induces changes in the geodynamic state of the

leading edge of continents by driving them into advancing compressional states of subduction and collisions involving arcs and continental blocks that favor crustal thickening (Lee et al., 2013). Increases in crustal recycling and thickness identified in the zircon proxy data correlate with an increase in passive margin abundance (Bradley, 2008) (Fig. 3C). These increases around the Proterozoic-Phanerozoic time interval also correlate with a decrease in thermal gradients of high dT/dP metamorphism (Brown and Johnson, 2018). Collectively, these patterns are consistent with supercontinent break-up driving a greater proportion of convergent margins into compressional advancing states and collisions with magmatism in thicker crust. High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in oceans during these periods are presumably due to increases in the proportion of exposed radiogenic sources and sedimentary flux from the continents associated with a reorganization of riverine drainage networks.

The correlations between the zircon proxy data and processes involving subduction outlined above warrants an examination of the U/Yb ratio in the zircon data set. The U/Yb ratio in zircon has been used as a proxy for crustal reworking (Verdel et al., 2021) but may also reflect the amount of subducting slab fluid addition in magmas, because U is a fluid-mobile large-ion lithophile element (LILE; K, Sr, Rb, Cs, Ba, Pb, U) extracted from slabs, and is, therefore, enriched relative to HREE such as Yb (Barth et al., 2013). U/Yb increases correlate with the increases in crustal assimilation and thickness we have identified (Fig. 3C), consistent with a higher amount of crustal recycling and flux of subduction fluid along a greater proportion of convergent margins during these periods. We, therefore, conclude that the increases in riverine Sr input into Earth's oceans were related to geodynamic changes in convergent margin networks, which were required to accommodate the birth and maturation of new ocean basins created by supercontinent break-up and dispersal. These episodes were associated with increased weathering and erosion of radiogenic rocks along convergent margins and greater expanses of uplifted, higher-elevation radiogenic crust found along the leading edges of continents. Increases in riverine Sr were likely amplified by the exhumation of continental crust associated with rifting (DeLucia et al., 2018), which is consistent with the general thesis supported here, that increases in riverine Sr are primarily driven by tectonism induced

by global changes in plate margin networks. Increasing $^{87}\text{Sr}/^{86}\text{Sr}$ compositions in Cenozoic marine sediments have also been associated with glaciation (Palmer and Elderfield, 1985). Snowball Earth deglaciation likely contributed to the Paleoproterozoic and Neoproterozoic Sr excursions (Sobolev and Brown, 2019), but the data reviewed here suggest that tectonism played a major role. Collectively, the balance of these processes is likely recorded in today's continental rock record by the great unconformities at the Precambrian-Phanerozoic and Archean-Proterozoic boundaries (Windley, 1984; Peters and Gaines, 2012).

BROADER IMPLICATIONS

Our results suggest that increases in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in oceans occur when a greater proportion of continental crust is thick and high, leading to increases in evolved felsic magmatism, radiogenic basement exposure, and riverine sedimentary flux. From a broader perspective, the results raise the important question of whether solid Earth processes play a fundamental role in modulating global climate and atmospheric oxygenation over geologic time scales. If the correlations outlined above are representative of a global tectonic pattern as we contend, then the generation of continental relief highlights the introduction of a significant silicate weathering sink associated with the drawdown of CO_2 and associated transition into periods of global glaciation (Hoffman and Schrag, 2002) (Fig. 3). Uplift associated with convergent margin tectonism may therefore have further enhanced CO_2 drawdown associated with the exhumation and weathering of rocks associated with continental rifting and dispersal (Donnadieu et al., 2004; DeLucia et al., 2018). Continental uplift has also been previously postulated to be linked to steps in oxygenation of Earth's atmosphere during the Paleoproterozoic and Neoproterozoic through enhanced erosion and nutrient supply to the oceans, as well as changes in the proportion of subaerial volcanism (Campbell and Allen, 2008; Gaillard et al., 2011) (Fig. 3B). Oxygenation may have fostered the decrease of CH_4 , a potent greenhouse gas (Fakhraee et al., 2019), while uplifts along convergent margins promoted nascent glaciation in cooler, high-elevation habitats, providing further feedback (albedo) for a runaway global glaciation. The ultimate drivers for these important steps in Earth's evolution are controversial and likely involved a complex set of variables and

inextricably linked feedbacks. However, in general terms, potential links between the solid Earth and the evolution of its climate, atmosphere, and oceans are highlighted by recent modeling that suggests that global climate may ultimately be modulated by changes in outgassing and weathering sinks associated with mantle thermal states during the assembly and break-up of supercontinents (Jellinek et al., 2020). While the oceans have played a fundamental role in the geochemical evolution of the continents (Campbell and Taylor, 1983), the continents have, in turn, shaped the oceans and perhaps major evolutionary steps in Earth's global climate and the oxygenation of its ocean-atmosphere system.

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