

Forming Earth's Continental Crust: A Nontraditional Stable Isotope Perspective

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1811-5209/21/0017-0413\$2.50 DOI: 10.2138/gselements.17.6.413

The formation of continental crust via plate tectonics strongly influences the physical and chemical characteristics of Earth's surface and may be the key to Earth's long-term habitability. However, continental crust formation is difficult to observe directly and is even more difficult to trace through time. Nontraditional stable isotopes have yielded significant insights into this process, leading to a new view both of Earth's earliest continental crust and of what controls modern crustal generation. The stable isotope systems of titanium (Ti), zirconium (Zr), molybdenum (Mo), and thallium (Tl) have proven invaluable. Processes such as fractional crystallization, partial melting, geodynamic setting of magma generation, and magma cooling histories are examples of processes illuminated by these isotope systems.

KEYWORDS: Continental crust; nontraditional stable isotopes; isotope geochemistry

EARTH'S CONTINENTAL CRUST

The composition and evolution of Earth's continental crust has received a great deal of attention, primarily for its links to habitability and its unique association with subduction and modern plate tectonics. Decades of research have found that modern continental crust is typically produced in convergent settings (e.g., oceanic arcs) (Taylor 1977), following the subduction of hydrated oceanic crust (altered oceanic crust). The compositions of magmas produced in these settings vary considerably, but are generally more buoyant and evolved than primitive mantle melts. Large volumes of these more evolved rocks have accumulated over time, forming what we know as continental crust, which has allowed for human life to evolve while maintaining a stable climate and providing a source of nutrients for life.

The timing of the onset of subduction, which is a mechanism of modern continental crust generation, and the evolving composition of Earth's crust through time are strongly debated (Korenaga 2018) (FIG. 1). Through recycling processes operating on the early Earth and by the subduction conveyor belt, rocks are carried into the mantle, erasing evidence of Earth's ancient crustal composition. Much of what we know about early Earth is gleaned from the zircon record—zircon being a mineral highly resistant to physical and chemical weathering—and the sedimentary rock record (e.g., shales and glacial diamictites), which

are representative of what has been physically and chemically weathered from a continent. Because interpretations of crustal history are gathered from incomplete, remnant, or complicated detrital records, the estimates for the initiation of plate tectonics range considerably, from ~0.85 Ga to >4.2 Ga (Korenaga 2018).

Presented with the challenge of interpreting an incomplete geologic record, geoscientists are employing innovative analytical techniques to learn more about Earth's continental crust: namely, the application of nontraditional

stable isotopes. The relatively recent development of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) has allowed geoscientists to measure extremely small variations in the isotope ratios of a majority of elements on the periodic table. Prior to the advent of MC-ICP-MS, the isotope compositions of most heavy elements were unable to be accurately and precisely measured. For this reason, isotopes of many common rock-forming elements are only now being leveraged to learn about different geological processes, such as crust-formation. Here, we highlight some recent work with the stable isotope systems of Ti, Zr, Mo, and Tl and so seek to

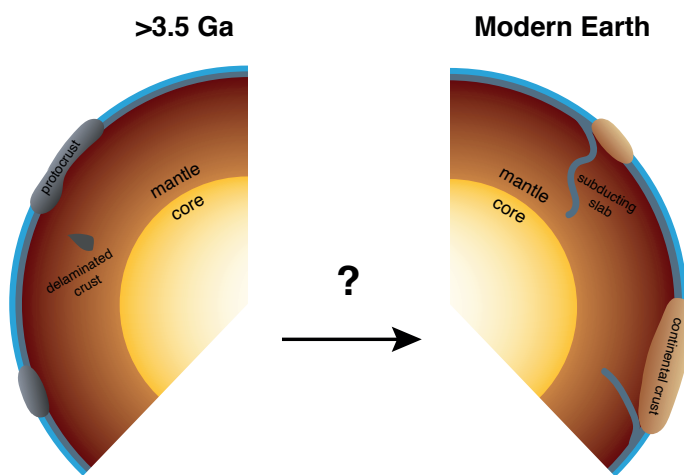


FIGURE 1 Schematic representation of Earth's transition from a (LEFT) protocontinent, stagnant lid regime to (RIGHT) modern-style subduction having our present continental crust composition. As indicated by the question mark, the timing of this transition is still under intense debate in the Earth science community.

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better understand continental crust formation, recycling, and composition through time.

Isotope Slang

Stable isotopic systems are denoted often using delta notation (symbol: δ), whereas for smaller variations, the epsilon (symbol: ϵ) or mu (symbol: μ) notations are used (see Ibañez-Mejía and Tissot 2021 this issue). The standards to which the systems described here have been normalized are listed in TABLE 1.

TABLE 1 ISOTOPIC RATIOS MOST COMMONLY USED FOR THE SYSTEMS DESCRIBED HEREIN, AND THEIR RESPECTIVE REFERENCE STANDARDS. Abbreviations: NIST = National Institute of Standards and Technology; SRM = standard reference material; OL = Origins Lab. *A universally agreed-upon Zr standard reference material is still under development. At this time, multiple standards are utilized with some being lab-specific.

Isotope system	Reference Material
$^{49}\text{Ti}/^{47}\text{Ti}$	OL-Ti
$^{94}\text{Zr}/^{90}\text{Zr}$	ZrNIST*
$^{98}\text{Mo}/^{95}\text{Mo}$	NIST SRM 3134
$^{205}\text{Tl}/^{203}\text{Tl}$	NIST SRM 997

WHAT IS THE ROLE OF INTRACRUSTAL DIFFERENTIATION?

Modern continental crust is unique in that it is highly evolved from most mantle melts, which is partially the result of extensive fractional crystallization, or differentiation within the crust. The early crystallization of dense, mafic minerals often leaves melts enriched in silica and other less refractory elements. The resultant buoyant, evolved melts may then ascend through the crust leaving cumulates of dense mafic minerals behind (FIG. 2). The compositional evolution of these silicate melts, sometimes referred to as the liquid line of descent, can be highly variable because the crystallizing mineral assemblage will continually change as a function of melt composition, pressure, temperature, oxygen fugacity, and water content. As a result, it is difficult to reconstruct liquid lines of descent and infer fractional crystallization histories from erupted products alone.

Nontraditional stable isotopes are helping us to overcome this limitation and understand those processes beneath Earth's surface which we cannot directly observe. As mantle melts crystallize, refractory elements are preferentially removed (FIG. 2). Elements with multiple isotopes will undergo isotope fractionation when there is a difference in the strength of the bonding environment between the crystallizing mineral and the melt. This fractionation could happen instantaneously or by diffusion-driven kinetic effects (see Guo et al. 2020; Méheut et al. 2020). Thus, the isotope composition of the rocks resulting from extensive differentiation may record the crystallization history, even when the earliest minerals to crystallize never make it to the surface.

Titanium

Stable titanium (Ti) isotopes have recently been leveraged to understand crustal differentiation because they are tracers of fractional crystallization (Millet et al. 2016; Greber et al. 2017; Deng et al. 2019a; Johnson et al. 2019). Titanium isotopes are sensitive to the crystallization of Fe–Ti oxides, which preferentially incorporate light isotopes such as ^{47}Ti over heavier isotopes such as ^{49}Ti . Fractionation of isotopes occurs during melt crystallization due to differences in the

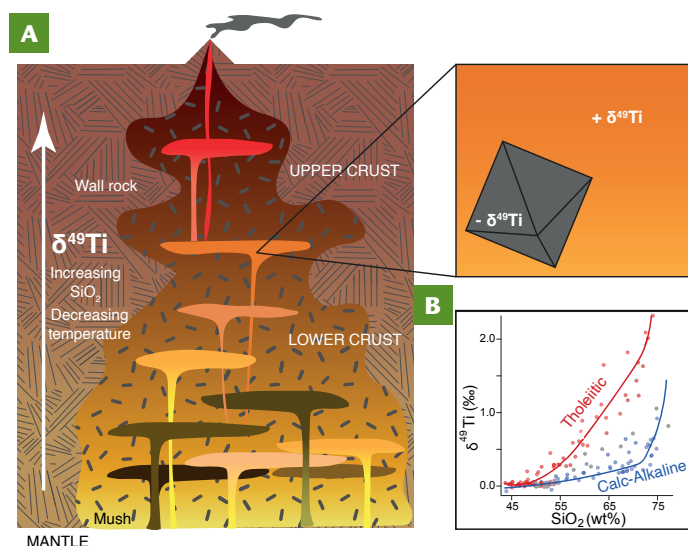


FIGURE 2 (A) Schematic of intracrustal differentiation where fractional crystallization can drive melts to have evolved, isotopically fractionated compositions of titanium compared to mantle values. Expanded inset shows how Fe–Ti oxides preferentially incorporate light isotopes of Ti leaving the melt isotopically heavier. MODIFIED FROM CASHMAN ET AL. (2017). (B) Relationship between $\delta^{49}\text{Ti}$ composition as a function of SiO_2 content. The $\delta^{49}\text{Ti}$ compositions of rocks are from calc-alkaline settings (blue circles), intraplate tholeiitic settings (red circles), and modern mid-ocean-ridge basalt (MORB) tholeiitic settings (gray circles). MODIFIED FROM AARONS ET AL. (2020) AND REFERENCES THEREIN.

coordination environment, which drives a preference of one isotope over another depending on the strength of the bond or number of bonds of an element of interest. The $\delta^{49}\text{Ti}$ values of evolved magmatic rocks record this process and are typically isotopically heavy compared to primitive mantle-derived melts, reflecting preferential removal of isotopically light Ti during fractional crystallization.

It was also demonstrated that Ti isotopes are sensitive to the liquid lines of descent of magmas produced in different tectonic settings (Deng et al. 2019a; Hoare et al. 2020). Specifically, rocks formed in settings with anhydrous (dry) magmas will fractionate Ti isotopes more significantly than those from hydrous (wet) magmas. In anhydrous magmas, the simultaneous crystallization of Fe–Ti oxides and plagioclase results in a rapid shift of melt $\delta^{49}\text{Ti}$ to heavier values with very limited changes in melt SiO_2 composition. Hydrous magmas, on the other hand, limit the crystallization of plagioclase, which results in an increase in both $\delta^{49}\text{Ti}$ and SiO_2 within the melt. This means that an anhydrous andesite is likely to have an elevated $\delta^{49}\text{Ti}$ compared to an andesite that crystallized from a hydrous melt. This sensitivity may make Ti suitable for tracing the contributions of different melt generation mechanisms in building continental crust and determining whether a rock was formed from wet versus dry magmatism.

It is also likely that because Ti isotopes reflect progressive Fe–Ti oxide crystallization that they are also sensitive to the FeO and TiO_2 contents of parental melts, in addition to oxygen fugacity and water content (Hoare et al. 2020). These conditions will not only control the timing of the appearance of Fe–Ti oxides in the crystallizing assemblage but also the Ti contents of the oxides and mineral–melt isotopic fractionation factors ($\Delta^{49}\text{Ti}_{\text{melt-mineral}}$). More work is needed to quantify the influence of these variables in natural settings, but ab initio investigations have made progress in calculating theoretical intermineral fractionation factors (Wang et al. 2020; Aarons et al. 2021), identi-

fying several controls that can be directly tested in future studies. These quantitative constraints on $\Delta^{49}\text{Ti}_{\text{melt-mineral}}$ and their dependence on temperature and mineral composition are essential for our understanding of what $\delta^{49}\text{Ti}$ compositions can tell us about redox conditions, water content, melt composition, and, potentially, the crystallization temperature. Together, these early studies demonstrate that Ti isotopes have much potential in tracing melt evolution and crust generation in the modern environment.

Zirconium

Similar to Ti isotopes, zirconium (Zr) isotopes show a potential to be valuable tracers of magmatic processes during the formation of continental crust. Zirconium draws special attention because it is a primary element within the mineral zircon (ZrSiO_4), which has been used extensively as a mineral chronometer and indicator of ancient felsic melts. Due to the sensitivity of Zr to the crystallization of zircon, Zr concentrations are often used as tracers of silicate differentiation. However, the measurement of Zr stable isotopes in igneous rocks has only recently begun.

Light Zr isotopes were initially suggested to be incorporated into zircon during crystallization, leaving the residual melt with higher Zr isotope compositions. This evolution in isotopic composition of the melt was hypothesized using highly evolved igneous rocks from Hekla Volcano (Iceland), which were found to be isotopically heavy compared to primitive mantle melts with an inferred fractionation factor of $\Delta^{94}\text{Zr}_{\text{melt-mineral}} = -0.5\text{‰}$ (Inglis et al. 2019). Contrastingly, Ibañez-Mejía and Tissot (2019) found that Zr-bearing accessory minerals can be isotopically heavy relative to the melt they crystallized from, indicating an opposite direction of Zr isotopic fractionation ($\Delta^{94}\text{Zr}_{\text{melt-mineral}} = +1.06\text{‰}$). Subsequent work suggests that rather than mass-dependent equilibrium isotope fractionation, it is more likely that diffusion-driven kinetic isotope fractionation is responsible, where lighter isotopes will diffuse or move more quickly (Méheut et al. 2020). Spatially resolved measurements of Zr isotopic compositions of zircons via laser ablation reveal zoning within the individual mineral grains, with generally isotopically lighter cores and heavier rims (Guo et al. 2020). Similar to the temperature dependence of zircon occurrence in crustal magmas noted by Watson and Harrison (1983), the observed fractionation of Zr isotopes within zircon crystals may be related to the cooling history of the host magma (Guo et al. 2020; Méheut et al. 2020), suggesting a new and exciting application of Zr isotopic compositions towards our understanding of continental crust formation.

New measurements of Ti and Zr stable isotope compositions in various magmatic settings suggest a wide variability in natural samples. However, more detailed work is required to understand the nuances of variables such as water content, oxygen fugacity, pressure, temperature, and initial geochemical composition on the isotopic composition and evolution of rocks during fractional crystallization. A well-characterized suite of measurements in modern environments typically shapes our understanding of the driving forces behind isotope fractionation and will aid in our understanding of continental crust generation in the past.

WHAT IS THE ROLE OF CRUSTAL RECYCLING AND DELAMINATION?

In addition to melting of the mantle, recycling crustal materials is another important component of forming continental crust. This can be accomplished via subduction or crustal delamination. Both mechanisms have long-term effects on the evolution of continental crust, and, as we are learning, can be traced by a handful of nontraditional

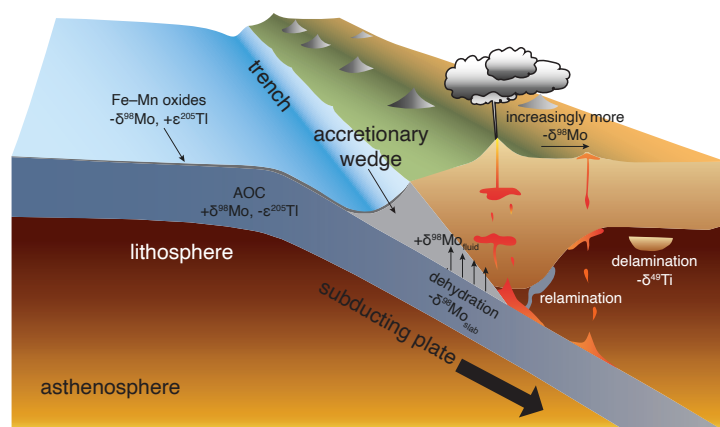


FIGURE 3 Cross-section of subduction of an oceanic plate beneath a continental plate. Various isotopic reservoirs related to subduction and delamination discussed herein are denoted with their relative magnitudes. Relamination is also shown, which, though currently unconstrained utilizing heavy stable isotopes, presents potential new frontiers for heavy stable isotope applications. Abbreviation: AOC = altered oceanic crust.

stable isotope systems (FIG. 3). Here, we focus on recycling via subduction.

Crustal recycling often occurs via subduction, in which materials are exchanged between Earth's surface and its interior. During subduction, hydrated oceanic crust and overlying sediments can either be returned to the continental crust via magmatic processes, and potentially relamination, or they can be carried to great depths in the mantle. If recycled via magmatism, volcanism in these arc systems is compositionally distinct and is a large source of volatiles to Earth's atmosphere. As such, subduction ultimately modulates the geochemical composition of the major Earth reservoirs, including the oceans, lithosphere, and atmosphere. However, the efficiency of this recycling process and the proportion of surface material that is returned versus the amount that reaches the mantle is difficult to observe directly, and the controls on this recycling are still poorly understood.

Nontraditional stable isotope systems have been implemented to better trace recycling mechanisms within subduction zones. In particular, isotopes of soluble, redox-sensitive elements are most helpful here because they experience large fractionations in ocean sediments and are often enriched to much higher concentrations in these settings compared to mantle values (e.g., Freymuth et al. 2015; Nielsen et al. 2017). These two characteristics allow geoscientists to trace the contribution of oceanic sediments to arc magmas, and, by extension, calculate the fraction of oceanic sediments returned to the mantle.

Thallium

Thallium (Tl) is one such redox-sensitive element that is highly mobile at Earth's surface and whose isotopes are strongly fractionated by low-temperature processes (Nielsen et al. 2017). Importantly, Tl isotopes were also shown to be largely unaffected by high-temperature magmatic processes such as intracrustal differentiation, greatly simplifying interpretations of Tl isotope signatures (Nielsen et al. 2017). There are two low-temperature processes that alter Tl isotopic compositions and that are relevant during crustal recycling: hydrothermal alteration of oceanic crust, shifting $\epsilon^{205}\text{Tl}$ compositions to much lighter values ($\epsilon^{205}\text{Tl} \approx -15$); adsorption onto authigenic Fe-Mn oxides in pelagic clays, which has produced the heaviest $\epsilon^{205}\text{Tl}$ values currently observed on Earth ($\epsilon^{205}\text{Tl} \approx +15$) (Nielsen et al. 2017).

These extreme variations in Ti reservoirs have been applied to determine the proportions of pelagic sediment and low-*T* altered oceanic crust contributing to arc rocks in a variety of locales (Shu et al. 2019). Through the use of Ti isotope compositions, we now have evidence that the transfer of slab sediments into arc magmas is fairly efficient, at least for incompatible elements such as Ti (Shu et al. 2019). This makes Ti isotopes a great resource for tracing and quantifying the contribution of different sediment sources to the subducting slab package, which ultimately influences arc magma compositions within our crust.

Molybdenum

Similar to Ti, molybdenum (Mo) is another redox-sensitive element that is highly mobile in modern, well-oxygenated oceans. During incorporation into pelagic sediments, Mo isotopes are often fractionated, with these sediments inheriting a relatively low isotopic composition compared to seawater (Gaschnig et al. 2017). Black shales, on the other hand, tend to be enriched in isotopically heavy Mo, resulting in isotopic compositions at the other end of the spectrum (Gaschnig et al. 2017). Hydrothermal alteration of oceanic crust has also been shown to fractionate Mo isotopes, generally pushing crustal compositions to variable but heavier values (Freythuth et al. 2015). Through these unique sedimentary reservoirs, Mo isotopes can act as a tracer for the input of various types of sediments into subduction zones (Gaschnig et al. 2017) because Mo isotopic compositions of arc lavas seem to track subducted sediments, much like the Ti system mentioned above.

Interestingly, there is an isotopic “mismatch” between the Mo isotope compositions of subducting slab material and resulting arc rocks in several locations, which may imply that Mo isotopes are fractionated during slab dehydration. Proponents of this model suggest that isotopically heavy Mo is partitioned into the slab-derived fluid phase while a residual mineralogical phase retains isotopically light Mo within the subducting slab (Freythuth et al. 2015). The isotopically heavy fluid contributes to the heavier isotopic composition of the bulk continental crust, while partial melting of the subducted, isotopically light sediments may contribute to lighter Mo isotope compositions observed within the subarc mantle (Freythuth et al. 2015). As a result, the heavier continental crust and the presumably lighter deep mantle are two complementary Mo reservoirs that may help track fluid fluxing in subduction zones (Freythuth et al. 2015). In some locales, however, this discrepancy can be modeled by mixing between a mantle end-member and various sediment sources present in the downgoing slab, as discussed above (Gaschnig et al. 2017). This simple binary mixing mechanism can explain the observed discrepancies and does not require isotopic fractionation of Mo during its removal from the subducting slab. As the utilization of Mo isotopes towards understanding subduction zones continues to expand and evolve, we hope to have a clearer understanding of the role various sediment sources and slab dehydration may play in shaping our continental crust, both now and in the past.

The development and application of novel isotope tracers discussed here have the potential to improve our understanding of crustal recycling components, mechanisms, and recycling efficiency, given that subduction zone processes are so difficult to observe directly. Utilizing several of these isotopic tracers in tandem may allow us to better quantify how much surface material is effectively recycled in the modern environment and will also provide insights into the prevalence of various recycling mechanisms through time.

HOW HAS THE CONTINENTAL CRUST CHANGED THROUGH TIME?

In addition to challenges in observing modern continental crust-forming processes, there is also the challenge of reconstructing these processes through time. The nature and composition of Earth’s ancient continental crust is still debated and a subject of continuing study. Because modern continental crust generation is, ultimately, a consequence of plate tectonics, extrapolating crust generation mechanisms through time naturally implicates larger questions, such as the timing of the initiation of subduction. For these reasons, the development of novel isotope tracers for the composition of ancient continental crust has been (and will likely continue to be) a driving motivator in studies of nontraditional stable isotopes.

Ideal candidates for understanding ancient magmatic differentiation are isotope systems of refractory elements that are lithophile, fluid immobile, and unlikely to be disturbed by metamorphic and metasomatic processes. Ancient rocks and sediments often experience complex histories, which may include fluid–rock interactions modifying their geochemical composition. This means that identifying stable isotope systems that are robust and resistant to these effects is increasingly crucial the further back in time we probe. Additionally, in order to be successful proxies, isotope systems need to have well-understood fractionation behaviors. Here, we summarize the progress and challenges of some of the most promising isotope proxies for ancient continental crust formation.

Titanium

Stable Ti isotopes were recently leveraged to trace differentiation in a variety of tectonic settings, with increasingly heavier isotope compositions observed among the most evolved rocks (FIG. 2B). Titanium was first shown to fractionate with calc-alkaline magmatic differentiation (Millet et al. 2016) and later shown to fractionate considerably more in intraplate settings (FIG. 2B) (Deng et al. 2019a). More detailed work on rocks from a variety of environments found a strong dependence of the $\delta^{49}\text{Ti}$ composition during magmatic differentiation on water content and oxygen fugacity (Hoare et al. 2020). Careful work detailing the processes responsible for these disparate trends in Ti isotope fractionation and their sensitivity to redox and melt water content will improve our understanding of initial magma composition and melt evolution during differentiation.

Greber et al. (2017) used the observed relationship between Ti isotope composition and SiO_2 content in magmatic rocks (Millet et al. 2016) to probe the ancient composition of Earth’s exposed continental crust, using a suite of shales from 3.5 Ga to the present. Their rationale was that more evolved rocks would have heavier $\delta^{49}\text{Ti}$ values (reaching +0.6‰) at SiO_2 contents of ~75 wt%, whereas mantle-derived rocks are close to 0‰. Thus, heavier $\delta^{49}\text{Ti}$ values in shales would indicate a silica-rich continental crust. Their investigation into the shale record found variable, but elevated, $\delta^{49}\text{Ti}$ values through time, with only a subtle shift towards heavier values from the Archean to present. Their conclusion was that felsic rocks were likely the primary type of exposed continental crust throughout the past 3.5 Ga.

This finding was complicated by a later study which found that rocks formed in intraplate settings also significantly fractionate Ti isotopes (Deng et al. 2019a), making it difficult to apply this proxy to the sedimentary record due to nonunique interpretations. As a result, we now understand that $\delta^{49}\text{Ti}$ values could correspond to a range of rock SiO_2 contents and are probably best used in conjunction with

other geochemical data to probe the ancient composition of continental crust. Due to the unique Ti isotopic fractionation that occurs during calc-alkaline and intraplate tholeiitic magmatism (Deng et al. 2019a), combining both $\delta^{49}\text{Ti}$ compositions and SiO_2 contents of igneous rocks could be a useful indicator of the geodynamic setting within which the rocks were initially formed. Understanding the processes that control magma generation early in Earth's history can provide valuable glimpses into when modern-style plate tectonics began. The Ti isotope approach was applied to Earth's oldest currently known rocks from the Acasta Gneiss Complex, which spans the Hadean–Eoarchean boundary between 4.02 Ga and 3.75 Ga (Aarons et al. 2020). Hadean tonalitic gneisses were found to have $\delta^{49}\text{Ti}$ compositions consistent with modern evolved dry tholeiitic magmas, and later crust (less than ~3.75 Ga) involved wetter magmas, possibly due to recycling of hydrated crust at subduction zones. The presence of wet magmatism early in Earth's history provides a small glimpse into the processes controlling continental crust generation, which appear to be consistent with a horizontal tectonic regime similar to modern subduction (Aarons et al. 2020).

Molybdenum

An alternative approach to reconstructing the relative growth/abundance of continental crust involves the isotopic fractionation between the depleted mantle and its complementary crust. This new approach can be challenging as we move back in time, because samples representative of the complementary reservoirs become increasingly rare. As mentioned above (see section *What is the role of crustal recycling and delamination?*), Mo isotopes may track the input of various sediment sources into subduction zones in many locales and can, therefore, act as a fairly straightforward tracer of sediment recycling mechanisms (Gaschnig et al. 2017). If this is the case, then well-preserved ancient arcs can likely be used to track the Mo isotope composition of subducting sediment through geologic time. Given the strong influence that redox states have on Mo isotope compositions, particularly in various sediment sources, then this methodology may also provide insight into the evolving marine redox conditions in the ancient past (Gaschnig et al. 2017).

As an alternative, complementary, approach, work on Mo isotopic compositions of the depleted mantle throughout Earth's history has sought to detect resolvable variations in the depleted mantle reservoir as a potential indicator of continental crust formation (McCoy-West et al. 2019). Data collected thus far indicates that the present-day depletion (light Mo isotopic compositions) of the mantle with respect to the continental crust (heavy Mo isotopic compositions) has been consistent since 3.5 Ga (McCoy-West et al. 2019). It is worth noting here that the crust extracted through this model was likely dominated by mafic lithologies, which are compositionally very different from modern continental crust. This finding suggests that rapid crustal growth and subsequent destruction may have occurred within the first billion years of Earth's history. It also implies that recycling of continental crust back into the mantle has been an ongoing process for most of Earth's history. Although subduction zone processes are not strictly required to produce this observed trend—which can be generated through mantle melting processes—approaches such as these, which quantify complementarity between the crust and the mantle, have the potential to increase our knowledge of how Earth's continental crust evolved through time.

AN ISOTOPE PERSPECTIVE INTO THE FORMATION OF EARTH'S CRUST

A firm grasp on the geochemical makeup of ancient crustal rocks and modern crust-forming processes is vital to understand the evolution of our planet. Work on this subject not only informs Earth's geophysical evolution but can also inform the evolution of our hydrosphere, atmosphere, and biosphere. Typical approaches employ elemental compositions of detrital sediments. However, this approach can be challenging because physical and chemical weathering, transport processes, and diagenesis can potentially skew these compositions. Ancient rocks are also extremely rare: outcrops older than 3.6 Ga represent only a few parts per million of the exposed crust. Through the use of nontraditional stable isotope systems, geochemists are able to more accurately model crust formation processes. Yet there are still many gaps in our understanding.

Many of the nontraditional stable isotopic systems mentioned here have only recently been measured with enough precision to detect natural variations. In that short period of time, incredible progress has been made in their utilization and application to geologic quandaries, such as moving towards a better understanding of the formation and evolution of continental crust. Examples of novel applications go well beyond those of Ti, Mo, Zr, and Tl summarized here, and include the following:

- **Application of stable Li isotopes to understand continental crust formation and evolution (e.g., Penniston-Dorland et al. 2017).** Stable Li isotopes have been used to understand continental crust formation and evolution (Penniston-Dorland et al. 2017 and references therein). Lithium isotope compositions of continental intraplate igneous rocks, unaltered mid-ocean-ridge basalts (MORBs), and most ocean island basalts (OIBs) overlap. Additionally, measurements of carbonatites (a carbonate-rich mantle-derived rock) over the past 2.7 Ga indicate that the Li stable isotope composition of the mantle has remained uniform over much of Earth's history (Halama et al. 2008), implying that crustal recycling has remained in a steady state. Recent measurements of Li isotope fractionation in regolith and water highlight the potential of using this system as a tracer of chemical weathering rates and compositional changes of the continental crust through time (Liu and Rudnick 2011). This isotope system has been used extensively to track links between continental crust generation, tectonic uplift, silicate weathering rates, and mass extinction events (Penniston-Dorland et al. 2017 and references therein).
- **Application of paired stable isotope systems (Fe, Zn, Mg, U) to understand magmatic differentiation (e.g., Telus et al. 2012).** Paired stable isotopic variations in felsic rocks can elucidate the mechanisms behind elemental and isotopic fractionation during magmatic differentiation, because each isotope system is sensitive to different processes. For example, zinc (Zn) isotopes should be mobile during fluid exsolution, whereas magnesium (Mg) isotopes are not fractionated by partial melting or magmatic differentiation, and are instead highly sensitive to diffusion [along with uranium (U) isotopes] and to low-temperature weathering processes (Teng et al. 2007; Telus et al. 2012). Combined with isotope systems such as iron (Fe), which are sensitive to fractional crystallization, studies that apply several isotope systems to one rock suite have the ability to rule out nonunique interpretations.
- **Application of silicon (Si) isotopes to ancient crustal recycling (e.g., Deng et al. 2019b).** Certain nontraditional stable isotopes are excellent tracers of

source assimilation during fractional crystallization, which is helpful in determining major reservoirs and mechanisms of continental crust formation. The recent application of stable silicon (Si) isotope compositions in Archean tonalite–trondhjemite–granodiorites found they were likely formed through the melting of subducted basaltic crust enriched in sedimentary silica inherited from seawater (Deng et al. 2019b). The application of Si isotopes to ancient rock samples demonstrated that horizontal tectonics and the downward transport of sediments was occurring at least on a local level early in the Archean. This has the potential to inform crustal recycling processes throughout other stages of Earth's history.

- **Application of potassium (K) isotopes to source attribution in subduction zones (e.g., Hu et al. 2021, others).** Like Ti and Mo, other isotopes susceptible to fractionation at low temperatures can be useful for high-temperature source attribution. For example, measurements of stable potassium (K) isotopes indicate that seawater has a ~0.5‰ heavier isotope composition compared to the mantle (Wang and Jacobsen 2016) due to low-temperature fractionation related to secondary mineral formation. Variability in K isotopic compositions

observed in volcanic rocks has subsequently been attributed to the recycling of both altered oceanic crust and subducted sediments (Hu et al. 2021). The susceptibility of K isotopes to fractionate and to move from one reservoir to another in low-temperature processes makes it a useful system for disentangling crustal components with distinctive K budgets and isotope compositions that have been imparted to magmatic rocks.

As demonstrated in the examples above, understanding geological processes that are hard to directly observe will continue to benefit from improvements and expanded use of novel stable isotope systems and on the new perspectives of how to apply these systems from upcoming generations of geochemists.

ACKNOWLEDGMENTS

We thank Roberta Rudnick, one anonymous reviewer, and the editors for constructive reviews, which greatly improved the manuscript. This work was supported by NSF-EAR 1946856 and start-up funds to S.M.A.; NSF-EAR PF 1952809 to A.C.J.; and NSF-EAR 1949655 to S.T.R.

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