Lu-Hf Dating: The Lu-Hf Isotope System

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Definition

The radiogenic isotope applications of the Lu-Hf system utilize variations in ^{176}Hf resulting from the radioactive decay of ^{176}Lu to ^{176}Hf and variations in the Lu/Hf ratios in rocks and minerals. It is used both in geochronology, primarily in rocks containing a high Lu/Hf phase, and in tracer isotopic applications, to track the chemical evolution of the Earth and other solar system materials and to constrain the sources of magmas and sediments.

Introduction

The Lu-Hf isotope system, with applications to geo- and cosmochemistry, was first investigated in the early 1980s (Patchett 1983b; Patchett and Tatsumoto 1980a, b, c, 1981) following the successful implementation of the Rb-Sr and Sm-Nd isotope systems several years earlier.

There are some obvious similarities between the Lu-Hf and Sm-Nd isotope systems and, as a result, they have long been used in concert in a wide range of studies (e.g., Beard and Johnson 1993; Blichert-Toft and Albarède 1997; Johnson and Beard 1993; Patchett and Chauvel 1984; Patchett 1983b; Salters and Hart 1991; Vervoort and Blichert-Toft 1999; Vervoort et al. 1999). In these two systems all elements are lithophile and refractory with high condensation temperatures. Because of these characteristics it has long been assumed that their abundances in the Earth can be approximated by chondritic meteorites (see discussion below). In addition, all elements in these systems behave incompatibly during melting and are concentrated in the melt over the residual solid. In both systems, the daughter element (e.g., Nd, Hf) is more incompatible than the parent, leading to lower Sm/Nd and Lu/Hf ratios in the melt than the residual solid. As a result, the ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf ratios in magmatic rocks are highly correlated (e.g., Chauvel et al. 2008; Johnson and Beard 1993; Patchett 1983a; Salters and Hart 1991; Vervoort and Blichert-Toft 1999). Both Lu and Hf are highly immobile and insoluble and, as is the case with the Sm-Nd system, are thought to be resistant to perturbations and retain their isotopic information through significant degrees of alteration and metamorphism.

In the case of the Lu-Hf isotope system, the parent is the heaviest of the rare-earth elements (REEs) and has broad geochemical similarities with all other +3 valence REEs. The daughter element, however, is not an REE, but a high-field-strength element (HFSE) with a +4 valence and, as such, can behave much differently than the REEs. These differences can confer some advantages to the Lu-Hf isotope system for both geochronology and tracer isotopic work as will be discussed below.

Although the Lu/Hf ratio is fractionated during magmatic processes, the degree of this fractionation, as is the case for Sm-Nd, is not very large. This results in small variations in Lu/Hf ratios between not only rocks within a comagmatic suite but also for most mineral phases within individual

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rocks. This lack of parent/daughter variation severely limits the application of the Lu-Hf chronometer, much as it does for the Sm-Nd isotope system. Therefore, whole-rock Lu/Hf isochrons of truly comagmatic suites of rocks either have too limited variation in Lu/Hf ratios to provide precise ages or, if there is a significant Lu/Hf variation, chances are the suite of rocks used in creating the isochron was not truly comagmatic. There are a few phases, however, with high affinity for Lu, which make them highly useful in geochronology in both magmatic (e.g., apatite) and metamorphic (e.g., garnet, lawsonite) rocks. In addition, some other phases (particularly phases with Zr or Ti as stoichiometric constituents) have strong affinities for Hf (e.g., zircon, baddeleyite, rutile), which make them useful in tracer isotopic studies – especially when used in conjunction with the U-Pb geochronologic information from these mineral phases.

Although the Lu-Hf system was introduced to the geochemical and cosmochemical communities in the 1980s, analytical challenges limited the widespread use of this technique until the late 1990s. The reason for this is that Hf has a very high first ionization potential (6.83 eV, Lide 2003), which prevented easy and routine analysis of Hf isotopes using thermal ionization mass spectrometry (TIMS). As a result there were only a few practitioners using this system in the 1980s and much of the 1990s. These difficult analyses utilized specialized techniques and required considerable amounts of Hf for the analyses to be successful. This all changed with the advent and development of the multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS), which combined the efficient ionization of Hf using an ICP ionization source with the high precision analysis afforded by multi-collector mass spectrometry (Blichert-Toft et al. 1997; Walder and Freedman 1992). This revolutionized the use of the Lu-Hf isotope system for geochronology and tracer isotope applications by allowing the routine analysis not only of Hf isotopes in general but also of much smaller amounts of Hf. This made several important things possible. *First*, it allowed for the more precise and accurate determination of the ^{176}Lu decay constant (Scherer et al. 2001; Söderlund et al. 2004). *Second*, the new MC-ICPMS instrumentation also facilitated the analysis of high Lu-Hf, but Hf-poor, phases like garnet or apatite, which made the use of these phases for geochronology possible. *Third*, it also made it possible to analyze Hf-poor rocks such as chondritic meteorites, which allowed more accurate constraints to be placed on the chondritic Lu-Hf value (e.g., Bouvier et al. 2008). *Finally*, MC-ICPMS technology has made it possible to determine the Lu-Hf isotope composition in very small, Hf-rich phases such as zircon. This latter application, particularly when done in conjunction with U-Pb geochronology, has enjoyed an explosion of use in recent years (e.g., Amelin et al. 2000; Fisher et al. 2014; Gerdes and Zeh 2009; Kemp et al. 2010; Woodhead et al. 2004; Xie et al. 2008; Yuan et al. 2008).

Background

Lutetium is the heaviest of the rare-earth elements (REEs) and shares a +3 valence with the lanthanides as a whole. It also has an odd atomic number (odd number of protons; Z = 71), which, in part, makes it the least abundant of the REEs (67 ppb; McDonough and Sun 1995). Lu has two isotopes (Table 1): ^{175}Lu is stable, is an odd-even nuclide, and is the most abundant isotope (97.4 %); ^{176}Lu is an odd-odd nuclide, has low abundance (2.6 %), and is radioactive, decaying primarily to ^{176}Hf by beta decay. A small percentage (<3 %) of ^{175}Lu is reported to decay to ^{176}Yb by electron capture (Dixon et al. 1954) although Amelin and Davis (2005) establish an upper limit of 0.9 % based on combined electron capture and positron emissions.

Hafnium is the next higher element from Lu on the periodic table (Z = 72) and is a high-field-strength element (HFSE) sharing geochemical similarities with other Group IVB elements, most

Table 1 Isotopic composition of Lu and Hf

	^{175}Lu				^{176}Lu	
Ratio to ^{176}Lu	37.666				1.0	
Atomic %	97.41				2.59	
Atomic weight	174.94079				175.94269	
Atomic weight Lu	174.96670 g/mol					
	^{174}Hf	^{176}Hf	^{177}Hf	^{178}Hf	^{179}Hf	^{180}Hf
Ratio to ^{177}Hf	0.0086743	0.282160	1.0	1.467170	**0.7325**	1.886660
Atomic %	0.1613	5.2474	18.5972	27.2852	13.6224	35.0865
Atomic weight	173.940065	175.94142	176.943233	177.94371	178.945827	179.946561
Atomic weight Hf	178.485367					

notably Zr and Ti. It is relatively under-abundant in the Earth (0.28 ppm, McDonough and Sun 1995) but enriched in the continental crust (5.3 ppm, Rudnick and Gao 2003). It has six isotopes, five of which are stable (Table 1). One isotope, ^{176}Hf (5.20 %), is radiogenic and produced, in part, by beta decay of ^{176}Lu and, together with ^{176}Lu, provides the basis of the Lu-Hf chronometer. By convention the reference stable isotope for the Lu-Hf system is ^{177}Hf (18.60 %).

In order to determine accurate Lu and Hf concentrations and, most importantly, the precise ^{176}Lu/^{177}Hf ratios required for geochronology and calculating accurate initial ratios, the "isotopic dilution" technique is required. This technique involves the addition of measured amounts of tracers of known isotopic composition (highly enriched in ^{176}Lu and ^{180}Hf, typically, with some labs using ^{178}Hf). These tracers, or "spikes," are generally mixed and precisely calibrated so that evaporative loss will not affect the precise determination of the parent/daughter ratios. These spikes are added to the sample solution following or during dissolution, equilibrated with the solution, and become part of the isotopic mixture of the sample. Ultimately the ^{176}Lu/^{177}Hf and ^{180}Hf/^{177}Hf ratios of the samples are measured to determine Lu and Hf concentrations and precise Lu/Hf ratios.

In order to correct for mass dependent fractionation during mass spectrometry (i.e., mass bias), the convention for the Hf isotope system is to normalize to ^{179}Hf/^{177}Hf = 0.7325 (Patchett and Tatsumoto 1980b), the value that has been used since the early days of Hf isotope analyses. Mass bias for Lu isotopic analyses is complicated by virtue of the fact that Lu has only two isotopes, making internal normalization impossible. In the early TIMS era of Lu-Hf isotope measurements, the small degree of mass bias (~ 0.1 % per amu) was not as significant for the less stringent requirements of the Lu isotope dilution analysis. With the advent of the MC-ICPMS analyses, however, mass fractionation that is over an order of magnitude larger than TIMS necessitated an accurate mass bias correction. The current approach is to use a different element with at least one invariant isotope ratio and which has a similar mass bias response, such as Yb, to correct for mass bias in the Lu isotopic measurement. Because of the similarity of behavior of the REEs (particularly for adjacent REEs), it is often difficult to quantitatively remove Yb from Lu. The current practice employed in most labs is to remove the majority of the Yb (recall that Yb is an even element and so is much more abundant than the odd numbered Lu) and use the Yb isotope measurements to determine the mass bias and then apply this to the Lu measurement. This approach is somewhat complicated by the uncertain isotopic composition of Yb (e.g., Amelin and Davis 2005; Chu et al. 2002; Segal et al. 2003; Vervoort et al. 2004) and the fact that ^{176}Yb is a relatively abundant isotope (12.70 %) with the same mass as the ^{176}Lu spike. The interference of ^{176}Yb on the spike isotope, ^{176}Lu, requires that most of the Yb be removed from the sample. In detail there are probably small differences in the mass bias of Yb and Lu, and there are approaches to quantify these differences

(e.g., White et al. 2000). Despite all of these challenges, ^{176}Lu/^{177}Hf ratios in rock samples can probably be determined to ~0.2 % accuracy (Vervoort et al. 2004).

The Hf solution standard employed throughout the history of Hf isotope analysis has been JMC-475, a Hf metal obtained from Johnson Matthey Corporation (Patchett and Tatsumoto 1980b) with a currently accepted ^{176}Hf/^{177}Hf value of 0.282160 (Vervoort and Blichert-Toft 1999). The JMC-475 Hf standard solution is available from the author on request.

Decay System Fundamentals

Lutetium-176 decays to ^{176}Hf by beta decay with a half-life of 37.12 Ga:

$$^{176}\text{Lu} \rightarrow\ ^{176}\text{Hf} + \beta^-.$$
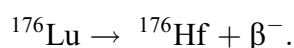
Only a small percentage (~1 %) of ^{176}Hf in rocks and minerals is radiogenic and produced in this way; the majority of ^{176}Hf is "common" Hf, produced primarily during nucleosynthesis. The radiogenic decay equation for the Lu-Hf isotope system describes how radiogenic ^{176}Hf in a rock or mineral will evolve over time:

$$^{176}\text{Hf}_{(p)} =\ ^{176}\text{Hf}_{(t)} +\ ^{176}\text{Lu}_{(p)} * \left(e^{\lambda t} - 1\right).$$

This expression shows that the ^{176}Hf present in a given sample today is a function of (1) the ^{176}Hf in that sample at some time, t, in the past; (2) the amount of radiogenic ^{176}Lu in that material; (3) the amount of time elapsed since formation; and (4) the decay constant. In practice, we reference these isotopes to ^{177}Hf, a stable isotope of Hf. Thus the equation above becomes:

$$^{176}\text{Hf}/^{177}\text{Hf}_{(p)} =\ ^{176}\text{Hf}/^{177}\text{Hf}_{(t)} +\ ^{176}\text{Lu}/^{177}\text{Hf}_{(p)} * \left(e^{\lambda t} - 1\right).$$

Therefore, the material with high Lu/Hf ratios, such as garnet, will generate proportionally more ^{176}Hf over time and evolve to higher ^{176}Hf/^{177}Hf ratios. Conversely, the material with low Lu/Hf ratios, such as zircon, will produce proportionally little ^{176}Hf with time and so its ^{176}Hf/^{177}Hf ratios will increase only very slowly.

An important part of using these radiogenic equations for geochronology and for determining precise initial isotopic compositions is not only measuring the present-day ratios accurately but also knowing the decay constant precisely and accurately. The ^{176}Lu decay constant has been a source of uncertainty, however, and this has limited the full application of the Lu-Hf isotope system. The first determination of the ^{176}Lu decay constant for use in geochemistry and cosmochemistry was performed by Patchett and Tatsumoto (1980a) who determined an isochron on a collection of basaltic and cumulate eucrite meteorites. Using a presumed age of 4.55 Ga for the differentiation event for the eucrites, they determined a value for $\lambda^{176}_{\text{Lu}}$ of $1.962 \pm 0.081 * 10^{-11}$ year^{-1} with a corresponding half-life of 35.3 Ga. This value was later revised by Patchett (1983b) to $\lambda^{176}_{\text{Lu}} = 1.94 \pm 0.07 * 10^{-11}$year^{-1} and a half-life of 35.7 ± 1.4 Ga. This revised value was similar to a decay constant value of $1.93 \pm 0.03 * 10^{-11}$ year^{-1} determined by physical counting experiments (Sguigna et al. 1982). The agreement between these results led, in part, to the use of the $\lambda^{176}_{\text{Lu}}$ value of $1.94 \pm 0.07 * 10^{-11}$ year^{-1} throughout the 1980s and much of the 1990s, with later studies (e.g., Blichert-Toft and Albarède 1997 and subsequent papers) using the Sguigna et al.'s

(1982) values. This early history of ^{176}Lu decay constant determinations is reviewed more thoroughly by Begemann et al. (2001).

The value determined for λ^{176}_{Lu} changed dramatically following age comparison studies by Scherer et al. (2001) and Söderlund et al. (2004). Scherer et al. (2001) suggested a λ^{176}_{Lu} value of $1.865 \pm 0.015 * 10^{-11}$ year^{-1} based on the age comparisons of 4 samples from diverse localities and with different ages. This included two pegmatites from Norway with ages ~1.1 and 0.9 Ga, an apatite-xenotime bearing gneiss from New York State with an age of ~1.0 Ga, and a carbonatite from South Africa with an age of ~2.1 Ga. The U-Pb crystallization ages for these samples were based on the measurements of gadolinite, xenotime, baddeleyite, and apatite in these rocks; the Lu-Hf isochron was determined using the high Lu/Hf ratios of gadolinite, xenotime, and apatite combined with low Lu/Hf phases in the rock (baddeleyite, zircon, biotite) or the whole-rock compositions.

In a similar study, Söderlund et al. (2004) determined a λ^{176}_{Lu} value of $1.867 \pm 0.008 * 10^{-11}$ year^{-1} based on age comparisons using two Proterozoic dolerite dikes from Sweden. The ages of these rocks were determined using baddeleyite U-Pb geochronology; apatite was the high Lu/Hf phase providing the spread in the Lu-Hf isochron. Additional determinations by Scherer et al. (2003) agreed with the slightly faster decay of Söderlund et al.'s (2004) value. As a result of this agreement, the isotopic community is now using the λ^{176}_{Lu} value of $1.867 \pm 0.008 * 10^{-11}$ year^{-1}. The half-life corresponding to this value is 37.12 Ga. The revision in the value for the ^{176}Lu decay constant from the Patchett (1983b) and Sguigna et al.'s (1982) values has two important consequences for Lu-Hf geochronology and isotope geochemistry. The first, and most obvious of these, is the change in calculated Lu-Hf ages. Using the Scherer/Söderlund decay constant results in ages that are 4 % older than ages determined with the Patchett/Sguigna value. The second consequence is that this lowers the calculated initial ^{176}Hf/^{177}Hf of rocks. The degree of this effect is a function of age but also of the ^{176}Lu/^{177}Hf ratios. For Archean and older samples, the lowering of the calculated initial ^{176}Hf/^{177}Hf for the Earth's oldest rocks has very significant implications for the record of the Hf isotope evolution of the Earth (e.g., Scherer et al. 2001, 2007).

Although the Söderlund/Scherer decay constant determinations, which used terrestrial samples in their age comparisons, have converged on a well constrained value of $1.867 \pm 0.008 * 10^{-11}$ year^{-1}, age comparison determinations based on meteorites continue to yield a faster ^{176}Lu decay rate. Blichert-Toft et al. (2002) reanalyzed a suite of basaltic and cumulate eucrites and concluded that their regression was consistent with the $1.93 \pm 0.03 * 10^{-11}$ year^{-1} value of Sguigna et al. (1982) and not the slower decay rates determined from terrestrial age comparisons. As was true with the earlier work of Patchett and Tatsumoto (1980a), however, the basaltic and cumulate eucrites plot at opposite ends of the isochron with the basaltic eucrites at the low Lu-Hf end and the cumulate eucrites at the high Lu-Hf end, which may indicate these are not truly cogenetic. Further, these samples appear to have different formation ages with the cumulate eucrites arguably younger (Mittlefehldt et al. 1998). In another study using meteorite age comparison, Bizzarro et al. (2003) determined a λ^{176}_{Lu} value of $1.983 \pm 0.033 * 10^{-11}$ year^{-1}, even faster than the Patchett/Sguigna values. The Bizzarro et al. (2003) study included analyses of ordinary chondrites, carbonaceous chondrites, and basaltic eucrites and used a common age of 4.56 Ga. As was true with the eucrite-based determination, this study included a diverse suite of meteorites of potentially different ages and metamorphic histories, and therefore, the decay constant determination may be affected in some way by the use of samples that do not strictly meet the requirements for an isochron. These caveats notwithstanding, there are indications that meteorite isochrons yield a faster decay constant. One possible explanation for this apparent difference between the terrestrial and meteorite determinations is the presence of excess ^{176}Hf in meteorites. This may have been produced by excitation of the long-lived radioactive isotope ^{176}Lu to a short-lived ^{176}Lu isomer early in the history of the solar

system that then decays quickly to ^{176}Hf, thereby producing the excess ^{176}Hf (Albarède et al. 2006; Thrane et al. 2010). The exact mechanism of how this might have occurred is still a matter of debate (Albarède et al. 2006; Thrane et al. 2010).

The Lu-Hf Isochron Method

All Lu-Hf geochronology uses the "isochron" method to determine absolute ages. Unlike some chronometers such as U-Pb in zircon where there is little, if any, daughter isotope at the time of mineral growth, in the Lu-Hf system, there is invariably an abundance of daughter isotopes present (i.e., "common Hf"). For this reason, it is not possible to determine the age of a single mineral sample by measuring the accumulation of daughter isotopes in the sample. Thus all Lu-Hf geochronometry relies on the isochron approach, which utilizes coexisting rocks and minerals to determine an age. Important assumptions in this approach include the following: (1) All the minerals formed at the same time (i.e., have the same age); (2) all samples are cogenetic (have the same isotopic composition at the time of formation); and (3) the sample being dated has been a closed system since the time of mineral growth.

The systematics of the Lu-Hf isochron method, using garnet geochronology as an example, is shown in Fig. 1: (1) Prior to mineral formation, whether in a magma or metamorphic protolith, the bulk rock has a low Lu/Hf ratio and (at least approximately) a uniform Hf isotopic composition at the hand sample scale. (2) During crystallization, or, in this example, metamorphism, different phases form with different Lu/Hf ratios, but all with the same initial ^{176}Hf/^{177}Hf. (3) Over time, the Hf isotopic compositions of the different components evolve as a function of their Lu/Hf ratios with high Lu/Hf components evolving more quickly to elevated ^{176}Hf/^{177}Hf and low Lu/Hf components evolving more slowly. (4) At some later time, if the rock has been a closed system with respect to Lu and Hf, all components will have compositions that plot along a line that is a function of time.
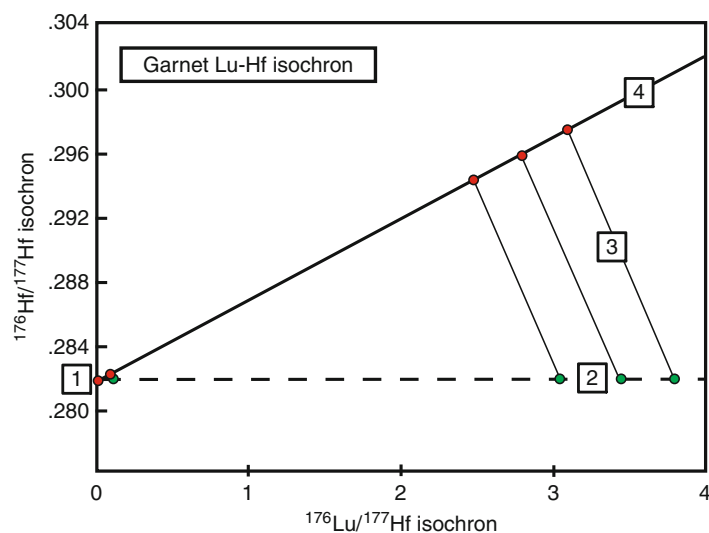

Fig. 1 The isochron method applied to garnet Lu-Hf geochronology. (*1*) uniform Hf isotopic composition at time $t = 0$; (*2*) phases in rock acquire different Lu/Hf ratios (garnets with high Lu/Hf), but all with the same ^{176}Hf/^{177}Hf; (*3*) Hf isotopic compositions of the different components evolve with time as a function of their Lu/Hf ratios; (*4*) if the rock has remained a closed system with respect to Lu and Hf, all components will plot along a line (isochron) that is a function of time

Regression of a line through these points yields a slope from which an age can be calculated using the formula:

$$\text{Age} = \ln(\text{slope} + 1)/\lambda^{176}\text{Lu}.$$

In detail, many of the assumptions of the garnet isochron method are not strictly met. In most cases the rock is certainly not in perfect isotopic equilibrium (i.e., homogeneous ^{176}Hf/^{177}Hf) prior to metamorphism. In addition, the time different phases in the rock form may not be precisely the same, especially in the case of prolonged garnet growth (e.g., Kohn 2009). These can be serious obstacles if there is a small range of Lu/Hf and ^{176}Hf/^{177}Hf variations in samples but are often overcome in isochrons with high Lu/Hf phases and large amounts of radiogenic Hf ingrowth.

Geochronologic Applications

Whole-Rock Lu-Hf Isochrons

Because of the limited fractionation in Lu/Hf that occurs during magmatic processes, there is rarely a sufficiently large range in Lu/Hf ratios in suites of rocks that are truly cogenetic to generate an isochron with enough precision to be useful (Patchett 1983b). If there is a large variation in Lu/Hf in a suite of samples, it is likely these samples are probably not strictly cogenetic. Examples of the former may be represented by the eucrite isochrons combining both basaltic and cumulate eucrites (Blichert-Toft et al. 2002; Patchett 1983b) and in the collective chondrite-eucrite isochron of Bizzarro et al. (2003). In practice, therefore, Lu-Hf whole-rock isochrons are rarely employed for geochronology, especially for terrestrial samples.

Apatite Lu-Hf Geochronology

There is potential in some magmatic rocks, however, to crystallize a high Lu/Hf phase (e.g., apatite, magmatic garnet) that can then be used in geochronology. The magmatic rocks that have the most promise for useful geochronometry are those that contain apatite as a crystallizing phase. As demonstrated by the decay constant work of Scherer et al. (2001) and Söderlund et al. (2004) and the pioneering work applying Lu-Hf geochronology to phosphates by Barfod et al. (2003), apatite generally has very high Lu/Hf ratios and can be used in generating meaningful isochrons. In addition, these phases are likely in isotopic equilibrium with the magma at the time of their formation and likely formed at the same time as the other phases in the rock. Furthermore, apatite can occur in mafic rocks that generally lack zircon and that may not contain baddeleyite. The potential of Lu-Hf apatite geochronology for providing important geochronologic information for some rocks that are notoriously difficult to date is high, and this should be a growth area in the future.

Garnet Lu-Hf Geochronology

The most successful geochronologic application of the Lu-Hf system has been garnet geochronology. This technique shares the same principles as Sm-Nd garnet geochronology in that it utilizes garnet's generally high affinity for HREEs which results in elevated Sm/Nd ratios and (generally higher) Lu/Hf ratios in the garnets as they grow. The potential of the garnet Lu-Hf technique was first demonstrated by a number of papers in the late 1990s (Blichert-Toft et al. 1999; Duchene et al. 1997; Scherer et al. 1997). Following this early proof-of-concept work, there have been a large number of studies in a wide variety of metamorphic rocks: garnet-bearing pelitic schists, para- and orthogneisses, amphibolites, eclogites, and granulites (Anczkiewicz et al. 2004; Bird et al. 2013;

Cheng et al. 2008; Herwartz et al. 2011; Kelly et al. 2011; Scherer et al. 2000; Smit et al. 2013; Wells et al. 2012; Zirakparvar et al. 2010). Reliable garnet Lu-Hf ages have been reported for rocks as old as Archean (e.g., Smit et al. 2013) and as young as Miocene (e.g., Zirakparvar et al. 2011) and everything in between.

Although there are many parallels between Lu-Hf and Sm-Nd garnet geochronology, there are important differences between these two systems. *First*, the decay rate of the parent isotope in the Lu-Hf system, ^{176}Lu, is ~3 times faster than ^{147}Sm in the Sm-Nd system. This results in a higher rate of ingrowth in the radiogenic daughter, ^{176}Hf, compared to ^{143}Nd. *Second*, owing to the different geochemical behavior between a REE and a HFSE, there is generally more fractionation in the Lu/Hf ratios compared to Sm/Nd, which is especially manifest in phases like garnet and apatite.

Third, Lu is partitioned into garnet most strongly of all the REEs, while Hf is incorporated into garnet only weakly (Table 2). This often results in pronounced Lu-Hf zoning in the garnet with high Lu/Hf ratios in the core, due to the strong incorporation of Lu during early garnet growth, and with lower Lu/Hf ratios toward the rim due to the depletion of Lu in the garnet feeding zones. Because the very high Lu-Hf in the cores will exert a strong control on the slope of the regression, it has been suggested that Lu/Hf ages will be biased toward the early stages of garnet growth (Lapen et al. 2003; Skora et al. 2006). In this way, we would expect slightly older Lu-Hf garnet ages compared with Sm-Nd ages in a slowly growing garnet (Lapen et al. 2003; Skora et al. 2006).

Fourth, there are significant differences in the apparent closure temperature ranges in garnet between the two isotopic systems with garnets closing for Lu-Hf at a higher temperature than for the Sm-Nd system. Debate continues on closure temperature estimates of the Sm-Nd chronometer (e.g., Dutch and Hand 2009; Ganguly et al. 1998; Scherer et al. 2000; Smit et al. 2013; Van Orman et al. 2002), but appear to be in the range of ~700–750 °C for garnets 1 mm diameter and larger (Smit et al. 2013; Van Orman et al. 2002) and significantly higher (perhaps 100 °C or more) for Hf. This can lead to differences between the garnet Lu-Hf and Sm-Nd ages with the Lu-Hf ages

Table 2 Melt-solid partition coefficients for Lu and Hf in various minerals

Mineral	D(Lu)	D(Hf)	Melt	References
Olivine	0.0015	0.01	Basalt	McKenzie and O'Nions 1991
Clinopyroxene	0.233	0.28	Basalt	McKenzie and O'Nions 1991
Clinopyroxene	0.223	0.623	Basaltic	Hauri et al 1994
Clinopyroxene	0.256	0.433	Alk. basalt	Zack and Brumm 1998
Plagioclase	0.025	0.01	Basalt	McKenzie and O'Nions 1991
Orthopyroxene	0.22	0.06	Thol. basalt	Green et al 2000
Ilmenite	0.084	0.38	Alk. basalt	Zack and Brumm 1998
Rutile	0.0124	4.98	Tonalite	Foley et al 2000
Amphibole	2.1	0.54	Andesite	Bacon and Druitt 1988
Garnet	5.5	0.23	Basalt	McKenzie and O'Nions 1991
Garnet	7.1	0.24	Basalt	Johnson 1998
Garnet	57	0.57	Andesite	Hauri et al 1994
Garnet	23.5	3.3	Dacite	Irving and Frey 1978
Apatite	13.8	0.73	Andesite	Bacon and Druitt 1988
Apatite	21.5	0.878	Dacite	Fujimaki 1986
Zircon	196	958	Andesite	Fujimaki 1986
Zircon	689	971	Dacite	Fujimaki 1986

The partition coefficient, D, is defined as the ratio of the concentration of the element in the solid compared to melt. Values are from GERM database (http://earthref.org/KDD/) compiled from the original references listed above

systematically older (e.g., Scherer et al. 2000). In some granulite terranes that may have remained buried at mid- to lower-crustal levels for a prolonged time during and following garnet growth, these age differences can be large – as much as 50–70 m.y. (Smit et al. 2013; Vervoort et al. 2013). Experimental work also indicates significantly slower diffusion for Hf in garnets than the REEs (Ganguly et al. 2010), which collectively have similar diffusion rates. One possible consequence of the slower diffusion of Hf than Lu is that the garnet may effectively close to Hf diffusion before Lu, leading to changing Lu/Hf ratios, but static Hf isotopic compositions (Ganguly et al. 2010). This could potentially result in "isochron rotation" and garnet Lu-Hf ages that are artificially too old.

Finally, the presence of accessory phases (e.g., zircon, apatite, monazite, allanite), especially as inclusions in the garnets, presents a special challenge (e.g., Anczkiewicz and Thirlwall 2003; DeWolf et al. 1996; Prince et al. 2000; Scherer et al. 2000; Thoni 2002), and each of these minerals affects the Lu-Hf and Sm-Nd system in different ways. For the Lu-Hf system, zircons provide the biggest challenge. Zircons are extraordinarily enriched in Hf (~10,000 ppm Hf in zircon) relative to garnet ($\ll$1 ppm) and, therefore, can easily overwhelm Hf concentration budget if present as inclusions in the garnets, thus lowering Lu/Hf ratios of the garnet dissolutions. Furthermore, inclusions of preexisting zircons, which are not likely to be re-equilibrated prior to metamorphic growth, can significantly lower the measured $^{176}Hf/^{177}Hf$ of the garnet sample since these zircons will have a less radiogenic Hf isotopic composition than the bulk rock. If these zircons are much older than the bulk rock, this difference can be significant. The incorporation of zircon Hf not in isotopic equilibrium with the protolith at the time of metamorphism in the analyses, either in garnet or as a dispersed accessory phase in the rock matrix, can result in erroneous ages (e.g., Scherer et al. 2000). Fortunately, what makes zircon resistant to isotopic equilibration during metamorphism also makes it resistant to dissolution, and thus zircon inclusions can be largely avoided with a nonaggressive dissolution protocol (e.g., Cheng et al. 2008; Lagos et al. 2007). Very high $^{176}Lu/^{177}Hf$ ratios (generally $\gg$ 1) in the garnet analyses is an indication that zircon (very low $^{176}Lu/^{177}Hf$ ratios, usually 0.002 to 0.001) has not been significantly dissolved. Apatite inclusions (very high $^{176}Lu/^{177}Hf$ ratios) in the garnet can also potentially have an effect on an isochron if they either are not in isotopic equilibrium with the garnet at the time of metamorphic growth or are formed or closed to Lu-Hf diffusion at a different time than the garnet. The effect of apatite inclusions on garnet Lu-Hf geochronology, however, has not yet been examined in the literature. For the Sm-Nd isotope system, the inclusions that are most problematic are phases enriched in REEs and with low Sm/Nd ratios such as monazite and allanite. The effect of these inclusions is generally to drastically reduce the spread in the isochron. If present within the garnets and incorporated in the dissolution, the garnets will have low Sm/Nd ratios – often as low as the whole rock – thus eliminating the possibility of producing a meaningful isochron.

Lawsonite Lu-Hf Geochronology

A recent addition to the Lu-Hf geochronology toolbox is the use of the mineral lawsonite to date subduction zone processes (Mulcahy et al. 2009; Vitale Brovarone and Herwartz 2013). Depending on its paragenesis, lawsonite can have sufficiently elevated Lu/Hf ratios to produce meaningful isochrons. Lawsonite is an important index mineral formed during low temperature-high pressure subduction zone metamoprhism and potentially provides one of the few tools we have available to date subduction zone processes. Initial work with this geochronologic tool has shown that when lawsonite forms on the retrograde path from the breakdown of garnet, it generally has elevated Lu/Hf

ratios and can yield robust Lu-Hf ages. When the lawsonite forms from the breakdown of zeolites on a prograde path, however, it may not develop elevated Lu/Hf ratios and, therefore, may not provide useful Lu-Hf ages (Mulcahy et al. in review). The full potential of this geochronologic tool is just now being explored.

Hf Radiogenic Isotope Geochemistry

As mentioned above, both Lu and Hf are lithophile and refractory elements with high condensation temperatures. Because of these characteristics, it has long been assumed that the abundance of these elements in the bulk Earth can be approximated by chondritic meteorites. It has also been long assumed that the isotopic composition of a refractory element such as Hf was homogeneous in the solar nebula and can also be approximated by chondritic meteorites. This is known as the Chondritic Uniform Reservoir model, or CHUR. Recent work, primarily based on the short-lived ^{146}Sm-^{142}Nd isotopic system, has questioned whether the Earth is strictly chondritic in composition (see discussion in Sm-Nd section). Regardless of whether the Earth is strictly chondritic, the CHUR model provides an important reference value for a plausible bulk Earth composition. The Lu-Hf and Sm-Nd systems are used in tandem for planetary evolutionary studies for the important reason that these are the only two such isotopic systems in which all elements are lithophile and refractory.

The Bulk Silicate Earth and CHUR

Because of the analytical challenges in measuring Hf isotope compositions in Hf-poor (~0.10 ppm; McDonough and Sun 1995) chondrites accurately and precisely, the early Lu-Hf CHUR values had considerable uncertainty. There have been two approaches used to determine a CHUR value for the Lu-Hf and Sm-Nd isotope systems. For Sm-Nd, because there is very little fractionation between Sm and Nd in chondrites and there are no phases with low Sm/Nd ratios, it has not been possible to determine a chondritic (Solar System) initial value for this system. Instead, the approach has been to take an average of representative present-day $^{143}Nd/^{144}Nd$ and $^{147}Sm/^{144}Nd$ values of undifferentiated chondrites. This works because the total Sm-Nd variation in chondrites is modest. Using this approach, Jacobsen and Wasserburg (1980, 1984) determined present-day CHUR values of $^{143}Nd/^{144}Nd = 0.512638$ and $^{147}Sm/^{144}Nd = 0.1966$, which corresponded to the composition of two CI chondrites, Allende and Murchison.

The situation for the Lu-Hf isotope system was initially different because of the difficulty in measuring Hf precisely in the Hf-poor chondrites and the large apparent spread in $^{176}Lu/^{177}Hf$ and $^{176}Hf/^{177}Hf$ in chondrites, which makes determining a mean chondritic value more ambiguous. In order to compare this system to the more established Sm-Nd isotope system, Patchett and Tatsumoto (1981) based the Hf CHUR values on the same CI chondrites used to define the Sm-Nd isotope system, Allende and Murchison. Using this approach, they arrived at present-day values of $^{176}Hf/^{177}Hf = 0.282860$ and $^{176}Lu/^{177}Hf = 0.0334$. The $^{176}Hf/^{177}Hf$ value was later adjusted to 0.282830 (Vervoort and Patchett 1996) to account for the high $^{176}Hf/^{177}Hf$ bias on the TIMS in Denver, the instrument on which all the early pioneering Hf isotope work was performed.

With the advent of the MC-ICPMS and its application to measuring Hf isotopes came the ability to analyze Hf-poor chondrites more precisely. In order to constrain the Lu-Hf CHUR values, Blichert-Toft and Albarede (1997) analyzed 25 chondritic meteorites including carbonaceous, ordinary, and enstatite chondrites. Because the measured values of these samples had a wide spread in $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$ (~ 18 %) and did not define an isochron, they took the weighted average of the 25 chondrites to arrive at present-day values of $^{176}Hf/^{177}Hf = 0.282772$ and $^{176}Lu/^{177}Hf = 0.0332$.

The ^{176}Hf/^{177}Hf values were significantly lower by 0.000058 from the adjusted Patchett and Tatsumoto values (Vervoort and Patchett 1996).

In order to address the problem of the spread in Lu/Hf ratios and the scatter about a reference isochron, Bouvier et al. (2008) analyzed only unequilibrated chondrites (lower metamorphic grade, petrologic types 1–3) including 12 carbonaceous chondrites, 13 ordinary chondrites, and 3 enstatite chondrites. The resulting data had a much smaller spread in Lu/Hf ratios (only 3 %) which allowed a more precise determination of the present-day CHUR values: ^{176}Hf/^{177}Hf = 0.282785 ± 11 and ^{176}Lu/^{177}Hf = 0.0336 ± 1. These are the values currently in use by the geochemical and cosmo-chemical communities. Bouvier et al. (2008) also measured the Sm-Nd isotopic compositions of the same solutions on which the Lu-Hf values were determined and arrived at new CHUR values for the Sm-Nd isotope system of ^{143}Nd/^{144}Nd = 0.512630 and ^{147}Sm/^{144}Nd = 0.1960. Although these are very close to the values of Jacobsen and Wasserburg (1980, 1984), the Bouvier et al.'s (2008) values are more appropriate to use in studies reporting both Hf and Nd data relative to the chondritic reference because they represent values determined on the same set of chondrites.

As is true for the Sm-Nd system, Hf isotope data are often expressed in epsilon values, which are variations in parts per 10,000 from the CHUR reference. Expressed in terms of present-day compositions, this expression is:

$$\varepsilon_{\text{Hf(0)}} = \left[\left({}^{176}\text{Hf}/{}^{177}\text{Hf}_{(\text{sample},0)} - {}^{176}\text{Hf}/{}^{177}\text{Hf}_{(\text{chur},0)} \right) / \left({}^{176}\text{Hf}/{}^{177}\text{Hf}_{(\text{chur},0)} \right) \right] \times 10^4.$$

Expressed in terms of compositions at any time in the past, t, this expression is:

$$\varepsilon_{\text{Hf(t)}} = \left[\left({}^{176}\text{Hf}/{}^{177}\text{Hf}_{(\text{sample},t)} - {}^{176}\text{Hf}/{}^{177}\text{Hf}_{(\text{chur},t)} \right) / \left({}^{176}\text{Hf}/{}^{177}\text{Hf}_{(\text{chur},t)} \right) \right] \times 10^4.$$

Frequently, when values are calculated back in time, they are expressed as "initial" values, signifying the formation age of that rock or mineral. (It is important to note that the CHUR value also needs to be calculated back to its composition at time, t, from the present-day values.)

Lu-Hf Tracers of Geologic Processes

The current paradigm for the evolution of the Earth holds that the crust was formed from silicate melts extracted in some way from the mantle. The crustal rocks resulting from this process are enriched in incompatible elements (hence the term enriched crust), and the mantle left from this extraction of crust is depleted in incompatible elements (hence the term depleted mantle). As a consequence of this differentiation occurring throughout the history of the Earth, including at its very beginning, the Earth's different reservoirs have evolved following different paths. The crustal reservoirs are enriched in incompatible elements but have lower Lu/Hf and Sm/Nd ratios than bulk Earth, and so their ^{176}Hf/^{177}Hf and ^{143}Nd/^{144}Nd evolve more slowly. Conversely, the depleted mantle components, while depleted in incompatible elements, have higher Lu/Hf ratios and Sm/Nd ratios, and so their ^{176}Hf/^{177}Hf and ^{143}Nd/^{144}Nd compositions evolve more quickly than bulk Earth (Fig. 2a). In terms of epsilon values relative to bulk Earth (i.e., CHUR), depleted mantle components evolve toward positive epsilon values, and enriched crustal values evolve toward negative epsilon values (Fig. 2b). This is a fundamental feature in both the Hf and Nd isotopic records of Earth's evolution and has been used to great utility in a wide range of crust/mantle petrogenetic/geochemical studies.
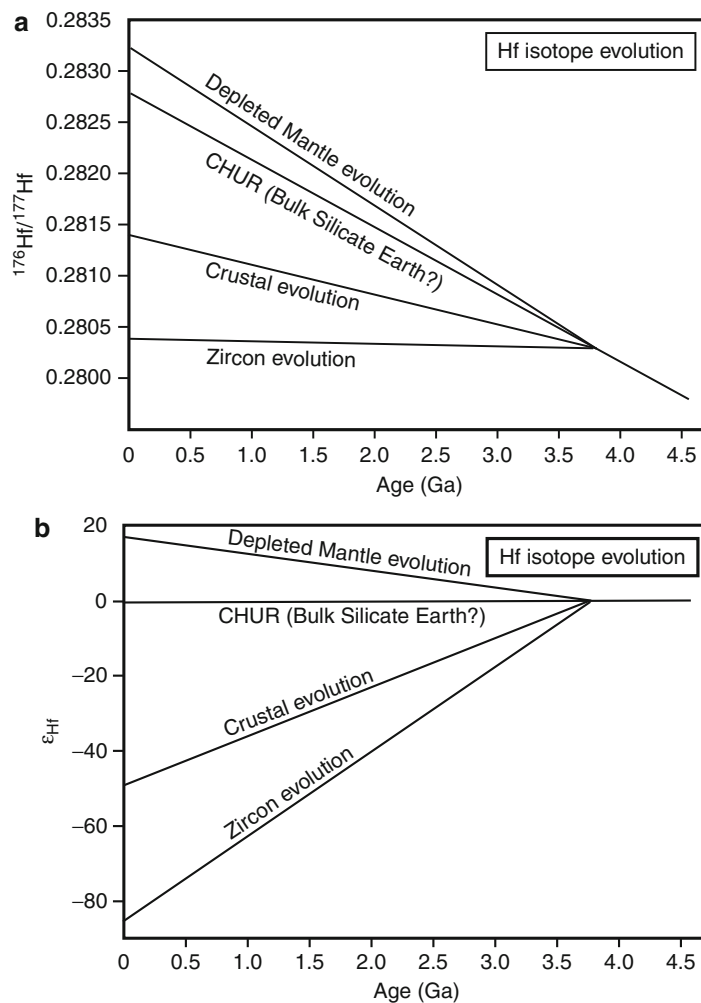
Fig. 2 Schematic diagram showing the hypothetical Hf isotope evolution of different terrestrial reservoirs following a major differentiation event at 3.8 Ga: Chondritic Uniform Reservoir (CHUR) broadly taken as representative of bulk silicate Earth (BSE), depleted mantle evolution from depletion at 3.8 Ga to its composition today, evolution of an enriched crustal reservoir ($^{176}Lu/^{177}Hf = 0.015$), and evolution of a typical zircon formed at 3.8 Ga ($^{176}Lu/^{177}Hf = 0.001$). (**a**) Evolution of $^{176}Hf/^{177}Hf$. (**b**) The same diagram in epsilon Hf notation

An important component in all radiogenic isotopes is time; time is an inherent aspect of Hf isotope evolution and therefore Hf isotope compositions can be used to qualitatively assess the time of separation from different reference reservoirs. These time estimates are called "model ages" and, although not ages in the strict sense, are still a useful way to represent and visualize data with a temporal framework.

The concept of a model age in the Lu-Hf isotope system follows that of Sm-Nd model ages (DePaolo 1981) and is illustrated in Fig. 3a. The $^{176}Hf/^{177}Hf$ isotopic composition of a sample is measured today, and the $^{176}Lu/^{177}Hf$ ratio of that sample is used to calculate its isotopic composition back in time until it intersects with a reservoir of interest such as the depleted mantle. The time, corresponding to this intersection, is a Hf model age – in this case, the Hf depleted mantle model age $Hf_{T(DM)}$. This model age has also been termed a crust-formation age, $Hf_{T(CR)}$, signifying the average time since separation from the depleted mantle or time of residence in a crustal reservoir (DePaolo 1981).

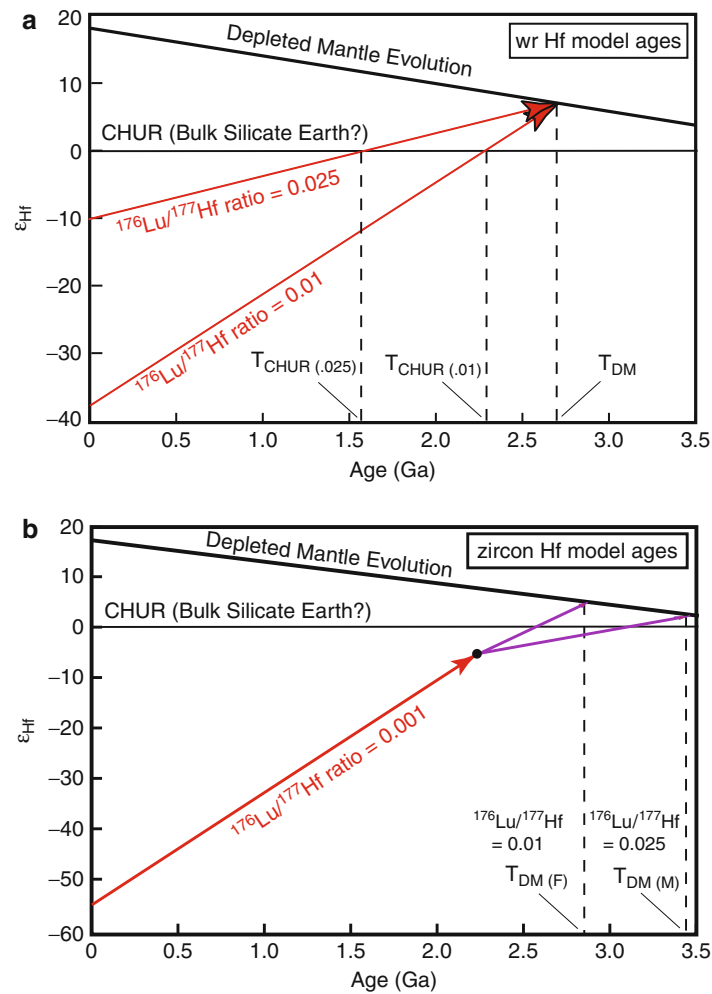**Fig. 3** (**a**) Schematic diagram showing the calculation of Hf model ages for two hypothetical whole-rock (wr) samples that formed from a depleted mantle reservoir at ~2.7 Ga: a mafic sample with a high Lu-Hf ratio (^{176}Lu/^{177}Hf = 0.025) and a negative present-day epsilon Hf value of approx. −10 and a felsic sample with a low Lu-Hf ratio (^{176}Lu/^{177}Hf = 0.010) and a highly negative present-day epsilon Hf value of ~ −38. Also shown in this diagram are the depleted mantle model ages (T_{DM}) and the CHUR model ages (T_{CHUR}). Note the different trajectories for the two samples and the differences in T_{CHUR}. (**b**) Schematic diagram showing the calculation of zircon Hf model ages. In this example the zircon has a present-day epsilon Hf value of ~ −55 and an initial epsilon Hf value of ~ −5 calculated at a crystallization age of ~2.2 Ga. Calculation of depleted mantle model ages (T_{DM}) requires an assumption of the ^{176}Lu/^{177}Hf of the source rock. If the source rock is more evolved (^{176}Lu/^{177}Hf = 0.01 in this case), the T_{DM} is ~2.85 Ga. If the source rock is more mafic (^{176}Lu/^{177}Hf = 0.025 in this case), the T_{DM} is much older, ~3.45 Ga. As can be seen from this diagram, the uncertainty in the T_{DM} increases dramatically the further the initial Hf value is away from the depleted mantle reference line. Further, unrecognized Pb loss in the zircon, which would yield anomalously young crystallization ages, exacerbates the difference between crystallization and depleted mantle ages. See text for further discussion of zircon Hf model ages

Depleted mantle model ages have been used to identify the sources of magmatic rocks; if the Hf T_{DM} values are older than the crystallization ages, then the interpretation is that these rocks were derived from older sources or sources that had a crustal prehistory – sources that had separated from the mantle some time in the past. In this way it is simply another means of conveying the Hf isotopic compositions in the context of time – in much the same way as an epsilon Hf isotope diagram places the Hf isotope compositions in a time context. Model ages are also applied to sediments to identify

the provenance of their sources: more juvenile mantle-derived sources, older evolved crustal sources, or some mixture of the two. This is identical to the approach used for Sm-Nd model ages in sediments with the caveat that Hf model ages are often more variable than Nd model ages because of the presence or absence of Hf-rich (and unradiogenic) zircons in the sediments (e.g., Prytulak et al. 2006; Vervoort et al. 1999).

A recent adaptation of Hf model ages – and one that has seen an explosion of use in recent years – is the use of Hf model ages of zircons. The way this works is shown in Fig. 3b. The Hf isotopic composition is measured in the zircon and the zircon's Lu/Hf ratio is used to calculate back to its crystallization age. At that point, the growth trajectory changes, assuming a source $^{176}Lu/^{177}Hf$ ratio. As was the case with the other model ages, the intersection with the depleted mantle reference line yields the zircon Hf depleted mantle model age. This technique has recently been applied to detrital zircon studies because of the facility of acquiring U-Pb crystallization ages and Lu-Hf isotope compositions on the same zircon grain by laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS).

There are several aspects of this approach, however, that result in considerable uncertainty in the zircon Hf model "ages." Because the context of the rock has been lost, the Lu/Hf ratio of the zircon's precursor rock has to be estimated, and this value can vary widely from a mafic precursor (high Lu/Hf) to a felsic precursor (low Lu/Hf). The further the composition of a zircon is from the depleted mantle (or other) reference, the greater the uncertainty in the model age. Another limitation of this technique is that the model ages rely on the intersection of the zircon + precursor rock trajectory with a depleted mantle reference curve. The depleted mantle, however, is not a discrete entity with a discrete isotopic composition. It is, in fact, typically defined by its most depleted, rather than average, compositions (Vervoort and Blichert-Toft 1999). Finally, it is not possible to determine the true ages of some detrital zircons precisely, due to the potential for ancient Pb loss and other factors. If ancient Pb loss exists in these grains, this would greatly exacerbate the differences between the crystallization and the Hf model ages with the former being too young and the latter being too old. In total, all of these factors contribute to very large uncertainties in Hf model "ages." It is tempting to treat these model ages, particularly for detrital zircons, as values with quantifiable age information rather than model-dependent estimates. It is important to recognize, however, that these model ages are not ages in any true sense of the word, but rather "models" with large uncertainties. While they provide some useful constraints on the timing and nature of crust forming events, it is imperative to understand the limitations of such "age" information.

Conclusions

The Lu-Hf isotope system is an important chronometer in geochemistry and cosmochemistry. Its utility as a chronometer in whole-rock samples, however, is limited by the relatively small degrees of Lu-Hf fractionation during magmatic processes. In rocks with high Lu-Hf phases, the Lu-Hf isotope system can be a powerful chronometer; this is especially true for garnet-bearing metamorphic rocks and magmatic rocks with apatite as a crystallizing phase.

There now appears to be widespread agreement on a value for the ^{176}Lu decay constant of $1.867 \pm 0.008 \times 10^{-11}$ Ga (Scherer et al. 2001; Söderlund et al. 2004). This value has important implications not only for Lu-Hf geochronology but also for early Earth differentiation and evolution based on calculated initial Hf isotope values. Similarly, there is currently widespread acceptance of the Bouvier et al. (2008) CHUR values of $^{176}Hf/^{177}Hf = 0.282785$ and $^{176}Lu/^{177}Hf = 0.0336$. Corresponding to these are the Sm-Nd CHUR values of $^{143}Nd/^{144}Nd = 0.512630$ and

^{147}Sm/^{144}Nd = 0.1960. Notwithstanding discussions of whether or not the Earth is strictly chondritic, these values provide a self-consistent baseline on which to reference the isotopic evolution of the Earth.

Tracer isotopic applications provide equal utility of the Lu-Hf isotopic system and, in conjunction with independent age information, can be used to determine the Hf isotopic composition of rocks and minerals back into time. This information is useful in constraining both the evolution and source regions of igneous systems as well as the provenance of sedimentary rocks. By far the most heavily utilized mineral for tracer isotope studies is zircon, which provides a unique opportunity for determining both age and Hf isotope compositions in individual crystals (and even separate growth zones within a single crystals), such as in the case of inheritance or overgrowths. For this reason, the integrated U-Pb and Hf isotope information from zircon has seen a rapid increase in use in recent years and will likely continue. Many of these studies often report zircon Hf model ages. While these provide useful qualitative, model-based data, these are not in any way truly ages and should not be interpreted as containing quantitative chronologic information.

In summary, with the full implementation of techniques and applications of the Lu-Hf isotope system following the advent of MC-ICPMS technology, Lu-Hf geochronology and tracer isotope work has finally taken its place at the table with the other main players in geochronology and radiogenic isotope geochemistry.

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