THE LU ISOTOPIC COMPOSITION OF ACHONDRITES:
CLOSING THE CASE FOR ACCELERATED DECAY OF $^{176}\text{Lu}$

JOSH WIMPENNY, YURI AMELIN, AND QING-ZHIU YIN

1 Department of Earth and Planetary Sciences, University of California, One Shields Avenue, Davis, CA 95616, USA; jbwimpenny@ucdavis.edu
2 Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia

Received 2015 April 24; accepted 2015 September 9; published 2015 October 2

ABSTRACT

Studies of Lu–Hf isotope systematics in meteorites have produced apparent “ages” that are older than Pb–Pb ages and older than the estimated age of our solar system. One proposed explanation for this discrepancy is that irradiation by cosmic rays caused excitation of $^{176}\text{Lu}$ to its short-lived isomer that then underwent rapid decay to $^{176}\text{Hf}$. This explanation can account for apparent excesses in $^{176}\text{Hf}$ that correlate with Lu/Hf ratio. Mass balance requires that samples with measurable excess in $^{176}\text{Hf}$ should also have measurable deficiencies in $^{176}\text{Lu}$ on the order of 1‰–3‰. To unambiguously test the accelerated decay hypothesis, we have measured the $^{176}\text{Lu}/^{176}\text{Hf}$ ratio in terrestrial materials and achondrites to search for evidence of depletion in $^{176}\text{Lu}$. To a precision of 0.1‰ terrestrial standards, cumulate and basaltic eucrites and angrites all have the same $^{176}\text{Lu}/^{176}\text{Hf}$ ratio. Barring a subsequent mass-dependent fractionation event, these results suggest that the apparent excesses in $^{176}\text{Hf}$ are not caused by accelerated decay of $^{176}\text{Lu}$, and so another hypothesis is required to explain apparently old Lu–Hf ages.

Key words: meteorites, meteor, meteoroids – methods: analytical – minor planets, asteroids: general – nuclear reactions, nucleosynthesis, abundances

1. INTRODUCTION

Age determination using decay of radioactive isotopes have played key roles in deciphering the evolution of the Earth and other planetary bodies. The $^{176}\text{Lu}$–$^{176}\text{Hf}$ system ($^{176}\text{Lu}$ decays to $^{176}\text{Hf}$ with a half-life of about $\sim$35–37 billion years) is widely used to understand crustal evolution processes on terrestrial and planetary bodies and to provide important chronological information in rocks and minerals that formed in the solar system. The decay constant of $^{176}\text{Lu}$ ($\lambda$) is well characterized at (1.865–1.867) $\times$ 10$^{-11}$ yr$^{-1}$ by studies of terrestrial rocks and minerals with independently known ages (Scherer et al. 2001; Söderlund et al. 2004) and in phosphate minerals from Richardson (ordinary chondrite) and Acapulco (primitive achondrite; Amelin 2005). However, several studies of Lu–Hf systematics in ancient meteorites are inconsistent with this $\lambda$ value, producing apparent Lu–Hf ages that are older than ages obtained by Pb–Pb dating and older than the age of the solar system. Examples include whole rock Lu–Hf studies in chondrites (Blichert-Toft & Albarède 1997; Bizzarro et al. 2003) and eucrites (Patchett & Tatsumoto 1980; Blichert-Toft et al. 2002) and an internal isochron from the quenched angrite SAH 99555, with an apparent Lu–Hf age of 4869 ± 34Ma (Bizzarro et al. 2012). In each case, the Lu–Hf data can only be reconciled with Pb–Pb data by inferring a greater $\lambda$ value of $\sim$1.96 $\times$ 10$^{-11}$ yr$^{-1}$. Accurate age determination is not possible without knowing the precise and accurate value of the decay constant. Consequently, the possible change in the decay rate of $^{176}\text{Lu}$ has important implications for our continued use of the Lu–Hf system to elucidate information about early solar system processes and crust–mantle evolution (e.g., Iizuka et al. 2015).

Several hypotheses have been investigated to explain the apparent excess in $^{176}\text{Hf}$. These have been discussed in detail elsewhere (Amelin & Davis 2005) but include the possibility of $^{176}\text{Lu}$ branch decay to $^{176}\text{Yb}$, interlaboratory bias related to mixed spike calibration used for Lu/Hf ratio determination, bias in terrestrial minerals induced by slow cooling, a suprachondritic early Lu/Hf ratio in the solar nebula, and nucleosynthetic heterogeneity. All are considered either highly unlikely or can be ruled out as a cause of the 5% discrepancy in $\lambda$ (Scherer et al. 2001; Söderlund et al. 2004; Amelin & Davis 2005). An alternative way to measure the $\lambda$ value is via direct physical counting of $^{176}\text{Lu}$ decay, but measurements have produced data that are highly scattered (1.7–1.96 $\times$ 10$^{-11}$ year$^{-1}$; Grinyer et al. 2003; Nir-El & Haquin 2003; Kostert et al. 2013) and cannot shed more light on the problem. The most recent explanation for the apparent rapid decay of $^{176}\text{Lu}$ in ancient meteorites hypothesized that irradiation, caused by a proximal supernova occurring during or after planetary accretion, produced gamma rays that, in turn, caused photoexcitation of $^{176}\text{Lu}$ to form the short-lived isomer $^{176}\text{mLu}$ (Albarède et al. 2006). The rapid decay of this isomer of Lu ($t_{1/2} = 3.7$ hr to $^{176}\text{Hf}$ could then explain why we observe correlated excesses of $^{176}\text{Hf}$ with Lu/Hf ratio. The energy source that caused photoexcitation was disputed by Thrane et al. (2010) because gamma rays have centimeter-scale penetration depths in solids and the excess $^{176}\text{Hf}$ has been observed in a range of meteorites, some of which are likely to have formed beneath the surface of their parent planetesimal. Neutrinos were also considered as an energy source but could not have delivered the necessary neutrino flux to cause the observed excesses in $^{176}\text{Hf}$. Instead, Thrane et al. (2010) proposed cosmic rays as a more viable energy source for production of the excited $^{176}\text{mLu}$. In theory, a supernova shock could have accelerated cosmic rays to high enough energies to penetrate rock to depths of 100–200 m. Irradiated samples will develop an excess in $^{176}\text{Hf}$, and assuming the sample has enough internal spread in Lu/Hf, this excess in $^{176}\text{Hf}$ will be measurable as excess slope on a Lu–Hf isochron line. The generation of excess $^{176}\text{Hf}$ may also offset the y-intercept (the initial $^{176}\text{Hf}^{176}\text{Hf}^{176}\text{Hf}^{176}\text{Hf}$ ratio) of the Lu–Hf isochron; however, this will be highly dependent on the timing of crystallization relative to irradiation. Samples that crystallized prior to
irradiation should have an identical initial $\text{^{176}Hf}/\text{^{177}Hf}$ ratio to samples that were not irradiated.

While the accelerated decay hypothesis can conveniently explain why some studies have observed excess $\text{^{176}Hf}$ in some meteorites, several recent studies have cast doubt on its validity. The irradiation hypothesis implicitly predicts that any excess in $\text{^{176}Hf}$ must be accompanied by a corresponding deficit in $\text{^{176}Lu}$ on the order of 1%–3% (e.g., Thrane et al. 2010). Recent analyses of the basaltic eucrite Agoult show that it has a $\text{^{176}Lu}/\text{^{175}Lu}$ ratio that is within error (0.2%) of terrestrial standards (Iizuka et al. 2015), although it is difficult to make robust conclusions from a single data point. Scherer et al. (2005) presented a wider set of $\text{Lu}$ isotopic data for eucrites, chondrites, and one calcium-alumina-rich inclusion (CAI) and observed no variation in $\text{^{176}Lu}/\text{^{175}Lu}$ to the 1% level but could not achieve the greater precision necessary to unambiguously confirm or reject the hypothesis. Amelin et al. (2011) presented whole rock $\text{Lu}$–$\text{Hf}$ systematics for angrites and eucrites that showed no excess slope, providing no support for the accelerated decay hypothesis (Amelin et al. 2011). Furthermore, recent $\text{Lu}$–$\text{Hf}$ analyses of the quenched angrite D’Orbigny observed no excess in $\text{^{176}Hf}$, with a $\text{Lu}$–$\text{Hf}$ age of 4510 ± 97 Ma (Sanborn et al. 2015). Other recent studies have also investigated internal $\text{Lu}$–$\text{Hf}$ systematics of angrites and eucrites, finding a wide range of apparent $\text{Lu}$–$\text{Hf}$ ages and initial $\text{^{176}Hf}/\text{^{177}Hf}$ values (e.g., Bast et al. 2012; Richter et al. 2013a, 2013b), some of which are consistent and some of which are inconsistent with the accelerated decay hypothesis.

In this study, we aim to finally settle the debate regarding the accelerated decay of $\text{^{176}Lu}$ by measuring the isotopic composition of $\text{Lu}$ in terrestrial samples and in achondrites to a precision of ~0.1%. Our study will test the accelerated decay hypothesis in two ways: first by comparison of the $\text{^{176}Lu}/\text{^{175}Lu}$ in terrestrial rocks and achondrites, and second by comparison of the $\text{^{176}Lu}/\text{^{175}Lu}$ ratio in quenched and plutonic angrites. Angrites are a group of meteorites that formed through melting of mantelike material on a planetesimal (Mittlefehldt et al. 2002; Keil 2012) that accreted and differentiated very early in the history of the solar system (<2 My after CAIs; Kleine et al. 2012). There are two subgroups: the quenched angrites and plutonic angrites that differ in crystal size and mineralogy. Petrographic evidence and crystallization experiments suggest that the quenched angrites probably cooled within a few meters of the APB surface (Mikouchi et al. 2000, 2001; Floss et al. 2003). In contrast, the plutonic angrites are coarse grained (e.g., Prinz et al. 1977), and some, such as Angra Dos Reis, contain homogeneous pyroxenes and olivines that are suggestive of much slower cooling (McKay et al. 1998). This is consistent with Pb–Pb and Hf–W dating, which show that plutonic angrites crystallized between 3.5 and 7 My after the quenched angrites (Kleine et al. 2012). Thus, while their exact formation depths are unknown, plutonic angrites probably formed at depths great enough to shield them from irradiation by cosmic rays, while the shallow formation depth of quenched angrites means they should show evidence of the irradiation event. Hence, the irradiation hypothesis predicts a greater deficit in $\text{^{176}Lu}$ in the quenched angrites relative to the plutonic angrites and terrestrial samples. The results of these analyses will provide an unambiguous answer to whether accelerated decay of $\text{^{176}Lu}$ is responsible for the measured excess in $\text{^{176}Hf}$ in ancient meteorites.

## 2. METHODS

A detailed description of the methodology used during sample preparation and analysis is given in Wimpenny et al. (2013). In brief, whole rock samples of two quenched angrites (D’Orbigny and Sahara 99555), four plutonic angrites (Angra dos Reis, NWA 2999, NWA 4590, and NWA 4801), two eucrites (Camel Donga and Ibitira), and three terrestrial basalts (BIR-1, BCR-2, and BHVO-2) were dissolved using a mixture of HF and HNO$_3$. The pure $\text{Lu}$ fraction was extracted using a multiple column procedure involving the removal of Fe and U using anion resin; separation of the heavy rare Earth elements using Ln-spec resin; and a further, more refined step using Ln-spec resin to separate $\text{Lu}$ from Yb. This final step was repeated several times to ensure the residual Yb content was as low as possible, reducing Yb/$\text{Lu}$ ratios by between 10$^4$ and 10$^5$ and maintaining a $\text{Lu}$ yield of >90%.

Lutetium isotope ratios were measured by a Neptune Plus Multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at UC Davis. To account for mass bias, all samples were bracketed and normalized to Ames $\text{Lu}$ metal, but due to the large isotopic fractionation between Ames $\text{Lu}$ and Lu in terrestrial standards, it is more convenient to present data normalized to a more representative standard, in this case, NIST 3130a (see the discussion in Wimpenny et al. 2013). Lutetium isotope ratios are presented in delta notation using the following formula:

$$\delta^{176}\text{Lu} = \left( \frac{^{176}\text{Lu}_{\text{sample}}}{^{175}\text{Lu}_{\text{sample}}} / \frac{^{176}\text{Lu}_{\text{NIST3130a}}}{^{175}\text{Lu}_{\text{NIST3130a}}} - 1 \right) \times 1000.$$

All samples were doped with 99.98% pure W solution to a concentration of 20 ppb W in order to correct for drift and instability in the mass bias. The $\text{Lu}$ and Yb concentrations in the pure W solution were both below detection limits. The total procedural blank was determined by isotope dilution and was 6 ± 4 pg. As a minimum of 10 ng of Lu was processed through the column procedure, this equates to ~0.06% of the total Lu and is thus negligible. To correct for potential isobaric interferences on $\text{^{176}Lu}$, we measured $\text{^{174}Yb}$ and $\text{^{176}Hf}$. External precision was determined from 76 repeat measurements of
differences in precision in this study is not sufficient to 
artifacts associated with correction for residual Yb. While the 
distinguish between true isotopic heterogeneity and analytical 
All achondrites and terrestrial standards have 
176Lu isotopic analyses show no evidence to suggest that 
that apparent excess in 176Lu is caused by the accelerated decay of 176Lu. Taken 
together, these data are inconsistent with the hypothesis of 
accelerated decay of 176Lu to explain an apparent excess of 176Hf in ancient meteorites. 
Ultimately, the homogeneous δ176Lu values can be explained in one of two ways. The simplest and most likely 
explanation is that the formation and rapid decay of the short-lived isomer of 176Lu did not occur or did so to such a small extent that it is not measurable at the current precision of 0.1‰. If this explanation is correct, then the observed excess in 176Hf is caused not by the accelerated decay of 176Lu, but by some other mechanism. The alternative explanation is that the 
irradiation and accelerated decay of 176Lu did happen, but a second process then caused isotopic fractionation of the 176Lu/177Lu ratio, favoring 176Lu in the residual mineral phases and thereby creating an apparently homogeneous pattern in early solar system materials. The latter scenario would seem remarkably fortuitous, requiring the second fractionation process to have been of opposite and equal magnitude to the initial change of Lu isotopic composition by the 
accelerated decay of 176Lu. This is despite samples originating from several different early planetary bodies that have experienced different thermal histories and loss of volatiles (e.g., Humayun & Clayton 1995). While this latter scenario appears unlikely, for completeness, it warrants further discussion.

Hypothetically, the mass-dependent fractionation of Lu isotopes could have occurred on the parent body (e.g., through volatilization) or as a result of terrestrial processes (i.e., weathering). We will first consider the possibility of terrestrial weathering causing fractionation of Lu isotopes. Stable isotopic systems more readily fractionate at low temperatures (e.g., Urey 1947); however, because the difference in mass between rare Earth elements is relatively small (26Mg and 44Ca values are corrected by internal normalization using an assumed 
common stable isotopic ratio (e.g., 177Hf/176Hf) that removes information about mass-dependent fractionation. For these reasons, there are no prior studies that document the behavior of Lu isotopes during weathering. Terrestrial alteration processes and contamination have been shown to cause fractionation of REE patterns, even in meteorites that seem fresh and unweathered. One example is SAH 99555, in which olivine grains exhibit LREE enrichments and positive Ce anomalies resulting from redox changes due to terrestrial weathering (Crozaz et al. 2003). Similarly, many Antarctic eucrites show Ce anomalies and the loss of Ca-phosphates due to interaction with water (Mittlefehldt & Lindstrom 1991; Floss & Crozaz 1991). Such processes could possibly cause the loss or gain of Lu and fractionation of Lu isotopes. However, the required magnitude of isotopic fractionation of Lu is large (1‰–3‰), similar in magnitude to the entire known natural range of δ26Mg and δ44Ca values (e.g., Tipper et al. 2006a). It is likely that any weathering process responsible for such a

AMES Lu with a δ176Lu value of −1.12 ± 0.08‰ relative to NIST 3130a.

3. RESULTS

Results are compiled in Table 1 and illustrated in Figure 1. All achondrites and terrestrial standards have δ176Lu values that are within error of 0.10 ± 0.16‰ (2 s.d.), representing a significant improvement over the 1‰ (2 s.d.) external reproducibility of Scherer et al. (2005). While small heterogeneities appear to exist between eucrites and angrites, the scale of the difference is small, with the eucrites having δ176Lu values of 0.22 ± 0.04‰ (n = 4), while angrites have on average δ176Lu values of 0.07 ± 0.15‰ (n = 18). Both are within error of the 


difference is small, with the eucrites having δ176Lu values of 0.22 ± 0.04‰ (n = 4), while angrites have on average δ176Lu values of 0.07 ± 0.15‰ (n = 18). Both are within error of the average δ176Lu value for three terrestrial basalts of 0.09 ± 0.14‰ (n = 20), which are also consistent with Lu isotopic data for the eucrite Agoult (Izuka et al. 2015). Thus, with our current level of precision, we cannot resolve differences in δ176Lu between eucrites, angrites, and terrestrial rocks. Furthermore, with a typical precision of ∼0.1‰, it will be difficult to distinguish between true isotopic heterogeneity and analytical artifacts associated with correction for residual Yb. While the precision in this study is not sufficient to resolve sub 0.1‰ differences in δ176Lu between samples, it is easily sufficient to resolve the predicted 1‰–3‰ deficits in 176Lu in objects that are hypothesized to have experienced an accelerated decay of 176Lu (Figure 1(b)).

4. DISCUSSION

Lu isotopic analyses show no evidence to suggest that 
achondrites are depleted in 176Lu relative to terrestrial rocks. Despite the likely differences in their burial depth on the 
angrite parent body (Mikouchi et al. 2001), there is no resolvable difference in 176Lu/177Lu ratio between the quenched and plutonic angrites as expected in the cosmic-ray 
irradiation hypothesis (Thrane et al. 2010; Bizzarro et al. 2012). Furthermore, despite the quenched angrite SAH 99555 having internal Lu–Hf systematics that are consistent with the excess production of 176Hf and an apparently old age (Bizzarro et al. 2012), it does not contain a deficiency in 176Lu. Taken 
together, these data are inconsistent with the hypothesis of 
accelerated decay of 176Lu to explain an apparent excess of 176Hf in ancient meteorites.

Figure 1. (a) Lu isotope data for terrestrial basalts, quenched and plutonic 
angrites, and eucrites, (b) comparing measured δ176Lu values with the range 
required to confirm that apparent excess in 176Hf is caused by the accelerated decay of 176Lu. All error bars are 2σ (s.d.).
significant fractionation would leave the sample highly enriched in alteration minerals such as clays and Al and Fe-oxides. Such altered samples are usually avoided as any extreme weathering event is also likely to significantly fractionate the Lu/Hf ratio, leaving any Lu–Hf isochrons severely disturbed, e.g., ALHA77302 (Patchett & Tatsumoto 1980). Furthermore, individual eucrites and angrites have been subjected to different degrees of terrestrial weathering (e.g., Crozaz et al. 2003), so any associated fractionation effects should also vary.

If fractionation of Lu isotopes by terrestrial weathering can be ruled out, then we must also consider whether isotopic fractionation of Lu could have occurred on the parent planetesimal during magmatic processes. Equilibrium fractionation decreases with increasing temperature (e.g., Urey 1947), so fractional crystallization is unlikely to cause significant fractionation of Lu isotopes. Instead, the HEDs and angrites are all known to be volatile depleted relative to the Earth (Humayun & Clayton 1995; Papik 1998; Sarafian et al. 2013), so the evaporative loss of Lu is a possible fractionating mechanism. Insight into isotopic fractionation of REE by possible parent body processes can be gained via a recent study by Albatal et al. (2012), who investigated the behavior of Er and Yb isotopes in a range of meteorite and terrestrial samples. Their results show that some samples, including lunar soils and terrestrial garnets, contain measurable mass-dependent fractionation effects, although perhaps predictably the fractionation is quite small (0.43‰ and 0.23‰ per a.m.u. for Yb and Er, respectively). Fractionation of Yb is ascribed to differences in Yb oxidation state in magmatic environments and to volatility effects causing a deficit in heavy Yb in lunar basalts, while fractionation of Er in lunar samples is likely due to the capture of thermal neutrons by 165Er. Lu-thetum only exists in one oxidation state (+3), so redox-induced fractionation processes that are important for Yb (Albatal et al. 2012) and other systems such as iron (e.g., Rouxel et al. 2005) are not relevant. Lu-thetum is also less volatile than Yb (1659 K and 1487 K as Lu2O3 and Yb2O3, respectively; Lodders 2003) with a similar 50‰ condensation temperature to Er, so we would predict that evaporative loss and related mass-dependent fractionation of Lu would be smaller than effects observed for Yb. Neutron capture effects are possible as the cross section of 176Lu is relatively large (2090 ± 70 barns; Mughabghab 2003; Wisshak et al. 2006), but this process would result in a further deficit in 176Lu, similar to the hypothesized irradiation event. Even if we assume that Lu isotopes could be fractionated with a similar magnitude to Er and Yb, ultimately, Albatal et al. (2012) show that any difference in their isotopic composition between chondrites, achondrites, and terrestrial rocks is far below the necessary 1‰–3‰ required to validate the accelerated decay hypothesis.

An alternative fractionating mechanism is some kind of distillation process analogous to processes involved in the refinement of metals. For example, we observe a large isotopic fractionation of Lu (–1.1‰) in the Ames metal standard, as discussed in Wimpenny et al. (2013). Though the metal is relatively enriched in 175Lu, presumably to account for mass balance, there must be a complementary component that is relatively enriched in 176Lu. Processed metals can be highly fractionated from natural values (e.g., Galy et al. 2001; Hippler et al. 2003); however, it is difficult to think of a natural process that can mimic the industrial processing of metals.

The evidence for a limited extent of secondary fractionation of rare Earth elements discussed above makes it highly unlikely that these processes removed the effect of accelerated decay of 176⁰Lu causing broad scale homogeneity of δ176⁰Lu across different planetary bodies. Therefore, the most straightforward and likely explanation for homogeneous δ176⁰Lu values in achondrites and terrestrial samples is that the hypothesized accelerated decay of 176⁰Lu did not occur. Clearly a different explanation is needed for why analyses of chondrites, eucrites, and angrites have given apparently old Lu–Hf ages. While the excess in 176⁰Hf could not have been derived from rapid decay of 176⁰Lu, our data cannot provide more insight into the likely cause of this age discrepancy. More data are needed, particularly internal isochrons that avoid the issue of sample co-genetics. Angrites are an ideal suite of samples to investigate further because they are old (>4557 Ma), formed rapidly, and have experienced little in the way of parent body alteration. Despite this, Lu–Hf isotope data for two quenched angrites, SAH 99555 (Bizzarro et al. 2012) and D’Orbigny (Sanborn et al. 2015), give discrepant results, with D’Orbigny showing no evidence of excess in 176⁰Hf. Similar inconsistencies in Lu–Hf data have been observed in recent preliminary analyses of angrites and eucrites (e.g., Bast et al. 2012, 2013; Righter et al. 2013a, 2013b). It is worth noting that many of these isochrons are based on data from a limited mineral set that does not include important Lu and Hf carrier phases such as phosphates and/or does not provide whole rock analyses to verify mass balance in cases where internal migration of Lu or Hf may have occurred (Debaille et al. 2014). More detailed studies that address these problems may be necessary in order to shed light on why apparent excesses in 176⁰Hf are observed in some ancient meteorites.

5. CONCLUSIONS

In this study, we measured the Lu isotope ratio of achondrites and terrestrial samples to a precision of ~0.1‰, sufficient to resolve the 1‰–3‰ depletion in 176⁰Lu necessary to validate or refute the hypothesis of accelerated decay to explain apparent excesses in 176⁰Hf in early solar system materials. Our results show that the isotopic composition of 176⁰Lu/175⁰Lu in these samples is homogeneous at the reported level of precision. Thus, barring an unlikely later fractionation event, our data are inconsistent with the accelerated decay hypothesis. Another mechanism is required to explain the apparent excesses in 176⁰Hf observed in bulk rock and internal isochrons.

This work was supported by NASA grants NNX11Ai51G and NNX14AM62G awarded to Q.Z.Y. The manuscript benefited from insightful review comments by Tom Lapen and one anonymous reviewer and from the editorial handling of Melissa McGrath.

REFERENCES

Amelin, Y. 2005, Sci, 310, 839
Amelin, Y., & Davis, W. 2005, GeCoA, 60, 465
Amelin, Y., Wimpenny, J., & Yin, Q-Z. 2011, LPICo, 1639, 9014
Bast, R., Scherer, E. E., Mezger, K., Fischer-Gödde, M., & Sprung, P. 2013, MinM, 77, 665

Wimpenny, Amelin, & Yin