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The role of phosphates for the Lu–Hf chronology of meteorites

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ABSTRACT

The ^{176}Lu–^{176}Hf isotopic system is widely used for dating and tracing cosmochemical and geological processes, but still suffers from two uncertainties. First, Lu–Hf isochrons for some early Solar System materials have excess slope of unknown origin that should not be expected for meteorites with ages precisely determined with other isotopic chronometers. This observation translates to an apparent Lu decay constant higher than the one calculated by comparing ages obtained with various dating methods on terrestrial samples. Second, unlike the well constrained Sm/Nd value (to within 2%) for the chondritic uniform reservoir (CHUR), the Lu/Hf ratios in chondrites vary up to 18% when considering all chondrites, adding uncertainty to the Lu/Hf CHUR value. In order to better understand the Lu–Hf systematics of chondrites, we analyzed mineral fractions from the Richardton H5 chondrite to construct an internal Lu–Hf isochron, and set up a numerical model to investigate the effect of preferential diffusion of Lu compared to Hf from phosphate, the phase with the highest Lu–Hf ratio in chondrites, to other minerals. The isochron yields an age of 4647 ± 210 million years (Myr) using the accepted ^{176}Lu decay constant of $1.867 \pm 0.008 \times 10^{-11}$ yr^{-1}. Combining this study with the phosphate fractions measured in a previous study yields a slope of 0.08855 ± 0.00072, translating to a ^{176}Lu decay constant of $1.862 \pm 0.016 \times 10^{-11}$ yr^{-1} using the Pb–Pb age previously obtained, in agreement with the accepted value. The large variation of the Lu/Hf phosphates combined with observations in the present study identify phosphates as the key in perturbing Lu–Hf dating and generating the isochron slope discrepancy. This is critical as apatite has substantially higher diffusion rates of rare earth elements than most silicate minerals that comprise stony meteorites. Results of numerical modeling depending of temperature peak, size of the grains and duration of the metamorphic event, show that diffusion processes in phosphate can produce an apparently older Lu–Hf isochron, while this effect will remain negligible in perturbing the Sm–Nd chronology. Our results suggest that only type 3 chondrites with the lowest metamorphic grade and large minerals with minimal diffusive effects are suitable for determination of the Lu–Hf CHUR values and the Lu decay constant respectively.

1. Introduction

The ^{176}Lu–^{176}Hf isotopic system is extensively used for dating cosmochemical and geological processes, and for studying planetary evolution. However, two uncertainties in the Lu–Hf systematic still need to be explained. First, Lu–Hf isochrons for many meteorites have steeper slopes than can be expected using the well-established decay rate of ^{176}Lu in terrestrial rocks. Isochron comparisons performed on terrestrial and extraterrestrial geological objects give similar values for λ^{176}Lu ("terrestrial" average of $\sim$1.864–1.867 $\times 10^{-11}$ yr^{-1}) (Amelin, 2005; Blichert-Toft and Albarède, 1997; Grinyer et al., 2003; Nir-El and Haquin, 2003; Nir-El and Lavi, 1998; Patchett et al., 2004; Scherer et al., 2001), whereas the isochrons obtained exclusively on some chondrites and achondrites indicate a less straightforward message. Some studies have proposed a λ^{176}Lu slightly higher than observed on Earth ("meteoritic" average of $\sim$1.95 $\times 10^{-11}$ yr^{-1}) (Bizzarro et al., 2003, 2012; Blichert-Toft et al., 2002; Patchett and Tatsumoto, 1980; Thrane et al., 2010) while other studies have found λ^{176}Lu similar to the "terrestrial value" either on mineral separates (Bast et al., 2017; Sanborn et al., 2015) or bulk rock isochrons (Bouvier et al., 2015). Direct counting experiments have, so far, not been particularly useful for understanding the apparent decay constant

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Table 1

Lutetium and Hf concentrations, and ^{176}Hf/^{177}Hf ratios obtained for the nine silicates fraction of Richardton.

		g	Hf (ppm)	Lu (ppm)	^{176}Lu/^{177}Hf	2σ	^{176}Hf/^{177}Hf	2σ
R1	initial fines	0.2537	0.15	0.05	0.0481	0.0005	0.284225	0.000035
R2	handground fines	0.1767	0.16	0.04	0.0382	0.0004	0.283335	0.000016
R3	coarse handground	0.249	0.20	0.03	0.0203	0.0002	0.281705	0.000007
R4	+100 mesh IF 0.2A	0.2233	0.12	0.02	0.0229	0.0002	0.281997	0.000007
R5	+100 mesh IF0.25A	0.2194	0.13	0.03	0.0318	0.0003	0.282717	0.000022
R6	−100 mesh IF0.25–0.35A	0.2213	0.07	0.01	0.0246	0.0002	0.282087	0.000034
R7	−100 mesh IF0.35–0.4A	0.2085	0.11	0.03	0.0327	0.0003	0.282915	0.000007
R8	−100 mesh IF0.4–0.45A	0.2232	0.10	0.03	0.0438	0.0004	0.283886	0.000007
R9	−40 & + 100 mesh freefall mag	0.1903	0.06	0.01	0.0354	0.0004	0.283016	0.000007

Mesh indicates the size of the sieve in micron, and + or − indicate if the fraction was larger or smaller than the sieve; IF is the current (in ampere) used for magnetic separation. See analytical method for details.

discrepancy, as even the most recent studies (Grinyer et al., 2003; Luo and Kong, 2006; Nir-El and Haquin, 2003; Nir-El and Lavi, 1998) show a considerable dispersion and give an average value of $1.848 \pm 0.212 \times 10^{-11}$ yr^{-1} with a relatively large uncertainty that encompasses the two groups. Several processes have been proposed to explain this discrepancy between terrestrial and extraterrestrial objects, such as accelerated decay of ^{176}Hf that may have occurred at the beginning of the solar system under the influence of irradiation by γ-rays and cosmic rays (Albarede et al., 2006; Thrane et al., 2010) and branched decay of ^{176}Lu (Amelin and Davis, 2005; Norman et al., 2004). Accelerated decay of ^{176}Lu is ruled out by the absence of variations in Lu isotopic composition between the meteorites of different ages that formed before and after the proposed irradiation event (Wimpenny et al., 2015). Branched decay is ruled out by the absence of Yb isotopic variations correlated with Lu/Yb ratios in ancient minerals (Amelin and Davis, 2005), and by γ-spectrometry measurements (Amelin and Davis, 2005; Norman et al., 2004). Hence there is a need to find another explanation for the observed excess slopes of meteorite Lu–Hf isochrons (e.g., Bizzarro et al., 2003; Thrane et al., 2010). It has recently been suggested that terrestrial contamination could cause excess radiogenic Hf and steeper Lu–Hf isochrons (Bast et al., 2017). However, it is not clear if this effect would be observable in all meteorites besides hot desert ones. Finally, because different minerals have different closure temperatures, they will provide different ages depending on the cooling rate (e.g., Amelin et al., 2005; Göpel et al., 1994). In that case, the whole-rock isochron will be shifted towards lower slopes and thus younger ages (i.e. an average value between the oldest and the youngest minerals), in contrast to a steeper slope that translates to higher λ^{176}Lu as investigated here.

Second, unlike the Sm/Nd ratios that show little variation in type 1–6 bulk chondrite samples and allow the Sm/Nd ratio in the chondritic uniform reservoir (CHUR) to be constrained within ∼2% (Bouvier et al., 2008; Jacobsen and Wasserburg, 1984; Patchett et al., 2004), the Lu/Hf ratios in chondrites vary up to 28% when all petrologic types (1–6) are considered (Bizzarro et al., 2003; Blichert-Toft and Albarède, 1997; Bouvier et al., 2008; Patchett et al., 2004). A difference in the variation range of Lu–Hf was also observed between un-metamorphosed (type 1–3) (ΔLu/Hf ∼4%) and metamorphosed chondrites (ΔLu/Hf ∼28%) (Bouvier et al., 2008), as well as a subsequent shift in the slope of the isochron (Bouvier et al., 2015). The initial ^{176}Hf/^{177}Hf in the early solar system has been constrained by direct analysis of meteorite zircons (Iizuka et al., 2015), but the uncertainty of the CHUR value for the Lu/Hf ratio remains. The discrepancy is also observed between the average chondritic ^{143}Nd/^{144}Nd vs. ^{176}Hf/^{177}Hf ratio (see compilation in Martin et al., 2013). This problem has been addressed by Bouvier et al. (2008) who suggested that only type 1–3 chondrites with the lowest metamorphic grade should be used to determine the Lu decay constant and the CHUR values, because they provide the smallest Lu–Hf variation amongst chondrites of 4%. It should be noted that the case is not totally closed, as even some type 3 chondrites were not considered in proposing this well-defined average (Bouvier et al., 2008). Bouvier et al. (2008) also proposed a new Lu decay constant of $1.884 \pm 0.060 \times 10^{-11}$ yr^{-1}, which is intermediate between the "terrestrial" and "meteoritic" values but has an uncertainty too large for usage of the ^{176}Lu–^{176}Hf system in geochemistry. Finally, Martin et al. (2013) observed a large redistribution of rare earth elements (REE) among different phases during metamorphism, while Hf is retained in its initial host phases. This raises the possibility that, under certain circumstances, preferential loss of Lu from phosphates, compared to Hf, may affect Lu/Hf isochron ages, even though this seems to be at odds with the study of Amelin (2005) who obtained a precise "terrestrial" Lu decay constant exclusively on phosphate grains from the Richardton H5 chondrite. We articulate in this paper that mineral grain size plays a significant role in determining whether or not a meaningful isochron can be obtained.

In order to better understand the Lu–Hf systematics of chondrites, various silicate fractions from the Richardton H5 chondrite have been analyzed to construct an internal Lu–Hf isochron. This meteorite has been well characterized, with an accurate U–Pb age on the pyroxene fraction of chondrules of 4.5627 ± 0.0017 billion years (Gyr), and one on phosphate of 4.5507 ± 0.0026 Gyr (Amelin et al., 2005). Besides, a Lu–Hf isochron has also been obtained on pure phosphate fractions, giving, by comparison with the U–Pb age, a "terrestrial" like (e.g., Scherer et al., 2001) Lu decay constant of $1.8640 \pm 0.0146 \times 10^{-11}$ yr^{-1} (Amelin, 2005). The data obtained here on the silicate fractions are first compared to these previous data. In a second step, diffusion modeling has been performed to evaluate the possibility that metamorphism can lead to an apparent variation in the Lu decay constant.

2. Analytical methods

The different fractions have been obtained by gently crushing the sample, followed by sieving and magnetic separation, as described in Table 1. Lutetium and Hf have been chemically purified at the Université Libre de Bruxelles (ULB) using the procedure described in Debaille et al. (2007), without any leaching. In brief, after dissolution, a 5% aliquot was separated to be spiked with a mixed ^{179}Hf–^{176}Lu spike. Hf and REE were separated on a cationic resin in HCl. Rare earth elements were subsequently purified on HDEHP resin in HCl in order to collect the Yb–Lu cut (Blichert-Toft et al., 1997). Finally, the Hf cut was first purified from Fe on an anionic column in 6N HCl, and the remaining matrix (notably Ti) was eliminated on Ln.Spec resin with 6N HCl plus traces of H_2O_2. Hafnium was collected in 4N HF. Hafnium cuts and spiked Lu and Hf cuts have been measured at ULB in 0.05N HNO_3 (+0.05 N HF for Hf cuts) on Nu-Plasma MC-ICP-MS equipped with a DSN-100 desolvating nebulizer. The repeated measurements of JMC stan-