

The Lu and Hf Isotopic Compositions of Meteorites: A Comparative Study of Alkali Flux Fusion and HF Parr Bomb Dissolution. A. Pourmand¹ and N. Dauphas^{1,2}, ¹The University of Chicago, Origins Lab, Department of Geophysical Sciences and Enrico Fermi Institute, 5734 South Ellis Avenue, Chicago, IL 60637 (pourmand@uchicago.edu), ²California Institute of Technology, Division of Geological & Planetary Sciences.

Introduction: The Lu and Hf isotopic compositions and concentrations have played an important role in our understanding of the evolution of terrestrial and extraterrestrial rocks [1-5]. Nevertheless, inhomogeneous distribution of Lu and Hf in meteorites and incomplete dissolution of samples that contain refractory phases have made it difficult to achieve a consensus on the chondritic value for the Lu/Hf ratio [1]. Two methods are commonly employed to dissolve terrestrial and extra-terrestrial material: i) hotplate dissolution of finely powdered material [2] or preferably Parr bomb dissolution with a mixture of hydrofluoric (HF), nitric and perchloric acids [6-7] and ii) fusion with an alkali flux (e.g., lithium metaborate LiBO_2) at temperatures $> 1000^\circ\text{C}$ and subsequent dissolution of the fusion glass in acid [8-9]. We present comparative results between Parr bomb dissolution and alkali flux fusion in different crucibles for Allende standard material. TODGA (N,N,N',N' tetraoctyldiglycolamide) and Ln (di(2-ethylhexyl) orthophosphoric acid, HDEHP) resins are used to separate Lu and Hf from the matrix and interfering elements. Results from bomb dissolution of 12 meteorites are also presented.

Analytical Methodology: HF Parr bomb. Approximately 100 mg of Allende standard powder (from the Smithsonian Institute, SI) was weighed into a clean 6 mL PFA Savillex beaker. A calibrated Hf-Lu spike mixture enriched in ^{180}Hf and ^{176}Lu was added together with 4 grams of HF and HNO_3 at a 3:1 ratio. The vial was heated inside a 45 mL PTFE Parr bomb at 160-170 $^\circ\text{C}$ for 5 days. The solution was then evaporated overnight at 90 $^\circ\text{C}$ to avoid sample/spike loss due to spattering. 100 μL of HClO_4 was added and fumed in several steps to convert insoluble fluorides to soluble chloride compounds. The residue was finally dissolved in 4 grams of concentrated HNO_3 and heated in the bomb for 5 days. In some cases, visible residues were still present and 2-5 days of extra heating were required to achieve complete dissolution.

LiBO_2 flux fusion. 100 μL of Pure LiBr (non-wetting agent) and Puratonic[®] LiBO_2 (Alfa Aesar, 99.997%) mixed with about 100 mg of the SI Allende powder were fused at a sample: flux ratio of 1:6 at 1070 $^\circ\text{C}$ for 15 minutes. Experiments were conducted in capped platinum, glassy carbon and high-purity graphite crucibles and the melt was quantitatively transferred to a 30 mL PFE Savillex beaker containing

25 mL of 3 mol $^{-1}$ L HNO_3 and the calibrated Hf-Lu spike. Although sample to flux ratios as low as 1:3 [8] and 1:4 [9] have been previously used, our tests have shown a sample to flux ratio lower than 1:6 leads to incomplete dissolution and inconsistent results.

Chromatography and MC-ICP-MS analysis. The solutions from the bomb and alkali flux dissolutions were loaded to a pre-conditioned 2-ml TODGA cartridge on a vacuum chamber and Hf was eluted in 3 HNO_3 + 0.2 mol L^{-1} HF after the matrix elements were removed. Lu was subsequently eluted in 6 mol L^{-1} HCl using a 2-ml Ln Spec cartridge utilized in tandem with the TODGA cartridge. The portions containing Lu and Hf were dried and analyzed in 3% HNO_3 + 0.03% HF on a Neptune MC-ICP-MS [10]. Hf and Lu isotopic compositions and concentrations were determined after processing the raw data in Mathematica[®] by correcting for isobaric interferences, instrumental mass-fractionation and accounting for the spike contribution to all Hf isotopes.

Results and discussion: We have performed extensive blank analyses to constrain the Hf and Lu contributions from labware, resins, LiBO_2 flux, double-distilled acids and platinum, high-purity graphite and glassy carbon crucibles. These tests are particularly important if a limited quantity of the sample is available (typically a few hundred mg for most meteorites). Procedural blanks for Lu are < 5 pg from HF bomb and flux fusion dissolution methods and pose no complications. As indicated in table 1, the amount of Hf in blanks from each possible source, however, must be well constrained and corrections should be implemented if the blank levels exceed ~ 0.5 % of the total Hf quantity in the sample. Capped high-purity graphite crucibles appear to give the best results for Hf blanks.

Figure 1 shows the $^{176}\text{Hf}/^{177}\text{Hf}$ (2σ based on average JMC-475 runs during each analysis session) as a function of $^{176}\text{Lu}/^{177}\text{Hf}$ for 8 samples of SI Allende powder that were dissolved using the Parr bomb, platinum crucibles and high-purity graphite crucibles (filled symbols). Our results are quite comparable with those obtained using hotplate [2] and HF Parr bomb dissolution [1,6] from the literature (open symbols in figure 1). Measured $^{176}\text{Hf}/^{177}\text{Hf}$ ratios in the current study are adjusted to the value of 0.28216 in JMC-475 Hf standard [1]. The Lu and Hf composition of 12 meteorites from Parr Bomb dissolutions are presented

in figure 2. Altered surfaces and fusion crusts were avoided during sampling. All meteorites plot close to the isochron. Provided results from a replicate analysis (L5) and one meteorite sample (LL6) with $^{176}\text{Lu}/^{177}\text{Hf}$ lower than 0.03 [1] are not taken into account, the arithmetic average of $^{176}\text{Lu}/^{177}\text{Hf}$ for all other analyzed types from this study is 0.0336 ± 2 , which is identical to the average of 22 unequilibrated meteorites (0.0336 ± 2) and CHUR from the literature (0.0336 ± 1) reported by Bouvier et. al. (2008) [6].

We plan to analyze more meteorite samples of all types using flux fusion in ultra-pure graphite crucibles. Both methods of dissolution produce consistent results, the flux fusion, however, has several advantages: i) No HF is used in the process of dissolution. In addition to safety hazards, the presence of trace amounts of HF can result in Hf loss, ii) intermediate evaporation steps necessary during bomb dissolution that may result in contamination and/or sample loss before spike/sample equilibration are avoided and iii) alkali flux fusion is superior in attacking all refractory phases (e.g., zircons) and dissolution of the fused disk is achieved within minutes compared with the HF Parr bomb method that may take several days to weeks.

Blanks	Hf (pg)
Savillex beakers (n=3)	< 5
LiBr (100 μl)	< 5
Double-distilled acids	< 5
TODGA cartridge (n=3)	< 5
LiBO ₂ Puratonic [®] 99.997 % (600 mg)	88
15 mL platinum crucibles (n=13)	130
8 mL Graphite crucibles (n=2)	29
15 mL glassy carbon crucible (n=3)	432
6 mL Savillex vial in Parr Bombs (n=2)	34

Table 1. Hf blank measurements. Graphite crucible blank is comparable to Parr Bomb dissolution.

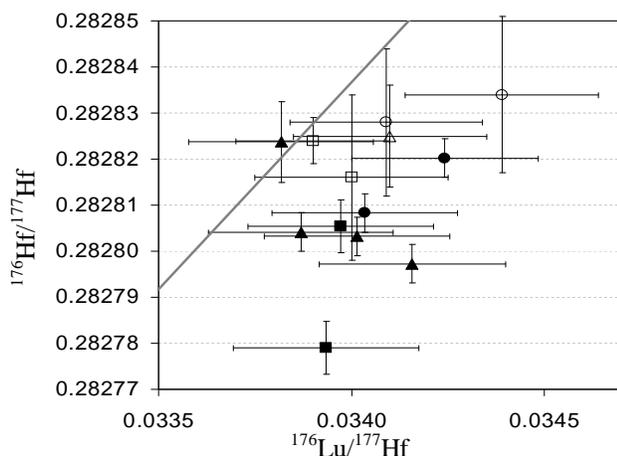


Figure 1. The Lu and Hf compositions for SI Allende powder dissolved using Parr bombs (filled triangles), platinum crucibles (filled circles) and graphite crucibles (filled squares). Open circles and squares represent Parr bomb dissolution from [1] and [6], respectively. The open triangle is from hotplate dissolution [2]. The line represents the isochron by combining data sets from several studies [6]. $^{176}\text{Hf}/^{177}\text{Hf}$ errors are 2σ standard deviations from the average JMC-475 runs during each analysis session.

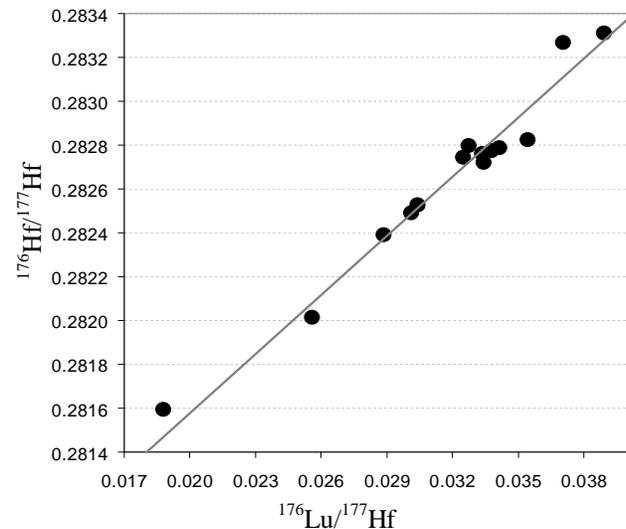


Figure 2. The Lu and Hf compositions of 12 meteorites dissolved in HF Parr bombs plot along the isochron line. The meteorite types are CM2, CO3, L5, LL5, LL6, H4, H6, EH4, EH5 and EH6. The average $^{176}\text{Lu}/^{177}\text{Hf}$ value with the exclusion of two measurements lower than 0.03 [1] is 0.0336 ± 2 , which is identical to the literature compilation value of 0.0336 ± 1 for unequilibrated meteorites [6]. The errors are smaller than the symbols.

References: [1] Patchett P. J. et al. (2004) *EPSL*, 222, 29-41. [2] Blichert-Toft J. et al. (1997) *Contrib Mineral Petrol.* 127, 248-260 [3] Amelin Y. et al. (2000) *GCA*, 64, 4205-4225. [4] Blichert-Toft J. and Albarède F. (1997) *EPSL*, 148, 243-258. [5] Bizzarro M. et al. (2003) *Nature*, 421, 931-933. [6] Bouvier A. et al. (2008) *EPSL*, 473, 48-57. [7] Mahlen. N. J. et al. (2008) *Geochem. Geophys. Geosyst.* 9, Q01002, doi:10.1029/2007GC001605 [8] Connelly J. N. et al. (2006) *Chem. Geol.*, 233, 126-136. [9] Ulfbeck D. et al. (2003) *Talanta*, 59, 365-373. [10] Pourmand A., Dauphas, N. (2008) *Lun. Planet. Sci. Conf.*, 39th, 1367.