

**PROGRESS REPORT ON Lu-Hf MEASUREMENTS OF SINGLE ZIRCON GRAINS AT THE UNIVERSITY OF CHICAGO.** X.C. Chen<sup>1</sup>, N. Dauphas<sup>1</sup>, K.D. McKeegan<sup>2</sup>, M. Barboni<sup>3</sup>, B. Schoene<sup>4</sup>, P. Boehnke<sup>1</sup>, <sup>1</sup>Origins Lab, Department of the Geophysical Sciences, and Enrico Fermi Institute, The University of Chicago, Chicago, IL ([chenxicindy@uchicago.edu](mailto:chenxicindy@uchicago.edu)), <sup>2</sup>Department of Earth, Planetary and Space Sciences, University of California, Los Angeles, Los Angeles, CA, <sup>3</sup>School of Earth and Space Exploration, Arizona State University, Tempe, AZ, <sup>4</sup>Department of Geosciences, Princeton University, Princeton, NJ.

### Introduction:

Previous studies coupled U-Pb and Lu-Hf isotopic analyses of single lunar zircon grains to derive a minimum age for the isolation of the KREEP reservoir; the very last residual melt produced by crystallization of the the Lunar Magma Ocean. The result of those analyses gives an early age of ~4.51 Ga [1,2]. This minimum age for the differentiation of the lunar crust is mostly based on four zircons with the least radiogenic Hf isotopic compositions. The age of KREEP from zircon analyses is ~120 to 150 Myr older than estimates based on Sm-Nd and Pb-Pb isochrons in ferroan anorthosites [3] and dating of Mg suite lunar crustal rocks [4].

There are several potential difficulties associated with the zircon approach. One is that most lunar zircons are small so that the amount of Hf available for isotopic analysis is small, which limits the precision attainable. Another is that it relies on extreme unradiogenic isotopic analyses of zircons so measurement accuracy of every single data point is critical. Previous lunar zircon  $\epsilon$ Hf results were reported at 1 to 4 epsilon uncertainty ( $2\sigma$ ). Higher precision and high-accuracy measurements are needed to provide more robust constraints on the minimum age of formation of the Moon and crystallization of the LMO. Here, we report our progress to implement the Lu-Hf technique at the University of Chicago for measurements of single zircon grains. We use an ion-exchange procedure to purify Zr and Hf from the interfering Yb and Lu elements [e.g. 5-8] in the digestion solutions of individual lunar zircons retrieved after U-Pb chemistry. This can potentially give smaller errors than applying a peak-stripping method [2]. It also allows us to recover the purified Zr for future isotopic studies.

### Method and Discussion:

A two-stage procedure (following the modified procedure of [7] and [9]) was developed for separating Zr and Hf. In the first step, TODGA resin is used to collect a zirconium-hafnium cut following the titanium separation methods [10]. In the second step, Ln-Spec resin is used to further separate Zr and Hf. Elution tests were done using a multi-element standard solution containing Zr, Hf and 24 other elements (including all the HFSEs and REEs). The Hf procedural blank was below detection limit and the yield was >80%. We also performed chemical separations on the solutions retrieved after U-

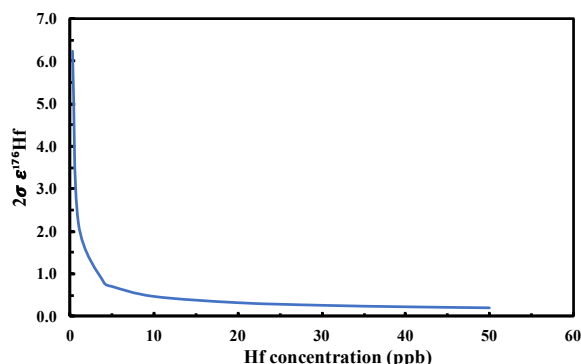
Pb chemistry of some zircon standards (AS3, 91500, and Mudtank).

The Hf isotope analyses were performed on a Neptune Plus multi-collector inductively coupled plasma mass spectrometer (ThermoFinnigan) connected to an Aridus II desolvating nebulizer. Matrix purification drastically decreases interferences and permits the use of high-transmission Jet sample and X-skimmer cones, which enhances the sensitivity of the instrument. The purified Hf fractions were dissolved in 0.3 M HNO<sub>3</sub> + 0.07 M HF. The achieved sensitivity was 1.5 V/10 ppb for <sup>177</sup>Hf (18.60%) at a sample uptake rate of ~150  $\mu$ L/min. For isotope ratio measurements of purified Hf fractions, the isotopes <sup>174</sup>Hf, <sup>176</sup>Hf, <sup>177</sup>Hf, <sup>178</sup>Hf, <sup>179</sup>Hf, and <sup>180</sup>Hf as well as <sup>172</sup>Yb, <sup>175</sup>Lu, and <sup>184</sup>W were monitored with static mode on nine Faraday cups. We found that the interferences of Yb, Lu, and W on Hf isotopes are negligible due to efficient separation of Hf in the ion exchange chemistry. Each measurement took 30 cycles with each cycle taking 8.389 seconds. Individual sample measurements were bracketed by the analysis of JMC-Hf 475 standard solutions whose concentrations are adjusted to match those of the samples that they bracket. The mass bias factor was calculated by normalizing the measured <sup>179</sup>Hf/<sup>177</sup>Hf to 0.7325 [11] with an exponential law. The Hf isotopic ratios of all samples corrected for mass bias were determined relative to the bracketing standard runs and are expressed as  $\epsilon^{174,176,178,180}\text{Hf}$ , which are the deviations of the <sup>174,176,178,180</sup>Hf/<sup>177</sup>Hf ratios from the standard solution (JMC-Hf 475) in parts per ten thousand. These  $\epsilon$ Hf ratios were further normalized to reference values of <sup>180</sup>Hf/<sup>177</sup>Hf = 1.886666, <sup>178</sup>Hf/<sup>177</sup>Hf = 1.467168, and <sup>176</sup>Hf/<sup>177</sup>Hf = 0.282160 for Johnson Matthey Company (JMC)-Hf 475 [6] to allow comparison with literature values. The external reproducibilities were evaluated by repeat analyses of the standard bracketing by itself.

The Hf isotopic compositions of lunar zircons are corrected for radiogenic <sup>176</sup>Hf ingrowth by combining TIMS high-precision U-Pb crystallization ages and Lu/Hf ratios in those samples. Each data is also corrected for neutron capture effects [2,12,13].

In Figure 1, we show the theoretically achievable precisions on Hf isotopes when measuring Hf isotopic composition bracketing with 1 ml JMC-Hf 475 standard

solution at given concentrations on a Neptune MC-ICPMS. This is done by calculating the isotope ratio uncertainties from counting statistics and Johnson noise [14]. More test results and lunar zircon data will be shown by the time of the conference.



**Figure 1:** Theoretical limit on the precision achievable on  $\epsilon^{176}\text{Hf}$  values as a function of the Hf concentration

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