

**AN IMPROVED METHOD FOR DETERMINING THE Hf ISOTOPIC COMPOSITION OF LUNAR BASALTS;** Erik E. Scherer<sup>1</sup>, Brian L. Beard<sup>2</sup>, Karin M. Barovich<sup>3</sup>, Clark M. Johnson<sup>3</sup>, Lawrence A. Taylor<sup>2</sup>;  
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**Introduction** Recently it has been suggested that the source region of high-Ti mare basalts contained residual garnet, if ilmenite was also a residual phase [1]. This may imply that the source region of high-Ti mare basalts was significantly deeper than previously thought. This conclusion is based on modelling of Lu-Hf isotopic and concentration data of lunar basalts reported by Unruh et al. [2], in the most recent Hf isotopic investigation of lunar rocks. Such interpretations highlight the exceptional ability of the Lu-Hf system to reveal the mineral assemblages involved in igneous processes like crystallization and partial melting, which produce strong mineral-dependent Lu-Hf fractionations. However, only 16 lunar samples have been analyzed for Hf isotopic composition to date, partly as a result of the formidable analytical challenges faced in separating Hf from other elements (e.g., Ti and Zr), and the poor ionization efficiency of Hf. Thus there are still large gaps in the Hf isotopic data set for lunar basalts. For example, the 7 high-Ti basalts that have been analyzed define an apparent horizontal trend on a plot of  $\epsilon_{\text{Hf}}$  versus  $\epsilon_{\text{Nd}}$  (Fig. 1). We observe that this trend is defined by high-Ti Apollo 11 samples that have low initial  $\epsilon_{\text{Nd}}$  values, and high-Ti Apollo 17 samples that have high  $\epsilon_{\text{Nd}}$  values. It is important to note, however, that Apollo 17 high-Ti basalts that have low  $\epsilon_{\text{Nd}}$  values (e.g., samples 77516 [ $\epsilon_{\text{Nd}} = +4.0$ ] and 78586 [ $\epsilon_{\text{Nd}} = +2.7$ ] [3]) and Apollo 11 samples that have high  $\epsilon_{\text{Nd}}$  values (e.g., samples 10044 [ $\epsilon_{\text{Nd}} = +7.1$ ] and 10047 [ $\epsilon_{\text{Nd}} = +7.4$ ] [4]) have not been analyzed to determine if this apparent horizontal trend between initial  $\epsilon_{\text{Hf}}$  and  $\epsilon_{\text{Nd}}$  is characteristic of individual landing sites. In preparation for new Hf isotope studies of these rocks, we have developed a new analytical technique that has been tailored to determining the Hf isotopic composition and Lu and Hf abundances of high-Ti basaltic rocks (up to 13 wt%  $\text{TiO}_2$ ).

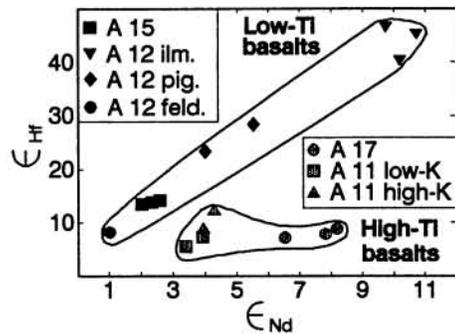


Figure 1

The Lu-Hf isotope investigation of lunar basalts conducted by Unruh et al. [2] used the analytical procedure of Patchett and Tatsumoto [5], which consists of a three stage process for separating Hf from other elements. They made analyses of Lu and Hf concentrations and Hf isotopic compositions from HF acid-digested rock solutions that were aliquotted into an isotopic composition (IC) fraction (~80%) and an isotope dilution (ID) fraction (~20%). For high-Ti basalts, this technique had to be modified to obtain a better separation of Hf from Ti by passing the sample through the final ion-exchange column two times. This separates Hf from Ti and Zr (although Ti does not have an isobaric interference with Hf, it considerably diminishes the ionization efficiency of Hf). Furthermore, determining the Lu/Hf ratio of high-Ti rocks using this method was susceptible to large uncertainties because any Ti-bearing precipitates present would fractionate Hf prior to aliquotting. In addition, if formation of alkaline-earth fluorides occurred prior to aliquotting, precipitation of insoluble Lu- and other REE fluorides would be likely. Aliquotting in HCl will produce no fractionation in Lu abundances, whereas this is an unfavorable acid for Hf equilibration. Conversely, aliquotting in HF will produce no fractionation of Hf abundances, but will form insoluble Lu- and other REE fluorides. With careful attention to these difficulties, Unruh et al. produced initial  $\epsilon_{\text{Hf}}$  values that were reproducible to  $\pm 1.8$  epsilon units, only a slightly larger range than other estimates of the  $\epsilon_{\text{Hf}}$  reproducibility for basaltic rocks [e.g., 6]. However, the aliquotting approach requires larger sample sizes than the total spike method, and ionization inhibition remains a problem with the chemical separation methods of Patchett and Tatsumoto. We stress that obtaining highly precise Lu and Hf abundances is critical for work on lunar rocks because of the large in situ correction required for  $^{176}\text{Lu}$  decay.

The Lu-Hf analytical method we are developing for our studies of high-Ti basaltic rocks is similar to that reported by Barovich et al. [7], and is ideally suited for avoiding the three biggest problems encountered by Unruh et al [2]: 1) inefficient separation of Hf from Ti, 2) large uncertainties in Lu/Hf ratios due to precipitation of cations prior to aliquotting, and 3) large sample sizes required by the aliquot method. The ion-exchange separation of Hf is accomplished using three columns. The 1st column separates Hf, Ti, and Zr from the major cations using anion exchange resin and 4M HF, followed by removal of Hf, Ti, and Zr with 29M HF (identical to the 1st stage column of [7]). The second column separates Ti from Hf and Zr using 0.20M  $\text{H}_2\text{SO}_4$ -1% $\text{H}_2\text{O}_2$  and anion exchange resin in a column that is 25 by 0.5 cm, followed by removal of Hf, some Zr, and any remaining Ti with 29M HF. This column is similar to the second stage column of [7], but the increase in the length of the column and the decrease in sulfuric acid molarity produces a better removal of Ti without Hf breakthrough. The third column is identical to that used by

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[7], and uses anion exchange resin and 0.65M H<sub>2</sub>SO<sub>4</sub> to elute any remaining Ti, then Hf, and finally Zr. Using this method to process a sample similar in Ti, Zr, and Hf contents to 1 gram of a high-Ti mare basalt produces a 90% Hf yield with insignificant contents of Ti or Zr. This is similar to the yield achieved by Patchett and Tatsumoto [5]), but the relative ion intensities of Ti to Hf and Zr to Hf, measured with a mass spectrometer, are smaller.

Our approach for avoiding problems of imprecise Lu/Hf ratios caused by precipitates is to spike the sample with a mixed Lu/Hf spike prior to complete dissolution. Our procedure is similar to that described by Patchett and Tatsumoto [5] which involves an initial evaporation of 29M HF to volatilize much of the Si from the sample, followed by a prolonged (~4 days) high temperature (190 °C) dissolution of the sample using concentrated HF and HNO<sub>3</sub> in high-temperature bombs. This acid is then evaporated and the sample is incrementally dissolved in 6M HCl - 0.1 M HF in the high-temperature bombs by periodically decanting the liquid and attacking remaining precipitates with fresh acid until a clear solution is obtained. Previous studies have avoided fully spiking a sample prior to dissolution because of the poor precision of sample <sup>176</sup>Hf/<sup>177</sup>Hf ratios obtained when subtracting the spike contribution from the measured isotope ratios. This limitation is largely a function of the vast difference between the <sup>176</sup>Hf/<sup>177</sup>Hf of the spike (e.g., 0.145) and that of naturally-occurring Hf (e.g., 0.2829). We have avoided this large subtraction by manufacturing a <sup>178</sup>Hf spike that has a <sup>176</sup>Hf/<sup>177</sup>Hf close to present day chondritic compositions. This tracer was made by adding a small amount of a <sup>176</sup>Hf tracer to a <sup>178</sup>Hf tracer, producing a Hf spike with a <sup>176</sup>Hf/<sup>177</sup>Hf of 0.2831±2 and a <sup>178</sup>Hf/<sup>177</sup>Hf of 61.17±9. Comparison of spike-subtracted <sup>176</sup>Hf/<sup>177</sup>Hf of spiked normal Hf solutions to the measured <sup>176</sup>Hf/<sup>177</sup>Hf of the unspiked normal indicates that there is no bias between these two sets of measurements (Figure 2), and the minor correction is very robust.

The Lu-Hf isotope system can be a powerful tool for determining the mineralogy, and hence the depths, involved in ancient igneous processes in planetary bodies. However, the potential of the Hf isotope system has not been widely utilized because of the analytical challenges in conducting Hf isotopic investigations. The procedure that we have outlined above avoids many of these problems and is ideally suited for determining the Hf isotopic composition and Lu and Hf concentrations of mare basalts. Hafnium isotopic analysis of carefully selected high-Ti mare basalts will allow us to determine whether or not high-Ti mare basalts from a single landing site have the same initial Hf isotopic composition regardless of initial ε<sub>Nd</sub> value. If such a relationship exists, it is in direct contrast to the ε<sub>Nd</sub> - ε<sub>Hf</sub> correlation of low-Ti basalts (Fig. 1), and implies that there are important differences between the source mineralogy of low-Ti and high-Ti mare basalts [e.g., 8].

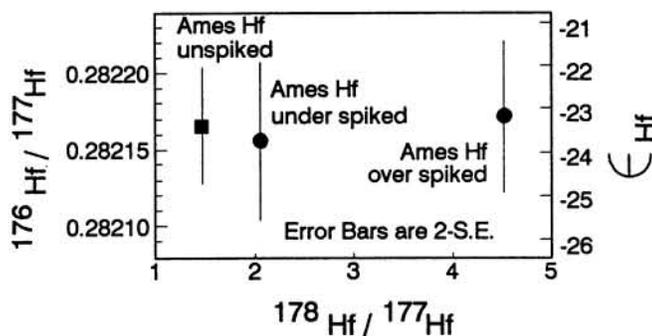


Figure 2

Plot of <sup>176</sup>Hf/<sup>177</sup>Hf versus <sup>178</sup>Hf/<sup>177</sup>Hf. The square indicates the average of 7 determinations of a normal Hf solution with no spike added. The circles show the average spike subtracted <sup>176</sup>Hf/<sup>177</sup>Hf ratios of two spiked normal solutions with differing amounts of <sup>178</sup>Hf spike added to each solution. These points are the average of 5 determinations on each solution and the error bars show the external 2 standard errors of the mean. These errors are similar to other estimates for the precision of Hf isotopic analysis. Errors for the <sup>178</sup>Hf/<sup>177</sup>Hf ratios are smaller than the size of the symbol and are typically 0.005%.

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