LA-MC-ICPMS LU-HF ISOTOPES IN LUNAR ZIRCONS: RELIABILITY OF PEAK STRIPPING PROTOCOL Dianne J. Taylor[1], Kevin D. McKeegan[1], Edward D. Young[1] and T. Mark Harrison[1,2], [1]Dept. of Earth and Space Sciences & IGPP, UCLA, Los Angeles, CA, 90095, dtaylor@ess.ucla.edu. [2]Research School of Earth Sciences, Australian National University, Canberra, A.C.T. 0200 AUSTRALIA

Introduction: The timescale for the cooling and crystallization of the lunar magma ocean has not been firmly established, yet it is essential for understanding the thermal history and the nature of silicate differentiation of the Moon (and other planetary bodies) as a whole [1]. Towards this end, we have undertaken an *in situ* LA-MC-ICPMS ^{176}Lu-^{176}Hf study of individual lunar zircons of well-determined crystallization (U-Pb) ages returned from the KREEP-rich portion of the Moon by the Apollo 14 mission. Zircons are ideal for this type of study because they concentrate Hf (up to 6 wt%) while excluding Lu (typical ^{176}Lu/^{177}Hf for lunar zircons = 0.001). Small deviations in the measured initial ^{176}Hf/^{177}Hf of the lunar zircons from the chondritic value allows us to calculate the differentiation age of KREEP. Since KREEP formed after the rest of the magma ocean had crystallized, an age at which KREEP became chemically isolated from the rest of the magma would establish an upper bound for the duration of LMO crystallization.

Unfortunately, laser ablation studies of zircons are complicated by the presence of isobaric interferences at mass 176 (zircons contain the rare earth elements Yb and Lu, resulting in ^{176}Yb$^+$ and ^{176}Lu$^+$ mass interferences with ^{176}Hf$^+$), necessitating a complex peak-stripping protocol. Our practice, as reported in [1] has been to use the protocol described by Harrison and co-workers [2] (and see below). Although this technique works well for Hadean zircons, Apollo 14 lunar zircons can contain up to 10 to 100 times the concentrations of heavy REEs compared to terrestrial zircons and therefore correspondingly larger corrections must be made. To establish the accuracy and reproducibility of the peak-stripping methods, we have carried out additional studies at UCLA using synthetic zircons (courtesy of Frank Mazdab, USGS, Stanford Ion Probe Laboratory) doped with either no Yb or ~800 ppm Yb (consistent with that found in lunar zircons).

Analytical Protocol: Laser ablation multi-collector ICPMS (LA-MC-ICPMS) was done at UCLA using a ThermoFinnigan Neptune plasma-source mass spectrometer coupled to a NuWave excimer laser (λ=193 nm). The laser was operated at a frequency of 3 Hz and fluence of 21-22 J/cm^2. Each measurement consisted of 50 cycles with 4 second integration time per cycle. Backgrounds were measured prior to each analysis (also 50 cycles) and cor-

rected using the Neptune software. Sixty to 80 μm diameter spots were ablated in polished, uncoated zircons. Ions of selected masses from 171 to 181 amu were collected simultaneously in 9 Faraday cups (10^{11} Ω resistors).

Peak stripping is accomplished by measuring non-interfered isotope pairs of Yb and Hf (^{173}Yb/^{171}Yb and ^{179}Hf/^{177}Hf) from which instrumental mass bias correction factors for Yb and Hf (β_{Yb} and β_{Hf}, respectively) are calculated by using an exponential mass fractionation law based on the accepted values for these ratios (^{173}Yb/^{171}Yb is normalized to 1.12345 [3] and ^{179}Hf/^{177}Hf is normalized to 0.7325 [4]). The fractionation factors (β's) thus calculated are applied to the other isotope ratios in the same run in which they are measured. The amount of ^{176}Yb$^+$ to be stripped from the measured ^{176}Hf$^+$ is calculated from the mass-fractionation corrected ^{173}Yb$^+$ intensity, normalized to ^{176}Yb/^{173}Yb as determined by [3]. Similarly, the amount of ^{176}Lu$^+$ to be stripped is calculated from the measured ^{175}Lu$^+$, normalized to ^{176}Lu/^{175}Lu determined by [5] and assuming that Lu follows the same mass fractionation law as Yb.

The accuracy of the mass bias fractionation factor determined from ^{179}Hf/^{177}Hf is checked by monitoring within-run ^{178}Hf/^{177}Hf, a second pair of stable, non-interfered isotopes of Hf.

Results: For the synthetic zircons containing 2 wt% HfO$_2$ and no Yb or Lu (and therefore not requiring any peak stripping) the reproducibility of the final ^{176}Hf/^{177}Hf ratio is within ±0.46ε (2 s.d.). Analyses of zircons containing ~800 ppm Yb, with a consequent 18-20% ^{176}Yb$^+$ correction at mass 176 (consistent with lunar zircons) show ^{176}Hf/^{177}Hf values, on average, 0.48ε units below the mean of the no-Yb zircons. This indicates that the Yb interference is slightly over-corrected for, but still accurate to within sub-epsilon levels. The stable, non-interfered ^{178}Hf/^{177}Hf for all synthetic zircons (with and without Yb) is found to be reproducible to within 0.14ε (2 s.d.) showing that the in-run mass bias fractionation factor for Hf is well-determined in both doped and undoped samples.

Also, the final ^{176}Hf/^{177}Hf result obtained for the well-characterized zircon standard, Mudtank, is compared to solution ICPMS results [6]. We found that the weighted mean of 13 analyses over two analysis

days deviated from the accepted value by -0.36 ± 0.28 (2 s.e.)ε.

Conclusions: In-situ measurement of Hf isotope compositions of zircon by LA-ICPMS can be made accurately to a level of ~0.5e even in samples which contain high (up to 10,000 times chondritic) levels of heavy rare earth elements. This accuracy level is commensurate with typical precisions achieved for 60 to 80 μm diameter analysis spots. Measurements of ε_{176Hf} in KREEP-rich lunar zircons reported previously [1] and containing up to ~800 ppm Yb appear to be precise and accurate at the sub-epsilon level.

References: [1] Taylor D.J. et al. (2007) *LPSC,* 163-164. [2] Harrison T.M. et al. (2005) *Science* **310,** 1947-1950. [3] Thirlwall M.F. and Anczkiewicz R. (2004) *International Journal of Mass Spectrometry,* **235,** 59-81. [4] Blichert-Toft J. and Albarede F (1997) *Contributions to Mineralogy and Petrology* **127,** 248-260. [5] Chu N.C. et al. (2002) *Journal of Analytical Atomic Spectrometry*, **17,** 1567-1574. [6] Woodhead, J.D. and Hergt J.M. (2005) *Geostandards and Geoanalytical Research* **29,** 183-195.
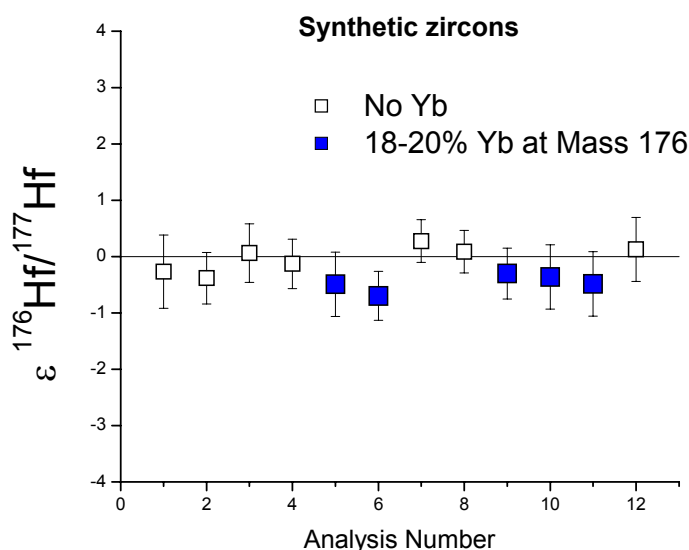

Fig. 2. Stable ^{178}Hf/^{177}Hf for all synthetic zircons. One standard deviation from the mean is 0.14 ε.

Fig. 1. ^{176}Hf/^{177}Hf for synthetic zircons containing 2 wt% HfO$_2$, with no Yb and ~800 ppm Yb. The mean of the zircons with Yb is 0.48ε below the Yb-free zircons.
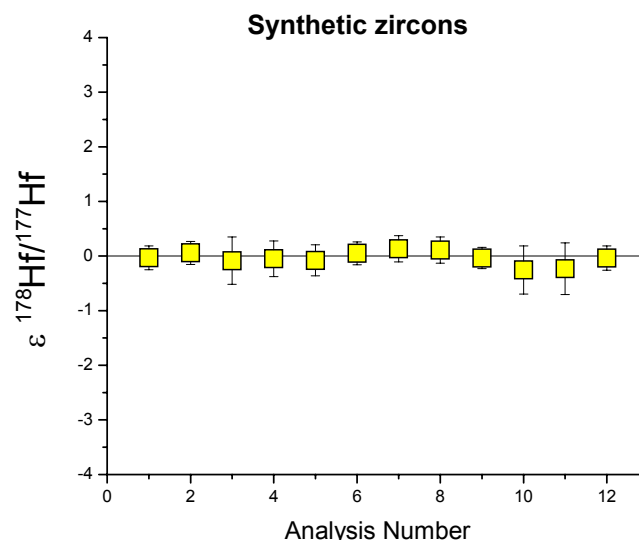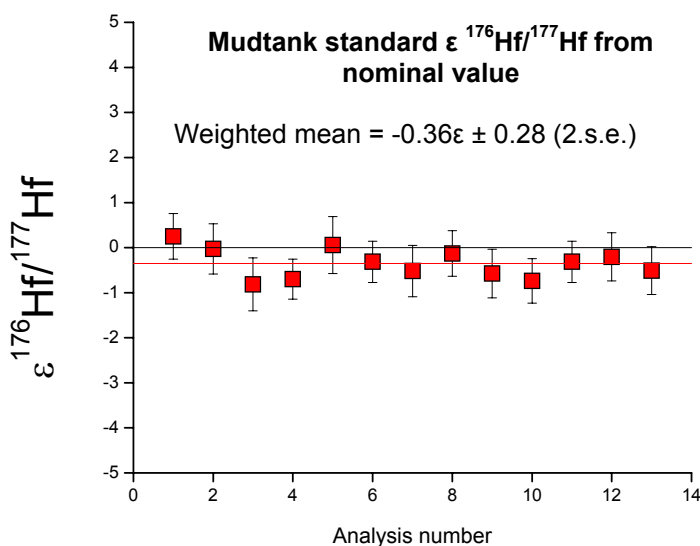

Fig. 3. The reliability of the dual peak-stripping procedure is monitored by analysis of Mudtank, a terrestrial zircon with well-characterized Hf isotopes