^{176}Lu-^{176}Hf Isochron Dating of Strongly Cosmic Ray Exposed Samples – A case study on Apollo 14 Impact Melt Rock 14310. T. Haber[1], E. E. Scherer[1], R. Bast[1,2] and P. Sprung[2], [1]Westfälische Wilhelms-Universität Münster, Institut für Mineralogie, Corrensstr. 24, D-48149 Münster, Germany (Contact: thomas.haber@wwu.de), [2]Institut für Geologie und Mineralogie, Universität zu Köln, Zülpicher Str. 49b, D-50674 Köln, Germany.

Introduction: The ^{176}Lu-^{176}Hf system promises to be a powerful tool for dating the crystallization of lunar impact melt rocks because it has a high closure temperature [e.g., 1]. Therefore, it should be less susceptible to loss of age information by later, impact-induced heating events than ^{40}Ar/^{39}Ar and, possibly ^{87}Rb-^{87}Sr, ^{147}Sm-^{143}Nd, and U-Pb. In addition, fractionation between Lu and Hf can be more extreme than that between Sm and Nd, potentially allowing improved precision on isochron dates and initial isotope compositions. The Lu-Hf method has already been successfully applied to date lunar igneous processes, such as the formation of mare basalts and Mg-suite rocks [2, 3], but it has yet to be applied to lunar impact melt rocks, despite its potential advantages over other dating methods.

There is, however, one major obstacle: Lunar samples that have been exposed to cosmic rays for tens or even hundreds of millions of years will be subject to neutron capture (NC) effects on the isotopes relevant for Lu-Hf and Sm-Nd dating [4]. This is especially critical for Lu-Hf because the main NC-induced shift occurs in ^{176}Hf/^{177}Hf and depends on the ^{176}Lu/^{177}Hf, which varies widely among minerals [5]. As a result, NC effects can change isochron slopes, affecting the accuracy of dates if they are not taken into account.

Fortunately, the thermal and epithermal neutron fluences can be estimated from the isotopic composition of an unspiked sample fraction. These fluences, in turn, can then be used to correct for the NC effects in spiked fractions. This approach was originally developed to correct the isotopic compositions of whole rocks [4, 5]. Here, we applied the method to mineral fractions to acquire the first *internal* Lu-Hf isochron for lunar impact melt rock 14310. In addition, measurements of the ^{87}Rb-^{87}Sr and ^{147}Sm-^{143}Nd isotopic systems on the same fractions are currently being performed. Concordant dates among these systems would likely reflect the true age of crystallisation, whereas dates that decrease with the closure temperatures of the respective isotopic systems might reveal a subsequent disturbance.

Sample Preparation and Methods: We were allocated a ~1 g aliquot (,115) of 14310 consisting of 4 clast-free pieces. Under the microscope, the sample appeared holocrystalline, with crystal sizes ranging mainly from 0.05 to 0.5 mm. Several 1-2 mm diameter vugs were visible.

The four pieces were crushed with an agate mortar and pestle and sieved under ethanol into 63-125 µm and <63 µm fractions. Metal grains were removed from both fractions using a hand magnet. The 63-125 µm fraction was then passed through a series of magnetic separations using a Frantz magnetic barrier separator, followed by density separations using methylene iodide-acetone mixtures.

Five of the resulting mineral fractions and a bulk fine fraction were processed and analyzed (Table 1). Additionally, an uspiked bulk fine fraction was analyzed to determine the natural isotopic composition of the sample.

Table 1: Mineral fractions obtained from 14310,115.

ID (mass)	Mineral Fraction	Description
CI-4 (32 mg)	fine	bulk fine fraction after removing highly magnetic minerals with a hand magnet (<63 µm)
CJ-1 (7 mg)	Pure plagioclase	clear, colourless plagioclase grains with a few ilmenite inclusions (63-125 µm)
CJ-2 (15 mg)	Impure plagioclase	some plagioclase colored yellow to orange; more ilmenite inclusions than CJ-1 (63-125 µm)
CJ-3 (8 mg)	Ilmenite-bearing plagioclase & pyroxene	Mix of mainly plagioclase and pyroxene containing large amounts of ilmenite inclusions and separate ilmenite grains (63-125 µm)
CJ-4 (30 mg)	Ilmenite-bearing pyroxene	Clear, brown pyroxene, containing moderate amounts of ilmenite inclusions (63-125 µm)
CJ-5 (25 mg)	Pyroxene	Like CJ-4, with fewer inclusions (63-125 µm)

Lutetium and Hf were separated following the two-stage elution scheme of [6] (cation followed by an Ln-Spec column) and measured on a Neptune Plus MC-ICP-MS. Rubidium, Sr, and LREE cuts were also collected for Rb-Sr and Sm-Nd chronology.

Ultimatley, the measured and reduced isotopic data will be corrected for neutron capture effects using the natural Hf and Sm isotopic compositions of the unspiked fraction using the model of [4,5]. As the LREE cut of the unspiked fraction has, at this stage, not been analyzed, we do not know the Sm isotope composition needed to calculate the exact epithermal and thermal fluences of our sample split. Therefore, we used the thermal (3.32×10^{16} n/cm^2) and epithermal (3.40×10^{16} n/cm^2) fluences obtained by [5] on a separate split of 14310 for a preliminary correction.

Results: The analyzed fractions contain 0.16 to 4.3 ppm Lu and 1.2 to 41 ppm Hf, with the highest and lowest concentrations in fractions CJ-3 and CJ-1 respectively. The uncorrected ^{176}Lu/^{177}Hf and ^{176}Hf/^{177}Hf data are shown in Figure 1. Five of the six analyzed fractions yield a 4033 ± 59 Ma (MSWD = 0.48) isochron. The "impure" plagioclase fraction (CJ-2, Table 1) lies above the isochron. The ^{180}Hf/^{177}Hf of the unspiked fine fraction is 277 ppm below that of the terrestrial Hf standard (see [5, 6]), indicative of significant neutron capture. Correcting for these NC effects changes the obtained date to 3995 ± 59 Ma and the initial ^{176}Hf/^{177}Hf from 0.280185(22) to 0.280064(22). Even after NC-correction, the impure plagioclase still lies above the isochron.

Discussion: The difference in date and initial ^{176}Hf/^{177}Hf obtained for uncorrected vs. NC-corrected data highlights the importance of this correction for samples that were subjected to significant neutron fluxes during lengthy exposure on the lunar surface. The exposure ages of 14310 range from 210 to 347 Myr, [7]). For this sample, the corrected Lu-Hf date is older than all ^{40}Ar/^{39}Ar dates (Figure 2), even when taking into account that the currently used decay constant for ^{40}K likely yields ages that are about 1% too young [8]. However, all spectra of the ^{40}Ar/^{39}Ar dates indicate significant loss of ^{40}Ar and should therefore only be considered as minimum ages [e.g., 8]. Two of the five Rb-Sr dates are also younger than our newly obtained date, whereas the other three are within error of it. The range of Rb-Sr dates indicates that this isotopic system might, at least partly, have been affected by at least one post-crystallisation disturbance. This would be consistent with the ^{40}Ar loss that is prevalant in published ^{40}Ar/^{39}Ar age data (Figure 2). The most likely event to introduce such a disturbance would be shock-induced heating of the sample during the cratering event that emplaced the sample on the lunar surface. In this case, the Lu-Hf system will be the most likely to preserve the actual crystallization age of the sample owing to its resistance to disturbance [1, 9]. Note, however, that the Lu-Hf date reported here may be revised once the NC correction has been further refined by using the natural Hf and Sm isotopic compositions of the ,115 aliquot rather than those of the aliquot measured by Sprung et al [4]. The change will likely be small, as the μ^{180}Hf of -277 obtained here is similar to the -292 value from [4], indicating that both splits were exposed to similar fluxes of epithermal neutrons, which dominate the NC effects on the Hf isotopes.

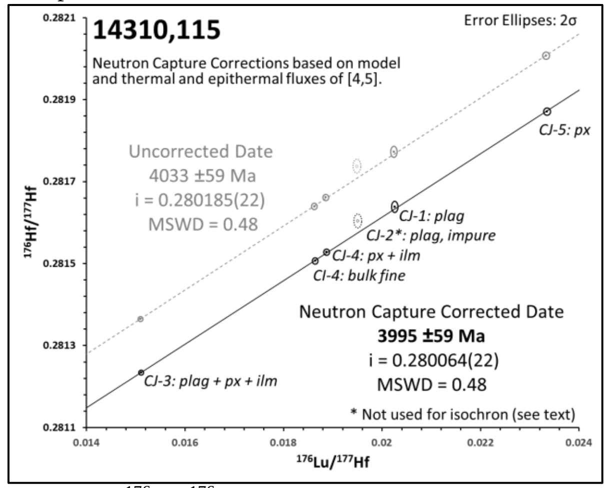

Figure 1: ^{176}Lu-^{176}Hf isochron using 4 mineral separates and one whole rock aliquot of 14310,115.

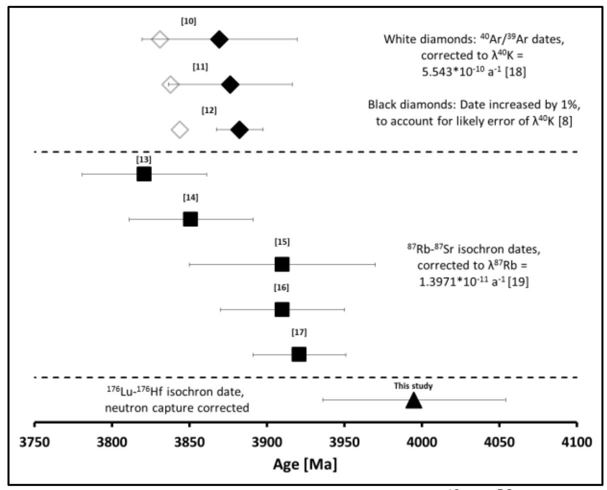

Figure 2: Comparision of literature ^{40}Ar/^{39}Ar and ^{87}Rb-^{87}Sr dates and our new ^{176}Lu-^{176}Hf date.

References: [1] Scherer E. E. et al. (2000) *GCA 64*, 3413-3432. [2] Sokol A.K. et al. (2008) *GCA 72*, 4845-4873. [3] Carlson R.W. et al. (2014) *Phil. Trans. R. Soc. A: 372*, 1-21. [4] Sprung et al. (2013) *EPSL 380*, 77-87. [5] Sprung et al. (2010) *EPSL 295*, 1-11. [6] Bast et al. (2015) *JAAS 30*, 2323-2333. [7] Meyer (2009) *LSC* #14310. [8] Jourdan (2012) *AJES, 59*, 199-224. [9] Bloch E. et al. (2014) *EPSL 395*, 173-183. [10] York D. et al. (1972) *LPS III*, 1613-1622. [11] Turner G. et al. (1971) *EPSL 12*, 19-35. [12] Stettler A. et al. (1973), *LPS IV*, 1865-1888. [13] Tatsumoto M. et al. (1972), *LPS III*, 1531-1555. [14] Papanastassiou D. A. and Wasserburg G. J. (1971) *EPSL 12*, 36-48. [15] Compston W. et al. (1972), *LPS III*, 1487-1501. [16] Murthy V. R. et al. (1972), *LPS III*, 1503-1514. [17] Mark R. K. et al. (1974), *GCA 38*, 1643-1648. [18] Steiger R. H. and Jäger E. (1977), *EPSL 36*, 359-362. [19] Rotenberg E. et al. (2012), *GCA 85*, 41-57.