Lu-Hf EVOLUTION OF THE MOON – IMPORTANCE OF NEUTRON CAPTURE EFFECTS.

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Introduction: The long-lived ^{176}Lu-^{176}Hf system is a powerful tool for unraveling the silicate differentiation history of planetary objects [1]. Previous Lu-Hf studies of lunar basalts [2-5] yielded results broadly consistent with a magma ocean history of the Moon as supported by Sm-Nd systematics [e.g., 6]. In detail, however, inconsistencies exist. For instance, mare basalts are characterized by radiogenic ^{176}Hf/^{177}Hf ratios, indicating derivation from mantle sources that were depleted in incompatible elements early in lunar history [2-5]. Consequently, it is expected that a complementary reservoir exists that is characterized by a long-term enrichment in incompatible elements and, hence, unradiogenic ^{176}Hf/^{177}Hf ratios relative to chondrites. This reservoir should be represented by KREEP, as is evident e.g., from its unradiogenic initial Nd isotopic composition. Surprisingly, however, KREEP-rich bulk rocks exhibit Hf isotope compositions at ~3.9 Ga that are too radiogenic, overlapping with those of chondrites at that time. The Lu-Hf and Sm-Nd systematics of KREEP are therefore inconsistent with each other and with a pure magma ocean origin for the KREEP source. Furthermore, 4.0-4.3 Ga zircon grains from KREEP-rich breccias have unradiogenic initial Hf isotope compositions, as expected for the origin of KREEP in a lunar magma ocean [7], but inconsistent with the values from KREEP-rich bulk rocks. While the origin of these inconsistencies are unclear, it has been proposed that the Lu-Hf systematics of KREEP may reflect non-chondritic Lu/Hf and Sm/Nd in the bulk Moon and perhaps also in the Earth [8]. Understanding the Lu-Hf evolution of the Moon, therefore, is important for constraining the early differentiation history of both the Moon and the Earth.

Recently, it was shown that the interaction with (epi)thermal neutrons produced during cosmic-ray exposure can significantly affect the Hf isotopic composition of extraterrestrial material including lunar samples and can result in measured ^{176}Hf/^{177}Hf ratios that are too high [9]. None of the previous Lu-Hf studies of lunar samples, however, has accounted for these neutron capture (NC) effects. Unrecognized NC effects in KREEP-rich whole-rocks thus possibly explain the aforementioned inconsistencies. To evaluate the relevance of NC for the Lu-Hf systematics of lunar samples we report new Lu-Hf data for 13 lunar samples, including two KREEP-rich whole rocks having relatively low exposure ages of <<100 Myr, [10].

Samples, analytical methods: Six low-Ti (12002, 12004, 15058, 15495, 15499, 15556) and 5 high-Ti mare basalts (10057, 70017, 70035, 74255, 74275), plus 2 KREEP-rich samples (68115, 68815) were analyzed for their Lu-Hf and non-radiogenic Hf isotope systematics. Complementing Sm isotope, ^{147}Sm/^{144}Nd, and ^{143}Nd/^{144}Nd analyses are underway.

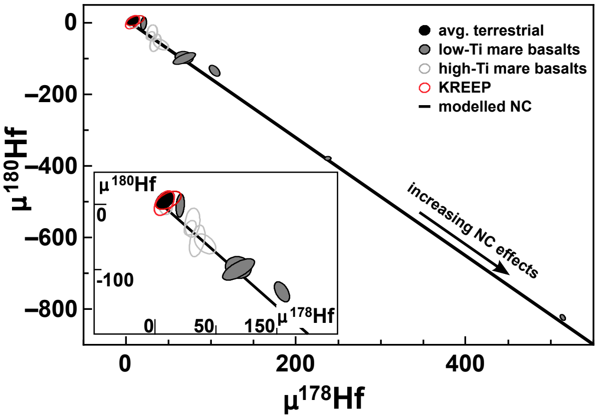

Fig. 1: μ^{180}Hf vs. μ^{178}Hf for all analyzed samples. NC trajectory modelled as detailed in [9].

Sample digestions and ion exchange chromatographic techniques followed [9]. Lu isotope compositions were analyzed at better than 0.3% (2 SD) precision on a NuPlasma MC-ICPMS at ETH Zürch using Yb for external mass bias correction. Isobaric interference from Yb was corrected by monitoring ^{172}Yb. Hf isotope measurements were performed on a Thermo-Scientific Neptune *Plus*® MC-ICPMS. Isobaric interferences from Yb, Lu, Ta, and W were monitored but were generally insignificant. The estimated [see 9] external reproducibility of ^{176}Hf/^{177}Hf was better than 25 ppm for all samples. For ^{180}Hf/^{177}Hf and ^{178}Hf/^{177}Hf, external 95% confidence limits of better than 20 and 10 ppm were achieved by replicate analyses ($N \geq 5$). Initial ^{176}Hf/^{177}Hf are reported as ε-unit deviations ('εHf_i') from the chondritic composition [11] at the sample's age. All ^{180}Hf/^{177}Hf and ^{178}Hf/^{177}Hf are given as ppm deviations (μ-values) from terrestrial Hf (Ames Hf standard).

Results: Nine lunar samples display clearly resolved ^{178}Hf and ^{180}Hf anomalies, fully consistent with calculated NC effects [9] (Fig. 1). Among the mare basalts investigated for this study, low-Ti mare basalts show the strongest effects with μ^{180}Hf up to -818±7 (sample 15556). The high-Ti mare basalts investigated so far generally display lower effects. The composition of both KREEP-rich whole-rock samples is indistinguishable from that of the terrestrial rocks analyzed with the lunar samples, indicating that NC effects are absent in these KREEP-rich samples and thus no correction was required for their ^{176}Hf/^{177}Hf (εHf$_i$ = -5.3). In contrast, NC effects in the mare basalts require corrections of up to ~12 ε-units. After NC correction, the εHf$_i$ values of the mare basalts range from +4.2 (15499) to +23.4 (12002). Our new data provide the lowest εHf$_i$ ever obtained for low-Ti mare basalts and KREEP-rich whole rock samples (Figs. 2,3).

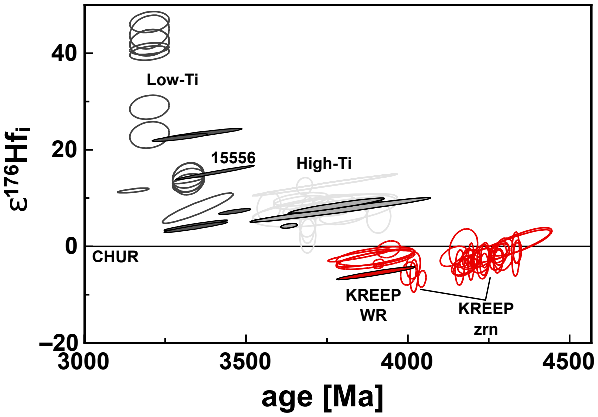

Fig. 2: εHf$_i$ of lunar samples. Open symbols: literature data [2-5,12]; filled: new data, corrected for NC effects on the basis of measured μ^{180}Hf. Color code as in Fig. 1; CHUR: chondritic evolution [11].

Discussion: The combined shift in μ^{178}Hf and μ^{180}Hf in 9 out of 13 lunar samples clearly demonstrates that NC effects on Hf isotopes are present in many lunar samples. Interpreting Lu-Hf data to infer the timescales and processes of lunar differentiation reliably thus requires quantifying NC effects on measured ^{176}Hf/^{177}Hf. With a correction on εHf$_i$ of ~12 ε-units, low-Ti mare basalt 15556 is ideal for assessing the relevance of NC effects in lunar samples. Its corrected εHf$_i$ overlaps that of relatively shortly exposed low-Ti mare basalt 15555 [2,13], whose initial Nd isotope composition is virtually identical to that of 15556 [14]. This agreement demonstrates the accuracy of our corrections, and underscores their importance. Note that even for an exposure age of only ~110 Myr, a correction of up to ~1.4 ε-units was necessary for one the low-Ti mare basalts. It thus seems likely that most previously obtained Lu-Hf data for lunar samples are compromised by NC effects.

The relatively shortly exposed KREEP-rich samples investigated here lack resolvable NC effects in Hf. Their εHf$_i$ are lower than those obtained in previously studied KREEP-rich samples, which had relatively long exposure times. It thus seems likely that NC effects on Hf isotopes are present in the latter, explaining why their reported εHf$_i$ appear too radiogenic. However, the εHf$_i$ of the KREEP-rich samples examined here still exceed the expected value based on Lu-Hf data for 4.0-4.3 Ga zircons from KREEP-rich breccias [7] (Fig. 3). Given that our KREEP-rich samples only have ~25% of the Hf contents expected for KREEP [3], their pristine KREEP compositions may have been diluted. This hypothesis will be tested with additional KREEP-rich samples.

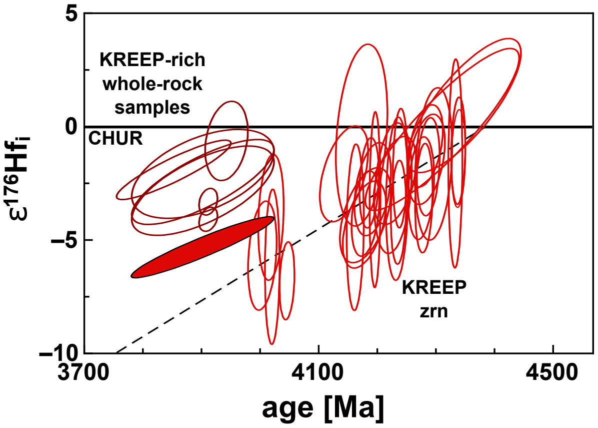

Fig. 3: εHf$_i$ of KREEP samples. Open symbols: literature data; of these in dark red: data for KREEP-rich whole rock samples; filled: new data virtually unaffected by NC reactions; dashed line: York-fit through all zircon data of [7] estimating the compositional evolution of KREEP.

Conclusions: Our new data clearly identify NC effects in 9 out of 13 lunar samples and show that necessary corrections on εHf$_i$ can be made accurately. NC effects on Hf can account for the as yet unexplained radiogenic initial Hf isotope compositions of KREEP-rich whole rocks. The presence of NC effects on Hf isotopes in many lunar samples thus requires a reinvestigation of the lunar Lu-Hf evolution.

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