HAFNIUM-NEODYMIUM ISOTOPIC EVIDENCE FOR A CHONDRITIC COMPOSITION OF THE MOON.

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Introduction: The paradigm that bulk planetary bodies have chondritic ratios of refractory lithophile elements forms the basis of using decay systems such as ^{176}Lu-^{176}Hf and ^{146,147}Sm-^{142,143}Nd to unravel the time scales and processes of early planetary differentiation and mantle-crust evolution [1,2]. On the basis of ^{142}Nd deficits in chondrites relative to the accessible silicate Earth [3] this paradigm has been challenged, however, and superchondritic Sm/Nd and Lu/Hf were proposed for Earth, Moon, and Mars [4,5].

The combined ^{176}Lu-^{176}Hf and ^{147}Sm-^{143}Nd isotope systematics of lunar samples provide a powerful tool for testing the hypothesis of superchondritic Lu/Hf and Sm/Nd of the bulk Moon [5]. The Hf-Nd isotope record of mare basalts [6-8] is broadly consistent with Lu/Hf and Sm/Nd fractionation during crystallization of the lunar magma ocean (LMO) [9], but the initial ^{176}Hf/^{177}Hf of KREEP (*i.e.*, the residual liquid of the LMO) appears too radiogenic for a chondritic Lu/Hf of the Moon [6,10]. This, and the fact that the chondritic composition is not the focal point of the Hf-Nd isotope arrays of mare basalts were used to argue against a chondritic Lu/Hf of the Moon [5].

The interpretation of the lunar Lu-Hf record is complicated, however, by neutron capture (NC) reactions that can strongly modify ^{176}Hf/^{177}Hf [11]. Here we re-investigate the lunar Hf-Nd isotope record in light of NC dosimetry based on non-radiogenic Hf and Sm isotope compositions. We show that the lunar Hf-Nd isotope record requires chondritic Lu/Hf and Sm/Nd of the Moon once NC effects are considered.

Samples and analytical methods: We investigated the combined Lu-Hf and Sm-Nd systematics of 20 Apollo lunar samples including 6 KREEP-rich whole rocks, 8 low-Ti-, and 6 high-Ti mare basalts. Non-radiogenic Hf and Sm isotope compositions were analyzed on spike-free powder aliquots. Sample dissolution and ion exchange chromatography followed [11]. Isotope analyses were conducted on a NuPlasma MC-ICPMS at ETH Zürich (Lu, Sm, Nd), and the Neptune *Plus* MC-ICPMS at the University of Münster (Hf). External reproducibilities (2 SD) were better than 30 ppm for ^{143}Nd/^{144}Nd and ^{176}Hf/^{177}Hf. Replicate analyses yielded 95% confidence intervals (CI) better than 11 and 20 ppm for ^{178}Hf/^{177}Hf and ^{180}Hf/^{177}Hf (all $n \geq 5$) and better than 40 ppm for ^{149}Sm/^{154}Sm (for $n \geq 3$). All ^{176}Hf/^{177}Hf and ^{143}Nd/^{144}Nd are given as ε-unit deviations from the chondritic composition [2], whereas ^{180}Hf/^{177}Hf and ^{178}Hf/^{177}Hf values are reported as ppm deviations (μ-values) from terrestrial Hf. The measured ^{149}Sm/^{154}Sm values are given as ε-unit deviations from terrestrial Sm.

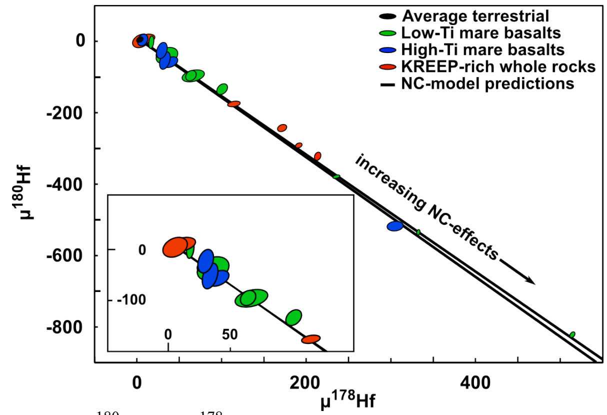

Fig. 1: μ^{180}Hf vs. μ^{178}Hf of all lunar samples. NC trajectories modeled after [11] for the entire range of neutron energy spectra observed in this study.

Results: Sixteen out of 20 samples show well resolved, coupled μ^{178}Hf and μ^{180}Hf variations up to +510 and -820 ppm that are typical for NC-induced effects (Fig. 1). Associated ε^{149}Sm values range down to -71.4 and correlate with μ^{178}Hf and μ^{180}Hf for chemically similar groups of samples, consistent with an NC origin of the Hf isotope shifts [11]. The new εHf_i and εNd_i agree well with previously reported values for similar types of lunar samples [6-8,10] except for two KREEP-rich samples (68115, 68815). These have the lowest εHf_i yet reported for KREEP-rich whole rocks (Fig. 2) and also exhibit terrestrial μ^{180}Hf and ε^{149}Sm.

Discussion: The presented data demonstrate that the lunar Lu-Hf record is strongly affected by NC reactions. Thus, its implications for the Lu/Hf and Sm/Nd of the bulk Moon need to be re-evalutated. The magnitude of NC effects is depth-dependent [e.g., 11] and we thus only discuss the new data for which comprehensive NC information exists for the same sample powders. Given the good agreement between the measured μ^{178}Hf -μ^{180}Hf pairs and the NC model (Fig. 1) and the fact that NC by ^{177}Hf and ^{178}Hf causes almost the entire NC-induced shift in *all* measured Hf isotope ratios [11], the NC model can be used to correct measured ^{176}Hf/^{177}Hf for NC effects. The investigated samples required downward corrections of up to 13.4 ε-units.

The corrected εHf_i of 3 out of 4 KREEP-rich whole rocks overlap the values of 68115 and 68815, which require no NC-correction (Fig. 2). Thus, after NC-correction, all KREEP-rich whole rocks have distinctly negative εHf_i, as expected in a chondritic LMO given the enriched composition and early formation of KREEP [e.g., 12-14]. The corrected εHf_i of KREEP-rich whole rocks are consistent with data for zircons from shortly-exposed KREEP-rich breccias [15] (Fig. 2). The chondritic model age for KREEP is 4400 ±25 using whole rock data (95% CI; 4440±50 Ma including Zrn data), which is in excellent agreement with other estimates for the crystallization age of KREEP [e.g., 12-14]. Hence, the Lu-Hf systematics of KREEP does not require a superchondritic Lu/Hf of the Moon.

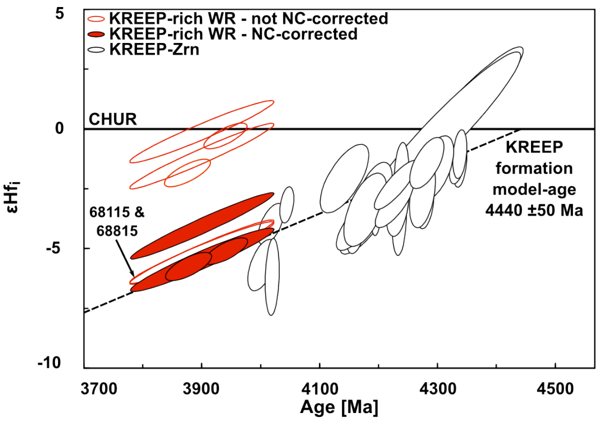

Fig. 2: εHf_i of KREEP-rich whole rocks (WR, this study) and KREEP zircons (Zrn) [15]. Dashed line: evolution of KREEP using $^{176}Lu/^{177}Hf = 0.01874$. Solid line: CHUR from [2].

The corrected Hf-Nd isotope systematics of low-Ti mare basalts is strongly correlated and indicates super-chondritic εHf_i values at chondritic εNd_i. To assess the origin of this Hf-Nd correlation and its significance for the lunar Lu/Hf and Sm/Nd, the Lu/Hf and Sm/Nd of LMO cumulates thought to be the mantle sources of mare basalts were modeled after [9]. For direct comparison, the corrected isotope data of samples are expressed as time-integrated parent-to-daughter ratios of their mantle sources (Fig. 3) assuming formation of these sources from a chondritic LMO at the time of LMO crystallization [12]. Assuming source-formation from a LMO having the superchondritic bulk composition 'SCHEM' [5] produces virtually identical sample-values. However, such a superchondritic LMO does not produce cumulate compositions (Fig. 3, brown trajectories) that are consistent with the least radiogenic low-Ti mare basalts. In contrast, cumulates of a chondritic LMO provide an excellent match to the observed Hf-Nd isotope systematics (Fig. 3). Thus, superchondritic εHf_i values at chondritic εNd_i, as observed for low-Ti mare basalts, would be expected of cumulates of a chondritic LMO but are no features expected of cumulates of a LMO having a SCHEM-like bulk composition.

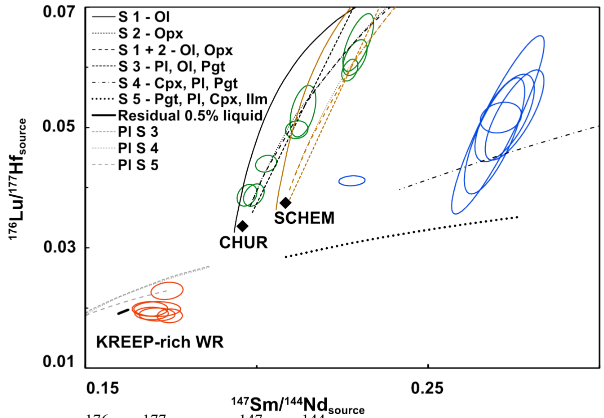

Fig. 3: $^{176}Lu/^{177}Hf$ vs. $^{147}Sm/^{144}Nd$ of lunar mantle sources compared to modeled cumulate compositions. Colors as in Fig. 1. Crystallization sequences S1 to S5 after [9]. Brown: S1 to S3 in a LMO having a SCHEM-like composition.

Conclusions: Our results indicate that the lunar Hf-Nd isotope record requires chondritic Lu/Hf and Sm/Nd of the bulk Moon. A previous study that concluded otherwise [5] did not consider the large NC effects on Hf isotopes in lunar samples. A chondritic Sm/Nd of the Moon is in apparent conflict with lunar ^{142}Nd data, which were taken as evidence for superchondritic Sm/Nd and $^{142}Nd/^{144}Nd$ of the bulk Moon [4,5]. However, the $^{142}Nd/^{144}Nd$ of the lunar mantle isochron [6,13,16] at a chondritic Sm/Nd is ~7 ppm below that of the modern terrestrial mantle and may be the best estimate for the bulk lunar $^{142}Nd/^{144}Nd$. This proposed lunar value may be slightly higher than values reported for enstatite chondrites [17] but overlaps these within uncertainties. The proposed lunar value and probably also that of enstatite chondrites slightly exceed the $^{142}Nd/^{144}Nd$ of ordinary chondrites, a difference that most likely is nucleosynthetic in origin [18].

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