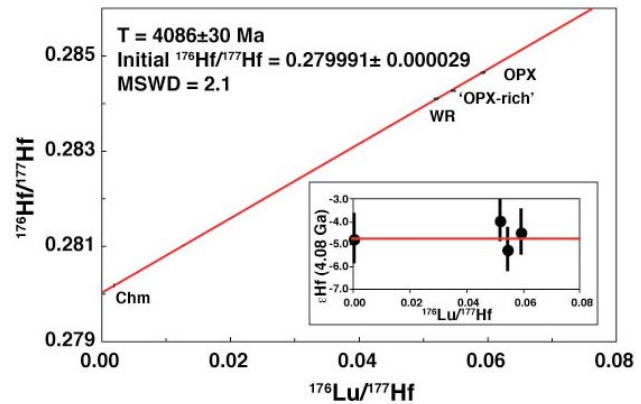


**LU-HF AGE AND ISOTOPE SYSTEMATICS OF ALH84001.** M. Righter<sup>1</sup>, T. J. Lapen<sup>1</sup>, A. D. Brandon<sup>2</sup>, B. L. Beard<sup>3,4</sup>, J.T. Shafer<sup>5</sup>, and A.H. Peslier<sup>2,6</sup> <sup>1</sup>Department of Earth and Atmospheric Sciences, University of Houston, Houston TX 77204-5007, USA (mrighter@uh.edu), <sup>2</sup>NASA-Johnson Space Center, Mail code KR, Houston TX 77058, USA, <sup>3</sup>Department of Geology and Geophysics, University of Wisconsin-Madison, Madison WI 53706, USA, <sup>4</sup>NASA Astrobiology Institute, <sup>5</sup>Lunar and Planetary Institute, Houston, TX 77058, <sup>6</sup>ESCG/JACOBS Engineering, Houston, TX 77058, USA

**Introduction:** Allan Hills (ALH) 84001 is an orthopyroxenite that is unique among the Martian meteorites in having the oldest inferred crystallization age (~4.5 to 4.0 Gyr) [e.g., 1-6 and references therein 7]. Its ancient origin makes this stone a critical constraint on early history of Mars, in particular the evolution of different planetary crust and mantle reservoirs. However, because there is significant variability in reported crystallization ages, determination of initial isotope compositions is imprecise making assessment of planetary reservoirs difficult. Here we report a new Lu-Hf mineral isochron age, initial  $^{176}\text{Hf}/^{177}\text{Hf}$  isotope composition, and inferred Martian mantle source compositions for ALH84001 that place constraints on long-lived source reservoirs for the ‘enriched’ shergottite suite of Martian meteorites including Shergotty, Zagami, NWA4468, NWA856, RBT04262, LAR06319, and Los Angeles. Sm-Nd isotope analyses are under way for the same mineral aliquots analyzed for Lu-Hf.

The Lu-Hf system was utilized because Lu and Hf are both lithophile and refractory and are not easily redistributed during short-lived thermal pulses associated with shock metamorphism. Moreover, chromite has relatively modest Hf concentrations with very low Lu/Hf ratios [9] yielding tight constraints on initial  $^{176}\text{Hf}/^{177}\text{Hf}$  isotope compositions [10].

**Analytical:** A carbonate-free ~2.5g aliquot from the interior of ALH 84001 consisting of roughly 98% opx and 2% chromite was gently crushed with a boron carbide mortar and pestle and sieved. Maskelynite, olivine, and phosphate phases were not observed during picking but were likely present in minor quantities. About 100 mg was taken as a ‘whole rock’ fraction from an aliquot of the <300 mesh material. Material in the size range of 200-300 mesh (~220mg) was separated by heavy liquids into orthopyroxene-rich and nearly pure chromite fractions. The pure orthopyroxene fraction was had picked under a binocular microscope. Prior to spiking and dissolution in high-pressure digestion vessels, the minerals were washed with ultrapure H<sub>2</sub>O to remove any surface contamination. All chemical separation procedures were carried out in clean lab facilities at the University of Houston and all Lu and Hf isotope analyses were carried out at the University of Wisconsin-Madison Radiogenic Isotope Laboratory using a GV Instruments *IsoProbe* MC-ICP-

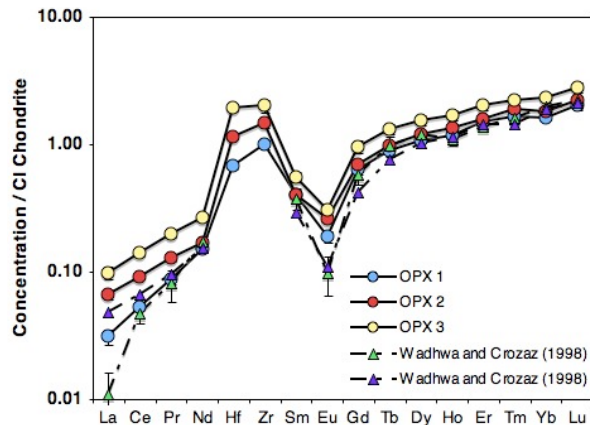


**Figure 1.** Lu-Hf isochron diagram of Martian meteorite ALH 84001. Inset is a plot of  $\epsilon^{176}\text{Hf}(\text{CHUR}; 4.08 \text{ Ga})$  versus  $^{176}\text{Lu}/^{177}\text{Hf}$ . Chm = chromite, OPX = pure orthopyroxene, ‘OPX-rich’ =  $\rho < 4.0$  fraction (mainly orthopyroxene), WR = whole rock. The isochron diagram was constructed with IsoPlot (v3.50) using a Model 1 age regression. All data are presented with  $2\sigma$  uncertainties.

MS. Total procedural blanks are <80 pg and <15 pg for Hf and Lu. Chemical analyses were carried out using a Cameca SX-100 electron microprobe at NASA-JSC for major elements and a CETAC LSX-213 laser ablation system coupled to a Varian 810-MS ICP-MS at University of Houston for trace element concentration measurement of orthopyroxene and chromite grains.

**Results:** Fig. 1 shows  $^{176}\text{Lu}/^{177}\text{Hf}$  and  $^{176}\text{Hf}/^{177}\text{Hf}$  data for four bulk and mineral samples of ALH 84001. The Lu-Hf data form a linear array yielding an age of  $4086 \pm 30 \text{ Ma}$  ( $2\sigma$ ;  $\text{MSWD} = 2.1$ ) for  $\lambda(^{176}\text{Lu}) = 1.867 \times 10^{-11} \text{ y}^{-1}$  and initial  $^{176}\text{Hf}/^{177}\text{Hf}$  isotope ratio of  $0.279991 \pm 0.000029$  ( $2\sigma$ ). Our Lu-Hf isochron age for ALH 84001 is consistent with  $^{39}\text{Ar}$ - $^{40}\text{Ar}$  ages of  $4.07 \pm 0.04 \text{ Ga}$  and  $4.10 \pm 0.20 \text{ Ga}$  [5, 6] but significantly younger than Sm-Nd and Rb-Sr ages of  $4.50 \pm 0.13 \text{ Ga}$  and  $4.55 \pm 0.30 \text{ Ga}$ , respectively [2]. The measured Lu-Hf age is similar to, but slightly older than Rb-Sr and U-Pb ages of secondary carbonate phases which yielded ages of  $3.90 \pm 0.04$  and  $4.04 \pm 0.10 \text{ Ga}$ , respectively [12].

Trace element concentrations of orthopyroxene have the characteristic LREE-depleted pattern (CI-normalized Yb/Nd ~10), with strong negative Eu anomalies ( $\text{Eu}/\text{Eu}^* \sim 0.2-0.4$ , where  $\text{Eu}^*$  is the value

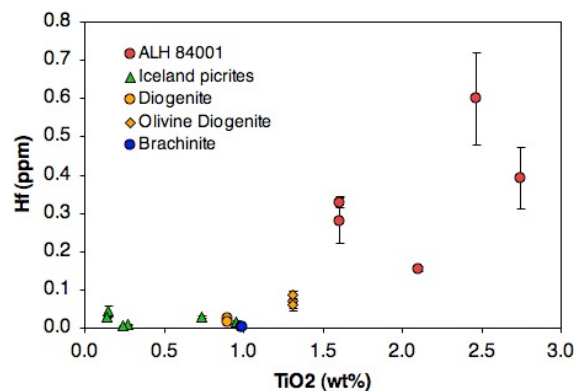


**Figure 2.** CI-normalized trace element abundances in three orthopyroxene grains of ALH 84001 measured by LA-ICPMS. For comparison, REE abundances in orthopyroxene from [11] are shown as triangles. Errors are  $1\sigma$ .

**Table 1.** Lutetium and Hf concentration of ALH 84001.

	LA-ICP-MS		Isotope Dilution	
	Lu (ppb)	Hf (ppb)	Lu (ppb)	Hf (ppb)
OPX	53	130	48.6	116.8
Chromite	<0.8 *	190	0.744	219.2

\* below detection limit.



**Figure 3.** Hf concentration versus  $\text{TiO}_2$  in ALH 84001 chromite grains with other meteoritic chromite data. Hf concentration in ALH 84001 chromites are much higher than other meteoritic chromites.

interpolated between CI-normalized values of Sm and Dy) (Fig. 2). These data are consistent with literature data [11] and also isotope dilution results from the hand picked pure orthopyroxene fraction (Table 1).

Chromite is euhedral to subhedral and occurs mainly within OPX. The Hf concentration of chromite determined by LA-ICPMS is much higher than various meteoritic and terrestrial chromite samples and shows a general positive correlation with Ti (Figure 3) which is consistent with our ID result of 0.22 ppm. The ALH 84001 chromite contains higher Ti contents than most other terrestrial and meteoritic chromites, and the Hf-

Ti correlation has been demonstrated experimentally in magmatic systems [9]. Lu concentrations were below the detection limits of our ICPMS, also consistent with the low Lu contents of 0.744 ppb measured by isotope dilution.

**Discussion:** Based on the trace element data of chromite and OPX, and the work of [11], we interpret the Lu and Hf contents of these phases to be of igneous origin. Therefore, we interpret the Lu-Hf isotope data to indicate that this rock crystallized from a magma at  $4086 \pm 30$  Ma and that this age does not reflect the age of metamorphism of a 4.5 Ga protolith.

An important outcome of this age is a robust measurement of the initial Hf isotope composition of  $\epsilon^{176}\text{Hf}_{(t, \text{CHUR})} = -4.76 \pm 1.04$  ( $2\sigma$ ) indicating that the source rocks of the magma that generated the orthopyroxene cumulate had a sub-chondritic  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio. Following [10,13], the modeled  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the source of ALH84001 is  $0.02358 \pm 0.00494$  which is within error of the average 0.027 source  $^{176}\text{Lu}/^{177}\text{Hf}$  ratio of the enriched shergottites.

Based on the new Lu-Hf age and isotope data, the source of the magma that ultimately imparted the Hf isotopic signature in ALH84001 is enriched relative to CHUR and the intermediate and depleted shergottites. The development of this enriched reservoir on Mars is likely similar to processes that produced lunar KREEP compositions which reflect late-stage, incompatible element rich residual liquids associated with late-stage crystallization of the Martian magma ocean. Although ALH84001 is depleted in incompatible trace elements due to its cumulate origin, its source magma, in terms of Lu/Hf ratio, was as enriched as that of the most enriched basaltic shergottites and a Lunar KREEP source. Indeed the  $^{176}\text{Lu}/^{177}\text{Hf}$  inferred for the enriched shergottite source (0.027) is the same as the source inferred from lunar rocks that are KREEP-rich (Brandon et al., unpublished).

**References:** [1] Jagoutz E. et al. (1994) *Meteoritics* 29, 478-479 (abstract). [2] Nyquist L. E. (1995) *LPS XXVI*, 1065-1066 (abstract). [3] Wadhwa M. and Lugmair G. W. (1996) *Meteoritics & Planet. Sci.*, 31, A145. [4] Turner G. et al. (1997) *GCA* 61, 3835-3850. [5] Ilg S. et al (1997) *Meteoritics & Planet. Sci.*, 32, A65. [6] Bogard D. D. and Garrison D. H. (1999) *Meteoritics & Planet. Sci.*, 34, 451-473. [7] Nyquist L. E. et al. (2001) *Space Sci. Rev.*, 96, 105-164. [8] Treiman A. H. *Meteoritics & Planet. Sci.*, 33, 753-764. [9] Righter M. et al. (2007) *Meteoritics & Planet. Sci.*, 43, A132. [10] Lapen T. J. et al. (2007) *LPS XXXIX*, Abstract #2073. [11] Wadhwa M. and Crozaz G. (1998) *Meteoritics & Planet. Sci.*, 33, 685-692. [12] Borg L. E. et al. (1999) *Science*, 286, 90-94. [13] Wadhwa M. and Borg L. E. (2006) *LPS XXXVII*, Abstract #2045. [14] Borg L. E. et al. (2003) *GCA*, 18, 3519-3536. [15] Debaille V. et al. (2007) *EOS Trans. AGU, Fall Meet. Suppl.*, Abstract V43F-02. [16] Debaille V. et al (2007) *Nature*, 450, 525-528.