A Rb-Sr and Sm-Nd isotope geochronology and trace element study of lunar meteorite LaPaz Icefield 02205

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Abstract

Rubidium-strontium and samarium-neodymium isotopes of lunar meteorite LaPaz Icefield (LAP) 02205 are consistent with derivation of the parent magma from a source region similar to that which produced the Apollo 12 low-Ti olivine basalts followed by mixing of the magma with small amounts (1 to 2 wt%) of trace element-enriched material similar to lunar KREEP-rich sample SaU 169. The crystallization age of LAP 02205 is most precisely dated by an internal Rb-Sr isochron of 2991 ±14 Ma, with an initial ^{87}Sr/^{88}Sr at the time of crystallization of 0.699836 ±0.000010. Leachable REE-rich phosphate phases of LAP 02205 do not plot on a Sm-Nd mineral isochron, indicating contamination or open system behavior of the phosphates. Excluding anomalous phases from the calculation of a Sm-Nd isochron yields a crystallization age of 2992 ±85 (initial ε^{143}Nd = +2.9 ±0.8) that is within error of the Rb-Sr age, and in agreement with other independent age determinations for LAP 02205 from Ar-Ar and U-Pb methods. The calculated ^{147}Sm/^{144}Nd source ratios for LAP 02205, various Apollo 12 and 15 basalts, and samples with strong affinities to KREEP (SaU 169, NWA 773, 15386) are uncorrelated with their crystallization ages. This finding does not support the involvement of a common KREEP component as a heat source for lunar melting events that occurred after crystallization of the lunar magma ocean.

1. Introduction

The return of lunar samples to Earth by six Apollo (Apollo 11, 12, 14, 15, 16, 17) and three Luna missions (Luna 16, 20, 24) produced a giant leap in our understanding of the age, compositional features and formation history of the Moon. Global spectroscopic coverage of the Moon obtained from orbit by the Clementine (1994) and Lunar Prospector (1998/99) missions allowed the sample data to be placed in the context of regional terranes (Jolliff et al., 2000). In particular, the global thorium concentration data collected by the Lunar Prospector spacecraft revealed a region on the Moon that is enriched in thorium and is now identified as the Procellarum KREEP Terrane (Haskin et al., 2000; Korotev, 2004; Lawrence et al., 1998, 1999, 2000, 2003). The KREEP reservoir (K - potassium, REE – rare earth elements, P – phosphorus, plus other incompatible elements like thorium) is commonly interpreted as a residual liquid resulting from the crystallization of a lunar magma ocean (LMO) that formed soon after accretion of the Moon (e.g., Warren and Wasson, 1979; Warren, 1985, 1988; Jolliff, 1998). One possible interpretation of the global thorium distribution thus suggests that this residual liquid concentrated in an area in the northwest quadrant of the lunar nearside [see discussions by Wieczorek et al. (2006) and Shearer et al. (2006)]. Later in lunar history, an impactor struck this area at ~3.9 Ga, forming the Imbrium basin and spreading thorium-rich ejecta over a vast portion of the Moon's surface (Haskin, 1998; Haskin et al., 2000; Jolliff et al., 2000; Wieczorek and Phillips, 2000). Hence, it appears that the Apollo samples (which were all collected from a geographically restricted area on the lunar near side) may present a biased view of the Moon by over-emphasizing the abundance of KREEP-rich lithologies (Giguere et al., 2000). This conclusion has been supported by studies of lunar meteorites (~40 different lunar meteorites are currently identified) that are typically Th-poor (Korotev, 2005; Korotev et al., 2003) and thus must originate from the broader and more representative portions of the Moon with low surface concentrations of thorium (Korotev, 2004).

LAP 02205 is a unbrecciated lunar low-Ti mare basalt found in the LaPaz Icefield in Antarctica during the 2002 Antarctic Search for Meteorites (ANSMET) field season. The LAP meteorite consists of six stones (LAP 02205, 02224, 02226, 02436, 03632 and 04841) with a combined mass of ~1.93 kg (Satterwhite and Righter, 2003, 2004a, 2004b, 2006). All the LAP stones are characterized by a positive slope in their light rare earth element abundance patterns as opposed to typical low-Ti mare basalts (cf. Fig. 6.4. of the Lunar Sourcebook (Taylor et al., 1991), and it has been speculated that this feature is inherited from a trace element enriched source region for the LAP basalts (Day et al., 2006; Anand et al., 2006). In order to obtain a precise crystallization age and to further examine if KREEP was involved in the genesis of the LAP basalts, new trace element and Rb-Sr and Sm-Nd isotope data for LAP 02205 are presented. Geochemical modeling indicates that the trace element-enriched signature observed for LAP 02205 (Anand et al., 2006; Day et al., 2006) likely represents mixing of a low-Ti magma similar to the Apollo 12 olivine basalts with small amounts of KREEP-rich material represented by lunar sample SaU 169. This in turn suggests that the LAP parent magma probably was generated in an area within or close to the Procellarum KREEP Terrane. The calculated source $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ for LAP 02205 are further used in conjunction with other well documented samples from the literature to investigate the involvement of progressively more trace element-enriched source materials to induce melting in a cooling Moon after the LMO had crystallized. (Borg et al., 2004; Hagerty et al., 2006; Wieczorek and Phillips, 2000).

2. Petrology and Geochemistry of LAP 02205

The LAP stones are all medium to coarse-grained, holocrystalline basalts with subophitic textures. In terms of its modal mineralogy, LAP 02205 mainly consists of pyroxene (57 vol%), plagioclase (33 vol%), minor ilmenite, silica, olivine, phosphates, and melt glass. There is no petrographic evidence for terrestrial weathering of LAP 02205 such as calcite, clay deposits or oxidized mineral rims (Anand et al., 2006; Day et al., 2006). This observation is substantiated by the absence of Ce anomalies in individual mineral phases (Anand et al., 2006), which may result from terrestrial weathering in the Antarctic environment (Crozaz et al., 2003). For detailed petrographic descriptions of the LAP stones see Anand et al. (2006), Day et al. (2006), Joy et al. (2006), Righter et al. (2005) and Zeigler et al. (2005).

Three petrographic features of LAP 02205 will be important for the following discussion. First, the occurrence of 0.3 to 0.7 percent by volume (vol%) of primary magmatic phosphate minerals in the groundmass of LAP 02205 (Anand et al., 2006; Day et al., 2006; Righter et al., 2005; Zeigler et al., 2005). These phosphates constitute the main host for the whole rock REE budget of LAP 02205. It has been shown that diffusion may decouple REE isotope and chemical signatures in apatite, with light REE isotope exchange proceeding much more rapidly than REE chemical diffusion that could alter total REE concentrations (Cherniak, 2000). Any post-magmatic disturbance of the LAP parent rock will thus be critical for the interpretation of the Sm-Nd isotope data for LAP 02205.

Second, ilmenite grains of LAP 02205 are characterized by the common occurrence of rounded K-Si-rich glass inclusions. The compositions of these inclusions are similar to the composition of K-Si-rich glass described in previous studies (Anand et al., 2006; Day et al., 2006; Righter et al., 2005; Zeigler et al., 2005). The K-Si-rich glass is restricted to the mesostasis areas in LAP 02205, often in symplectitic intergrowth with fayalitic olivine, and associated with phases that appear late in a basaltic crystallizing sequence such as Fe-pyroxenes, free silica, and troilite. Because ilmenite has generally low distribution coefficients for large-ion lithophile elements (like Rb and Sr) and the REE (McKay et al., 1986; Zack and Brumm, 1998), it will be argued (section 4.1) that the isotope analyses of ilmenite separates of LAP 02205 are dominated by the trace element budget of the contained K-Si-rich inclusions. Hence, for the interpretation of the isotope data in sections 5.2 and 5.4, the ilmenite separates are considered to represent the composition of the very last fractions of the crystallizing LAP parent magma.

Third, the LAP stones all contain pockets and veins of glassy shock melt that cross the primary igneous texture of the basalt. The formation of the shock melts is attributed to localized partial melting (Anand et al., 2006; Righter et al., 2005) during impact and ejection of the LAP meteorite at 55 ±5 ka (Nishiizumi et al., 2006), and therefore represents a zero-age event for the Rb-Sr and Sm-Nd isotope systems. To distinguish the melt vein glass from the K-Si-rich mesostasis glass and inclusions in ilmenite, they are referred to here as ‘melt veins’.

3. Sample preparation and analytical techniques

3.1. Sample preparation

For mineral separation procedures (Figure 1), a 944 mg subsample of LAP 02205.23 (4.647 g total) was gently crushed to <100 mesh in a boron carbide mortar and pestle. After sieving using a nylon sieve stack, the 100 to 200 and 200 to 325 mesh fractions were split repeatedly with a Franz magnetic separator according to their magnetic susceptibility. Clean fractions of plagioclase (plag, plag1, plag2), and fractions rich in clinopyroxene (cpx-Fe, cpx-Mg) and ilmenite (0.25M, 0.3NM, MM, cpx-ilm) were purified using methylene iodide (ρ=3.32 g/cm^3), which allowed isolation of the glassy melt-vein material. All fractions were further purified by hand-picking in ethanol under a binocular microscope.

3.2. Major and trace element analyses of mineral separates

Major element concentrations (Table 1) of individual grains picked from the mineral separates (cpx-Fe, cpx-Mg, plagioclase and ilmenite) of LAP 02205 were determined by wavelength-dispersive electron microprobe (EMP) using a focused beam with an acceleration voltage of 15 kV, 20 nA beam current, 20 sec peak count times, 2x10 sec count times for a two-sided background determination, a $\phi(\rho Z)$ data reduction (Merlet, 1994), and calibrated against natural mineral standards. The melt veins were analyzed under the same conditions but using a 20 µm diameter defocused beam. Because of their small diameters, the K-Si-rich inclusions in ilmenite could only be analyzed by energy-dispersive spectrometry (EDS).

Trace element data (Table 1) were obtained on the same grains used for EMP analysis by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). Ablation was accomplished under a He atmosphere using a custom built 193 nm excimer laser system operated with a 65-μm-diameter laser beam and a laser repetition rate of 4 Hz. Ablated material was analyzed for trace element abundances using an Agilent 7500 quadrupole ICPMS operated in time-resolved mode using a dwell time of 20 ms per mass. The CaO or TiO_2 contents of the minerals were used for internal normalization of the LA-ICPMS analyses. For all data, the NIST 612 glass was used for calibration of element sensitivity. The USGS synthetic basaltic glasses BCR-2G, BHVO-2G, BIR-1G and TB-1G were analyzed for quality control. Replicate LA-ICPMS analyses of BCR-2G, BHVO-2G and TB-1G demonstrate external reproducibilities of <10.2% (2σ) for the trace elements listed in Table 1 (Norman et al., 2004) at abundances similar to those found in LAP 02205 melt veins. Replicate LA-ICPMS analyses of the LREE-depleted glass BIR-1G, that has trace element abundances closer to plagioclase and clinopyroxene mineral separates, resulted in an external reproducibilities of <7.8% (2σ) for the trace elements listed in Table 1, except Rb (21%, 2σ), Ta (29.8%, 2σ), and Th (26.6%, 2σ) (Norman et al., 2004).

3.3. Isotope analyses

Whole rock powders WR 2, 3, and all hand-picked mineral fractions were leached for 10 min with cold 1N HCl in an ultrasonic bath (Figure 1). The leachates were pipetted from the residues and combined (leachate, Table 2). Samples WR A and B were leached for 10 min in ultrapure H_2O in an ultrasonic bath before leaching in 1N HCl to check for the presence of water-soluble REE-bearing phases (samples WR A H2O, WR A-L, WR B H2O and WR B-L; Figure 1, Table 2). All samples were dissolved without further crushing in HF-HNO_3 for 3 days at 120°C using sealed PFA beakers, then taken to dryness. The residues were subsequently dried down three times with small amounts of concentrated HNO_3 to break down insoluble fluoride compounds. The samples were finally taken up in 2 ml of 6N HCl, which produced a clear solution for all sample fractions. A 100 µl aliquot of each sample solution was removed and spiked with mixed ^{87}Rb-^{84}Sr and ^{149}Sm-^{150}Nd tracers for the determination of Rb/Sr and Sm/Nd by isotope dilution (ID). This mixed solution was taken to dryness and redissolved in HCl to ensure sample-spike isotope equilibration. Rubidium, strontium and the REE group were separated from the major elements using cation exchange chromatography (White and Patchett, 1984). The strontium fractions were then purified using Eichrom Sr-spec resin. Neodymium and samarium were separated from the REE using Eichrom Ln-spec resin. Total procedural blanks for Rb, and Sr ranged from 11-20 pg, and 120-320 pg, respectively. Total procedural blanks for Sm isotopic composition (IC) and ID measurements ranged from 2-4 pg, those for Nd ID measurements ranged from 12-16 pg. Blank contributions to Nd IC measurements ranged from 41-94 pg. The corrections from chemistry blank contributions were <0.5% for Rb and Sr ID concentration data, and <0.7% for Sm and Nd ID concentration data. Blank corrections were taken into account in the calculation of final concentration data (Table 2). Blank contributions to all IC measurements were negligible.

3.4. Mass spectrometry

Rubidium and strontium were loaded on rhenium filaments and measured on a Finnigan MAT 261 thermal ionization mass spectrometer. Rubidium isotope ratios were corrected for instrumental mass fractionation by comparison to contemporaneous runs of the NBS 727 isotope standard. Strontium isotope ratios were corrected for instrumental mass fractionation by normalizing to ^{86}Sr/^{88}Sr = 0.1194 using an exponential law. The results are presented in Table 2. Repeated measurements of the NBS 987 isotope standard gave average ^{87}Sr/^{86}Sr of 0.710242 ±0.000021 (±30 ppm, 2σ, n=9). For neodymium isotope measurements, 20 to 600 ng of neodymium were loaded with phosphoric acid on double rhenium filaments and measured as Nd^{+}-ions in static mode on a Thermo Finnigan Triton® thermal ionization mass spectrometer (TIMS). Cerium and samarium were monitored as ^{140}Ce and ^{147}Sm, respectively. Neodymium isotope ratios were corrected for instrumental mass fractionation by normalizing to ^{146}Nd/^{144}Nd = 0.7219 using an exponential law. Repeated measurements of the La Jolla and AMES 97 Nd isotope standards gave average ^{143}Nd/^{144}Nd of 0.511844 ±0.000002 (2σ, n=13) and 0.512132 ±0.000002 (2σ, n=9), respectively. Five high intensity measurements of a Sm standard solution produced mean ^{144}Sm/^{152}Sm, ^{148}Sm/^{152}Sm, ^{149}Sm/^{152}Sm, ^{150}Sm/^{152}Sm and ^{154}Sm/^{152}Sm of 0.114985 ±0.000006, 0.420454 ±0.000007, 0.516864 ±0.000009, 0.275997 ±0.000003 and 0.850781 ±0.000013, respectively (normalized to ^{147}Sm/^{152}Sm = 0.560828; all errors are 2σ). The results are in agreement with values previously reported (Wasserburg et al., 1981).

In order to calculate neodymium concentrations, an offline iterative spike stripping procedure was applied to each scan of the measured raw data from the ID runs. This resulted in precise concentration data and provided an independent determination of the

^{143}Nd/^{144}Nd ratios to check for inconsistencies with IC measurements. For the calculation of Sm concentrations, accurate sample Sm isotopic compositions (see discussion on neutron capture effects below) were obtained from contemporaneous unspiked runs and included in the spike stripping algorithm. Interferences on masses ^{144}Sm, ^{148}Sm and ^{150}Sm from ^{144}Nd, ^{148}Nd and ^{150}Nd were corrected for by monitoring ^{143}Nd and using the appropriate ^{143}Nd/^{144}Nd, ^{143}Nd/^{148}Nd and ^{143}Nd/^{150}Nd ratios of each sample. Application of individual corrections for the calculation of Sm concentrations led to significant improvements of the Sm/Nd reproducibility. Because use of mixed Rb-Sr and Sm-Nd spikes cancels out errors introduced from sample/spike weighing, the accuracy of the measured Rb/Sr and Sm/Nd is primarily a function of the instrumental mass fractionation (Rb) and the accuracy of the spike calibrations, and were set to fixed values of 0.5% and 0.1%, respectively. The error on Sm/Nd was derived from repeated analyses of solutions of a Sm-Nd standard (Wasserburg et al., 1981) equilibrated with the mixed Sm-Nd spike.

4. Results

4.1. Major and trace elements

Incompatible trace element concentrations and molar MgO/MgO+FeO$_{tot}$ (mg#) of average melt veins (mg# 0.33) overlap published LAP 02205 whole rock compositions (mg# 0.31 to 0.34) (Anand et al., 2006; Day et al., 2006; Zeigler et al., 2005) (Figure 2). When compared to more primitive members of the Apollo 12 and 15 low-Ti mare basalt suite, LAP 02205 exhibits a similar shape of the CI-normalized incompatible trace element pattern (Figure 2), but at overall elevated concentrations (30 to 80 times CI chondrites) and a slightly steeper highly incompatible element section (Ba to Ta). LAP

02205 is also distinguished from the low-Ti mare basalts by lower Eu/Sm and V/Sc (Figure 2). Major element compositions of individual grains picked from the clinopyroxene mineral separates of LAP 02205 range in compositions from high-Mg augite and pigeonite to ferroaugite and encompasses clinopyroxene compositions previously measured for LAP 02205 (Anand et al., 2006; Day et al., 2006; Joy et al., 2006; Righter et al., 2005; Zeigler et al., 2005). Chondrite-normalized REE abundances of individual pyroxene grains picked from the mineral separates of LAP 02205 show subparallel LREE-depleted patterns with pronounced negative Eu anomalies, whereas plagioclase is LREE-enriched with large positive Eu anomalies (Figure 3). Concentrations of the trace elements Rb, Sr, Sm and Nd from LA-ICPMS analyses of individual clinopyroxene, plagioclase, and melt vein grains of LAP 02205 generally agree with the results from ID-TIMS analysis of the mineral separates (Tables 1 and 2), consistent with the observed high purities of the picked mineral separates during optical examination. The exception are the two clinopyroxene separates (cpx-Fe and cpx-Mg) that show much higher Sr concentrations in the TIMS analysis of the bulk mineral concentrate compared to the LA-ICPMS determination of individual grains.

An examination of four LAP thin sections (02205, 02224, 02436, and 03632) by scanning electron microscopy demonstrates the frequent occurrence of rounded inclusions (~10 micron diameter) in ilmenite host grains (Figure 4). EDS data for the major element compositions of these inclusions are 77 to 80 wt% SiO_2, 11.3 to 12.6 wt% Al_2O_3, 7.1 to 8.2 wt% K_2O, and 1.6 to 4.8 wt% FeO. The encounter of such K-Si-rich inclusions during time-resolved single spot LA-ICP-MS analyses of ilmenite grains is manifested by strongly elevated count rates for all incompatible elements compared to ‘pure’ ilmenite background count rates. Judging from analyses of multiple ilmenite grains, ilmenite A (Table 1) is the best representation of an inclusion-free grain, whereas ilmenites B and C are representative of ilmenite with numerous enriched inclusions. Total abundances of the REE in bulk ilmenite are hence highly variable and span a range from abundances close to or at the detection limit of the LA-ICP-MS (ilm A) to abundances of, for example, La reaching 390 times the chondritic value in ilmenite B (Table 1, Figure 3). Rare earth element abundance patterns of individual ilmenite grains (Figure 3) also show a transition from slightly LREE-enriched (ilmenite B) to LREE-depleted (ilmenite C) with increasing overall REE abundances.

Analyses by ID-TIMS (Table 2) of unleached whole rocks (WR 1, C), leached whole rocks (WR 2, 3, D) and whole rock leachates (WR A-L, B-L, D-L) revealed that 73 to 83% of the whole rock Nd, and 20 to 29% of the whole rock Sr was transferred to the HCl-leachates. In contrast, the H_2O-leachates (WR A H2O, WR B H2O) contained only 53 and 390 pg of Nd, or 0.003 to 0.01% of the total Nd of the unleached whole rock (Table 2). The calculated concentrations of 191 to 10361 ppm Nd in the leachates are consistent with predominant leaching of phosphate phases (merrillite, fluorapatite) that contain 2700 to 15000 ppm neodymium (Anand et al., 2006; Day et al., 2006; Zeigler et al., 2005).

4.2. Rb-Sr isotopes

The results from Rb-Sr analyses of eleven LAP 02205 whole rocks and mineral separates are summarized in Table 2. When plotted in an isochron diagram (Ludwig, 1999), the data points define an age of 2990 ±18 Ma (λ^{87}Rb = 1.402×10^{-11} year^{-1}; MSWD

= 1.7; error represents the 95% confidence limit) and initial $^{87}Sr/^{86}Sr$ of 0.699839 ±0.000014 (Figure 5). Only the combined 1N HCl-leachate (Table 2) does not overlap the isochron within the analytical reproducibility of ±30 ppm (other leachates have not been analyzed for Rb-Sr isotopes, Table 2). Omitting the leachate from the calculation leads to insignificant changes with an age of 2991 ±14 Ma (MSWD = 1.1) and an initial $^{87}Sr/^{86}Sr$ ratio of 0.699836 ±0.000010 (Figure 5).

4.3. Sm-Nd isotopes

The results from Sm-Nd analyses of LAP 02205 mineral separates are summarized in Table 2. When plotted in a $^{147}Sm/^{144}Nd$ versus $^{143}Nd/^{144}Nd$ isochron diagram (Figure 6), the data shows considerable scatter. All data points combined yield a crystallization age for LAP 02205 of 3144 ±71 Ma (MSWD = 20) and a $\varepsilon^{143}Nd_i$ of +1.2 ±0.5. However, three plagioclase separates consistently show higher $^{143}Nd/^{144}Nd$ for a given $^{147}Sm/^{144}Nd$ ratio when compared to whole rocks, leachates and melt veins (Figure 6). The line fitted separately through the leached fractions (minerals and rocks) yields an age of 2992 ±85 Ma (MSWD = 9.8) and initial $\varepsilon^{143}Nd$ ($\varepsilon^{143}Nd_i$) of +2.9 ±0.8 (Fletcher and Rosman, 1982), in agreement with the age estimate from Rb-Sr chronology (Figure 5), although the high MSWD precludes this being a rigorous isochron. The subset of LAP 02205 whole rocks, leachates and leached residues, instead, define a linear array with a slope corresponding to a slightly older age of 3245 ±25 Ma (MSWD = 1.8) and lower $\varepsilon^{143}Nd_i$ of +0.8 ±0.2. In the following discussion, we propose that this older Sm-Nd age has no chronological meaning. Instead, it represents a mixing line between the leached mineral residues and isotopically anomalous REE-rich phosphates that are preferentially extracted by the acidic leachate. Discarding the phosphates, the initial Sr and Nd isotopic compositions are compared in section 5.4 to those obtained from studies of Apollo rocks in order to put constraints on the source region of the LAP basalt.

5. Discussion

5.1. The relationship of Si-K-rich inclusions to ilmenite host grains

Thermodynamic modeling of the closed system crystallization sequence of a magma of LAP 02205 whole rock composition using the MELTS code (Asimow and Ghiorso, 1998; Ghiorso and Sack, 1995) suggests that ilmenite appears on the liquidus after ~92 wt% equilibrium crystallization of (in the order of appearance) 36% pigeonite, 22% plagioclase, 4% spinel, 26% clinopyroxene and 2% olivine. The late appearance of ilmenite is supported by textural evidence such as equilibrium contacts of ilmenite grains with free silica (Figure 4) and Fe-pyroxene in the mesostasis. The mesostasis areas have been proposed to be the result of silicate liquid immiscibility that occurs after >95% melt crystallization (Anand et al., 2006). Glassy inclusions observed in mineral grains are frequently interpreted as trapped portions of the melt from which the mineral grains crystallized (Roedder and Weiblen, 1970). Assuming that the Si-K-rich inclusions in ilmenite sample the evolved host melt from which ilmenite crystallized, and perfectly incompatible behavior of potassium, the remaining liquid fraction F (represented by the Si-K-rich inclusions) is calculated from the whole rock potassium concentration C_0 in LAP 02205 (0.11 wt% K_2O) and the concentration C_L in the Si-K-rich inclusions (7 to 8 wt% K_2O) as $F = C_0/C_L = 1.4$ to 1.6 wt%.

The evolved melt from which the ilmenite formed would also have higher absolute abundances of incompatible trace elements compared to the composition of the LAP whole rock. This expectation is confirmed by the analysis of 'clean' ilmenite A, i.e., ilmenite that did not show evidence of the encounter with distinct trace-element enriched inclusions during LA-ICP-MS analysis (Table 1). Ilmenite A has a Zr concentration of 592 ppm (Table 1). Using the proportions of crystallized phases at the point of ilmenite saturation indicated by the thermodynamic model (F = 7.4%), a LAP 02205 whole rock Zr concentration of 200 ppm (Anand et al., 2006), and published distribution coefficients for pigeonite, plagioclase, clinopyroxene (Norman et al., 2005), olivine (Kennedy et al., 1993) and spinel (McKay et al., 1986), a Zr concentration in the residual liquid at the onset of ilmenite crystallization of 1880 ppm is calculated. Taking D_{Zr}(ilm/melt) = 0.330 (McKay et al., 1986), this translates to a concentration of Zr in first formed ilmenite of 622 ppm, which compares well with the measured value in the inclusion-free ilmenite A of 592 ppm. Likewise, for a remaining liquid fraction representative of the Si-K-rich inclusions (F = 1.5 wt%), the Zr concentration in the residual liquid and crystallizing ilmenite is calculated to be 3465 ppm and 1143 ppm, respectively. This result is not intended to give a detailed model of late-stage crystallization of LAP 02205, but to illustrate that the combined effect of crystallization from an evolved melt and the presence of inclusions can produce ilmenites with highly elevated trace element compositions.

The observed transition from the slightly LREE-enriched trace element abundance pattern of ilmenite B to the LREE-depleted pattern of ilmenite C with overall increasing trace element abundances (Figure 3) is explicable by the onset of additional phosphate crystallization. The phosphates are LREE enriched, as indicated by their low $^{147}Sm/^{144}Nd$ of ~0.17 (leachates, Table 2). Crystallization of phosphates will thus lead to a LREE-depletion in the residual liquid. The bulk ilmenite $^{147}Sm/^{144}Nd$ from ID-TIMS analysis is 0.27 (i.e., strongly LREE-depleted). This suggests that the bulk ilmenite isotope analyses are dominated by those melt inclusions that show a LREE-depleted pattern and are characterized by high absolute abundances of the incompatible elements.

In summary, these relationships between trace elements and the timing of mineral crystallization show that the high abundances of incompatible trace elements in the ilmenites and their specific abundance patterns are inherited from a progressively fractionating LAP 02205 host melt. Ilmenite-melt distribution coefficients for Rb, Sr, Nd and Sm are not well constrained for evolved lunar materials, but are estimated to be in the range of 0.001 to 0.01 (Nakamura et al., 1986; Snyder et al., 1992). Thus, the measured Rb, Sr, Sm and Nd isotopic compositions of ilmenite separates should be entirely dominated by their K-Si-rich inclusions, consistent with the observations presented above. Moreover, ilmenite likely acted as a protective shield around the melt inclusions, inhibiting their post-crystallization diffusive re-equilibration. Hence, the Sr-Nd isotope analyses of the bulk ilmenite separates are taken to be reliable representatives of the last fractions of the crystallizing LAP 02205 parent magma in the following discussion.

5.2. Neutron irradiation effects on measured isotope ratios

Rocks exposed at the lunar surface may show alterations in their initial isotopic composition because of neutron capture (Eugster et al., 1970). Figure 7 shows results from Sm isotope analyses of LAP 02205, normalized to $^{147}Sm/^{152}Sm = 0.560828$.

Calculated ε^{149}Sm [defined as $(^{149}\text{Sm}/^{152}\text{Sm})_{\text{meas}}/(^{149}\text{Sm}/\ ^{152}\text{Sm})_{\text{Std}}-1)*10^4$] for the different sample splits form a tight cluster with a mean of -3.51 ±0.21 (2σ). The regressed line has a slope of -0.99 ±0.17, consistent with the assumption that the observed isotopic variation is affected by neutron capture. Using the major element compositions of LAP 02205 (Anand et al., 2006; Joy et al., 2006; Zeigler et al., 2005) and ε^{149}Sm = -3.5 (this work), an effective cross section σ_{eff} (^{149}Sm) of ~5.6×10^4 barns and an effective neutron fluence of ~0.63×10^{16} n/cm^2 (Lingenfelter et al., 1972) is calculated. Assuming that LAP 02205 was part of a lava flow that extruded on the lunar surface at 3 Ga and that its relative position to the surface has not changed markedly by lunar gardening processes, the approximate average shielding depth can be calculated by comparing this neutron fluence to the theoretical depth dependence derived for the Apollo 11 soil (Lingenfelter et al., 1972). The calculated macroscopic effective neutron absorption cross section Σ_{eff} (Lingenfelter et al., 1972) of 0.0094 cm^2/g for LAP 02205 is similar to the value of 0.0103 cm^2/g for the Apollo 11 soil (Lingenfelter et al., 1972). The latter can therefore be used to estimate the shielding depth of LAP 02205 without introducing large errors. From Figure 4 of Lingenfelter et al. (1972), the ε^{149}Sm = -3.5 is consistent with 3 Ga irradiation at a shielding depth of ~800 g/cm^2, or ~2.7 m below the surface in a rock with the density of LAP 02205 (~3 g/cm^3). A similar estimate of ~700 g/cm^2 for the ejection depth has recently been proposed for the LAP basalts on the basis of cosmogenic (^{10}Be, ^{26}Al, ^{36}Cl, ^{41}Ca) radionuclides (Nishiizumi et al., 2006). Comparable estimates were also derived from textural and petrological studies of the LAP meteorites (Anand et al., 2006; Day et al., 2005; Righter et al., 2005). For example, an estimate of 2 to 10 m depth was derived from the subhedral to skeletal morphology of olivine (Lofgren et al., 1975; Righter et al., 2005), and calculated mineral cooling rates are consistent with derivation of the LAP basalts from the central part of a lava flow of 5 to 20 m thickness (Day et al., 2005).

All relevant nuclides in the Rb-Sr system have very low thermal neutron capture cross sections (≤16 barns) and the neutron fluence correction on measured isotope ratios is negligible. The reaction ^{143}Nd(n,γ)^{144}Nd with a larger capture cross section of 336 barns affects the ^{143}Nd/^{144}Nd ratio directly, but also indirectly via the ^{146}Nd/^{144}Nd normalization scheme. A correction term of +4.6 ppm on ^{143}Nd/^{144}Nd ratios is calculated for LAP 02205 in this study from the isotopic shift of the samarium isotopes (Nyquist et al., 1995). This correction term is similar to the external 2σ-reproducibility of the standard (4.5 and 3.9 ppm for the AMES 97 and La Jolla isotope standards, respectively). Applying a uniform correction term on individual ^{143}Nd/^{144}Nd ratios of the mineral fractions will have no effect on the slope (and thus calculated age) in an isochron diagram, but will shift the calculated initial ^{143}Nd/^{144}Nd ratio by the same amount. The correction from neutron irradiation on sample LAP 02205, however, is negligible when compared to the uncertainties associated with the calculated ε^{143}Nd$_i$ values [±0.9 and ±0.2 ε^{143}Nd-units, or ±90 and ±20 ppm, respectively (Figure 6)].

5.3. Rb-Sr and Sm-Nd chronology of LAP 02205

A precise Rb-Sr crystallization age of 2.990 ±0.018 Ga is obtained for LAP 02205 in this study (Figure 5), consistent with the previously reported Rb-Sr age of 3.02 ±0.03 Ga (Nyquist et al., 2005). It is important to note that the analysis of the LAP 02205 ilmenite separate does not deviate from the Rb-Sr reference isochron (Figure 5), supporting the conclusion from Ar-Ar analysis (Fernandes and Burgess, 2006) that the Si-K-rich phase (a major host for radiogenic ^{40}Ar from the decay of ^{40}K) has remained isotopically undisturbed.

The Sm-Nd isochron defined by the leached mineral separates (excluding the melt veins) yields an age of 2992 ±85 Ma (Figure 6) that is within error identical to the more precise 2990 ±18 Ma Rb-Sr age (Figure 5), and ages obtained from independent Ar-Ar [2.915 ±0.010 and 2.95 ±0.04 Ga (2σ), (Fernandes and Burgess, 2006; Nyquist et al., 2005)], and U-Pb studies [2.93 ±0.15 Ga (2σ) (Anand et al., 2006). If taken separately, the subgroup of whole rocks, leachates and leached residues, however, defines an older age of 3245 ±25 Ma in the Sm-Nd isotope diagram (Figure 6). This older age compared to the 2992 ±85 Ma mineral isochron could be interpreted as the crystallization age of LAP 02205. In such a case, the younger ages obtained from the Rb-Sr, Ar-Ar, and U-Pb methods represent post-crystallization resetting of the different isotope systems. The Ar-Ar isotopic system is more sensitive to post-crystallization disturbance than the Rb-Sr or Sm-Nd isotope systems, because gaseous phases are likely to be more easily lost or redistributed during shock or heating events (Bogard et al., 1987). However, the consistent ages obtained from the Ar-Ar, Rb-Sr and U-Pb isotope systems, and the finding that plagioclase is in trace element equilibrium with the whole rock (Anand et al., 2006), argues against post-crystallization resetting at 2990 Ma. Instead, it is proposed that the observed scatter in the Sm-Nd isochron diagram is caused by isotopically altered phosphates.

It has been shown that REE transport in apatite is considerably faster than REE diffusion in other accessory minerals (Cherniak, 2000). REE isotope and chemical signatures can become decoupled in apatite, with light REE isotope exchange proceeding much more rapidly than REE chemical diffusion altering total REE concentrations. It seems unlikely that only the LAP 02205 phosphates should record an older crystallization age, whereas minerals with much lower REE-diffusivities than phosphates such as clinopyroxene (Cherniak, 2000; Van Orman et al., 2001) have been efficiently reset. A straightforward interpretation of the deviant composition of the REE-bearing phosphates in the Sm-Nd isochron diagram (Figure 6) is thus open-system behavior of the phosphates that occurred after the Sm-Nd isotope system was effectively closed in the other mineral phases of LAP 02205. The ilmenite separates contain significant amounts of Nd and show highly evolved Sm/Nd ratios (Table 2), yet they plot on the Sm-Nd reference isochron, consistent with the finding from Rb-Sr isotopes (Figures 5 and 6). Isotopic exchange and alteration of the phosphates thus must have occurred in the prolonged time span between final stages of crystallization (marked by isotopically undisturbed Si-K-rich inclusions in ilmenite) and formation of the melt vein glass (which incorporated isotopically altered phosphates) during relatively recent [55 ±5 ka (Nishiizumi et al., 2006)] impact and ejection of the LAP meteorite from the lunar surface.

The specific mechanism, by which LAP 02205 phosphate grains that appear fresh and intact in thin section have been isotopically altered, remains enigmatic. Although a reasonable heat source to cause such open-system behavior could have potentially been provided by the prolonged meteorite bombardment of the lunar surface, there is no evidence for disturbed Sm-Nd isotopes in phosphates of samples collected by the Apollo missions that are compositionally similar to LAP 02205. The Rb-Sr isochron, however, is only minimally disturbed by the inclusion of the leachate (Figure 5). This finding is consistent with the low strontium concentration in the leached phosphates. The bulk of the strontium of LAP 02205 resides in plagioclase (Table 1), which is expected to be less susceptible to open-system behavior than the phosphates (Cherniak, 2000, 2003).

It is concluded that the phosphate phases record open-system behavior during the latest stages of crystallization of the LAP parent basalt; or more likely, during in the prolonged time period between final crystallization and ejection of the LAP meteorite from the lunar surface. If anomalous phases (leachates, whole rocks and melt veins) are excluded from the age calculations, similar crystallization ages are obtained from Rb-Sr (2991 ±14 Ma, Figure 5) and Sm-Nd isotopes (2992 ±85 Ma, Figure 6), respectively. The calculated initial $^{87}Sr/^{86}Sr_i$ of 0.699836 ±0.000010 and $\varepsilon^{143}Nd_i$ of +2.9 ±0.8 for LAP 02205 obtained from these Rb-Sr and Sm-Nd isochrons are used to model the isotopic evolution of the LAP source region. It must be noted, however, that the calculated $^{87}Rb/^{86}Sr$ and $^{147}Sm/^{144}Nd$ inferred for the LAP source region are only applicable if the LAP magma evolved as a closed system (i.e., no isotopic exchange has occurred between generation of the magma in the mantle source region and final crystallization of the mineral phases). Trace element inversions of individual minerals and thermodynamic modeling suggests that the whole rock composition of LAP 02205 reflects a melt composition and that no cumulus phase is present in the rock sample (Anand et al., 2006; Day et al., 2006). The lack of cumulus phases, however, implies that there is no direct evidence for the differentiation processes that occurred between formation of the primary LAP parent magma in the lunar mantle, and extrusion and solidification of the evolved lava parental to the LAP meteorite. However, assuming a general petrologic relationship between LAP 02205 and lunar samples from the Luna and Apollo missions, some constraints on the mantle source region and differentiation history of LAP 02205 may be derived.

5.4. Constraints on the LAP source region

In terms of its major element chemistry and low mg# of 0.31, LAP 02205 closely resembles evolved low-Ti lunar mare basalts from the Apollo 12 and 15 olivine and pigeonite basalt suites (Anand et al., 2006; Day et al., 2006; Joy et al., 2006; Righter et al., 2005; Zeigler et al., 2005). Experimental work has shown that samples of the low-Ti olivine-normative basalt suite have multiple saturation points at pressures from 5 to 13 kb, corresponding to depths of 100 to 250 km in the Moon with dominantly low-Ca pyroxene and olivine on the liquidus (Chappell and Green, 1973; Green et al., 1971; Longhi, 1992). This source assemblage is believed to have formed as magmatic cumulates in the LMO (Snyder et al., 1992, 1997). If the cumulate mantle sources formed globally with similar compositions, then the most straightforward assumption is that similar primitive low-Ti liquids were parental to both LAP and Apollo samples. In this case, the Apollo samples can be used to model the magmatic evolution of the LAP basalt. Primitive Apollo 12 and 15 basalts that have been suggested to represent parental compositions for their particular petrographic suites (olivine, pigeonite and ilmenite basalts), have MgO ranging from 8 to 13 wt% (Neal et al., 1994; Ryder and Schuraytz, 2001; Snyder et al., 1997). Thermodynamic modeling of the crystallization sequence of primitive low-Ti Apollo 12 and 15 olivine basalts such as 12009, 12072 and 15555, using the MELTS and MAGFOX codes yield major element compositions that match the LAP basalts (Righter et al., 2005).

If the LAP parent magma shares a common source region with the Apollo 12 or 15 low-Ti olivine basalt suites, then they should also have similar source ^{87}Rb/^{86}Sr and ^{147}Sm/^{144}Nd, which are inferred from the ^{87}Sr/^{86}Sr$_i$, ^{143}Nd/^{144}Nd$_i$, and the crystallization ages obtained from internal isochrons (Figure 8). However, the source ^{87}Rb/^{86}Sr and ^{147}Sm/^{144}Nd may have been changed by metasomatism of the mantle source regions, or alternatively, by assimilation of exogenous material during ascent of the magma through the lunar mantle and crust. Such mixing scenarios will be discussed for Sr and Nd isotopes as well as trace element abundances in the following sections.

5.4.1. Sr-Nd isotope mixing models

The ^{87}Sr/^{86}Sr and ^{143}Nd/^{144}Nd isotopic evolution of the lunar mantle source regions of the LAP parent magma, Apollo 12 and 15 olivine basalts, and KREEP are modeled assuming two-stage models (Figure 8A and B) with the mixing parameters listed in Table 3 (data from this study, Borg et al., 2004; Gnos et al., 2004; Jolliff et al., 2003; Neal, 2001; Nyquist and Shih, 1992; Nyquist et al., 1995; Rankenburg et al., 2006; Snyder et al., 1997). Because the trace element abundances in the SaU 169 impact melt breccia are the highest among the KREEP-rich samples, it probably represents a relatively ‘pure’ KREEP composition, and the REE and Sr concentrations of SaU 169 (Gnos et al., 2004) are therefore used in the mixing calculations. However, no Rb-Sr isotope data is available for SaU 169, and the ^{87}Sr/^{86}Sr composition of NWA 773 (Borg et al., 2004) is used instead. This is justified by the similar ^{147}Sm/^{144}Nd$_s$ of SaU 169 and NWA 773 (Table 3), indicating a similar degree of source fractionation for the two samples.

For simplicity, the stages that lead to the bulk lunar Rb/Sr (volatilization of Rb during accretion of the lunar precursor materials and during the Moon-forming giant impact) are integrated to one single step leading from the initial ^{87}Sr/^{86}Sr of the solar system to the lunar initial ^{87}Sr/^{86}Sr (Figure 8A). The initial ^{87}Sr/^{86}Sr ratio of the solar system is taken from the initial ^{87}Sr/^{86}Sr = 0.69892 ±0.00002 (normalized to ^{87}Sr/^{86}Sr = 0.71025 for NIST SRM 987) of calcium-aluminum-rich inclusions (CAI) (Podosek et al., 1991) that formed from the solar nebula at 4.567 Ga (Amelin et al., 2002). The lunar initial ^{87}Sr/^{86}Sr has been estimated to 0.69903 at 4.55 Ga (Nyquist, 1977). Estimates for the timing of the giant impact on the basis of tungsten isotopes are model-dependent and range from ~30 to 50 Ma after CAI formation (Halliday, 2004; Jacobsen, 2005; Kleine et al., 2002; Yin et al., 2002). The specific choice of the formation age of the Moon, however, does not greatly change the slopes of the tie lines connecting the bulk lunar initial with the initial ^{87}Sr/^{86}Sr ratios of the samples at the time of their crystallization (Figure 8A), and thus the long-term integrated ^{87}Sr/^{86}Sr source ratios of these samples. A duration of 30 to 50 million years for the first stage in the model that connects CAI's to the Moon's initial ^{87}Sr/^{86}Sr = 0.69903 (Figure 8A), corresponds to a time-integrated first-stage ^{87}Rb/^{86}Sr ratio of 0.245 to 0.147, respectively, which is lower than the mean ^{87}Rb/^{86}Sr value for CI carbonaceous chondrites of ~0.91 at that time (Anders and Grevesse, 1989), and thus indicates formation of the Moon from precursor materials that were already volatile depleted (Halliday and Porcelli, 2001).

Assuming that the LAP 02205 parent magma was derived from a source that is similar to the Apollo 12 and 15 low-Ti olivine basalt mantle sources, the amount of admixture of KREEP-like material can be inferred from binary mixing calculations. Mixing is assumed to take place at 2991 Ma between SaU 169 and Apollo 12 and 15 low-Ti olivine basalt sources (Table 3, mixing lines in Figure 8A). The Sr isotopic compositions of the SaU 169 and Apollo 12 and 15 low-Ti olivine basalt sources at 2991 Ma were calculated by projecting their calculated long-term averaged ^{87}Rb/^{86}Sr to the crystallization age of LAP 02205 of 2991 Ma (Table 3). Binary mixing calculations on the basis of Sr isotopes suggest additions of 1.3 and 3.0 wt% SaU 169 to the Apollo 12 and 15 sources, respectively, to form LAP 02205 with an initial ^{87}Sr/^{86}Sr = 0.69984 (Table 3).

In contrast to Rb/Sr, the bulk lunar Sm/Nd is not expected to deviate from the solar value because both Sm and Nd are refractory elements, and thus should not be fractionated from each other by volatilization processes occurring during accretion of the lunar precursor materials. A chondritic bulk lunar Sm/Nd has been confirmed by combined ^{146,147}Sm/^{142,143}Nd isotopes (Rankenburg et al., 2006). The formation interval for the lunar mantle, however, is model dependent and ranges between 30 to 50 Ma after solar system formation from Hf-W isotopes (Kleine et al., 2005; Shearer and Newsom, 2000) and 215 to 250 Ma from ^{146,147}Sm/^{142,143}Nd isotopes (Nyquist et al., 1995; Rankenburg et al., 2006). For the two-stage mixing model on the basis of Sm-Nd isotopes (Figure 8B), a lunar mantle formation interval of 215 Ma (Rankenburg et al., 2006) was chosen. Although the calculated source isotope ratios vary slightly depending on the source formation age, the results from the mixing calculations are model-independent and give identical answers. Using the age and $\varepsilon^{143}Nd_i$ from the Sm-Nd mineral isochron (2992 Ma and +2.9, Figure 6), a $^{147}Sm/^{143}Nd$ source ratio of 0.2126 is calculated for the LAP region (Table 3). This ratio is similar to the ratios calculated for the Apollo 15 olivine-normative basalts (average 0.2105, Figure 8B) and thus no addition of SaU 169 is necessary to generate the LAP parent magma from source regions similar to that which produced the Apollo 15 olivine-normative basalts. This result is in conflict with the 3.0 wt% KREEP admixture required from Sr isotopes. In contrast, to explain the offset in $\varepsilon^{143}Nd_i$ between Apollo 12 low-Ti olivine basalts and LAP 02205, binary mixing calculations suggest 1.0 wt% admixture of KREEP (Table 3), similar to the 1.3 wt% derived from Sr isotopes.

5.4.2 Trace element constraints

This result from isotope mixing calculations can be further refined by constraints from trace element concentrations (Figure 9). The hypothetical primary liquid derived from mixing of KREEP and Apollo 12 sources must undergo substantial fractional crystallization to match the major element composition of LAP 02205, thereby increasing trace element concentrations in the residual liquid. It has previously been shown on the basis of major element modeling that the major element composition of LAP 02205 is consistent with fractional crystallization of 7 to 10 wt% olivine, 0 to 13 wt% orthopyroxene, 13 to 18 wt% low-Ca clinopyroxene and ~1 wt% chromite (Righter et al., 2005) from more primitive members of the Apollo 12 low-Ti olivine basalt suite such as 12009 and 12072. Using these phase proportions and published distribution coefficient data for Sr and Nd (Kennedy et al., 1993; McKay et al., 1986; Norman et al., 2005), the trace element concentrations for the REE elements La, Nd, Sm, Eu, Yb and Lu are calculated for residual liquids that are derived from mixtures of average Apollo 12 low-Ti olivine basalt and SaU 169 (Table 4). Excellent agreement between the modeled final LAP 02205 REE pattern and measured concentrations (Anand et al., 2006) is achieved for 2.2 wt% addition of SaU 169 (Figure 9, Table 4), thus substantiating the results from the Sr and Nd isotope systems.

In summary, the major element compositions, Rb-Sr and Sm-Nd isotopes, REE concentrations, and Ni/Co anomalies in Fe-Ni metals (Day et al., 2006), are consistent with derivation of the LAP basalts from a lunar mantle source region akin to the Apollo 12 low-Ti mantle source. The LAP parent magma can be successfully modeled by mixing of 1 to 2 wt% SaU 169 (i.e. KREEP-rich material) to average Apollo 12 low-Ti olivine basalt.

5.4.3 Additional constraints on the mixing process

The mixing calculations presented here do not necessarily imply mixing in the mantle source region of the LAP parent magma. The LREE-enriched signature observed in LAP 02205 may also have been acquired by a combined assimilation/fractional crystallization processes (AFC) during ascent of the LAP parent magma to the lunar surface. AFC model results are strongly dependent on the ratio chosen for the mass of assimilated rock to mass of fractionating minerals, the bulk distribution coefficients, and a number of other factors (for a review of the full potential of AFC modeling see Spera et al., 2004). As such, without the determination of isotope ratios/trace element data in a larger suite of cogenetic lunar rocks, where these factors can be better constrained, it is questionable whether the AFC models are meaningful, but they cannot be ruled out.

Figure 8A illustrates the previously observed correlation between age and apparent source enrichment indicated by elevated calculated source ^{87}Rb/^{86}Sr ratios of the mare basalts. This source enrichment has been used to argue for the involvement of trace element-enriched material similar to KREEP-rich samples as a heat source for lunar melting events after crystallization of the LMO (Borg et al., 2004; Hagerty et al., 2006; Wieczorek and Phillips, 2000). In model of Borg et al. (2004), the correlation between younger crystallization ages and higher Rb/Sr source ratios of pristine KREEP-rich rocks was suggested to reflect the need for source regions of young magmas to contain a greater abundance of heat-producing elements to offset cooling associated with heat loss of the Moon through time. However, samples with strong KREEP affinities (15386, NWA 773) are not part of the trend defined by the olivine basalts and LAP 02205 (inset in Figure 8A). Moreover, if the same reasoning is applied to the Sm-Nd isotope system, an opposite trend should be observed, meaning lower (incompatible element-enriched) ^{147}Sm/^{144}Nd source ratios should correlate with younger crystallization ages for the same sample suite. This is not observed (Figure 8B). Instead, the ^{147}Sm/^{144}Nd source ratios for Apollo 12 and 15 low-Ti olivine basalts, LAP 02205 and KREEP samples SaU 169, 15386 and NWA 773 are randomly distributed when plotted versus their crystallization ages (Figure 8B). The inclusion of Apollo 12 ilmenite basalts that have similar ages to other Apollo 12 basalts of ~3200 Ma but strongly positive ε^{143}Nd of 10.5 to 11.2 (Snyder et al., 1997), reinforce the discrepancy between the model prediction (Borg et al., 2004) and observation. It is more likely that the reasons for the melting events that occurred after the LMO episode in lunar history are more complex, and may require additional sources of energy such as large impact events, or ascending plumes within the lunar mantle.

5.5. Summary

The formation history of low-Ti mare basalt meteorite LAP 02205 is considered within the context of an Apollo-based understanding of lunar petrogenesis. There is evidence for multi-stage processing from the trace element and isotopic characteristics of LAP 02205. The LAP parent magma was generated from a mantle source similar to that which produced the Apollo 12 low-Ti olivine basalts. This was followed by addition of approximately 1 to 2 wt% KREEP-rich material similar to SaU 169 to the LAP parental melt and fractional crystallization of approximately 27 to 33 wt% of olivine, orthopyroxene, pigeonite and spinel to account for the observed major and trace element composition of LAP 02205. The crystallization age of LAP 02205 is most precisely dated by an internal Rb-Sr isochron of 2991 ±14 Ma. Excluding phases that are dominated by isotopically anomalous phosphates that are likely reset subsequent to crystallization, a Sm-Nd crystallization age of 2992 ±85 Ma is obtained, which is within error from the Rb-Sr age, and is in general agreement with other independent age determinations for LAP 02205 from Ar-Ar and U-Pb methods. Impact and ejection of the LAP parent meteorite from the lunar surface occurred 55 ±5 ka ago before it finally fell on Antarctica 20 ±5 ka ago (Nishiizumi et al., 2006).

Although the involvement of KREEP as a heat source in generating melts in the lunar interior is appealing, there is a general discrepancy between predictions of the model and observed Sr-Nd isotopic compositions of lunar basalts. The model calls for the generation of lunar basalts from progressively more enriched source regions with younger age to yield basaltic magmas in a constantly cooling Moon (Borg et al., 2004). In contrast, Rb-Sr and Sm-Nd data for the Apollo 12 and 15 low-Ti olivine basalt suites, LAP 02205 and the samples with strong KREEP affinities display no general trend that connects source enrichment indicated by lower calculated source ^{87}Rb/^{86}Sr and higher ^{147}Sm/^{144}Nd ratios with the crystallization age of the lavas.

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References

Amelin Y., Krot A. N., Hutcheon I. D., and Ulyanov A. A. (2002) Lead isotopic ages of chondrules and calcium-aluminium-rich inclusions. *Science* **297**, 1678-1683.

Anand M., Taylor L. A., Floss C., Neal C. R., Terada K., and Tanikawa S. (2006) Petrology and geochemistry of LaPaz Icefield 02205: A new unique low-Ti mare-basalt meteorite. *Geochimica et Cosmochimica Acta* **70**(1), 246-264.

Anders E. and Grevesse N. (1989) Abundances of the elements; meteoritic and solar. *Geochimica et Cosmochimica Acta* **53**(1), 197-214.

Asimow P. D. and Ghiorso M. S. (1998) Algorithmic modifications extending MELTS to calculate subsolidus phase relations. *American Mineralogist* **83**, 1127-1131.

Begemann F., Ludwig K. R., Lugmair G. W., Min K., Nyquist L. E., Patchett P. J., Renne P. R., Shih C. Y., Villa I. M., and Walker R. J. (2001) Call for an improved set of decay constants for geochronological use. *Geochimica et Cosmochimica Acta* **65**(1), 111-121.

Bogard D., Hoerz F., and Johnson P. (1987) Shock effects and argon loss in samples of the Leedey L6 Chondrite experimentally shocked to 29-70 GPa pressures. *Geochimica et Cosmochimica Acta* **51**(7), 2035-2044.

Borg L. E., Shearer C. K., Asmerom Y., and Papike J. J. (2004) Prolonged KREEP magmatism on the Moon indicated by the youngest dated lunar igneous rock. *Nature* **432**, 209-211.

Canup R. M. (2004) Simulations of a late lunar-forming impact. *Icarus* **168**, 433-456.

Chappell B. W. and Green D. H. (1973) Chemical compositions and petrogenetic relationships in Apollo 15 mare basalts. *Earth and Planetary Science Letters* **18**(2), 237-246.

Cherniak D. J. (2000) Rare earth element diffusion in apatite. *Geochimica et Cosmochimica Acta* **64**(22), 3871-3885.

Cherniak D. J. (2003) REE diffusion in feldspar. *Chemical Geology* **193**(1-2), 25-41.

Crozaz G., Floss C., and Wadhwa M. (2003) Chemical alteration and REE mobilization in meteorites from hot and cold deserts. *Geochimica Et Cosmochimica Acta* **67**(24), 4727–4741.

Day J. M. D., Taylor L. A., Floss C., Patchen A. D., Schnare D. W., and Pearson D. G. (2006) Comparative petrology, geochemistry, and petrogenesis of evolved, low-Ti lunar mare basalt meteorites from the LaPaz Icefield, Antarctica. *Geochimica Et Cosmochimica Acta* **70**, 1581-1600.

Day J. M. D., Taylor L. A., Hill E., and Liu Y. (2005) Textural analysis and crystallization histories of La Paz mare basalt meteorites (abstract). *Annual Meeting of the Meteoritical Society* **68th**, #5185 [CD-ROM].

Eugster O., Tera F., Burnett D. S., and Wasserburg G. J. (1970) The isotopic composition of Gd and the neutron capture effects in samples from Apollo 11. *Earth and Planetary Science Letters* **8**(1), 20-30.

Fernandes V. A. and Burgess R. (2006) Ar-Ar studies of two lunar mare rocks: LAP 02205 and EET 96008 (abstract). *Lunar & Planetary Science Conference* **37th**, #1145 [CD-ROM].

Fletcher I. R. and Rosman K. J. R. (1982) Precise determination of initial epsilon Nd from Sm-Nd isochron data. *Geochimica Et Cosmochimica Acta* **46**, 1983-1987.

Ghiorso M. S. and Sack R. O. (1995) Chemical Mass-Transfer in Magmatic Processes IV. A Revised and Internally Consistent Thermodynamic Model for the Interpolation and Extrapolation of Liquid-Solid Equilibria in Magmatic Systems at Elevated-Temperatures and Pressures. *Contributions to Mineralogy and Petrology* **119**(2-3), 197-212.

Giguere T. A., Taylor G. J., Hawke B. R., and Lucey P. G. (2000) The titanium contents of lunar mare basalts. *Meteoritics & Planetary Science* **35**(1), 193-200.

Gnos E., Hofmann B. A., Al-Kathiri A., Lorenzetti S., Eugster O., Whitehouse M. J., Villa I. M., Jull A. J. T., Eikenberg J., Spettel B., Kraehenbuehl U., Franchi I. A., and Greenwood R. C. (2004) Pinpointing the source of a lunar meteorite; implications for the evolution of the Moon. *Science* **305**(5684), 657-660.

Green D. H., Ringwood A. E., Ware N. G., Hibberson W. O., Major A., and Kiss E. (1971) Experimental petrology and petrogenesis of Apollo 12 basalts. *Proceedings of the Lunar Science Conference* **2nd**, 601-615.

Hagerty J. J., Shearer C. K., and Vaniman D. T. (2006) Heat-producing elements in the lunar mantle: Insights from ion microprobe analyses of lunar pyroclastic glasses. *Geochimica Et Cosmochimica Acta* **70**(13), 3457-3476.

Halliday A. N. (2004) Mixing, volatile loss and compositional change during impact-driven accretion of the Earth. *Nature* **427**, 505-509.

Halliday A. N. and Porcelli D. (2001) In search of lost planets - the paleocosmochemistry of the inner solar system. *Earth and Planetary Science Letters* **192**, 545-559.

Hartmann W. K. (1985) Giant impact on Earth seen as Moon's origin. *Geotimes* **30**(6), 11-12.

Haskin L. A. (1998) The Imbrium impact event and the thorium distribution at the lunar highlands surface. *Journal Of Geophysical Research-Planets* **103**(E1), 1679-1689.

Haskin L. A., Gillis J. J., Korotev R. L., and Jolliff B. L. (2000) The materials of the lunar Procellarum KREEP Terrane: A synthesis of data from geomorphological mapping, remote sensing, and sample analyses. *Journal Of Geophysical Research-Planets* **105**(E8), 20403-20415.

Jacobsen S. B. (2005) The Hf-W isotopic system and the origin of the Earth and Moon. *Annual Review of Earth and Planetary Sciences* **33**, 531-570.

Jolliff B.L. (1998) Large-scale separation of K-frac and REEP-frac in the source regions of Apollo impact melt breccias, and a revised estimate of the KREEP composition. *Int. Geol. Rev.* **40**, 916-935.

Jolliff B. L., Gillis J. J., Haskin L. A., Korotev R. L., and Wieczorek M. A. (2000) Major lunar crustal terranes: Surface expressions and crust-mantle origins. *Journal Of Geophysical Research-Planets* **105**(E2), 4197-4216.

Jolliff B. L., Korotev R. L., Zeigler R. A., Floss C., and Anonymous. (2003) Northwest Africa 773; lunar mare breccia with a shallow-formed olivine-cumulate component, inferred very-low-Ti (VLT) heritage, and a KREEP connection. *Geochimica et Cosmochimica Acta* **67**(24), 4857-4879.

Joy K. H., Crawford A. J., Downes H., Russell S. S., and Kearsley A. (2006) A petrological, mineralogical, and chemical analysis of the lunar mare basalt meteorite LaPaz Icefield 02205, 02224, and 02226. *Meteoritics & Planetary Science* **41**(7), 1003-1025.

Kennedy A. K., Lofgren G. E., and Wasserburg G. J. (1993) An Experimental-Study of Trace-Element Partitioning between Olivine, Ortho-Pyroxene and Melt in Chondrules - Equilibrium Values and Kinetic Effects. *Earth and Planetary Science Letters* **115**(1-4), 177-195.

Kleine T., Münker C., Mezger K., and Palme H. (2002) Rapid accretion and early core formation on asteroids and the terrestrial planets from Hf-W chronometry. *Nature* **418**(6901), 952-955.

Kleine T., Palme H., Mezger K., and Halliday A. N. (2005) Hf-W chronometry of lunar metals and the age and early differentiation of the Moon. *Science* **310**, 1671-1674.

Korotev R. L. (2004) A unique chunk of the Moon. *Science* **305**(5684), 622-623.

Korotev R. L. (2005) Lunar geochemistry as told by lunar meteorites. *Chemie der Erde* **65**, 297-346.

Korotev R. L., Jolliff B. L., Zeigler R. A., Gillis J. J., Haskin L. A., and Anonymous. (2003) Feldspathic lunar meteorites and their implications for compositional remote sensing of the lunar surface and the composition of the lunar crust. *Geochimica et Cosmochimica Acta* **67**(24), 4895-4923.

Lawrence D. J., Elphic R. C., Feldman W. C., Prettyman T. H., Gasnault O., and Maurice S. (2003) Small-area thorium features on the lunar surface. *Journal Of Geophysical Research-Planets* **108**(E9).

Lawrence D. J., Feldman W. C., Barraclough B. L., Binder A. B., Elphic R. C., Maurice S., Miller M. C., and Prettyman T. H. (1999) High resolution measurements of absolute thorium abundances on the lunar surface. *Geophysical Research Letters* **26**(17), 2681-2684.

Lawrence D. J., Feldman W. C., Barraclough B. L., Binder A. B., Elphic R. C., Maurice S., Miller M. C., and Prettyman T. H. (2000) Thorium abundances on the lunar surface. *Journal Of Geophysical Research-Planets* **105**(E8), 20307-20331.

Lawrence D. J., Feldman W. C., Barraclough B. L., Binder A. B., Elphic R. C., Maurice S., and Thomsen D. R. (1998) Global Elemental Maps of the Moon: The Lunar Prospector Gamma-Ray Spectrometer. *Science* **281**, 1484-1489.

Lingenfelter R. E., Canfield E. H., and Hampel V. E. (1972) The lunar neutron flux revisited. *Earth and Planetary Science Letters* **16**(3), 355-369.

Lofgren G. E., Donaldson C. H., and Usselman T. M. (1975) Geology, petrology and crystallization of Apollo 15 quartz-normative basalts. *Proceedings of the Lunar Science Conference* **6th**, 79-99.

Longhi J. (1992) Experimental petrology and petrogenesis of mare volcanics. *Geochimica Et Cosmochimica Acta* **56**, 2235-2251.

Ludwig K. R. (1999) Isoplot 2.10. Berkeley Geochronology Center.

McKay G. A., Wagstaff J., and Yang S. R. (1986) Zirconium, hafnium and rare earth element partition coefficients for ilmenite and other minerals in high-Ti lunar mare basalts. *Journal of Geophysical Research* **91**, 229-237.

Merlet C. (1994) An Accurate Computer Correction Program for Quantitative Electron Probe Microanalysis. *Mikrochim. Acta* **114/115**, 363-376.

Nakamura Y., Fujimaki H., Nakamura N., Tatsumoto M., McKay G. A., and Wagstaff J. (1986) Hf, Zr, and REE partition coefficients between ilmenite and liquid: implications for lunar petrogenesis. *Journal of Geophysical Research* **91**(B4), D239-D250.

Neal C. R. (2001) Interior of the Moon: The presence of garnet in the primitive deep lunar mantle. *Journal of Geophysical Research* **106**(E11), 27865-27885.

Neal C. R., Hacker M. D., Taylor L. A., Schmitt R. A., and Liu Y.-G. (1994) Basalt generation at the Apollo 12 site, part 1: New data, classification, and re-evaluation. *Meteoritics* **29**(334-348).

Nishiizumi K., Hillegonds D. J., and Welten K. C. (2006) Exposure and terrestrial histories of lunar meteorites LAP 02205/02224/02226/02436, MET 01210, and PCA 02007 (abstract). *Lunar & Planetary Science Conference* **37th**, #2369 [CD-ROM].

Norman M. D., Garcia M. O., and Bennett V. C. (2004) Rhenium and chalcophile elements in basaltic glasses from Ko'olau and Moloka'i volcanoes: Magmatic outgassing and composition of the Hawaiian plume. *Geochimica Et Cosmochimica Acta* **68**(18), 3761-3777.

Norman M. D., Garcia M. O., and Pietruszka A. J. (2005) Trace-element distribution coefficients for pyroxenes, plagioclase, and olivine in evolved tholeiites from the 1955 eruption of Kilauea Volcano, Hawai'i, and petrogenesis of differentiated rift-zone lavas. *American Mineralogist* **90**, 888-899.

Nyquist L. E. (1977) Lunar Rb-Sr chronology. *Physics and Chemistry of the Earth* **10**, 103-142.

Nyquist L. E. and Shih C. Y. (1992) The isotopic record of lunar volcanism. *Geochimica et Cosmochimica Acta* **56**(6), 2213-2234.

Nyquist L. E., Shih C. Y., Reese Y., and Bogard D. E. (2005) Age of lunar meteorite LAP 02205 and implications for impact-sampling of planetary surfaces (abstract). *Lunar & Planetary Science Conference* **36th**, #1374 [CD-ROM].

Nyquist L. E., Wiesmann H., Bansal B., Shih C. Y., Keith J. E., and Harper C. L. (1995) ^{146}Sm-^{142}Nd formation interval for the lunar mantle. *Geochimica et Cosmochimica Acta* **59**(13), 2817-2837.

Podosek F. A., Zinner E. K., MacPherson G. J., Lundberg L. L., Brannon J. C., and Fahey A. J. (1991) Correlated study of initial ^{87}Sr/^{86}Sr and Al-Mg isotopic systematics and petrologic properties in a suite of refractory inclusions from the Allende Meteorite. *Geochimica et Cosmochimica Acta* **55**(4), 1083-1110.

Rankenburg K., Brandon A. D., and Neal C. R. (2006) Neodymium Isotope Evidence for a Chondritic Composition of the Moon. *Science* **312**, 1369-1372.

Righter K., Collins S. J., and Brandon A. D. (2005) Mineralogy and petrology of the LaPaz Icefield lunar mare basaltic meteorites. *Meteoritics and Planetary Science* **40**(11), 1703-1722.

Roedder E. and Weiblen P. W. (1970) Silicate Liquid Immiscibility In Lunar Magmas, Evidenced By Melt Inclusions In Lunar Rocks. *Science* **167**(3918), 641-&.

Ryder G. and Schuraytz. (2001) Chemical variation of the large Apollo 15 olivine-normative mare basalt rock samples. *Journal of Geophysical Research* **106**(E1), 1435-1451.

Satterwhite C. and Righter K. (2003) *Antarctic Meteorite Newsletter* **26**(2), 23.

Satterwhite C. and Righter K. (2004a) *Antarctic Meteorite Newsletter* **27**(3), 21.

Satterwhite C. and Righter K. (2004b) *Antarctic Meteorite Newsletter* **27**(1), 21.

Satterwhite C. and Righter K. (2006) *Antarctic Meteorite Newsletter* **29**(2), 21.

Shearer C. K. and Newsom H. E. (2000) W-Hf isotope abundances and the early origin and evolution of the Earth-Moon system. *Geochimica et Cosmochimica Acta* **64**(20), 3599-3613.

Shearer C. K., Hess P. C., Wieczorek M. A., Pritchard M. E., Parmentier E. M., Borg L. E., Longhi J., Elkins-Tanton L. T., Neal C. R., Antonenko I., Canup R. M., Halliday A., Grove T. L., Hager B. H., Lee D.-C., and Wiechert U. (2006) Chapter 4: Thermal and Magmatic Evolution of the Moon. In *New views of the Moon - Reviews in Mineralogy and Geochemistry*, Vol. 60 (ed. B. L. Jolliff, C. K. Wieczorek, C. K. Shearer, and C. R. Neal). Mineralogical Society of America.

Snyder G. A., Borg L. E., Taylor L. A., Nyquist L. E., and Halliday A. N. (1998) Volcanism in the Hadley-Apennine region of the Moon: Geochronology, Nd-Sr isotopic systematics, and depths of melting. *Lunar & Planetary Science Conference* **29th**, #1141 [CD-ROM].

Snyder G. A., Neal C. R., Taylor L. A., and Halliday A. N. (1997) Anatexis of lunar cumulate mantle in time and space: Clues from trace-element, strontium, and neodymium isotopic chemistry of parental Apollo12 basalts. *Geochimica Et Cosmochimica Acta* **61**(13), 2731-2747.

Snyder G. A., Taylor L. A., and Neal C. R. (1992) A chemical model for generating the sources of mare basalts: Combined equilibrium and fractional crystallization of the lunar magmasphere. *Geochimica Et Cosmochimica Acta* **56**, 3809-3823.

Spera F. J., Bohrson W. A., Niu Y., Herzberg C., and Wilson M. (2004) Open-system magma chamber evolution; an energy-constrained geochemical model incorporating the effects of concurrent eruption, recharge, variable assimilation and fractional crystallization (EC-E'RAXFC). *Journal of Petrology* **45**(12), 2459-2480.

Taylor G. J., Warren P. H., Ryder G., Delano J., Pieters C. M., and Lofgren G. E. (1991) Lunar Rocks. In *Lunar Sourcebook: A Users Guide to the Moon* (ed. G. H. Heiken, D. T. Vaniman, and B. M. French), pp. 183-284. Cambridge University Press.

Van Orman J. A., Grove T. L., and Shimizu N. (2001) Rare earth element diffusion in diopside: influence of temperature, pressure, and ionic radius, and an elastic model for diffusion in silicates. *Contributions to Mineralogy and Petrology* **141**(6), 687-703.

Warren P. H. (1985) The magma ocean concept and lunar evolution. *Annual Review of Earth and Planetary Sciences* **13**, 201-240.

Warren P.H. (1988) The origin of pristine KREEP: Effects of mixing between urKreep and the magmas parental to the Mg-suite cumulates. *Proceedings of the Lunar Science Conference* **18th**, 233-241.

Warren P. H. and Wasson J. T. (1979) The origin of KREEP. *Reviews of Geophysics and Space Physics* **17**, 73-88.

Wasserburg G. J., Jacobsen S. B., Depaolo D. J., McCulloch M. T., and Wen T. (1981) Precise determinations of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica Et Cosmochimica Acta* **45**(12), 2311-2323.

White W. M. and Patchett J. (1984) Hf-Nd-Sr Isotopes and Incompatible Element Abundances in Island Arcs - Implications for Magma Origins and Crust-Mantle Evolution. *Earth and Planetary Science Letters* **67**(2), 167-185.

Wieczorek M. A. and Phillips R. J. (2000) The "Procellarum KREEP Terrane": Implications for mare volcanism and lunar evolution. *Journal Of Geophysical Research-Planets* **105**(E8), 20417-20430.

Wieczorek M. A., Jolliff B. L., Khan A., Pritchard M. E., Weiss B. P., Williams J. G., Hood L. L., Righter K., Neal C. R., Shearer C. K., McCallum I. S., Tompkins S., Hawke B. R., Peterson C., Gillis J. J., and Bussey B. (2006) Chapter 3: The Constitution and Structure of the Lunar Interior. In *New views of the Moon - Reviews in Mineralogy and Geochemistry*, Vol. 60 (ed. B. L. Jolliff, C. K. Wieczorek, C. K. Shearer, and C. R. Neal). Mineralogical Society of America.

Yin Q., Jacobsen S. B., Yamashita K., Blichert-Toft J., Télouk P., and Albarède F. (2002) A short timescale for terrestrial planet formation from Hf-W chronometry of meteorites. *Nature* **418**, 949-952.

Zack T. and Brumm R. (1998) Ilmenite/liquid partition coefficients of 26 trace elements determined through ilmenite/clinopyroxene partitioning in garnet pyroxenite. *7th International Kimberlite Conference*, 986-988.

Zeigler R. A., Korotev R. L., Jolliff B. L., and Haskin L. A. (2005) Petrography and geochemistry of the LaPaz icefield basaltic lunar meteorite and source crater pairing with Northwest Africa 032. *Meteoritics and Planetary Science* **40**(7), 1073-1101.

Table 1: Results from EMPA major elements analyses of mineral separates of LAP 02205 compared to LAP 02205 whole rock data (Anand et al., 2006).

LAP 02205	whole rock Anand et al.	melt veins	plag	cpx Fe-rich	cpx Mg-rich	cpx (+ilm)	ilmenite
mean wt%		n=6	n=3	n=5	n=3	n=3	n=2
SiO_2	45.2	44.45	45.44	48.65	50.55	45.55	0.08
TiO_2	3.38	3.64	0.06	1.32	0.87	1.06	51.31
Al_2O_3	10.0	11.89	32.91	2.04	2.19	1.21	0.13
Cr_2O_3	0.19	0.23	0.01	0.51	0.82	0.03	0.12
FeO	23.2	20.76	0.62	22.53	17.86	39.83	44.86
MnO	0.23	0.25	0.01	0.35	0.34	0.50	0.38
MgO	5.99	5.64	0.23	12.25	17.43	1.59	0.05
CaO	11.2	11.35	17.20	11.22	9.58	9.17	0.05
Na_2O	0.33	0.43	1.12	0.03	0.03	0.03	0.01
K_2O	0.11	0.13	0.06	0.00	0.00	0.00	0.00
Total	100.00	98.76	97.67	98.91	99.68	98.99	96.98
mg#	0.31	0.33		0.49	0.63	0.07	

Table 1 cont.: Results from LA-ICP-MS trace elements analyses of mineral separates of LAP 02205 compared to whole rock data for LAP 02205 (Anand et al., 2006). n.m.: not measured.

LAP 02205	whole rock	melt veins	plag	cpx	cpx	ilm	ilm	ilm
	Anand et al.			Fe-rich	Fe-poor	A	B	C
mean ppm		n=3	n=5	n=4	n=6		(+ incl.)	(+ incl.)
Li	11.7	12	25	8	5	<2.8	5.6	n.m.
Sc	58.6	53	1.8	111	98	21.6	12.7	n.m.
V	129.0	91	2.3	221	242	498	299	n.m.
Cr	1300	1743	9	3900	3865	18526	10802	n.m.
Co	37.3	38	1.3	51	39	211	92.2	n.m.
Ni	27.6	34	1.6	19	18	77	9	n.m.
Cu	n.m.	13	0.5	5	3	7	11	n.m.
Zn	n.m.	3	0.4	3	3	36.6	34.4	n.m.
Ga	n.m.	20	11	2	1	17.6	51.7	n.m.
Rb	2.1	1.5	<0.2	<0.1	<0.08	<0.24	32	<4.3
Sr	135.3	140	251	3.9	3.9	-	63	352
Y	73.2	53	0.29	19	18	0.63	212	3818
Zr	200.3	177	<0.04	13	14	592	2328	3176
Nb	14.7	13	<0.02	0.07	0.08	50.9	268	19
Ba	164.7	147	33	0.23	0.08	0.2	225	92
La	13.40	11	0.34	0.33	0.30	0.11	91.5	68.4
Ce	37.31	30	0.79	1.4	1.4	0.08	221	305
Pr	5.15	4.1	0.09	0.29	0.29	0.02	31.2	68.3
Nd	25.12	20	0.41	2.1	2.0	0.17	152	450
Sm	7.56	6.3	0.18	1.2	1.0	<0.14	40.7	235
Eu	1.24	1.2	1.44	0.08	0.08	<0.03	1.61	12.1
Gd	9.95	7.9	0.13	2.2	2.0	<0.02	6.65	417
Tb	1.93	1.4	<0.02	0.44	0.41	<0.1	48.6	84
Dy	12.08	9.7	<0.1	3.2	3.0	<0.1	41.7	663
Ho	2.45	2.1	<0.02	0.73	0.70	<0.02	7.82	151
Er	6.71	6.0	<0.06	2.2	2.1	<0.06	19.2	457
Yb	6.37	5.7	<0.1	2.2	2.1	0.151	11.8	515
Lu	0.88	0.79	<0.03	0.35	0.31	<0.02	1.6	81.1
Hf	5.39	4.5	<0.09	0.63	0.65	11.2	55.8	128
Ta	0.77	0.64	<0.03	<0.02	<0.02	1.9	12	0.63
Th	2.33	1.9	<0.04	<0.02	<0.01	<0.03	15.7	4.96
U	0.55	0.43	<0.03	<0.02	<0.01	0.038	4.33	2.18