

ILMENITE PARTITIONING REVISITED: CONFIRMATION OF ZIRCONIUM RESULTS FOR HIGH-Ti MARE BASALTS. G. McKay (SN4, NASA-JSC, Houston, TX 77058) and J. Wagstaff (Lockheed, 1830 NASA Rd. 1. Houston, TX 77258).

Introduction. Because of large differences in distribution coefficients, the Lu-Hf isotopic system is particularly sensitive to ilmenite fractionation, and hence is potentially of great value in constraining the chronology and nature of events leading to the formation of high-Ti lunar mare basalts and KREEP-rich, Ti-depleted late-stage liquids residual to the primary lunar differentiation. Last year, in collaboration with the Denver isotope group, we initiated a study of the partitioning of Lu, Hf, Zr, and other REE, between ilmenite and mare basalt melts to provide basic partitioning data for application to mare basalt petrogenesis. Synthetic melts were held at appropriate temperatures for growth of a few per cent ilmenite. Crystals and glass were analyzed in situ by electron microprobe, and as mineral separates by isotope dilution. Initial results were reported at the Fifteenth LPSC [1,2].

These initial results were marred by an apparent disagreement between the two analytical techniques. For example, the value obtained for $D(\text{Zr, IL/L})$ from electron microprobe analyses was 0.4, vs. 0.8 as measured from mineral separates by isotope dilution [1,2]. We believe this apparent disagreement resulted from the nature of the materials subjected to mineral separation procedures. As a result of inadequate control of Fe loss, some experimental charges crystallized armalcolite in addition to ilmenite. The mineral separation techniques [2,3] do not separate ilmenite from armalcolite. Hence we proposed [1] that the mineral separates actually consisted of mixtures of these two minerals. Because armalcolite has a much higher value for $D(\text{Zr})$ than ilmenite (1.2 vs. 0.4, [1]) the separates yielded an intermediate value of 0.8. Moreover, we proposed orally that the skeletal crystals which formed in last year's experiments as a result of cooling from above the liquidus contained glass inclusions which produced artificially high apparent D values for the LREE. Unfortunately, we did not retain any chips from the charges from which mineral separates were obtained, and the separates were completely consumed by the analyses, so that it is not possible to directly confirm this proposition.

To remove any resulting uncertainty regarding these important distribution coefficients, we have performed experiments under conditions producing only ilmenite and glass. Results from these experiments are reported here and in the companion abstract by the Denver group [3].

Experimental. Loss of Fe to Pt sample containers is an important factor in the relative stabilities of armalcolite and ilmenite in experimental runs. The decrease in melt Fe/Ti resulting from Fe loss promotes crystallization of armalcolite at the expense of ilmenite. Experiments indicated that under our run conditions, quenched glasses with more than 18% FeO contained only ilmenite, while glasses with less than 18% FeO also contained armalcolite. By using Pt suspension loops onto which 3±.5mg was electroplated, we successfully controlled Fe loss and consistently produced charges yielding glass with about 21% FeO, and with ilmenite as the only crystalline phase.

Experimental starting material consisted of synthetic glass (composition: $\text{SiO}_2=38.6$; $\text{TiO}_2=11.9$; $\text{Al}_2\text{O}_3=9.5$; $\text{Cr}_2\text{O}_3=0.2$; $\text{FeO}=23.89$; $\text{MnO}=0.56$; $\text{MgO}=5.4$; $\text{CaO}=9.2$; $\text{Na}_2\text{O}=0.35$; $\text{K}_2\text{O}=0.17$, in wt.%) spiked with 50-100 ppm of several REE and Hf, and with 500-1000 ppm of Zr. Beads of this starting material were suspended on Fe-plated Pt loops in a gas mixing furnace at 1125°C and $f\text{O}_2$ of $10^{-11.7}$, 0.5 log units above IW, held for 2-4 days, and air quenched.

The resulting charges were coarsely crushed, and 1 or 2 1mm chips from each charge were mounted for microprobe analysis. After verification of proper run products (see below), the remaining material from each run was sent to Denver for mineral separation and ID analysis.

Results. Run products consisted of ~90% glass (typical composition: $\text{SiO}_2=43.5$; $\text{TiO}_2=8.6$; $\text{Al}_2\text{O}_3=10.7$; $\text{Cr}_2\text{O}_3=.14$; $\text{FeO}=20.5$; $\text{MnO}=0.56$; $\text{MgO}=5.3$; $\text{CaO}=10.2$; $\text{Na}_2\text{O}=0.42$; $\text{K}_2\text{O}=0.20$), and ~10% ilmenite (typical composition: $\text{TiO}_2=54.9$; $\text{Al}_2\text{O}_3=0.44$; $\text{Cr}_2\text{O}_3=1.6$; $\text{FeO}=37.9$; $\text{MnO}=0.70$; $\text{MgO}=5.3$; $\text{CaO}=0.20$). Ilmenite occurs as euhedral crystals 10-80 μm in size. Vertical sections through charges show strong effects of crystal settling, with ilmenite concentrated in the lower portion of the charge, and almost absent from the upper region. In contrast to the skeletal ilmenites from last year's runs [1], crystals from the current series of runs are euhedral, and do not appear to contain inclusions of glass. Thus LREE D values from this year's ilmenite separates [3] are much less likely to be artificially high because of glass inclusions.

A high-sensitivity microprobe technique involving repeated wavelength profiling across characteristic x-ray peaks [4] and fitting of background spectra obtained on trace-element "free" samples was used to measure abundances of Zr, Hf, Lu, and Gd in glass, ilmenite, armalcolite, pigeonite, spinel, and olivine in charges from last year's per cent level experiments [1], of Zr in glass and ilmenite in charges from this year's lower concentration experiments. (Last year's experiments produced armalcolite, spinel, and pigeonite as a result of substantial Fe loss.) Resulting distribution coefficient values are shown in Table 1. Some of these results were reported in [1], some were only reported orally at the 15th LPSC, and some are previously unreported.

Conclusions. (1) Excellent agreement between the 1985 and 1986 microprobe values for $D(\text{Zr,IL/L})$ indicates that the differences in experimental techniques have no important effects on partitioning behavior. (2) Good agreement between microprobe and new ID results for ilmenite [3], including downward revision of the ID values for Zr and LREE, strongly supports our hypothesis that last year's ID results were affected by the presence of armalcolite and glass inclusions in the ilmenite separates. New experimental techniques have avoided this problem, and permitted separation of much higher purity ilmenite. (3) D values reported in Table 1 and in [3] represent the best values currently available for high-Ti mare basalt petrogenesis. (4) One remaining unresolved issue is the difference between microprobe and ID results for $D(\text{Zr/Hf})$.

Table 1. Crystal/liquid weight ratio partition coefficients. Uncertainties correspond to the last figure, and represent the larger of the standard deviation of the mean of replicate measurements, or the uncertainty contributed by x-ray counting statistics.

Mineral:	Hf	Zr(1984)	Zr(1985)	Lu	Gd
Ilmenite	0.40+3	0.38+2	0.40+1	0.085+3	0.006+1
Armalcolite	1.45+1	1.24+2		0.045+3	0.006+1
Pigeonite	0.05+1				
Spinel	0.81+7	0.55+3			
Olivine				0.25+5	

References. [1] McKay G. and Wagstaff J. (1984) *PLPSC XV*, 532. [2] Fujimaki H. and Tatsumoto M. (1984) *PLPSC XV*, 282. [3] Tatsumoto et al. (1985) This volume. [4] Miyamoto et al. (1985) *Abs. 47th Ann. Mtg. Met. Soc.*, in press.