APOLLO SAMPLE 12032,366-18: CHARACTERIZATION AND EXPERIMENTAL INVESTIGATION OF A CHEMICALLY EVOLVED LUNAR BASALT.
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Introduction: We examine an Apollo 12 basaltic soil fragment that is unlike other Apollo 12 basalts [1, 2]. Sample 12032,366-18 is enriched in Th (7 ppm) and other incompatible elements compared to other mare basalts [1]. Barra et al. found that 123032,366-18 has a minimum crystallization age of 2.3 Ga, and a disturbance age of 500–700 Ma [3]. For these reasons, it may be a sample of basalt delivered by impact from western Oceanus Procellarum [1]. This lithology has a subophitic texture and regions of Si+K-rich mesostasis that may have formed by silicate liquid immiscibility (SLI). We seek to determine if the bulk composition of 12032,366-18 is representative of its parent magma, how the residual melt evolved as the melt crystallized, whether or not immiscible liquids were involved in the formation of 12032,366-18, and if so how did minor and trace elements partition between these liquids.

We addressed these questions using the bulk chemistry and in-situ mineral chemistry of the lunar sample, and by performing petrologic experiments to observe the chemical evolution of the residual melt.

Methods: The sample was irradiated and analyzed by instrumental neutron activation analysis (INAA) to determine its bulk concentrations for some elements (including Fe, Ca, Ba, Na, K, Zr) [1]. The sample was sawn in two, one half mounted in epoxy & polished for electron probe microanalysis (EPMA). The bulk composition of 12032,366-18 was estimated using modal recombination, constrained to match the elements determined for the bulk sample by INAA (Table 1).

The bulk composition of 12032,366-18 was used as the starting composition for five melting and crystallization experiments in a 1 atm vertical gas mixing furnace. These non-isothermal cooling experiments descended in temperature, from 1106 °C to 975 °C (Table 2). The 1106 °C began with the bulk composition of 12032,366-18, but the 1050 °C experiment started with the composition of the glass in the 1106 °C charge. The remaining experiments, at 1030 °C, 1002 °C, and 975 °C, each used the glass from the 1050 °C charge.

Using phase compositions obtained by EPMA, we used an isometric log-ratio transform algorithm, Log-ratio Inversion of Mixed Endmembers (LIME), to determine phase proportions [4].

Oxide	wt.%
SiO$_2$	44.3
TiO$_2$	4.22
Al$_2$O$_3$	11.7
Cr$_2$O$_3$	0.22
FeO	19.5
MnO	0.26
MgO	7.2
CaO	11.5
BaO	0.056
Na$_2$O	0.69
K$_2$O	0.25
P$_2$O$_5$	0.28
ZrO$_2$	0.08
Total	100.3

Table 1: Bulk composition of 12032,366-18.

Results: We first present results from characterization of the sample 12032,366-18. Following this, we report on the petrologic experiments mimicking the fractional crystallization of the magma from which 12032,366-18 formed.

Characterization of 12032,366-18. The sample 12032,366-18 contains zoned plagioclase (An$_{90-60}$), zoned pyroxene (from ~En$_{42}$Fs$_{20}$Wo$_{38}$ to ~En$_{15}$Fs$_{75-}$Wo$_{10}$), Fe-rich olivine (Fo$_{38-16}$), ilmenite, titanian chromite, chromian ulvöspinel, and mesostasis regions containing minor phases Ba-K-feldspar, silica, rare-earth-merrillite (RE-merrillite), apatite, zircon, and troilite. In addition, the mesostasis regions contain the most sodic plagioclase (An$_{54-57}$).

Petrologic experiments. We performed five petrologic experiments, starting with the bulk composition of the sample 12032,366-18 (Table 1). These experiments exhibited a total of eight unique minerals and either residual liquid or immiscible residual liquids (Table 2).

The crystallization sequence begins with olivine of an intermediate composition (Fo$_{45-46}$), olivine disappeared as a crystallizing phase in the 1030 °C charge, then reappeared as fayalitic compositions (Fo$_{11}$ and Fo$_5$ in the 1002 °C and 975 °C charges, respectively). The An content of plagioclase steadily decreased with decreasing temperature (An$_{85-81}$ at 1106 °C to An$_{73-64}$ at 975 °C) and the range of compositions in a given experiment increased with lower temperatures. The pyroxene composition started at ~En$_{42}$Wo$_{35}$Fs$_{23}$ at 1106 °C. With lower temperatures pyroxene compositions became more variable and less magnesian. At 975 °C, pyroxene had compositions of En$_{<21}$, with Wo$_{15-37}$ and Fs$_{49-79}$.

T (°C)	t (hr)	Resulting Phases (Calculated Mode)	PC
1106	22	olv (9.4) + plag (12.9) + pyx (10.4) + sp (tr) + liq (67.3)	32.7
1050	96	olv (2.1) + plag (2.1) + pyx (24.4) + ilm (5.3) + liq (66.0)	55.6
1030	140	plag (1.1) + pyx (2.9) + ilm (1.4) + sil (1.2) + metal (tr) + liq (93.3)	58.6
1002	192	olv (10.6) + plag (17.1) + pyx (16.2) + ilm (5.0) + sil (6.8) + merr (1.4) + Lfe (17.0) + Lsi (26.1)	80.9
975	163	olv (8.9) + plag (23.9) + pyx (34.3) + ilm (5.2) + sil (9.0) + merr (2.1) + bdy (tr) + Lfe (7.1) + Lsi (10.5)	92.2

Table 2: *Experimental charges, with final temperature (T), duration (t), phases present and their mode, and the system's percentage crystallized (PC) after each step. Abbreviations: olv: olivine; plag: plagioclase; pyx: pyroxene; sp: spinel; liq: residual liquid/glass; ilm: ilmenite; sil: silica; metal: iron metal; merr: merrillite; Lfe: iron-enriched liquid; Lsi: silica-enriched liquid; bdy: baddeleyite; tr: trace, not included in LIME calculation.*

Chromian ulvöspinel was only present in the first, 1106 °C experiment, and ilmenite was present in the last four experiments (1050 °C to 975 °C). A silica phase was present in experiments at and lower than 1030 °C. At 1002 °C and 975 °C, merrillite was present in the experimental charge. Baddeleyite was present in the lowest temperature charge, 975 °C. Two liquids (one Fe-rich, Lfe, and one Si-rich, Lsi) were present in the 1002 °C and 975 °C experiments (Figure 2). Lsi is rich in Si, Al, Na, and K, whereas Lfe is rich in Ti, Fe, Mn, Mg, Ca, P, and Zr. Barium partitioned roughly equally between Lfe and Lsi, slightly favoring Lfe at 1002 °C, but slightly favoring Lsi at 975 °C.

Discussion: The petrologic experiments suggest that the sample 12032,366-18 underwent SLI. The timing of phosphate saturation and onset of SLI occurred in the same window between the 1030 °C and 1002 °C experiments, so we cannot constrain which process occurred first. Typical mare basalts undergo SLI at ≥85% crystallized [5–7], but we observed SLI in our experiments at just 80% crystallized (Table 2). The petrologic experiments imply that the sample may have undergone SLI at a lower percent crystallized as well.

The progression of major phase compositions in the experiments match that of the zoning and ranges found in 12032,366-18, indicating that our experiments are reasonable analogs to the lunar basalt. Furthermore, the high incompatible trace-element content of 12032,366-18 is anomalous compared to other mare basalt samples [1]. Even though it is enriched in incompatible elements, it is not a KREEP basalt because it is not sufficiently enriched in those indicator elements (Figure 3). Combined, these two characteristics suggest that 12032,366-18 may represent a composition not previously identified at any of the Apollo landing sites.

Comparing to remote sensing data for Th [9], 12032,366-18 may represent a basalt from western Oceanus Procellarum, owing to its Th-rich composition [1] and young age [3], perhaps delivered to the Apollo 12 site via an impact occurring sometime 500–700 Ma [1]. It will be interesting to compare this sample with those collected by the Chang'e-5 mission.

References: [1] Jolliff B. L. et al. (2005) *LPSC XXXV*, #2357 [2] Neal C. R. et al. (1994) *Meteoritics, 29*, 3, 334–348. [3] Barra F et al. (2006) *Geoch. Cosmoch. Acta 70*, 24, 6016–6031. [4] Krawczynski M. J. and Olive J. L. (2011) *AGU Fall Mtg.*, Abstract V53B-2613. [5] Roedder E. and Weiblen P. W. (1970) *Science 167*, 641 LP – 644. [6] Rutherford M. J. et al. (1974) *LPSC V*, 569–583. [7] Pernet-Fisher J. F. et al. (2014) *Geoch. Cosmoch. Acta 144*, 326–341. [8] Snape J. F. et al. (2014) *Meteoritics & Planet. Sci. 49*, 5, 842–871 [9] Lawrence D. J. et al. (2000) *J. Geophys. Res. 105*, 20307–20331. [10] Warren P. H. (1989) *Worksh. on Moon in Transition*, 149–153.
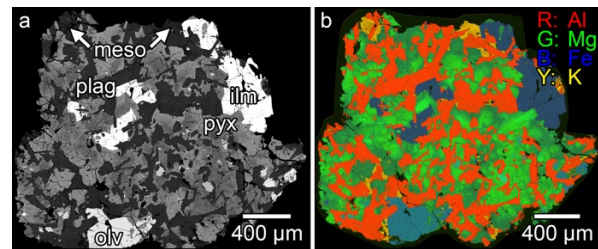

Figure 1: *(a) Backscattered electron (BSE) image showing the crystalline, non-vesicular, medium grained, subophitic, texture dominated by clinopyroxene (50% by weight) and plagioclase (33%), with relatively coarse ilmenite grains (7%). Olivine (8%) is found as a large grain (labelled) and small grains intergrown with pyroxene and plagioclase (pyroxene and olivine in reaction relationship). Areas of silica-rich mesostasis are noted by arrows and appear gold in the X-ray composite. (b) X-ray composite, with Al in red, Mg in green, Fe in blue, and K in yellow. Abbreviations: meso: mesostasis; plag: plagioclase; ilm: ilmenite; pyx: pyroxene; olv: olivine.*
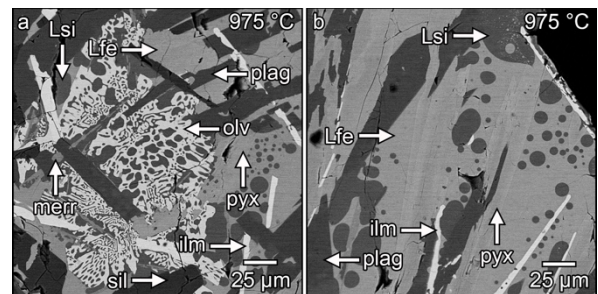

Figure 2: *BSE images of the lowest-T experimental charges. Abbreviations: olv: olivine; plag: plagioclase; pyx: pyroxene; ilm: ilmenite; sil: silica; Lsi: silica-rich liquid; Lfe: iron-rich liquid; merr: merrillite.*
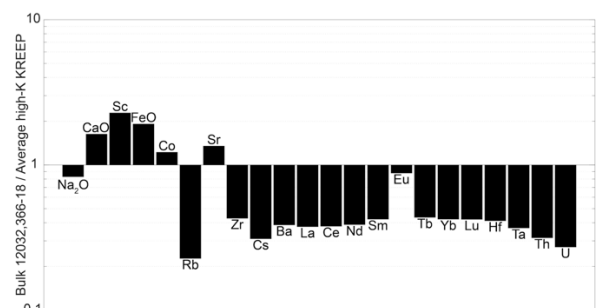

Figure 3: *Ratio of bulk elemental concentrations in 12032,366-18 to that of average high-K KREEP (enriched in K, REE, P). Concentrations for 12032,366-18 come from INAA data; KREEP composition from [10].*