



	Experiment title: <i>In situ</i> study of the density and structure of primitive lunar melts at high pressure and temperatures	Experiment number: HD151
Beamline:	Date of experiment: from: 12/06/2007 to: 16/06/2007	Date of report: January 24, 2008
Shifts:	Local contact(s): J-P Perrillat and M. Mezouar	<i>Received at ESRF:</i>

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Introduction: Accurate knowledge of the density of lunar materials at high pressures and temperatures is critical for models of the dynamic evolution of the interior of the Moon. Lunar silicate magma density variations during crystallisation of a lunar magma ocean are particularly important, as formation of both plagioclase-rich highland rocks and mare basalts are ultimately linked to density differences between lunar magma and co-existing minerals. To date, densities of lunar melts have only been determined using indirect quench methods [1,2]. Here we introduce a X-ray absorption technique, initially developed by Katayama [3] for work on *metallic* melts, to determine the density of silicate magma *in situ*. Preliminary density measurement experiments using a synthetic equivalent of Apollo 14 black glass [4], performed during beamtime HD151, are presented here along with subsequent detailed microscopic analysis of recovered samples. Our results show that this technique can indeed be used to obtain *in situ* silicate magma densities. We also provide details of several minor adjustments to the experimental procedures that will significantly improve our ability to expand the lunar magma density database to wider pressure, temperature and compositional ranges in future experiments.

Experimental techniques: Eight *in situ* experiments were conducted at beamline ID 27, using X-ray absorption in the toroidal Paris-Edinburgh cell. Starting material was packed in CVD diamond cylinders (inner diameter: 0.5 mm) with graphite end caps. Diamond cylinders, chosen because it is a low absorbing, incompressible material, were surrounded by other low-Z materials (hexagonal boron nitride sleeves, graphite furnace and boron epoxy pressure medium) to maximise X-ray throughput (Fig. 1, [5]).

Samples were first pressurized followed by stepwise heating. During pressurisation and heating, angle-dispersive X-ray diffraction patterns of both samples and calibrants were obtained. A monochromatic beam (33 KeV, I k-edge, $\lambda = 0.3738 \text{ \AA}$ for the 1st experiment and 20 KeV, Mo k-edge, $\lambda = 0.6199 \text{ \AA}$ for experiments 2-8). Pressure-temperature conditions were calculated offline by combining X-ray diffraction measurements of the unit-cell volumes of hBN, MgO, and/or Pt calibrants with equation-of-state parameters. The crystalline vs. molten state of the sample was assessed by monitoring angle-dispersive X-ray diffraction patterns. An example of the evolution of diffraction patterns during temperature increase is shown in the left

panel of Fig. 2. After the disappearance of sample diffraction peaks and appearance of the diffuse scattering signal of the liquid, X-ray absorption across the sample was measured (Fig. 2, right panel). Pressure-temperature conditions were determined from the unit-cell volumes of the internal calibrants using the equations of state of [6-8].

To calculate the density of the molten black glass, the Beer-Lambert law was fit to the near-parabolic absorption scans [5], giving values for the product $\mu_{\text{liq}}\rho_{\text{liq}}$. The constant mass absorption coefficient μ_{liq} was derived at room conditions, from a free standing sample, using the calculated density of the sample at room conditions [9-12], 3.78 g/cm^3 . Major element compositions of selected recovered run products were obtained using a JEOL JXA 8800M electron microprobe at the VU University Amsterdam. The boron content of selected run products was measured on Ag-coated samples at IOM (University of New Mexico, Albuquerque).

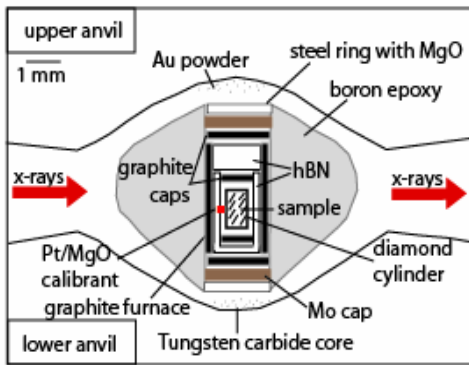


Figure 1. Experimental set-up (adapted from [5])

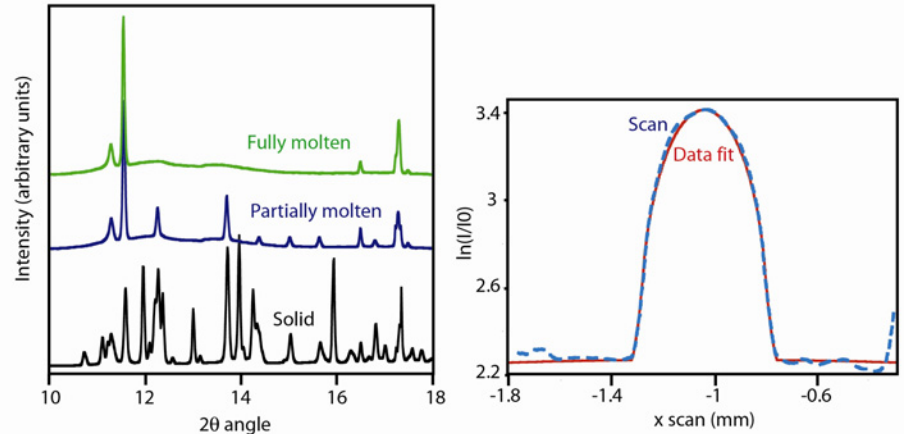


Figure 2: Left panel: Typical sequence of X-ray diffraction spectra upon progressive heating, showing disappearance of sample mineral reflections. In fully molten spectrum, only peaks from the hBN sleeve surrounding the diamond sample capsule remain. Right panel: Dotted line: measured absorption scan; solid line: model fit.

Results: Table 1 summarises the pressure-temperature conditions for experiments in which X-ray diffraction patterns indicated total melting had occurred, and shows sample densities calculated from fits to absorption scans. The uncertainty in μ_{liq} introduces an error of $\pm 0.10 \text{ g/cm}^3$ in the determination of these density values. Experimental temperatures are compared to liquidus temperatures of Apollo 14 black glass at the corresponding sample pressure [4].

Discussion: Our results highlight several solvable experimental problems. Table 1 illustrates two main issues. First, although the eventual disappearance of sample diffraction peaks (Fig. 1) suggested all samples reached superliquidus conditions, in several experiments (e.g. 6, 7) subsequent PT calibrant calculations indicate subliquidus conditions when compared with the published liquidus of black glass [4].

Exp. No.	Density (g/cm^3)	Previously reported density values (g/cm^3) (at similar P, T conditions)	P (GPa)	T (K)	T _{liq} at P	Heating duration before melting (minutes)	total
2-1	3.64	< 3.26 @ 2.5GPa, 1758 K	2.45	1783	1758	177	
2-2	3.75	< 3.25 @ 2.0GPa, 1738K	2.31	1552	1746		
2-3b	3.61		2.33	1700	1750		
5-3*	3.15	3.65 @ 5.5GPa, 2073K	5.17	2241	?	122	
5-4*	3.10	> 3.64 @ 5.0GPa, 2048K	5.08	2241	?		
5-5*	3.08		4.95	2211	?		
5-6*	3.03		4.95	2224	?		
5-7*	2.89	> 3.62 @ 4.0GPa, 1983K	4.32	2109	?		
6-2	3.42		1.6	1478	1711	36	
6-3	3.10		1.64	1576	1715		
6-4	3.06	3.30 @ 1.5GPa, 1707K	1.46	1610	1703		
6-5*	3.16		1.41	1492	1698		
7-1*	3.00	> 3.22 @ 1.0GPa, 1688K	0.99	1384	1683	103	
7-2*	2.93		0.87	1406	1678		
8-1	3.55		1.54	1593	1709	61	
8-2	3.29	3.30 @ 1.5GPa, 1707 K	1.68	1755	1717		
8-3	3.32		1.46	1664	1703		

Table 1. Experimental pressure-temperature conditions (calculated using BN and Pt, or BN and MgO (*) calibrants), and measured density at these conditions. Liquidus temperatures at calculated pressures taken from [4]. Time (in minutes) from start of heating until total melting was observed from the diffraction patterns is given in final column. Previously reported values are from [1], obtained using sink/float quench experiments. Signs > and < denote magma density was larger or smaller than that of a mineral sphere of known density in these quench experiments, respectively.

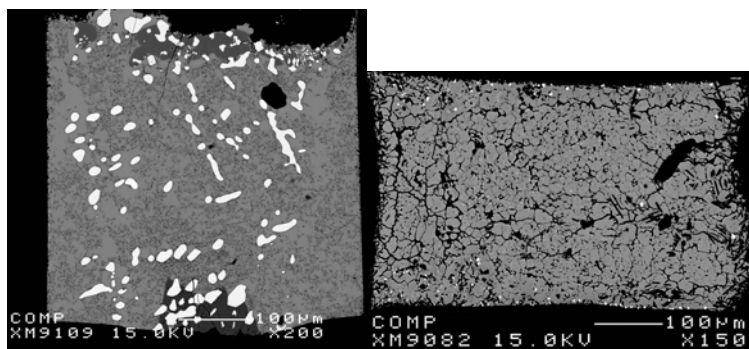


Figure 3. BSE images of experiment 1 (left) and 8 (right). Left image shows white ilmenite crystals in a glassy matrix. Right image shows glass with minor graphite laths and < 1 vol% micron-sized Fe crystals indicating minor sample reduction.

Microprobe glass totals for these samples range from 88 to 98 wt%. Subsequent analyses showed these samples were contaminated with up to 10 wt% of B₂O₃, derived from the hBN sleeves surrounding the diamond cylinder and graphite end caps. The lowering of the sample liquidus by addition of the light element B explains (1) why fully molten samples were formed at conditions far below the well-constrained black glass liquidus (2) why measured densities are significantly below previously published values from quench experiments. The unexpectedly low densities measured for experiment 5 (a sample that was not recovered) must also be a result of such B contamination. Clearly B contamination is a bigger problem in silicate magma density measurements than in the metal density measurements that our setup was successfully used for in the past. A simple remedy for this problem is to enlarge the graphite end caps that separate sample from hBN (Figure 1) in future experiments.

Second, several run products contain non-trivial amounts of rounded ilmenite crystals (Fig. 3). These were formed in the subliquidus field during heating of the samples. Ostensibly dissolution of these crystals is slow on the timescale of these synchrotron experiments (0.5-3 hrs, see Table 1). In future experiments, time spent at subliquidus temperatures should be minimised to prevent crystal nucleation and growth.

In experiment 8 (right panel Fig. 3) these problems were absent. Experiment 8-2 in particular has calculated PT conditions above the published liquidus, the recovered sample is free of ilmenite, and there is no evidence for B contamination (microprobe total 100.5 wt%). The measured density in this case should reflect a true *in situ* magma density value. The calculated density value of 8-2 (3.29 g/cm³) lies within error of the previously reported quench technique at very similar P-T conditions (3.30 g/cm³) [1]. This proves that our technique is suitable for *in situ* measurements of silicate magma density.

A final issue is the use of multiple calibrants to constrain both pressure and temperature in the experiments. Pressure-temperature conditions were derived from simultaneous volume determination for the calibrants, using the equations of state of BN and Pt or BN and MgO. The main problem here was the uncertainty of the equations of states themselves. Using the average literature values [7] for MgO, the difference between BN- Pt and BN-MgO stayed smallest, with a maximum of 300 K and 0.4 GPa difference. In future experiments we strongly advise using a thermocouple to measure sample temperatures. This will minimise the uncertainty in pressure-temperature conditions, and will avoid having to depend completely on equations of state for both P and T. Thermocouples have been used in conjunction with this assembly in the past, so this adjustment will not require additional development.

Summary and outlook: We have successfully obtained the first *in situ* density measurements of lunar silicate magma. In a next set of experiments the contamination and disequilibrium effects we identified can easily be solved by slightly adjusting the cell assembly and heating trajectory, and by adding a thermocouple to the assembly. Our study highlights the necessity of sample recovery and characterization after *in situ* studies to exclude contamination issues that cannot be identified from *in situ* observations.

A follow-up study to complete our data set of lunar magma densities is highly anticipated. The results presented here have put us in pole position to do so.

References: [1] Circone and Agee (1996) *GCA* 60, 2709. [2] Smith and Agee (1997) *GCA* 61, 2139. [3] Katayama (1996) *High Pressure research* 14, 383. [4] Wagner and Grove (1997) *GCA* 61, 1315. [5] Sanloup et al. (2000) *GRL* 27, 811. [6] Zhao et al. (1997) *HPR* 15, 369. [7] Dewaele et al. (2000) *JGR* 105, 2869. [8] Fei et al. (2004) *PEPI* 143, 515. [9] Lange and Carmichael (1990) *Reviews Mineral.* 24, 25. [10] Lange (1997), *Contrib. Min. Petr.* 130, 1. [11] Ochs and Lange (1999) *Science*, 283, 1314. [12] Liu and Lange (2006) *Am. Mineral.* 91, 385.