DEVELOPMENT OF AN *IN-SITU* X-RAY ABSORPTION TECHNIQUE TO MEASURE LUNAR MAGMA DENSITIES AT HIGH PRESSURE. M. van Kan[1], C. Sanloup[2], E. J. Tronche[1], JP. Perrillat[3], M. Mezouar[3], C. B. Agee[4], W. van Westrenen[1], [1]Faculty of Earth and Life Sciences, VU University Amsterdam, The Netherlands, Mirjam.van.kan@falw.vu.nl, [2]Laboratoire MAGIE, University Paris-6, France, [3]ESRF, Grenoble, France, [4] Institute of Meteoritics, UNM, Albuquerque, USA.

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 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], to determine the density of silicate magma *in situ*. Preliminary density measurements of a synthetic equivalent of Apollo 14 black glass [4] are presented. Our study shows this technique can be used to construct a comprehensive data set describing density variations in lunar magmas as a function of pressure, temperature, and composition.

Methods: Starting materials were packed into CVD diamond cylinders (inner diameter: 0.5 mm) with graphite end caps. Diamond cylinders were surrounded by low-Z materials (hexagonal boron nitride sleeves, graphite furnace and boron epoxy pressure medium) to maximise X-ray throughput (Fig. 1, [5]). *In situ* measurements were conducted at beamline ID27 of the European Synchrotron Radiation Facility (ESRF) using a toroidal Paris-Edinburgh cell [6]. 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.
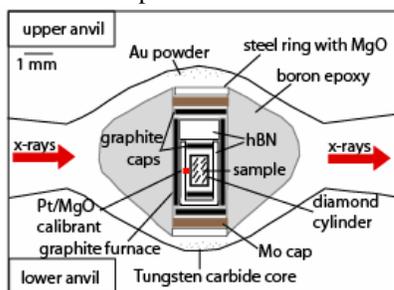

Figure 1. Experimental set-up (adapted from [5])

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 top 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, bottom panel). 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 $\mu_{liq}\rho_{liq}$. The constant mass absorption coefficient μ_{liq} was derived using the calculated density of the sample at room conditions [7-10], 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).
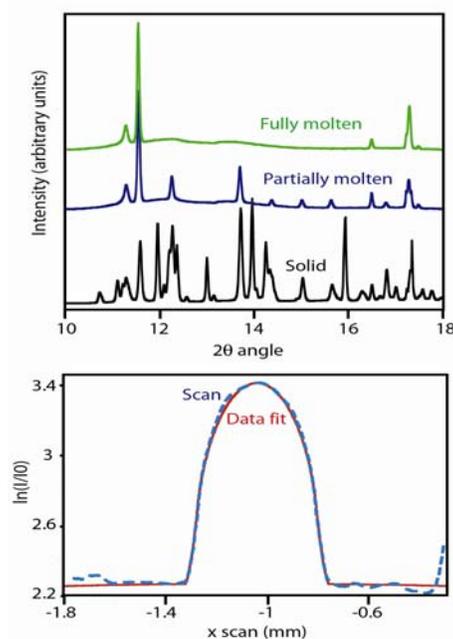

Figure 2. Top panel: Typical sequence of X-ray diffraction spectra upon progressive heating, showing disappearance of sample mineral reflections. In fully molten spectrum, only peaks from the hBN sleeve surrounding the diamond sample capsule remain. Bottom panel: Dotted line: measured absorption scan;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

Exp. No.	Density (g/cm^3)	P (GPa)	T (K)	Tliq at P	Melt t_{min}
2-1	3.64	2.45	1783	1758	177
2-2	3.75	2.31	1552	1746	
2-3b	3.61	2.33	1700	1750	
5-3*	3.15	5.17	2241	?	122
5-4*	3.10	5.08	2241	?	
5-5*	3.08	4.95	2211	?	
5-6*	3.03	4.95	2224	?	
5-7*	2.89	4.32	2109	?	
6-2	3.42	1.6	1478	1711	36
6-3	3.10	1.64	1576	1715	
6-4	3.06	1.46	1610	1703	
6-5*	3.16	1.41	1492	1698	
7-1*	3.00	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	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 melting was observed from the diffraction patterns is given in final column.

Fig. 3 shows BSE images of two recovered run products (from experiments 1 and 8).
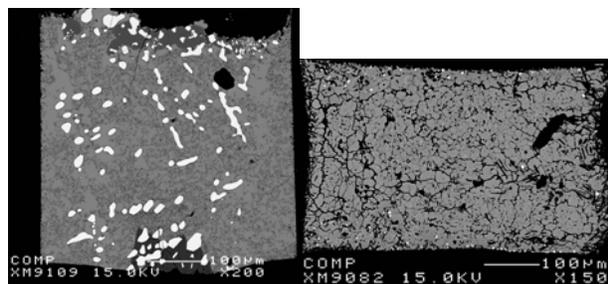

Figure 3. BSE images of experiment 1 (left) and 8 (right). Left image shows white ilmenite crystals in a glassy matrix. Right image shows glass with minor graphite laths and < 1 vol% micron-sized Fe crystals indicating minor sample reduction.

Discussion: Our preliminary experiments highlight several solvable experimental problems. Table 1 partly illustrates two main issues: 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 results [4]. 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 B_2O_3, derived from the hBN sleeves surrounding the diamond cylinder and graphite end caps. The resulting lowering of the sample liquidus explains why fully molten samples were formed at conditions far below the well-constrained black glass liquidus.

In addition, several samples 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). Clearly, in future experiments, time spent at subliquidus temperatures should be minimised.

In experiment 8 (right panel Fig. 3) these problems were mostly 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 calculated density in this case should reflect a true *in situ* magma density value. The calculated density value of 8-2 lies within error of the previously reported quench technique at very similar P-T conditions (3.30 g/cm^3) [1].

Outlook: The technique developed in this study is suitable for making *in situ* density measurements of silicate magma. Contamination and disequilibrium effects can easily be solved by slightly adjusting the cell assembly and heating trajectory. 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.

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] Besson et al. (1992) *HPR, 8,* 625. [7] Lange and Carmichael (1990), *Rev. in Min., 24,* 25. [8] Lange (1997), *Contrib. to Min. and Petr., 130,* 1. [9] Ochs and Lange (1999), *Science, 283,* 1314. [10] Liu and Lange (2006), *AM, 91,* 385.