



	Experiment title: <i>In situ</i> study of the density and structure of primitive lunar melts at high pressure and temperatures	Experiment number: HD330
Beamline: ID 27	Date of experiment: from: 29/01/2009 to: 03/02/2009	Date of report: August 27, 2010
Shifts: 15	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 (P) and temperatures (T) is critical for models of the dynamic evolution of the interior of the Moon. Densities of lunar melts have mostly been determined using indirect quench methods [1,2]. In a previous session at ESRF (HD151) we attempted to use an *in situ* X-ray absorption technique originally developed for high-Z molten metals [3,5] to measure the density of the densest lunar magma known (Apollo black glass, containing > 16 wt% TiO₂).

Although we showed that from a technical point of view, such measurements are indeed feasible, this initial beamtime did not produce useable density measurements. As detailed in the HD151 experimental report, we identified several key issues including (1) sample contamination due to slow heating paths and (2) P-T calibration uncertainties, both of which we had not anticipated. This time, we used our improved experimental and analytical protocol, circumventing the problems identified during HD151. In addition to validating this improved methodology we aimed to extend our *in situ* density measurements to a lunar magma composition with a significantly lower density (Apollo green glass, containing < 1 wt% TiO₂).

Experimental techniques: Ten technically successful *in situ* experiments were conducted at beamline ID 27, using X-ray absorption in the Paris-Edinburgh press. In addition to seven lunar magma density experiments we performed three calibration experiments to quantify the P-T conditions in our sample holder (single crystal diamond). A key assumption in using diamond capsules is that the P and T deduced from X-ray diffraction measurements of the unit-cell volumes of calibrants placed *outside* the diamond, are identical to P and T experienced by the sample *inside* the diamond. This assumption had never been tested previously. The starting materials for the calibration experiments were mixtures of MgO and Pt powders. For the density experiments the starting materials were synthetic lunar green and black glass analogues. Starting materials were packed in single crystal diamond cylinders with graphite end caps, and surrounded by other low-Z materials (hBN sleeve, graphite furnace, boron epoxy gasket) to maximise X-ray throughput [5].

In all experiments the assemblies were pressurized followed by stepwise heating. In case of the calibration experiments, we frequently collected X-ray diffraction patterns of the external and internal calibrants. For the density experiments we heated all samples to a constant power of 150 W and then heated rapidly until full melting, to minimise the heating time and thus exposure to the contamination that was identified during prior beamtime HD151 (e.g. reaction with graphite or BN). Absorption scans were taken for density evaluation of fully molten samples using techniques pioneered at ESRF [5]. Additionally absorption scans of the quenched, and quenched free standing sample were taken to assess the effect of sample environment.

Results: The calibration experiments significantly improved our understanding of the behaviour of a diamond sample capsule assembly during compression and heating in a Paris-Edinburgh press. Our results show that this assembly is indeed highly suitable for density determinations of high-melting point silicates such as our lunar compositions, but that it should not be used for low-liquidus temperature systems. The reason for this is that the pressure shielding effect of single-crystal diamond leads to a significant difference between inside and outside P at low T. Inside and outside P only become the same at $T > \sim 1250$ K. A paper detailing these findings is now in press [6]. Our improved experimental strategy led to significantly less sample contamination and complete melting of our samples, unlike most of the experiments done during HD151.

Densities of lunar melts were estimated using the Beer-Lambert law through fitting to the absorption scans (Fig 1., [5]). Upon normal compression and heating all molten materials should show an increase in density reflected by a decrease of the transmitted X-ray intensity. However, to our great surprise we found that density significantly decreases. A dramatic example of this is shown in Fig. 1. Almost all of our experiments lead to physically implausibly low density values for our lunar materials.

We have struggled for several months trying to find an explanation for these strange results (leading to the long delay in submission of this experimental report). We have excluded effects related to the assembly and to changes in the composition of the sample. Together with the beamline scientist **we have identified a possible fault in the electronics of one or both of the photodiodes** used to measure the absorption intensity

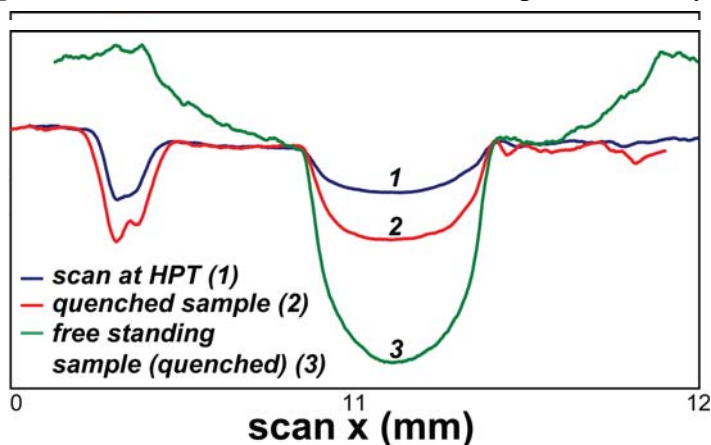


Fig.1. Typical sequence of absorption scans

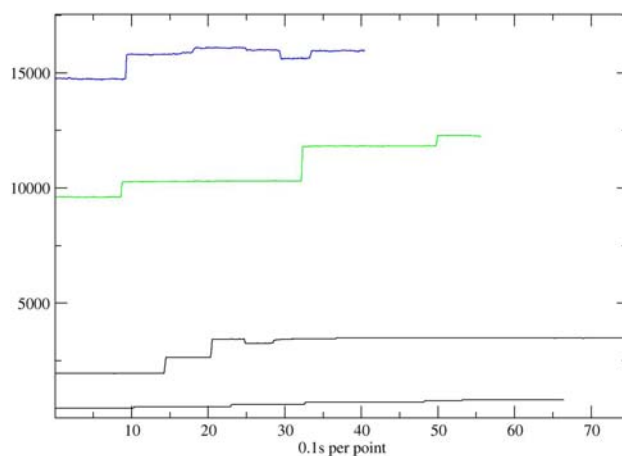


Fig. 2. Time series of upstream diode counts (in counts per second) for a series of measurements done during beamtime HD330. Variations between time series can be related to changes in beam intensity or beam size, but variations within each time series show unexpectedly large variations.

profiles shown in Fig. 1 as the most likely reason for our observations. In addition, unexpectedly large variations of the upstream photodiode counts were observed (Fig.2). This signal should be constant, but clearly it is not.

The beamline scientist is currently working on fixing this problem. **As it stands, it looks like virtually all of our analyses were affected, and that our project did not produce the required results as a consequence.**

Conclusion: Our beamtime resulted in a peer-reviewed publication of the calibration of this Paris-Edinburgh assembly. This will be of great use to other ESRF users using the same or a similar setup in the future. In principle, our improved methodology should allow for *in situ* density determinations of silicate liquids. Unfortunately, due to the problems that seem to have occurred with the X-ray absorption measurements it was impossible to derive reliable density measurements during this particular beamtime. Clearly these issues need to be resolved before further *in situ* density measurements using the Paris-Edinburgh press can be attempted.

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] Delano (1986) *JGR* 91, D201. [5] Sanloup et al. (2000) *GRL* 27, 811. [6] van Kan Parker M, Sanloup C, Tronche EJ, Perrillat JP, Mezouar M, Rai N, van Westrenen W (2010) Calibration of a diamond capsule cell assembly for *in situ* determination of liquid properties in the Paris-Edinburgh press. *High Pressure Research*, in press.