



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: The viscosity of carbonated silicate melts; implications for the state of the lithosphere-asthenosphere boundary	Experiment number: ES 220
Beamline: ID27	Date of experiment: from: 28 nov. 2014 to: 03 déc. 2014	Date of report:
Shifts: 15	Local contact(s): Mohamed Mezouar	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Dr. Yves Moussallam (ISTO, CNRS-Orléans) *Dr Jean philippe Perrillat (Univ. Lyon 1) *Dr Yann Morizet (Univ. de Nantes) *Dr. Fabrice Gaillard (ISTO, CNRS-Orléans) *Mr David Sifre (ISTO, CNRS-Orléans) *Dr. Rémi Champallier (ISTO, CNRS-Orléans)		

Report:

Abstract

Carbon-rich, silica-poor melts are suspected to be the most common type of melts in the asthenosphere. These melts, formed by very low degree (< 1%) partial melting of the upper mantle, play a key role in the global geochemical cycles of our planet, notably by concentrating mantle volatiles. These carbonated melts are assumed to be very mobile, owing to their (expected) high wetting properties and low density. This presumed mobility however is at odd with seismic¹ and electrical conductivity² investigations hinting to the presence of partial melts accumulated over a laterally continuous region at the Lithosphere - Asthenosphere boundary (LAB). One hypothesis that might reconcile these observations is if carbonated melts are more viscous than currently thought, impeding ascent despite their low density. It is this hypothesis we attempted to challenge during a 15 shift period at the ESRF ID27 beamline in December 2014, by performing falling sphere experiments under relevant high pressure and temperature conditions.

Experiment details

In the falling sphere technique, the viscosity relies on the measurement of the settling velocity of a dense metallic sphere within the melt using time-resolved X-ray radiography. The high pressure and temperature measurements were performed in a large volume Paris-Edinburgh press.

The sample was located in a diamond cylinder with an inner diameter of 0.5 mm and an outer diameter of 1.0 mm in order to minimize changes in the sample shape during heating and pressurisation while maximising X-ray throughput. The diamond capsule were sealed by Pt discs on both sides although we experienced sealing with Re, Mo, Pd and Au₈₀Pd₂₀ disks. Only the diamond capsule and the Pt lid were in direct contact with the melt to prevent undesired chemical reactions. The capsules were placed in a graphite heater, with h-BN as pressure transmitting medium and the whole furnace assembly was then placed inside a standard 7 mm boron-epoxy gasket³. The samples was compressed at room temperature to the desired pressure, and then melted by resistive heating with a graphite heater at a rate of 100W/min. Sample melting was monitored by X-ray diffraction using a

monochromatic beam and pressure and temperature were calculated from the X-ray diffraction patterns of Pt-hBn calibrants (double isochor method) with equation-of-state parameters. A ~100 μm diameter sphere of Pt was placed on top of each sample and used as viscosity markers. X-ray shadow images of the probing sphere falling through the melt were recorded using a single-crystal YAG phosphor converting the X-ray absorption contrast into visible light recorded by a high speed CCD camera^{4,5}. Magma viscosity could then be determined on the basis of the terminal velocity of the falling sphere using the Stokes equation:

$$\eta = \frac{gd_s^2(\rho_s - \rho_l) F}{18\nu E}$$

Where η is the viscosity, g is the acceleration of gravity (9.81 m/s²), ρ and d are density and diameter, respectively, with subscripts s and l denoting the probing spheres and liquid, ν is the terminal velocity of the falling sphere and F and E are correction factors for wall and end effect respectively. The accuracy of viscosity estimates relies on a precise knowledge of the density of the melt under high P-T. We therefore also performed density measurements using the X-ray absorption method developed by ref.6,7 based on the Beer-Lambert's law.

Experiment difficulties

During the session we encountered a number of technical difficulties:

1. The first issue was to find that for one of the sample suite investigated (various mix of a hydrated basalt with a carbonate), a strong chemical reaction occurred between the melt and the probing sphere. The diamond capsules were also found to react with the melt and fractured during experiments. We assigned this reaction to the peculiar chemistry of this sample suite (notably containing Cl) and did not pursue its investigation too long before moving to a different composition.
2. The second difficulty was related to the high melting point (> °C) of some compositions free of CO₂ so that parts of the assemblage (lid and probing sphere) would start melting before the sample. We therefore experienced different metals (Re, Mo, Au₈₀Pd₂₀, Au₉₀Pd₁₀, Pd, Pt) as lids before settling on Pt which combined a high-enough melting point with mechanical properties ensuring a good seal of the diamond capsule and an effective transmission of pressure to the sample.
3. The nature of the technique we used, in which the temperature is estimated from the X-ray diffraction patterns of Pt-hBn calibrants, means that radiography imaging of the sample could not be done concurrently with temperature determination (or XRD on the sample to assess if it has reached a completely molten state). In one occasion this limitation meant that we missed the fall of the probing sphere while on XRD mode.
4. Finally, on multiple occasions we could not get the probing sphere to fall through the sample, while the X-ray diffraction signal showed the absence of solid crystalline phases. The accuracy of the viscosity determination is a direct function of the number of radiography images that are acquired during the sphere fall. In order to maximise this number we tried using very small probing spheres, down to 30 μm diameter. The problem with small probing spheres however is that if the viscosity of the liquid is too high they will not fall at the timescale of our experiment. The problem is therefore a circular one with experimental assemblages needing to be tuned to the viscosity of the liquid (the unknown we're trying to determine).

Confronting experimental difficulties

In this section we detail our future plans to tackle the issue presented above.

1. In order to limit reactions of the sphere and diamond capsule with the melt we plan on coating both with a thin Al₂O₃ film (few μm).
2. Our experience with various materials has now allowed us to define the best experimental assemblages to investigate the compositions of interest.
3. The issue of indirect temperature determination cannot be answered entirely. During our experiments however, we have repeatedly established calibration curves for the graphite furnaces so future experiments will benefit from an a priori determination of the experiment temperature based on the imposed current intensity. We are also now know that some compositions being more viscous than expected, we should expect a delay before the sphere begins to fall.
4. We are currently performing a series of "classical" piston-cylinders viscometry experiments in order to obtain a first order determination of the viscosity of the investigated liquid. Results from these experiments should allow us to design experimental assemblage better adapted to accurately probe the viscosity of carbonated melts.

Results

We performed a total of nine experiments. In no occasion were we able to record the fall of the probing sphere through a pure melt. One fall was successfully recorded but the sphere fell through a mush rather than a pure liquid. Despite the experimental difficulties we were successful, for several samples, in obtaining X-ray transmission profiles through the quenched glass at ambient conditions and through the melt at high pressure and temperature (Fig. 1). These data will allow us to determine the density of these melts at the pressure and temperature conditions of their expected formation in the mantle.

Although we initially hoped to determine the viscosity of carbonated melts we note that density measurements on such low silica high - CO₂ compositions are a first. Given the scarcity of data and importance of such melts in the deep carbon cycle we are confident in our ability to publish the results within a year. We are currently determining the density of the glass by an independent method in order to calibrate the obtained absorption profiles.

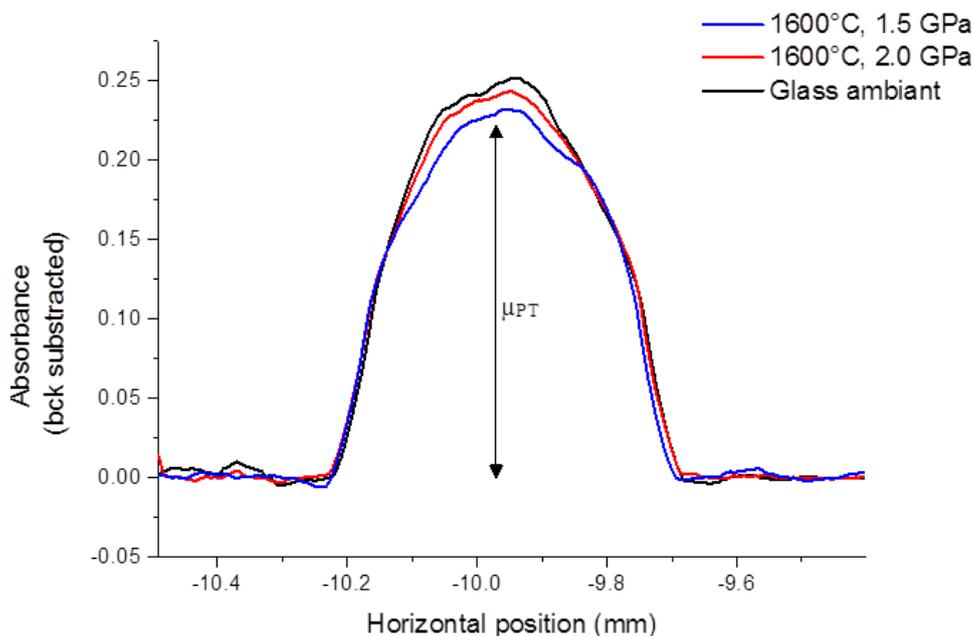


Figure 1: Example of a background-subtracted X-ray absorbance scan through the diamond capsule and a sample containing 32 mol% SiO₂ (calculated dry) and 18 mol% CO₂ at (i) ambient conditions, (ii) 1600°C and 1.5 GPa, (iii) 1600°C and 2.0 GPa. The density can be derived from the attenuation coefficient of the sample (μ_{PT}).

Conclusions and Future work

Our experimental session has highlighted a number of problems impeding us from obtaining *in situ* viscosity measurements on carbonated melts. We have now improved the experimental setup in order to target each problem specifically and are currently performing a number of *ex-situ* experiments which will help us further constrain the experimental assemblage design for future experiments. We believe that the originally proposed experiments are feasible and hope to perform them in the near future. We are therefore re-applying for beamtime.

References

1. Kawakatsu, H. *et al.* Seismic Evidence for Sharp Lithosphere-Asthenosphere Boundaries of Oceanic Plates. *Science* **324**, 499–502 (2009).
2. Naif, S., Key, K., Constable, S. & Evans, R. L. Melt-rich channel observed at the lithosphere-asthenosphere boundary. *Nature* **495**, 356–359 (2013).
3. Van Kan Parker, M. *et al.* Calibration of a diamond capsule cell assembly for in situ determination of liquid properties in the Paris-Edinburgh press. *High Pressure Research* **30**, 332–341 (2010).
4. Sakamaki, T. *et al.* Ponded melt at the boundary between the lithosphere and asthenosphere. *Nature Geoscience* **6**, 1041–1044 (2013).
5. Perrillat, J.-P., Mezouar, M., Garbarino, G. & Bauchau, S. In situ viscometry of high-pressure melts in the Paris–Edinburgh cell: application to liquid FeS. *High Pressure Research* **30**, 415–423 (2010).
6. Katayama, Y. Density measurements of non-crystalline materials under high pressure and high temperature. *High Pressure Research* **14**, 383–391 (1996).
7. Sanloup, C. *et al.* Density measurements of liquid Fe-S alloys at high-pressure. *Geophys. Res. Lett.* **27**, 811–814 (2000).