



Trace-element coordination in carbonate-silicate melts measured in-situ at high pressure and temperature		Experiment number: ES 191
Beamline: BM23	Date of experiment: from: 29.10.14 to: 04.11.14	Date of report: 19.1.14
Shifts: 18	Local contact(s): Olivier Mathon	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

Julia Pohlenz*, Max Wilke*, Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany
 Andrei Shiryayev* IPCE RAS Moscow, Russia
 Alexey Veligzhanin*, Kurchatov Institute, Moscow, Russia
 Oleg Safonov, IEM RAS Chernogolovka, Russia
 Tetsuo Irifune, Ehime University, Matsuyama, Japan

Report:

This study aims at understanding the structural properties of carbonate-silicate melts relevant to magmatic processes in the deep Earth. Carbonate melts show extraordinary properties, especially in regard to their low melt viscosities and densities, high surface tensions and electrical conductivities as well as distinct geochemical affinities to a wide range of trace elements¹. Understanding the structural properties of carbonate-bearing melts is fundamental to explaining their chemical and physical behaviour as well as processes operating in the deep Earth, such as trace element partitioning. This study focuses on elucidating the local structural environment of Y and Sr in silicate melts with varying carbon contents (Figure 1). Whereas Sr is expected to represent the alkali earths, Y is expected to represent the role of heavy rare earth elements.

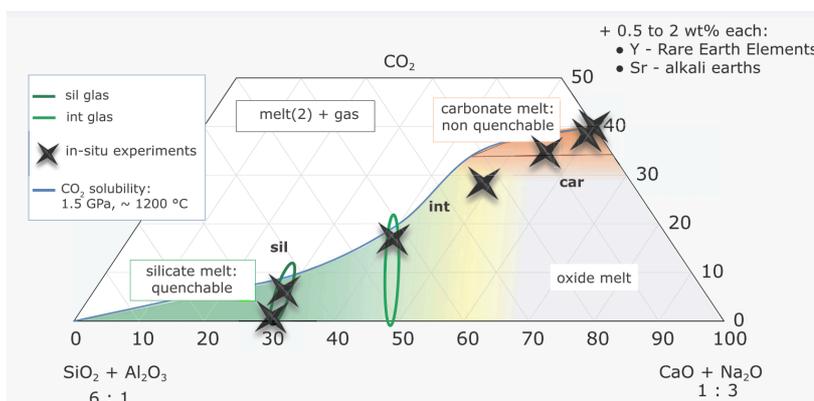


Figure 1: Chemical composition of investigated samples. The ellipses indicate the chemical compositions, which were quenched to glass and measured ex-situ in June 2014. Black stars indicate the chemical compositions, which were investigated in-situ using the Paris-Edinburgh-Press.

Former EXAFS studies conducted at BM23 (June 2014) on silicate glasses (Figure 1, green ellipses) synthesized at high pressure and temperature revealed a systematic increase of bond lengths between the incorporated trace element Sr and O with increasing CO₂-contents, whereas Y-O bond lengths did not show a systematic change (Figure 2).

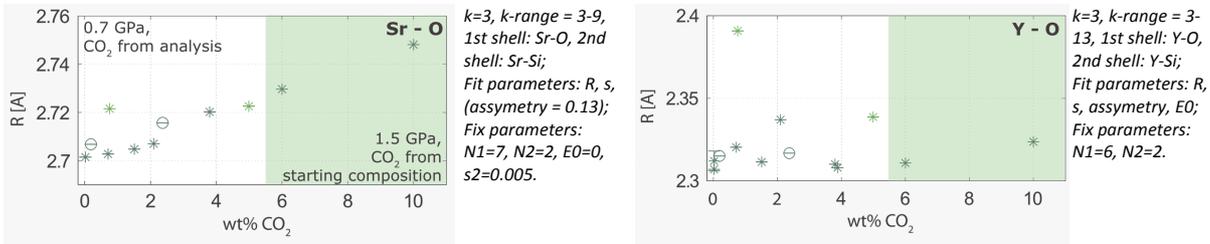


Figure 2: Dependence of bond lengths incorporated trace element (~0.5 wt%) and coordinating oxygen and CO₂-content in silicate glasses synthesized under high pressure and temperature. While Sr-O distances increase with rising CO₂-content, the Y-O distances do not show a systematic variance. Data derived from EXAFS fits using XAFS.

In order to also investigate CO₂-rich compositions, which are not quenchable, and to test for possible quench effects on the local structure, we performed in-situ experiments using the Paris Edinburgh press (PEP) on samples with chemical compositions covering the whole chemical system (Figure 1, black stars, with ~2 wt% trace element each). We determined the liquid state by the absence of crystalline phases using in-situ XRD. Silicate melts were analyzed at 2.2 GPa, 1330 °C and carbonate melts at 2.6 GPa, 730 °C as determined by a calibration run with XRD on BN and MgO. We collected Y and Sr K-edge EXAFS at BM23 using the Si(111) double-crystal monochromator in transmission mode.

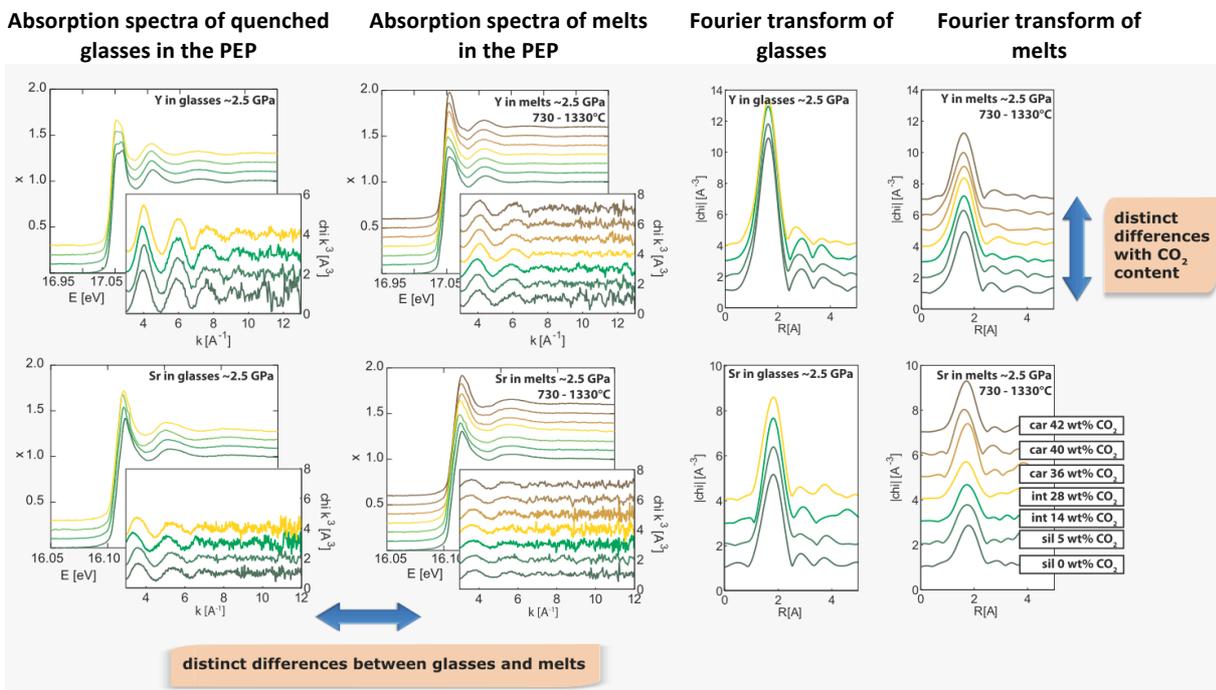


Figure 3: Collected Y and Sr EXAFS spectra and their fourier transforms of melts and quenched glasses along the join CO₂-free silicate glass – pure carbonate mix (colors of spectra correspond to colors in the phase diagram in Figure 1). There are distinct differences in the absorption features along the chemical join itself as well as between melts and quenched glasses.

As known from former fitting procedures in this system, a fit based on an asymmetric distribution function is required, which is still in progress. First qualitative analysis already reveals a strong dependence of the absorption spectra on chemical composition as well as distinct differences of the spectra of Y and Sr between glasses and in melts (Figure 3). This first view on our data reveals that there is a significant effect of the melt composition on the local structure of these trace elements. Moreover, they show that the structure of glasses quenched from high temperature in this chemical system is considerably effect during the cooling process.

1. Jones, A. P., Genge, M. & Carmody, L. Carbonate Melts and Carbonatites. Rev. Mineral. Geochem. 75, 289–322 (2013).

Acknowledgements:

The great help and support of Olivier Mathon, Sakura Pascarelli, Innokenty Kantor, Sebastian Pasternak, Mohamed Mezouar and the BM23-team is highly appreciated.