Structural properties of sodium-rich carbonate-silicate melts: An *in-situ* high-pressure EXAFS study on Y and Sr

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2016 J. Phys.: Conf. Ser. 712 012083
(http://iopscience.iop.org/1742-6596/712/1/012083)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 131.169.95.162
This content was downloaded on 11/11/2016 at 11:11

Please note that terms and conditions apply.

You may also be interested in:

Characterization and EXAFS Studies of Cobalt Synthesized by sol-gel auto Combustion Method
Ashutosh Mishra, Priya Singh and Samrath Ninama

EXAFS Study on the Local Structure of Cu in Bi-Pb-Sr-Ca-Cu-O Systems
Yasushi Uehara, Nagao Kamijo, Hiroyuki Kageyama et al.

A Laboratory EXAFS Study with Higher-Order Bragg Reflection by Means of the Fluorescence Monitoring Technique
Kazuhiko Omote, Kazuyuki Tohji and Yoshio Waseda

Superconductivity in pressurized Rb0.8Fe2ySe2xTex
Dachun Gu, Qi Wu, Yazhou Zhou et al.

EVOLUTIONARY CLIMATE TRACKS OF EARTH-LIKE PLANETS
S. Kadoya and E. Tajika

EVOLUTIONARY TRACKS OF THE CLIMATE OF EARTH-LIKE PLANETS AROUND DIFFERENT MASS STARS
S. Kadoya and E. Tajika

Positive or Negative Thermal Expansion in Anharmonic Vibrational Systems in EXAFS study
Dong-Seok Yang and Jay Min Lee
Structural properties of sodium-rich carbonate-silicate melts:
An in-situ high-pressure EXAFS study on Y and Sr

J Pohlenz¹, S Pascarelli², O Mathon², S Belin³, A Shiryaev⁴, O Safonov⁵, A Veligzhanin⁶, V Murzin⁷, T Irifune⁸ and M Wilke¹

¹Helmholtz Centre German Research Centre for Geosciences, Potsdam, Germany, ²ESRF European Synchrotron Radiation Facility, Grenoble, France, ³Synchrotron SOLEIL, GIF-sur-YVETTE, France, ⁴IPCE, Moscow, Russia, ⁵Institute of Experimental Mineralogy RAS, Chernogolovka, Russia, ⁶Kurchatov Institute, Moscow, Russia, ⁷DESY, Hamburg, Germany, ⁸Ehime University, Matsuyama, Japan.

E-Mail: julia.pohlenz@gfz-potsdam.de

Abstract. In-situ EXAFS combined with a Paris-Edinburgh press (PEP) is an outstanding tool to investigate the local environment of trace elements in melts at high pressure and temperature. A novel design of the pressure assembly ensures a highly stable experimental setup (reaching temperatures of up to 2000 K at 2.5 GPa) while permitting the necessary level of X-ray transmission. This study focuses on the structural incorporation of the geochemically important trace elements Y and Sr in sodium-rich silicate-carbonate melts. Y and Sr K edge EXAFS were collected in transmission mode of the melt (at ~2.5 GPa, 1600 K) and its respective quench products. Distinct changes in the XANES region suggest a change in site symmetry during the cooling process.

1. Introduction
Carbonate-bearing silicate and carbonate melts possess unique physical properties. Especially the latter is characterized by extremely low melt viscosities and densities, high surface tensions and electrical conductivities. Of special interest are the distinct geochemical affinities of a wide range of trace elements in carbonate versus silicate melts. The processes of carbonatite genesis and evolution as well as the interaction between carbonate-bearing reservoirs are still unresolved. The only active carbonatitic volcano is the Oldoinyo Lengai, Tanzania, which generates sodium-rich carbonatites in close association with phonolites and nephelinites [1]. Additionally, carbonate-bearing melts evidently play a crucial role during mantle melting, in diamond formation and as metasomatic agents [2]. Understanding the structural properties of carbonate-bearing melts is fundamental to explaining their chemical and physical behavior as well as modeling their role in geochemical processes in the deep Earth. Applying in-situ Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy with a large volume Paris-Edinburgh press (PEP) allows for investigating the local structure around geochemically important trace elements in melts at high pressure (HP) and high temperature (HT) conditions, as found in the Earth’s crust and upper mantle.
2. In-situ EXAFS using a Paris-Edinburgh press

![Image of XRD setup](image1.png)

**Figure 1.** (a) Photograph of the Paris-Edinburgh press (PEP) at beam line BM23, ESRF with the XRD detector on the right hand side of the picture. (b) Pressure assembly used in the Paris-Edinburgh press based on zircon dioxide (ZrO$_2$), boron epoxy (BE) and hexagonal boron nitride (hBN) as pressure media. In order to heat, the molybdenum (Mo) parts transfer the current from the wolfram carbide (WC) core of the anvil to the graphite heater. The outer ring made of polyether ether ketone (PEEK) ensures the stability of the setup.

Originally, the Paris-Edinburgh press (Figure 1a) was developed for HP experiments on neutron sources [3], but was progressively adapted to XRD and X-ray absorption experiments [e.g. 4]. The press is operated with oil pressure, which is transmitted to the sample-containing pressure assembly through a set of anvils with tungsten-carbide cores. The newly introduced pressure assembly (Figure 1b) used in these in-situ experiments is a refined version of the pressure assembly used by Yamada et al. [5] for XRD experiments. The layered setup of the novel assembly firstly assures high stability at high $P$ and $T$ conditions due to robust and low heat-conducting zircon dioxide parts at the top and the bottom of the assembly. Secondly it assures a sufficient level of X-ray transmission at respective energies due to the radiation penetrated parts consisting of the light materials of boron nitride (as thermal insulator), boron-epoxy (as pressure medium), and polyether ether ketone (for mechanical stabilization). The center of the pressure assembly contains a graphite heater around a nano-polycrystalline diamond, which serves as an inert pressure capsule for the sample itself.

![Graph of pressure vs. oil pressure](image2a.png)

![Graph of temperature vs. power](image2b.png)

**Figure 2.** Pressure (a) and temperature (b) calibration as determined by the equation of states of reference materials (gold (Au), NaCl, hexagonal boron nitride (hBN), and platinum (Pt)). Volume changes at HT/HP are detected by XRD. Temperature calibration was conducted at ~2 GPa and ~3 GPa sample pressure.
Heating is accomplished by applying high current at low voltage through the anvils, which is transmitted to the graphite heater by central Mo rods and foils at the top and the bottom of the assembly. To avoid high temperature induced damage, the anvils are connected to a water cooling system. With this setup, we were able to reach temperatures of 2000 K at ~2.5 GPa, while retaining a stable gap between the anvils of ca. 300 μm. Pressure and temperature determination is based on the double isochore technique [6] applied to reference materials (e.g. hexagonal boron nitride (hBN), magnesium oxide (MgO), Au, Pt) in calibration runs. The volume changes of these materials are detected with XRD and used in their equation of states, which’s intersections indicate the prevailing pressure and temperature conditions.

### 3. Y and Sr incorporation in carbonated silicate melts

This study focuses on unraveling the influence of carbonate concentration on the structural incorporation of the geochemically important trace elements Y (representing rare earth elements) and Sr (representing alkali earths) in silicate and carbonate melts in the system Na₂O-CaO-Al₂O₃-SiO₂-CO₂ (Figure 3), which resembles a simplified composition of the rocks found at the Oldoinyo Lengai. Starting materials were prepared by mixing carbonate powders (Na₂CO₃ + CaCO₃) and grinded silicate glass (Na₂O-CaO-Al₂O₃-SiO₂ produced by melting the oxide powders) in the respective proportions and then introduced into the diamond capsule.

In order to obtain EXAFS spectra in transmission, the samples were doped with approximately 2 wt% Y and Sr. The in-situ experiments were conducted using a Paris-Edinburgh press, installed at BM23, ESRF [7]. CO₂-bearing silicate compositions were investigated in-situ at 2.2 GPa and 1600 K as well as at the quenched glass after the run. The quench was accomplished by cutting the power supply to the graphite heater. During this process the pressure drops to 1.8 GPa. Pure carbonate melts with CO₂ contents between 35 and 42 wt% do not quench to a glass and were investigated only in-situ at 2.6 GPa and 1000 K. We determined the liquid state by the absence of crystalline phases as indicated by in-situ XRD. The EXAFS measurements were carried out using a Si(111) monochromator. The beam was vertically focused to 50 μm and horizontally collimated to 0.1 mm.

Figure 4 presents Y and Sr K edge EXAFS of a silicate composition containing 5 wt% CO₂. The XANES region, especially of Y, shows distinct differences between the measurements taken in-situ at HP/HT and the quenched glass at HT, which might indicate a change in site symmetry during the cooling process. The most prominent difference between EXAFS at in-situ conditions and on the quenched sample is the reduction in amplitude. This results in a considerable shortening of the EXAFS spectrum range. It is related to thermally induced vibrations of atoms around their equilibrium position or even migration in the liquid state. This leads to an anharmonic reduction in amplitude and shift in frequency. In order to analyse these data and determine structural parameters of the Y-O and Sr-O pair-distribution an asymmetric pair distribution model needs to be applied. Evaluation of in-situ data is still in progress.
In conclusion, we show the feasibility of detecting differences in structural incorporation of elements only being present in low amounts in glasses and melts by transmission EXAFS at high pressure and temperature using the large volume Paris-Edinburgh press.

Figure 4. Normalised XANES and reduced EXAFS ($\chi$) of Y (a, b) and Sr (d, e) K edge and their Fourier Transforms (FT) (c, f) of in-situ (bright) and quenched (dark) samples. Note the reduced amplitude of in-situ compared to quench measurements due to enhanced anharmonicity of atomic vibrations. Data was processed with the software xafsX [8].

References
[1] Klaudius J and Keller J 2006 Peralkaline silicate lavas at Oldoinyo Lengai, Tanzania Lithos 91 173–90
[2] Jones A P, Genge M and Carmody L 2013 Carbonate Melts and Carbonatites Rev. Mineral. Geochem. 75 289–322
[3] Besson J M, Nelmes R J, Hamel G, Loveday J S, Weill G and Hull S 1992 Neutron powder diffraction above 10 GPa Phys. B Condens. Matter 180–181, Part 2 907–10
[4] Morard G et al. 2007 Optimization of Paris–Edinburgh press cell assemblies for in situ monochromatic X-ray diffraction and X-ray absorption High Press. Res. 27 223–33
[5] Yamada A, Wang Y, Inoue T, Yang W, Park C, Yu T and Shen G 2011 High-pressure x-ray diffraction studies on the structure of liquid silicate using a Paris–Edinburgh type large volume press Rev. Sci. Instrum. 82 015103
[6] Zhao Y, Dreele R B V, Weidner D J and Schiferl D 1997 P-V-T Data of hexagonal boron nitride h BN and determination of pressure and temperature using thermoelastic equations of state of multiple phases High Press. Res. 15, 369–386
[7] Mathon O et al. 2015 The time-resolved and extreme conditions XAS (TEXAS) facility at the European Synchrotron Radiation Facility: the general-purpose EXAFS bending-magnet beamline BM23 J Synchrotron Radiat. 22 1548–54
[8] Winterer M 1997 XAFS - A Data Analysis Program for Materials Science J. Phys. IV 7 C2-243–244