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

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**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 trance elements in melts at high pressure (*HP*) and high temperature (*HT*) conditions, as found in the Earth's crust and upper mantle.

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## 2. *In-situ* EXAFS using a Paris-Edinburgh press

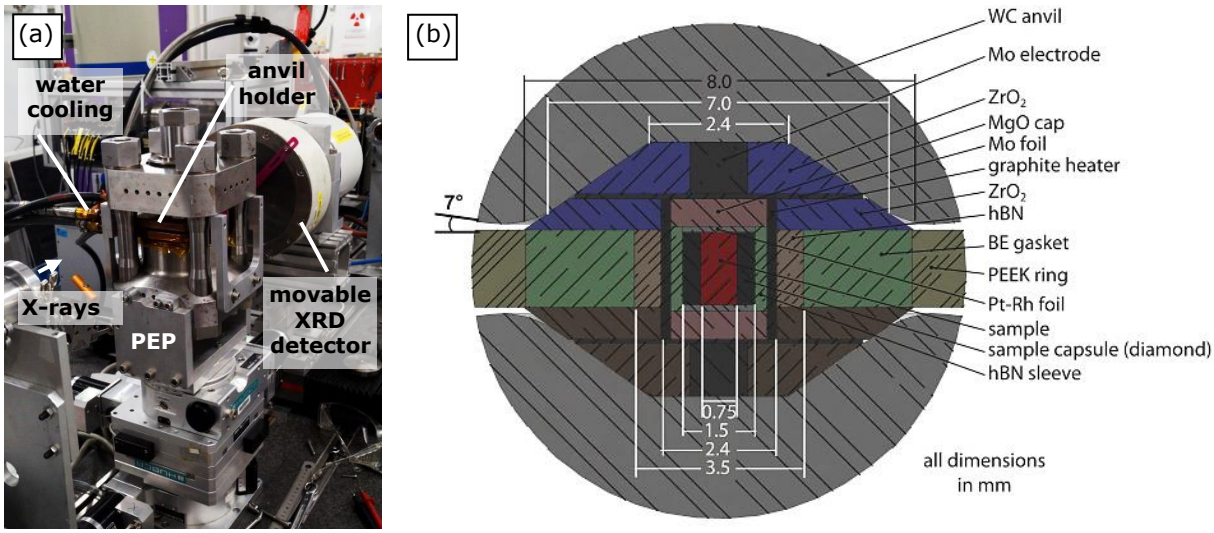


**Figure 1.** (a) Photograph of the Paris-Edinburgh press (PEP) at beam line BM23, ESRF with the XRD detector on the right hand side of the picture. (b) Pressure assembly used in the Paris-Edinburgh press based on zircon dioxide ($ZrO_2$), boron epoxy (BE) and hexagonal boron nitride (hBN) as pressure 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.

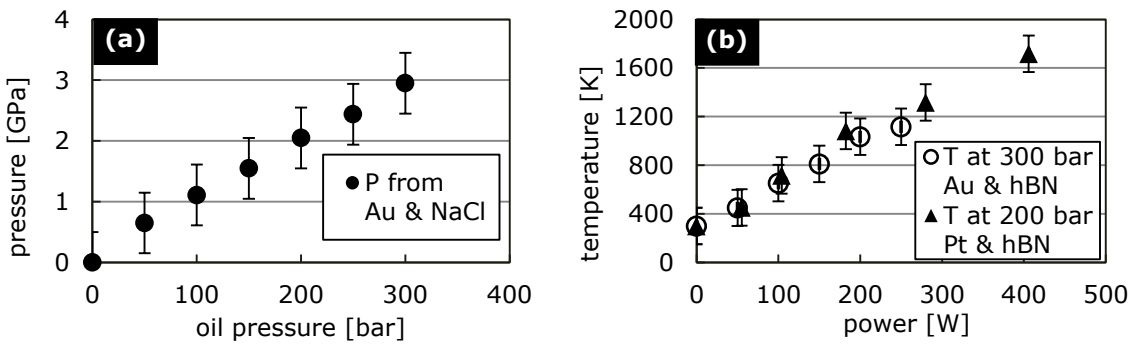


**Figure 2.** Pressure (a) and temperature (b) calibration as determined by the equation of states of reference materials (gold (Au), NaCl, hexagonal boron nitrite (hBN), and platinum (Pt)). Volume changes at *HT/HP* are detected by XRD. Temperature calibration was conducted at ~2 GPa and ~3 GPa sample 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 $Na_2O$-$CaO$-$Al_2O_3$-$SiO_2$-$CO_2$ (Figure 3), which resembles a simplified composition of the rocks found at the Oldoinyo Lengai. Starting materials were prepared by mixing carbonate powders ($Na_2CO_3$ + $CaCO_3$) and grinded silicate glass ($Na_2O$-$CaO$-$Al_2O_3$-$SiO_2$ produced by melting the oxide powders) in the respective proportions and then introduced into the diamond capsule.

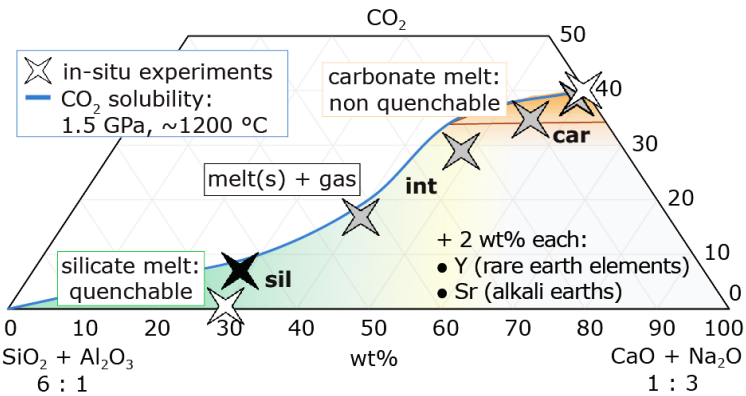


**Figure 3.** Chemical composition of investigated melt samples ranging from silicate (sil) over intermediate (int) carbonate bearing silicate to carbonate (car) compositions. White stars indicate the end members of carbonate free silicate and pure carbonate composition. Grey stars indicate samples prepared out of mixtures between them. The black star indicates the sample of which EXAFS data are presented in this paper.

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]. $CO_2$-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 $CO_2$ 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% $CO_2$. 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.

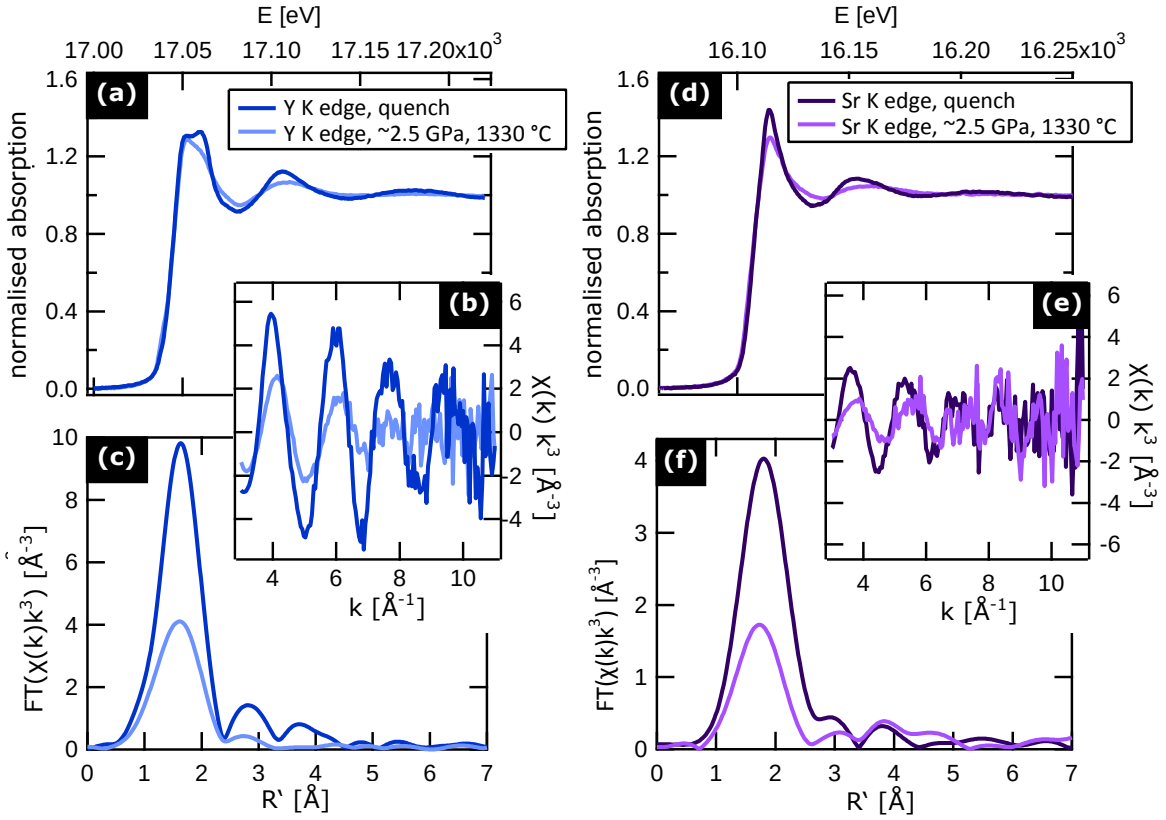


**Figure 4.** Normalised XANES and reduced EXAFS (χ) of Y (a, b) and Sr (d, e) K edge and their Fourier Transforms (FT) (c, f) of *in-situ* (bright) and quenched (dark) samples. Note the reduced amplitude of *in-situ* compared to quench measurements due to enhanced anharmonicity of atomic vibrations.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

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