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DISSERTATION FOR THE DEGREE OF PHILOSOPHIAE DOCTOR (PhD)

Experimental constraints on Earth's lower mantle melting and core formation

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“I am among those who think that science has great beauty.

A scientist in the laboratory is not a mere technician but a child
confronting natural phenomena that impresses as though they were fairy tales.”

Maria Skłodowska-Curie

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Preface

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The majority of the experimental and analytical work presented in this thesis was performed at School of Earth Sciences, University of Bristol in the United Kingdom. Various experimental facilities and analytical equipment were used including: Petrology Laboratories (Diamond Anvil Cell Lab, Large Volume Solid Media Lab, One-Atmosphere Lab, Micro-Raman Lab and Microscopy and Sample Preparation Lab) and Micro-beam Laboratory (Field Emission Electron Microprobe Lab). The experimental and analytical work was carried through with the assistance and under the supervision of Prof. Michael J. Walter and Dr. Oliver T. Lord, but also Dr. James W. E. Drewitt, Dr. Marion Louvel, Dr. Richard Brooker, Dr. Stuart Kearns and Dr. Benjamin Buse, to name a few.

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During the last three and a half years PhD candidate was also involved in additional collaboration with Prof. Michael J. Walter, Dr. Oliver T. Lord and Dr. James W. E. Drewitt on separate side projects, the results of which are not included in this PhD thesis but can be found in:

- Walter, M.J., Thomson, A.R., Wang, W., Lord, O.T., Ross, J., McMahon, S.C., **Baron, M.A.**, Melekhova, E., Kleppe, A.K., Kohn, S.C., 2015. *The stability of hydrous silicates in Earth's lower mantle: experimental constraints from the systems MgO-SiO₂-H₂O and MgO-Al₂O₃-SiO₂-H₂O*. Chem. Geol. 418, 16–29.
- Dobson, D.P., Hunt, S.A., Ahmed, J., Lord, O.T., Wann, E.T.H., Santangeli, J., Wood, I.G., Vočadlo, L., Walker, A.M., Thomson, A.R., **Baron, M.A.**, Mueller, H.J., Lathe, C., Whitaker, M., Morard, G., Mezouar, M., 2016. *The phase diagram of NiSi under the conditions of small planetary interiors*. Phys. Earth Planet. Inter. 261(B), 196–206.
- Drewitt, J.W.E., McMahon, S., Lord, O.T., **Baron, M.A.**, Daisenberger, D., Anzellini, S., Kleppe, A. Walter, M.J. (in prep.) *Carbon in the Deep Mantle: Sub- and Super-Solidus Phase Relations in the System CaO-MgO-FeO-SiO₂-CO₂ in Earth's Lower Mantle*.

Another scientific contribution published by the PhD candidate during the PhD research at CEED involves earlier work performed at the Institute of Mineralogy and Petrography, University of Innsbruck in Austria, with Prof. Roland Stalder and Prof. Jürgen Konzett, is not included in this thesis but can be found in:

- **Baron, M.A.**, Stalder, R., Konzett, J., Hauzenberger, C.A., 2015. *OH-point defects in quartz in B- and Li-bearing systems and their application to pegmatites*. Phys. Chem. Miner. 42(1), 53–62.

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Marlene A. Baron

Introduction

Earth's formation through accretion of primordial and differentiated material, led to extensive melting, resulting in multiple global magma oceans and differentiation into several layers, including metallic core and silicate mantle. These processes were extremely complex and shaped our Earth and the other terrestrial planets in very unique ways. Luckily, it has left behind geophysical and geochemical signatures preserved to this day in both the core, and the mantle. By studying Earth's structure, composition and dynamics, we attempt to understand more about its past by testing different evolution scenarios, which might have led to the formation of such a fascinating and diverse planet that we live on.

The main direct data concerning the structure of our planet comes from global seismology. Geophysicists use P (compressional) and S (shear) wave travel times and normal mode vibrational spectra to construct globally averaged Earth's models, upon which the layered picture of our differentiated planet is based (e.g. PREM, **Fig. 1**). Linking geological observations of processes happening near and at the Earth's surface (e.g. volcanic activity and deep earthquakes related to the movement of the lithospheric plates) with seismic tomography images (e.g. van der Hilst et al., 1997; Fukao and Masayuki, 2013), provides clear evidence of the dynamic nature of the Earth's interior. Three-dimensional geodynamic simulations (e.g. Tackley et al., 1993; Nakagawa and Tackley, 2008) of the Earth's interior seem to support the concept of the whole-mantle convection, driven by the energy delivered from the core and from radioactive heat generated in the mantle. The convective mantle follow a nearly adiabatic temperature gradient between the two major thermal boundary layers in the D'' zone and the lithosphere. The upwelling via slow pervasive flow above the two antipodal LLSVPs and hot plumes over the LLSVP-margins and

Fig. 1 The Preliminary Reference Earth Model (PREM, Dziewonski and Anderson, 1981) which underlines the layered structure of the Earth based on the globally averaged seismic velocity profiles (S-green and P-blue). The density profile is shown in red.

Fig. 2 Simplified equatorial section of the Earth (modified from Trønnes, 2010). Blue regions represent the downwelling motions where subduction occurs and red regions represent upwelling motions related with the two large low shear velocity provinces (LLSVP) which reside on top of the CMB.

Fig. 3 Mineral phase proportions of fertile peridotite (top) and basalt (bottom) in the Earth's crust and mantle down to the CMB (modified from Stixrude and Lithgow-Bertelloni, 2012).

heterogeneous D'' zone near the CMB (e.g. Garnero and McNamara, 2008, Lay et al 2008, Torsvik et al., 2010, 2016). The origin, composition and properties of these heterogeneities remain uncertain. **Fig. 2** provides a general overview of the present-day structure and mechanisms governing the mantle dynamics. The two antipodal large low shear wave velocity provinces (LLSVPs) located underneath Africa and the Pacific and more localized ultra-low velocity zones (ULVZs) may be a result of either fractional crystallization of the magma ocean during the earliest history of the Earth and/or the continued accretion of subducted basaltic oceanic crust at the CMB (e.g. Labrosse et al., 2007, Elkins-Tanton 2012, Torsvik et al. 2016). In order to test both hypotheses a good understanding of the melting phase relations of peridotitic and basaltic compositions are required throughout the whole mantle pressure range. Recent experiments on natural multi-component peridotitic and basaltic compositions (Fiquet et al., 2010; Andraut et al., 2011; Nomura et al., 2014; Andraut et al., 2014; Pradhan et al., 2015) yield a range of solidus and liquidus temperatures. Systematic studies of chemically simpler systems are therefore needed in order to assess the uncertainties and understand the melting behaviour of lower mantle lithologies in more detail. **Chapter 1** approaches this goal by studying eutectic melting of analogues for peridotitic and basaltic lithologies within the simplest MgO-SiO_2 system, which captures the major mineralogy of the lower mantle. The near-eutectic compositions (de Koker et al., 2013 and Liebske and Frost, 2012) produced large enough melt fractions to determine more precisely the eutectic melting curves through the lower mantle pressure range, despite the temperature gradients in the laser-heated diamond anvil (LH-DAC).

Based on the seismological observations, another important aspect of the Earth's structure and composition arises: the Earth's core seems to be lighter than pure iron-nickel alloy (e.g. Birch, 1952, Kennett et al., 1995), hence the present-day core most likely contains a small portion of lighter element(s) in order to account for the observed density deficit (e.g. Alfè et al., 2002; Badro et al 2007; Antonangeli et al 2010). On the other hand, geochemical measurements of the primitive mantle rocks reveal strong depletion of many siderophile ('iron loving')

downwelling via subduction of cold slabs govern the movements in the present-day, mostly solid mantle (**Fig. 2**) and suggests an on-going exchange and interaction between the surface, mostly made of basaltic material (e.g. oceanic crust), and the mantle, dominated by peridotitic material (see **Fig. 3** for more details on mineralogical characteristics).

Although the averaged structure of the bulk mantle resembles the mineralogy of peridotite (**Fig. 3**, top) with major phase transitions at the seismically resolvable discontinuities 410 and 660 km depth (**Fig. 1**), a more heterogeneous picture emerges from a detailed study of the geophysical data. For example, one of the most distinct features in the lowermost part of the Earth's mantle is laterally and vertically

elements relative to primordial chondrites (e.g. McDonough and Sun, 1995; McDonough, 2003; Becker et al., 2006). Therefore, their present-day mantle abundances must have been influenced by differentiation processes (see **Fig. 4**). An approach to understand processes which have led to gravitational segregation of metallic core from silicate mantle during Earth's accretion involves experimental simulations of the metal (core) - silicate (mantle) interaction and equilibration at various pressure and temperature conditions. Thanks to the results of numerous metal-silicate partitioning experiments (e.g. Righter et al., 1997; Wade and Wood, 2005; Siebert et al., 2011, Tsuno et al., 2013) unique hints about the Earth's evolutionary history has been collected

over the last couple of decades. Studying the partitioning behaviour of various trace and major elements in a broad range of pressures, temperatures and compositions has therefore been established as a powerful tool to deduct plausible core formation scenarios. Based on the extrapolation of partitioning coefficients of the refractory and moderately siderophile elements such as Ni, Co, W and V obtained in the large volume presses, it has been proposed that as the Earth grew, the core-mantle equilibration must have occurred in a relatively deep magma ocean (e.g. Wade and Wood, 2005, Wood et al., 2006). However, only very recently, thanks to the advancements of the experimental (LH-DAC) and analytical (focused ion beam milling with SEM, field-emission microprobe analyser, etc.) methods, the metal-silicate partitioning experiments of the refractory siderophile elements have been performed at more realistic pressures and temperatures of core formation (e.g. Bouhifd and Jephcoat, 2011; Siebert et al., 2012 and 2013 and Fisher et al., 2015). Following the same approach, understanding the fate and abundances of other elements can be assessed by studying their metal-silicate partitioning tendencies during core formation. **Chapter 2** presents an experimental investigation of the geochemical affinity of several volatile elements (Ga, Ge, Zn, As and Pb; **Fig. 4**) over a range of pressures (25 – 60 GPa) along with the mantle liquidus in order to understand the budget and genealogy of Earth's volatile elements in a context of core formation during planetary accretion.

Knowledge of the phase relations, physical and chemical properties of the relevant mantle and core materials under the conditions of the deep interior provide essential keys to encode and interpret the geophysical observations but can also help to simulate and understand processes that have shaped our planet over the last 4,57 Gyr. Studying mantle and core materials has been a major task of the experimental mineral physicists in the last couple of decades. Applying the most technologically advanced tools used in high-pressure physics, material science and nanotechnology, to address geoscientific questions, enables us to probe and understand the building blocks of the unsampled Earth, and helps to test scenarios of distant

Fig. 4 Elemental abundances of the Earth's present-day mantle normalized to CI chondrite and Mg vs. 50% condensation temperatures from the solar nebula at 10^{-4} atm(modified from Siebert and Shahar et al., 2015, see references therein).

time phenomena. However, each technology has its limitations. In the case of laser heated diamond anvil cell (LH-DAC) experiments, one of the most challenging technological aspect concerns temperature gradients. The extreme thermal conductivity of diamonds, which are usually in a direct contact with the laser-heated sample, causes severe heat loss and therefore heterogeneous heat distribution within the sample. The thermo-chemical (Soret) diffusion might cause artificial chemical segregation and biased distribution of elements in co-existing phases (e.g. Heinz and Jeanloz, 1987, Andrault and Fiquet, 2001, Sinmyo et al., 2008; Sinmyo and Hirose, 2010), leading to unrepresentative results. **Chapter 3** discusses some of the challenges related to the temperature distribution in LH-DAC experiments and presents a new technological approach of advanced sample micro-manufacturing in the form of metal-encapsulation, which enables more controlled and uniform laser-heating of fully encapsulated silicate samples at pressures and temperatures relevant for studying geo-materials at lower mantle conditions.

In brief, this thesis focuses on experimental investigation of the lower mantle melting phase relations of the simplest MgO-SiO₂ system (**Chapter 1**) and core-mantle equilibration processes through metal-silicate partitioning of several volatile and siderophile elements (**Chapter 2**). Our findings are relevant for understanding present-day Earth's structure and composition, but also its evolution through time since the early stages of its accretion and differentiation. The laser-heated diamond anvil cell (LH-DAC) technique was used in order to generate pressures and temperatures relevant for studying Earth's Interior. We have also developed a novel metal-encapsulation method for LH-DAC experiments to provide more controlled and uniform temperature distribution (**Chapter 3**).

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~~Chapter 1~~

Experimental constraints on melting temperatures in the MgO-SiO₂ system at lower mantle pressures*

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Abstract

Eutectic melting curves in the system MgO-SiO_2 have been experimentally determined at lower mantle pressures using laser-heated diamond anvil cell (LH-DAC) techniques. We investigated eutectic melting of bridgmanite plus periclase in the MgO-MgSiO_3 binary, and melting of bridgmanite plus stishovite in the $\text{MgSiO}_3\text{-SiO}_2$ binary, as analogues for natural peridotite and basalt, respectively. The melting curve of model basalt occurs at lower temperatures, has a shallower dT/dP slope and slightly less curvature than the model peridotitic melting curve. Overall, melting temperatures detected in this study are in good agreement with previous experiments and *ab initio* simulations at ~ 25 GPa (Liebske and Frost, 2012; de Koker et al., 2013). However, at higher pressures the measured eutectic melting curves are systematically lower in temperature than curves extrapolated on the basis of thermodynamic modelling of low-pressure experimental data, and those calculated from atomistic simulations. We find that our data are inconsistent with previously computed melting temperatures and melt thermodynamic properties of the SiO_2 endmember, and indicate a maximum in short-range ordering in MgO-SiO_2 melts close to Mg_2SiO_4 composition. The curvature of the model peridotite eutectic relative to an MgSiO_3 melt adiabat indicates that crystallization in a global magma ocean would begin at ~ 100 GPa rather than at the bottom of the mantle, allowing for an early basal melt layer. The model peridotite melting curve lies ~ 500 K above the mantle geotherm at the core-mantle boundary, indicating that it will not be molten unless the addition of other components reduces the solidus sufficiently. The model basalt melting curve intersects the geotherm at the base of the mantle, and partial melting of subducted oceanic crust is expected.

Keywords:

lower mantle; eutectic melting; diamond anvil cell; Early Earth Evolution; basalt; peridotite.

1. Introduction

Seismic velocity and density profiles of Earth's lower mantle as depicted in 1-D radially averaged models (Dziewonski and Anderson, 1981) are generally consistent with a peridotitic bulk composition. However, the exact proportions of the primary mineral phases, bridgmanite, ferropericlase, Ca-perovskite and possibly stishovite, are not yet uniquely constrained, and it is not known if the upper and lower mantle are compositionally similar, or if the lower mantle composition has a higher Si/Mg ratio due to a more chondritic primitive composition (e.g. Murakami et al., 2012) or through accumulation of mafic material via subduction. Seismology also reveals the presence of both small (e.g. Helffrich, 2006) and large-scale velocity anomalies (e.g. Garnero and McNamara, 2008) in the lower mantle. Large-scale features include two antipodal large low shear wave velocity provinces (LLSVP), as well as the more localized ultra-low velocity zones (ULVZ; Garnero and McNamara, 2008 and Lay et al., 2008) just above the core-mantle boundary (CMB). Depending on their origin and mineralogical constitution, these structures may exert a strong control on the distribution and magnitude of heat flow at the CMB and, therefore, on the convective dynamics and evolution of the Earth (e.g. Nakagawa and Tackley, 2008 and Torsvik et al., 2016).

One possible explanation for large-scale features in the deep lower mantle is mineralogical layering inherited from solidification of a deep global magma ocean during the earliest part of the Hadean Eon. Although geochemical arguments strongly preclude large-scale fractionation, segregation of bridgmanite-rich domains constituting up to ~15% of the lower mantle remain plausible (e.g. Walter et al., 2004 and Liebske et al., 2005). Another possible mechanism is the continued accretion of subducted oceanic crust at the base of the mantle, and the potential for melting of that material at the CMB (e.g. McNamara and Zhong, 2005). Testing these possibilities requires a detailed knowledge of the melting behaviour of mantle materials at the extreme conditions of the lower mantle.

Recent experiments on natural peridotitic and basaltic compositions (Fiquet et al., 2010; Andrault et al., 2011; Nomura et al., 2014; Andrault et al., 2014 and Pradhan et al., 2015) yield a range of solidus and liquidus temperatures at lower mantle pressures, and it is difficult to discriminate between the effects of bulk composition, the presence or absence of volatiles in starting materials, and the different melting criteria and detection techniques used to establish the melting curves. In this study, we focus on eutectic melting in the system MgO-SiO₂ in order to eliminate the complexity inherent in natural multi-component systems. The MgO-SiO₂ system describes ~95% of the mineralogy of peridotite and ~70% of basalt at lower mantle conditions. Importantly, because melting is eutectic, compositions can be chosen that produce large amounts of melt at an invariant melting temperature, facilitating greatly our ability to detect melting in experiments at extreme pressures and temperatures.

1.1 Previous Work in the System MgO-SiO₂ at Lower Mantle Pressures

Eutectic melting in the MgO-MgSiO₃ binary has been studied experimentally using the multi-anvil apparatus up to pressures of 26 GPa (Gasparik, 1990; Presnall et al., 1997 and Liebske and Frost, 2012). There is good agreement between these studies that the bridgmanite + periclase = melt eutectic is located at ~2775 K at 25 GPa, and that the eutectic liquid becomes progressively enriched in MgO with increasing pressure. Liebske and Frost (2012) presented a thermodynamic model for eutectic melting in this system, and based on extrapolation predicted that the eutectic liquid composition becomes richer in MgO up to about 80 GPa (from ~57 mol% at 24 GPa to ~60 mol% at 80 GPa), at which point it maintains a nearly constant Mg/Si ratio that

is close to model bulk silicate earth (BSE). Atomistic simulations in the MgO-SiO₂ system by de Koker et al. (2013) show a similar increase in MgO content from 58 to 60 mol% for the bridgmanite + periclase eutectic liquid throughout the lower mantle pressure range (25 – 135 GPa). These authors also simulated melting in the MgSiO₃-SiO₂ binary, and found a reduction in the MgO content of the bridgmanite + stishovite eutectic liquid from 37 to 33 mol% over the same pressure range; the silica phase is either stishovite or modified stishovite in the CaCl₂ crystal structure (referred to as stishovite from here onwards).

No previous experimental studies have investigated eutectic melting in the MgO-SiO₂ system throughout the lower mantle pressure range. The melting curves of the unary compounds MgO, MgSiO₃ and SiO₂ have been investigated in the laser-heated diamond anvil cell (LH-DAC) at pressures between ~30 and 60 GPa (e.g. Shen and Lazor, 1995), and results from these studies are in broad agreement with corresponding melting curves calculated from atomistic simulations (Stixrude and Karki, 2005; de Koker and Stixrude, 2009 and de Koker et al., 2013). The experimentally derived melting curve of bridgmanite (Zerr and Boehler, 1993 and Shen and Lazor, 1995), however, maintains a considerably higher dT/dP slope and less curvature than the computationally derived curve (de Koker and Stixrude, 2009 and Di Paola and Brodholt, 2016) through the 24-60 GPa pressure range.

In this study we performed double-sided laser-heated diamond-anvil cell experiments to constrain eutectic melting temperatures in the MgO-SiO₂ binary system up to 110 GPa. The two eutectics in the MgO-SiO₂ system are considered model analogues for the melting of the natural lower mantle candidate lithologies, peridotite and basalt, respectively.

2. Experimental and Analytical Methods

2.1 Starting Compositions

The compositions of the starting materials used in this study are listed in **Table 1**. In selecting starting compositions we aimed to be close to the eutectic melt composition in both the MgO-MgSiO₃ and MgSiO₃-SiO₂ binary systems, as predicted in the studies of Liebske and Frost (2012) and de Koker et al (2013). In the MgO-MgSiO₃ system we chose a composition with 58 mol% MgO, whereas in the MgSiO₃-SiO₂ system we chose two mixes, one with 40 mol% MgO and the other with 35 mol% MgO.

Fig. 1 shows our starting compositions relative to the predicted eutectic compositions derived from the atomistic computations of de Koker et al. (2013), and by applying the lever rule we calculate that our near-eutectic starting materials should yield from ~50% to 96% melt at lower mantle pressures. Producing such a large liquid fraction upon melting aids considerably in melt detection during laser heating and therefore enables precise eutectic temperature assessment.

Table 1. Experimental starting compositions (in mol%)

Starting mixtures	SiO ₂	MgO	Components*
M ₅₈ S ₄₂	42	58	En + Fo
M ₄₀ S ₆₀	60	40	En + SiO ₂
M ₃₅ S ₆₅	65	35	En + SiO ₂

*En: enstatite glass (MgSiO₃), Fo: crystalline forsterite (Mg₂SiO₄), SiO₂: silica glass

The MgO-MgSiO_3 binary composition was made by mixing enstatite glass with crystalline forsterite in the desired proportions, followed by grinding in an agate mortar under ethanol to a powder with a grain size of $\sim 1 \mu\text{m}$. Enstatite glass was made from a 1:1 molar mix of pure MgO and SiO_2 oxides, which were fused three times at 1 atm and $\sim 1700^\circ\text{C}$ for 30 minutes. The pure, crystal free glass product was ground after each fusion to a very fine powder. Crystalline forsterite was synthesized from a 2:1 molar mix of pure MgO and SiO_2 oxides, which were sintered three times at 1 atm and 1500°C for one hour and was verified as a pure phase by X-ray diffraction. The $\text{MgSiO}_3\text{-SiO}_2$ binary compositions were made by mixing enstatite glass (prepared as above) and high purity optical-grade silica glass (99.997%) in the desired proportions followed by grinding in an agate mortar under ethanol to a powder with a grain size of $\sim 1 \mu\text{m}$. Before weighing, all powdered components were dried at 120°C and stored in a desiccator to prevent adsorption of water. To provide an absorber for the IR laser radiation, $\sim 10 \text{ wt}\%$ of sub-micron tungsten powder was added to each starting composition. These mixtures were then further ground in an agate mortar under ethanol to ensure that the W absorber was homogeneously distributed throughout the sample on the micron scale to provide as uniform heating as possible. All mixtures were stored at 120°C under vacuum before use.

2.2 LH-DAC Experiments

2.2.1 High Pressure generation

High-pressure experiments were performed in ‘Princeton-type’ symmetric DACs, using Type Ia diamond anvils with culet diameters of 120, 150, 200 or $250 \mu\text{m}$. Re gaskets were pre-indented to $\sim 30 \text{ GPa}$ and sample chambers were drilled by UV laser ablation in each indentation. We drilled multiple sample chambers in a single Re-gasket where space allowed; 3 holes when using $200 \mu\text{m}$ diameter culets for pressures of 60-90 GPa, and 4 holes when using $250 \mu\text{m}$ diameter culets for pressures of 24-60 GPa (Walter et al., 2015; Thomson et al., 2014). The initial sample chamber diameters were 25-30 μm , and all sample chambers drilled in one gasket were filled with the same starting material. Before sealing and pressurising, the loaded DAC was

Fig. 1. Liquidus phase relations in the MgO-SiO_2 system at 24 and 136 GPa, adopted from de Koker et al. (2013). The initial fractions of eutectic melt (in percent) for the bulk starting compositions at 42, 60 and 65 mol% silica are calculated by the lever rule and shown beneath the red arrows representing the three starting compositions. Used abbreviations: per – periclase, bdg – bridgmanite, stv – stishovite L – melt.

heated at 125 °C under Ar gas flow for at least one hour to remove adsorbed water and then closed at the same high temperature conditions.

We opted not to use an additional thermally insulating material between the sample and the diamond anvils in order to avoid chemical reactions and mechanical effects at high pressures (e.g. sample tearing and separation) that might affect the observed melting temperatures. This is especially important as we have designed the bulk compositions to produce high melt fractions at the invariant temperature to aid in melt detection.

2.2.2 Pressure Measurement

Pressure was determined on the basis of the Raman shift of the singlet peak related to stress in the (001) direction at the diamond culet surface (Hanfland et al., 1986), and is calibrated relative to the ruby fluorescence scale of Mao et al (1986) (see Walter et al., 2015 for more detail). Confocal Raman measurements were made using a Jobin-Yvon T64000 Raman microscope at a spectral resolution of $\sim 0.4 \text{ cm}^{-1}$ within a diffraction limited focal volume. The calibrations based on diamond peak-shift are shown in **Figure S1** in the supplementary information. In each experiment, pressure was directly measured on each sample chamber before and after laser-heating. All reported pressures in this study are post-heating measurements. No correction has been made for thermal pressure during heating due to lack of *in situ* EoS data. The thermal effect on pressure is not expected to be more than $\sim 10\%$ of the initial pressure measured at room temperature (Fiquet et al., 2010 and Andrault et al., 2011). None of the results reported here came from heating of the sample chambers that contained ruby as it was added only for the purpose of pressure calibration.

2.2.3 Laser Heating

Double-sided laser heating was performed at the University of Bristol using two 100 W Yb-doped fiber lasers ($\lambda=1070 \text{ nm}$) combined with beam-shaping and beam-expanding optics to minimise radial temperature gradients. Beams were shaped to an approximately ‘flat-top’ energy distribution, with the spot size matched as closely as possible to the diameter of the sample chamber. The melting experiments were heated using an automated ‘ramp mode’, in which the laser power is continually and automatically increased by ~ 0.2 watts on each side every 4-6 seconds until quenching, resulting in a heating rate of 500-1500 K/min. We also performed a series of subsolidus experiments, where samples were heated to target temperatures below our melting curve and maintained at that temperature for ~ 30 minutes before quenching.

2.2.4 Temperature Measurement

At each step, temperatures were measured using standard spectroradiometric techniques (e.g. Walter and Koga, 2004). The thermal emission spectra were measured on both sides of the sample simultaneously over a wavelength range of 570 - 830 nm along an approximately $2 \mu\text{m}$ wide strip across the sample. Spectral intensity profiles were converted to temperatures by normalising to a NIST calibrated W-lamp of spectral radiance, with spectra fitted to the idealised grey-body Wien function. Maximum temperature precision is achieved by selecting the best-fit 200 nm bandpass within the 570 - 830 nm window that minimizes the average analytical error on the fits; temperature precision is typically better than 10 K at 3000 K. Uncertainty in temperature accuracy related to possible wavelength dependent sample emissivity (e.g. non-grey body behaviour) is unknown. A boxcar smoothing procedure was performed on all

temperature profiles to eliminate artefacts that arise because the spatial resolution of the CCD at the object plane ($\sim 1 \mu\text{m}$) is smaller than the actual system optical resolution of $\sim 3 \mu\text{m}$. For more details on the laser heating and temperature measurement system employed here, including calibration, benchmarking and uncertainties, see Lord et al. (2014a).

In several experiments we also obtained 2D temperature maps using four-color imaging radiometry similar to that described in Campbell (2008). In brief, a 50x image of the sample is focussed onto a large format, high resolution CCD (SBIG Model ST-402ME) at four different wavelengths (550, 650, 750 and 850 nm). The images are superimposed in software to a precision of ± 1 pixel. Temperature is calculated from a four-color Wien fit at each pixel, with spectral intensity calibrated as described above for the 1D spectroradiometry system.

2.3 Analytical Methods

After decompression, the culet region of the gaskets were cut out by UV laser ablation, transferred to a 1-inch epoxy mould and embedded in standard epoxy. The cured epoxy discs were polished axially to expose the approximate centre of the sample chambers, first manually using water based $9 \mu\text{m}$ diamond suspension on a polishing cloth, and later using a Buehler EcoMet® grinder-polisher with $3 \mu\text{m}$ and $1 \mu\text{m}$ diamond suspension. Because the samples were very thin ($\sim 10 - 25 \mu\text{m}$) and usually not completely flat after decompression, approximately 50% of all the sample chambers were lost during this process. Successfully polished samples were coated with a thin layer of carbon or gold and analysed using a JEOL JXA8530F Field Emission Gun Electron Microprobe at the University of Bristol. Textural and chemical analyses were carried out with beam conditions of 5 keV and 20 nA. Wave-length dispersive elemental calibration was performed with the following standards: Si - synthetic SiO_2 crystal, Mg - synthetic MgO crystal, Al - Amelia albite and W - tungsten metal.

3. Results

3.1 Melt Detection: Thermal Signal Processing

Perturbations in the temperature-power relation as laser power increases have been shown to be an extremely robust indicator of melting. These perturbations commonly manifest as a distinct plateau in temperature as laser power increases; temperature plateaus are especially well defined during invariant melting of metals, but have also been used to effectively detect melting in low-variance silicate, silicate-carbonate, and silicate-water systems (e.g. Shen and Lazor, 1995; Anzellini et al., 2013; Lord et al., 2014a; Thomson et al., 2014 and Walter et al., 2015). A comprehensive understanding of the factors resulting in thermal signal perturbations related to phase changes is elusive due to the diabatic nature of the sample environment and a lack of knowledge of material specific factors including changes in optical, thermal and mechanical properties upon crystallisation and/or melting (see for example: Geballe and Jeanloz, 2012; Lord et al., 2014a and b). Critically, this method has been corroborated using independent techniques, including direct observation of melt by *in situ* X-ray diffraction, often simultaneously (e.g. Fiquet et al., 2010; Anzellini et al. 2013; Lord et al. 2014a and b).

Fig. 2. Example of automatically ramped melting experiments showing: **(a)** Peak temperatures measured on the right (purple squares) and left (pink diamonds) sides of the DAC vs. total laser power in experiment MB_E8_C, and showing a well-developed temperature plateau. The pale grey band represents a 1σ uncertainty in the mean of the points within the plateau (defined by the grey band); **(b, c)** temperature profiles across the heated spot recorded on both sides of the DAC for experiment MB_E8_C. The ranges highlighted in colour reflect the selected windows used to define peak temperature. The sample chamber size is approximately $30\text{ }\mu\text{m}$ and the selected window is about $15\text{ }\mu\text{m}$. Error bars reflect the precision of the Wien fits and are $\pm 1\sigma$; **(d)** Peak temperatures vs. laser power for experiment MB_E48_C showing a rapid increase in temperature before reaching a maximum temperature plateau; **(e, f)** temperature profiles across the heated spot for MB_E48_C.

In all automatically ramped experiments, temperature was measured continuously at $\sim 5\text{ s}$ intervals during the heating ramp. We observe in some cases the appearance of a well-defined plateau in temperature as power continues to increase (**Fig. 2a-c**), but also commonly observe a rapid rise in temperature to a distinct temperature plateau that occurs after a gradual rise in temperature (**Fig. 2d-f**). These perturbations are likely a consequence of the indirect heating of the silicate due to laser absorption by the dispersed W particles and mechanical segregation of a high-degree melt and W particles. We observe the temperature maxima at these perturbations to be pressure dependent, and we correlate these with eutectic melting of the sample. Textural observations support this interpretation.

3.2 Melting Detection: Textural Analysis

Textural and compositional analysis of recovered samples using backscattered electron imaging (BSE) and elemental mapping provide additional evidence for melting. To establish the baseline subsolidus texture, experiments were made well below the expected melting temperatures and at conditions

approaching the solidus (**Tables S1** and **S2** in supplementary materials). All subsolidus samples we inspected using BSE imaging showed a relatively uniform distribution of W particles

embedded in the silicate matrix, with no obvious indication of melting in the heated area (**Fig. 3a** and **b**). However, we do observe a distinct coarsening of the W grains at higher temperatures approaching the solidus (**Fig. 3b**). In sharp contrast, samples where melting was detected by thermal signal processing show a range of textures consistent with melting, typical examples of which are shown in **Fig 3c**. The samples show segregation of W grains into a ring, or in a radial geometry about a central region that is relatively W-free. We also commonly observed a more centrally located large W aggregate (**Fig. 3c**). We suggest that once a large melt fraction forms at the eutectic temperature, W grains are mechanically displaced by the melt, resulting in the observed segregation of silicate melt pool and W aggregates. Melt-W segregation may also provide at least a partial explanation for the increased power needed to maintain constant temperature at the eutectic.

Fig. 3. BSE images of recovered DAC samples from: **(a)** cold-subsolidus (MB_E44_B $P = 53.3$ GPa and $T_{\text{max},s} = 2350$ K), **(b)** hot-subsolidus (MB_E36_C $P = 36.7$ GPa and $T_{\text{max},s} = 2500$ K), and **(c)** melted experiments (left: MB_E11_B $P = 43.7$ GPa and $T_m = 2930 \pm 124$ K, right: MB_E3_C $P = 28.6$ GPa and $T_m = 2753 \pm 35$ K).

The formation of a central aggregate and radially distributed W could indicate melting of the W absorber. However, we are confident that our melting curves represent the melting of the silicate rather than the W absorber because the 1 atm melting point of W (3687 K; Handbook of Physics and Chemistry) is considerably higher than most of our melting data. Another possibility is melting of the absorber as a consequence of carbide formation by reaction with the diamond. This is also an unlikely explanation as we observe no carbide formation in our electron probe analyses, and the diamond anvil culet surfaces show no indications of reaction with the sample. Moreover, the melting point of tungsten carbide at 1 atm (3003–3103 K, Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens) is higher than most of our data points below 40 GPa for the MgO-rich eutectic and 60 GPa for the SiO₂-rich eutectic, and as we will show below, our melting data at the lowest pressures investigated are consistent with results from multi-anvil apparatus experiments and *ab initio* simulations.

3.3 Melt Detection: Chemical Analysis

Polished samples were analysed with the electron probe to generate high-resolution X-ray elemental maps for Si, Mg and W. **Fig. 4** shows an example using the M₃₅S₆₅ starting material, where samples were pressurized to almost identical pressure (~50 GPa) but heated to different temperatures. **Fig. 4a** shows a sample heated to 2000 K for 35 minutes, and **Fig. 4b** represents a sample heated to 2300 K for a few minutes. Both samples show a relatively uniform distribution of W, indicating the samples remained subsolidus.

The Si- and Mg-chemical maps and spot analyses indicate the presence of two phases in the heated region, one of pure SiO₂, which we interpret as stishovite, and one with an intermediate

Mg/Si ratio consistent with bridgmanite (the grains were too small <500 nm for individual mineral analyses). The sample shown in **Fig. 4c** (MB_E44_C) was heated in ramp mode with melting detected by thermal signal processing at 3026 ± 178 K at 48,3 GPa. Here again, we observe the typical W-ring around the quenched melt pool and also a W-aggregate in the middle.

The subsolidus chemical maps (**Fig. 4a,b**) show phase separation between bridgmanite and stishovite, which is likely due to Soret or saturation gradient diffusion in response to the temperature gradient through the sample (e.g. Sinmyo and Hirose, 2010). We observe SiO_2 crystallizing within the hottest region, with bridgmanite intergrown or forming an annulus around stishovite, as expected. Temperature gradient induced phase segregation is also common in multi-anvil experiments where the temperature gradients are much less extreme (e.g. 100 C/mm), and have been reported previously to occur in the MgO-SiO_2 system (Presnall and Walter, 1993).

Fig. 4. Backscattered electron images (BSE) and wavelength dispersive elemental maps for Mg and Si of run products in the $\text{MgSiO}_3\text{-SiO}_2$ sub-system. **(a,b)** Two subsolidus samples (MB_E44_D and A) showing a homogeneous distribution of W grains in the BSE images, and phase segregation between bridgmanite (bdg) and stishovite (stv) in the heated region. **(c)** The melted sample (MB_E44_C) shows the typical annulus of W grains and a central aggregate in BSE, whereas the heated region shows a single homogeneous silicate with a composition close to that of the starting eutectic composition (67 wt% SiO_2 and 31 wt% of MgO), which we interpret as quenched melt.

3.4 2D-Sample Temperature Distribution

The radial temperature distribution, as measured by 2-D imaging radiometry, varies in detail from sample to sample but has common features. **Fig. 6** shows two examples, one showing a subsolidus temperature distribution (**Fig. 5a**), and another showing the temperature distribution after a temperature-power perturbation interpreted as melting (**Fig. 5b**). In the subsolidus, we commonly observe a $\sim 15\ \mu\text{m}$ diameter region with roughly constant temperature ($\sim \pm 50\ \text{K}$), surrounded by a region where temperature decreases with increasing distance from the centre at $\sim 20\text{-}30\ \text{K}/\mu\text{m}$, mimicking the energy distribution of the incident laser radiation. This gradient continues up to the radius at which the intensity of the incandescent light drops to $\sim 10\%$ of the maximum and an accurate temperature fitting becomes impossible (the dark blue region in **Fig. 5**). This masks the steep gradient of $\sim 10^3\ \text{K}/\mu\text{m}$ that defines the edge of the laser heated region. Such a temperature distribution is stable for extended duration (e.g. tens of minutes). However, with continuous increase in laser power and temperature, we observe a drastic, time-dependent change in temperature distribution (e.g. **Fig. 5b**) that correlates with the melting perturbation (plateau). **Fig. 5b** shows a central temperature peak and an annulus of high temperatures separated by a slightly cooler zone that mimics closely the distribution of W typically observed upon melting of the sample (**Fig. 3 and 4**).

An axial temperature gradient must also be present between the diamond anvils over a thickness of $\sim 10\text{-}25\ \mu\text{m}$ (depending on pressure), but is not well defined because we cannot measure it directly. We expect an $\sim 5 - 10\ \mu\text{m}$ region in the centre across which temperature decreases at the modest rate ($\sim \pm 50\ \text{K}/\mu\text{m}$), and a steep gradient over a few microns toward the highly thermally conductive diamond surfaces on each side.

Fig. 5. 2-D temperature maps over the laser-heated region in LH-DAC experiment MB_48_C at 48.3 GPa as determined using 4-color imaging radiometry. **(a)** Subsolidus temperature map collected at the beginning of laser-heating at $\sim 2300\ \text{K}$. **(b)** Super-solidus temperature map collected just before quenching at $\sim 3000\ \text{K}$. Contour lines represent light intensity relative to the maximum at intervals of 10%. The dark blue regions are not fitted because of insufficient light intensity that coincides with the very steep temperature gradient ($\sim 10^3\ \text{K}/\mu\text{m}$) separating the laser heated region from its unheated surrounding. See text for more details.

3.5 Melting Curves

The melting temperatures reported in this study are calculated as the mean of the smoothed maximum temperatures ($T_{\text{max},s}$ data in **Table S1** and **S2** in **supplementary materials**) from both sides of the sample, from the start of the temperature plateau until quenching. The reported uncertainties include the analytical precision in the greybody spectral fitting and one

standard deviation of the temperature variation within the melting plateau, which results in total uncertainties of $\sim 50 - 300$ K. We do not include an uncertainty related to non-greybody sample emissivity. Similarly, in subsolidus experiments we report temperatures calculated as the mean of the measured maximum temperatures on both sides of the sample, starting from the power at which the target temperature was reached until quenching. The run conditions of melting and subsolidus experiments are listed in **Tables S1** and **S2** in the supplementary materials and the results are plotted in **Fig. 6**.

All ramped experiments that resulted in detectable melting plateaus were used to constrain the melting curves. We could not detect any statistical difference between the melting data for the two Si-rich compositions we studied in the $\text{MgSiO}_3\text{-SiO}_2$ system, as expected for a eutectic system. Therefore, we fitted all the data simultaneously to produce a single eutectic melting curve. The P-T data are fitted using a modified Simon-Glatzel equation (Simon and Glatzel, 1929):

$$T_m = T_{24} \left(1 + \frac{P_m}{A} \right)^{\frac{1}{C}} \quad (1)$$

where T_m is the melting temperature at pressure P_m , A and C are fitting parameters (see **Table S3** in supplementary materials), and T_{24} is the melting temperature at 24 GPa from this study, which is consistent with both Liebske and Frost (2012) and de Koker et al. (2013). Because the lower mantle mineral assemblages differ from those at ambient pressure conditions, we use T_{24} as the starting point for our fits rather than the commonly used T_0 in the original Simon-Glatzel equation (Simon and Glatzel, 1929). The reference melting temperature at 24 GPa (T_{24}) represents approximately the pressure at which bridgmanite becomes stable. The melting temperatures for the two eutectics can be fitted with curves with positive and decreasing dT/dP slopes through the lower mantle pressure range.

Fig. 6. Results of this study for **(a)** the MgO-MgSiO_3 eutectic ($M_{58}S_{42}$), and **(b)** the $\text{MgSiO}_3\text{-SiO}_2$ eutectic ($M_{35}S_{65}$ and $M_{40}S_{60}$). The melting curves (solid lines) are fitted using a modified Simon-Glatzel equation (Simon and Glatzel, 1929) with parameters listed in **Table S3** and extrapolated to 136 GPa with associated 95% confidence intervals (dashed lines).

4. Discussion

4.1 Comparison with Previous Work in the MgO-SiO₂ System

In **Fig. 7** we compare our experimentally determined eutectic melting curves with previously published results from atomistic simulations (de Koker et al., 2013), previous experiments, thermodynamic modelling (Liebske and Frost, 2012), and endmember melting temperatures for MgSiO₃ (Stixrude et al. 2009), SiO₂ (Shen and Lazor, 1995) and MgO (Alfé, 2005). Our MgO-MgSiO₃ eutectic melting curve is in excellent agreement with the experimental data of Liebske and Frost (2012) in the lower pressure range (24 – 26 GPa). However, at higher pressures our melting curve is systematically lower than their extrapolated melting curve predicted on the basis of thermodynamic modelling. The predicted melting curve of Liebske and Frost (2012) is a maximum of ~350 K higher than our curve; at the pressure of the core-mantle boundary it lies within our uncertainty envelope. The bridgmanite + periclase eutectic as calculated by de Koker et al. (2013) is higher than our curve by about 100 K at 24 GPa, and about 450 K at 136 GPa.

Fig. 7. Eutectic melting curves from this study (solid lines with shaded area) compared with results from atomistic calculations (solid diamonds - de Koker et al., 2013), thermodynamic modelling (dashed line - Liebske & Frost, 2012) and melting curves of endmembers MgSiO₃ (Stixrude et al. 2009), SiO₂ (Shen and Lazor, 1995) and MgO (Alfé, 2005). The green and pink melting curves represent the peridotitic (M₅₈S₄₂) and basaltic (M₃₅S₆₅ and M₃₀S₆₀) model eutectics, respectively. The model basalt melting curve has a lower dT/dP-slope and less curvature than the model peridotite melting curve throughout the lower mantle pressure range.

The systematically lower melting points in our work compared to the first principles calculations might be explained by the difficulty in obtaining accurate melting points (T_m) in polyatomic systems using *ab initio* molecular dynamics. Simulations of relatively small systems (66-78 atoms, de Koker et al., 2013) with periodic boundary conditions tend to overestimate T_m due to the lack of defects and surfaces on which melt can nucleate.

4.2 Comparison with Melting Curves of Natural Compositions

Fig. 8 compares our eutectic melting curves with experimentally determined solidi for natural basalts and peridotites. Eutectic melting curves in the MgO-SiO₂ binary system should be higher than in systems that contain additional components. The multi-component peridotite solidi of Fiquet et al. (2010), Andrault et al. (2014) and Nomura et al. (2014) are shown in **Fig. 9a** for comparison. Fiquet et al. (2010) used a combination of X-ray scattering and textural evidence to detect melting in a model upper mantle composition (KLB-1), and found a solidus that is about 200 K lower than the bridgmanite + periclase eutectic determined here, but with an almost identical curvature. Andrault et al. (2011), also relying on X-ray diffraction and textural evidence for melt detection, found a solidus for model chondritic peridotite that has little or no curvature and which is located below the bridgmanite + periclase eutectic by a maximum of ~600 K at 80 GPa, but is within 300 K at the lower and higher pressure extremes. The pyrolitic solidus determined by Nomura et al. (2014) also has small curvature, but is about 1000 K below the bridgmanite + periclase eutectic at 80 GPa, and well below the other natural peridotite melting curves. Our peridotite melting curve is higher than those of natural compositions due to the reduction in temperature caused by the solution of additional components into the melt, with iron likely to have the most significant effect. For example, de Koker et al. (2013) suggest that adding around 10 mol% Fe to the MS system would reduce the solidus by 250±50 K. Such a reduction would bring our melting curves into much closer agreement with those of Fiquet et al. (2010) and Andrault et al. (2011) in the peridotitic system, though the curvature would still more closely resemble the study of Fiquet.

The different melting temperatures observed among studies in multi-component systems must reflect compositional differences to some degree (e.g. Mg/Si ratio, H₂O content), but differences in melt detection criteria are also likely to be relevant. In natural systems melting occurs over a temperature interval, rather than at a eutectic temperature. The X-ray scattering techniques used in the studies of Fiquet et al. (2010) and Andrault et al. (2011) (e.g. diffuse scattering; grain growth; phase disappearance) likely lead to overestimation of the solidus temperature because a substantial melt fraction may need to be present before melt can be detected. Nomura et al. (2014) attribute their lower temperature solidus to a combination of more sensitive melt detection technique based on X-ray tomographic imaging, and to the presence of ~400 ppm H₂O in their starting composition.

The multi-component basalt solidi of Hirose et al. (1999), Andrault et al. (2014) and Pradhan et al. (2015) are shown in **Fig. 8b**. Both Hirose et al. and Pradhan et al. use thermal signal processing as a primary melting criterion, their melting curves are nearly identical, and are supported at the low-pressure end by multi-anvil press (MAP) experiments. The melting curves from these studies have a nearly identical shape to the bridgmanite + stishovite eutectic curve found in our experiments, and lie close to our bridgmanite + stishovite melting curve. This would suggest that addition of iron and other components has little effect on solidus temperature. However, in contrast, the basaltic solidus of Andrault et al. (2014), determined using X-ray diffraction and temperature plateaus as melting criteria, falls ~600 K below our

bridgmanite + stishovite melting curve at 30 GPa, and ~ 300 K below at pressures greater than about 60 GPa.

Fig. 8. A comparison of experimentally determined melting curves (thick black solid lines) in this study of: **(a)** the periclase + bridgmanite eutectic compared with the peridotite solidi determined in LH-DAC experiments by Fiquet et al. (2010), Andrault et al. (2011), Nomura et al. (2014) and MAP experiments by: Trønnes and Frost (2002), together with the MgSiO₃ liquid isentrope from Stixrude et al. (2009); **(b)** the bridgmanite + stishovite eutectic compared with the basalt solidi determined in LH-DAC experiments by Hirose et al. (1999), Andrault et al. (2014) and Pradhan et al. (2015) together with a single MAP experiment from Hirose et al. (1999). The mantle adiabat of Anzellini et al. (2013, supplementary) is shown for comparison.

As with peridotite melting, melt detection in multi-component basaltic systems will depend on the melt fraction exceeding the detection limit. For example, in the study of Hirose et al. (1999) the basaltic sample was ‘sandwiched’ between Re absorbers, and melting was detected by a rapid rise in temperature. It may be that melting occurs at a lower temperature, and the runaway heating occurs only after considerable melt is present such that the solidus temperature is overestimated.

We reiterate that the advantage of working in the MgO-SiO₂ system using near-eutectic starting compositions is that large amounts of melt are produced at a single eutectic temperature, allowing more accurate determination of melting. In contrast, the melting curves produced in studies on natural compositions may represent the temperature at which the melt fraction exceeds the detection limit of the method used for melt determination, whether it be thermal signal processing or *in situ* X-ray diffraction methods.

4.3 Implications for Thermodynamic Modelling of the MgO-SiO₂ System

The eutectic melting curves presented in this study provide constraints on the thermodynamic properties of the MgO-SiO₂ liquid solution. By employing *ab initio* derived endmember models for the solids (periclase and stishovite) and liquids (MgO and SiO₂) from de Koker et al. (2013) and references therein, we calculated the activities (a_i) of MgO and SiO₂ in the two eutectic liquids using the equilibrium relation:

$$\mu_i = G_i^\circ + RT \ln a_i \quad (2)$$

where G_i° is the Gibbs free energy of component i (e.g. MgO or SiO₂) in the pure endmember melt and μ_i is the chemical potential of that component in the melt. At the bridgmanite + periclase eutectic, the chemical potential of MgO liquid is equal to the Gibbs free energy of periclase (assuming no SiO₂ is incorporated into periclase, equation 2). The same is true of SiO₂ liquid and stishovite for the bridgmanite + stishovite eutectic (equation 3). The thermodynamic relationships can be described as:

$$\mu_{MgO}^{liquid} = \mu_{MgO}^{solid} \quad (3)$$

$$\mu_{MgO}^{\circ,liquid} + RT \ln a_{MgO} = \mu_{MgO}^{\circ,solid} \quad (4)$$

and

$$\mu_{SiO_2}^{liquid} = \mu_{SiO_2}^{solid} \quad (5)$$

$$\mu_{SiO_2}^{\circ,liquid} + RT \ln a_{SiO_2} = \mu_{SiO_2}^{\circ,solid} \quad (6)$$

As the resulting activities only rely on endmember properties, they can be used to assess the accuracy of MgO-SiO₂ solution models (**Fig. 9**). We demonstrate this by comparing our calculated activities with predictions from a Margules-like mixing model that reasonably reflects the *ab initio* results (de Koker et al., 2013) at lower mantle pressures (**Fig. 9**). Margules interaction parameters (W_i) in a asymmetric regular solution model describe and fit the excess Gibbs free energy of the binary liquid mixture (e.g. Thompson, 1967 and Haselton and Newton, 1980) as:

$$G_{mix} = G_{ideal} + W_A Y^2(1 - Y) + W_B Y(1 - Y)^2 \quad (7)$$

where $Y = \frac{X}{X + \lambda(1 - X)}$ and $X = X(\text{SiO}_2)$ (molar fraction of SiO₂) so that $X = Y$ when $\lambda = 1$. However, de Koker et al. (2013) suggests using $\lambda = 1.43$, which allows for additional asymmetry

in G_{mix} and enables a match to their low pressure enthalpy of mixing data. The resulting Margules parameters for the binary mixture are the following:

$$W_A = 80 \cdot 10^3 - 70T \quad (8)$$

$$W_B = -245 \cdot 10^3 - 25T \quad (9)$$

In **Fig. 9** we observe the pressure-driven increase in the activity of SiO_2 derived from the de Koker et al. (2013) endmembers and bridgmanite + stishovite eutectic temperatures, and at face value the indication is that bridgmanite + stishovite eutectic melts become markedly more SiO_2 -rich. Such a dramatic change in the bridgmanite + stishovite eutectic composition would require a rapid change in melt solution properties at high pressures, which seems unlikely, and so a different explanation is required. We note that the calculated increase in silica activity is a direct consequence of the marked flattening of the de Koker et al. (2013) SiO_2 melting curve at high pressures (based on first-principles simulations by Karki et al., 2007; **Fig. S2a**), which is not mirrored in the pressure dependence of bridgmanite + stishovite eutectic temperatures presented in this study. Our results may thus indicate that the melting curve and properties of SiO_2 melt require reassessment. Especially as a number of ab initio studies note that obtaining accurate thermodynamic properties of silica-rich solids and liquid remains challenging due to

Fig. 9. A comparison between the activities of **(a)** MgO and **(b)** SiO_2 in eutectic liquids calculated based on the thermodynamic model of de Koker et al. 2013 using experimentally determined eutectic melting curves from this study (solid lines) compared with previous estimates (dashed lines) which reflects the variation of periclase + bridgmanite (green) and bridgmanite + stishovite (pink) eutectic compositions with pressure. The dotted lines are calculated for different melt compositions at the experimentally derived eutectic temperature, according to the modified Margules mixing model described in the main text.

a high degree of polarization and very slow diffusion of viscous liquid silica (e.g. Tangney and Scandolo, 2002).

Our experimental results also provide considerable constraints on the mixing properties of MgO-SiO₂ liquids. Specifically, the 100 – 500 K difference between the periclase + bridgmanite and bridgmanite + stishovite eutectic temperatures is a sensitive function of the shape of the free energy mixing curve. Although the results of de Koker et al. (2013) produce similar temperature differences between the eutectics, we note that this prediction is dependent on large entropies of mixing, coupled with a model in which bridgmanite is about 40 kJ/mol more stable relative to periclase + stishovite than in experimental datasets at 24 GPa (e.g. Stixrude and Lithgow-Bertelloni, 2011; Holland and Powell, 2011; more explanation can be found in supplementary materials, **Fig. S2b**).

If we assume instead that the experimentally derived datasets provide accurate estimates of the free energy of the reaction bridgmanite = periclase + stishovite, then our eutectic melting curves tell two things about the mixing and endmember properties of the MgO-SiO₂ melt system. First, a low temperature bridgmanite + stishovite eutectic (relative to periclase + bridgmanite) indicates that SiO₂ melting temperatures are probably overestimated, at least at pressures corresponding to shallow parts of the lower mantle. Second, to ensure that melting of bridgmanite remains congruent despite a relatively low stability (relative to its constituent oxides), the minimum in the liquid Gibbs free energy of mixing must be quite angular and shifted to the MgO-rich side of bridgmanite. This angularity can be explained by a maximum in short range order around the Mg₂SiO₄ composition, which has been proposed on the basis of both theoretical considerations and low pressure experimental results (Wu et al., 1993 and Harvey et al., 2015). This maximum implies that the activities of MgO and SiO₂ in ultramafic melts change quite abruptly as a function of silica content, which could strongly influence phase equilibria in a partially molten mantle.

4.4 Implications for Melting in the Deep Mantle

4.4.1 Crystallization of a Deep Magma Ocean

During the late stage accretion of Earth one or more giant impacts probably resulted in deep magma ocean(s) on a global scale (e.g. Benz and Cameron, 1990). Crystallization of a Hadean magma ocean would have set the initial state of the mantle, with crystal-melt fractionation potentially leading to large-scale early mantle heterogeneity. Near-equilibrium crystallisation of a magma ocean, as a result of efficient convective mixing of suspended crystals, would not be an effective fractionation mechanism (e.g. Solomotov and Stevenson, 1993). Fractional crystallization due to crystal settling or floating, or liquid segregation and trapping due to negative buoyancy could, however, lead to extensive primordial differentiation. The density contrast between crystals and liquid is therefore a key parameter controlling magma ocean evolution. Another important factor is the depth at which the magma ocean begins to crystallize, which depends on the relationship between the magma ocean adiabatic temperature gradient and the slope of the peridotite liquidus.

First principles molecular dynamics simulations of melts in the MgSiO₃ system (Stixrude and Karki, 2005 and Stixrude et al., 2009) show that the liquid adiabat, due to a continuous increase in the Gruneisen parameter of the liquid with pressure, is steeper than the melting curve, such that crystallization should begin in the middle of the lower mantle, rather than from the bottom up. On the basis of the shape of the bridgmanite + periclase eutectic curve found here, and assuming that the MgSiO₃ liquid adiabat is an adequate representation of the eutectic

liquid, the adiabat would intersect the melting curve at about 100 GPa (**Fig. 8a**). That is, our eutectic curve is consistent with crystallization beginning deep within a global magma ocean, but not at the bottom.

A middle-outward style of crystallization creates the potential for residual melts to become trapped near the bottom of the lower mantle forming a ‘basal magma ocean’, the remnants of which may manifest themselves in the modern Earth as seismic low velocity structures (LLSVP, ULVZ) (e.g. Labrosse et al., 2007). The melt-solid density difference will determine the fate of the basal liquid. Petitgirard et al. (2015) measured the density of amorphous MgSiO_3 at high pressures, and predicted a very small density contrast between crystalline and molten bridgmanite. With the strong preference for iron to partition from periclase and bridgmanite into melt relative to magnesium (e.g. Tateno et al., 2014; Pradhan et al., 2015 and Boukaré et al., 2015) it is probable that a melt-solid density cross-over exists in the lower mantle, and that basal melt derived from mid-mantle magma ocean crystallisation would remain negatively buoyant.

4.4.2 Melting of Peridotite and Basalt at the CMB

The mantle adiabat by Anzellini et al. (2013) extended to an outermost core temperature of 4050 K, is shown in **Fig. 8**. The bridgmanite + periclase eutectic melting curve (model peridotite) does not intersect the adiabat, so melting would not be predicted to occur at the base of the modern mantle based on the simplified system. The melting curves of Fiquet et al. (2010) and Andrault et al. (2011) also lie just above the adiabat at the CMB, although within uncertainty. Only the melting curve of Nomura et al. (2014) lies clearly below the adiabat such that melting at the base of the mantle is predicted to occur.

In contrast, our bridgmanite + stishovite melting curve (model basalt) intersects the mantle adiabat just above the core-mantle boundary, as do all melting curves for natural basalt. This region above the CMB is where localised but significant reductions in both P- and S- wave velocities are observed in seismic data (e.g. Williams and Garnero, 1996 and Garnero and Helmberger, 1998). Thus, partially molten recycled basalt is considered a possible candidate material for the thin ultra-low velocity zones (ULVZs) located directly above the outer core surface (e.g. Andrault et al., 2014 and Pradhan et al., 2015). Subducted oceanic crust is slightly denser than the ambient peridotite (e.g. Ballmer et al., 2015) and may partially segregate downwards in the low-viscosity D'' zone during conductive heat transfer from the outer core and lateral flow towards the LLSVPs (Torsvik et al., 2016). Basaltic material near the bottom of the D'' flow may interact and replenish the ULVZs, which are frequently confined to LLSVP-margins (e.g. Thorne and Garnero, 2004). Moreover, most deep plumes seem to be rooted near the edges of the LLSVPs and therefore may partially entrain basaltic material from the ULVZs (French and Romanowicz, 2015 and Torsvik et al., 2016).

5. Conclusions

Eutectic phase relations in the system MgO-SiO_2 involving the assemblages bridgmanite + periclase + melt and bridgmanite + stishovite + melt provide analogues for melting in equilibrium with peridotite and basalt at lower mantle conditions, respectively. Our experimental melting curves from ~20-110 GPa provide constraints on the maximum melting temperatures in peridotitic and basaltic lithologies relevant to the Earth's mantle. The bridgmanite + periclase (peridotite) melting curve is ~100 K higher at the top of the mantle than the bridgmanite + stishovite (basalt) melting curve, but is ~500 K higher at the CMB. The

bridgmanite + periclase eutectic curve has a shape indicating that a deep, peridotitic global magma ocean would begin crystallizing at ~100 GPa, favouring the possibility of residual, basal melt layer at the base of the mantle. Relative to estimates of the mantle geotherm, our data indicate that basalt will melt near the core-mantle boundary. The model peridotite eutectic is about 500 K higher than the mantle geotherm at the core-mantle boundary, but melting may occur due to the depression of the solidus caused by additional components (e.g. FeO, CaO, Al₂O₃, Na₂O).

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Supplementary materials

This Supplement contains additional information, figures and tables which completes and supports the manuscript by Baron et al., 2017 entitled ‘Experimental constraints on melting temperatures in the MgO-SiO₂ system at lower mantle pressures’.

1. Pressure calibration

In our experimental setup pressure was determined based on the Raman shift of the singlet peak related to stress in the (001) direction at the diamond culet surface (Hanfland et al., 1986), and was calibrated relative to the ruby fluorescence scale of Mao et al (1986). The calibration curve of the Raman shift of the singlet peak is shown in **Figure S1**. To calibrate the diamond peak shift, ruby was added to one of the sample chambers in many of our multi-chamber experiments. After laser heating we measured both the R1 ruby fluorescence peak from the ruby-bearing sample chamber and the Raman shift of the singlet peak from the diamond culet at the same position. Thomson et al. (2014) and Walter et al. (2015) found that the calibration can vary depending on the sample material and pressure medium. However, we observe no difference between the three compositions studied here.

Figure S1. Calibration of the stress-induced Raman shift of the diamond singlet peak measured at the culet surface relative to pressure measured by ruby fluorescence, both measured after quenching. The linear regressions for MgO-rich (green) and SiO₂-rich (pink and purple) samples resulted in slopes of 0.4937 and 0.4954 GPa/(cm)⁻¹ that are within uncertainty. We therefore fitted all the data simultaneously yielding a slope of 0.495 GPa/(cm)⁻¹ when forced through the origin.

2. Experimental data and fitting parameters

A summary of all the experimental conditions and measured melting temperatures are presented in **Table S1** and **S2** for MgO-MgSiO₃ and MgSiO₃-SiO₂ sub-systems, respectively. The melting temperatures reported in this study are calculated as the mean of the smoothed maximum temperatures ($T_{\max,s}$ data in **Table S1** and **S2**) from both sides of the sample, from the start of the temperature plateau until quenching. The reported uncertainties include the analytical precision in the greybody spectral fitting and one standard deviation of the temperature variation within the melting plateau, which results in total uncertainties of ~50 – 300 K. In subsolidus experiments we report temperatures calculated as the mean of the measured maximum temperatures on both sides of the sample, starting from the power at which the target temperature was reached until quenching.

Table S1. Experimental conditions and melting temperatures (K) in the MgO-MgSiO₃ sub-system.

C	Experiment	P (GPa)	$T_{\max}$	σ	$T_{\max,s}$	σ
M ₅₈ S ₄₂	MB_E4_A	30,7	2831	65	2793	65
	MB_E4_D	44,3	3304	185	3323	184
	MB_E4_C	50,0	3603	91	3506	93
	MB_E9_A	20,4	2734	109	2705	161
	MB_E9_C	55,7	3509	15	3502	14
	MB_E10_D	32,7	3145	50	3142	50
	MB_E16_D	27,4	2782	101	2770	98
	MB_E18_A	35,4	3112	60	3071	63
	MB_E18_B	40,3	3193	56	3174	62
	MB_E18_C	47,8	3448	166	3433	156
	MB_E32	99,1	4161	131	4072	130
	MB_E33_A	69,8	3687	103	3637	112
	MB_E33_C	63,6	3630	91	3617	93
	MB_E33_B	77,4	4004	118	4013	175
	MB_E43_C	48,2	3164	57	3150	101
	MB_E43_B	54,1	subsolidus ~2400 K			
	MB_E43_A	58,0	subsolidus ~2150 K			
	MB_E43_D	50,7	long subsolidus ~1800 K (30 minutes)			
	MB_E48_C	58,2	3556	89	3484	93
	MB_E48_A	63,3	subsolidus ~2450 K			
	MB_E48_B	60,0	long subsolidus ~2200 (30 minutes)			
	MB_E50_C	40,1	3324	108	3291	102
	MB_E50_A	47,3	subsolidus ~2500 K			
	MB_E50_B	45,0	subsolidus ~2400 (30 minutes)			

Table S2. Experimental conditions and melting temperature (K) in the MgSiO₃–SiO₂ sub-system

C	Experiment	P (GPa)	T _{max}	σ	T _{max,s}	σ
M ₃₅ S ₆₅	MB_E3_C	28,6	2757	36	2753	35
	MB_E5_A	23,1	2645	109	2640	108
	MB_E5_D	42,5	3112	94	3102	93
	MB_E5_C	45,3	2796	72	2784	47
	MB_E7_A	32,3	3004	45	2997	45
	MB_E29	108,5	3887	156	3852	271
	MB_E34	89,3	3448	289	3449	274
	MB_E37	91,4	3690	299	3675	304
	MB_E44_C	48,3	3038	186	3026	178
	MB_E44_B	53,3	subsolidus ~2350 K			
	MB_E44_A	49,1	subsolidus ~2300 K			
	MB_E44_D	44,8	long subsolidus ~2000 K (30 minutes)			
	MB_E47_B	80,0	subsolidus ~2900 K			
	MB_E47_C	86,1	subsolidus ~2450 K			
	MB_E47_A	78,3	long subsolidus ~2200 K (30 minutes)			
M ₄₀ S ₆₀	MB_E8_D	30,6	2910	42	2894	38
	MB_E8_A	55,2	3066	74	3055	70
	MB_E8_B	67,0	3188	44	3162	39
	MB_E8_C	68,7	3472	42	3444	40
	MB_E11_A	21,7	2497	120	2486	115
	MB_E11_D	29,3	2719	128	2669	203
	MB_E11_B	43,7	2938	121	2930	124
	MB_E12_D	30,1	2982	82	2949	78
	MB_E12_B	51,3	3281	123	3269	116
	MB_E19_C	35,4	2938	323	2916	312
	MB_E19_A	77,2	3479	181	3468	177
	MB_E19_B	73,7	3151	60	3144	58
	MB_E22_A	42,7	2968	115	2957	112
	MB_E22_B	60,2	3334	105	3312	105
	MB_E36_A	37,8	2775	146	2760	141
	MB_E36_C	36,7	subsolidus ~2500 K			
	MB_E36_B	53,1	subsolidus ~2700 K			
	MB_E49_B	62,3	subsolidus ~2900 K			
	MB_E49_A	71,8	subsolidus ~2400 K			
	MB_E49_C	68,0	long subsolidus ~2700 K (30 minutes)			
	MB_E45_A	80,1	3625	51	3573	45
	MB_E45_B	80,8	subsolidus ~2400 K			
	MB_E45_C	81,3	long subsolidus ~2000 K (30 minutes)			

All the automatically ramped melting experiments that resulted in detectable melting plateaus (listed in Table S1 and S2) were used to constrain the melting curves by fitting a modified Simon-Glatzel equation (Simon and Glatzel, 1929):

$$T_m = T_{24} \left(1 + \frac{P_m}{A} \right)^{\frac{1}{C}}$$

where T_m is the melting temperature at pressure P_m , A and C are fitting parameters (see **Table S3**), and T_{24} is the melting temperature at 24 GPa from this study (see more explanation in the main text of the manuscript).

We could not detect any statistical difference between the melting data for the two Si-rich compositions we studied in the MgSiO₃-SiO₂ system (M₄₀S₆₀ and M₃₅S₆₅), therefore, we fitted all the data simultaneously to produce a single eutectic melting curve for the bridgmanite-stishovite eutectic.

Table S3. Fitting parameters for the melting curves defined in this study

eutectic:	T_{24} (K)	A (GPa)	C
MgO-MgSiO ₃	2705	19.156 ± 7.38	3.7796 ± 0.878
MgSiO ₃ -SiO ₂	2605	29.892 ± 16.2	3.6770 ± 1.28

3. Thermodynamic modelling

In **Fig. S1a** we report and compare the experimentally determined eutectic melting curves from this study with all the *ab initio* results determined by de Koker et al. (2013) together with the melting curves of the end-members, MgO and SiO₂ used in the thermodynamic modelling of de Koker et al. (2013) and our thermodynamic calculations of the activity of MgO and SiO₂ in the eutectic liquids. The endmember melting curves were originally determined by Koker and Stixrude (2009) and Karki et al. (2006) for MgO and Karki et al. (2007) for SiO₂. A recently determined melting curve for SiO₂ based on shock data extended to 500 GPa by Millot et al. (2015) and previous shock data by Boslough (1988) suggests that the melting curve of SiO₂ may be lower but steeper than originally thought; hence thermodynamic models of the Si-rich eutectic might require further reassessment.

In order to understand the discrepancies between the various experimental, *ab initio* and modelling studies, we have also summarized the differences in Gibbs energy of solids and liquids at 24 GPa and 2605 K (de Koker et al., 2013 and Stixrude and Lithgow-Bertelloni, 2011) and at 1 bar (Wu et al., 1993) (**Fig. S2b**).

Figure S2. (a) The periclase + bridgmanite (green solid line) and bridgmanite + stishovite (pink solid line) eutectic melting curves experimentally determined in this study, *ab initio* results by de Koker et al. (2013; dashed green and pink lines) and endmembers MgO and SiO₂ melting curves used in the thermodynamic modelling (de Koker et al., 2013 and this study). Recently determined melting curve for SiO₂ based on shock data extended to 500 GPa by Millot et al. (2015) and previous shock data by Boslough (1988) are shown for comparison. **(b)** The difference in Gibbs energy of solids and liquids at 24 GPa and 2605 K from de Koker et al. (2013) (dK - 13) study in comparison with experimental datasets for solids by Stixrude and Lithgow-Bertelloni (2011) (S and L-B 2011) and 1 bar experimental liquid Gibbs free energy of mixing curve from Wu et al. (1993) (W - 93).

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Chapter 2

Partitioning of Ga, Ge, Zn, As and Pb between silicate and metal liquids in a deep magma ocean by LH-DAC experiments and μ -XRF measurements*

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Abstract

The volatile elements in the Earth's mantle are depleted relative to primitive solar system materials. However, many of them fall below the conventional volatile depletion trend postulated for Earth. This is largely related to a moderately siderophile (iron-loving) nature, such that their mantle depletion below the volatile depletion trend may be caused by core formation processes. The dual geochemical affinity for these elements makes it difficult to identify the relative importance of core formation and volatile depletion. Better constraints on the metal-silicate partitioning behaviour of the volatile and siderophile elements at pressures and temperatures relevant for core formation is therefore needed. Here, we present new experimentally determined partition coefficients for a series of volatile elements (Ga, Ge, Zn, As and Pb) between metal and silicate melts under high pressures and temperatures (25 – 60 GPa and 3000 – 4000 K) to test if the observed volatile abundances can be explained by core formation in deep magma oceans at conditions deduced from the partitioning behaviour of many refractory siderophile elements (e.g. Ni, Co, W and V). Laser-heated diamond anvil cell (LH-DAC) experiments were performed with doped silicate glasses and pure Fe-metal at superliquidus conditions. The quenched experimental products were prepared by focused ion beam milling for analysis by field emission electron microprobe and novel high resolution synchrotron-based μ -XRF, and the two analytical methods gave similar results, confirming the robustness of the data. The partitioning coefficients were corrected with respect to the Si and O contents in the metal and available element interaction parameters. The oxygen fugacity of the experiments, estimated by the Fe and FeO concentrations in the metal and silicate, respectively, varied from -1,0 to -0,6 log units below the iron-wustite buffer. The majority of our 25-60 GPa partitioning data agree with and extend to higher temperatures and pressures the already existing datasets from large volume press (LVP) experiments. Our experimental data suggest that Ge, Ga and As become less siderophile with increasing temperature and pressure. In contrast, Zn and Pb appear to become slightly more siderophile with increasing pressure and temperature. The Ge partitioning data, well-constrained by interaction parameter corrections, turned out to be very temperature dependent. These data were therefore used in the multi-stage core segregation model of Badro et al. (2015) along with other existing and well-constrained partitioning data for Ni, Co, Cr and V, in order to test different scenarios of core-formation. The favoured solutions involved metal-silicate equilibration along a high-temperature peridotite liquidus at 50-70 GPa and 4000-4200 K, independent of the redox state of the accreting material. Depending on the fO_2 scenario, the model predicts various Si- and O-concentrations in the Earth's core. A moderately reduced initial condition yields 4.5 and 2 wt% Si and O and a moderately oxidised initial case results in 3.5 and 2.5 wt% Si and O in the core, which roughly satisfies the requirement for a core-density deficit due to light-element incorporation. Overall, our partitioning data support the deep and very hot magma ocean scenario during Earth's accretion.

Keywords:

Earth's core formation; magma ocean; metal-silicate partitioning; volatile elements; laser heated diamond anvil cell

1. Introduction

The violent genesis of Earth and other terrestrial planets through collision of many planetary embryos and other smaller planetesimals and the decay of radiogenic isotopes provide substantial energy to induce melting of the proto-planetary material which differentiated and separated into layers (e.g. Stevenson, 1990; Murthy, 1991 and Chambers, 2005). Earth's accretion and core formation occurred within about 60 Myr of the beginning of the solar system (e.g. Kleine et al., 2002; Yin et al., 2002 and Barboni et al. 2017), and is best modelled and understood as a process of metal segregation from a relatively deep silicate magma ocean (e.g. Li and Agee, 1996; Wade and Wood, 2005; Wood et al., 2006 and Siebert et al., 2012). Dynamical models can simulate and illustrate the physics of planetary formation (Canup, 2004), whereas geochemical observations combined with experimental simulations of the core (metal) – mantle (silicate) interaction can place constraints on the conditions of the core segregation. The geochemical models of core formation are based on knowledge of the partitioning behaviour of refractory and moderately siderophile elements such as Ni, Co, W and V, which undergo very limited volatilisation so that their overall abundance patterns are largely controlled by core formation. Although models are dependent on specific data sets and assumptions made about the core formation processes (e.g. Walter and Cottrell, 2013), a general picture of metal-silicate equilibration in the pressure range of 25 – 60 GPa and at temperatures close to the silicate liquidus has emerged, supporting the core-mantle equilibration in a deep magma ocean scenario (e.g. Wood et al., 2006; Bouhifd and Jephcoat, 2011; Siebert et al., 2012).

Among nearly 30 siderophile elements, a particular subgroup includes elements which are also volatile in terms of their geochemical affinity (volatile siderophile elements). Their dual nature can be used to study not only core-formation processes but also the behaviour of volatile elements and their abundances. The volatile elements are depleted in Earth's mantle relative to primary solar system materials (chondritic reference) and follow a volatile depletion trend as a function of condensation temperature (e.g. Lodders 2003). However, many volatile elements falling well below the trend, were either sequestered into the core, lost during impact accretion or never delivered to Earth (Witt-Eickschen et al., 2009; McDonough and Palme, 2014). A first order test is to see whether or not the observed volatile element abundances can be solely explained by core formation at the appropriate PT conditions deduced from the refractory siderophile elements partitioning experiments (e.g. Wood et al., 2006; Siebert et al., 2011 and Siebert et al., 2012).

Following the concept of high-pressure core segregation, and given the importance of the high-pressure metal-silicate partitioning data for testing models of core formation and planetary differentiation, we have investigated the partitioning behaviour of five volatile siderophile elements, Ga, Ge, Zn, As and Pb, at 25-60 GPa and 3000-4000 K. Whereas Ga and Zn fall on the volatility trend, Ge and especially As are depleted by about 1-2 orders of magnitude. Although the depletion of Pb is more difficult to estimate, its partitioning behaviour at high PT is particularly important because of its use in geochronometry, and because there appears to be a Pb-loss event early in the Earth history (so called 'Pb paradox' of Allègre, 1969 and Allègre et al., 2001).

The superliquidus metal-silicate partitioning experiments were performed using the laser-heated diamond anvil cell (LH-DAC) method followed by sample recovery and preparation of thin sections by focused ion beam system (FIB). The quenched metal and silicate liquids were analysed for major and trace element concentrations by a standard field emission electron microprobe analysis (FE-EMPA) and novel synchrotron-based micro X-Ray fluorescence method

(μ -XRF) which provides a new opportunity to obtain high-quality quantitative data with spatial resolution on a sub-micron scale, particularly important for analyses of small DAC samples.

2. Experimental and Analytical Methods

2.1. Starting Compositions

The starting compositions used in this study were prepared by weighing the appropriate stoichiometric quantities of high purity oxide powders SiO_2 (Merck kGaA, proanalysis), Al_2O_3 (Sigma-Aldrich, 99.95 %), CaCO_3 (Alfa Aesar, 99.95 %), and MgO (Alfa Aesar, 99.95 %). After weighing, the material was ground for 1 hr in ethanol in an agate mortar and heated slowly to 1000°C in a Pt crucible for 24 hr to decompose the carbonate. Powdered Fe_2O_3 (Alfa Aesar, 99.99 %) was mixed into the decarbonated material to form a model basaltic composition (simplified BHVO-2, Wilson, S.A., 1997, Data compilation for USGS reference material BHVO-2, Hawaiian Basalt: U.S. Geological Survey Open-File Report). Subsequently, the material was split in two parts, and dopants were added and homogenised by grinding in an agate mortar for a further 1 hr. Dopants of ZnO (BDH Chemicals Ltd., 99.5 %), As_2O_3 (Sigma-Aldrich, 99.995 %) and PbO (Johnson Matthey, specpure) were added to the composition PC_4, whereas Ga_2O_3 (OSAKA, 99.99 %) and GeO_2 (Wako pure chemical industries Ltd., 99.9999 %) were added to PC_5 (see **Table 1**). In order to obtain meaningful analyses by FE-EMPA and high resolution μ -XRF and metal-silicate partition coefficients, the concentration level of the dopants varied between 1 and 3 wt%. The two starting oxide mixtures were loaded in Pt capsules with diameter of 2 mm and height of about 7 mm, pre-annealed at 1000°C and sealed using a micro-spot welder. The capsules were placed in MgO sleeves in a graphite furnace in a 12.5 mm pyrex-NaCl assembly. The two compositions were melted and vitrified in a 50-ton end-loaded piston-cylinder apparatus at 1.5 GPa and 1650°C .

The melts were held at high temperature for 10 mins in order to reach chemical equilibrium and quenched by switching off the power. The recovered capsules were carefully extracted from the high pressure assembly and opened to reveal the quenched glasses, initially checked for homogeneity using an optical microscope. The glasses were subsequently ground to a fine

Table 1

Microprobe analyses of silicate glasses synthesised in piston cylinder apparatus and used as starting materials for LH DAC experiments.

Wt.%	PC_4	1 σ	PC_5	1 σ
MgO	6,84	0,53	7,08	0,10
SiO_2	52,06	0,06	52,12	0,13
Al_2O_3	13,29	0,13	12,92	0,11
FeO	10,48	0,02	11,06	0,10
CaO	11,31	0,16	11,62	0,08
ZnO	1,07	0,14	-	-
Ga_2O_3	-	-	2,67	0,09
GeO_2	-	-	1,12	0,05
As_2O_5	3,14	0,13	-	-
PbO	1,42	0,10	-	-
Total	99,62	-	98,58	-

powder under alcohol and used for the LH-DAC experiments. A small portion of the synthesised products were embedded in epoxy and prepared for electron microprobe analyses to confirm the vitreous state of the samples and their chemical integrity. FE-EMPA WDX spot analyses of the synthesised products PC_4 and PC_5 are summarised in **Table 1**. We did not seek to control or measure the ferric-ferrous Fe ratio of the silicate starting material, because the $f\text{O}_2$ relevant to the LH-DAC partitioning experiments is governed by the silicate-metal equilibration at high pressures and temperatures.

2.2. LH-DAC Experiments

All experiments were performed using the laser-heated diamond anvil cell (LH-DAC) system installed at the School of Earth Science, University of Bristol, UK. We used ‘Princeton-type’ symmetric DACs with Type 1a diamond anvils of 300, 250 and 200 μm culet sizes. Re-gaskets were pre-indented to about 25 GPa, resulting in a final thickness of 30–35 μm . A sample chamber of 80–100 μm in diameter was drilled in each gasket by UV laser ablation. The starting materials were loaded as two pre-fabricated discs of compressed silicate powder with a Fe-metal foil in between. The glass powder was first mechanically squeezed into thin sheets (10–15 μm thick), using a hydraulic press, and cut into discs with the UV laser ablation unit to fit the sample chamber in the Re-gasket. A pure Fe-metal foil of about 10 μm thickness and 10–20 μm diameter was loaded between the two silicate powder discs in the middle of the chamber (Fig. 1a).

Fig. 1. (a) An optical image of the indentation in Re-gasket with a sample chamber of 100 μm in the diameter filled with a bottom layer of silicate glass and a small piece of Fe-foil in the middle. (b) Photomicrograph of a pressurised sample with a ruby sphere in a Re-gasket inside the DAC in the early stage of heating. The ruby piece (pink circle) is to the right of the laser-heated zone (orange rectangle) (c) 2D temperature map of the laser-heated zone in experiment no. 138 just before quenching. The temperature in the centre reaches 3050 K at 40 GPa. (d) Temperature vs. total laser power profile recorded during laser-heating of experiment no. 138 (40 GPa, 3050 K). The green and red squares represent standard 1D spectroradiometric measurements from left and right side, respectively, and the green circles refers to the temperature measurements based on the 2D temperature map from the left side. The grey band represents $\pm$ one standard deviation of the data in the last 10 s of the experiment, which was kept at 3050 ± 50 K.

For pressure estimation, a small ruby sphere was added on the side of the silicate and metal foil layers, away from the centre of the sample chamber to avoid contamination with the starting material in the laser heated zone (see photomicrograph in **Fig. 1b**). No additional thermal insulating and pressure medium was used as the silicate glass layers were relatively thick and provided enough chemical and thermal insulation. Before closing and pressurising, the loaded DACs were heated for an hour at 125°C under Ar gas flow to remove any absorbed moisture.

The pressure was measured at room temperature before and after each laser-heating experiment, using the R1 ruby fluorescence peak shift measurements (Mao et al., 1986). After each experiment, the Raman shift of the diamond stress peak was also measured at the culet surface in the middle of the heated area, using a Jobin-Yvon T64000 Raman Spectrometer which has been described in Baron et al., (accepted). The central pressure from the Raman measurements was only up to 3 GPa higher than the peripheral pressure from ruby fluorescence measurements, indicating a very small uncertainty arising from the radial pressure gradient. The reported pressures are post-heating measurements based on the ruby fluorescence method, checked and corrected by Raman measurements. No correction was made for the thermal pressure effect.

Pressurised samples were laser-heated from both sides using two 100 W Yb-doped fiber lasers ($\lambda=1070$ nm). The application of beam-shaping and beam-expanding optics restricted the heated area to about 20-30 μm in diameter (see **Fig. 1c**). Temperature was measured using a spectroradiometric technique (e.g. Boehler, 2000 and Walter and Koga, 2004). The thermal emissions were measured from both sides of the samples simultaneously fitted with the idealised grey-body Wien function over the 570-830 nm spectral range. More details about the design and technical features of the installed laser-heating setup, including calibration and uncertainties are described in Lord et al., 2014. The temperature in each experiment was first adjusted by levelling the laser power and coupling and focusing the lasers until both sides were in good agreement. Then the laser power was gradually and automatically increased by about 0.2 watts on each side every 3-4 seconds until reaching the target temperature. As the laser power was ramped up, the temperature profile typically recorded plateaus caused by melting of the Fe metal, followed by melting of the silicate (**Fig. 1d**). In order to overcome the highest plateau and achieve even higher temperatures for studying the influence of temperature on the partitioning character in some of the experiments, the lasers were manually focused until the target temperature was reached. Reported temperatures represent averaged measurements from both sides recorded during the last 10-15 s before quenching.

2.3. Focused Ion Beam (FIB) sample preparation

After laser-heating the DAC samples were slowly decompressed, recovered and excavated by the Zeiss Crossbeam Auriga FIB-SEM system at the IPGP in Paris, France. The flat and indented culet areas of the Re-gaskets were cut out by UV laser ablation and placed in the middle of carbon conductive tabs fixed to alumina SEM-stubs and carbon coated for FIB milling. The FIB system at IPGP allows electron imaging during the milling, enabling selection of the most representative area of the sample. When the quenched metallic and silicate melts were exposed in an axial section from one side, the milling was continued from the other side (**Fig. 2**). Thereby, we could locate approximately the centre of the laser-heated hot spot, expose similar proportions of the quenched metal and silicate liquids on both sides and prepare relatively thin (3-4 μm) but large (30-50 μm) section for extraction. The axial cuts were made through the entire thickness of the LH-DAC samples (15-30 μm) with a gallium beam operating at 30 kV.

During the milling we reduced the initial current of 20 A for efficient and fast milling to a very low current of 0.05-1 nA for final polishing of the sample surfaces in order to avoid Ga-implantation from the gun. The pre-cut sample sections were subsequently hitched to the remotely manipulated needle by Pt-deposition, cut off and lifted from the Re-gaskets. Then, the sample was transferred and mounted onto a copper TEM grid, where final thinning and cleaning of the sample surface took place.

Fig. 2. Secondary electron images of the LH-DAC sample retrieval and preparation using focused ion beam (FIB). **(a)** The initial cut into the sample and exposure of the entire laser-heated zone with metal blob, silicate melt around it and unreacted material on the sides. **(b)** After rotating by 180° the milling is continued from the other side and identical quenched features are exposed. **(c)** The section is thinned to about 3-4 μm thick slice and cut off from the sides **(d)** Once the thin section is partly detached from the surrounding material, a tungsten needle is inserted and fixed to the sample by electron-beam-deposited film of Pt, and after a complete cut off, it is transferred to the copper TEM grid **(e)** The sample is then fixed to the Cu-grid by Pt deposited strips and ready for further thinning and gentle polishing at the lowest current conditions (~ 1 nA). **(f)** The final overview of the sample prepared for further analytical measurements.

2.4. μ -XRF measurements

X-Ray fluorescence measurements were performed at the P06 beamline at PETRA III, DESY synchrotron in Hamburg, Germany. All measurements were taken from recovered LH-DAC

samples at room temperature and ambient pressure. The samples prepared by FIB and mounted on copper TEM grids were placed in the beam pathway with a sample holder rotated by 10° toward the detector to optimise the angle for XRF measurements. The XRF spectra were collected with a Vortex® detector set at about 90° from the incident beam. The monochromatic beam was tuned to 16 keV and focused to a beam size of approximately 250 nm in diameter. First we collected quick and low-resolution XRF spectra over the entire sample area, with a step size of 2-3 μm . The overview maps were used to identify optimal locations for smaller grid analyses with longer acquisition times (90–600 s).

Fig. 3. (a) An example of the XRF data collected along the linear grid in the silicate melt from sample 134 (PC_5, 41.5 GPa, 3200 K). The distinctive anomaly in the dataset (shaded point) represents high concentration of Fe and Ge which suggests that a sub-micron metal ball has been detected in the silicate matrix. The anomalous data points were excluded from the dataset to calculate the average amount of the dopant elements in the silicate melt. *normalised peak intensity refers to the area under the characteristic fluorescence line in the XRF spectrum after the background removal. **(b)** A BSE image of the sample 134 showing the linear grid location in the silicate melt along which the high-quality XRF spectra shown in (a) was collected.

Depending on the type of material, we used different acquisition times per spectrum, ranging from 90 to 180 s for metallic melts and from 300 to 600 s for silicate melts. Typically, we collected spectra along small square grids (5x5 or 4x4 μm) in the middle of the metallic melts and even smaller square, rectangular or linear grids (4x4, 3x3, 3x2 or 4x1 μm) in different areas of the silicate melts around the metallic blob in order to check the homogeneity, be able to resolve sub-micron features (e.g. small metal balls quenched in the silicate matrix, **Fig. 3**) and improve our statistics. Only the high-quality (longest acquisition time), representative and well-resolved spectra were used to accurately determine the relative concentrations of each element in the silicate and metal phases. In this study, we focussed on determining the partition coefficients of the elements Ge, Ga, Zn, As and Pb between the metal and silicate melts but because the fluorescence peaks of some of the elements overlap, we designed two starting material compositions PC_4 and PC_5 (see **Table 1** for details). Thereby, we were able to carefully separate and detect the characteristic K α lines for Ga and Ge in experiments with PC_5 starting composition (**Fig. 4a**) and K α lines for Zn, K β line for As and L β and L γ lines for Pb in experiments made using PC_4 (**Fig. 4b**)

Fig. 4. An example of two typical XRF spectra, showing the raw data (black lines) and applied fits (red dashed lines) and backgrounds (dotted orange lines) used for the calculations of the elemental contributions of all the elements of interest. The spectra were collected from a segregated metal ball from **(a)** sample 131 (scan19_0_1) after melting at 30 GPa and 3300K, **(b)** sample 134 (scan7_0_3) quenched at 41.5 GPa and 3200 K. The black dashed lines indicate the fluorescence lines which were well-resolved and used for calculation of the partition coefficients of the Ga and Ge in (a) and Zn, As, Pb in (b).

The high-resolution spectra were individually fitted using the PyMca software (Solé et al., 2007) and the areas under the specific fluorescence lines indicated in **Fig. 4** were calculated for each element after the background removal. All the results were first normalised to the incident beam intensity. The fluorescence lines at 6,403 (Fe - K α), 7,057 (Fe - K β), 8,63 (Zn - K α), 9,25

(Ga – K α), 9,89 (Ge – K α), 11,73 (As – K β), and a sum of two peaks: 12,61 and 14,76 kV (Pb – L β and L γ) were well-resolved and have been used for further partitioning calculations (described in Section 3).

In the XRF spectra of samples synthesised with PC_4 starting material one peak results from an overlap of two fluorescence signals from As (K α line) and Pb (L α line) at 10,55 kV (**Fig. 4b**). This peak was not selected and fitted because it would lead to false partitioning coefficient estimates. Another peak observed in some of the XRF spectra, in the region of interest (5 – 16 kV), comes from the fluorescence of Cu (K α line) and is attributed to the Cu-TEM grid which holds all the samples and is present due to the specific geometry of the beam-sample-detector pathway.

2.5. FE-EMPA measurements

The sample sections prepared with FIB were further investigated with the JEOL JXA8530F field emission electron microprobe analyser (FE-EMPA) at the School of Earth Science, University of Bristol, UK. The copper grids with samples were mounted as flat as possible on previously polished graphite SEM-stubs, fixed with Cu-tape and coated with a thin layer of carbon. All the chemical analyses were carried out at 15 kV accelerating voltage and 10-20 nA beam current. The calibration was performed with the same beam conditions using several standards for each element: Si – diopside and SiO₂, Ca – wollastonite, Al – albite and Al₂O₃, Mg – diopside and MgO, Zn – Zn metal, Ge – Ge metal, Ga and As – GaAs, Pb – galena, Fe – andradite, but also pure Fe metal and hematite (especially for O measurement in the metallic alloys). In most samples the metallic phases were relatively large (approximately 15x20 μ m) and homogeneous, and FE-EMPA spot analyses with 1 μ m beam size were therefore reliable and reproducible.

In the silicate melts, the regions without small metallic droplets were carefully chosen for the spot analyses, allowing us to measure the chemical composition of the silicate without metal phase contribution. The sub-micron metal droplets were most likely not able to coalesce with the main metal blob in the centre of the hot spot and therefore ended up being trapped in the silicate matrix during quenching. This has commonly been observed in a large number of metal-silicate partitioning studies performed with large volume presses (LVP) but also more recently in the DAC studies (e.g. Siebert et al., 2012; 2013 and Fisher et al., 2015).

3. Quantification of metal-silicate partitioning

The basic reaction which describes the distribution of an element M between a metal and silicate phase is:

where n is the valence of the cation M in the silicate melt. The partition coefficient D_M of an element M is defined as the ratio of the molar fractions of M in the metal over $MO_{n/2}$ in the silicate:

$$D_M = \frac{X_M^{metal}}{X_{MO_{n/2}}^{silicate}} \quad (2)$$

With the equilibrium constant, K, of reaction (1) and activity coefficients, γ_i we can derive a relation:

$$\log D_M = -\frac{n}{4} \log fO_2 - \log K + \log \frac{\gamma_{MO_{n/2}}^{silicate}}{\gamma_M^{metal}} \quad (3)$$

This defines a linear relationship between the logarithm of partition coefficient ($\log D_M$) and oxygen fugacity (fO_2) and the slope of the function ($-\frac{n}{4}$) provides the valence n of an element M in the silicate melt. In order to understand the effect of P , T or melt composition, it is important to compare the results at constant oxygen fugacity. Another way to characterise partition of an element M between metal and silicate is to consider the chemical exchange reduction-oxidation reaction of iron presented by Wade and Wood, (2005) and Corgne et al., (2008):

The equilibrium constant K associated with the reaction (4) is:

$$K = \frac{(a_M^{metal})(a_{FeO}^{silicate})^{n/2}}{(a_{MO_{n/2}}^{silicate})(a_{Fe}^{metal})^{n/2}} \quad (5)$$

where a is the activity of the component indicated in the subscript, so that:

$$a_i = \gamma_i X_i \quad (6)$$

where γ_i is the activity coefficient and X_i is the mole fraction of the element i . Therefore, the equation (5) can be written as:

$$K = \frac{(X_M^{metal})(X_{FeO}^{silicate})^{n/2}}{(X_{MO_{n/2}}^{silicate})(X_{Fe}^{metal})^{n/2}} \cdot \frac{(\gamma_M^{metal})(\gamma_{FeO}^{silicate})^{n/2}}{(\gamma_{MO_{n/2}}^{silicate})(\gamma_{Fe}^{metal})^{n/2}} \quad (7)$$

The first part of the equation (7) is commonly referred as K_D^M (O'Neill, 1992) which can be expressed as:

$$K_D^M = \frac{(X_M^{metal})(X_{FeO}^{silicate})^{n/2}}{(X_{MO_{n/2}}^{silicate})(X_{Fe}^{metal})^{n/2}} = \frac{D_M}{(D_{Fe})^{n/2}} \quad (8)$$

and is the molar ratio of partition coefficients D_M and D_{Fe} which are calculated based on the experimental measurements. In this way, the partitioning coefficients are normalised to the iron partitioning coefficients, allowing the experimental results to be compared independently of the oxygen fugacity (fO_2) of each individual experiment.

Following the same approach as presented in Wade and Wood (2005), the ratio of oxide activity coefficients in equation (7) is considered constant, thus taking the logarithm of the equilibration constant, the equation (7) can be reduced to:

$$\log K = \log K_D^M + \log \frac{(\gamma_M^{metal})}{(\gamma_{Fe}^{metal})^{n/2}} \quad (9)$$

because the partitioning behaviour seems to be insensitive to the silicate melt composition and its structure (e.g. Wade and Wood, 2005, Corgne et al., 2008, Siebert et al., 2011), especially for divalent elements, like Ge^{2+} , Zn^{2+} and Pb^{2+} but also for Ga^{3+} (Blanchard et al., 2015). For highly charged cations (e.g. As^{5+}) the validity of equation (9) needs to be re-addressed as their bonding mechanisms are more complex and depend on the degree of polymerisation of the silicate melt. In this study, however, no correction has been applied for the dependence of the silicate melt composition on partitioning behaviour.

Following the thermodynamic approach described by Wade and Wood (2005) and Corgne et al. (2008) summarised in equation (9), our experimentally determined and calculated partitioning coefficients (K_D^M), were corrected for the solute interactions and thus the activity coefficients γ_M^{metal} and $\gamma_{Fe}^{\text{metal}}$ were determined using the interaction parameters (ε_i^j) approach developed by Ma (2001). The following equations (10 and 11) thermodynamically describe the activity coefficients of iron (γ_{Fe}) and N-1 solutes (γ_i), in a multicomponent metallic solution (made up of N constituents) at the temperature of interest, in terms of the first-order interaction parameters (ε):

$$\begin{aligned} \ln \gamma_{Fe} = & \sum_{i=1}^{N-1} \varepsilon_i^i (X_i + \ln(1 - X_i)) - \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon_j^k X_j X_k \left(1 + \frac{\ln(1 - X_j)}{X_j} + \frac{\ln(1 - X_k)}{X_k} \right) \\ & + \sum_{i=1}^{N-1} \sum_{\substack{k=1 \\ k \neq i}}^{N-1} \varepsilon_i^k X_i X_k \left(1 + \frac{\ln(1 - X_k)}{X_k} - \frac{1}{1 - X_i} \right) \\ & + \frac{1}{2} \sum_{j=1}^{N-2} \sum_{k=j+1}^{N-1} \varepsilon_j^k X_j^2 X_k^2 \left(\frac{1}{1 - X_j} + \frac{1}{1 - X_k} - 1 \right) \\ & - \sum_{i=1}^{N-1} \sum_{\substack{k=1 \\ k \neq i}}^{N-1} \varepsilon_i^k X_i^2 X_k^2 \left(\frac{1}{1 - X_i} + \frac{1}{1 - X_k} + \frac{X_i}{2(1 - X_i)^2} - 1 \right) \end{aligned} \quad (10)$$

and

$$\begin{aligned} \ln \gamma_i = & \ln \gamma_{Fe} + \ln \gamma_i^0 - \varepsilon_i^i \ln(1 - X_i) - \sum_{\substack{j=1 \\ j \neq i}}^{N-1} \varepsilon_i^j X_j \left(1 + \frac{\ln(1 - X_j)}{X_j} + \frac{1}{1 - X_i} \right) \\ & + \sum_{\substack{j=1 \\ j \neq i}}^{N-1} \varepsilon_i^j X_j^2 X_i \left(\frac{1}{1 - X_i} + \frac{1}{1 - X_j} + \frac{X_i}{2(1 - X_i)^2} - 1 \right) \end{aligned} \quad (11)$$

where γ_i^0 is the activity coefficient of solute i when it is infinitely dilute in pure liquid Fe and the interaction parameters ε_i^j reflects the measured effect of component i on the activity of component j in the alloy and depends on the mole fraction of $i(X_i)$ and $j(X_j)$. Values of many ε_i^j and γ_i^0 are tabulated in the Steelmaking Data Sourcebook (The Japan Society for the Promotion of Science and The Nineteenth Committee on Steelmaking, 1988) at a reference temperature of 1873 K (T^0). We extrapolate the values to the experimental temperatures (T) following the suggested correction presented in the Steelmaking Data Sourcebook:

$$\ln \gamma_i^0(T) = \frac{T^0}{T} \ln \gamma_i^0(T^0) \quad (12)$$

and

$$\varepsilon_i^j(T) = \frac{T^0}{T} \varepsilon_i^j(T^0) \quad (13)$$

The principles and equations used for the formalization of the metal-silicate partitioning coefficients are directly applicable to the results of chemical analyses using EMPA. However, in this study we aim to compare the partitioning results based on standard EMPA analyses with more advanced μ -XRF analyses which have not previously been used for the determination of metal-silicate partitioning coefficients. We simplify the estimation of the metal-silicate partitioning coefficients based on μ -XRF data by assuming that the areas under the characteristic fluorescence peaks (see Section 2.4 for more details) of the XRF spectra represent the relative concentrations of the elements of interest in the metal and silicate melt phases. The partition coefficients (D_M) can therefore be obtained from the ratio of the area under the specific fluorescence line in the metal to the area under the same line in the silicate. Subsequently, the K_D is calculated using equation (8) where D_{Fe} is the ratio of the area under the main fluorescence line of Fe ($K\alpha$ – at 6,403 eV, see **Fig. 4**) in the metal phase to the area under the same line in the silicate melt. This approach is a first order approximation and does not fully address the complex nature of metal-silicate interaction. Because the partitioning results obtained with the two methods (EMPA and XRF) are very similar (see **Table 2** and **Fig. 5**), we have not applied any further corrections to the XRF data.

All the uncertainties reported for D_M and K_D are derived from the propagation of uncertainties in the analytical measurements (both for EMPA and XRF data). Calculated values for $\log K_D^M$ and related uncertainties are summarised in **Table 2** and plotted in **Fig. 5** for comparison.

4. Results and Discussion

4.1. Experimental results

The LH-DAC experiments were performed with basaltic starting compositions at temperatures at or above their liquidus (Andrault et al., 2014 and Pradhan et al., 2015) in order to ensure superliquidus conditions, necessary for equilibration. During laser-heating we commonly observed two distinct perturbations, in the form of temperature plateaus, in the temperature vs. laser power curve. **Fig. 1f** illustrates a typical temperature profile. Temperature plateaus are well known as good indicators of melting, and are especially well resolved during invariant melting of metals but are also useful to determine the melting of various silicates (e.g. Shen and Lazor, 1995; Anzellini et al., 2013; Lord et al., 2014a; Walter et al., 2015 and Baron et al., (accepted)). As mentioned in Section 2.2 and illustrated in **Fig. 1f**, the first plateau in our experiments is likely attributed to melting of the pure Fe-metal (~ 2500 K at 40 GPa, in agreement with Anzellini et al., 2013). After further increase beyond the plateau, the temperature stagnated again at about 2800 K, corresponding to the solidus determined by Pradhan et al. (2015) for natural basalt (at ~ 40 GPa). To achieve superliquidus conditions, the laser power was further increased to the target temperature above the liquidus, before rapid quenching by switching off the lasers.

The recovered samples comprise one central blob of metallic alloy surrounded by quenched silicate melt with quench-textures similar to those observed in previous studies (**Figs. 2f** and **3b**; Bouhifd and Jephcoat, 2003; 2011; Siebert et al., 2012; 2013 and Fisher et al., 2015). The quenched silicate melt is very homogeneous and fine-grained with an almost glassy appearance, indicating rapid quenching of a metal-silicate assemblage. Another commonly observed quenched feature in the silicate matrix is an occurrence of small (~ 200 nm to 2 μ m in diameter) regularly spaced and rounded metallic blobs, trapped in the silicate upon quench, before they managed to coalesce with the main central molten iron blob. These particles were avoided

during EMPA and μ -XRF analysis of the silicate glass (see **Fig. 3** for more details). As previously observed in numerous studies, the silicate melts were commonly enriched in FeO relative to the solid starting material (see **Table 1** and **Appendix A** for comparison) which reflects the preferential partitioning of FeO into the melt (e.g. Corgne et al., 2008; Tateno et al., 2014; Andrault et al., 2014 and Pradhan et al 2015). The characteristics of the metallic blobs varied with run temperature and composition of the alloy. In most experiments the metallic alloys were very homogeneous (like in **Fig. 2f**) but a few exhibited more heterogeneous quenched textures (**Fig. 3b**), due to the presence of Fe-Si-O-rich quench exsolutions, also featured in run products from large volume press (LVP) experiments (e.g. O'Neil et al., 1998; Ricolleau et al., 2011 and Siebert et al., 2011) and previous LH-DAC (e.g. Frost et al., 2010 and Siebert et al., 2012) partitioning experiments.

The partitioning results (with one sigma uncertainties) from seven experiments constraining the partitioning behaviour between liquid metal and liquid silicate of 5 volatile elements regarded as moderately (Ge, As) and weakly (Ga, Zn and Pb) siderophile are presented in **Table 2**. The average results of the FE-EMPA chemical analyses of the silicate and metallic melts are available in **Appendix A**.

Table 2

Experimental conditions and partitioning coefficients calculated based on microprobe and micro-XRF measurements.

XRF measurements														
No.	130		131		138		128		134		129		127	
P (GPa)	24,5		29,2		40		59		41,5		41,4		33,4	
T (K)	3400±100		3300±200		3050±50		3600±200		3200±200		3300±200		4000±300	
starting material	PC_4		PC_4		PC_4		PC_4		PC_5		PC_5		PC_5	
fO_2														
(ΔIW) ^a	-0,99		-0,62		-0,65		-0,64		-0,70		-1,03		-0,63	
	LogK _D	σ	LogK _D	σ	LogK _D	σ	LogK _D	σ	LogK _D	σ	LogK _D	σ	LogK _D	σ
Partitioning results based on microprobe analyses														
Zn	-1,05	0,02	-1,12	0,08	-0,62	0,07	-0,48	0,07	-	-	-	-	-	-
As	0,17	0,15	0,22	0,04	0,53	0,15	0,10	0,13	-	-	-	-	-	-
Pb	-0,13	0,08	-0,65	0,08	-0,10	0,04	0,02	0,06	-	-	-	-	-	-
Ga	-	-	-	-	-	-	-	-	-0,61	0,04	-0,81	0,05	-1,05	0,17
Ge	-	-	-	-	-	-	-	-	0,25	0,08	0,38	0,07	0,23	0,03
Partitioning results based on micro-XRF analyses														
Zn	-1,30	0,10	-0,87	0,11	-0,47	0,15	-0,64	0,02	-	-	-	-	-	-
As	0,33	0,46	-0,23	0,09	-0,06	0,10	0,45	0,40	-	-	-	-	-	-
Pb	-0,02	0,03	-0,39	0,19	-0,17	0,03	0,05	0,02	-	-	-	-	-	-
Ga	-	-	-	-	-	-	-	-	-0,81	0,05	-1,11	0,02	-1,03	0,15
Ge	-	-	-	-	-	-	-	-	0,28	0,10	0,17	0,03	0,16	0,11

^aOxygen fugacity (f_{O_2}) was calculated relative to the iron-wüstite (IW) buffer assuming ideal mixing behaviour (i.e. $IW = 2 \cdot \log(X_{FeO}/X_{Fe})$).

The quenched silicate and metallic melts were compositionally very homogeneous. The metal foil used as a starting material in the experiments did not contain any light elements (LE), and therefore the concentrations of oxygen, silicon and other elements solely come from the silicate-metal interaction at high pressures and temperatures. The LE content of the metallic alloys increases with increasing temperature and pressure, up to ~ 9 wt% of O and ~ 6 wt% of Si at 60 GPa and 3600 $\pm$ 200 K (**Appendix A**). Potential carbon contamination through diffusion

from diamond anvils was not measured, although the relatively high totals of the microprobe analyses (even of the metallic alloys) suggest very low C-contribution.

All the experiments were performed at similar redox conditions (from -1 to -0,6 relative to the IW buffer, see **Table 2**), which are similar to conditions reported in other DAC partitioning studies (e.g. Siebert et al., 2012; 2013 and Fisher et al., 2015). Previous studies have shown that the oxidation fugacity is somewhat higher in LH-DAC than in LVP experiments. This has been attributed to stronger partitioning of Si into the metal at higher temperatures and pressures, enriching the silicate melt in FeO, which increases the oxidation state (Siebert et al, 2012 and Fisher et al, 2015).

4.2. μ -XRF vs. EMPA data

Analysis by FE-EMPA has been used in the most recent LH-DAC metal-silicate partitioning studies (e.g. Siebert et al., 2012 and 2013). We followed the same procedures of sample preparation and used similar FE-EMPA analytical conditions as described in Siebert et al., 2012 and obtained reliable and reproducible minor and major concentrations of all elements in the systems (**Appendix A**). However, the microprobe analyses of the DAC samples need to be interpreted with caution and remain challenging due to potential analytical errors associated with the small size of the analysed material (e.g. Wade and Wood, 2012). The contribution of secondary fluorescence arising from the neighbouring phases, the effect of sample thickness and a relatively large beam size, unable to resolve all the quenched features, are examples of the potential sources of analytical errors. The sample thickness is especially crucial for analyses of low-atomic number silicates in which the primary X-Ray excitation depth is greater than that of metals. More advanced spectroscopic methods based on the high-brilliance synchrotron X-Ray radiation can therefore provide more accurate results and improve our understanding of the metal-silicate partitioning on the sub-micron scale.

Although synchrotron-based μ -XRF analysis has been used to determine partitioning of various major or trace elements between solid and liquid silicates (e.g. Andrault et al., 2012 and Petitgirard et al., 2012), as well as fluid-melt partitioning and dissolution of different elements at high PT conditions, using hydrothermal DAC (e.g. Sanchez-Valle et al., 2003; Petitgirard et al., 2009; Louvel et al., 2013 and 2014), this analytical technique has not been used in metal-silicate partitioning studies so far. Our new approach provides very high resolution and quality of the obtained spectra. The most important advantage of the new μ -XRF measurements compared to the FE-EMPA analyses is greater spatial resolution and therefore ability to resolve quenched features on a sub-micron scale. The high-energy X-Ray beam diameter can be focused to about 250 nm, providing the finest possible tool for spectroscopic measurements. This aspect is particularly important for analysis of the silicate melts, which commonly contain trapped metal blobs, which should be avoided in order to obtain more reliable chemical analysis of the quenched silicate melt phases (**Fig. 3**).

Fig. 5 shows uncorrected exchange coefficients ($\log K_D$) for the five investigated trace elements derived by the FE-EMPA and μ -XRF analyses. The two methods give similar results, especially for Ga and Ge. This can be related to the homogeneity of the quenched metallic and silicate melts synthesised with the PC_5 starting material (**Table 1**), compared with more scattered results from experiments performed with PC_4 starting material, containing Zn, As and Pb.

Fig. 5. A comparison of the exchange coefficients ($\log K_D$) of all studied elements (Ga, Ge, Zn, As and Pb) calculated based on the concentration data obtained by FE-EMPA (white dots) and μ -XRF (black dots) measurements. Both methods gave similar results, especially for Ga and Ge, which can be related to the starting material (Ga and Ge were doped in starting material PC_5, see Table 1) or to the homogeneity of the quenched metallic and silicate melts. The error bars are derived from the propagation of uncertainties in the analytical measurements.

partitioning coefficients are calculated as ratios between the elemental concentrations in metals and the concentrations in silicate melts, that issue is less relevant. Although our simplified XRF-approach does not address the full complexity of the metal-silicate interaction, it provides partitioning coefficients in good agreement with the data from the well-established EMPA methodology. To fully understand and correctly assess the potential of the μ -XRF measurements, further work on the calibration and potential correction of the XRF spectra is needed.

4.3. Epsilon correction and thermodynamic parametrization

To correct for the effect of the metallic melt composition, we applied the epsilon method developed by Ma (2001) (equations 10-13) to our experimentally derived partitioning coefficients (K_D^M) and other available data from the literature for comparison. We consider interactions parameters between elements of interest ($i = \text{Si, O, Ga, Ge, Zn, As and Pb}$) and four light elements (Si, O, S and C), influencing the partitioning of other elements in the system. The self-interaction parameters were considered for Si and O, only, and assumed to be negligible for the trace elements. The interaction parameters (ϵ_i^j) which are not available in the literature (e.g. ϵ_O^{As}) are also assumed to be negligible. The evaluated values of epsilon that best fit our experimental dataset are listed together with references in **Table 3**. Although our DAC experiments did not contain C and S, we include their interaction parameters for correction of previously published LVP data which were performed in graphite capsules and contained C and/or S in the starting material.

Comparison of the results from the two different methods, however, is not straightforward. Whereas the partitioning coefficients derived from the EMPA data are calculated using the molar oxides and molar elemental fractions of the silicates and metallic melts, respectively, the XRF-based partitioning coefficients rely on the elemental concentrations in silicate and metallic melts derived from the fitted fluorescence peak areas. Although the XRF-values represent absolute abundances of a particular element in the measured medium, they would need to be calibrated with external standards to obtain fully quantitative information (in wt%). However, because the

Table 3
Activity models for liquid metal.

i	ε_{Si}^i	ε_O^i	ε_S^i	ε_C^i	$\ln \gamma^o (T)$	References ^b
Si	12,41	-5	8,92	9,69	-6,65*1873/T	(1) and (2)
O	-5	-1	-17,14	-20,04	4,29-16500/T	(1) and (2)
Ga	-	-	-	-	-	-
Ge	15	0 ^a	7,03	2,09	1	(2), (3) and (4)
Zn	-	-	-	-	-	-
As	45	-	0,81	12,93	1	(3) and (2)
Pb	5,91	9,41	-3,47	5,61	1	(2), (5) and (6)

^anot resolvable

^bReferences: (1) Tsuno et al. [2013]; (2) Steelmaking Data Sourcebook [1988]; (3) Righter al. [2017]; (4) Wood et al. [2014]; (5) Wood and Halliday [2010]; (6) Siebert et al. [in prep.]

Table 4
Summary of the regression coefficients for all the studied elements from metal-silicate partitioning experimental studies.

i	a	±	b	±	c	±	References ^b
Si	0,364	0,280	-16520	716	0	-	(1) and (2)
O	2,736	0,140	-11439	387	0	-	(1) and (2)
Ga	-	-	-	-	-	-	-
Ge	-0,517	0,152	4478	323	0 ^a	-	(3)
Zn	-	-	-	-	-	-	-
As	1,460	0,560	2389	870	-121	18	(3)
Pb	1,217	0,250	-2984	495	0 ^a	-	(3) and (4)

^anot resolvable

^bReferences: (1) Siebert et al. [2013]; (2) Badro et al. [2015]; (3) this study; (4) Siebert et al. [in prep.]

Following the thermodynamic parametrization presented by many authors of metal-silicate studies (e.g. Righter et al., 1997; Wade and Wood, 2005; Corgne et al 2008; etc.), to understand the effect of the three main thermodynamic variables (P, T and composition) on the partitioning behaviour of studied elements, a relation is applied:

$$\log K = a + \frac{b}{T} + \frac{c \cdot P}{T} + d \cdot (nbo/t) \quad (14)$$

where a , b , c and d are regression constants obtained from least squares multivariable regression, T is temperature in K, P is pressure in GPa and nbo/t is the molar ratio of non-bridging oxygens over tetrahedral cations in the silicate melt. As shown in Siebert et al. (2011) the partitioning of elements studied here is rather independent of the silicate composition (especially for divalent elements) therefore equation (14) can be simplified to:

$$\log K = a + \frac{b}{T} + \frac{c \cdot P}{T} \quad (15)$$

In order to provide the most reliable and sensitive regression analyses of the metal-silicate partitioning behaviours in a wide range of pressures and temperatures, results obtained in this study were combined with data from previously published partitioning experiments available in the literature. Values of the regression coefficients a , b and c with corresponding uncertainties are listed together with references in **Table 4**.

Due to discrepancies between our high pressure data and recently published LVP partitioning results for Ga at 2 GPa (Blanchard et al., 2015) and slight inconsistencies between our Zn data and 2 GPa data (Mahan et al., 2017) and higher pressure results from Mahan et al. (in prep.), we were unable to correct and fit all the available data. We only report uncorrected partitioning coefficients values for Ga and Zn and will perform more detail regression analyses of the data set in the future. Similarly for As, due to the lack of essential interaction parameters (especially ε_O^{As}) and inconsistencies with the recent estimates of ε_{Si}^{As} (Richter et al., 2017), we decided to report and discuss only uncorrected K_D^M values for clarity.

4.4. Characterisation of the metal-silicate partitioning

4.4.1. Si and O partitioning (all experiments)

Si and O are two of the most likely major light element candidates contributing to the density deficit of the outer core (e.g. Poirier, 1994; Allègre et al., 1995 and McDonough, 2003). Constraints on their geochemical affinity for different bulk compositions and PT conditions can therefore help to understand the Earth's core evolution. The quenched metallic melts from our experiments contain 0,09-6,36 wt% Si and 3,04-9,98 wt% O, and the upper parts of these concentration ranges may likely exceed the Si and O contents of the Earth's core, based on the geophysical observations compared with the density of pure Fe. It is necessary to correct the experimental data for the Si and O concentrations in the metallic phase in order to relate our metal-silicate partitioning data for the investigated trace elements to plausible core-formation scenarios.

Fig. 6 summarises the results from previous studies on Si and O partitioning including DAC experiments above 30 GPa (Bouhifd and Jephcoat, 2011; Siebert et al., 2012; 2013; unpublished data and Fischer et al., 2015) and various large volume press experiments below 25 GPa (see figure caption for all the references) and the results obtained in this study. All the experimentally derived data are corrected following the approach developed by Ma et al. (2001) (explained in Section 3). Applied interaction parameters and activity coefficients are given in **Table 3** (see references therein).

Least-squares regressions of the full dataset published in previous studies (regression constants a , b and c are given in **Table 4**) show that the partitioning of O, and of especially Si, is strongly temperature dependent with no resolvable pressure effect. Our dataset is consistent with the previously published results for both elements, which indicates reliable P-T estimates and chemical equilibration of our experiments. To limit the influence of compositions, the plotted results are restricted to (1) experiments with silicate melts, (2) experiments without high sulphur contents in the iron metal, and (3) experiments performed in MgO capsules (LVP experiments).

Fig. 6. Equilibrium constants (K) **(a)** $\text{FeO}_{\text{sil}} = \text{Fe}_{\text{met}} + \text{O}_{\text{met}}$ (the log K term appears in equation 3) and **(b)** equation 4: $\text{SiO}_{2\text{sil}} + 2\text{Fe}_{\text{met}} = 2\text{FeO}_{\text{si}} + \text{Si}_{\text{met}}$, plotted as a function of reciprocal temperature. Equilibrium constants represent the measured exchange coefficients values corrected for the effect of metal composition (see text). K values of this work (white crosses) and other studies at different pressure conditions including LH-DAC experiments above 30 GPa (Bouhifd and Jephcoat, 2011; Siebert et al., 2012; 2013; unpublished data and Fischer et al., 2015) and large volume press experiments below 25 GPa (Hilgren et al., 1994; Kilburn and Wood, 1997; Gessmann and Rubie, 1998; Li and Agee, 2001; Wade and Wood, 2001; 2005; Chabot et al., 2005; Asahara et al., 2007; Wood et al., 2008; Mann et al., 2009; Ricolleau et al., 2011; Tsuno et al., 2013 and Fischer et al., 2015) are summarized for comparison. Solid lines are the result of least-squares regressions of the full dataset.

4.4.2. Ga-Ge - system

4.4.2.1. Ga partitioning

Fig. 7. Exchange coefficients (K_D) for Ga plotted as a function of pressure: this work (red dots) and other studies including DAC experiments (green dots Siebert et al., unpublished data, **Appendix F**) and large volume press experiments at lower pressure (white circles: Siebert et al., 2011; Mann et al., 2009; Blanchard et al., 2015) at different temperature conditions. See text for more detail.

strong negative pressure effect inferred from other lower P-T experiments (Siebert et al., 2011 and Mann et al., 2009). This also applies to the DAC results from this study and that of Siebert et al., (unpublished data, **Appendix F**). Further experiments and thermodynamic modelling are required to constrain a set of regression parameters that would allow proper parameterization of Ga partitioning as a function of P, T and metal composition after more detail evaluation and correction of the available datasets.

4.4.2.2. Ge partitioning

In **Fig. 8a** we present a summary of the Ge partitioning coefficients (K) available in the literature (Siebert et al., 2011; Wood et al., 2014 and Righter et al., 2017) together with our results, obtained for the first time with LH-DAC technique at realistic conditions of a deep magma ocean. To fully understand the pressure and temperature effect on the Ge partitioning behavior, the measured partition coefficients (K_D) were corrected for the effect of metal composition, using the interaction parameter approach developed by Ma (2001). Previously published partitioning data obtained with LVP (Siebert et al. 2011; Wood et al. 2014 and Righter et al. 2017) were corrected for the effect of S, Si and C, using the interaction parameters in **Table 3**. Because our samples did not contain C or S, the partitioning data were only corrected for the strongly reducing effect of Si on Ge partitioning predicted from Righter et al. (2017) (i.e. $\epsilon_{Si}^{Ge} = 15$), which lead to K values consistent with the LVP experiments.

Fig. 7 summarises the partition coefficients (K_D) obtained in this study and selected results from previously published LVP experiments (Siebert et al., 2011; Mann et al., 2009 and Blanchard et al., 2015) and DAC experiments (Siebert et al., unpublished data, see **Appendix F** for more details). The Ga valence state in silicate melt is assumed to be 3+ as proposed by Siebert et al. (2011) and the temperature effect on partitioning is assumed to be negligible (Siebert et al., 2011 and Mann et al., 2009). For the sake of comparison, we selected LVP data which do not contain light elements in the liquid metal. Only the exchange coefficients (equation 4) are presented here because the influence of light elements on Ga partitioning predicted from Blanchard et al. (2015) would lead to elevated K values for DAC experiments, inconsistent with the

Fig. 8. (a) Corrected equilibrium constant (K) of the redox exchange reaction (equation 4) for Ge plotted as a function of reciprocal temperature: Our data (red dots; first partitioning data for Ge obtained with the LHDAC technique at direct conditions of a deep magma ocean) and LVP experiments (other filled circles, Siebert et al., 2011; Wood et al., 2014 and Righter et al., 2017) at different pressure conditions. Our data are corrected only for the large Si negative effect predicted from Righter et al. (2017) ($\epsilon_{Si}^{\text{Ge}} = 15$), red empty circles, the K_D values from this work, are reported for comparison. Solid line represents result of least square regression of the full dataset (see regression constants in **Table 4**). **(b)** Molar partition coefficient (D_{Ge}) as a function of the oxygen fugacity expressed relative to the IW buffer. Following the relationship in equation (3) the valence state of Ge in silicate melt is estimated to be 2+ based on LVP data at similar P-T conditions without light elements (LE) in metal.

The result of least square regression of the full dataset with the regression constants in **Table 4** shows that pressure effect and O content of the metal have no resolvable influence on Ge partitioning. Increasing temperature, however, has a strong effect, reducing the metal-silicate partition coefficients, in good agreement with Siebert et al. (2011). This temperature effect

provides a powerful tool to estimate the plausible temperature conditions of core formation processes and was therefore implemented in the multi-stage core-formation models presented below in section 6.

Following the relationship presented in equation (3) and using selected LVP data which were performed at similar P-T conditions (1 - 3 GPa, 1838 - 2173 K) without light elements in metal (Siebert et al 2011; Wood et al., 2014 and Righter et al., 2017), we also confirm that the Ge valence state in silicate melt is 2+ (**Fig. 8b**) which agrees with previously published studies (Siebert et al., 2011 and Righter et al., 2017).

Fig. 9. Exchange coefficients (K_D) for Zn plotted as a function of **(a)** pressure and **(b)** reciprocal temperature: this work (red dots) and other studies including DAC experiments (green dots Mahan et al., unpublished data, **Appendix F**) and LVP experiments at lower pressures (white circles Siebert et al., 2011; Mann et al., 2009; Wood et al., 2014, Wang et al., 2016, Mahan et al., 2017) at different pressure and temperature conditions. See text for more detail.

4.4.3. Zn-As-Pb – system

4.4.3.1. Zn partitioning

Fig. 9 shows the uncorrected partition coefficient (K_D) of Zn plotted against pressure and reciprocal temperature from this study together with selected results from previously published LVP (Siebert et al., 2011; Mann et al., 2009; Wood et al., 2014; Wang et al., 2016 and Mahan et al., 2017) and DAC experiments (Mahan et al., unpublished data, see **Appendix F** for more details). For the sake of comparison and because C and S in the metal are known to affect the partitioning behaviour of Zn (Siebert et al., 2011; Wood et al., 2014 and Mahan et al., 2017), we have selected only LVP experiments performed in MgO capsules (not graphite or other capsule types) and without

significant amount of S in the starting material.

The valence state of Zn in silicate melt is assumed to be 2+ as confirmed by Siebert et al. (2011). A combination of LVP and DAC experiments shows that the metal-silicate Zn partition coefficient increases towards unity with increasing temperature (**Fig. 9**). Although the pressure effect is questionable, the general correlation between pressure and temperature in the combined datasets from LVA and DAC experiments gives the appearance of a weak positive correlation between the Zn partitioning coefficient and pressure (**Fig. 9a**). Based on the compilation of the individual LVP data sets, however, Siebert et al., (2011, their Fig. 9) and Mann et al., (2009, their Fig. 5) show indications that Zn becomes slightly less siderophile with increasing pressure. In contrast, the DAC experimental datasets from this study and Mahan et al. (unpublished, **Appendix F**) indicates a weak positive correlation between pressure and the metal-silicate partitioning coefficient for Zn, although the effect is not significant. Further investigations (experiments and thermodynamic modelling) are required to constrain a set of regression parameters that would allow proper parameterization of Zn partitioning as a function of P, T and metal composition. As noted by Mahan et al., (2017), the higher pressure (9-24 GPa) results of Mann et al., (2009) displayed significant discrepancies with the rest of the available data, and we therefore excluded these from our comparison.

4.4.3.2. As partitioning

In **Fig. 10** we present the first partitioning coefficients (K_D) for As obtained from LH-DAC experiments. These are plotted against pressure, together with previously published LVP data (Siebert et al., 2011). The valence state of As in silicate melt is assumed to be 5+ which was also quantitatively determined by Siebert et al. (2011). However, Richter et al., (2017) assumed trivalent arsenic although did not provide sufficient explanation for such a choice. In this study, we only present measured exchange coefficients due to the fact that the influence of light elements (Si, O) on As partitioning is poorly understood and remains controversial. Although the predictions from Richter et al. (2017) suggest very strong Si-As interaction with $\varepsilon_{Si}^{As} = 47$, a corresponding correction would lead to inconsistent K values with respect to the strong negative pressure effect on partitioning inferred from previous LVP experiments (Siebert et al., 2011) supported by our results. Other interaction parameters (e.g. ε_O^{As}) are also lacking in the literature, limiting

Fig. 10. Exchange coefficients (K_D) for As plotted as a function of pressure: this work (red dots; first partitioning data for As obtained with the LH-DAC technique) and previous large volume press experiments at lower pressure (Siebert et al., 2011) at different temperature conditions. Selected large volume press data do not contain light elements in the liquid metal. Solid line represents result of least square regression of the full dataset (see regression constants in **Table 4**)

a comprehensive understanding of the partitioning behaviour of As. In **Table 4** we report the regression parameters obtained for K_D values which are first order approximations and further work is required to constrain regression parameters that allow consistent thermodynamic parameterization of As partitioning as a function of P, T and metal composition (i.e. ε_{Si}^{As} and ε_O^{As}).

4.4.3.3. Pb partitioning

Fig. 11. Equilibrium constant (K) of redox reaction (3) for Pb plotted as a function of reciprocal temperature: LH-DAC data (our work: red dots, and Siebert et al., in prep. (**Appendix F**): red empty diamonds) and large volume press (LVP) experiments at lower pressure (white and yellow circles, Wood and Halliday, 2010; Bouhifd et al., 2013; Wood et al., 2014) at different pressure conditions. Solid line represents result of least square regression of the LVP dataset (see regression constants in **Table 4**).

P and T, using regression constants listed in **Table 4**. This shows a positive effect of T on Pb partitioning and a negligible pressure effect. Subsequently, the K values for the DAC experimental data were corrected by assuming that the discrepancy between DAC values and the regression line is due to the influence of oxygen solubility in the metal on the activity coefficients of Pb in the metal. A value of $\varepsilon_O^{Pb}=9$ was obtained (see **Table 3** and **4** for full details of Pb partitioning parameterization). The partitioning values obtained from our experiments are slightly more scattered than the other DAC data (Siebert et al., in prep., **Appendix F**) but agree and lie on the same trend.

5. Comparison to Earth mantle abundances

Based on our experimental determination of the pressure and temperature dependences of the metal-silicate partitioning coefficients of a range of elements classified as volatile and moderately siderophile, we compare the geochemical affinities of these elements with their terrestrial abundances in the context of core formation processes. Pb and Zn have an additional

Corrected partitioning coefficients (K) of Pb from this study, together with previously published LVP results (Wood and Halliday, 2010; Bouhifd et al., 2013 and Wood et al., 2014) and another DAC results from Siebert et al., (in prep.) which experimental details are listed in **Appendix F**, are summarised in **Fig. 11**.

The Pb valence state in silicate melt is assumed to be 2+ (Wood and Halliday, 2010). The full dataset is corrected for the effect of metal composition on partitioning using the interaction parameter approach (Ma, 2001) with available interaction parameters for S, Si and C (ε_{Si}^{Pb} and ε_C^{Pb} from the Steelmaking Data Sourcebook and ε_S^{Pb} from Wood et al., 2014; **Table 3**). First we used the corrected K values from LVP experiments to parameterise the partitioning of Pb as a function of

chalcophile affinity. For Earth, the “final” or “accumulated” metal-silicate partitioning coefficients of all the elements ($D^{\text{core-mantle}}$) are given by the core to the mantle concentration ratios of the elements. These concentration ratios can be estimated by mass-balance calculations involving the observed mantle abundances of the elements, assumed bulk Earth and mantle compositions and a core mass fraction of about 0,32. The bulk Earth and bulk mantle compositions are commonly assumed to be CI chondritic and pyrolitic, respectively (e.g. McDonough and Sun, 1995). **Table 5** gives ranges of the apparent core-mantle partitioning coefficients of the five elements investigated in this study based on data available in the literature.

Table 5
Apparent core-mantle partition coefficients

Element	$D^{\text{core-mantle}}$	Lithophile element ^a	References ^b
Ga	0-0.8	Na (Tc ~950 K)	(1) and (2)
Ge	9-17	Rb (Tc ~950)	(1) and (2)
Zn	0-8	F (Tc ~730K)	(1) and (2)
As	40-100	Li (Tc ~ 1150 K)	(1) and (2)
Pb	13-38	-	(3) and (4)

^aLithophile element used to determine the bulk Earth abundance of the siderophile element with similar volatility trend.

^bReferences: (1) McDonough and Sun [1995]; (2) Palme and O'Neil [2003]; (3) Wood and Halliday [2010]; (4) Bouhifd et al. [2013].

Experimentally derived partition coefficients have traditionally been used to define a single set of P-T conditions of the core-mantle equilibration. However, core formation processes have more likely evolved in a multi-stage manner over the whole or most of the accretion history, including several impact-induced magma ocean scenarios which would result in core-mantle equilibration at progressively higher pressures as the Earth grows (Wade and Wood, 2005 and Rubie et al., 2007). Hence, understanding the metal-silicate partitioning behaviour of different elements with various geochemical affinities over a broad range of pressures, temperatures and fO_2 provides essential foundations to model core-formation processes and explain the terrestrial concentrations of the studied elements. The complexities of core segregation have recently been modelled by Badro et al., 2015. In section 6 we present results of Badro's multi-stage core formation model supplied with our most robust and geochemically relevant data for Ge. Here we will take the traditional approach and briefly discuss general tendencies of the experimentally derived metal-silicate partitioning coefficients of all studied elements with respect to the observed Earth's core-mantle values. Such a simple approach helps to assess the potential influence and imprint of core formation processes on the present-day elemental abundances.

In **Fig. 12** we compile and compare the partitioning results from our and other relevant experimental studies with inferred core-mantle element partitioning coefficients and PT-ranges for core segregation happening in a hot and deep magma ocean (see section 6 for more detail). The inferred present-day values for the core-mantle ratio, expressed as $\log K_D$ for an element M with valency n , is calculated as:

$$\log K_D^{\text{core-mantle}} = \log \frac{D_M^{\text{core-mantle}}}{(D_{Fe}^{\text{core-mantle}})^{n/2}} \quad (16)$$

where $D_M^{core-mantle}$ are taken from the literature (listed in **Table 5**) and $D_{Fe}^{core-mantle}=13,6$ (Wood et al., 2006).

Because the inconsistencies with some of the previously published data prevented a coherent thermodynamic modelling of the Ga, Zn and As data, we only show uncorrected values of the partitioning coefficients ($\log K_D$) and tentative interpretation of their partitioning tendencies. Ga and Zn are almost exactly on the volatility trend defined by most lithophile and volatile elements like Li, Na, Rb (e.g. McDonough, 2003 and Morbidelli and Wood, 2015). However, low-pressure metal-silicate partitioning experiments (Siebert et al., 2011 and Blanchard et al., 2015) have shown that Ga is moderately siderophile and therefore the anomalously high concentrations of Ga in the mantle (4 ppm) cannot be matched with the experimental values or explained by late veneer addition. The strong pressure effect on the Ga partitioning resolved in our dataset and supported by other studies (Siebert et al., 2011 and Siebert et al., unpublished data) indicates that Ga becomes decreasingly siderophile (more lithophile) with increasing pressure. Core-mantle equilibration at high enough pressures (50-70 GPa) and temperatures (4000-4500 K) can potentially explain the present-day mantle abundances (**Fig. 12**) and provide an additional indication that core-mantle equilibration occurred in very hot and deep magma ocean.

Fig. 12. A summary of the metal-silicate partitioning results from this study (red dots) and data from the literature (black, grey and white dots, references can be found in figure captions of Fig. 7-11) compared with core-mantle values and plausible core formation PT condition. The horizontal shaded areas correspond to the Earth's apparent core-mantle partition coefficients (with its uncertainties). The vertical bar corresponds to plausible pressure or temperature ranges of core-mantle equilibration (50-70 GPa and 4000-4400 K) determined based on multi-stage core formation model supplied by the partitioning data of four well established elements (Co, Ni, Cr and V) together with Ge data from this study (details of the modelling are presented in section 6). The solid lines are least square regression lines for the datasets (see regression constants in **Table 4**). See text for more detail.

Because Zn plots directly on the volatility trend and has very similar 50% condensation temperature to S, the abundance of both elements in the bulk Earth are related and has been used as indicators of how much S can be present in the core (Dreibus and Palme, 1996 and Mahan et al., 2017). Our DAC data suggest that Zn becomes slightly more siderophile with increasing temperature, which is consistent with more recent work (Siebert et al., 2011 and Mahan et al., 2017). In this study we also observe that Zn becomes slightly more siderophile with increasing pressure (**Fig. 12**), although some other lower pressure experiments (e.g. Mann et al. 2009) tend to indicate the opposite pressure effect. The weak trend towards increasingly siderophile Zn with increasing pressure and temperature is seen in the present DAC experiments, as well as those of Mahan et al., (in prep.). If the Earth's core equilibrated with the silicate magma ocean at very high pressures and temperatures, it might therefore host more Zn than the mantle alone (Mahan et al., 2017), and an estimate of the S content of the Earth based on the assumption that Zn is exclusively lithophile (Dreibus and Palme, 1996) needs to be revised. Recent studies have also resolved the weakly or moderately chalcophile nature of Zn at realistic oxygen fugacities of about 2 log-units below the Fe-FeO equilibrium and 5-10 wt% FeO in the silicate melt (e.g. Wood et al. 2014 and Wood and Kiseeva, 2015).

In spite of a substantial depletion of As in the mantle relative to CI chondrites, the apparent $\log K_D$ for bulk core-mantle partitioning of As is about -1 (**Fig. 12**). The low K_D -value is consistent with the decreasingly siderophile nature of As with increasing pressure. This trend, indicated by Siebert et al. (2011) in the 0-18 GPa range, is confirmed by our DAC experiments at 25-60 GPa. Unfortunately, the effect of light elements (especially Si and O) on As partitioning is poorly understood, and the interaction parameter $\varepsilon_{Si}^{As} = 47$ at 2073 K in C-saturated experiments with an assumed 3+ valence state, suggested by Righter et al. (2017), cannot be directly applied to our dataset. Another important aspect of understanding partitioning behaviour of such a high valence cation as As^{5+} is the potential effect of silicate melt composition, which can be expressed by the silicate melt structure parameter nbo/t (Mysen et al., 1982, equation 14). The affinity of the high valence cations for silicate melt seems to increase in highly depolymerised melts (high nbo/t ; e.g. Ryerson, 1985). Therefore, an additional correction of our dataset might be required when a more comprehensive thermodynamic model is established.

Both of the siderophile elements in this study, Ge and As, fall below the Earth's volatility trend. The mantle depletion of Ge has been seen as a result of core segregation, although previous LVP metal-silicate partitioning data (Siebert et al., 2011; Righter et al., 2011; Wood et al., 2014 and Righter et al., 2017) were not able to match the present-day mantle concentration with any kind of core formation scenario. However, Righter et al. (2011) has suggested a strong decrease in D_{Ge} with increasing temperature and roughly predicted that metal-silicate equilibration at 30($\pm$ 5) GPa, 3500($\pm$ 400) K and $\Delta IW = -1$ might explain the very low mantle concentration of Ge. Our LH-DAC experiments on the Ge metal-silicate partitioning agree and extend previously published large volume press results to temperatures of about 4000 K and pressures of about 40 GPa. These conditions are more directly applicable to a realistic core segregation scenario in a hot and deep magma ocean, and the high pressure and high temperature data confirm the increasingly siderophile nature of Ge with increasing temperature. Moreover, the new synchrotron-based μ -XRF method allowed us to precisely detect and fit characteristic $K\alpha$ lines for Ge, even in the strongly depleted silicate glass, which then was confirmed by the FE-EMPA analyses (see **Table 2** and **Fig. 5**). Since the metal-silicate partitioning of Ge has been measured for a range of compositions and under various P, T, fO_2 experimental conditions, all the essential interaction parameters have been determined and are available in the literature. We applied relevant corrections for the light element to the full

dataset. A comprehensive thermodynamic model and regression analysis enabled application of the most recent multi-stage core formation model of Badro et al. (2015) with the refined Ge partitioning data, which will be described in more detail below.

The two most volatile elements in our selection, Zn and Pb, have nearly identical 50% condensation temperatures of 726-727 K (Lodders, 2003). Whereas the combined geochemical affinity of Zn is weakly siderophile to lithophile and weakly chalcophile, Pb is siderophile and strongly chalcophile. It is especially important to gain further insights into the core-mantle partitioning behaviour of Pb due to its role as a decay product of U and Th and involvement in Earth and planetary chronometry (e.g. Halliday and Wood, 2009). The fact that Earth's mantle and crust have too radiogenic Pb isotopic signature to be explained by simple evolution of chondritic material over the last 4.57 (the 'Pb paradox' of Allègre, 1969 and Allègre et al., 2001) begs a better understanding of the partitioning of Pb between silicate, sulphide and metal during core formation and possible later core-mantle chemical exchange. Several LVP experimental studies (e.g. Wood and Halliday, 2010; Bouhifd et al., 2013 and Wood et al., 2014) have determined the partitioning of Pb between metallic and silicate melts at elevated PT conditions. It has been shown that high C and Si content in the Fe-dominated metallic liquid suppresses the Pb (Steelmaking Data Sourcebook, 1988 and Malhotra et al., 1998) resulting in underestimation of Pb partitioning coefficients (Lagos et al., 2008 and Malavergne et al., 2007). More recently, it has been shown by Wood and Halliday (2010), that at about 24 GPa and 2500 K, Pb becomes more siderophile and its mantle depletion can be solely explained by core formation. Our DAC results combined with those of Siebert et al., (in prep.) extend the positive correlation between log K and temperature to +0.5 and 4000K. The fairly strong Pb mantle depletion below the volatility trend, compared to Zn which is on the volatility trend supports a stronger partitioning of Pb to the core as a result of high temperatures and the presence of some S in the core. An additional portion of Pb delivered as volatile-rich material during the late veneer stage may therefore be required to match the upper mantle concentrations (Albarède, 2009).

6. Core formation model supplied by Ge partitioning data

With the well constrained metal-silicate partitioning coefficient of Ge derived from our DAC-experiments and previously published LVP-experiments, corrected for Si, O and C interaction in the metallic melt, based on the recent findings by Righter et al., (2017), we were able to use our data and supply the multi-stage core formation model by Badro et al. (2015). This model combines previously determined partitioning coefficients of Ni, Co, Cr and V (Siebert et al., 2012 and 2013) to deduce the most plausible scenarios of core-formation. Three main parameters: magma ocean depth, magma ocean geotherm and redox path were tested for a broad range of conditions. For more details about the applied core-formation model, including information about the input data, variables and relevant equations the reader is referred to the original work by Badro et al. (2015) and the supporting material therein.

Figs. 13 and 14 show the outcome of the core formation modelling performed with two different redox paths for four different geotherms (A-D), constrained based on the following experimental melting curves: peridotite solidus (A; Fiquet et al., 2010), model chondrite liquidus (B; Andraut et al., 2011), intermediate liquidus (C; arithmetic mean of B and D) and peridotite liquidus (D; Fiquet et al., 2010). In **Fig. 13** the accretion starts at very reducing conditions (constant $\sim IW-4$ until 28% of accretion) as proposed by Wade and Wood, (2005) and then evolves through time to the current core-mantle fO_2 value ($\sim IW-2$). The other model, presented in **Fig. 14**, begins with more oxidised material than the present mantle (following Badro et al.,

2015 and Siebert et al., 2013), and during accretion the magma ocean becomes more reduced. In both cases it is evident that the two first, lower temperature geotherms (A and B) do not satisfy all the partitioning data correlated with present day mantle abundances. However, once the temperature is high enough (geotherm C and D) the partitioning of all five elements match present day abundances when the core formation takes place at pressures of 50-70 GPa, independently of the redox scenario. We have simulated several other redox paths during accretion, by varying the initial FeO concentration in the magma ocean which then evolves to present-day value for the primitive upper mantle (5.9 mol% FeO). Results of models testing all redox scenarios for selected higher temperature geotherms (C and D) are shown in **Appendix D** and **Appendix E**.

Previous estimates of the P-T- fO_2 conditions of the terrestrial core-mantle equilibration processes, were mainly based on studying moderately and slightly refractory siderophile elements (e.g. Ni, Co, Cr and V) and focused on the pressure/depth aspect of the magma ocean (e.g. Wade and Wood, 2005 and Siebert et al., 2012) and the fO_2 evolution during accretion (Siebert et al., 2013). The strong temperature dependence on the Ge partitioning behaviour, puts more direct constraint on the temperature of the core-mantle equilibration, which must have occurred at or above the silicate liquidus. This implies a very hot magma ocean scenario and rules out core formation occurring near the silicate solidus (A and B geotherms).

Experimentally determined geochemical tendencies of Ge presented in this study combined with previously determined metal-silicate partitioning data for Ni, Co, V and Cr gives new hints about the pressure and temperature of the core-mantle equilibration during the Early Earth history. The models predict core-mantle equilibration temperatures of 4000-4200 K at pressures of 50-70 GPa. This hot and deep magma ocean hypothesis is also in agreement with recent study by Badro et al. (2016) in which the very high temperature during accretion is required for MgO dissolution in core-forming alloy which subsequently exsolves and drives an early geodynamo.

Obtained ranges of pressures and temperatures are largely independent of the redox state of the accreting material, at least if the two hottest geotherms (models C and D) are applied (see **Fig. 13** and **14** and **Appendix D** and **E**). With highly variable fO_2 , the models C and D predict only slightly different Si- and O-concentrations in the Earth's core for an average segregation pressure of about 60 GPa: 8-10 wt% Si and about 2 wt% O for the very reduced initial conditions (Wade and Wood, 2005, **Fig. 13**) and 3-4 wt% Si and about 2 wt% O for the most oxidised initial case (Badro et al, 2015, **Fig. 14**). These light element contents would generally satisfy the requirement for an outer core density deficit. The predicted Si and O contents of the core are even more similar, and slightly lower, when using the two moderate core evolution scenarios for oxidation and reduction during core growth, based on the C and D models presented in **Appendices D** and **E**, respectively. With model C (**Appendix D**) the moderate oxidation (increase from 4 to 6 wt% FeO in the magma ocean) gives about 4 and 1.8 wt% Si and O in the core and the moderate reduction (from 8 to 6 wt% FeO) results in about 3 and 2 wt% Si and O, respectively. Model D (**Appendix E**) results in about 4.5 and 2 wt% Si and O, respectively, for the moderately oxidising scenario and about 3.5 and 2.5 wt% Si and O, respectively, for the moderately reducing core evolution.

Fig. 13

Fig. 13 and 14. The result of a series of multi-stage core formation models where the pressure (magma ocean depth) varied from 0 to 135 GPa, testing the whole possible range of the core-mantle equilibration depths during Earth differentiation. In the first row, we present the redox path which we used in the following accretion models performed with four different geotherms: A-D (second row, see main text for more explanation). Each column represents the outcome of the accretion model performed with one of the four geotherms. In the third-row Si (solid black line) and O (dotted black line) core concentrations are plotted at different plausible pressures of the core-formation. The five bottom rows show the partitioning coefficient (D_i , Equation (2)) behaviour for Ni (red), Co (blue), Ge (turquoise), Cr (pink) and V (green) at different pressures of core-formation.

Fig. 14

(continuation)
Core concentrations and the D s represent the final values reached at the end of accretion. The horizontal shaded areas correspond to the Earth's core-mantle partition coefficients (with its uncertainties). The vertical bar corresponds to the pressure range for which all five partition coefficients match the terrestrial observables. Selected redox scenario involves accretion beginning with more oxidised material than present day mantle which becomes more reduces and evolves to present-day primitive mantle values (5,9 mol% FeO, ~IW-2). This has been suggested as the most plausible redox evolution by Badro et al., (2015).

7. Conclusions

We have determined the partitioning of the volatile and moderately siderophile elements Ga, Ge, Zn, As and Pb between liquid Fe-dominated metal and silicate melt at 25-60 GPa and 3000-4000 K by LH-DAC experimentation, followed by analysis of the run products by synchrotron-based μ -XRF and FE-EMPA. The derived metal-silicate partitioning coefficients agree with and extend the existing experimental results from moderate pressures and temperatures achievable with large volume press experiments. The new data, especially for Ge, put important additional constraints on the temperatures, and thereby on the pressures and depths, of the final metal-silicate equilibration during core segregation in the growing and largely molten Earth.

Whereas Ga and Zn lie approximately on the terrestrial volatility trend (condensation temperature versus primitive mantle concentration), the mantle concentrations of Pb, Ge and As are depleted (in that order) relative to the simple volatility trend. Although a chalcophile affinity of Zn and especially Pb may influence core segregation, we have chosen a system (starting assembly of pure Fe foil sandwiched between layers of model basaltic glass discs) containing only Si and O as light elements in the metal. The fO_2 -values calculated from our coexisting metal and silicate phases cover the range of -1.0 to -0.6 log-units below the IW-buffer.

Our experimental data confirm that Ge and As are the most siderophile of the investigated elements and that they become less siderophile with increasing temperature (Ge) and pressure (As). A similar behaviour of decreasingly siderophile affinity with increasing pressure is seen for Ga. In contrast, Zn appears to become slightly more siderophile with increasing pressure and temperature above 3000 K and 25 GPa, although that trend may be opposite in the 1-20 GPa and 2000-2500 K range. Also the other, and more strongly, chalcophile element, Pb, becomes increasingly siderophile with increasing temperature. This might reduce the impact of their chalcophile affinity during core segregation at high temperatures and pressures.

A simple evaluation of the experimentally derived metal-silicate partitioning coefficients with Earth's values of each of the five elements discussed in this study indicate that the protracted metal segregation from early magma ocean(s) occurred at high pressures and temperatures (on order of 60-90 GPa and 3000-6500 K). These pressure and temperature ranges, however, are associated with considerable errors. We have therefore performed more rigorous multi-stage core segregation modelling based on the best-constrained and coherent metal-silicate partitioning of Ge, as well as previously published Ni, Co, Cr and V data, using the Badro et al. (2015) core-formation model. This resulted in more precise estimation of the final core-mantle equilibration at 60 ± 10 GPa and 4000-4200, corresponding to a magma ocean geotherm following a hot peridotite liquidus (Fiquet et al., 2010). This conclusion is independent of the redox state of the accreting material. However, models starting with moderately reducing (4 wt% FeO in the silicate magma) or moderately oxidising (8 wt% FeO in silicate) conditions followed by oxidation or reduction to present-day 6 wt% FeO in the mantle, result in relatively similar Si and O content of the core. The reduced and oxidised initial conditions yield 4.5 and 2 wt% Si and O and 3.5 and 2.5 wt% Si and O, respectively. A model with gradual oxidation, starting from a very reduced initial condition (from 0.6 to 6 wt% FeO in the silicate melt) yields about 9 wt% Si and 2 wt% O in the core. Although there is still a large array of suggested light element contents in the core, the Si and O contents described above agree with several recent compositional models of the Earth's core.

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Supplementary material

Appendix A.

FEG microprobe analyses of the silicate and metallic melts

No.	130		131		138		128		134		129		127	
	wt.%	1 σ	wt.%	1 σ	wt.%	1 σ	wt.%	1 σ	wt.%	1 σ	wt.%	1 σ	wt.%	1 σ
silicate melts														
MgO	5,94	0,03	7,08	0,08	7,25	0,21	6,97	0,21	5,57	0,08	7,93	0,16	5,71	0,05
SiO ₂	39,89	1,01	32,72	0,07	38,06	0,20	37,62	0,20	35,25	0,89	44,46	0,65	31,13	0,18
Al ₂ O ₃	9,31	0,14	11,21	0,05	13,02	0,52	16,85	0,52	13,09	0,31	15,48	0,82	10,47	0,28
FeO	29,61	0,57	35,34	0,27	31,01	2,34	30,43	2,34	27,50	0,95	22,95	0,56	42,84	0,51
CaO	9,99	0,06	6,34	0,04	6,57	0,16	6,17	0,16	5,20	0,08	5,87	0,13	4,73	0,07
ZnO	0,89	0,04	1,14	0,06	0,88	0,10	0,76	0,10	-	-	-	-	-	-
Ga ₂ O ₃	-	-	-	-	-	-	-	-	2,27	0,09	1,70	0,19	2,10	0,11
GeO ₂	-	-	-	-	-	-	-	-	0,42	0,07	0,19	0,03	0,78	0,05
As ₂ O ₅	0,18	0,06	2,62	0,22	0,35	0,11	0,42	0,11	-	-	-	-	-	-
PbO	1,01	0,18	2,52	0,09	1,31	0,09	0,79	0,09	-	-	-	-	-	-
Total	96,81	0,28	98,97	0,39	98,44	1,74	99,99	1,74	89,30	0,44	98,58	0,56	97,76	0,86
metallic melts														
O	3,04	0,02	4,01	0,01	9,98	0,19	9,79	0,19	7,98	0,00	6,79	0,19	3,75	1,83
Fe	88,63	0,14	67,05	0,10	72,98	0,04	73,17	0,04	67,70	2,40	82,73	0,54	84,20	3,08
Si	0,39	0,03	0,32	0,10	2,39	0,07	6,36	0,07	3,68	0,00	5,19	0,15	0,09	1,26
Mg	n.d.	0,01	0,00	0,01	0,00	0,01	0,18	0,01	0,00	0,01	0,09	0,00	0,00	0,03
Ca	0,04	0,01	0,09	0,01	0,08	0,01	0,17	0,01	0,05	0,00	0,08	0,01	0,05	0,02
Al	n.d.	0,01	0,04	0,01	0,20	0,02	0,64	0,02	0,17	0,00	0,53	0,02	0,04	0,09
Zn	0,25	0,00	0,17	0,03	0,52	0,05	0,63	0,05	-	-	-	-	-	-
Ga	-	-	-	-	-	-	-	-	1,63	0,08	1,36	0,05	0,41	0,16
Ge	-	-	-	-	-	-	-	-	1,94	0,07	1,80	0,12	2,73	0,06
As	4,04	0,00	22,35	0,20	8,12	0,04	3,73	0,04	-	-	-	-	-	-
Pb	2,68	0,20	1,28	0,24	2,95	0,04	2,39	0,04	-	-	-	-	-	-
Total	99,05	0,36	95,30	0,50	97,21	0,06	97,06	0,06	83,13	2,57	98,57	0,29	91,26	0,25

Appendix B. XRF spectra from Ga and Ge doped system (134; 41.5 GPa and 3200 K) showing the raw data (black lines) and applied fits (dashed lines: green and red for silicate and metallic melt, respectively) and backgrounds (dotted orange lines).

Appendix C. XRF spectra from Zn, As and Pb doped system (131; 30 GPa and 3300 K) showing the raw data (black lines) and applied fits (dashed lines: green and red for silicate and metallic melt, respectively) and backgrounds (dotted orange lines).

Appendix D. Multi-stage core formation modelling, using the second hottest geotherm (model C) in Figs. 13-14 (see those figure captions) and five different fO_2 evolution trends (FeO in silicate, row 2).

Appendix E. Multi-stage core formation modelling, using the hottest geotherm (model D) in Figs. 13-14 (see those figure captions) and five different f_{O_2} evolution trends (FeO in silicate, row 2).

Appendix F

Experimental conditions of the additional DAC data used for comparison in this study but obtained at IPGP in Paris.

Element	P (GPa)	T (K)	composition	author	included in
Ga	46	3100	pyrolite	Siebert et al., (unpublished)	Fig. 7
Ga	58	3600	pyrolite	Siebert et al., (unpublished)	Fig. 7
Zn	62	3600	basalt	Mahan et al., (unpublished)	Fig. 9
Zn	72	3700	basalt	Mahan et al., (unpublished)	Fig. 9
Zn	49	3500	basalt	Mahan et al., (unpublished)	Fig. 9
Zn	70	3700	basalt	Mahan et al., (unpublished)	Fig. 9
Zn	81	4000	basalt	Mahan et al., (unpublished)	Fig. 9
Zn	54	4000	pyrolite	Mahan et al., (unpublished)	Fig. 9
Zn	71	4100	pyrolite	Mahan et al., (unpublished)	Fig. 9
Pb	62	3600	basalt	Siebert et al., (in prep.)	Fig. 11
Pb	72	3700	basalt	Siebert et al., (in prep.)	Fig. 11
Pb	49	3500	basalt	Siebert et al., (in prep.)	Fig. 11
Pb	70	3700	basalt	Siebert et al., (in prep.)	Fig. 11
Pb	81	4000	basalt	Siebert et al., (in prep.)	Fig. 11
Pb	49	3700	pyrolite	Siebert et al., (in prep.)	Fig. 11
Pb	71	4000	pyrolite	Siebert et al., (in prep.)	Fig. 11

Chapter 3

Metal-encapsulation of silicate samples for LH-DAC experiments at lower mantle conditions – technical development, preliminary results and numerical modelling of the thermal distribution*

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Abstract

In order to overcome and understand the significant temperature gradients experienced in conventional laser-heated diamond anvil cell (LH-DAC) experiments, we have developed a novel technique involving total metal-encapsulation of the silicate samples. Here we present the details of the sample preparation and preliminary experimental results together with numerical modelling of the temperature distribution in the new experimental setup. Glassy samples of natural (BIR-1) and simplified model basaltic composition ($\text{MgSiO}_3 - \text{SiO}_2$ system) were held in an annulus of molybdenum metal of $\sim 10 \mu\text{m}$ thickness and $30\text{-}40 \mu\text{m}$ diameter, with a centrally located sample chamber $\sim 10\text{-}15 \mu\text{m}$ in diameter. The samples were coated on both sides with $\sim 3\text{-}4 \mu\text{m}$ of molybdenum in an argon atmosphere using a magnetron sputtering system, which entirely encapsulates the sample and enables infra-red laser-heating using IR lasers. The capsules were loaded between two layers of insulation ($\sim 15 \mu\text{m}$ thick) and pressurised in a DAC. High temperatures were achieved by using double-sided laser-heating with spot sizes of $\sim 30 \mu\text{m}$, somewhat larger than the sample diameter. With this setup, we achieved stable uniform heating at temperatures in excess of 4100 K and pressures up to $\sim 100 \text{ GPa}$. The majority of experiments were performed off-line, although several samples were laser-heated with simultaneous synchrotron-based XRD measurements. Recovered samples were prepared for further TEM analyses using a focused ion beam (FIB) system. Powdered glass samples held under subsolidus conditions for extended periods of time ($15\text{-}60 \text{ min}$) were found to be homogeneous in composition, containing the expected subsolidus phases. Samples which were laser-heated to target temperatures (near solidus) in a ramp mode show more heterogeneous hour-glass shaped textures, with unreacted areas on the side of the capsule. Based on numerical models of the temperature distribution inside the LH-DAC assemblage, we found that the temperature gradients inside the encapsulated samples were still substantial (on the order of 500 to 1000 K at 42 and 72 GPa , respectively). A parametric study in which we tested the importance of different capsule dimensions at various laser setups, shows that a reduction of the encapsulated sample thickness, and most importantly of the Mo-capsule and sample radius, combined with a 'doughnut shaped' laser beam, can decrease the temperature gradients to only a few tens of K at pressures of the lower mantle. Thus, further development of the metal-encapsulated setup has a great potential to achieve isothermal LH-DAC experiments.

Keywords:

laser heating; diamond anvil cell; temperature gradients; thermal diffusion; numerical modelling

1. Introduction

Geochemical and geodynamic models of the evolution of planetary interiors require detailed knowledge of the melting and subsolidus phase relations of lower mantle candidate materials (e.g. basalts, peridotites or their simplified analogues), as well as elemental partitioning among coexisting phases at high pressures and temperatures. Experiments at the extreme conditions relevant to melting in the lower mantle (24-136 GPa and 2500-4500 K) remain challenging and have led to somewhat inconsistent results. Undoubtedly, diamond anvil cell (LH-DAC) experiments have provided a unique opportunity to make indirect inferences about the phase relations in parts of our planet from where samples are unavailable. However, large uncertainties often arise in LH-DAC investigations of melting temperatures, relations between the solidus and liquidus and solid-melt partitioning due to the large temperature gradients of the laser-heated samples.

To determine the properties of the lower mantle lithologies and thus understand the structure and evolution of planetary bodies, a good understanding of the melting phase relations of relevant basaltic and peridotitic compositions are required throughout the mantle pressure range. Recent experiments on natural peridotitic and basaltic compositions (e.g. Fiquet et al. 2010; Andraut et al. 2011; Andraut et al. 2014 and Pradhan et al. 2015) have given relatively wide ranges of solidus and liquidus temperatures at lower mantle pressures. On the other hand, the computational approach to study materials under extreme conditions via *ab initio* atomistic simulations, due to its limitations, has only been applied to simple silicate melts and coexisting minerals at PT-conditions of the lower mantle (e.g. Stixrude et al., 2009, de Koker et al., 2013). Even the simplest *ab initio* determinations of the melting temperatures of endmember components, such as MgO (periclase) and MgSiO₃ (bridgmanite), remain computationally demanding and often results in unrealistic melting temperatures due to lack of defects and surfaces on which melt can nucleate (Belonoshko et al., 2005). Recently, however, so-called two-phase equilibria simulations where solid and liquid coexist with each other have yielded reliable results although the 2-phase method turns out to be even more computationally demanding (e.g. Alfie, 2005 and Di Paola and Brodholt, 2016).

Part of the problem in interpreting the experimental data is lack of systematic studies of simple analogue systems, like MgO-SiO₂, CaO-MgO-SiO₂, FeO-MgO-SiO₂, etc., at pressures beyond those achievable in the multi-anvil press (e.g. Liebske and Frost, 2012). Baron et al. (accepted) show that near-eutectic compositions in the simplest MgO-SiO₂ system produce large enough melt fractions to precisely determine the eutectic melting curves through the lower mantle pressure range, despite the large temperature gradients, typical for conventional LH-DAC setups. However, studies of more complex non-eutectic systems where solidus and liquidus curves are not the same, are often plagued with difficulties in capturing and interpreting the low-degree melt due to debatable melt detection criteria yielding unreliable results.

Strong temperature gradients during LH-DAC experiments commonly cause thermochemical (Soret) diffusion, which has a serious effect on segregation of various elements along the thermal gradient (Sinmyo and Hirose, 2010). It has been shown that in gases, heavier elements and elements with large ionic radii tend to migrate from hot to cold region, whereas lighter and smaller elements migrate from cold to hot regions (Grew and Ibbs, 1952). In silicate melts, similar Soret diffusion has been studied as one of the mechanisms of chemical segregation in magma chambers (e.g. Leshner and Walker, 1986). For basaltic melts Leshner and Walker (1991) noticed that Mg, Fe and Ca diffuse towards colder areas and Si, Na and K diffuses towards hotter areas. This suggests that Soret diffusion in silicate melts is more complex than in gases.

Soret diffusion occurs also in the solid state, which has been noted in many subsolidus LH-DAC experiments. Commonly, Fe tends to migrate towards the colder areas at the edges of the laser-heated spot (e.g. Heinz and Jeanloz, 1987; Andrault and Fiquet, 2001; Sinmyo et al., 2008 and Sinmyo and Hirose, 2010). Associated effects of Soret diffusion include heterogeneous Mg/Si ratios (Ozawa et al., 2009) and inconsistent Fe-Mg partitioning coefficients between subsolidus phases, e.g. between bridgmanite, post-perovskite and ferropericlase (e.g. Kobayashi et al., 2005; Auzende et al., 2008; Sinmyo et al., 2008 and 2010). On the other hand, the melting studies of the lower mantle lithologies (peridotites and basalts) consistently report Fe-enrichment of the melt phase (e.g. Fiquet et al., 2010; Nomura et al. 2011; Andrault et al., 2012; Tateno et al. 2014; Nomura et al. 2014 and Pradhan et al., 2015), although precise measurements of the partitioning of iron and other elements between low-degree melts and solids remain challenging and no correction for the Soret effect has been proposed so far. Potential Soret diffusion in the melting experiments on peridotitic and basaltic compositions would presumably reduce the observed strong partitioning of Fe into melt and Mg into bridgmanite and post-bridgmanite.

To quantify the temperature gradients in LH-DAC experiments, several numerical models (e.g. Dewaele et al., 1998 and Rainey et al., 2013) have been used to describe the temperature distribution both in the axial and radial directions. The temperature gradients observed in the simulations largely depend on the laser-heating setup (shape of the beam intensity profile, e.g. Gaussian, 'flat top' or 'doughnut shape'), geometry and type of the sample (e.g. partially absorbing sample or metals), thickness and type of pressure medium and thermal conductivity of the materials used in the model. So far, only a very few experimental scenarios of different geometries have been tested numerically. More comprehensive understanding of the importance of all the different parameters controlling the thermal distribution applied to more realistic thicknesses of the DAC assemblages (less than 40 μm thick, especially at high pressures) is therefore needed to improve the design of the high pressure cells.

The reduction of temperature gradients is possibly achievable by modifying the geometry of the sample and/or laser absorber and pressure medium. One of the first technological improvements of the LH-DAC experimental configuration for melting experiments was described by Hirose et al. (1999) where the sample was sandwiched between two Re-foils acting as hot plates, heating the sample from two sides. In LH-DAC experiments lasting around 60 min at subsolidus conditions, Sinmyo and Hirose (2010) found uniform radial temperature profiles across the laser-heated region and no undesirable chemical segregation, when the samples were coated with thin layers of gold on each side and sandwiched between two thick layers of SiO_2 glass acting as a pressure medium.

Careful preparation of samples for LH-DAC experiments have recently been improved by advanced micro-fabrication and micro-machining, utilizing pulsed lasers (e.g. Hrubíak et al., 2015) and focused ion beam (FIB) system (Pigott et al., 2011 and Marquardt and Marquardt, 2012). Another technological advancement in preparing controlled-geometry double hot-plate samples ($\text{Ni/SiO}_2/\text{Ni}$) has recently been suggested by Pigott et al., 2015. Their nanofabricated samples were prepared by a combination of vapour deposition, photolithography and wet and plasma etching. None of these studies, however, aimed to heat at extreme conditions (>2500 K) and melt the sample.

Here we present a new approach for total metal-encapsulation of silicate samples suitable for LH-DAC experiments which can be readily pressurised up to 100 GPa and laser-heated up to 4100 K. The manufacturing procedures and new experimental setup provides a uniform heating of 10-15 μm samples, encapsulated radially by a Mo metal annulus and axially by thin layers of

Mo coat. The Mo capsule acts like a micro-heater (laser absorber) and mechanical barrier between the sample and pressure medium, preventing chemical contamination.

We aimed to study the subsolidus and melting phase relations of natural basalt (BIR-1) and an analogue for subducted basaltic crust within the simple $\text{MgSiO}_3\text{-SiO}_2$ (MS) binary. In addition, we tested the possibility of making encapsulated samples with synthetic peridotite (KLB-1) and an analogue for the mantle peridotite within the MgO-MgSiO_3 system which can be found in the supplementary material.

Two methods of encapsulation were developed for experiments using glass disc ('filament method') or powdered glass ('gasket method') samples. Various parameters including laser-heating styles, heating duration, pressure medium materials, and thickness of the Mo-layers have been tested, although the final outcome and interpretation of the recovered samples studied using transmitted electron microscope (TEM) remains ambiguous. In order to understand our experimental results and to improve the experimental setup, we have performed numerical simulations of the thermal distribution in the LH-DAC experiments with metal-encapsulated samples. The model enables us to simulate and quantify the radial and axial temperature gradients in different encapsulated sample configurations. We varied the thickness of the whole assemblage, tested different laser power density distribution profiles (Gaussian, 'flat top' and 'doughnut shape') and different width of the laser beam (10-40 μm). Additionally, we have performed a parametric study in which we varied the size and thickness of the encapsulated sample in order to test possible ways to improve and achieve more isothermal conditions in the LH-DAC experiments in the future.

2. Methodology

The development and production of the metal-encapsulated samples and all the off-line laser heated diamond anvil cell (LH-DAC) experiments were performed at the School of Earth Sciences, University of Bristol, UK. The LH-DAC experiments coupled with *in situ* X-Ray Diffraction (XRD) measurements were carried out at beam line ID-27 of the European Synchrotron Radiation Facility. XRD measurements of two experimental run products were done at the Diamond Light Source Synchrotron Facility. Preliminary focused ion beam (FIB) preparation was carried at the Institut de Physique du Globe de Paris, France. Further FIB sample preparation and transmitted electron microscopy (TEM) analyses were performed at the Bayerisches Geoinstitut, University of Bayreuth, Germany.

Section 2.1 details the two encapsulation manufacturing procedures ('filament method' and 'gasket method', respectively) and section 2.3 describes the LH-DAC experiments. A summary of applied analytical methods includes the synchrotron-based XRD (section 2.4), FIB preparation (section 2.5) and TEM analyses (section 2.6). The last section (2.7) includes foundations of the numerical model, simulating thermal distribution in the LH-DAC experiments with metal-encapsulated samples.

2.1. Capsule manufacturing

2.1.1. 'Filament method' for glass discs samples

The encapsulation of the glass disc samples with so called 'filament method', illustrated in **Fig. 1**, consists of multiple steps of manufacturing to fully enclose the silicate samples by laser absorbing metal. The capsule preparation starts with manufacturing a metal filament made of 10 μm thick pure metal foil (e. g. Mo), which is cut into a bow-tie shaped filament of about 4 x 9-10 mm size (**Fig. 1a**) by using a UV laser ablation unit (New Wave research, LUV series, operating

wavelength 266 nm). In the narrowest part of the bow-tie shaped Mo-filament, a grid of 40-70 sample chambers is laser-drilled with the smallest diameter achievable with the UV laser (10-15 μm). After laser-drilling, the filaments are polished by hand with very fine 0.1 μm alumina-impregnated biaxially-oriented polyethylene terephthalate (BoPET) polishing sheets and cleaned several times using acetone in an ultrasonic bath until all the sample chambers were perfectly free of polishing residue. Subsequently, a pressed pellet of powdered starting material is fixed on the neck of the Mo-filament where the drilled sample chambers are (**Fig. 1b**) using a minimal amount of Loctite Super Glue. The assemblage is then carefully transported and connected with the resistive heating device, made in the machine shop in the School of Earth Science, University of Bristol (**Fig. 1c**). The heating device has two brass electrodes, holding a metal filament which closes an electrical circuit and is heated by electrical current from a power supply (Spectra-Physics, Oriel Instruments USA. 69931 Power Supply) which provides a highly stable current up to a maximum of 15 A. The system is enclosed in a chamber, connected to a supply tube of Ar gas on one side with an open outlet on the other side, allowing the flow of inert gas. A transparent window allows for detailed observation under a microscope of the heating filament. Once the filament with starting material is tightly screwed to the brass electrodes, the electrical resistivity is checked with Ohmmeter. Subsequently, the chamber is flushed with Ar for few minutes and resistively heated under Ar gas flow. The electrical power is increased manually until the neck of the filament with sample pellet, starts to glow and the starting material on top melts (**Fig. 1d**). The temperature during resistive heating is not measured directly, but we have noticed that different materials melt at different power, although it also depends on the quality of the conducting materials and the electrical contact of all the components. When the starting material melts, it permeates into the holes of the Mo-filament. The sample is then rapidly quenched to form a glass by switching off the power (**Fig. 1e** and **Fig. S1c**). Subsequently, the filament, with its glass-filled chambers, is detached from electrodes and the residual glass on the top of the filament is stripped away with a sharp razor blade. Because the melt tends to migrate and move during heating, leaving some of the sample chambers empty, each sample chamber is documented and checked from both sides using high-magnifying optical microscope. Only the sample chambers completely filled with glass were used for further LH-

Figure 1. A schematic detailing the fabrication technique for the metal encapsulated glass disc samples using the so called 'filament method'. See main text for more detail explanation.

DAC experiments. The glass-filled sample chambers were cut almost free from the filament, using the UV laser ablation unit leaving a thin (about 10-15 μm) wall of Mo around each sample and a small neck to ensure the pre-cut capsule remained attached to the Mo-filament (**Fig. 1f**). To finish the encapsulation, the filament with pre-cut capsules containing glassy discs was coated on both sides by a 3-4 μm layer of pure Mo metal by magnetron sputtering deposition (Q150R S Rotary-Pumped Sputter Coater, Quorum Technologies). A thick coat of Mo is essential for the mechanical stability of the capsule during LH-DAC experiments at high temperatures and pressures. Too thin Mo-layer could potentially break and result in poor laser absorption, lack of temperature control and contamination of the sample by the pressure medium. After detachment from the Mo-gasket by a manipulating needle, the encapsulated samples were ready to be loaded into the standard DAC assemblage.

The final encapsulated glass disc samples are approximately 15-20 μm thick and 30-50 μm in diameter before pressurization (**Fig. 1h**). Additional photographs of all described products at different steps of the encapsulated samples preparation, as well as the resistive-heating device with a Mo-filament with sample powder on top are shown in **Fig. S1** in the supplementary material.

Table 1

FEG microprobe analyses of starting materials used in this study

Wt.%	BIR-1_LL*	1 σ	BIR-1_FM*	1 σ	S65_FM*	1 σ
MgO	9,66	0,07	11,64	0,64	24,34	0,14
SiO ₂	47,79	0,99	49,77	0,41	73,87	0,55
Al ₂ O ₃	14,86	0,06	14,50	0,33	-	-
FeO	10,60	0,19	6,78	0,42	-	-
CaO	13,27	0,12	13,72	0,37	-	-
Na ₂ O	1,85	0,08	0,80	0,05	-	-
K ₂ O	0,02	0,01	0,02	0,01	-	-
MnO	0,17	0,01	0,18	0,01	-	-
P ₂ O ₅	0,03	0,02	0,08	0,05	-	-
TiO ₂	1,02	0,03	0,00	0,01	-	-
Total	99,27	-	97,49	0,84	98,21	-

*LL – laser levitated starting material; *FM – material melted on top of the filament.

Starting materials encapsulated with ‘filament method’ included natural BIR-1 basalt (Flanagan, 1984) and one selected near-eutectic composition in the MgSiO₃-SiO₂ system (65 mole% SiO₂ and 35 mole% MgO; de Koker et al., 2013 and Baron et al., 2017, (accepted)), prepared as a mixture of enstatite and silica glass. The powder samples were ground in an agate mortar under ethanol for an hour to ensure homogeneity. The crystal-free glasses residing in the Mo-filament chambers were analysed by a JEOL JXA8530F Field Emission Gun (FEG) Electron Microprobe at the University of Bristol (**Table 1**). Wavelength dispersive elemental calibration was performed using a series of synthetic and natural mineral standards.

2.1.2. 'Gasket method' for powdered glass samples

The steps for manufacturing the encapsulated glass powder samples with the so called 'gasket method' are illustrated in **Fig. 2**. Mo-foil of about 100 μm thick (or less if accessible) was placed in between two diamond anvils in the DAC apparatus and thinned by applying pressure (**Fig. 2a**). We used 300 μm culet size diamonds and pressurised the foil to 18-19 GPa in order to obtain 15-20 μm thick indentation. The pressure was monitored by ruby fluorescence (Mao et al. 1986) and the thickness was measured by using a mechanical micrometer with an accuracy of $\pm 2 \mu\text{m}$. Once the Mo-foil was indented to the desired thickness ($\sim 10\text{-}15 \mu\text{m}$), a grid of approximately 9 sample chambers with 10-15 μm diameter, was drilled using the UV laser ablation unit in the thin part of the indentation (**Fig. 2b**). The foil was then washed using acetone in an ultrasonic bath. Subsequently, the 'gasket like' foil was placed back on the base diamond anvil of the DAC apparatus and powdered starting material was loaded on top of the indentation and pressed into the sample chambers (**Fig. 2c and d**).

After removing the residual powder, the sample chambers were laser-cut into the same shape as in the previous method (**Fig. 2e**) so that the capsule walls were almost cut out but still attached to the Mo-foil by a small neck. The Mo-gaskets were then coated with Mo-layers on top and the bottom by magnetron sputtering (Q150R S Rotary-Pumped Sputter Coater, Quorum Technologies), so that the capsules were fully sealed and wrapped by two Mo layers (**Fig. 2f**).

The final dimensions of the 'powder glass' encapsulated sample were similar to those fabricated using the 'filament method' although, achieving the appropriate thickness of the Mo-indentation during pressurization was sometimes difficult such that the capsules were slightly taller (20-25 μm) but similar in terms of the capsule diameter (**Fig. 2g**). After detachment from the Mo-gasket by a manipulating needle, the samples were ready to be loaded into pre-prepared DAC assemblages.

Here we only present results from experiments using a glass made from the natural basalt BIR-1 as starting material. The fine BIR-1 powder was compacted into $\sim 0.10 \text{ g}$ pellets and melted under nitrogen gas flow in a laser-levitation system equipped with a single YAG laser at

Figure 2. A schematic of the microfabrication technique for the metal encapsulated samples with powdered starting material using the 'gasket method'. See main text for more detailed explanation.

the University of Bristol. The chemical composition of quenched glasses made from BIR-1 starting material was also checked with FE-EMPA and is presented in **Table 1**.

2.2. LH-DAC Experiments in Bristol

All the laser heated diamond anvil cell (LH-DAC) experiments were performed in Princeton-type symmetric DACs with 250, 200 and 150 μm culet sizes. The setup of a typical DAC assemblage is illustrated in **Fig. 3**. In this study we have mainly used KCl as the pressure medium material. Other materials like SiO_2 glass, Al_2O_3 glass and MgO have been tested but we have found that KCl had optimal thermal and mechanical properties and was easy to work with due to its transparency and softness. Gaskets made from 250 μm thick Re-foil, indented to about 30-40 μm thickness at 20-25 GPa were used to achieve relatively deep sample chambers, which were laser-drilled in the middle of the indentation. In order to accommodate the capsules and as much pressure medium as possible, the sample chambers were about 90 and 50 μm in diameter for 250 and 150 μm culets, respectively. Before sample loading, an approximately 10 μm thick disc of KCl was emplaced in the sample chamber. The encapsulated sample detached from the Mo-filament or Mo-gasket by breaking the connective neck (see capsule manufacturing and **Fig. 1** and **2** for the details) was then loaded onto the lower KCl disc. In order to keep the capsule in the center of the assemblage and for pressure monitoring a few ruby spheres were added aside the encapsulated sample (**Fig. 3b,c**). A second disc of KCl was loaded on top of the encapsulated sample and gently compacted by squeezing in between the anvils to ensure that the pressure medium fills the space and separates the sample circumference from the inner Re gasket wall.

Figure 3. (a) A schematic cross section showing the experimental setup with an encapsulated sample loaded together with a few ruby spheres for pressure estimation and surrounded by KCl pressure medium inside the pre-indented Re-gasket. (b) Magnified view of the experimental configuration of the loaded encapsulated sample and laser heating area (red shaded) (c) Axial view of an encapsulated sample.

Before closing the cell and pressurization, each loaded DAC was heated at about 125 $^{\circ}\text{C}$ in an Ar-filled chamber for at least an hour to remove adsorbed moisture. Final closing and initial compression were performed while the cell was still hot. Target pressure compression was aided by ruby fluorescence measurements. Before and after the laser-heating, the pressure was also monitored by the Raman peak shift of the diamond anvil near the sample surface (after Hanfland et al., 1986, calibration presented in Baron et al. 2017 (accepted)). This approach allows measuring the pressure exactly where the encapsulated sample is located. Usually, the difference in pressure measured by the diamond peak shift next to the central part of the sample was about 3-5 GPa higher than the more peripheral pressure determined by ruby fluorescence.

During the double-sided laser heating, the temperature was measured on each side, using standard spectroradiometric techniques (e.g. Walter and Koga, 2004). For better understanding of the temperature distribution, we also obtained 2D temperature maps using four-color spectroradiometry (Campbell, 2008). More details on the laser heating system and the temperature measurement are provided by Lord et al. (2014) and Baron et al. 2017 (accepted).

Figure 4. (a) A microphotograph of a typical metal encapsulated sample loaded and pressurized inside the DAC. (b) A closer look at the encapsulated sample during laser-heating. (c) Two-dimensional temperature map of the laser-heated area in the middle of the encapsulated sample. (d) Radial temperature profiles across the laser heated zone from the beginning of the automatically ramped laser heating experiment starting at about 2300 till ~ 3100 K. Note the uniform temperature distribution across the hot spot and lack of temperature gradient.

Fig. 4 presents an example of laser-heating of an encapsulated sample. The metal capsule acts like a double hot plate which is powered by two 100 W Yb-doped fiber laser beams, shaped and expanded to so-called ‘flat-top’ energy distribution mode which matched as closely as possible the diameter of the encapsulated sample (**Fig. 4a** and **b**). Because the Mo-layers above and below the sample are much thinner than the cylindrical Mo-walls and the thermal conductivity of Mo is considerably higher than of KCl and the sample itself, the heat transfer into and heat loss out of the sample is dominantly axial and radial, respectively. The central part of the capsule heated easily and homogeneously, resulting in flat temperature profiles (**Fig. 4c** and **d**) and therefore straightforward fit of the spectra to the idealised grey-body Wien function.

The laser-heating of the encapsulated samples has been performed in two main modes: high-temperature runs (automatically or manually ramped to the target temperature and

Figure 5. Examples of a typical (a) low-temperature run (long subsolidus experiment) kept at 2400 ± 50 K for about 60 minutes. The temperature on the right and left side of the LH-DAC remains almost identical throughout the entire run duration (sample BIR-1_24 at 41 GPa and ~ 2500 K). (b) high-temperature run (automatically ramped experiment) showing maximum temperatures measured on both sides of the DAC as a function of time until reaching a target temperature (3500K at 75,5 GPa for S65 starting material).

rapidly quenched by switching off the lasers) and low-temperature run (manually ramped to the target temperature, kept for 15 to 60 minutes and then quenched). We aimed to test the kinetics of the re-crystallization reaction of glass disc and powder glass samples and the possibility of detecting low-degree partial melt just at the solidus temperature. Two examples of the measured temperature vs. time during laser heating from both sides are shown in **Fig. 5**. In the long low-temperature run (subsolidus experiment, **Fig. 5a**) the elevated temperature is kept for up to an hour to assure thermal equilibration. In the automatically ramped high-temperature run the laser power is continually and automatically increased by ~ 0.2 watts on each side every 3-5 seconds until reaching the intended temperature and rapidly quenched by switching off the lasers (see **Fig. 5b** for an example). In both laser-heating modes the temperature was very stable and almost identical on each side, regardless of the type of encapsulated sample used in the experiment.

2.3. Synchrotron X-Ray measurements (in situ LH-DAC, ex-situ analyses)

The *in situ* LH-DAC experiments were performed at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The experimental assemblies and encapsulated samples were prepared in an almost identical way to those used in off-line experiments (as described in section 2.3), although the encapsulated samples were slightly bigger (40-60 μm in diameter and 20-25 μm thick) as the Mo-foil for filament preparation was thicker (15-20 μm) in the preliminary design. Also, the coated Mo-layers on top and the bottom of the silicate sample were significantly thinner (1-2 μm) due to lack of efficient depositing equipment at the time of preparation for the beam time. All encapsulated samples used for the experiments at ESRF were the glass disc type manufactured using the 'filament method' (described in section 2.1.1.).

Laser heating was performed from two sides with off-axis geometry and the heated spot was about 20-30 μm in diameter. The incandescent light from a $2 \times 2 \mu\text{m}^2$ area in the center of the laser-heated spot was selected using a pinhole and analysed spectroradiometrically to determine the temperature. In order to equalise the temperatures by varying the laser power on each side, we first tested the laser power versus temperature response in the 1500-2000 K range. This was required because only upstream side T-measurements were possible during XRD-collection. The downstream light-collecting optics for T-measurements had to be removed from the path of the diffracted X-ray detector (Schults et al., 2005). For more details of the beam-line setup see Mezouar et al. (2005).

A monochromatic incident X-Ray beam ($\lambda=0.3738 \text{ \AA}$) of about 3 μm size was co-aligned with the center of the laser-heated area by X-ray induced fluorescence of the KCl pressure medium. Diffracted X-Rays were collected on a MAR345 image plate (MarResearch) with exposure times of 5–30 seconds. The distance between the sample and detector was calibrated with a LaB₆ standard (399.954 mm).

We aimed to laser-heat the samples with ~ 150 K steps and with collection of XRD patterns at each step, until loss of the diffraction signal caused by large-degree melting. This would allow a determination of the phase relations throughout the experimental temperature range. Pressure at ambient and high temperature was determined from the thermal equations of state of the Mo capsule (Huang et al., 2016) using the method of Campbell et al. (2009). The 2-D diffraction patterns were subsequently integrated into 1-D diffraction patterns using the Fit2D (Hammsrsley, 1997) and Dioptas (Prescher and Prakapenka, 2015). The final diffraction patterns were fitted and interpreted using the Le Bail method (Le Bail et al., 1988) in the GSAS software package (Larson and Von Dreele, 1994 and Toby, 2001).

2.4. Focused Ion Beam (FIB) preparation for TEM

After laser-heating and decompression some of the successfully laser-heated samples were recovered and excavated by focused ion beam (FIB) milling and subsequently analysed by transmitted electron microscopy (TEM). Preliminary excavation of the laser-heated samples by FIB was performed at IPGP (Paris, France) using Zeiss Auriga instrument. Electron transparent foils for TEM analysis were prepared using a FEI Scios FIB device at Bayerisches Geoinstitut (Bayreuth, Germany).

The flat cullet area was first cut out of the remaining Re-gasket using UV laser ablation and placed on a carbon tape fixed to an SEM aluminium stub and carbon coated for subsequent focused ion beam (FIB) milling (**Fig. 6**). In most cases the pressure medium was very homogeneous and it was not obvious where the laser-heated area was located. Therefore, it was important to mark and pre-cut the gaskets to be able to orient the whole assemblage with respect to the capsule location (**Fig. 6a**). The section was cut over the entire thickness of the indentation and after exposing the sample encapsulated in the Mo-sleeve from one side, milling was continued from the other side (**Fig. 6b,c**). After exposing the sample from the other side and making sure that both sides looked similar, a stripe of platinum, 3-5 μm thick and 25-35 μm wide, was deposited on the top edge of the slice, on top of the pressure medium. This Pt bridge protects the sample from beam damage and promotes parallel section walls during the thinning steps (**Fig. 6d**). The exposed section was later fixed to a micro-manipulating tungsten needle (**Fig. 6e**), transported to the TEM copper grid and fixed to one of the parking positions on the grid for further thinning and cleaning (**Fig. 6f,g**).

The extracted thin sections have areas of about $10 \times 20 \mu\text{m}^2$ and thickness of 3 – 4 μm . Ion thinning reduced the final sample thickness to about 100 nm or less. The last steps of thinning and cleaning of the thin foil surface was performed at the lowest current conditions (5 kV, 100 pA), giving a very smooth finish and reducing the possibility of Ga implantation into the sample.

Figure 6. Electron images of the LH-DAC sample recovery procedure using focused ion beam system (FIB). The detail description of all the procedures is presented in the main text. The marked and colour coded elements (dashed boxes) represents the same parts of the setup in different perspectives.

2.5. Transmitted Electron Microscopy (TEM)

The samples were studied using transmission electron microscope (ATEM, Philips CM-20FEG) and a new generation FEI Titan 80–200 microscope at the Bayerisches Geoinstitut (Bayreuth, Germany). The microscopes were operated at an acceleration voltage of 200 kV to image the sample in Bright Field as well as High Angle Annular Dark Field modes. Chemical maps were collected in STEM mode for about 200–500 seconds. Due to very time-consuming sample preparation of the thin sections and limited access to the FIB and TEM microscopes we were only able to prepare and analyse about 10% of the laser-heated samples but further analyses are planned as an extension of this study.

2.6. Numerical modelling

Because we cannot directly measure the temperature distribution inside the encapsulated samples, we used idealised numerical models to estimate the probable temperature gradients and their dependence on sample thickness, laser beam width and power density distribution. For simplicity, we assumed that radiative and convective heat transfer is negligible (Heinz and Jeanloz, 1987, Manga and Jeanloz, 1998). In this case, the steady state thermal diffusion equation reads as:

$$\rho c \frac{\partial T}{\partial t} = \nabla(k \nabla T) + q, \quad (1)$$

where ρ , c and k are density, specific heat capacity and thermal conductivity, respectively. q is the power density and relates to heating by the laser. As we are only interested in the steady state temperature field and because thermal diffusion time scales are on the order of 10^{-4} s, we set the left term in equation (1) to zero. As the sample assembly can be regarded as axisymmetric, it is convenient to rewrite equation (1) in cylindrical coordinates:

$$\frac{1}{r} \left(kr \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial}{\partial \theta} \left(k \frac{\partial T}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + rq = 0. \quad (2)$$

Due to the axial symmetry, the term $\partial T / \partial \theta$ equals 0, and we obtain an equation where T is only dependent on the variables r and z , thus reducing the dimensionality of our problem from three to two:

$$\frac{1}{r} \left(kr \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(k \frac{\partial T}{\partial z} \right) + rq = 0 \quad (3)$$

The final setup, including the boundary conditions for our numerical model, is shown in **Fig. 7**. Because the assembly is heated from both sides, we can further reduce the two-dimensional model domain to one fourth of the entire LH-DAC configuration.

The laser used in the simulations has an optimised profile so that the power density distribution is mostly constant. We tested three scenarios to evaluate the impact of the laser profile on the temperature distribution: a Gaussian profile (TEM₀₀ mode), an idealised flat profile ('flat top') with constant power density distribution and a 'doughnut-shaped' power density (TEM₀₁^{*} mode) distribution with maxima on the two sides and a local minimum in the middle of the profile. Assuming that the top of the Mo coat is located at $z = 0$, the respective power density distribution for the TEM₀₀ mode is given by

$$Q(r, z) = Q_0 e^{-\alpha z} e^{-r^2/R^2}, \quad (4)$$

where Q_0 is the maximum power density, α the absorption coefficient and R the half width of the Gaussian power density distribution. The power density distribution for the ‘flat top’ profile is then

$$Q(r, z) = Q_0 e^{-\alpha z} \Theta(-r + R), \quad (5)$$

where $\Theta(-r + R)$ is the Heaviside function and R the width of the heated region. Finally, the ‘doughnut-shaped’ (TEM₀₁ mode) power density distribution is given by:

$$Q(r, z) = Q_0 e^{-\alpha z} r^2 e^{-r^2/R^2}. \quad (6)$$

For each setup, equation (3) is solved numerically by employing a finite element solver based on MILAMIN (Dabrowski et al., 2008). The model domain is discretised using triangular elements (Shewchuk 1996, 2002) with quadratic shape functions. Due to the small absorption length in Mo (~10 nm), the region on top of the Mo coating has to be very well refined to correctly capture heating due to laser absorption. Node distances are therefore reduced to 1 nm in this region. Numerical models are designed to obtain a certain maximum temperature at the surface of the Mo capsule. This goal is achieved by iteratively solving equation (3) for varying values of the maximum power density Q_0 until the desired temperature is reached.

The assembly thicknesses varied due to the different pressures exerted on the assembly. In our idealised numerical models, we therefore changed assembly thicknesses based on a fit of the measured thicknesses from recovered samples (see **Fig. 8**). The thickness measurements were made based on the BSE images taken during FIB extraction of the recovered samples and no additional correction has been made to account for the effect of decompression. The remaining assembly dimensions were kept constant for all numerical experiments presented in the Sections 3.4.1-3.4.3 (see **Table 2**). In the parametric study (Section 4.2) we tested more experimental geometries by varying the sample thickness (ST), sample radius (SR) and Mo-capsule radius (CR). In **Table 2** we also listed the physical properties of all the materials used in the model of the LH-DAC assemblage. For simplicity, all simulations were performed with one type of sample material (quartz glass) which has very low thermal conductivity and heat

Figure 7. The setup of the idealised numerical model. Different colours denote different units. For symmetry reasons, the transparent parts of the model do not have to be modelled. Boundary conditions for the reduced model are indicated in the schematic sketch.

capacity, therefore represents the most heat resistant case scenario. Such an approach might closely represent the experiments performed with the S65 starting material (near-eutectic composition in $\text{MgSiO}_3\text{-SiO}_2$ system) but would certainly overestimate the potential temperature gradients when more conductive sample materials (e.g. natural basalts or peridotites) are laser-heated. Thus, the values of the temperature gradients calculated in this numerical simulation should be taken as a rough approximation rather than an explicit result.

Figure 8. Observed and fitted thickness variation of the different parts of the DAC assemblage due to compression during experiments. Different colours denote different units. The data for each unit was fitted using a simple linear fit. The fitted values were then used as input for the numerical model.

Table 2

Summary of the model parameters

	Quartz glass	KCl	Mo	Re	Diamond
thermal conductivity at					
300 K (W/m K)	1,38	6,66	138,00	48,00	1000,00
heat capacity (J/g K)	0,68	0,69	0,25	0,14	0,50
density (g/cm ³)	2,20	1,98	10,28	21,02	3,51
Dimensions of the modelled assembly (one fourth of the entire configuration)					
thickness (μm)	5,5-11	3,5-14	0,5-3	3,5-14	120,00
radius (μm)	7,50	62,50	37,50	112,50	112,50

3. Results and Discussion

3.1. LH-DAC Experimental conditions

Table 3 lists the experimental P-T conditions and details of the experimental setup (pressure medium, type of the capsule, heating style and time etc.). In **Figure 9** all performed experiments presented in this study are plotted on the P-T diagram together with previously published and experimentally determined melting curves of natural basalts (Hirose et al., 1999, Andrault et al., 2014, Pradhan et al., 2015) and eutectic melting curves in the simple $\text{MgSiO}_3\text{-SiO}_2$ system (Baron et al., 2017 (in review.)).

The LH-DAC experiments with encapsulated samples were performed with two types of capsule ('glass disc' and 'glass powder') and heated in two manners (described in Section 2.4). The analytical errors, in the form of standard deviation of the mean temperature measurements in the selected window assigned to the sample location, were lower than 100 K. Therefore, in **Table 3** we only report the final (in the ramped experiments) or averaged (in the long subsolidus experiments) temperatures. The long subsolidus experiments at lower temperatures (up to 2600 K) and ramped experiments to temperatures below the solidus of the starting material (see **Fig. 9** for references) were reproducible and technically easy to perform. However, in the ramped experiments at the extreme temperatures (3000 – 3900 K at 40 – 90 GPa, respectively) near the solidus of the starting material the mechanical stability of the experimental assembly was sometimes affected. In a few cases, the capsule material melted and therefore it was difficult to maintain high temperature conditions for longer periods of time.

The majority of the experiments were performed in the high-temperature ramp mode, the goal of such a strategy was to be able to detect and analyse the composition of the low-degree melt and compare samples heated and quenched at different temperatures but similar pressures in order to locate the solidus temperature as precisely as possible. Because we expected to observe melting of the samples in the ramped experiments, we assumed that relatively short experiments would be sufficient for equilibration, particularly at very high temperatures - although in the low-temperature subsolidus experiments we aimed to heat the sample for longer time to ensure equilibration.

Due to time constraints and limited access to synchrotron-based XRD, FIB and TEM, combined with the considerable challenges associated with improving the technological setup of the encapsulated samples, we were not able to comprehensively describe and investigate all the experimental products. Only about 10% of the synthesised samples were analysed with the TEM, although about 30% of the samples were at least partly cut with the FIB. Out of 40 laser-heated experiments, only 10 were performed with *in situ* XRD measurements. Therefore, within the limited scope of this study, we present mainly the technological details of the new experimental setup of the metal-encapsulated samples, preliminary results and the thermal distribution modelling which helps to understand the experimental outcome.

Table 3

Experimental conditions

No.	Pressure medium	Pressure [GPa]	Temperature [K]	ramp/time	Capsule type	XRD
S65_1	KCl	76	3500	ramp	glass disc	
S65_2	KCl	49	3000	ramp	glass disc	
S65_3	KCl	82	2300	ramp	glass disc	
S65_4	KCl	27	2600	ramp	glass disc	
S65_5	KCl	67	2950	ramp	glass disc	
S65_6	KCl	54	2600	15 min	glass disc	
BIR-1_1	Al ₂ O ₃	82	3100	ramp	glass disc	ESRF
BIR-1_2	Al ₂ O ₃	60	2080	ramp	glass disc	ESRF
BIR-1_3	KCl	58	3130	ramp	glass disc	ESRF
BIR-1_5	KCl	40	3050	ramp	glass disc	ESRF
BIR-1_6	KCl	36	2850	ramp	glass disc	ESRF
BIR-1_7	KCl	45	3200	ramp	glass disc	ESRF
BIR-1_8	KCl	90	3950	ramp	glass disc	ESRF
BIR-1_9	KCl	78	2750	ramp	glass disc	ESRF
BIR-1_10	MgO	108	2450	ramp	glass disc	ESRF
BIR-1_11	KCl	42	3000	ramp	glass disc	
BIR-1_12	MgO	42	2350	ramp	glass disc	
BIR-1_13	MgO	57	2500	ramp	glass disc	
BIR-1_14	Al ₂ O ₃	43	2800	ramp	glass disc	
BIR-1_15	SiO ₂	42	2400	ramp	glass disc	
BIR-1_16	Al ₂ O ₃	41	2930	ramp	glass disc	
BIR-1_17	KCl	29	1860	ramp	glass disc	
BIR-1_18	KCl	37	2870	ramp	glass disc	
BIR-1_19	KCl	53	3240	ramp	glass disc	
BIR-1_20	KCl	65	2901	ramp	glass disc	
BIR-1_21	KCl	88	2882	ramp	glass disc	
BIR-1_22	KCl	87	3440	ramp	glass disc	
BIR-1_23	KCl	41	3000	ramp	glass powder	
BIR-1_24	KCl	41	2500	60 min	glass powder	
BIR-1_25	KCl	66	3300	ramp	glass powder	
BIR-1_26	KCl	60	3370	ramp	glass disc	
BIR-1_27	KCl	77	3600	ramp	glass disc	
BIR-1_28	KCl	36	2040	20 min	glass disc	
BIR-1_29	KCl	40	2600	ramp	glass disc	
BIR-1_30	KCl	61	2900	ramp	glass disc	
BIR-1_31	KCl	83	3050	ramp	glass disc	
BIR-1_32	KCl	52	2800	ramp	glass disc	
BIR-1_33	KCl	72	2800	ramp	glass disc	
BIR-1_34	KCl	55	3300	ramp	glass disc	
BIR-1_35	KCl	70	3100	ramp	glass disc

Figure 9. A summary of all the encapsulated experiments performed with S65 (pink circles) and BIR-1 (orange diamonds) starting compositions. Selected samples were recovered and prepared with FIB (black squares), analysed by TEM (large black diamond frames) and analysed with XRD at the synchrotron (large black circles). Previously published melting curve of the bdg+stv eutectic by Baron et al. 2017 and natural basalt solidi of Pradhan et al. (2015) (dashed line), Andraut et al. (2014) (dash-dotted line) and Hirose et al. (1999) (dotted line) are listed for comparison.

3.2. *In situ* XRD results (ESRF)

In situ high-pressure and high-temperature experiments were performed with encapsulated glass disc samples of BIR-1 starting composition at pressures from 36 to 108 GPa and temperatures ranging from 2000 to almost 4000 K. At first, X-ray transmission maps of the pressurised samples were made in order to find the centre of the DAC assembly and precisely locate the glassy sample embedded in the Mo-capsule (**Fig. 8a**). Before laser heating a typical XRD pattern collected from encapsulated BIR-1 samples contained only peaks from Mo (capsule material) and KCl (pressure medium) (see **Fig. 8b**), confirming full vitrification of the starting material during sample preparation (see section 2.1.1 and 2.1.2). With increasing laser power, the XRD patterns changed due to crystallization of characteristic phases including stishovite, Ca-perovskite, the calcium-ferrite structured Al-rich phase, and bridgmanite (**Fig. 8c,d**). After reaching sufficiently high temperatures we expected to see the disappearance of some of the phases accompanied by the diffuse scattering of the produced melt, but due to insufficient data and difficulties in reaching the extreme melting temperatures we were unable to perform more systematic study.

Another factor worth mentioning is that the samples prepared for the *in situ* experiments were only coated with 1-2 μm layer of Mo which turned out to be insufficient for the mechanical stability of the capsule at extreme conditions, resulting in an unsustainable thermal environment. The encapsulated samples were also slightly bigger than described in section

2.1.1 due to technological limitations at the time of the sample preparation for the synchrotron experiments.

Although the synchrotron-based study do not provide comprehensive documentation of the experimental products, it is worth mentioning that the quality of the obtained XRD spectra is very high and that the crystallizing phases are readily resolved, even though the sample quantity is much smaller than the pressure medium (KCl) and Mo-coating. This provides good evidence that metal-encapsulated samples can be successfully studied by *in situ* synchrotron-based XRD.

3.3. FIB and TEM observations

Based on the BSE images of the recovered samples, obtained using the FIB system, we selected the most promising and representative samples to test and compare the outcome of the experiments using both types of the encapsulated samples ('glass disc' or 'glass powder'), performed with different heating modes (short ramps and long subsolidus). In total, eleven samples were successfully recovered using FIB apparatus, but due to time limitations, only four samples were prepared for detailed TEM analyses.

In the ramped experiment (BIR-1_34: 55 GPa and 3300 K) performed with a 'glass disc' encapsulated sample, (see section 2.1.1) the starting material only partially recrystallised at the high-pressure and high-temperature conditions. The crystallization occurred in hour-glass shape pockets near the surface of the Mo-capsule, where the temperature was the highest, but a large part of the glass disc, especially on the side and in the centre, remained unreacted (**Fig. 9a**). Based on the observed textures and phase separations, the temperature gradients inside the capsule must have been very substantial and the laser-induced heating

Figure 8. (a) A map of the Mo-encapsulated sample (elevated transmission in the middle) surrounded by Mo-walls of the capsule (low transmission region around the sample) surrounded by KCl pressure medium (elevated ring around the capsule). (b-d) Le Bail fits (red lines), backgrounds (green lines) and residuals (blue lines) for XRD data (black pluses) from a Mo-encapsulated BIR-1_3 sample before laser heating (b), in situ at 3130 K and (c) after quenching (d). The post heating pressure was 58 GPa. The tick marks represent reflections of, from top to bottom, KCl, Mo, stishovite, Ca-perovskite, calcium-ferrite structured phase, and bridgmanite.

of the metal-encapsulated sample was not sufficient to achieve isothermal conditions. Moreover, due to the rigid character of the starting material (glass disc) and very short heating at the target temperature, the kinetics of the crystallization reaction was insufficient to achieve equilibrium.

In the ramped experiments performed with 'glass powder' encapsulated sample (described in Section 2.2, BIR-1_25: 66 GPa and 3300 K) the crystallization at high pressures and temperatures was more efficient, because powdered glass with many nucleation centres on grain boundaries is more reactive than a glassy disc. As documented in **Fig. 9b**, the crystallization occurred in the majority of the sample chamber with only few unreacted regions on the sides. Also, the grains close to the Mo-layer on the top and the bottom were larger than in the centre, reflecting the hourglass-shaped geometry of the temperature gradients. The laser heating time at the target temperature was also very short and probably insufficient for equilibration, as in the previously described case.

Figure 9. TEM images of three laser-heated diamond anvil cell experiments with metal-encapsulated samples. **(a)** BIR-1_34 glass disc sample recovered from 55 GPa and 3300 K (ramp heating), bright field images. **(b)** BIR-1_25 glass powder sample recovered from 66 GPa and 3300 K (ramp heating), bright and dark field images. **(c)** BIR-1_24 glass powder sample recovered from 41 GPa and 2500 K (60 min heating at subsolidus conditions), bright field images.

The longer experiments, kept at target temperature from 15 to 60 minutes, with both types of encapsulated samples recrystallised to a large extent at the experimental PT conditions (**Fig. 9c** and **Fig. 10**). The lower temperature experiments were intentionally kept at the target temperature for longer time in order to ensure equilibration. Because it was easy to control and maintain a constant temperature on both sides of the sample, the temperature gradients were most likely less severe than in the short ramped experiments at extreme temperatures. The grain size distribution was similar to the previously described examples with slightly larger crystals near the Mo-layers and smaller grains in the centre and on the side of the capsules, reflecting the hourglass-shaped temperature distribution. Based on the chemical analyses of the products synthesised in the capsules, the observed phases agree with the high pressure phases observed in other studies at similar lower mantle conditions for complex basaltic and simplified $\text{MgSiO}_3\text{-SiO}_2$ analogue compositions.

In the basaltic sample (BIR-1_24: 41 GPa and 2500 K, for 60 min, **Fig. 9c**), bridgmanite, Ca-perovskite, stishovite and an Al-rich phase (probably: NAL-phase) crystallised. Additional small Fe metal droplets could have been a result of iron redox disproportionation related to the incorporation of the $\text{Fe}^{3+}\text{AlO}_3$ component in bridgmanite (e.g. Frost et al., 2004 and Sinmyo et al, 2011). Because the crystals were too small for high-quality diffraction analyses of single grains, even though the experiment was conducted for over 60 minutes, the phase identification was only based on EDX chemical maps. Previously presented XRD (**Fig. 8 b-d**) data from the *in situ* experiments seems to confirm the observed phases.

The recovered sample from an experiment on the model basalt analogue in the $\text{MgSiO}_3\text{-SiO}_2$ system (S65_6: 54 GPa and 2600 K, **Fig. 10**) contains very distinctive grains of stishovite surrounded by bridgmanite, which became amorphized by the electron beam. The distribution of both phases in the sample is very homogeneous with no observed chemical segregation, suggesting that the temperature gradients did not cause Soret diffusion. An additional feature of this particular sample is that it is slightly smaller than all the previous examples (see **Fig. 6** for FIB-SEM images of the entire capsule) hence even though the sample was manufactured using the ‘filament method’ resulting in a glass disc, the crystallization occurred throughout the

Figure 10. TEM images and EDX elemental maps of the recovered diamond anvil cell experiment S65_6 synthesised at 54 GPa and 2600 K (15 min heating, ‘glass disc’ sample). The chemical maps were taken in the smoothest and the thinnest part of the sample marked by the blue dashed square, although the sample was very homogeneous in the entire volume. The Si-rich grains represent stishovite surrounded by lighter in colour amorphous bridgmanite matrix which contains some remanences of the bridgmanite crystals.

entire sample chamber, unlike the basaltic sample shown in **Fig. 9a**. This suggests that the temperature gradients were less pronounced in this experiment, and this can be attributed to longer heating (15 min.), but might also be related to the smaller dimensions of the laser-heated sample. The dependence of the sample size on the thermal distribution has therefore been tested numerically and promising results of the parametric study (presented in section 4.2) gave us directions on how to improve the experimental setup in order to be able to perform more isothermal experiments at extreme conditions.

3.4. Modelling of thermal distribution with encapsulates samples

As described in section 2.8, we performed various numerical models to understand the temperature distribution in the encapsulated samples at high pressure and high temperature conditions. Here, we present the results of simulations involving different types of laser power density profiles. We tested three different laser power profiles: a conventional Gaussian profile (TEM_{00}), a flat-top mode representing most closely our experiments and a doughnut-shaped profile (TEM_{01}), which has a potential to minimize the lateral heat loss. The absolute temperature difference (ΔT) between a maximum at the capsule surface and a minimum inside the sample has been chosen as a criterion in the comparison of the numerical results of different pressure cell designs and laser power profiles.

3.4.1. Gaussian power density profile

Fig. 11 shows two examples of thermal distribution in pressure cells with metal encapsulated samples heated to a temperature of 3000 K with a laser beam with a half-width R of 10 μm at 42 and 72 GPa, resulting in a total thicknesses of the DAC assembly of 25 and 13.5 μm , respectively (see section 2.6 for more details on the parameters and **Fig. 7** for the thickness vs. pressure correlation).

The temperature varies strongly at the capsule surface, as well as in the sample itself. The heating reaches a maximum in the central part of the Mo-layer above and below the sample and the heat loss through diffusion is most evident along the peripheral edge of the sample. The temperature difference ΔT between the maximum temperature at the capsule surface and the minimum temperature in the sample is very large (1100 and 1600 K at 42 and 72 GPa, respectively) but different parameters need to be considered for a more comprehensive understanding of the modelling outcome. To assess the impact of the laser half-width on the above-mentioned temperature difference, we ran several simulations where we changed assembly dimensions according to the linear fit to the measured data at 42 and 72 GPa, laser half-width (5 – 20 μm) and target temperature (2500 – 4000 K). The resulting maximum temperature difference (ΔT) of this set of simulations are plotted in **Fig. 12**.

We observe a strong reduction in the temperature difference, with increasing laser power density half-width. In a 42 GPa experiment at a nominal temperature of 3000 K the temperature difference decreases from 2300 K at a half-width of 5 μm to ~ 670 K at a half-width of 20 μm . The gradients in these simulations are also very sensitive to the thickness of the whole assembly, which thins with increasing pressure (details in **Fig. 7**), resulting in the highest temperature differences at more extreme pressures (e.g. 72 GPa) and smaller differences at lower pressures (e.g. 42 GPa). Moreover, the temperature gradients are significantly lower when the simulated experimental temperatures are lower, but the relative differences in simulations with different target temperatures become less prominent with increasing laser beam diameter.

Figure 11. Numerically computed temperature distribution in an idealised sample assembly at **(a)** 42 GPa and **(b)** 72 GPa heated with a laser beam with a Gaussian power density profile with a half width of 10 μm. The desired temperature at the capsule surface was 3000 K. Colours indicate temperature. The outer and inner black lines show the diamond culet surface and the surface of the Mo-capsule, respectively. The white line denotes the boundary between the sample (quartz glass model) and the capsule. The insets in the top right corners show magnified views of the samples and their immediate surroundings.

Figure 12. Temperature differences (ΔT) between maximum capsule surface temperature and minimum temperature of the sample inside the capsule for different half-widths of the Gaussian power density profile applied at two pressures: 42 (warm colours) and 72 (cold colours) GPa and different maximum temperatures denoted with different symbols.

Figure 13. Numerically computed temperature distribution in an idealised sample assembly at **(a)** 42 GPa and **(b)** 72 GPa which is heated with a laser beam with a ‘flat top’ power density profile with a half width of 10 μm. The desired temperature at the capsule surface was 3000 K. Further explanations in Fig. 11.

Figure 14. Temperature differences (ΔT) between maximum capsule surface temperature and minimum temperature of the sample inside the capsule for different half-widths of the ‘flat top’ power density profile applied at two pressures: 42 (warm colours) and 72 (cold colours) GPa and different maximum temperatures denoted with different symbols.

Figure 15. Numerically computed temperature distribution in an idealised sample assembly at **(a)** 42 GPa and **(b)** 72 GPa which is heated with a laser beam with a 'doughnut' power density profile with a half width of 10 μm . The desired temperature at the capsule surface was 3000 K. Further explanations can be found in Fig. 11.

Figure 16. Temperature differences (ΔT) between maximum capsule surface temperature and minimum temperature of the sample inside the capsule for different half-widths of the 'doughnut' power density profile applied at two pressures: 42 (warm colours) and 72 (cold colours) GPa and different maximum temperatures denoted with different symbols.

1.1.1. Flat-top power density profile

The results for the same set of numerical simulations using a perfectly flat power density profile (equation 5, section 2.7), show no significant difference in ΔT relative to the Gaussian power density profile (see **Fig. 13** for two examples at 42 and 72 GPa, 3000 K, and 10 μm half-width laser beam).

Fig. 14 summarises the results of the selected simulations with ‘flat top’ mode (performed at 42 and 72 GPa). As for the Gaussian power profile, the temperature difference (ΔT) in this set of models is reduced with increasing laser width, decreasing target temperatures and decreasing pressures (directly related to the thickness of the whole assembly).

Such a similarity between the simulations with Gaussian and ‘flat top’ laser beams suggests that the main difficulty in obtaining uniform heat distribution in the LH-DAC experiments with encapsulated samples is related to the radial heat loss at the edges of the capsule rather than to the shape of the thermal distribution at the surface of the Mo-layer or the axial gradient. Therefore, we tested a possibility to reduce the radial T gradient within the samples by applying a laser beam with a more complex doughnut-shaped laser profile which potentially maximises the heating along the periphery (circumference) of the sample but also keeps the central part of the capsule hot enough.

1.1.2. Doughnut-shaped power density profile

The last set of models involves a doughnut-shaped laser profile (see equation (6) in section 2.7). The thermal distribution in sample assemblies heated to a temperature of 3000 K with a laser beam with a half-width of 10 μm at 42 and 72 GPa are presented in **Fig. 15**.

In comparison with the previously described examples, the simulations with the doughnut-shaped power density profile seem to provide a lot more isothermal conditions. The significant reduction of the temperature gradients is due to the specific laser beam shape with two maxima which matches the geometry of the experimental assembly and compensates for the radial heat loss.

As the thermal distribution governed by the doughnut-shaped laser profile is more elaborate, the influence of the laser beam width, the pressures and the target temperatures on the ΔT is also more complex (**Fig. 16**). In simulations with 5 μm laser radius the temperature differences show similar variation to the previously described cases but lower values (by about 1200 K). However, in the simulations with laser half-width of 10 μm , the temperature gradients are significantly lower (between 180 and 320 K) regardless the target temperature or pressure (thickness of the whole assembly). This observation is related to the specific geometry of the experimental setup and points out the optimal conditions at which almost isothermal LH-DAC experiments with the metal-encapsulated samples can be performed, independently of the sample size and therefore the target experimental pressure. **Fig. 16** shows that a laser beam half-width of 15 μm minimises ΔT for the 42 GPa pressure cell ($\Delta T < 90$ K) but increases ΔT for the 72 GPa cell. Adjustments of the laser beam width to the sample size would therefore be beneficial, especially for doughnut-shaped power profiles.

The striking improvement of the modelled thermal distribution in the LH-DAC experiments with metal-encapsulated samples achieved by application doughnut-shaped power density laser profile, especially with half-widths of 10-15 μm , provides great potential to reduce the severe horizontal temperature gradients of the current experimental setup without any further adjustment of the manufacturing processes.

2. Discussion

Although LH-DAC experiments can generate pressure and temperature regime of the entire Earth, the task of performing isothermal experiments at high temperatures, relevant for studying melting phase relations, partitioning behaviour of different elements and properties of melts at extreme conditions, remains challenging. The temperature gradients drive chemical segregation which alters the bulk composition of the experiment and impacts our understanding of the phase equilibria. To solve this long-standing problem we developed a novel micro-fabrication technique that allows silicate samples to be fully encapsulated. This method is based on the general idea of using a laser absorber (Mo metal) as a heater, allowing iron-free samples to be heated using Nd:YAG lasers. The metal capsule also acts as a barrier and prevents the sample from reacting with the pressure medium.

2.1. Summary of the experimental observations and future approach

A new metal-encapsulated sample configuration designed for LH-DAC experiments has been successfully manufactured using micro-fabrication techniques and applied in the high-pressure and high-temperature experiments. Two methods of encapsulation presented in this study enable starting materials of almost any kind to be fully enclosed in a Mo-sleeve which acts like a mechanical barrier and metallic heater which absorbs the laser light and allows conduction of heat to the inner part of the capsule. The capsule approach keeps the sample fully isolated from the pressure medium and therefore limits contamination. The encapsulated samples are mechanically stable at high pressures, do not tear in the stress field and can survive at high temperatures during laser heating, up to a point when the target temperature is close to the melting temperature of the capsule material (Mo in this study). We have tested and described two methods of sample encapsulation: ‘the filament method’ and ‘the gasket method’, used to prepare glass disc and glass powder starting samples, respectively. The crystallization kinetics turned out to be significantly slower in the massive glass disc samples compared to in the glass powder samples.

In the ‘filament method’, the starting material was resistively heated and melted to fill 10-15 μm holes in the pre-fabricated filament. After quenching the glass discs were cut out of the filament and coated with the Mo-layers on the top and bottom. This produced up to about 40 Mo-encapsulated and homogeneous glass disc samples with identical composition to be used for experiments at different PT conditions. The filament method to produce massive glass discs is limited to starting materials which can be melted at 1 bar pressure in an inert gas and quenched to homogeneous glass. The method is therefore problematic for a variety of materials, for example peridotitic compositions (see supplementary material for more details) or volatile-bearing starting compositions. Although the mechanical stability of the encapsulated glass disc samples is advantageous for the LH-DAC experiments at extreme conditions, the low reactivity of the massive glass disc material can be problematic. We have noticed that the glassy disc samples exhibit less profound recrystallization, limited to an hourglass pattern near the laser-heated Mo-walls (see **Fig. 9a**). The slow and limited recrystallization can be attributed to scarcity of nucleation centres and/or to less efficient thermal diffusion resulting in larger temperature gradients. However, the glass disc sample presented in **Fig. 10** (S65_6, 54 GPa and 2600 K, 15 min heating) shows homogeneous crystallization which can be attributed to longer heating time and/or smaller capsule size, suggesting that with some small improvement the samples obtained with the ‘filament method’ can provide successful results.

Following the ‘gasket method’ procedures, the metal-encapsulated glass powder samples are made by micro-manufacturing using the DAC as a press to thin the Mo-foil to the appropriate thickness and to press glass powder starting material into the previously drilled sample chambers in the indented foil. This technique is less efficient and results in only up to 9 capsules per gasket made with 300 μm culet size diamonds mounted in the DAC. Moreover, during loading of the starting material some sample chambers collapse or break and therefore more care needs to be taken in order to identify successfully prepared samples. On the other hand, with this method a wide variety of starting material can be encapsulated, e.g. samples containing volatiles or samples which require more complex synthesis using large volume presses (LVP) or laser-levitation under different redox conditions, which makes it more versatile and applicable. In terms of the mechanical stability and robustness of the capsule at high pressure and temperature, the samples containing powdered glass tend to deform slightly more extensively and irregularly due to the small voids and pore space inside the capsule. However, in most cases the capsule integrity is maintained, and we did not observe any contamination of the sample by the KCl pressure medium. The glass powder samples resulted in more extensive crystallization compared to the glass disc samples, suggesting that the powdered glass with its abundant grain boundaries is more reactive.

2.2. Summary of the thermal modelling results and future approach

The exact values of the temperature gradients, expressed as ΔT , are not definitive, but they can be used for comparison and as an indication of how different parameters influence the temperature distribution in the LH-DAC assemblies with metal-encapsulated samples. Although the temperature gradients resulting from the Gaussian and ‘flat-top laser beam profiles are substantial, they are also very similar. We therefore conclude that these two laser beam power profiles can be used with the same confidence. As all the experiments presented in this study were heated with flat-top laser beams, we attribute the large temperature gradients observed in our samples based on the textural interpretations of the recovered samples to the irregular heat distribution and strong heat loss in the radial direction where there is no laser power input. The uneven temperature distribution captured in the numerical models reflects accurately the hourglass-shaped crystallization and grain size distribution observed in the recovered samples, and we are therefore confident that the modelled scenarios largely represent the LH-DAC experiments. After discovering that the radial gradients are the most extensive and that the heat escapes efficiently also in the radial direction where there is no laser power input, we performed a number of simulations with a doughnut-shaped laser beam, providing maximum power intensity in the peripheral zone. This reduced the temperature gradients significantly, and we plan to implement this laser-heating mode in future LH-DAC experiments with metal-encapsulated samples.

In order to investigate the effect of the dimensions of the different pressure cell components on the modelled temperature gradients, we performed a parametric study in which we varied dimensions of the Mo-capsule and the sample itself in a systematic way. We tested if the temperature distribution can be improved by reducing the sample thickness (ST), sample radius (SR) and Mo-capsule radius (CR). Because the Gaussian and ‘flat top’ models gave almost identical results in previous simulations, our study was limited to the flat-top and doughnut-shaped laser power density profiles. The results of a series of parametric simulations performed with a constant total assembly thickness of about 25 μm , corresponding to our 42 GPa experiments, are presented for the flat-top and doughnut-shaped laser beam profiles in **Figs. 17** and **18**, respectively. All of these simulations use a target temperature of 3000 K, a laser half-

width of 10 μm and a constant Mo-coat of about 1.5 μm which closely represents our LH-DAC setup. In **Fig. 17a** and **18a** the thermal distribution was computed for different sample radii (SR ~ 7 or 4 μm) and Mo-capsule radii (CR ~ 35 or 12 μm) but constant thickness of the encapsulated sample (ST=8 μm), corresponding to the thickness of DAC samples recovered from 42 GPa. The effects of a sample thickness reduction to ST=4 μm on the temperature gradients are presented in **Fig. 17b** and **18b**.

The parametric study demonstrates that a reduction of the thickness of the encapsulated sample from 8 to 4 μm improves the temperature distribution only marginally (compared to the original setup presented in **Fig. 13a** and **15a**). A more significant reduction of the T-gradient, however, can be achieved by reducing the sample and/or Mo-capsule radius (SR and CR). Scaling down the encapsulated sample radius can lead to more uniform heat distribution and reduction of the temperature gradients to about 200 – 300 K in the experiments with a flat-top laser beam and 70 – 80 K for a doughnut-shaped laser beam.

The temperature gradients in the LH-DAC experiments with metal-encapsulated samples, which have been observed, characterised and numerically modelled in this study, can be reduced by a few modifications of the already developed setup. The application of a doughnut-shaped laser beam, instead of a more conventional Gaussian or flat-top beam, can potentially provide more uniform heat distribution and temperature gradients (ΔT) of about 100-300 K with the current experimental configuration or to less than 100 K by using a smaller capsule. Due to the extensive net heat loss in the radial direction, in which there is no laser power input, the most sensitive parameters controlling the temperature gradients are the diameters of the sample and surrounding Mo-capsule. Thus, our goal for the future development is to manufacture narrower elements and possibly use an additional component (e.g. MgO or SiO₂ ring around the capsule) to keep the capsule more confined by a frame of robust material and therefore prevent potential spreading of the Mo-ring under pressure.

Preparation and manufacturing of metal-encapsulated samples smaller than those used in the present (reconnaissance) study is currently in progress. Although this manufacturing is laborious, some assemblies with the BIR-1 basalt (glass powder samples) have already been run at stable high pressure and temperature conditions. However, the experimental run products need to be studied analytically in more detail.

3. Conclusions

LH-DAC experiments at the lower mantle conditions (~ 25 – 110 GPa and 2000 – 4100 K or more), using metal-encapsulated samples can significantly reduce the thermal gradients within the capsules. We developed such a technique and performed test experiments with a natural basalt (BIR-1) and a simple basaltic analogue composition in the MgSiO₃-SiO₂ system (65mol% SiO₂). Two types of encapsulated samples were tested: glass disc ('filament method') and powdered glass ('gasket method') samples. Based on observations of the recovered samples analysed by FIB-SEM and TEM, we noticed that the temperature gradients remained substantial as the crystallization of high pressure phases occurred in hourglass-shaped zones reflecting the hottest part of the sample chamber, close to the laser-heated metal surfaces. Based on the textural interpretations and chemical analyses of the recovered samples, the powdered glass samples resulted in more pronounced and homogeneous crystallization than the glass disc ones.

Figure 17. A comparison of numerically computed temperature distribution in the LH-DAC experiments at constant pressure (42 GPa), temperature (3000 K), with ‘flat top’ laser beam of 10 μm radius but varying capsule dimensions: sample thickness (ST), sample radius (SR) and Mo-capsule radius (CR). In **(a)** the ST has a constant value of 8 μm (original setup) but different SR and CR whereas in **(b)** the ST is reduced to 4 μm with varying SR and CR in order to understand the effect of all the sample/capsule parameters on the generated temperature gradients and to test possibilities for further improvement of the thermal distribution in the encapsulated LH-DAC experiments.

Figure 18. A comparison of numerically computed temperature distribution in the LH-DAC experiments at constant pressure (42 GPa), temperature (3000 K), with ‘doughnut shape’ laser beam of 10 μm radius but varying capsule dimensions: sample thickness (ST), sample radius (SR) and Mo-capsule radius (CR). In (a) the ST has a constant value of 8 μm (original setup) but different SR and CR whereas in (b) the ST is reduced to 4 μm with varying SR and CR in order to understand the effect of all the sample/capsule parameters on the generated temperature gradients and to test possibilities for further improvement of the thermal distribution in the encapsulated LH-DAC experiments.

This difference can be attributed to more efficient nucleation in the powdered samples, containing abundant grain boundaries.

In order to understand and improve the thermal distribution of the encapsulated samples, we modelled the experimental setup and performed numerical simulations for different laser beam shapes (Gaussian, flat-top and doughnut-shaped beams), laser half-widths (5-20 μm), different target temperatures (2500 - 4000 K) and varying thickness of the whole assemblage, directly related to the experimental pressure. The thermal modelling also included a systematic study of how the dimensions of the Mo-capsule and sample affect the T-gradients. The combination of a doughnut-shaped laser beam and reduced sample and capsule diameters can limit the temperature range (ΔT) to 100-300 K ('flat top' mode) or even <100 K ('doughnut shape' mode). Further experimental work using the refined laser beam profile and reduction of the capsule and sample dimension is required in order to test the promising findings obtained from the numerical simulations.

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Supplementary material

1. Capsule manufacturing – ‘filament method’

Additional photographic documentation of the manufactured products with the ‘filament method’ technique is presented in **Fig. S1**.

Figure S1. Pictures of the Mo-filament **(a)** laser-drilled to the bow-tie shape; **(b)** loaded with starting material glued on top of the middle part of the filament and connected to the circuit of the resistance heater. **(c)** recovered after melting the starting material and removal of the excess glass quenched on top of the filament **(d)** after cutting the capsule walls around the sample and leaving a little neck which keeps the sample attached to the filament. **(e)** single sample disk surrounded by the Mo-wall. **(f)** fully encapsulated sample disk coated with Mo metal layer.

2. LH-DAC experimental results of the KLB-1 encapsulated samples

In parallel to the experimental study on natural basalt and simplified analogue for basaltic material in $\text{MgSiO}_3\text{-SiO}_2$ system (S65 - 65 mole% SiO_2 and 35 mole% MgO) presented in the main text, we have also performed a number of LH-DAC experiments with metal-encapsulated samples containing KLB-1 model peridotite starting material (Trønnes and Frost, 2002) and analogue for mantle peridotite in the simple MgO-MgSiO_3 system (S36 - 36 mole% SiO_2 and 64 mole% MgO). The preparation of the encapsulated samples containing peridotitic material, experimental setup and laser-heating procedures were the same as for the basaltic samples described in the main text, but because of the more complex features of the peridotitic material and difficulties in obtaining homogeneous starting material we have decided to describe it separately.

Table S1

FEG microprobe analysed of starting materials

Wt.%	KLB-1_LL*	1 σ	KLB-1_FM*	1 σ	Si36_FM*	1 σ
MgO	38,11	0,21	35,01	0,49	54,54	0,21
SiO ₂	43,03	0,36	45,81	0,50	44,23	0,32
Al ₂ O ₃	3,81	0,06	5,00	0,08	-	-
FeO	7,87	0,12	7,43	0,07	-	-
CaO	3,92	0,05	4,85	0,01	-	-
Na ₂ O	0,12	0,01	0,10	0,02	-	-
K ₂ O	0,01	0,01	0,00	0,00	-	-
MnO	0,11	0,02	0,10	0,02	-	-
P ₂ O ₅	0,05	0,01	0,03	0,06	-	-
NiO	0,22	0,02	0,02	0,02	-	-
Cr ₂ O ₃	0,17	0,05	0,28	0,04	-	-
TiO ₂	0,17	0,01	0,01	0,01	-	-
Total	97,59	-	98,63	-	98,77	-

*LL – laser levitated starting material; *FM – material melted on top of the filament.

The capsules containing glass discs ('filament method' described in the main text, section 2.1.1) were particularly difficult to manufacture due to the fact that MgO -rich peridotitic material has a very high melting temperature and does not easily quench to homogeneous glass at 1 atm. We were able to manufacture only a very limited number of filaments and in most cases the samples comprise quench crystals. The chemical compositions of the peridotite glass produced by laser levitation were measured by FE-EMPA and are listed in **Table S1** (KLB-1_FM and S36_FM). However, The obstacles related to the synthesis of the starting material by melting of powder on a perforated filament prompted us to load glassy and powdered samples directly into holes in Mo-filaments (the 'gasket method' described in the main text, section 2.1.2).

We have performed a number of LH-DAC experiments at pressures and temperature of the lower mantle (27 – 85 GPa and 2200 – 3600 K). A summary of the experimental conditions together with the heating parameters can be found in **Table S2**.

Table S2

Experimental conditions

No.	Pressure medium	Pressure [GPa]	Temperature [K]	ramp/time	Capsule type	XRD
S36_1	KCl	64	3500	ramp	glass disc	
S36_2	KCl	45	3200	ramp	glass disc	
S36_3	KCl	65	2900	ramp	glass disc	
S36_4	KCl	32	2800	ramp	glass disc	
S36_5	KCl	35	3000	ramp	glass disc	
S36_6	KCl	56	3400	ramp	glass disc	
S36_7	KCl	55	3000	ramp	glass disc	
KLB-1_1	KCl	27	3150	ramp	glass disc	ESRF
KLB-1_2	Al ₂ O ₃	51	2980	ramp	glass disc	
KLB-1_3	Al ₂ O ₃	30	2260	ramp	glass disc	
KLB-1_4	KCl	69	3060	ramp	glass disc	
KLB-1_5	KCl	34	2900	ramp	glass disc	
KLB-1_6	KCl	54	3200	ramp	glass disc	
KLB-1_7	KCl	85	2800	ramp	glass disc	
KLB-1_9	KCl	72	3600	ramp	glass disc	
KLB-1_10	KCl	53	2450	60 min	glass disc	
KLB-1_11	KCl	31	2400	15 min	glass disc	DLS
KLB-1_12	KCl	85	3100	ramp	glass powder	
KLB-1_13	KCl	54	2900	ramp	glass powder	
KLB-1_15	KCl	53	3100	ramp	glass disc	
KLB-1_16	KCl	37	3200	ramp	glass disc	
KLB-1_18	KCl	36	3100	ramp	glass disc	
KLB-1_19	KCl	27	2550	ramp	glass disc	

The PT conditions of our experiments in comparison with previously published experimentally determined solidus curves for peridotitic compositions or analogues in the simple system are plotted in **Fig. S2**.

A few selected peridotitic run products were recovered and prepared by FIB for TEM analyses (**Figs. S3, S4**).

Figure S2. A summary of all the encapsulated experiments performed with S36 (green circles) and KLB-1 (blue diamonds) starting compositions. The temperatures refer to average temperature measured from both sides during laser heating. Pressure is based on the diamond Raman shift peak. Selected samples were recovered and prepared with FIB (black squares), analysed by TEM (large black diamond frame) and analysed with XRD at the synchrotron (large black circle). Previously published melting curve of per+bdg eutectic by Baron et al. 2017 and natural peridotite solidi of Fiquet et al. (2010) (dashed line), Andrault et al. (2011) (dash-dotted line) and Nomura et al. (2014) (dotted line) are listed for comparison.

Figure S4. (a) Electron image of the thin sections prepared using focused ion beam system (FIB) of KLB-1_13 sample synthesised at 54 GPa and 2900 K (glass powder, ramp heating). (b) TEM image of the KLB-1_13 sample (BF: bright field image). (c) EDX elemental maps of a small region indicated with red and white dashed squares on TEM images b. and d. respectively. (d) A TEM image of the homogeneous and crystallised area near the Mo-wall of the KLB-1_13 sample (BF: bright field image). In this case the sample shows more homogeneous texture and all the different phases are uniformly distributed inside the capsule. The chemical maps document occurrence of phases typical for peridotitic compositions synthesised at lower mantle conditions including: bridgmanite, ferropervicite, Ca-perovskite and Fe-metal droplets. In the centre and near the edges on the side of the capsule there are fragments of amorphous material which suggests that the temperature gradients were still substantial in those regions.

Figure S3. (a,b) Electron images of the thin sections prepared using focused ion beam system (FIB) of KLB-1_11 sample recovered from 35 GPa and 2400 K (glass disc, heated for 15 min.). **(c-g)** TEM images of the KLB-1_11 sample (BF: bright field images, DF: dark field images). The TEM images show complex and dynamic texture which is difficult to interpret and might be a consequence of several processes. The chemical heterogeneity can be attributed to the fact that the starting material during sample manufacturing did not quench to glass and therefore the chemical heterogeneity was inherited and did not re-equilibrated at the high pressure and high temperature despite the relatively long (15 min.) heating time.

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Summary

“Learn from yesterday, live for today, hope for tomorrow.

The important thing is to not stop questioning.”

- *Albert Einstein*