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ABSTRACTS

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Fractional crystallization of melilitite and Mg-nephelinite at 1 GPa: An experimental study on the petrogenesis of carbonatite magmas

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The most common sources of Rare Earth Elements (REE) are carbonatite deposits and associated alkaline magmas. Amongst widely distributed carbonatites in the world, the only active extrusive carbonatite lavas are found at Oldoinyo Lengai volcano (Tanzania), and are unique due to their high-alkali content, named as natrocarbonatites. The supposed parental melts of these carbonatites, namely melilitites and Mg-nephelinites, are believed to be formed by low-degree partial melting in the upper mantle due to their high alkali contents. At late stage evolution, the primitive melts are likely to produce immiscible carbonatite and alkaline silicate melts. However, the crystallization process by which the evolution of these parental melts would evolve toward immiscible melts in the upper mantle has not yet been fully understood.

In the present study, a series of fractional crystallization experiments is performed in order to understand the differentiation of carbonatites' parental magmas. Both starting compositions, melilitite and Mg-nephelinite, were prepared with 1.2 wt.% of H_2O and 0.6 wt.% of CO_2, based on previous melt inclusion studies. The conditions of the first fractional crystallization step were established to be just below the liquidus temperature of each composition, i.e., for melilitite = 1250°C and for Mg-nephelinite = 1200°C and the subsequent experiments are performed with 30°C steps. At each step, the melt composition in equilibrium with crystallized minerals is determined by chemical analysis (using electron microprobe) and mass balance calculations. All the experiments are performed at a nominal pressure of 1 GPa, using a piston-cylinder apparatus and AuPd alloy capsules. A double capsule setup is employed to avoid iron and volatile losses during the experiments.

The experimental results will ultimately show how the fractional crystallization could explain the association of alkali carbonatites together with alkaline lavas.

Formation of jack-straw olivine in siliceous dolomite contact aureoles by reaction overstepping

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The forsterite zone of the Ubehebe Peak contact aureole consists of an outer zone of tabular/jack-straw olivine and an inner zone of equant olivine. The change in habit is abrupt. Previous work has proposed that this shift in morphology reflects variation in reaction affinity across the contact aureole [1,2]. Here we present an experimental study which sheds light on the mechanism for the formation of tabular forsterite.

Forsterite precipitation experiments done in cold seal pressure vessels at 1.7 kbar and 650°C were done in gold capsules with 15 µL H_2O, powdered natural dolomite, and quartz at 1.7 kbar Capsules were heated rapidly at ca. 22°C/min; the final, steady temperature of

650°C was reached after approximately 30 minutes. Each experiment was held at the peak temperature for a different amount of time. Experiments were isobarically cooled to room temperature in a air stream, resulting in a fast initial quench, with the final temperature reached after approximately 30 minutes. Each capsule was punctured and the amount of CO_2 formed during the experiment was estimated by weight loss. Run products were imaged with a scanning electron microprobe. Finally, the phases were identified by a combination of energy dispersive X-ray spectroscopy and Raman spectroscopy.

Forsterite precipitation in the system Ca-Mg-Si-C-O-H involves three separate chemical reactions. In the beginning of the experiments, quartz rapidly reacts with dolomite to simultaneously form tabular forsterite and tremolite. Tabular forsterite exhibits pseudohexagonal twinning. After all the quartz in the capsule has reacted away, forsterite precipitation continues at a slower rate by tremolite dissolution. This second generation of forsterite precipitates around of some of the tabular forsterite, with a different habitus and tracht; it lacks the (100) face and is stubby.

After all of the tremolite in the capsule has reacted away, forsterite crystallisation continues at an even slower rate by dissolution of the tabular forsterite. Dissolution of the early tabular scaffolding on which later stubby forsterite formed results in subequant crystals that preserve the tabular twin relationships but that have voids within them. Long time experiments (30 days) at 650°C eventually develop euhedral equant crystals that we interpret as reflecting a chemical, structural, and textural equilibrium.

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Geology, 25(9), 823-826.
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The role of substrate roughness on overgrowth morphology and trace element partitioning during precipitation from low temperature aqueous fluids: a case study of Sr-in-calcite

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Seed crystals are commonly used in crystal growth experiments to overcome nucleation issues. Although it is common practice to use oriented, polished seed crystals it is unclear to what extent seed crystal surface roughness influences overgrowth formation. Furthermore, growth on fractured, cleaved, abraded, or chemically weathered surfaces is common in many natural environments. To ascertain how substrate roughness influences overgrowth formation and trace element partitioning, we modified calcite cleavage surfaces by abrading them with various grits of silicon carbide sandpaper (physical weathering analogue substrates) or by etching them in 5 M HCl (chemical weathering analogue substrates). All substrates were characterized by imaging with a scanning electron microscope; 3D reconstructions of the surfaces allowed for quantification of roughness parameters. After imaging, the seeds were suspended in a calcite-supersaturated, 1 mM Sr-doped solution at 25°C.

Each substrate type developed a unique overgrowth morphology. Calcite grown on physical weathering analogue substrates had a shingled appearance and consisted of 3D crystallites that failed to coalesce into a homogeneous overgrowth. Calcite grown on pristine cleavage surfaces was homogeneous and optically continuous with the substrate when observed in a transmitted light microscope. Calcite grown on chemical weathering analogue substrates had characteristics that were intermediate between the cleavage surface overgrowth and the physical weathering analogue substrate overgrowths.

Each substrate has a unique mean Sr concentration, indicating that substrate roughness influences overgrowth impurity incorporation, as well as morphology. However, the magnitude of this deviation from expected partitioning is small.

Experimentally exploring the production and pre-eruptive storage conditions of phonolitic magmas from Mayotte (France)

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Between May 2018 till the end of 2021, Mayotte island was the locus of a major submarine volcanic eruption characterized by the emission of more than 6.5 km^3 of basanitic magma. The eruption occurred along a WNW-ESE trending submarine ridge on the east flank of Petite Terre where, in addition, several seemingly recent phonolitic bodies were also identified at 10-15 km from the island. To have a precise understanding on the plumbing system operating below this system and for defining realistic scenarios of evolution and ascent, it is crucial to have accurate constraints on magma temperature, storage depths and on the characteristic amount of volatiles (H_2O, CO_2, S, F, Cl, etc.) dissolved into the magmas. In this work we experimentally explore 1) the putative relationships between the basanites emitted by the new volcano and the recent phonolites and 2) the crustal storage and ascent conditions of phonolites. To achieve these goals, we first performed crystallization experiments on a representative basanite over a large range of pressures (up to 400 MPa). The results show that the ≥65 wt.% crystallization of an assemblage of olivine, plagioclase, amphibole, clinopyroxene, biotite, magnetite, ilmenite and apatite from a parental basanite at crustal levels (≤12–15 km) yields a phonolitic residual liquid containing up to 3-4 wt.% H_2O. The depth/pressure of fractionation exerts an important control on the final iron content of the residual phonolitic liquids. Fe-rich phonolites from the submarine ridge can be only produced at 6–8 km depth, while a shallower differentiation (≤4–5 km) results in the production of liquids with trachyte-benmoreite affinities. If the fractionation process occurs at depths higher than 8 km, the resulting phonolitic melts are progressively enriched in SiO_2-Al_2O_3 but depleted in FeO*, i.e. unlike those erupted [1].

A complementary set of crystallization experiments are currently being performed on a representative Fe-rich phonolite from the submarine active ridge at Mayotte, characterized by the presence of a dry mineral assemblage consisting of fayalite+olivine+anorthoclase+magnetite+apatite. Based on the basanite crystallization experiments, the conditions explored were P ≤ 200 MPa, T 1000-750°C, and a large range of H_2O/CO_2 ratios. The liquidus assemblage is characterized by the presence of magnetite+apatite, followed by alkali feldspar, fayalitic olivine, clinopyroxene, biotite, amphibole and sodalite as T, P, H_2O decrease. Our experiments not only reproduce the mineralogy and composition of submarine phonolites but can be also used to set tight constraints on the storage conditions of on-shore equivalents, these representing a major hazard for the local population. Compared to previous estimates [2], we therefore conclude that phonolitic magma production and storage at Mayotte is a rather shallow process [1].

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Temperature-emissivity relationship: the key parameter to understand heat transport in surface and deep geological processes

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The understanding and modelling of magmatic and volcanic processes like cooling, solidification, crystallization and mixing occurring in magmatic reservoirs or progressing lava flows requires precise data on the thermal properties of the surrounding media and magmas. Hence, it is crucial to accurately determine magma Temperature (T) since this parameter controls the rheological evolution (i.e., crystal content, viscosity) of the emitted lava flows, lava lake surface and eruptive columns. During eruptions, T is mostly retrieved by measuring the infrared (IR) radiance of the lava flow, however this is subjected to important errors related to the poor knowledge of one of the most critical parameters, namely spectral emissivity (ε), which is commonly considered constant. In this study, we performed in situ spectral emissivity measurements on representative basalts at relevant magmatic temperatures (from RT to 1800 K) over a wide spectral range (400-8000 cm^{-1}) covering TIR, MIR and SWIR regions, using a non-contact IR emissivity apparatus [1-3]. Structural, chemical and textural analyses of studied samples performed prior and after IR measurements, reveal that ε has a complex relationship with temperature, wavenumber and is greatly affected by micro-scale crystallization and small changes in the silicate network. Hence, considering a constant emissivity when determining the T of a magma is an important oversimplification that results in important source of uncertainties. Our ε -T data were used to develop new algorithms that account for the effect of T and melt structure on spectral ε when calculating radiative heat fluxes. They allowed to refine up to 50% the remote sensing thermal data of the 2014-2015 Holuhraun eruption in Iceland [2], obtained with a constant emissivity value.

The above results retrieved on anhydrous magmas clearly show that crystals have a significant impact on their radiative properties. In this light, the case of deep reservoirs appears even more challenging since magmas can contain up to several percent of volatiles (mainly H_2O). Water is an important network modifier element in silicate melts and its solubility is mostly controlled by pressure. In order to determine the radiative properties of volatile (H_2O)-bearing magmas we will present a new experimental setup developed in the framework of Planex project [4] allowing high temperature- high pressure in-situ measurements of magma spectral emissivity. This new apparatus will allow to improve the knowledge on the radiative heat transfer occurring in deep magma reservoir processes such as cooling, crystallization, mixing as well as predicting reservoir-lifetime.

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Recent advances in determining equations of state of minerals

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Equations of State (EoS) describe the variation of volume and elasticity of a mineral with pressure and temperature. EoS are a foundation of all thermodynamic databases for minerals and mineral equilibria, and the basis for interpreting seismic wave velocities in terms of the mineralogy and structure of planets. Precise and accurate EoS are also needed for the recently revived and rapidly developing methods of piezobarometry, which uses the remanent pressures, stresses and strains in inclusion phases trapped in host minerals to determine the conditions of their entrapment or resetting and hence P,T points in the history of rocks.

Despite the challenges of performing accurate and precise measurements of elastic properties of minerals at high P and T, there is an ever-increasing amount of new internally-consistent and precise data, especially measurements of their bulk moduli at simultaneous high P and T. However, these data are usually fitted on their own to obtain EoS parameters. Such independent fits of individual datasets inevitably suffer from large uncertainties in the parameter values, because of the small numbers of data points. And the correlations between the values of parameters are almost never reported or considered, although these are critical for evaluating whether one set of parameters is statistically the same as, or significantly different from, another set of parameters. Fitting individual datasets does not allow the leverage of different types of data such as elastic moduli compared to volume to be exploited; elastic moduli data do not determine volumes.

In this contribution we will use end-member garnets [1] as an example to demonstrate how to determine the EoS of minerals with the EosFit program (www.rossangel.net) from all of the available data for volume, density, and elasticity. We introduce the use of heat capacity data to identify individual and sets of volume and elasticity data that are in error. Dataset scaling [2] then allows some of these datasets to be used to better constrain the EoS parameters.

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Inclusions in a natural diamond studied by in situ Mössbauer spectroscopy, tomography, single crystal X-ray diffraction, infrared and Raman spectroscopy and electron microprobe

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The investigation of mineral inclusions trapped in diamonds represents a valuable tool to access the deep Earth and improve our understanding about its chemistry and mineralogy.

More in detail, inclusions can provide multiple information such as pressure, temperature, and redox conditions of diamond formation, as well as their rock source. This study focused on the identification and characterization of multiple mineral inclusions by a combination of synchrotron-based diffraction and spectroscopic techniques to reveal the origin of the host diamond.

The investigated diamond comes from the area of Rio Soriso, Juina (Brazil), typically known for the abundance of lithospheric and sublithospheric diamonds [1]. It is double polished along [100] and characterized by eight visible, transparent and greenish inclusions, with size ranging between ~20 micron and ~200 micron.

The inclusions were analysed by synchrotron X-ray tomography and diffraction at 13BM-D (GSECARS) beamline at the Advanced Photon Source (Argonne, US), equipped with a new Pilatus 1M CdTe detector. Analyses of the $Fe^{3+}/\Sigma Fe$ were performed by in situ synchrotron Mössbauer spectroscopy at ID 18 beamline of the European Synchrotron Radiation Facility (Grenoble, France), with a 6x15 μm^2 focused beam. Additional non-invasive analyses consisted of both transmittance and reflectance Fourier Transform infrared spectroscopy coupled with Raman spectroscopy to verify either the presence of O-H-N molecules and evidence of residual stresses by looking at the frequency shift of the vibrational bands. Finally, chemical analyses were performed on an exposed inclusion.

Our preliminary results provide evidence of a wehrlitic environment where the investigated diamond might have formed. Based on the measured $Fe^{3+}/\Sigma Fe$ of the trapped minerals we propose a possible redox reaction through which syngenetic inclusions can be encapsulated in the upper mantle.

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Efficiency of immobilization of hazardous elements: towards a sustainable ceramic process

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The ceramic tile industry is a high throughput sector. With a global production exceeding 18 billion square meters in 2021 [1], tile industry requires a huge and constant supply of raw materials, with estimates of ~400 million tons per year. In Europe, especially in Italy, the ceramic tile sector is heavily dependent on imports of strategic raw materials, and this dependence is a critical aspect in the supply chain. Several measures can be taken to mitigate a potential supply-chain disruption, such as the substitution of natural raw materials with secondary raw materials in a circular economy context. In this sense, the ceramic industry proved to be able of recycling its processing residues in a very efficient way (index of reuse ~100%), but this cannibalistic way of recycling is not enough to meet the market demand.

A strong contribution to the sustainability of the ceramic tile manufacturing process can derive from the recycling of waste, even when it contains hazardous elements (HEs). On the other hand, the range of secondary raw materials would be broadened to include elements that, however, must undergo a total inertization into the crystalline lattice of the residual phases or in the glass matrix of ceramic bodies through the so-called ceramization process [2]. Namely, before any possible resort to HEs (e.g., Ba, Co, Cr, Cu, Mo, Pb, Sb, Sn, Sr, V, Zn), their degree of inertization within different ceramic matrices have to be quantitatively assessed.

In this contribution seven ceramic batches were formulated to obtain: three largely vitrified products (i.e., two different porcelain stoneware bodies and a red stoneware), three largely recrystallized products (i.e., plagioclase-, melilite-, and clinopyroxene-enriched porous tiles and bricks), and a largely unreacted body (low fired brick). These formulations, taken as ceramic standards, were then admixed with 10 wt.% of two different type of waste: bottom ashes (BA) from MWI and an artificial waste (an aluminosilicate matrix containing all the HEs of above to simulate the BA composition). Fired products from all 21 ceramic formulations, experimented at the laboratory scale simulating the industrial tile-making process, were characterized through a combined analytical approach (QPA-XRPD, SEM, water absorption, and bulk density), and then subjected to a leaching test (EN 12457-2:2002) to evaluate the HEs mobility. Both specific HE and ceramic formulation have influence on the degree of inertization and mobilization mechanism of HEs. Significant criticisms are related to the ceramization of Mo, Cr, V and Sb, mostly in the largely unreacted body.

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Dendritic plans crystallization inside barred olivine (BO) textures and their relations with border: Experimental investigation and X-ray tomography

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Chondrules, the major constituent of chondrites, are millimeter-sized igneous objects resulting from the crystallization of silicate liquids produced by the partial or complete melting of chondritic precursors, whose exact nature remains disputed. Various chondrule textures are observed and are attributed to the extent of the initial melting event [1,2]. Here, we report dynamic crystallization experiments using a 1-atm vertical furnace, performed with a broad range of cooling rates (20-700°C h^{-1}) at superliquidus initial conditions to decipher the mechanisms of crystallization leading to the textures observed in chondrule Barred Olivines (BO). The dendritic textures were reproduced in all experiments, regardless of the cooling rate investigated. However, the closest texture to the so-called BO texture of the chondrules (smooth bar, border, inclusions [3]) is obtained using a low cooling rate (< 50°C h^{-1}). The border and the bars are linked but can present embayments, a feature which is analogous with the natural objects. In addition, a rare dendritic plan (101) is observed in low cooling rate experiments (20°C h^{-1}) and shows a start of ripening with assembly of small units in a medium direction <101> and with dissoluted parts [4]. X-ray tomography is used to observe the organization of barred texture in 3D. Based on petrographic observations, we propose thermal and temporal formation models for BO chondrules and provide constraints to the thermal conditions prevailing during the early solar system history.

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Elastic properties of fayalite $(Mg_{0.2},Fe_{0.8})_2SiO_4$ at high pressures and temperatures

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The elastic properties of a pure, synthetic fayalite aggregate, $(Mg_{0.2},Fe_{0.8})_2SiO_4$, were studied by coupled synchrotron X-ray diffraction and ultrasonic interferometry in a DIA-type multi-anvil press at beamline X17B2 (NSLS, Brookhaven Laboratory, USA). The sample was prepared by mixing nanosize oxide powders (MgO + Fe_2O_3 + SiO_2) in stoichiometric proportions and densified by spark plasma sintering prior the experiment. The sintered sample showed no preferred orientation and an average grain size of about 2 microns. Ultrasonic interferometry, using the DIASCoPE system

[1], allowed us to measure sound wave velocities at pressures up to about 7 GPa and temperatures up to 873K. Results from both the ultrasonic measurements and Xray diffraction will be presented as well as the effect of Fe content on the elastic properties of olivine. Finally, the implications for the determination of a mineralogical model in the context of the Mars Insight SEIS experiment will be discussed.

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Elastic geobarometry using omphacite in eclogites: a Raman spectroscopy approach

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Raman scattering is very sensitive to structural deformations in crystal structures developed upon heating or compression. Raman elastic geobarometry uses deformation recorded by a mineral inclusion trapped in its host to retrieve the pressure and temperature conditions at which the inclusion has been entrapped [1]. Several host-inclusion systems have been studied, but clinopyroxenes have not yet been investigated. Because of their widespread occurrence in several geological settings and rock-types (e.g. high pressure eclogites, mantle xenoliths etc.), omphacitic clinopyroxenes (solid solution of jadeite, augite and aegirine, with chemical formula $(Ca,Na)(Mg,Al)Si_2O_6$) should be exploited for application of elastic geothermobarometry. However, he application of this methodology to omphacites requires the accurate knowledge of their elastic behaviour and at least a detailed Raman spectroscopy calibration as a function of external compression.

For this purpose, we have studied ordered and disordered omphacite crystals (belonging to Münchberg Massif, Bavaria, Germany [2]) by in situ high-pressure Raman spectroscopy and the results have been compared against calculated Raman spectra obtained by performing ab initio simulations on a completely ordered omphacite. Ab initio simulations have been carried out at variable pressures by means of ab initio hybrid HF (Hartree-Fock)/DFT (Density functional theory) simulations using the CRYSTAL17 software [3] following the protocol developed by [4]. The calculations resulted to be in good agreement with the experimental data. The full set of 60 Raman active modes and their intensities have been calculated at variable pressures and the main Raman peaks have been assigned to specific atomic motions.

Our results readily enabled us to calculate the entrapment pressure of omphacite inclusions still trapped in their host rocks by determining the changes in the Raman shift of the main peaks.

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A comparative study of crystal-fluid interaction phenomena in ABC-6 zeolites group: the case of ERI, OFF and EAB topologies

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The pressure-mediated intrusion of molecules, along with solvated ions, into the nano-cavities of microporous or layered materials is one of the most spectacular routes to promote a mass transfer from fluids to crystalline solids. This phenomenon, observed for example in synthetic and natural zeolites, is now exploited in order to expand their industrial utilization, developing new functional materials and enhancing catalytic performance [1,2]. From a geological perspective, a full understanding of the P-induced crystal-fluid interaction could lead to a re-evaluation of the role played by zeolites as fluid carriers during the early stages of subduction, considering that this class of open-framework silicates can have even up to 20 wt.% H_2O. In this study, we have investigated the crystal-fluid interaction, promoted by pressure, of three different natural zeolites belonging to the ABC-6 group: erionite (ERI framework, 6-membered ring sequence of AABAAC), offretite (OFF, sequence of AAB), and bellbergite (EAB, sequence of AABCCB). The goals of the experiments were twofold: 1) to understand the potential role of erionite as a fluid carrier during subduction, given its status as one of the alteration minerals in oceanic floor basalts, and 2) to compare the mechanisms used by structurally similar frameworks in accommodating bulk compression and adsorbing new molecules. Synchrotron XRD experiments were conducted to investigate erionite, offretite, and bellbergite single crystals, using a diamond anvil cell and both potentially penetrating and non-penetrating P-transmitting fluids. The latter were used as a benchmark for evaluating crystal-fluid interaction, as the adsorption of new molecules decreases the bulk compressibility due to the "pillar" effect played by guest species in structural voids [1]. The results showed that erionite experiences the highest adsorption magnitude among the three zeolites. Furthermore, the occurrence and magnitude of the crystal-fluid interaction phenomena were found to be strongly governed by the H_2O content of the hydrous P-transmitting fluids used for the experiments. Ne atoms were observed to penetrate into the offretite framework, making weak Van der Waals interactions with the extra-framework population. Natural bellbergite was found to be almost impenetrable for guest molecules from the P-transmitting fluids, highlighting the key role played by "secondary factors", such as the extra-framework content of the mineral, in crystal-fluid interaction phenomena.

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The oxidation state of peridotite mantle xenoliths from Tallante (Betic Cordillera, Spain) coupled with oxygen isotopes: implication for the oxidizing role of the subducted crust

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The determination of the oxidation state of peridotite mantle xenoliths allows modeling the volatile speciation within the C-O-H system and helps estimating the oxidizing role played by subduction-driven metasomatic fluids. Recent measurements of the oxygen isotopes (i.e., $^{18}O/^{16}O$ ratios) in rock-forming minerals from mantle xenoliths provide evidence for recycling of the continental crustal into the deep mantle [1]. However, no data exists that couple the oxygen fugacity (fo_2) of mantle rocks through the determination of the $Fe^{3+}/\Sigma Fe$ in coexisting spinels with the $^{18}O/^{16}O$ ratios from the same upper mantle assemblages.

In this study, we investigated the $Fe^{3+}/\Sigma Fe$ of coexisting spinel (spl), clinopyroxene (cpx) and orthopyroxene (opx) from four rare peridotite (lherzolite) xenoliths from Tallante (Betic Cordillera, Spain) within a post-collisional tectonic setting. The pressures and temperatures of equilibrium of these rocks are 0.7-0.9 GPa and 830-1000°C. The petrography and geochemistry of these rock samples have been widely studied to the present [2,3] and the results have been interpreted as representative of the interaction between mantle and crustal-derived Si-rich fluids.

Measurements of the $Fe^{3+}/\Sigma Fe$ in spl, cpx and opx single crystals were performed by in situ synchrotron Mössbauer spectroscopy at ID 18 beamline of the European Synchrotron Radiation Facility (Grenoble, France) with a 6 x 15 μm^2 focused beam. The chemical composition of the same crystals was analyzed by scanning electron microscopy.

The resulting $Fe^{3+}/\Sigma Fe$ of spinel varies between 10 to 14%, which is lower than what generally reported for spinel-peridotites (up to about 40%). Interestingly, in peridotite samples that show-textural and geochemical evidence of interaction with a rhyolitic melt, the $Fe^{3+}/\Sigma Fe$ of opx varies between the matrix and the metasomatized portion from 3% (e.g., in agreement with literature data) to 8%, respectively. The $\log fo_2$ was calculated by using the available oxythermobarometry [4] at the equilibration P of 0.8 GPa and T of 1000°C and ranges from -1.80 to -0.68 as normalized to the fayalite-magnetite-quartz reference buffer.

Our results of both $Fe^{3+}/\Sigma Fe$ and $\log fo_2$ were coupled with the $\delta^{18}O$ available for the same minerals of the studied peridotite samples and, interestingly, they show a positive correlation in the case of spinel, opx and cpx, while show an opposite trend for olivine that can be preliminarily explained in terms of preferential $^{18}O/^{16}O$ partitioning.

These data combined with thermodynamic modeling of the C-O-H fluid speciation at the given P, T and fo_2 can be taken as first evidence of the oxidizing role of CO_2-bearing Si-rich fluids that formed from the subducted continental crust deep in the mantle.

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Nitrogen solubility in silicate melt under controlled hydrogen and oxygen fugacity

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Nitrogen is an important volatile element when it comes to habitability because of its omnipresence both in our atmosphere and in the molecules that form the basis of life. Studies are multiplying, whether to trace the origin of terrestrial nitrogen, identify Earth's main reservoirs, or define N-exchange between the different reservoirs. Our work seeks to address these last two points. We tackle nitrogen speciation and solubility in silicate melts under magmatic conditions, in order to model the exchange between a silicate melt and a fluid phase at equilibrium via degassing/solubilization phenomena.
The two main parameters highlighted by most studies controlling nitrogen solubilization in silicates melts are oxygen and nitrogen fugacity (fO_2, fN_2). Three main nitrogen species have been described in silicate melts: N^{3-} and NH_3 dominant under reduced conditions (i.e. 2 in more oxidized melts).
Here we present our latest results on the study of nitrogen in silicate melts. We will discuss the effect of the fH_2 parameter. We will present results of double-capsule experiments using piston cylinders at high-pressure (10 kbar). We will also present results at low pressure (~250 bar), i.e. magma ocean like conditions, on the solubilization of nitrogen in the C-H-O-N-S system. These data will be compared with the results of other studies, and tested against pre-existing solubility models [1,2].
For low pressure data, both models predict different results but close to the measured values. For high pressure data, both models tend to underestimate the measured values as the fH_2 and temperature values become higher. This call for a formulation of new nitrogen solubility model considering the fH_2 parameter.

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The oxidation state of titanium in silicate melts

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Titanium occurs exclusively as Ti^{4+} in most natural terrestrial materials, however, under reduced conditions it may also occur as Ti^{3+}. For example, Ti^{3+} is found in armalcolite in high-Ti Lunar basalts and in both hibonite and fassaite in chondritic meteorites. The proportion of Ti as Ti^{3+} in these minerals is a potential indicator of the oxygen fugacity

(fO_2) of the process during which they formed. However, predicting Ti^{3+}/Ti^{4+} in the system from which these minerals may have crystallised is experimentally challenging because of the extremely reduced conditions. The oxidation states of Ti in five synthetic silicate glass compositions, quenched from melts equilibrated at 1400°C, atmospheric pressure, and fO_2s in log units relative to the fayalite-magnetite-quartz (FMQ) buffer from FMQ+3.3 to FMQ-10.2 (from +6.6 to -6.9 log units relative to iron-wüstite, IW), were investigated by Ti K-edge X-ray absorption near edge structure (XANES) spectroscopy. All spectra could be well fit by a linear combination of the spectra recorded from the most oxidised and reduced samples of the same composition, indicating that the samples only contain two Ti species. Ti^{3+}/Ti_{Tot} (where $Ti_{Tot} = Ti^{3+} + Ti^{4+}$) = 0 for the most oxidised samples but is unknown for the most reduced. Thus, the linear combination fit results were used in a regression model in which Ti^{3+}/Ti_{Tot} of the reduced end-member was varied to give Ti^{3+}/Ti_{Tot} values of the other samples that best fit the thermodynamically expected dependence of Ti^{3+}/Ti_{Tot} on fO_2. The most reduced samples were found to have $Ti^{3+}/Ti_{Tot} \sim 0.6$. The resulting modified equilibrium constants of the Ti oxidation reaction, logK', are linearly correlated with the optical basicity parameterisation of melt composition, such that as optical basicity increases, Ti^{3+}/Ti increases, at constant fO_2. This correlation allows Ti^{3+}/Ti_{Tot} to be predicted for other compositions and, assuming that the temperature dependence of Ti^{3+}/Ti^{4+} is parallel to FMQ, a general equation relating Ti^{3+}/Ti^{4+} to fO_2 was obtained. This equation was used to predict Ti^{3+}/Ti_{Tot} as a function of fO_2 for high-Ti Mare basalt, chondrule (CV and CM), and calcium aluminium inclusion (CAI; Type A and B) compositions.

Experimental insight on the carbonaceous matter stability during subduction

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Thermodynamic, experimental and field studies have suggested that organic compounds can be stable, and even dominate over inorganic carbon species, in subduction zones up to high pressure (HP; 0.5-6 GPa) and high temperature (HT; 600-1000°C). Slab-hosted organics can be formed either by carbonate destabilization during subduction or inherited from hydrothermal circulation at mid-ocean ridges. Of widespread occurrence in these settings are polycyclic aromatic hydrocarbons (PAHs) and/or genetically-related condensed carbonaceous matter, all spatially related to serpentine, and whose behavior during subduction is still unknown. To assess the fate of these organic compounds during subduction, HP-HT experiments using either a piston-cylinder device or a multi-anvil press have been run at 500-1000°C and 3-7 GPa. Different anhydrous starting solids were tested, including either synthetic PAHs alone, with (1-hydroxypyrene, 1-pyrenebutyric acid) or without (pyrene) oxygen-bearing functional groups, or a mix of pyrene and powdered natural antigorite.

Our results show that the maturation of PAHs at HP-HT leads to the formation of graphitic carbon preserving a high structural disorder, possibly related to the persistence of O and H atoms in its network, far from pure graphite structure. We also observe the formation of aqueous fluids during oxygen-bearing PAHs experiments, suggesting water release from organics at HP-HT. Mix experiments involving pyrene and antigorite show various assemblages depending on experimental redox conditions, with oxidizing conditions stabilizing magnesite-enstatite-quartz over olivine-enstatite-graphitic carbon under reducing conditions. Our results highlight the poor reactivity of solid organic carbon towards serpentine-derived aqueous fluids under reduced conditions suggesting that the latter might facilitate the cycling of organic compounds to the deep mantle.

Investigating C-O-H/S bearing systems at mantle pressures: challenges and opportunities

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Even though they have a low abundance, volatile elements, such as carbon, sulfur, hydrogen and halogens, have long been recognized as one of the key controlling factors of processes occurring in the Earth's mantle [e.g. 1]. For example, melting phase relations, as well as rheology of deep mantle rocks have been shown to be sensitive to the presence of C-O-H-S liquids [e.g. 2]. Due to the incompatibility of volatile species with most deep mantle minerals (lithosphere to the mantle transition zone) and their tendency to concentrate in a liquid, it is important to identify, control and quantify the effects of volatiles in experiments. Conducting experiments at high pressures and high temperatures, while maintaining closed-system behavior, is one of the key challenges of experimental geosciences. Problems arise from the difficulty of finding sample containers that can withstand the conditions of Earth's interior and that are also inert and impermeable to the elements of interest for long enough to reach chemical equilibrium. The speciation of the elements as a function of oxygen fugacity adds another layer of complexity that needs to be addressed to obtain phase assemblages that are representative of the redox state of Earth's mantle [3]. We will present results related to the effect of sulfide composition on the melting of magmatic sulfides and the migration of sulfide liquids at conditions relevant for the lunar mantle cumulates, Earth's lithospheric mantle and transition zone. In another example, we will propound our recent findings on diamond formation from reduced C-O-H fluids in eclogites and peridotites. Lastly, we will discuss the challenges of ground truthing the possibility of isochemical precipitation of graphite/diamond from C-O-H fluids [4] at conditions of the lithospheric mantle with high-pressure experiments.

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Exotic accessory minerals within supra-subduction mantle metasomatic domains

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The petrographic and mineralogical investigation of ultramafic xenoliths is fundamental for our understanding of the nature and evolution of the upper mantle. These xenoliths are commonly brought to surface by the eruption of alkaline basic magmas in intraplate settings. On the contrary, in convergent settings, their occurrence is rare and usually associated with post-collisional anorogenic volcanism, being of paramount importance since they represent the supra-subduction mantle sources. A particular case is represented by the ultramafic xenolith occurrence in the Betic Cordillera of southern Spain, where decimetre-sized metasomatised mantle xenoliths (lherzolites and harzburgites) were brought to the surface by the eruption of post-orogenic Na-alkaline basalts of the Cabezo Negro de Tallante volcano. Interestingly, a few of them are also crossed by felsic veins and veinlets which have been interpreted as the interaction of crustal-derived melts released in the mantle wedge and peridotite during the subduction [1,2]. Petrographic and mineral chemistry analyses show that these veins and veinlets are mainly made up of plagioclase, orthopyroxene and quartz, or by phlogopite/amphibole, diorite and gabbronorite. In centimetric veins the parageneses include sporadic pargasite amphibole, whereas the network (apophysis) of millimetric veinlets contain a large variety of accessory minerals such as amphibole, phlogopite, apatite, zircon, rutile, and peculiar mineral phases pertaining to the apatite and monazite-huttonite/thorite solid solutions. Preliminary investigation with SEM and EMPA revealed that the compositional range of huttonite/thorite is SiO_2 15-18 wt.%, ThO_2 69-85 wt.%, P_2O_5 2-5 wt.%, La_2O_3 0-3 wt.%, Ce_2O_3 2-6 wt.%. Apatite contains Cl up 3 wt.%. The rutile compositional data indicate that this mineral dominates the budget of Ti (TiO_2 80-100 wt.%) and Nb (Nb_2O_5 5-13 wt.%). Further major and trace elements analyses will be performed to better constrain the composition of these mineral phases. These xenoliths will offer valuable information about the nature and composition of the metasomatic agents in subduction-related mantle sections, as well as the element redistribution in the metasomatic parageneses through the interaction with the mantle wedge. This is of great importance because they represent the unique (or very rare) direct explanation for the observed geochemical signature of orogenic magmas.

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Relationship between plagioclase shape, size and density during the cooling of a basaltic andesite under various pre-treatment conditions

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Experimental studies of dynamic crystallization are important to better understand the different parameters (cooling rates, temperature, pressure) leading to the different terrestrial or extra-terrestrial rock textures. In most studies, the starting material (synthetic or natural) is preheated over the liquidus to ensure a homogeneous melt [1]. However, some studies have shown the impact of relic crystals on the texture and density of newly formed crystals and crystal overgrowths [2-4].

In this project we conducted a series of experiments at 1 atm to determine the nucleation and growth rates of plagioclase as a function of the initial thermal treatment above the liquidus as well as the presence or absence of plagioclase seeds in the starting material. Experiments were conducted on an anhydrous natural basaltic andesite from Osorno volcano (Central Southern Volcanic Zone, Chile) under NiNiO oxygen fugacity conditions (buffered with a CO-CO_2 gaz flow). Three series of cooling-driven experiments were conducted and quenched at 1100-1165°C: (A) initial equilibration at 1190°C, ~10°C above the for 24h followed by different cooling rates (1°C/h, 3°C/h, 9°C/h); (B) Initial equilibration at 30°C to 50°C above the liquidus followed by a cooling rate of 1°C/h; (C) initial heating at 1450°C followed by a 1°C/h cooling rate. The series (A) is supposed to retain a certain number of germs from the starting material. The growth and nucleation rates of plagioclase have been determined by batch method (image analyses) and maximum size (lmax). The results show a great variability of texture ranging from few large skeletal crystals to abundant, small, tabular/bladed crystals in 2D sections. The degree of superheating and the presence or absence of an initial dwell time near the liquidus modify the presence of plagioclase seeds (>70 An mol%) as well as the size and texture of new plagioclase for which nucleation is delayed by overheating. We also observe a large variability of plagioclase shape in a single sample for each degree of undercooling that we tested.

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The glass transition of amorphous calcium-magnesium carbonate as a function of water content

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Amorphous calcium-carbonate (ACC) has recently gained attention due to its critical role in biomineralization and in the formation of hard tissue, as well as applications in pharmaceutical products. Carbonate melts are also gaining significance in the evaluation of the evolution of planetary interiors. Amorphous carbonates are apparently unstable at temperatures near the glass transition and thus have been inaccessible to scanning calorimetry until very recently. Fast Scanning Differential Scanning Calorimetry (FDSC) provides significantly higher heating and cooling rates than conventional DSC. The FDSC technique permits to investigate relaxational processes inapproachable to conventional DSC by suppressing phase transitions (e.g., crystallization, unmixing, vesiculation). We applied FDSC using a *Mettler Toledo Flash-DSC 2+* to study the glass transition of amorphous calcium-magnesium carbonate (ACMC) with different water contents. We used ACMC in which Ca ions are partly substituted by Mg ions to obtain an enhanced stability under ambient conditions. The ACMC standard material ($Ca_{0.95}Mg_{0.05}CO_3 \cdot 0.5H_2O$) was synthesized by precipitating from a $MgCl_2$-$NaHCO_3$ solution. We have recently demonstrated that FDSC heating curves of anhydrous ACMC indeed reveal an endothermic signal that is related to a transition from a non-ergodic state (i.e., glass) to an ergodic state (supercooled liquid) followed by crystallization (exothermic) towards higher temperatures. This relative stability of amorphous carbonates vs. their tendency to crystallize have substantial implications for biomineralization and for pharmaceutical applications. ACC and ACMC so synthesized, are hydrous phases and thus provide an opportunity to study the effect of water content on the glass transition and crystallization dynamics of carbonate glass. We held ACMC at 110°C in air for 3 weeks, to inhibit water adsorption. ACMC-110 was proved to maintain its amorphous structure after heat treatment and was ongoing stable under laboratory conditions. The typical heating program to study the glass transition and crystallization of ACMC with different water contents consisted of an initial isothermal segment at temperatures of 110, 200, 225, and 250°C for 10 min to obtain ACMC with different water contents as a function of annealing temperature. This was followed by four heating-cooling cycles at rates of 500, 1000, 1500, and 2000°C/s up to 500°C. The water contents of variably dried samples have been quantified by TGA and using an elemental analyzer. Glass transition temperatures (T_g) were determined after Richardson & Savill [1] and corrected for the effect of the heating rate. Our results indicate that T_g decreases from 376°C for anhydrous ACMC to 201°C for ACMC-110. A Gordon Taylor model has been applied to describe the compositional dependence of T_g in the ACMC-H_2O system. The presented results on changes in the glass transition temperature of ACMC caused by different water contents have implications for the overall stability of the amorphous state as it occurs in nature.

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Novel experimental methods to study hydrogen diffusion in glasses and minerals at low temperatures

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Diffusion of fast-diffusing elements such as H in minerals and glasses at relatively low temperatures (e.g., < 600°C) are finding use in an increasing number of areas ranging from serpentinization on the ocean floor, seafloor weathering and alteration, and applications in Archaeometry. These data find applications in various Material Science problems as well. However, quantification of diffusion rates through direct measurements has been a challenge, and extrapolations of high-temperature data were necessary.

We present two novel methods, which make it possible to study diffusion at low temperatures in both, minerals, and glasses. Method A combines the production of thin-film diffusion couples by Pulsed Laser Deposition (PLD) with diffusion experiments followed by Nuclear Resonance Reaction Analysis (NRRA) and numerical modeling. This method was successfully applied to silicate glasses. The polished surface of an anhydrous glass substrate was coated with a layer of the same glass composition that had been hydrated with a known amount of H in a previous step. Diffusion of H from the hydrous thin film into the dry glass substrate resulted in nanoscale diffusion profiles that are resolvable using NRRA and from which diffusion rates could be extracted using numerical modeling. Method B describes an alternative route that uses ion implantation to create a concentration gradient instead of using the thin film technique. This method has been used for clinopyroxene and it is especially valuable for materials that respond only weakly to ablation by a laser and/or that should be crystalline from the beginning. Our results highlight the ability to verify where extrapolation may be permitted (e.g., the clinopyroxene example in our study) and where there is a need to characterize diffusion rates and mechanisms through direct experiments at low temperatures (e.g., where structural transformations such as glass transition occur in the temperature range of interest).

Experimental constraints on the influence of major element activities and coupled substitutions on Li diffusion in zircon

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Diffusion of Li in zircon has gained considerable attention over the past few years, predominantly due to its consequences for using Li either to fingerprint magmatic sources or as a diffusion chronometer [1-7]. Recent studies have shown that Li diffusion in zircon occurs by at least two mechanisms, which are associated with coupled substitutions (primarily with Y and REE) and diffusion coefficients differing by orders of magnitude. With the aim of better understanding and further quantifying multi-mode Li diffusion in zircon, we have recently begun a series of experiments in which both major element activities and tetravalent cations available for coupled substitution with Li are carefully controlled. All experiments thus far were conducted within the SiO_2-ZrO_2-Li_2O±Al_2O_3 system and were designed such that all diffusion occurred parallel to the c-axis in zircon. In experiments in which no excess trivalent cation is available, both a Li-in diffusion profile and a complimentary H-out diffusion profile are observed. The Li and H profiles exhibit reflectional symmetry and complex shapes, characterized by an initial flat region, followed by a relatively steep gradient and then by a final plateau. The high-quality polish of the zircon was maintained throughout the diffusion anneal, which rules out the possibility of a surface reaction and or/recrystallization. Nonetheless, a transmission electron microscope image was taken from this sample within ~2 microns of the polished diffusion interface, which confirms that the zircon structure was not compromised. Although these profiles cannot be fit using standard diffusion models, they can be well fit using a simple numerical multi-site diffusion model, in which Li is assumed to occupy two sites within zircon (e.g., possibly the octahedral zirconium site and an interstitial site). For experiments in which Al is available to substitute with Li, the surface concentration is considerable higher and results in Li diffusion that is both clearly coupled with Al and exhibits a diffusion coefficient that is more than 10 orders of magnitude lower than the Al-free experiments. Diffusion of Li in zircon appears to be faster when silica activity is lower, but more experiments are needed in order to fully clarify this trend.

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Acoustic wave velocities in Mars' mantle minerals

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With the successful landing of a seismometer (SEIS) at the surface of Mars (Mars InSight mission), the interior structure of the red planet is now better constrained. However, these advances raise further questions as mineralogical models of the interior of Mars are debated.

Mineral physics experiments conducted at high temperature and pressure (HT/HP) are essential to accurately measure the physical properties of the materials that potentially constitute the Martian mantle. These properties, for example the thermoelastic parameters of possible mantle mineral phases, are needed to interpret the seismic data and construct accurate models of mineralogical composition and structure of the martian upper mantle. The inversion of seismic and geodetic data depends on density, seismic velocities and rheology, properties themselves related to the presence of mineral phases at equilibrium, liquidus and solidus curves, equations of state, thermoelastic and viscoelastic properties of the constituent materials at Martian P, T conditions.

We present here results on the elastic properties measured in representative minerals from Mars' mantle. The experiments were carried out on synthetic aggregates of pyroxenes (Fe/(Fe+Mg) = 0.25) under HP-HT (from room PT conditions up to 12 GPa and 1200°C) in a large volume press on a synchrotron light line (APS, Chicago, USA). Equations of state and sound wave velocities were determined by coupled synchrotron X-ray diffraction and ultrasonic interferometry. Implications for the mineralogical composition of the upper mantle of Mars will be discussed.

Metasomatism of mantle rocks via interaction with granitic melt: reaction experiments at 1.5-2.9 GPa

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Subduction of continental lithosphere at mantle depth allows elements transfer from the crust to the mantle via melts and fluids. Mantle sequences of Granulitgebirge (Bohemian Massif) record the interaction with crustal melts in a subduction environment. Investigations on melt inclusions in garnet from eclogite lenses embedded in mantle peridotites documented the granitic composition of infiltrating melt and the conditions of metasomatism at about 1000°C and 2.2 GPa [1]. However, the effect of mantle metasomatism via interaction with granitic melts is still poorly known mostly due to the scarcity of experimental data. We performed melt-rock reaction experiments to define the role of crustal melt-mantle interaction in generating garnet-bearing rocks at the conditions at which metasomatism took place in the Granulitgebirge.

Reaction experiments were carried out using a piston cylinder apparatus at 1.5, 2.2 and 2.9 GPa and equilibrated at 1100°C, after an initial stage at 1300°C for 1 hour. Starting materials are homogeneous mixtures of synthetic glass with the same composition of the granitic melt (SiO_2 = 70.95 wt.%, Al_2O_3 = 16.84 wt.%, Na_2O = 5.43 wt.%, K_2O = 5.06 wt.%) measured in the inclusions in the Granulitgebirge eclogites and two mantle protoliths: a fertile lherzolite pre-synthesized starting from a gel and a pyroxenite made by clinopyroxene and Al-rich spinel separated from a mantle mafic rock (bulk X_{Mg} = 0.74). Initial melt:rock weight proportion is 1:9, in order to simulate a rock-dominated metasomatic reaction

The reaction between lherzolite and anhydrous granitic melt at 2.2 GPa results in melt consumption and crystallization of orthopyroxene-rich garnet-bearing websterite showing trace of phlogopite. At 1.5 GPa the same reaction does not include garnet and produce opx-rich websterite with few amount of phlogopite + pargasitic amphibole. Metasomatized peridotites have clinopyroxenes with higher Al and Na and lower Cr contents and garnet with higher grossular with respect the pristine mantle phases. Experimental products after the reaction between granitic melt and spinel clinopyroxenite are garnet and clinopyroxene coexisting with an andesitic residual melt. Coarse poikilitic grain of garnet developed at 1.5 GPa suggesting high crystallization rate likely promoted by high amount of reacted melt. Modal abundance and grossular content of garnet resulting from the reaction increase with pressure. Garnets have composition similar to those in Granulitgebirge eclogites. On contrary, clinopyroxenes crystallized by reacted melt are Al-rich diopside with very low jadeite content (Jd < 0.14), much lower than clinopyroxene in eclogites. Experimental results suggest, therefore, that Granulitgebirge eclogites might originate from the interaction between granitic melts and a pristine mafic rock.

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Challenges and perspectives in experimental studies of high-temperature ore deposits

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In contrast to common rock-forming processes in magmatic and magmatic-hydrothermal systems, selective mineralization and concentration of metal as an ore deposit is complex, episodic and rare. Enrichment in the metal of interest must be several orders of magnitude relative to its content in the source or in the host rocks and the accumulation of metal must occur in a limited volume, which is however large enough to classify the mineralization as economically valuable. Often, ore formation is a function of many consequent processes occurring not only in space but also in time as well as across different geological systems and conditions. This requires efficient transport of the metal and hence, availability of transport agents, condition gradients and mineralization traps.

These complexities obviously challenge the experimental and analytical investigation of ore formation processes. The difficulties are imposed by technical and analytical limitations as well as by conceptual and implementation approaches. The experimentalists should be able not only to simulate specific P-T-fO_2 conditions but also to create and control physical and chemical gradients in space and time, and to preserve the system of interest for further analysis. The experimental techniques must account for the appropriate proportion of metal and transport agent as well as for the kinetic aspects of equilibration process. Hence, the choice of the reliable experimental method is defined not only by technical characteristics of the equipment but also by the conceptual formulation of the simulated process. It, in turn, has crucial consequences for the interpretation of the results and implications for natural systems (e.g., upscaling in space and time).

The multiscale nature of ore-forming processes requires experimental methods either with step-wise equilibrium approaches or with gradient-imposed kinetically-controlled techniques or with in-situ analytical determinations. All these methods have their own advantages and disadvantages and, in some cases, a combination of methods provides the best result. The experimental approach often relies on the analytical technique available for the analysis of the experimental products but the analytical methods can be also adapted for the purposes of experimental research.

Since experiments are challenged by numerous variables imposed by conditions, compositions and related technical obstacles, a simple “cook-and-look” approach can be very time consuming and non-effective. In order to set up the most appropriate and reliable experimental method and to minimize the number of reconnaissance attempts, a preliminary modeling of the system behavior in a set of conditions/composition is very useful. The development in computational techniques and facilities, including multiparameter optimization, mechano-chemical coupling and artificial intelligence, allows for prediction of favorable conditions for future experiments.

Hydrogen in an early magma ocean: implications for Earth's core composition

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Hydrogen is the most abundant element in the universe, making it one of the most plausible light elements of the Earth's core. However, by compiling the existing data we found that the hydrogen content of the core varies from about 50 ppm to very high content of about 1 wt.% (10^4 ppm). Such differences on the hydrogen content of the core have important implications not only on the physical and chemical properties of the Earth's core, but also on the sources of planetary volatiles and the timing at which they were accreted to growing planets.

Here we present new experiments simulating the earliest conditions of planet accretion by performing molten metal - silicate liquid partitioning experiments between 1 and 5 GPa, and use them to determine an accurate picture of the behaviour of hydrogen during terrestrial core formation. The originality of our approach is to use concentrations of volatile elements (C, H, and S) that are close to those supposed to be during the accretion of the Earth and segregation of its core. The results show that the metal-silicate partition coefficients of hydrogen are within 5×10^{-3} – 9.3×10^{-1} for pressures < 5 GPa, consistent with the experimental studies at similar conditions [e.g. 1,2]. These coefficients are mainly dependent on the chemical composition of the metallic phase, but consistent with interaction parameters of H with C, Si and S (being the lowest for C-rich alloys and the highest for S-rich phases). The final stages of Earth's core formation that involve high pressures and high temperatures conditions, hydrogen seems to be siderophile with > 20.

By taking into account all parameters that affect the partition of hydrogen to the core: contents of hydrogen available during core formation and especially the interactions of the major light elements of the core with hydrogen (C, Si, S and O) we found that the H content of the core is in the range of 150-530 ppm. This range of concentrations is consistent with the low content of water on bulk Earth and also with the terrestrial volatility trend as determined from geochemical models.

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The effect of mantle and mush assimilation on the crystallization path of MORB-type melts: IHPV and piston cylinder experiments at 200 and 250 MPa

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Oceanic crust accretion processes and magma reservoir models have been gradually shifting over the last decades from melt-filled to mush-filled reservoirs, and from (fractional) crystallization-dominated differentiation towards processes that increasingly involve an assimilated component of either mantle or magmatic origin [1,2]. These models result in particular from both textural and geochemical observations of drilled magmatic sections of oceanic crust and ophiolites. Comparison between the minerals' major and trace element compositions and expected compositions after differentiation of MORB-type melts by fractional crystallization show systematic discrepancies (e.g., high-Mg# high-Ti Cpx). However, the origin of these discrepancies is yet to be fully established. We propose here an experimental study of the two types of processes suspected to impact melt differentiation, i.e. crystallization and assimilation. The design of the experiments relies on the magmatic system identified in the Atlantis Bank Oceanic Core Complex, where recovered lithologies have been extensively studied and where both types of processes have been identified [3].

We conducted equilibrium and fractional crystallization experiments of a primitive MORB-type melt on an IHPV at 200 MPa (IfM Hannover, Germany). Two series of crystallization experiments were conducted for both equilibrium and fractional crystallization experiments at controlled fO2 = FMQ, with either ~0.2 wt.% or 1.5 wt.% initial H2O contents. Six temperature steps between 1200 and 1030°C have been investigated. Associated crystallized assemblages range from troctolitic to typical olivine gabbro and gabbro-type, with the onset of oxide crystallization in 3 of the four series of crystallization. First-order comparison with natural samples and thermodynamic models shows differences, for example in the minerals' composition or the expected melt fractions at various crystallization steps. The second set of experiments consists of the crystallization of the same starting MORB-type melt, this time mixed with either a peridotite component or a cumulate component representative of a primitive olivine gabbro mush. Experiments were conducted on a piston-cylinder at 250 MPa, with starting materials equilibrated at fO_2 = FMQ (LMV Clermont-Ferrand, France). The idea is to test the effect of the potential assimilation of these components (at two different melt mass-assimilated mass ratios) on the crystallization path of the melt. The results eventually help us evaluate the impact on the crystallization assemblages and minerals' composition of the series by comparison between the two series of experiments, and test the hypothesis that assimilation plays a key role in melt differentiation in oceanic reservoirs.

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Solubility of H_2 in primitive melts as determined by experiments

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New data from telescopes such as JWST will allow us to characterize exoplanet atmospheres. To interpret and contextualize these data, scientists are modeling how solid planets and their atmospheres evolve. However, geochemical models that are applied to exoplanets are based on Earth's chemistry and petrological relationships, many of which are still not well understood. For example, the models needed to interpret exoplanet atmospheric data depend on the solubility of volatile species in molten rock, but studies of reduced volatiles in magma are not common. H_2 is the most abundant species in primary (nebula-derived) planetary atmospheres that may be in direct contact with primitive magma oceans for an extended time [1]. How much H_2 could be ingassed to, or degassed from, a magma ocean is important because this partitioning sets the internal water budget of the planet and can affect future melting behavior and habitability. An increase in mantle H_2 may also lead to more H partitioned into the planet's metallic core.

We present the results of H_2 solubility experiments performed at high and near-ambient pressures. Previous work determined the solubility of H_2 in andesitic and basaltic compositions [2]; we extend this data to primitive and pyrolitic silicate compositions at multiple pressures and temperatures. Preliminary data suggest that H_2 is more soluble than previously suggested at all conditions currently investigated, and that ionic porosity may not be a reliable parameter to use to extrapolate H2 solubility to more primitive magma ocean compositions.

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Partitioning of elastic strain in polycrystalline materials at high pressures and seismic frequencies

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In Earth's mantle, seismic waves propagate by elastic deformation. The minerals that form the rocks of the mantle, however, have different and anisotropic elastic properties. As a result, the strain imposed by a seismic wave is partitioned between mineral grains with different elastic properties and orientations. Although the effect of strain and stress partitioning is often evaded by calculating bounds on the elastic behavior of a polymineralic rock, these bounds may differ by several percent and impede unique interpretations of seismic observations [1]. This is of particular importance for Earth's lower mantle where seismic tomography suggests variations in wave speeds of only a few percent. Inverting seismic data of the lower mantle into information about its composition and dynamics therefore requires improved models for the elastic behavior of mantle rocks.

To observe and analyze strain partitioning at high pressures and at frequencies of seismic waves, we performed cyclic loading experiments on binary powder mixtures of reference materials as well as on sintered polycrystals of mantle minerals. To subject samples to strain oscillations at seismic frequencies, a diamond anvil cell was attached to a piezo-actuator that generates sinusoidal compression cycles [2]. During cyclic loading, the strain state of the sample inside the diamond anvil cell was probed by time-resolved X-ray diffraction in radial diffraction geometry. All experiments were performed at the Extreme Conditions Beamline at PETRA III/DESY. The time series of diffraction patterns were analyzed for strain along different directions relative to the compression axis of the diamond anvil cell. By converting elastic strains into stresses, we evaluate the partitioning of stress and strain between phases and along different crystallographic directions.

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Assessment of total CO_2 content and entrapment conditions of primary mantle melts: high-pressure homogenization of CO_2-rich melt inclusions in a piston-cylinder

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Experimental homogenization of olivine-hosted melt inclusions representative of near-primary basic magmas is a powerful approach to investigate the nature of their source regions and the melting conditions in Earth’s mantle. There is growing evidence that the total CO_2 contents of olivine-hosted melt inclusions may reach values of the order of a single to several weight percent, especially in intraplate continental basalts. To be able to homogenize melt inclusions with such high CO_2 contents, we developed a new technique to heat melt inclusions at 1300°C under hydrostatic pressures up to 3-4 GPa in a piston cylinder, using thick-walled Au80-Pd20 containers and molten NaCl as the surrounding medium for the inclusion-bearing olivines. We applied this technique to olivine phenocrysts from Bas-Vivarais volcanic province (French Massif Central, Ardèche). These melt inclusions were chosen because of their high CO_2 contents, as indicated by up to 1.9 wt.% dissolved CO_2 in the glass phase and by the presence of bubbles containing large amounts of CO_2. We characterized melt inclusion bubbles by Raman spectrometry and focused ion beam scanning electron microscope (FIB-SEM), and obtained that, in addition to the fluid CO_2, the walls of the bubbles were covered with microcrystals. These microcrystals, mainly carbonates (Mg-calcite, ferromagnesite), represent more than 30% of the bubble volume and contain more than 41% of the total CO_2 of melt inclusion. The homogenization experiments were conducted at pressures of 1.5 to 2.5 GPa, temperatures of 1300°C, and run durations of 30 min. In all the melt inclusions treated at 2.5 GPa-1300°C and half of those treated at 2 GPa-1300°C, we were able to completely homogenize the inclusions, as indicated by the disappearance of the starting bubbles. The total CO_2 contents in melt inclusions were increased to as high as 4.8 wt.% (3.4 wt.% in average). The presence of some bubbles at 2 GPa and their absence at 2.5 GPa suggest that trapping conditions of these CO_2-rich basanitic magmas are between 2 and 2.5 GPa, near mantle source beneath Bas-Vivarais volcanic province. These high CO_2 contents, the highest ever measured in melt inclusions, have direct implications on the eruptive dynamics in particular by driving to highly explosive eruptions. They also imply the presence of a carbon-rich mantle source (> 500 ppm CO_2) beneath French Massif Central.

Experimental development of new oxybarometers based on V-Sc exchange between mafic minerals and hydrous silicate melts

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Redox conditions have a significant impact on phase equilibrium and the physical-chemical behavior of volatiles, such as sulfur, in magmas. Therefore, a better understanding of the initial redox state of magmas and its evolution during magma differentiation may help assess the fertility for associated magmatic-hydrothermal ore deposit genesis and provide new insights into the importance of magmatism and volcanic degassing in the redox evolution of the Earth's upper spheres. However, there are only a few studies on oxybarometric methods calibrated at elevated pressure in the presence of hydrous melts, conditions typical of magma differentiation at convergent plate boundaries.

We conducted experiments in a rapid-quench Molybdenum-Hafnium Carbide pressure vessel apparatus equipped with an in-house-made Shaw membrane for in-situ hydrogen pressure control. It allows the application of continuous hydrogen fugacity steps and thus in turn flexible oxygen fugacity values within the experimental capsule compared to restricted values when solid redox buffers are applied [1]. With this experimental setup, we developed oxybarometers based on the exchange coefficient of V and Sc between mafic minerals and hydrous silicate melts of medium-K basaltic and shoshonitic compositions. These oxybarometers are expected to exhibit reduced dependence on pressure, temperature, and silicate melt composition in comparison to those relying solely on the partition coefficient of V [e.g. 2]. The first set of experiments was performed at constant pressure (200 MPa) and temperature (1030°C), under water-saturated conditions at oxygen fugacity varied from +0.5 to +3.5 log units relative to the FMQ buffer, resembling the relevant range for arc magmatic systems. The exchange coefficient of V and Sc between olivine and silicate melt can be described by the following linear regression equations for medium-K calc-alkaline (Eq.1) and shoshonitic (Eq.2) systems, respectively:

$$logK_{V/Sc}^{Ol/melt} = -1.26 \pm 0.03 - 0.22 \pm 0.02 * \Delta FMQ$$

(Eq.1)

$$logK_{V/Sc}^{Ol/melt} = -1.50 \pm 0.05 - 0.18 \pm 0.04 * \Delta FMQ$$

(Eq.2)

In the case of clinopyroxene, which is more abundant in shoshonitic systems, the exchange coefficient can be defined by using Equation 3 below:

$$\log K_{V/Sc}^{Cpx/melt} = -0.93 \pm 0.08 - 0.13 \pm 0.03 * \Delta FMQ$$

(Eq.3)

These values are consistent with the expected degree of variation in V-partitioning as a function of *f*O_2 based on previous studies. Both the olivine- and clinopyroxene-based oxybarometer can in turn be applied to mafic volcanic rocks with suitable silicate melt inclusions-host mineral pairs to reconstruct the redox history of deep-seated magma reservoirs.

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Exploring quartz inclusions within garnet (QuiG) under high external pressure via in situ Raman spectroscopy

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Quartz inclusions in garnet (QuiG) represent one of the most widespread host-inclusion mineral systems in many metamorphic rocks and they are often used in the framework of elastic geothermobarometry to determine pressure and temperature conditions of rock formation. This method relies on the contrast between the thermal expansion and compressibility of a mineral inclusion and its surrounding host, which leads to a residual pressure in the inclusion (P_{inc}) that may significantly differ from the external pressure [e.g. 1].

We have investigated the stress interaction of natural quartz-in-garnet (QuiG) host-inclusion systems under external pressure by in situ Raman spectroscopy in a diamond-anvil cell at room temperature. A particular challenge is preparing the QuiG samples to fit into the DAC while preserving their natural stress state.

The results confirm that, as predicted by elastic theory, upon pressure increase the garnet host acts as a shield to the softer quartz inclusion. Up to external pressure of 2.5 GPa the evolution of quartz P_{inc} calculated from the Raman data agrees very well with predictions from the equations of state. At higher pressures the pressure dependence of the FWHM of the A_1 207cm^{-1} mode indicates that a quartz inclusion becomes metastable with respect to coesite at an *external* pressure applied to the garnet of ~4.4 GPa, apparently ca. 2 GPa above the pressure of the coesite-quartz equilibrium at room temperature. However, this external pressure corresponds to a measured inclusion pressure P_{inc} ~2.4 GPa, the pressure of the quartz-coesite phase boundary [2]. This suggests that the non-hydrostatic stresses in these quartz inclusions do not significantly shift the mean stress of the quartz-coesite transformation, even though the stresses are sufficiently large to induce measurable splitting of some Raman modes that indicate the symmetry of the quartz inclusion has been reduced.

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Deep recycling of boron through Dense Hydrous Magnesium Silicates

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In the recent years, the role of Dense Hydrous Magnesium Silicates (DHMSs) as geochemical reservoir has been gaining ground, particular for boron (B), which is widely considered the most powerful tracer to understand geological processes involving serpentinized materials. As a matter of fact, the genesis of blue B-bearing diamonds in the lower mantle has been proposed as witness for the deep recycling of serpentinized materials through DHMSs. However, we still do not know if and how much the DHMSs are able to incorporate and transport B to great depth. In this contribution, we attempt to fill this gap providing the results of a pilot experiment aimed to investigate the B content in Phase-A, the first DHMS replacing antigorite along a prograde subduction path in cold thermal setting. By using a Walker-type Multi Anvil module, we synthetize Phase-A at high temperature and ultra-high pressure (700°C and 7.0 GPa) starting from a stoichiometric composition modelled in the MSH system (2 SiO_2 : 7 MgO) and adding 1000 ppm of B as ultrapure boric acid (H_3BO_3) in H_2O plus trace of NH_4OH. We characterize the experimental product with EMPA and single-crystal X-ray diffraction, confirming the crystallization of the Phase-A. By means of LA-ICP-MS analyses, our pilot study indicates that hundreds of ppm of B can be structurally incorporated in the Phase-A, thus pointing to its role as viable B source to depth. Further experiments are required to understand how B can be incorporated within DHMSs in more complex system (i.e., Fe-Al-bearing) and, concurrently, to gather information regarding the B isotope composition of DHMSs. Our result extends the current knowledge of the B cycle thus opening new perspectives to better disclose deep recycle and feeding of geochemical heterogeneities in the Earth’s mantle at geological timescales.

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Mechanisms of zircon crystallization in mafic melts at high temperatures and pressures: insights from an experimental study

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The recent discovery of zircons in mafic or ultramafic systems have provided much information on terrestrial geodynamics (e.g. processes of crustal recycling or extraction of melts from source regions in the mantle), but the high solubility of zircons in mafic melts at high temperatures have also raised the question: How are zircon crystals stable in the presence of melt in such systems? Recent numerical calculations and experimental studies [1,2] indicate that local saturation conditions and available melt volumes are key parameters that control zircon survivability. In this study we have carried out experiments to constrain the roles of temperature and pressure in situations where (a) excess zircon is available in the form of inherited zircon crystals and (b) zircon contents are similar to those in average basaltic melts. In a first series of experiments, 1 atm and $fO_2 \approx$ QFM buffer (CO-CO_2 gas mix), a cooling ramp was imposed from super liquidus conditions, 1250°C, to low crystallization degree conditions, 1150°C, at a rate of 10°C/h. A zircon cube of 1 mm side was suspended in a dry-MORB basaltic glass to simulate the behavior of an inherited zircon crystal in a mafic magma during cooling. The zircon shows clear dissolution and growth textures in the crystal rim, whereas far in the matrix other Zr-bearing phases like baddeleyite, srilankite and Zr-rich ilmenite crystallized. Notably, in these far field regions zircon can crystallize as an interstitial phase. In these cases, the zircon crystallizes under conditions of high Zr concentration due to the high dissolution rate of the initial crystal. To evaluate if zircon can crystallize in mafic magmas without an excess of available Zr, we carried out a second set of experiments where a dry-MORB basaltic glass was doped with 150 ppm of Zr, which is a typical Zr content of a basalt. Gas mixing furnace experiments reveal the crystallization of baddeleyite as the Zr-bearing phase. We studied the effect of pressure on this system by conducting the same experiments in a piston-cylinder apparatus at 15 kbar. In this case, new zircon crystallized in the interstitial melt along with newly formed clinopyroxene. Textural relationships reveal intergrowth textures between cpx and zircon. The experimental results demonstrate how zircon can precipitate in mafic systems under very low zircon saturation conditions in environments where there is a low volume of melt that allows zircon to saturate locally. This process is also facilitated by the crystallization of other phases, like cpx, that do not fractionate Zr (thereby raising the local zircon concentration). This zircon crystallization mechanism explains the wide range of crystallization temperatures displayed by zircons of mafic rocks and the textural evidence where zircon is crystallized at high-temperature conditions (e.g., as inclusions in Ca-rich plagioclase).

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Experiments on unmixing of fluids or carbonate melts in ultramafic lamprophyres

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Liquid immiscibility is known to be important in carbonate-bearing magmatic systems, particularly due to the Oldoinyo Lengai volcano in northern Tanzania, which erupts natrocarbonatite and melilitite magmas. Several experimental studies have delineated a miscibility gap between carbonatite melts with approximately 5-6 wt.% SiO_2 and silicate melts resembling melilitites with around 35 wt.% SiO_2 [1]. Very few igneous rocks are known with SiO_2 contents intermediate between carbonatite and melilitite. However, in high-pressure experiments on melting of peridotite, melt compositions progress continuously from carbonatite close to the solidus to silicate melts with >30 wt.% SiO_2 at higher degrees of melting. Under geothermal conditions of the subcontinental asthenosphere, melts with ≈20 wt.% SiO_2 are more likely to occur than carbonatite melts. If these intermediate melts migrate towards the surface, a miscibility gap must open at lower pressures, but it is not known at which pressure this occurs. Aillikites are carbonate-rich ultramafic lamprophyres that fall consistently in this intermediate SiO_2 range (average 24 wt.%) [2]. These rocks are mica-rich with K_2O > Na_2O; potassic systems have not been studied in experiments on liquid immiscibility. The aillikites occur in parallel fracture systems as discontinuous dykes, with cracks coloured yellow by small-volume deposits from either fluids or low-viscosity carbonate melts [3]. Many are banded with carbonate-rich and carbonate-poor layers that may indicate separation of carbonate-rich and carbonate-poor parts of the magma.

We have conducted experiments at 0.8-1.2 GPa to search for the conditions at which the miscibility gap opens during ascent. These experiments have not found liquid immiscibility, but demonstrate the evolution of a carbonate-rich fluid rather than an immiscible melt, as evidenced by large voids taking up half the capsules. Fluid separated from melt in experiments at 0.8 GPa, 900°C and 1100°C, whereas at 1.2 GPa fluid formed at 900°C but not at 1100°C. This separation of fluids appears to be the source of the deposits in cracks and may explain the opening of the parallel fracture systems. This is approximately the same pressure range as the crystallization conditions of cognate inclusions in the aillikites [2].

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First in-situ single crystal determination of IIa polytype in clinochlore and its relevance in the high-pressure behavior of chlorite

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Chlorite is one of the most important water-bearing phases and its behavior at high pressure conditions has a significant role in the modeling of dehydration processes in subduction zones [1,2] and volatile transfer. Due to its propensity for stacking disorder, finding natural undistorted single crystals of chlorite is difficult, leading to a lack of available accurate data on its high-pressure crystallographic and physical properties.

The adequate sample selection (natural clinochlore, Val d'Ala, Italy) allowed us to assess the stability conditions of a natural clinochlore single-crystal sample (nominally $Mg_5Al_2Si_3O_{10}(OH)_8$), performing a high-pressure in-situ diffraction experiment with high-flux synchrotron radiation up to 20 GPa. Between 8 and 9 GPa, a polytypic phase transition from the IIb- to the IIa-structure occurs, resulting in the stabilization at high pressure of an uncommon chlorite polytype. It corresponds to the highest energy polytipe [3], to date never found in natural chlorite samples. The technically challenging experiment unequivocally allowed the ab-initio experimental structural determination of this high-pressure polymorph, and it confirms predictions of polytypic stability dating back to the 1960s and subsequently widely discussed based on X-ray powder diffraction data [4]. The transition is reversible upon decompression.

Our results offer valuable insights into the high-pressure structural properties of chlorite, and we believe it has far-reaching implications in mineralogy and planetary sciences. We confirm that these phyllosilicates can undergo multiple reversible polytypic phase transitions to compensate and counterbalance important stress states without decomposition or amorphisation. Since phyllosilicates are considered primary candidates among the minerals present in meteorites for transferring volatiles during the accretion of planetary covers, the persistence of their metastable states in a suitable region of P-T-Time space could be a mechanism for the accumulation of volatile components in planetary bodies.

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The high pressure behavior of jamesonite using single crystal synchrotron X-ray diffraction

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Jamesonite ($Pb_4FeSb_6S_{14}$) is a sulfosalt, of a rod-layer structure type (monoclinic symmetry, $P2_1/c$) where Fe atoms in octahedral coordination connect $(Pb_4Sb_6S_{14})_\infty$ rods to layers. Fe coordination octahedra share two opposite edges forming $(FeS_6)_\infty$ rows parallel to *a* axis.

The mineral represents a valuable source of antimony, together with stibnite (Sb_2S_3), a very important metal for industrial development with a wide application in metallurgy and semiconductor fields.

The chemical and structural building units of sulfosalts allow material engineering and designing: band gap can be continuously adjusted from close to 0 eV to more than 2.0 eV, that is, a wide variety of semiconductor applications are possible for this group of minerals. Between them, jamesonite is an intrinsic semiconductor with an optical band gap equal to 0.48 eV.

Jamesonite is usually associated with other sulfides in ore bodies, and the similar floatability of these minerals seriously affects their separation. New strategies are needed, i.e. green flotation and metallurgic technology, to improve the separation efficiency, that are dependent on the physical properties of these minerals.

Some sulfosalts showed interesting pressure (P) induced structural phase transitions, and P may be an important parameter to tune the transport and structural properties of these thermoelectric materials.

In the present study, the crystal structure of jamesonite was investigated at P between 0 and 16.6 GPa by synchrotron single-crystal X-ray diffraction using a diamond anvil cell, collected at the ID-15B beamline at ESRF (Grenoble). Helium was used as a P transmitting medium and a ruby sphere was loaded as a fluorescent P calibrant together with the samples.

The volume (V) - pressure data, collected up to 16.6 GPa, were fitted with a third-order Birch-Murnaghan Equation-of-State (BM-EoS), yielding V0 = 1214 (5) A3, K0 = 35(5) GPa, and K' = 4.4(5); K0 becomes equal to 37.0(9) fitting the data with a second order BM-EoS. The compressibilities of the lattice parameters, up to 16.6 GPa, was studied by fitting the data with a third-order BM-EoS and the following values were found: M0a = 55GPa, M'a = 19, M0b = 129 M'b = 11.0, M0c = 147 and M'c = 10; by using second-order BM-Eos the data were Ma = 90, Mb = 121, Mc = 130 GPa.

The comparison of structural refinements at different P indicates that Fe and Sb do not change their coordination number (CN) over the whole investigated P range: Fe has CN 6 whereas the three Sb polyhedra have CN 5+1. On the other hand, both Pb polyhedra increase their coordination around 12 GPa: Pb1 passes from 6+1 to 7 (with 7 bond lengths lower than 3Å) whereas Pb2 passes from CN 6+2 to 8+1.

The effect of temperature (T) on the baric behavior of jamesonite will be presented by using data collected at different P along three isotherms (room T, 426K and 523K).

Experimental high-pressure behavior of germanium during core-mantle differentiation

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The concentration and isotopic signature of siderophile elements in the Earth's mantle is the consequence of planetary accretion and core-mantle differentiation. These elements were partitioned either between core-forming, iron-rich metallic phases and residual mantle-forming silicate. While the mantle abundances of several siderophile elements (Ni, Co, Cr, Mn, Mo, W, Zn) are resolvable with a single-stage core formation model, the concentration of Ge in the mantle cannot be reproduced by such a scenario. To resolve this discrepancy, several models have been proposed, such as 1) accretion under oxidizing conditions, 2) the significant role of light elements (S, C, Si, O) or 3) a late veneer providing such siderophile elements to the silicate reservoir. However, none of them in isolation can account for the estimated core/mantle concentrations. This is mainly due to the scarcity of germanium partitioning data between metal and silicate at high pressure within variable accretion conditions. Here we performed multi-anvil experiments to constrain the elemental partitioning and isotopic fractionation of germanium between metal and silicate at high pressure (5 - 10 - 15 GPa) and high temperature (1800 - 2000°C). Variable amounts of S and C were added to the starting metal to investigate their influence on germanium partitioning. In addition, a series of experiments has been performed with different Si amounts to probe the role of oxygen fugacity on germanium behavior. Finally, a series of experiments at 1 GPa has been performed to understand the fractionation of Ge isotopes as a function of time. Together with previous experimental metal-silicate partitioning studies at low pressure, we build upon our new partition coefficient dataset to explore the conditions (P - T - X - fO_2) prevailing during the Earth's core-mantle differentiation.

High-pressure and high-temperature equation of state of $CaFe_2O_4$-type aluminous silicates

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Understanding the fate of subducted basaltic crust in the Earth's lower mantle is critical to constrain the mantle dynamics and evolution. $CaFe_2O_4$-type (CF) aluminous silicate is considered to be one of the most abundant minerals in basaltic phase assemblages at pressures above 25 GPa, corresponding to topmost lower mantle depths. The dominant component is $NaAlSiO_4$ but can be substituted by $MgAl_2O_4$, $Fe^{2+}Al_2O_4$ and $Fe^{2+}Fe^{3+}{}_2O_4$, altering its thermodynamic and elastic properties. Understanding the link between the crystal chemistry and physical properties of the CF-type phase is therefore essential to model the density and seismic velocities of subducted basaltic crust in the lower mantle.

Here, we report on the high-pressure and high-temperature equations of state of high-quality CF-type single crystals in the $NaAlSiO_4$, $NaAlSiO_4$-$MgAl_2O_4$, and $NaAlSiO_4$-$MgAl_2O_4$-Fe_3O_4 systems synthesized in a multi-anvil press and investigated using resistively heated diamond anvil cells and synchrotron X-ray diffraction. Diffraction data at room temperature and up to 73 GPa revealed that, out of the samples investigated, the end member $NaAlSiO_4$ is the most compressible, while the Mg-bearing and Fe,Mg-bearing samples have similar compressibility, at least in the low-pressure range. Moreover, $NaAlSiO_4$ has the highest compressional anisotropy, which has maximal value at room pressure and decreases upon compression. Above 25 GPa, the Fe,Mg-bearing sample displayed a slight change in the compression mechanism, which is most evident in the *a* lattice parameter evolution and highlights the onset of a high-spin to low-spin crossover of Fe^{3+} in octahedral coordination, as has been suggested in previous studies. Structural refinements confirmed this hypothesis and show an increase in the compressibility of the Fe^{3+}-bearing octahedra with respect to the Fe-free samples. High-temperature measurements were conducted on the $NaAlSiO_4$ and Fe,Mg-bearing CF-type samples up to 50 GPa and 800K. Mie-Grüneisen-Debye equations of state were used to fit the two pressure-volume-temperature datasets, suggesting that the Grüneisen parameter and thus the volumetric thermal expansion coefficient decrease with increasing Mg and/or Fe substitution. The newly determined thermoelastic parameters of CF-type phases will be used to update existing mineral physical models of Earth's lower mantle, enhancing our understanding of how the density and seismic velocities of basaltic crust are affected by changes in temperature and bulk chemical composition.

Modal and chemical changes related to high-pressure melt-harzburgite reaction: experiments at 1-2 GPa

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Earth's upper mantle mostly consists of peridotites that can evolve over time through events of chemical depletion via partial melting and/or refertilization (i.e. incompatible element addiction) via reactive melt percolation. At sub-ridge oceanic settings, mantle peridotites experience melt extraction and concomitant incompatible element depletion that may be soon followed by refertilization via variable extent of equilibration with transient melts. The interaction between depleted peridotite and MORB-like infiltrating melts is widely recognized to significantly modify the mineralogy and chemistry of residual mantle and, in turn, to affect the isotopic evolution of large portions of lithospheric mantle. However, the extent and mechanism of chemical equilibration between mantle minerals and percolating melts during melt-peridotite reactions are still poorly known. This work aims to provide new experimental constraints by performing piston cylinder experiments of melt-harzburgite interaction at P-T conditions consistent with those of lithosphere-asthenosphere boundary.

Starting material is a mixture of mantle minerals and glass. Harzburgite is modeled as a mix of San Carlos olivine (Fo_{90}) and orthopyroxene separated from a depleted spinel peridotite of Mt. Maggiore (Corsica, France) ophiolitic massif (residual after MORB-producing partial melting; opx

$Ce_N/Yb_N = 0.022$; [1]). Initial reacting melt is a tholeiitic basaltic glass sampled at the Romanche Fracture zone, with a relatively low X_{Mg} (0.60), high alkali (Na_2O = 3.48 wt.%, K_2O = 0.81 wt.%) and enriched-MORB signature ($La_N/Yb_N = 5.49$). Previous crystallization experiments at 1-2 GPa on the selected starting glass have indicated that clinopyroxene is the liquidus phase. We performed experiments starting with basalt:orthopyroxene:olivine proportions of 1:1:1 at 1, 1.5 and 2 GPa and 1250-1350°C. Preliminary results indicate that mantle minerals are chemically modified by the interaction with the basaltic melt. Run products consist of orthopyroxene, olivine and reacted glass, with few grains of new crystallized clinopyroxene at 2 GPa. Rims of partially reabsorbed orthopyroxene acquired high TiO_2 and low Cr_2O_3 with respect to initial orthopyroxene composition. Olivine is homogeneous and chemically modified with respect the San Carlos olivine towards higher CaO and lower NiO contents.

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The distribution of H_2O between melt and clinopyroxene in a hydrous and hydrous-carbonated mantle

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Volatiles, such as H_2O and CO_2, are concentrated in surface environments such as the oceans and the atmosphere but, at the same time, they are continuously recycled into and out of the mantle by geodynamic processes (i.e., subduction and volcanism). In fact, water can be stored in the lattice of nominally anhydrous minerals as H^+ point defects, making the Earth's mantle a potentially major reservoir for H_2O. Even if present in very low amounts (ppm wt), H_2O greatly affects the physico-chemical properties of minerals, for example by lowering their melting temperature and influencing rheological and elastic properties. Therefore, a precise knowledge of the behavior and distribution of H_2O in the mantle is required in order to understand the dynamics and evolution of our planet.

The partitioning of H_2O between nominally anhydrous minerals and coexisting silicate melts ($D_{H2O}^{min/melt}$) is crucial for constraining the storage and behavior of H_2O in the mantle and the melting of mantle rocks, and several studies have investigated the $D_{H2O}^{min/melt}$ in both peridotitic and basaltic systems in the past decades [see e.g., 1 for a review]. However, these previous works principally determined values of $D_{H2O}^{min/melt}$ in purely hydrous-silicic systems, i.e., without considering CO_2, the 2nd most abundant volatile stored in the mantle, which inevitably decreases the activity of H_2O of a system and, possibly, affects its distribution between minerals and fluids/melts. To the best of our knowledge, only one study investigated the partition of H_2O between olivine and melt in the presence of CO_2 at 6.3 GPa and 1400°C [2]. Therefore, the effect of CO_2 on $D_{H2O}^{min/melt}$ remains strikingly unconstrained at mantle conditions and for most mantle minerals, especially those that can host large amounts of H_2O, including clinopyroxene [e.g., 1].

We present here the results of a set of piston cylinder experiments performed at conditions representative of the shallow upper mantle (i.e., 2 GPa, 1200°C) and employing hydrous-carbonated basaltic compositions with variable XCO_2 with the aim of improving our knowledge of $D_{H2O}^{min/melt}$ in a representative mantle composition containing CO_2. Large (>100 µm) and inclusion-free clinopyroxene crystals were crystallized in equilibrium with hydrous-carbonated melts with different volatile contents. Fourier transform infrared (FTIR) spectroscopy analyses were used to measure the H_2O contents of minerals and melts, allowing to determine $D_{H2O}^{min/melt}$. The new data, constraining the evolution of $D_{H2O}^{min/melt}$ in a hydrous-carbonated mantle, will be examined in the context of mantle dynamics and particularly melt productivity and H_2O storage in the deep mantle.

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New C and S metallic reference materials for SIMS analysis

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Major planetary processes occurred when planets were partially to completely molten, i.e., during their magma ocean stages. This primordial stage encompassed the segregation of a metallic core from the silicate magma ocean, setting the initial distributions of volatile elements (H, C, N, and S) between main planetary reservoirs and modifying rocky planets' original volatile element concentrations and isotopic compositions. High-pressure experiments can quantify elemental and isotopic fractionations during core-mantle differentiation. However, no volatile element reference materials are available that are adapted to local micro-analyses by secondary ion mass spectrometry (SIMS) in experimental metals and silicate glasses, respective analogs of core-forming metals and magma oceans.

To address this lack of standards, we synthesized a series of 56 metallic reference materials comprising four FeNi(±Si) compositions ($Fe_{95}Ni_5$, $Fe_{90}Ni_{10}$, $Fe_{80}Ni_{20}$, or $Fe_{80}Ni_{15}Si_5$) with C, N, and S contents varying from 100 ppm to 4 wt.%. These materials were synthesized in the metallurgy laboratory at the Institute Jean Lamour (Nancy, France) by the "melt-spinning" method, which guarantees that the metal alloys are very efficiently quenched at ~10^6 K/sec. The samples are pieces of ~100-µm-thick ribbons with homogeneous Fe, Ni, Si, C, and/or S contents. Carbon and sulfur contents were analyzed at the Service d'Analyse des Roches et Minéraux at the CRPG. Samples' S contents and $d^{34}S$ values were determined by multicollector inductively coupled plasma mass spectrometry (ThermoScientific Neptune). Characterizations of C, N, and S contents and isotopic compositions by isotope ratio mass spectrometry are ongoing.

Preliminary SIMS results do not show any effect of the FeNi(±Si) composition on measurements of C and S contents and isotopic compositions, suggesting that there is no matrix effect on concentration determinations nor on instrumental mass fractionation. These new reference materials will soon become available to the CRPG's SIMS facility for C, N, and S analyses of not only experimental samples, but also terrestrial and extra-terrestrial samples, and will later be shared with other laboratories worldwide.

Isotope fractionation in magma oceans: seeking new constraints on primitive mantle heterogeneity

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Estimates of $^{28}Si/^{30}Si$ and $^{26}Mg/^{24}Mg$ indicate that the Bulk Silicate Earth (BSE) is isotopically heavy compared to chondrites [1,2]. While processes such as core formation and vapor loss have been proposed to explain this, isotopic heterogeneity in the mantle created during crystallization of a magma ocean could contribute to this observation. For example, structures such as BEAMS, bridgmanite-enriched ancient mantle structures, [e.g. 3], could be potential reservoirs for light Si and Mg isotopes. However, the necessary constraints on equilibrium isotope fractionation at the relevant high pressure and temperature conditions to probe this hypothesis are not available. Provisional density functional theory (DFT) calculations exhibit a 0.4‰ $^{28}Si/^{30}Si$ and 0.15‰ $^{26}Mg/^{28}Mg$ ratio between diopside-forsterite at 1300°C and 1 atm. In the near future, our DFT calculations will be performed for other mantle minerals (e.g. bridgmanite & pyrope). We aim to combine DFT calculations with experiments to constrain isotopic fractionation factors between forsterite-diopside-melt. To limit variables that impact isotope fractionation (e.g. Fe, Na, K), the experiments were performed in the basalt analog system anorthite-enstatite-diopside or CMAS. Several bulk compositions have been prepared in this system and near liquidus experiments were carried out at 1 atm. Big (≥ 20 µm) homogeneous crystals of forsterite, anorthite and diopside are successfully grown at 1300°C with run durations of 7 days. Experiment samples will be prepared for micro-drilling and Si/Mg isotope analysis using a double spike method and multi-collector inductively coupled plasma mass spectrometer [e.g. 1,2]. Isotope ratios will be compared with computational work to test the capabilities of heterogeneous mantle reservoirs, such as BEAMS to incorporate ^{28}Si and ^{26}Mg.

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Effect of composition and oxygen fugacity on Fe-Mg interdiffusion in orthopyroxene

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Fe-Mg interdiffusion in orthopyroxene, Opx, has a broad range of interest in petrological studies. The available experimental data for the diffusion coefficient of Fe-Mg, $D_{Fe\text{-}Mg}$, were determined for a limited compositional range that does not always fulfil the needs of the applications, in particular for diffusion chronometry with volcanic rocks, which typically contain Opx with higher ferrosilite contents [e.g., 1,2]. We addressed this issue using a new experimental approach to measure $D_{Fe\text{-}Mg}$ in Opx parallel to the [001] crystallographic axis as a function of oxygen fugacity, fO_2, and for different Al contents, as well as quantitatively constrain the compositional dependence of $D_{\text{Fe-Mg}}$ on the ferrosilite content.

Gem-like quality Opx single crystals were oriented and polished perpendicular to the [001] axis. The chosen compositions show similar Fe contents (Fs_9 - Fs_8) but different Al contents. Diffusion couples were produced by depositing ferrosilite-rich thin films (300 nm to 1 µm thick) on the single crystals by pulsed laser deposition [3]. Diffusion experiments were carried out at atmospheric pressure in CO-CO_2 vertical gas mixing furnaces at temperatures between 950 and 1100°C and at varying fO_2. Thin lamellae (100-400 nm thick) of cross sections of the diffusion couples were prepared by application of a focused Ga ion beam. Chemical zoning was extracted from these cross sections by using a combination of back-scattered electron imaging and energy dispersive X-ray mapping. The extracted diffusion profiles were fitted by least-squares regression to the solution of a 1-D diffusion equation, that accounts for the compositional dependence of the diffusion coefficients and mass balance between film and substrate.

The measured diffusion rates are consistent with earlier determinations for the T and fO_2 range of available experimental data [1]. Our study shows that the compositional dependence of $D_{\text{Fe-Mg}}$ on the ferrosilite content is considerable higher than estimated in previous experimental work [1] and seemingly increases with temperature. For T > 1000°C, the determined compositional dependence is similar to what has been found for olivine [4] and is in agreement with theoretical predictions of Ganguly & Tazzoli obtained from experimental data on Fe-Mg ordering kinetics on the M-site in Opx [2]. Our preliminary data suggests that Fe-Mg diffusion rates are slightly slower (0.1-0.2 log units) when the Al content increases from 0.3 to 0.7 wt.% Al_2O_3. It was not possible to identify any significant effect of fO_2 on $D_{\text{Fe-Mg}}$, confirming previous experimental results [1].

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Trace element diffusion in olivine

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With the advances in analytical capabilities and improved detection limits trace elements in olivine became increasingly important for various applications in petrology. Trace and minor element zoning in olivine in particular was used as diffusion chronometer. Published diffusion coefficients of trace elements that substitute as heterovalent ions into olivine are often controversial (REE) or show a complex behaviour (Li, Al). We have performed a series of experiments to measure diffusion rates of various trace elements in olivine simultaneously and have investigated potential coupling of trace element diffusion. Experiments were performed in CO/CO_2 mixing furnaces in the temperature range 800-1300°C using thin-film diffusion couples or the powder source method with San Carlos olivine single crystals. Thin films with approximate olivine stoichiometry were enriched with Lu, Ce, and Eu to various degrees. The powder was composed of ground San Carlos olivine enriched with synthetic fayalite and/or doped with Li in different degrees. Diffusion profiles were analysed using Rutherford-Back Scattering spectroscopy, Time of Flight Secondary Ion Mass Spectrometry in the depth profiling mode, and Laser Ablation Inductively Coupled Mass Spectrometry in the scanning as well as depth-profiling mode. Our preliminary results indicate a diffusive coupling of elements like Li and Al or Al and REE due to charge balance constraints, depending on the concentration range of the respective trace element. There appears to be a threshold value below which most trace elements occupying the metal site in olivine diffuse at about the same rates (order of magnitude) as Fe-Mg interdiffusion. Above this threshold value the diffusion rate of, for example, Li or REE, can be a couple of orders of magnitude faster or slower, respectively. Our results indicate that the diffusion rates for trace elements that substitute heterovalently into the olivine structure could be indirectly controlled by the exchange medium (melt or adjacent crystal) if the incorporated amount of the trace element reaches the critical amount. However, due to their commonly low concentrations in natural olivine crystals, trace element zoning measured in these crystals seem to show that in most cases their diffusion rates are similar to Fe-Mg interdiffusion rates.

A novel method to measure in situ stress of a sample in large volume presses

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For decades, researchers have strived to develop experimental methods that reproduce the high pressures and temperatures within Earth's interior. These approaches simulate conditions from the surface to the core, and ongoing advancements, such as recent progress in redox control, continually improve their accuracy. A comprehensive understanding of Earth's dynamic interior, unique in its mantle convection and plate tectonics, necessitates considering the added complexity of stresses and strains.

Stresses play a crucial role in affecting the stability fields of mineral phases concerning temperature and pressure, altering the ratio of stable phases, and impeding phase transitions. However, there has been limited research on how Earth's interior is influenced by stresses. While ex situ stress measurement methods like pressure markers exist, in situ stress measurements have traditionally depended on X-ray diffraction (XRD) and highly competitive beamtime allocations.

At the Bayerisches Geoinstitut (BGI), a cutting-edge method has been developed to measure in situ stresses without relying on XRD. Piezoelectric crystals generate an electric charge when subjected to mechanical stress or strain. As the crystals change shape, a charge forms on opposing faces [1]. By placing a crystal along the deformation axis within the assembly and connecting electrodes to opposing faces, the induced charge can be measured. With the crystal's known piezoelectric coefficient, the deviatoric stress experienced can be accurately determined. This innovative technique allows for real-time stress measurement during sample deformation under high pressures and temperatures.

The assembly's validation involved experiments at PETRA III and ESRF synchrotrons, where stress was measured in situ using both XRD and the novel piezoelectric assembly. The stress measurement comparison confirmed the assembly's accuracy and precision on a sub-second timescale. Further off-beam studies showed consistent results between subsequent experiments and verified stress measurements within expected ranges for single-crystal MgO and forsterite, up to 1500K. The assembly has been effectively used at pressures up to 6 GPa, temperatures up to 1500K, and strain rates between 10^{-6} and 10^{-4}. This precise, accurate, and reproducible method opens up new possibilities for deformation experiments, enabling any large volume press capable of deformation to conduct experiments that once required synchrotron access.

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Fluorine- and Li-enrichment in the late-stage fluids in a tourmaline-bearing LCT-pegmatite from Fonte del Prete, San Piero in Campo, Elba Island (Italy)

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The zonation of a pale pink tourmaline with about 8 mm in diameter from a cavity in an LCT-family pegmatite at Fonte del Prete, San Piero in Campo, Elba Island (Italy), was investigated. Fonte del Prete is a historic mineralogical locality which produced nice tourmaline crystals in the 19th Century [1]. While the most part of the investigated sample (#18292 from 1882; Natural History Museum of Milan) can be assigned to an Al-rich elbaite, significant chemical changes can be observed near the rim. The tourmaline composition of the outer rim (~30 µm) displays a dominant fluor-elbaite component. Towards the rim, the F content increases from ~0.2 to ~0.5 apfu and the Li content from ~0.7 apfu to ~1.1 apfu. This investigated tourmaline crystal consists of different proportions of the tourmaline end-members elbaite, fluor-elbaite, rossmanite, alumino-oxy-rossmanite and possibly others. Towards the rim, the fluor-liddicoatite component increases from 1% to 5%. The simplified chemical formula of the main tourmaline portion dominated by the elbaite component is: $(Na_{0.5}\square_{0.5})(Al_{2.2}Li_{0.7}\square_{0.1})Al_6(BO_3)_3[Si_{5.6}B_{0.3}Al_{0.1}O_{18}](OH)_3[(OH)_{0.5}O_{0.3}F_{0.2}]$. The refinement of the single-crystal structure with lattice parameters *a* ≈ 15.80 Å, *c* ≈ 7.09 Å agrees well with the chemistry determined by EPMA and SIMS. The simplified chemical formula of the fluor-elbaite-dominant outer rim is: $(Na_{0.6}\square_{0.4})(Al_{1.9}Li_{1.1})Al_6(BO_3)_3[Si_{5.5}B_{0.3}Al_{0.2}O_{18}](OH)_3[F_{0.5}(OH)_{0.3}O_{0.2}]$. Such a zonation can be explained by a F- and Li-enrichment of the late-stage fluids in this pegmatitic system.

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Influence of FeO content on the degassing behavior of hydrous phonolitic melts

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The degassing of volatiles from magma is the key factor in volcanic eruption dynamics [e.g. 1]. H_2O is the most important volatile driving volcanic eruptions and the degassing properties have been studied in several experimental studies [e.g. 2,3]. The key property to linking experimentally degassed samples to natural volcanic products and the corresponding degassing dynamics is the number density of bubbles (*BND*) [e.g. 4]. The prevalent formation process of such bubbles in silicic magma is attributed to homogeneous and heterogeneous nucleation [e.g. 2]. In both cases, the phase separation of H_2O from the melt is occurring in the metastable region of the melt-H_2O system. This diffusion-controlled process leads to an exponential increase in bubble nucleation rate with increasing supersaturation and to an exponential increase of the *BND* with decompression rate (dP/dt) [2,4]. This correlation is key to reconstructing ascent rates of magmas from the analysis of *BND*s in volcanic pumice and ashes. However, for hydrous phonolitic melt with 2.7 wt.% FeO, Allabar & Nowak [3] found high *BND*s of $10^5/\text{mm}^3$ and a narrow bubble size distributions (*BSD*) independent of dP/dt in experimental samples, inconsistent with nucleation theory. These results have been attributed to spinodal decomposition as a non-activated phase separation process occurring at the thermodynamic limit of stability.

As such a process would prevent the derivation of magma ascent rates from *BND* of natural samples, it is important to identify possible causes for the different phase separation mechanisms in e.g., phonolitic melt. We performed continuous decompression experiments following the protocol of Allabar & Nowak [3] with hydrous FeO-free melts based on their phonolitic melt composition. Over a broad dP/dt range of 0.17 to 5 MPa/s the observed *BND*s in our quenched experiments increase notably with d*P*/d*t* and produce a broad *BSD*. The results are well approximated by the *BND*-dP/dt correlation of Toramaru [4] with an increase of ~1.5 in log*BND* (*BND* increase from $10^1/\text{mm}^3$ to $10^4/\text{mm}^3$ over the dP/dt range) per order of magnitude of dP/dt. Our results indicate that even small variations of melt composition can fundamentally change the degassing behavior of silicate melts. The interaction process between FeO component and H_2O leading to such a fundamental change in the phase separation mechanism is at this point not clear. However, our results emphasize the need to consider both, nucleation and spinodal decomposition in magma-degassing models to determine the ascent history of magma by analyzing the bubble texture of natural samples.

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Constraining the pre-eruptive conditions of the 2021 Tajogaite eruption (Cumbre Vieja volcano, La Palma, Canary Islands)

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La Palma is one of the most historically active volcanic islands of the Canary Islands. The last eruption was produced by Tajogaite cone in the Cumbre Vieja ridge (La Palma, Canary Islands), which erupted between 19 September and 13 December 2021. The pre-eruptive conditions of the Cumbre Vieja volcano, which produced exceptionally fast and fluid lava at high discharge rates, are not well constrained. Here, we combine phase equilibria experiments and thermodynamic simulations to constrain the pre-eruptive conditions of the shallow reservoir, located at 8-12 km depth [1], of the 2021 Cumbre Vieja eruption. A rock from a lava flow erupted on the 2nd of October 2021 [2] as well as a series of analogous synthetic compositions were used as starting materials to perform the experiments in the temperature (T)/water content (wt.% H_2O) space at 275 MPa. The experimental results highlight that: i) up to 1 wt.% water added, olivine crystallizes between 1175 and 1150°C and it is followed by clinopyroxene between 1125 and 1100°C; ii) with increased water contents (i.e. 3, 5 wt.% H_2O) the appearance of olivine is lowered to the temperature range 1125-1100°C (3 wt.% H_2O) and to less than 1000°C (5 wt.% H_2O); iii) the appearance of clinopyroxene is not affected by the water content (0-5 wt.% H_2O), which is always in the temperature interval 1125-1100°C; iv) the crystallization temperature of oxides (Cr-spinel) is strongly influenced by the water content decreasing from ~1200°C at anhydrous conditions to ~1000°C with 5 wt.% H_2O added; v) amphibole and apatite were found only at 1000°C/1 wt.% H_2O. The experiments reproduce the natural phenocryst assemblage, comprised mainly of clinopyroxene, olivine and oxides [3]. Rhyolite-MELTS simulations partially reproduce the experimental results and the observed natural phenocryst assemblage, confirming that the assemblage likely formed at pressures $\geq$ 275 MPa. Simulations with Rhyolite-MELTS also suggest that amphibole is stable above 400 MPa, therefore, the reaction rims observed in the natural amphiboles [3] indicate disequilibrium conditions during magma ascent below 400 MPa. Moreover, the formation of natural plagioclase microlites (<50 μm) in the groundmass [3] are predicted at low pressures (< 20 MPa) and temperatures between 1050 and 1140°C. This indicates that plagioclase crystals grow up during the final ascent in the magmatic conduit and/or during cooling of the erupted lava outside of the vent.

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The effect of oxygen fugacity on sulphur speciation in magmatic fluids based on in situ Raman spectroscopy experiments at elevated P-T

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Sulphur speciation in magmatic fluids controls metal solubility, transport, and magmatic-hydrothermal ore deposit formation. To study sulphur speciation, we first trapped pre-equilibrated sulphur-bearing aqueous fluids as synthetic fluid inclusions (SFI) at 875°C, 2 kbar, and eight different oxygen fugacities ranging from ~NNO-1 to ~NNO+2.5, in our prototype externally heated molybdenum-hafnium carbide pressure vessel apparatus with hydrogen membrane simultaneously allowing for rapid quenching and flexible, precise, and accurate redox control [1]. Then, we reheated the SFI to their entrapment temperature in a microscope heating stage and analysed them using in situ Raman spectroscopy. During our heating experiments we observed several reactions, including sulphur comproportionation and the formation of sulphur radical species, underlining the unquenchable nature of sulphur speciation in magmatic fluids and the need for in situ approaches. Our experimental design, including the employment of two different laser excitations, allowed the quantification of sulphur-bearing aqueous species, including sulphide, sulphate, SO_2 and sulphur radical species, at previously inaccessible temperature and oxygen fugacity conditions and the assessment of their role in ore deposit formation. Our speciation model differs significantly from the results reported in previous studies [2,3].

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Reflectance spectra of mascagnite and salammoniac minerals with varying viewing geometry

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We analyse the quantitative effects of viewing geometry variations on the near-infrared reflectance spectra of mascagnite-$(NH_4)_2SO_4$ and salammoniac-NH_4Cl samples. Bi-directional reflectance spectra are collected in the 1 - 4.2 μm range considering a set of 3 incidence (*i*) angles (*i* = 0°; 30°; 60°) and 9 emergence (*e*) angles between -70° and 70° at room temperature and computed with respect to the normal direction. The NH_4^+ overtone and combinations bands located at ~ 1.09, 1.32, 1.62, 2.04, 2.2 and 3.05 μm are experimentally investigated. The bidirectional reflectance spectra of these samples show significant variations with the observation geometry in terms of reflectance values, spectral slope, and absorption bands parameters. The band positions remain essentially unchanged by varying the incident and emergence angles. On the other hand, bands' area and depth show the highest variability for $i \geq 30°$ and e greater than ±40° (up to a factor 2.3 in relative mean variation). The area and depth parameters of these bands show a dual behaviour: (i) for the weak-medium spectral features below 2 µm the area and depth decrease as the phase angle increases. (ii) The strong spectral features above 2 µm increase their values only at phase angles above 90°, but also at low phase angles for high incidences, $i \geq 30°$. This behaviour is linked both to the non-linear radiative transfer in particulate media and to the way the band depth and area are defined, relative to the local continuum. We observe important dependence (up to ~60% relative mean variation) of band depth and area on the incidence angle, up to 60°, compared to moderate variation with emergence angles (up to ~20% relative mean variation). Furthermore, the ~ 3 µm features becomes more less saturated at ± 70° emergence angles. A general trend of spectral bluing with change in observation geometry is observed. The current dataset is a contribution in the framework of present and future space missions focused on understanding the nature and quantification of ammonium-bearing minerals on icy bodies. The NH_4^+ – bearing minerals identification could provide information on: (i) ocean/brine compositions, (ii) possible explanations of geological phenomena and (iii) implications for biological activity. The two samples analysed in this work could represent the two most promising candidates as ammonium-bearing minerals. Also, their sensitivity to solar ray alterations and phase transitions should have direct consequences on the internal structure and dynamic of the bodies.

The solidus position and partial melting relations of amphibole- and mica-bearing peridotites in the presence of H_2O, CO_2 and F

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The chemical heterogeneity and compositional evolution of the lithospheric mantle are largely attributed to the partial melting of peridotite lithologies [1]. Volatile elements play a crucial role in promoting partial melting and metasomatism of the depleted mantle through melts and fluids, ([2] and see [3] for a review). Hence experimental data are crucial for understanding the metasomatism and geochemical evolution of the subcontinental lithosphere, and its connection to the sequestration of volatiles and the generation of volatile-rich melts, which are essential for the geodynamic and geochemical evolution of Earth's crust and mantle.

The impact of volatiles on the melting of metasomatized mantle sources was investigated by melting experiments involving two amphibole- and phlogopite-bearing peridotitic compositions. Experiments were conducted under H_2O- and CO_2-undersaturated conditions, with the addition of F, at pressures between 1 and 2 GPa and temperatures ranging from 950°C to 1300°C.

The solidus position of the two lherzolitic compositions was found at 1050°C at 1 GPa, and 1175°C at 2 GPa. Amphibole remains stable for 50°C above the solidus at 1-1.5 GPa, but it is present until the solidus at 2 GPa. Phlogopite is not present in any of these runs. For the K-enriched lherzolite, the solidus coincides with the lherzolite solidus up to 1.5 GPa and is slightly lower at 2 GPa at ~ 1140°C. Amphibole and phlogopite are present in all the sub-solidus and super-solidus runs. Both amphibole and phlogopite persist 15-50°C above the solidus, becoming less stable with increasing pressure.

The composition of the melts in both systems is initially controlled by the breakdown of amphibole and/or phlogopite at 1050-1100°C. The melts generated in both systems show a decreasing SiO_2 content with increasing P-T, with this drop being more significant in the K-enriched system. In this system, the SiO_2 content of the melts drops from 59 wt.% to ~ 51 wt.% at 2 GPa and 1250°C.

Our data will be utilized to determine the melting relations for amphibole- and phlogopite-bearing mantle sources and develop a quantitative mantle melting model. Such a model will provide quantitative constraints on the amount of melt generated, hence improving our understanding of the role of volatiles during the melting of metasomatised mantle sources.

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The case for metal saturation in the lunar mantle

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One of the more idiosyncratic features of lunar basalts is that they are more reduced than their terrestrial counterparts. This is shown, for example by the ubiquity of native metal in some basaltic samples recovered from the lunar sample. If these basalts formed due to melting of a similarly reduced lunar mantle, then it is quite possible that mare basalts' mantle sources are themselves metal-saturated. However, regardless of whether the oxygen fugacities (fO_2) determined for lunar samples, which are typically more reduced than the Fe-FeO reference redox equilibrium (or IW), are representative of their mantle sources has been long a matter of debate. Several a posteriori processes, like H-implantation by solar wind and CO-degassing during mare basalt eruption, can result in localized reduction of lunar samples. Depending on how pervasive these processes are, they may lead to underestimations of mare basalt fO_2, with the possible consequence that partial melting of their mantle sources occurred at more oxidizing conditions than otherwise estimated from the lunar rock record. Furthermore, the apparent positive correlation between siderophile elements like W and Cu with similarly incompatible elements like U and Yb, appears to preclude the presence of metal in the sources of mare basalts, as the former would have been retained in a metal-saturated lunar mantle. However, it is generally agreed that the median fO_2 of the lunar interior sits at around one log unit below the IW redox buffer. If this is true, then the question becomes whether the redox conditions prevalent during partial melting of the lunar interior were reducing enough to stabilize a residual Fe-bearing metal phase. Here we give an overview of the evidence for and against the presence of residual metal in the lunar mantle, and then discuss the consequences of this presumptive metal saturation. As constrained by basic equilibrium thermodynamics, at a log fO_2 of IW-1 or lower, metal-saturation of lunar mantle sources is not just a possibility but an inevitability. The behavior of the highly siderophile elements (HSE), W and Mo during lunar mantle melting is also modelled using a combination of literature data and from metal/silicate-melt partitioning experiments (Mo and W) assuming different starting compositions (bulk silicate Earth or canonical bulk silicate Moon), and the saturation of mantle sources in either Fe metal or Fe-S melt. We reconcile two apparently mutually exclusive possibilities, lunar core formation and lunar mantle metal saturation by suggesting that inefficient metal segregation during lunar core formation may have led to metal being retained in already partially crystallized lunar mantle cumulates.

Partitioning coefficient of sulphur between apatite and melt in basanite, preliminary experimental results

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The study of sulphur is fundamental for understanding magmatic degassing processes. Our attention has been focused on the partitioning coefficient between apatite and the melt as a first step in attempting to achieve a relationship between fugacity and sulphur concentrations in basaltic melt. This calcium phosphate mineral was chosen because it is ubiquitous in magmatic rocks. Moreover, its structure incorporates most of the volatile elements produced by volcanic activity such as water, halogens, and sulphur. Since previous studies on apatite/melt partitioning have mainly focused on evolved magmas, we decided to investigate the basanite-tephrite composition (Cumbre Vieja - La Palma).

We performed experiments with an internally heated pressure vessel (IHPV) at 200 MPa and 1040°C under both oxidizing and reducing conditions. Individual capsules were doped with different concentrations of native sulphur, between 2% and 0%, under water-saturated conditions. Our preliminary results show an increase of $K_d^{ap/melt}$ in the reduced experiments with a maximum of about 3-4. $K_d^{ap/melt}$ appears to decrease with increasing SO_3 wt.% in the glass. The amount of SO_3 in the apatite is directly correlated to the amount of S added to the charges. Furthermore, it appears that the concentration of SO_3, both in the apatite and in the melt, is higher in the more oxidizing series of experiments, which could indicate

that a greater amount of S is released into the liquid phase at reduced conditions.
Comparing our results with the literature, the $K_d^{ap/melt}$ increases with SiO_2, reaching a maximum around 20.

The reduced component in the Earth's upper mantle: Chemical composition the Fe-Ni-S dominated metallic melt and implications for oxygen fugacity (5-16 GPa)

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For a moderately oxidized mantle (near fayalite-magnetite-quartz), a typical Fe-Ni-S component at <6 GPa has atomic proportions of M/S (M = Fe+Ni) close to monosulfide stoichiometry [1]. With pressures increasing to >6 GPa, garnet becomes enriched in majorite component, which is associated with ferrous iron disproportionation according to 3 FeO (silicates) = Fe^0 (reduced component) + Fe_2O_3 (garnet). The increasing amount of Fe^0 is then expected to dissolve in the monosulfidic component, leading to a reduced phase with higher M/S and lower Ni/(Fe+Ni) ratios. A quantitative understanding of the chemical composition of this metallic phase is still lacking.
To shed light on the equilibrium systematics between Fe-Ni-S-C alloys and a bulk silicate Earth (BSE)-like composition, we performed multianvil experiments at 5 GPa in graphite capsules and at 6, 9, 12, and 16 GPa in single-crystal olivines. Temperatures were near-adiabatic between 1420-1590°C, and Fe-Ni-S atomic proportions of the reduced starting component was varied from 1.3 to 8.7 M/S and 0.4-0.6 Ni/(Fe+Ni), the latter scaled for the expected Ni-content of the reduced phase in a BSE composition. Similarly, bulk carbon contents were scaled to correspond to a BSE concentration of 150 ppm and are on the order of 1-5 wt.% in the reduced phase. Silicate and the reduced starting materials were mixed in subequal weight proportions, which is required to produce sufficiently large liquid pools of the unquenchable metallic melt for chemical analysis.
The results show that the reduced component consists of a Fe-Ni-S-C-O melt, saturated in graphite or diamond, and coexists with olivine (ol) or wadsleyite (wad), high-Ca px, garnet, and ± low-Ca px. M/S ratios of the equilibrated reduced melts range from 1.1-6.9, and X_{Mg} (ol or wad) varies from 0.76-0.91. Calculated distribution coefficients (K_D) for the equilibrium 2Fe (Fe-Ni-S-C-O melt) + Ni_2SiO_4 (ol/wad) = 2Ni + Fe_2SiO_4 yield values of 8-29. A positive linear relationship exists between the X_{Mg} of olivine and the M/S of the coexisting melt at 5-12 GPa. Calculated f_{O2}, expressed relative to the iron-wüstite (IW) buffer, ranges from ΔIW -1.3 to 0.7.
A thermodynamic model was then developed to describe the relations between f_{O2}, K_D, X_{Mg} (ol/wad), pressure and temperature. The model is used to predict f_{O2} and K_D at BSE-like X_{Mg} (ol/wad) values of 0.89-0.91. At a given S concentration, the proportions of Fe, Ni and S in the liquid alloy can then be calculated. Assuming 200-250 ppm S in the BSE, the abundance of the reduced melt relative to BSE steadily increases from ~600-750 ppm (42 wt.% Fe, 23 wt.% Ni, 35 wt.% S) at 5 GPa to ~1000-1300 ppm (61 wt.% Fe, 20 wt.% Ni, 19 wt.% S) at 16 GPa. Modeled f_{O2} values increase from ΔIW -1.8 (5 GPa) to -0.2 (13 GPa) and drop to a value of ca. -0.7 across the phase transition of olivine to wadsleyite.

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The perils of H_2O retention in quartz-hosted melt inclusions

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Pre-eruptive H_2O contents of rhyolites are difficult to determine directly because most is lost by degassing during ascent. Quartz-hosted melt inclusions (MIs) are potential recorders of pre-eruptive H_2O contents. The main uncertainty is whether the MIs retain their pre-eruptive H_2O, or some is lost via decrepitation or diffusion through the host crystal during ascent and degassing of the host magma. Results from the experimental study of Severs et al. [1] suggest that diffusive loss is possible, but the mechanism of H_2O loss was not unambiguously identified. We investigated this problem by conducting dehydration experiments and measuring both H_2O concentration and the deuterium-to-hydrogen ratio (D/H or dD_{VSMOW}) of the MIs by secondary ion mass spectrometry. Fractionation of D/H with increasing dehydration provides an unambiguous indication that H_2O loss occurred via diffusion of hydrogen through the host crystal [2]. Experiments were conducted by placing a single Bishop Tuff quartz crystal into a Vernadsky heating stage and raising the temperature to 750°C. Crystals were held in high purity helium for durations ranging from 24 to 336 hours. Within the first ~12 hours, some of the inclusions formed vapor bubbles while others remained bubble free. The concentration of H_2O in MIs containing vapor bubbles decreased by ~50 %, but with no corresponding increase of dD_{VSMOW}. The mechanism resonsible for this loss is clearly identifiable as decrepitation. Most of the MIs did not form vapor bubbles, and show little-to-no evidence for diffusive loss at 750°C for experimental durations as long as 336 hours. A few of the bubble-free MIs, however, show decreasing H_2O and increasing dD_{VSMOW} after only 120 hours, suggesting diffusive loss. We interpret these differences in behavior to be attributable to interactions among H_2O being diffusively lost from multiple MIs within a single grain. When a quartz grain contains a small number of inclusions diffusive loss can be detected, whereas in a grain containing a large number of inclusions it cannot. Our results demonstrate that H_2O loss from quartz-hosted MIs may occur either through decrepitation or diffusion, and that quartz grains containing multiple, bubble-free inclusions are likely to provide the most accurate record of pre-eruptive H_2O.

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The effects of minor element substitutions on trace element partitioning between pargasitic amphibole and melt

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The effects of minor components on mineral/melt partition coefficients are poorly understood, but may be significant due to charge-balance and other thermodynamic factors. Here we investigate the behaviour of titanium and fluorine on the partitioning of trace elements between synthetic pargasitic amphibole and silicate melt. Fluorine is particularly interesting because it does not impinge on the charge-balance of the substitutions. Experiments were performed at 10 kbar and 950 and 1050°C in the system K_2O-Na_2O-Al_2O_3-CaO-MgO-SiO_2-(OH,F) ± TiO_2 for molar F/(F+OH) from 0 to 1, and TiO_2 in the melt from 0 to 2.5 wt%. Iron was not included to avoid ambiguities in amphibole structural formulae arising from variable Fe^{3+}/Fe^{2+} ratios. The experiments were done in the piston-cylinder apparatus using Pt capsules. The experiments at 950°C crystallized pargasite (OH, F), with some also containing augitic clinopyroxene and accessory titanite coexisting with melt, while at 1050°C, only clinopyroxene with melt was found except in the experiments with high F/(F+OH), which did produce fluor-pargasite. There is a extremely strong negative correlation between REE pargasite/melt partition coefficients and F/OH in the system, which change by an order of magnitude as F/(F+OH) goes from 0 to 1. There is also a positive correlation with TiO_2, requiring the two effects to be deconvoluted by varying the F/OH and the TiO_2- contents of the starting compositions independently. The interpretation of results is further complicated by significant changes in the major-element compositions of the amphiboles between experiments, notably their Al_2O_3 contents. However, at least part and perhaps most of the effect of F can be ascribed to REE-F interactions stabilizing REE cations in the melt rather than to the F/OH ratio in the pargasite, since a similar effect is observed in the clinopyroxene/melt partition coefficients. This implies that F would influence mineral/melt REE partition coefficients generally.

For each individual experiment, the logarithms of the REE partition coefficients fall on a parabola when plotted against the REE ionic radii, with maxima near Dy, that is, near the middle of the REEs. The data thus provide a sensitive test affirming the asymmetry in the parabola is, within uncertainty, that predicted by the lattice strain model, as deduced from simple theoretical considerations. The shapes of the parabolas does not depend on the minor element substitutions. Partition coefficients were also obtained for Y, Rb, Sr, Ba, Zr and Hf, and Nb and Ta. The Large Ion Lithophile elements Rb, Sr and Ba are significantly less incompatible in pargasite than clinopyroxene. The partition coefficients for Hf are greater than those for Zr in both phases, whereas those of Nb and Ta are more similar to each other.

How to measure the isotopic fractionation of hydrogen at high pressure

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The most abundant mineral in the mantle, olivine, is described as nominally anhydrous whereas its high-pressure polymorph, wadsleyite, can contain up to 3% H_2O by weight. This study aims to measure the effect of polymorphism on isotopic fractionation as well as the effect of hydrogen speciation in relation with fO_2. Samples were synthesized in the multi-anvil press at 12-14 GPa and low temperature conditions of 550-1100°C, like conditions prevailing in a subducting slab. Experiments are performed under fluid saturated conditions. The study focuses on the quantification of the water contents and speciation of olivine, wadsleyite and enstatite and their respective D/H isotope ratios using a multi-instrumental approach. Raman spectroscopy is used to monitor hydrogen speciation while Secondary Ion Mass Spectrometry (SIMS) provides total hydrogen contents and D-H ratios. The calibrations of Raman and SIMS analyses are performed using samples characterized with Fourier Transform Infrared Spectroscopy (FTIR) and the Elastic Recoil Detection Analysis (ERDA) nuclear probe respectively. We assumed that OD and OH molecules are characterized by the same optical activity. A correlation close to 1:1 is obtained between the ratio of OD/OH Raman intensities and the SIMS D/H ratio measured for 6 high-pressure wadsleyite samples. We report the D-H fractionation between olivine and its high-pressure polymorph, using enstatite as a control for the isotopic composition of the fluid. We report the D-H fractionation between olivine and its high-pressure polymorph, using enstatite as a witness of the fluid isotopic composition. We find that Deuterium fractionates more into olivine compared to wadsleyite with a $ln(\alpha)^{adselyite\_olivine}$ negative up to 1100°C.

Towards a quantitative model for the prediction of fluid/melt partitioning of ore metals in porphyry systems: the effect of chlorine and melt aluminosity

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Aqueous fluids released from crustal magma reservoirs are the key source of metals for magmatic-hydrothermal ore deposits. The metal content of these fluids is dependent on fluid/melt partitioning within the source pluton during fluid exsolution, a process in turn dependent on a variety of factors including pressure (P), temperature (T), the availability of ligands, and melt composition (X). Despite the importance of fluid/melt partitioning, no comprehensive models have yet been established to predict the fluid/melt partition coefficients of porphyry ore metals in P-T-X space. Therefore, we aim to understand the influence of the fluid Cl content and melt aluminum saturation index (ASI) on the fluid/melt partitioning of Au, Cu, Ag, and Mo as the first step towards an accurate fluid/melt partitioning model applicable to porphyry and arc-magmatic systems. For this purpose, a series of experiments were conducted at 800°C and 1750 bar in René 41 alloy cold-seal pressure vessels. Au-Ag-Cu alloy capsules were filled with a synthetic, rhyolitic glass and aqueous fluids with cation ratios calculated to be in equilibrium with the melt at run conditions. Natural quartz cylinders were added and fractured in situ after the attainment of equilibrium to trap synthetic fluid inclusions. Experiments were conducted with four different fluid Cl concentrations (1, 3, 9, and 27 molal) and a melt ASI range of 0.8-1.2. Experimental results show a partitioning dependence of all metals on both fluid Cl content and melt ASI. Cu, Ag, and Mo partition coefficients all strongly increase with increasing Cl concentration in the fluid and decrease slightly with increasing melt ASI. Mo displays the lowest fluid/melt partition coefficients (up to ~60), while the highest values were seen for Au (up to ~1300), being about 3-5 times higher than those of Cu and Ag. Drawing from these results, a metal extraction efficiency from a crystalizing and degassing magma chamber of Au > Cu > Ag > Mo is expected, and is further supported by rough preliminary modelling of the experimental data. Modeling of the crystallization-driven degassing of granitic magmas with initial Cl concentrations of 2000 ppm and three different ASI values shows rapid Au and Cu uptake into the fluid, even at low crystal fractions. Over 60% of Au in all cases is present in the fluid phase after only 10% of the melt has crystallized. Mo has the lowest melt extraction efficiency, with 50% of Mo being present in the fluid after 60-70% melt crystallization. Peralkaline melts display the highest metal extraction efficiency, while peraluminous melts display the lowest, in line with the partition coefficients derived from the experimental data. Overall, experimental evidence shows that low melt ASI values and high initial Cl concentrations are the most conducive to metal extraction from felsic magmas, consistent with the high magmatic Cl abundances and metaluminous melt compositions often associated with porphyry deposits.

Concentration profiles in the melt embayments: Are they really significant?

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One dimensional, cylindrical entry of silicate melt into a mineral phenocrysts, embayment, is commonly found in volcanic rocks, and it is often quenched and preserves a profile of concentration variation, caused by diffusive loss of volatile component from the embayment, reflecting the last minutes to seconds of ascent dynamics of magma. Over the years, there have been many models that fit the concentration profile using a diffusion equation with a boundary condition that changes during the period of diffusion (e.g. EMBER, [1]). With such the models, magma ascent rates were found to be in a range from 0.02 $MPa.s^{-1}$ to 3 $MPa.s^{-1}$. As more embayment studies are engaged on various volcanoes of the world, there are discoveries of profiles that are not monotonic decrease of concentration expected from a degassing driven diffusion, showing increase, or even oscillation. Furthermore, there are concentration profiles of H_2O and CO_2 that cannot be derived from a simple degassing path (closed or opened). To understand such complexity in nature, we have modified pre-existing diffusion degassing model and ran several forward models to explore various scenarios. One of such scenarios considers the disequilibrium degassing in which the rate of decompression is too fast to transfer volatile species from magma to bubble. For example, CO_2 concentration in melt may not reach equilibrium as it diffuses significantly slower than H_2O. Our pre-liminary tests indicate that the quantity of exsolved gas in magma and disequilibrium degassing allows typical deviations from a simple diffusive degassing in which CO_2 appear to record slower decompression than H_2O when calculated individually.

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Does the polymorphic transition in quartz trigger lower crustal earthquakes?

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The change in the wavenumbers of Raman active vibrational modes of crystals are dependent on the strains applied to the crystal. The relationship between changes in the Raman wavenumber of a mode and the applied anisotropic strain is defined by the modes' Grüneisen tensor [e.g. 1]. The components of these tensors can be determined by ab-initio DFT simulations of the crystal structure [e.g. 2]. The strains of inclusions such as quartz in garnet can then be determined by in-situ Raman measurements, converted to stress and used to determine the entrapment conditions of the inclusion.

We have now performed in situ high-temperature Raman spectroscopy on quartz inclusions in garnet to study the evolution of inclusion stress and strain. The wavenumbers of the inclusion are higher than those of a free quartz at the same temperature which is the result of the inclusion being under confining stress imposed by the garnet host. This confining effect is also responsible for a different dω/dT between a free quartz and the inclusion and for the persistence of modes E 128 and A1 355 (Raman-inactive in the β-phase) well above the transition temperature expected for a quartz at ambient pressure. Crossing the α-β transition causes the garnet around the quartz inclusion to fracture or even, in some cases, shatter due to the large differential stresses developing in the inclusion at this transition. Inclusions of other minerals involved in the same experiment (e.g., apatite or zircon) remain unchanged at the same condition, excluding the fracturing being related to the host garnet. Calculations show that the deviatoric stress and strain in a confined quartz inclusion increase rapidly as the α-β transition is approached, and this will impose strong differential stresses on the surrounding host garnet crystal. We propose that this process can create sufficient fracturing in lower–crustal garnets, which in turn accumulate into planar fractures along garnet-rich layers and thus trigger brittle failure and seismicity. This would explain why estimates of the temperatures and pressures of several lower-crustal paleo-earthquakes (recorded as pseudotachylytes) place them at, or just below, the α-β phase boundary in quartz.

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Mineral-like copper oxychloride-vanadates: Nature-inspired synthesis, thermal stability and magnetic behavior

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Today, one of the most unique mineralogical objects are the scoria cones of the Great Tolbachik Fissure Eruption (GTFE, 1975-1976), in the fumaroles of which more than 135 new minerals have been discovered and studied over the past decades. These exhalative mineral associations from fumaroles in particular of the Second scoria cone of the Northern Breakthrough of the GTFE are well known for their wide diversity of Cu^{2+} oxysalt minerals [1]. An important characteristic feature of the of Cu^{2+} oxysalt exhalation minerals is the frequent presence of "additional" oxygen atoms forming the oxocentered tetrahedra $[OCu_4]^{6+}$ [2]. Their presence in the structures of these minerals suggests a vapor transfer mechanism of their formation [1].

On the other hand, such Cu^{2+} compounds are of great interest from the point of view of physics and materials science. Divalent copper compounds with the lowest spin-1/2 value are a promising platform for the design of low-dimensional and quantum magnets for technological applications. One of the prototypes for such promising functional materials are representatives of the group of copper oxychloride-vanadates.

Within this work, synthetic compounds based on rare exhalative minerals of the copper oxychloride-vanadates group were obtained: α-$Cu_4O_2(VO_4)Cl$ (*Pbcm*) (**1**), β-$Cu_4O_2(VO_4)Cl$ (*P*2/*n*) (**2**), $Cu_5O_2(VO_4)_2\cdot(KCl)_{0.5}$ (*C*2/*m*) (**3**), $Cu_5O_2(VO_4)_2\cdot(CuCl)$ (*P*-3*m*1) (**4**) and $Cu_9O_2(VO_4)_4Cl_2$ (*P*-1) (**5**). The method of chemical vapor transport reactions with approximate conditions to the fumaroles of the GTFE was used. The crystal structures of the presented compounds **1**-**5** are based on complexes of various dimensions constructed by $[OCu_4]^{6+}$ tetrahedra. For all the presented synthetic compounds **1-5**, the limits of thermal stability and the features of thermal expansion, including with the manifestation of negative thermal expansion, are determined using powder and single-crystal X-ray diffraction in situ methods [3,4]. From the point of view of magnetism, the magnetic spins of spin-1/2 Cu^{2+} form complex systems of interactions with the manifestation of strong competition between magnetic couplings, that is, magnetic frustration. The magnetic order is established in the low-temperature region, and the general magnetic behavior is complicated by quantum effects. Thus, magnetic moments in the structure of **5** are ordered antiferromagnetically, and an uncompensated moment is created, as a result of the deviation of the spin canting. The report will present the results of a detailed consideration of the features of the formation of these mineral-like materials **1-5**, as well as their crystal chemistry, thermal and magnetic studies.

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Experimental constraints on the exchange of metals between supercritical fluids and silicate melts

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Fluids generated in magmatic-hydrothermal systems are the primary means by which metals can be transported through the crust and be either deposited in the crust or outgassed at the surface. In order to understand these transport processes, it is necessary to characterize how metals are removed from silicate melts. To this end, experiments were performed in internally-heated pressure vessels, wherein a rhyolitic melt (Macusani Rhyolite or Bishop Tuff) was equilibrated with a saline fluid of up to ~11 wt.% NaCl equiv. at a fluid-melt ratio of between 0.5 and 1. A quartz core was also added to fix the activity of SiO_2 in the system to unity. Additionally, in some experiments fluorine was added as a mixture of AlF_3:NaF:KF. Experiments were performed at 800°C and 200 MPa at an oxygen fugacity of either FMQ ± 0.5 or NNO for a duration of up to 644 hours. Upon completion of the experiments, the glass was quenched by turning off the power to the furnace and the melt reached the glass transition temperature in <10 minutes. Solid and liquid run products were recovered according to the method of Gion et al. [1] and analyzed for major and trace elements by EPMA, (LA-) ICP-MS, and ion chromatography. The distribution of the metals in fluid as chlorides, fluorides, and hydroxides was calculated by using an in-house built fluid speciation calculator (SoAP: Solutes in Aqueous Phases). In total, the concentration of 134 aqueous species (including H_2O, HCl, and HF) for Li, Be, B, Al, K, Ca, Sc, V, Mg, Mn, Co, Cu, Zn, Ga, Rb, Sr, Y, Nb, Mo, Ba, Pb, Th, U, and REE's were determined. The concentration of each species and the trace element compositions in the melt were then used to determine apparent equilibrium constants, which are expressed relative to either NaCl, NaF, or NaOH, for example

$$K' = \frac{KCl^{Fluid} \times NaO_{0.5}^{Melt}}{NaCl^{Fluid} \times KO_{0.5}^{Melt}}$$

Apparent equilibrium constants (K') vary as a function of the HCl and HF content of the fluid phase and the K' can either decrease or increase with increasing HCl depending on the considered cation. Generally, chloride species with divalent cations have K' values greater than 1; all fluoride species except for those containing Al, Fe, Be, Co and Rb have K' values greater than one; and all hydroxide species except for those contain Sc have K' values of greater than one. The apparent equilibrium constants calculated as part of this study describe the exchange of metals between a felsic silicate melt and any saline fluid and can be used to predict the metal loads of those fluids as they exsolve from a melt that is decompressing and crystallizing.

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Spin transitions in (ultra)mafic silicate glasses: implications for the electronic state of Fe in melts at high pressure

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Iron, with its multiple valence states, plays a key role in controlling the oxygen fugacity (fO_2), density and viscosity of liquids in the deep Earth. However, the electronic and structural states of Fe in silicate melts with relevant compositions for magma oceans, and at pressures up to those of the core-mantle boundary, are still poorly understood. Here, we perform in situ-high pressure synchrotron Mössbauer studies of ^{57}Fe-peridotitic and basaltic glasses of unprecedented quality synthesised under different fO_2 and compressed, at ambient temperature, up to 193 GPa. Peridotitic glasses synthesised under reducing conditions, at 1 bar, contain Fe with 91% of a Fe^{2+} high spin (HS), 'd1', and a 9% contribution from a second site, known as the 'd2' feature, with hyperfine parameters intermediate between those of Fe^{2+} LS and Fe^{3+} HS. With increasing pressure, the contribution of d2 increases at the expense of d1 to become the predominant site at pressures beyond 124 GPa, suggesting therefore that d2 is actually Fe^{2+} in the low spin (LS) configuration, which is in agreement with its hyperfine parameters at higher pressure. Ferric iron-bearing basaltic glass is entirely composed of Fe^{3+} HS at ambient conditions, but, beyond ~6 GPa, a second doublet with hyperfine parameters unlike those of any Fe^{2+}-bearing species is required to precisely fit the data and its intensity increase with pressure at expense of the other site. We tentatively assign this second doublet to either Fe^{3+} LS or Fe^{3+} in a higher coordination environment due to an increase in quadrupole splitting (from 3.37 mm/s to 3.62 mm/s) with pressure and its low central shift (0.42-0.57 mm/s). The presence of a second site suggests a closer-packed arrangement of Fe^{3+} moieties, consistent with a decrease in the molar volume of $FeO_{1.5}$ with increasing pressure. At high pressures, both Fe^{2+}- and Fe^{3+}- end-members undergo significant changes to their electronic structures that may affect their molar volumes, and hence, the density of silicate melts as well as the chemical-and physical properties of silicate melts. Accordingly, investigations of the redox state of magma oceans should take into account the electronic structure change of Fe and its implication for the volume variation with pressure of primitive melts to constrain the fO_2 of the early Earth mantle and of the primordial atmosphere.

Experimental determination of the effect of limestone and dolomite assimilation on the viscosity of a phonotephritic melt

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The assimilation of carbonate rocks by magmas can dramatically change their chemistry and differentiation path, thereby affecting the rheological properties of the derived products. Here we present a set of viscosity measurements exploring the effect of variable degrees of carbonate assimilation on the melt viscosity (η) of a phonotephrite from Vesuvius (Italy). We doped the starting material with different amounts (0, 10, and 20 wt.%) of CaO and CaO+MgO, mimicking the effects of limestone and dolomite assimilation, respectively.

Through this approach, we focused on the composition change liquid phase, regardless of the effect of CO_2 bubbles produced by the decarbonation on the rheological properties. The high and low temperature liquid viscosity of the decarbonated melts were measured by concentric cylinder viscometry (CC) and differential scanning calorimetry (DSC), respectively. Melt fragility (m) were measured as a function of spectroscopic parameters of glass using Brillouin technique.

Viscosity data show non-Arrhenian trends, well described by both Vogel-Fulcher-Tammann (VFT) and Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equations. Trends obtained at high-T, low-η differ from those at low-T, high-η conditions. In the high-T regime, all decarbonated melts show lower viscosity than the pristine melt, the effect being more pronounced when only CaO is added. The opposite trend is observed in the low-T-regime, due to different fragility of the investigated melt.

The most recent predictive viscosity models well reproduce the high-T, low-η regime, or in the low-T, high-η regime, but they do not simultaneously perform well over the entire investigated temperature regime. This discrepancy is apparently caused by the lack of decarbonated melt (i.e., Si poor, Ca-Mg-rich compositions) in the calibration dataset of viscosity models.

Titanite fluid alterations – Experimental study

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Metasomatism experiments have been performed on a natural titanite (Lake Tahoe (USA)) with homogeneous REE and trace element composition for 16 days at 700°C and 200 MPa using NaF-, KCl-, NaCl-, $CaCl_2$-, NaOH-, KOH-, $Ca(OH)_2$-, and

$Na_2Si_2O_5$-bearing hydrothermal fluids. The goal of the study was to experimentally metasomatically alter titanite under known P-T-X conditions. Titanite metasomatism experiments involving NaF- and $Ca(OH)_2$-bearing fluids, showed the most intense alteration. In the experiment involving NaF + H_2O, perovskite ($CaTiO_3$) was the only alteration product via the reaction: titanite + NaF + H_2O → Na,REE-rich perovskite. In contrast, in the experiment involving $Ca(OH)_2$ + H_2O perovskite, wollastonite, and calcite grew at the expense of titanite according to the reaction: titanite + $Ca(OH)_2$ + H_2O → perovskite + wollastonite + calcite. Although perovskite formed in both experiments, there are noticeable differences in the composition and texture of the perovskite grains. In the NaF + H_2O experiment, perovskite shows weak zonation in the form of REE enrichment in the core (visible on BSE images). This is due to an admixture of Na_2O (up to 5 wt.%) and LREE (up to 8% wt.%) where REE and Na are replacing 2 Ca in the perovskite structure via the coupled substitution: $REE^{3+} + Na^{+} = 2Ca^{2+}$, for which the end member phase is loparite ($NaCeTi_2O_6$) [1]. Fluoride ions form strong complexes with REE which would promote their mobilization out of the titanite into solution. This fact, along with the presence of Na in the fluid, allowed for major uptake of REE by the perovskite. In contrast, perovskite from the $Ca(OH)_2$ + H_2O experiment contains much lower LREE concentration (up to 1 wt.%) which most likely is due to the lack of Na in the fluid.

In general, titanite alteration products are more pronounced with a more diverse mineralogy in the case of the $Ca(OH)_2$ + H_2O experiment compared the NaF + H_2O experiment. Element maps of titanite from the NaF + H_2O experiment support the remobilization of REE and their preferential incorporation into perovskite. Whereas, element maps of titanite from the $Ca(OH)_2$ + H_2O experiment show a distinct reaction front along the titanite grain rim and along apparent cleavage planes in the grain rim.

Metasomatically induced alteration of titanite to perovskite has been observed in a Ca-Mg skarn-porphyry deposit in Slovakia [1]. Here the REE's as well as Th, are found to be irregularly distributed in the perovskite.

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Experimental melting of kaersutite-diopside metasomes + lherzolite at 1-4 GPa and its constraints for the origin of Na-alkaline magmatism

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A traditional view suggests that basaltic magmas sourced within the upper mantle are generated by the melting of a homogenous peridotite dominated by olivine. An alternative to the homogeneous mantle paradigm is the melting of hydrous heterogeneous mantle rocks that contain the so-called hydrous "metasomes" [1-3]. Metasomes comprise mineral assemblages, with the dominant presence of hydrous minerals like mica or amphibole. The melting of hydrous mantle lithologies has been proposed to explain the origin of Na-alkaline lavas [2], traditionally linked to small degree of partial melting of a peridotitic mantle source [4].

We present a new experimental dataset for reaction experiments between natural amphibole-clinopyroxene metasomes and lherzolite that produced Na-rich alkaline melts. Experiments were conducted at 1-4 GPa and 1000 to 1300°C. The generated melts range from foidite over basanite to phonotephrite. At 1 GPa between 1000 and 1100°C amphibole is unstable. Instead, amphibole decompression-breakdown products generate phonotephritic melts. At T > 1100°C, the composition of the melt is controlled by amphibole melting. At 3 and 4 GPa the melt composition is additionally influenced by phlogopite melting and by the presence of garnet in the residue. The melt residues are generally wehrlitic and imply that incongruent melting of metasome produces wehrlitic residue. The melt then reacts with opx from the lherzolite, which again produces wehrlitic residue with different ol/cpx ratios. Therefore, wehrlite formation does not require separate metasomatic processes and can be a direct by-product of alkaline volcanism.

We applied a metasome melting model to the magmas of the Kula volcanic province, Turkey, and show that at 1 GPa basanite melts and phonotephrite melts can cover the whole range of known Kula lava compositions. The Kula lava trend can be therefore generated not by differentiation of basanite but by basanite-phonotephrite melt mixing.

A comparison of high-pressure (3-4 GPa) melts with global nephelinite data shows overlap with most elements but suggest also that the natural nephelinite data are slightly more evolved and do not represent primary metasome melts.

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The effect of strain on crystal alignment and clustering during crystallisation of basalt in experiment

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During magma transport and effusive eruption, crystallisation often occurs. Investigating the effect of crystallisation in flowing melt on microstructure, crystallographic preferred orientation (CPO), and cluster formation can shed light on the interaction between crystallisation and rheological behaviour of magma, and provides new tools to detect syn-eruptive crystallisation in nature.

At the University of Perugia Petro-Volcanology Research Group lab, basaltic glass synthesised from crushed Mt. Etna lava was placed in a cylindrical crucible in a furnace (at 1 atmosphere in air). After melting and super-liquidus homogenisation, a central spindle was inserted, rotating at a fixed strain rate of $1 s^{-1}$ at its rim. The sample was cooled to 1170°C (~ 30°C undercooling), then subjected to ten sub-liquidus temperature oscillations of 40°C to create chemical zoning. After ~ 18 hours, spindle rotation was stopped, and the sample was annealed for 48 hours at 1150°C before quenching in air.

Electron backscatter diffraction scans were acquired at different distances from the spindle to quantify microstructure, CPO, and crystallographic orientation relationships (CORs). The sample contains glass (42-51%), subhedral plagioclase (Plg, 25-27%) and clinopyroxene (Cpx, 18-25%), and skeletal magnetite (Mt, 5-6%). In general, phase proportions are constant, whereas average grain size increases and average number density decreases with increasing distance from the spindle for all phases. Only Plg shows a strong shape preferred orientation (SPO), weakening far from the spindle. Near to the spindle, Plg exhibits a weak CPO (J-index 1.3-1.4), while Cpx exhibits a very weak CPO (J-index ≤ 1.2). Far from the spindle, both CPOs weaken further but do not disappear. In detail, variations occur at the same radial distance. Very close to the spindle, localised very fine grained domains with reduced melt fraction occur. Far from the spindle, phase proportions remain constant, but some domains have weaker Plg SPO and larger Cpx grains. Heterogeneous radial distribution of microstructures underlines the complex relationship between microstructure and rheology in crystallisation under strain.

Near to the spindle, low-index planes in crystals are preferentially aligned subparallel to low-indexed planes in their touching neighbours. $\{110\}_{\mathrm{Plg}}$ aligns preferentially with $(010)_{\mathrm{Cpx}}$, and there is also an increased fraction of low angle Cpx-Cpx grain boundaries. Far from the spindle, these alignments become more dispersed, but do not disappear. Both the statistical nature of CORs and their variation with radial distance suggest they arise due to physical interaction of grains in the melt. The fact that simultaneous deformation and crystallisation led to weak or very weak CPOs, but CORs resulting from physical crystal alignment were always clearly detectable, suggests CORs may be a key indicator of crystallisation in flowing magma.

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Synchronizing acoustic emission detection and X-ray tomography: application to carbonatite magma degassing

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Carbonatite magmas forming at equilibrium with the mantle have a composition that is close to dolomite $CaMg(CO_3)_2$ and are stable only at pressures above ca. 2 GPa (corresponding to ca. 60 km depth). Phase diagrams predict that the melts should release their CO_2 at once, by crossing the so-called carbonate ledge, a boundary that limits the stability of molten carbonates to the high-pressure side [1]. This abrupt liberation of CO_2 has the potential to generate high-energy eruptions.

In order to investigate the consequences of the forceful release of CO_2 and its fracturing potential, we monitored acoustic emissions (AE) in situ, at high pressure and high temperature during controlled decompression. We also performed in situ x-ray tomography to follow the formation of vapor in the molten samples.

The experiments were performed in a multianvil apparatus (MA), using the 250-ton press installed on 13-BM-D beamline of GSECARS facility at the Advances Photon Source [2] and in a Paris-Edinburgh (PE) press for combined AE and high-pressure x-ray microtomography (HPXMT) [3]. We used an AE setup that was initially designed for studies of solids at mantle conditions [4]. In the MA, we positioned the transducers at the back of the 6 anvils, for acoustic emission location and focal mechanism characterization. In the PE, we positioned 2 transducers along the vertical axis of the HPXMT and attached 4 transducers on the lower PE anvil, slightly off the sample plane. A combination with X-ray diffraction is necessary to verify that the emissions coincide with phase transformations occurring in the sample.

We performed several runs on systems with pure CO_2 or mixed H_2O-CO_2 as a fluid. In all cases, acoustic emissions were detected at the crossing of the carbonate ledge. Focal mechanism analysis confirms the presence of an explosive component and the potential for carbon-rich magmas to initiate fracturing at mantle P-T conditions. X-ray tomography performed in situ at high pressure and temperature confirms the formation of bubbles at the crossing of the carbonate ledge.

The eruption of CO_2-rich magmas such as carbonatites and kimberlites have long been suspected to be very deeply rooted. This work documents the fracturing potential of these magmas at mantle depths.

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Investigating the origin of the young lunar Chang'E5 basalts with high-P high-T experiments

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The latest returned lunar samples from the Chinese national Space Administration's Chang'E5 mission (CE5) comprise young (1.96 Ga) basalts, which lack any KREEP (K-REE-P) or volatile element component [1,2]. The origin of these rocks remains highly debated and the CE5 samples are hence a unique chance to study volcanism very late in lunar history. To further our understanding of the petrogenesis of the CE5 basalts, we conducted high-P high-T phase equilibria experiments on two CE5 basalt compositions [3] to examine whether these samples could be primary melts of lunar mantle cumulates [4]. Additionally, we used a fractional crystallization model to evaluate if the CE5 basalts could be products of extensive fractionation [1]. The experimental results show that multiple phase saturation with Fe-Ti oxides and clinopyroxene occurs at P-T conditions corresponding to a depth of ~250 km within the lunar mantle. This observation indicates that the basalts could indeed be primary melts of a late-stage lunar mantle cumulate. Fractional crystallization modeling attests the possibility, that the basalts could originate from primitive parental Mg-rich melts that fractionated large amounts of olivine and minor plagioclase. Thermal constraints of the lunar mantle at 1.96 Ga clearly favour one of these hypotheses.

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Enhancing the understanding of lunar magma ocean evolution using appropriate mineral/melt partition coefficients

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Partition coefficients (D) are not constant values but depend on temperature, pressure, redox conditions, and on the chemical composition of the liquid and the solid [1,2]. Recent models of the chemical evolution of the Lunar Magma Ocean (LMO) [3] rely on accurate trace element partition coefficients [4,2]. Experimentally produced mineral-melt D's are extremely valuable to assess and model natural processes, as P-T-fO_2 conditions of the experiments are usually well constrained. Computational models can be enhanced and developed, based on experimental observation and predictions.

In order to better constrain the solidification history and thermo-chemical evolution of the Moon, we conducted 1-atm vertical tube furnace experiments and piston cylinder experiments with compositions relevant for the LMO. Starting materials are doped with a variety of trace elements (e.g., REE, transition metals, large ion lithophile and high field strength elements). The experiments cover a range of fO_2 conditions and temperatures relevant for the Moon. Run products contain large and homogeneous minerals (e.g., pyroxene, olivine, plagioclase) and quenched melts, and were characterized with SEM. Major element were analyzed by EPMA and trace element concentrations of minerals and glasses were determined with LA-ICP-MS.

The highly accurate new trace element mineral-melt partition coefficients were implemented into geochemical and petrological models to predict isotopic signatures of e.g., the different lunar mantle cumulates. Our data show that existing models need to be refined to explain isotope signatures of natural lunar samples.

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A high-pressure (≤250 MPa) high-temperature (≤1120°C) rheometer: measuring the viscosity of volatile-bearing magmas

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Magma rheology exerts a primary control on a wide range of volcanic processes, from the extraction of magma in the deep earth, its transport to the surface, and finally its eruptive style at the surface. Throughout this journey, the magma experiences significant changes in pressure and temperature, that affect the viscosity of the melt, but also the role of crystal and volatile phases (especially H_2O) in the bulk rheology. Direct viscosity measurements of volatile-bearing magmas at high pressures and high temperatures (HPHT) are needed to constrain models and predict transport and eruptive behaviour. Previous direct viscosity measurements of high temperature magmas are generally limited to anhydrous, ambient pressure conditions as a consequence of the difficulty posed in adding a pressurised chamber to a rheometer. Indirect viscosity measurements, using variations on the falling-sphere method, in high-pressure apparatuses (diamond-anvil cell, piston-cylinder, etc.) allow for high pressure and volatile-bearing investigations. However, the method is limited to low viscosity materials, prone to larger uncertainties (> 15%) and cannot be applied to dynamic conditions. Here, we introduce a new HPHT rheometer capable of direct viscosity measurements over high pressure (≤ 250 MPa) and temperature (≤ 1200°C) ranges, measuring viscosities in the range 100 Pa s - 30,000 Pa s. The rheometer combines a cold-seal high-pressure apparatus and a concentric cylinder rheometer. It is able to achieve HPHT conditions due to a magnetically coupled measuring system which links an internal spindle within a sealed pressure chamber to an external rheometer head (supplied by Anton Paar). The HPHT rheometer produces viscosity measurements with an uncertainty of ±5%, the technical features and challenges that contribute to this uncertainty will be presented.

Experimental insights into the formation of Archean continental crust

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Remnants of Earth’s juvenile continental crust are preserved in the form of Archean Tonalite-Trondhjemite-Granodiorites (TTGs). However, much controversy surrounds the composition of TTG protoliths and whether the geodynamic setting involved convergent-style plate tectonics. Thus, a combination of high-pressure and high-temperature experiments combined with robust geochemical proxies are required to gain insight into TTG petrogenesis. Over the last three decades, numerous experimental studies have demonstrated that partial melting of hydrated basalt at pressures ranging from 0.8 to 2 GPa is sufficient to produce TTG-like melts [e.g., 1-2]. The compositions of starting materials used in these partial melting experiments vary significantly between studies and has profound implications for the solidus and compositions of TTG melts, and the type, composition and modal abundance of solid phases [1-3]. This is problematic especially given most studies have utilised MORB-like starting compositions, which differ significantly in composition to the least altered samples of Archean metabasalts, namely in their higher MgO and lower Al_2O_3 contents [4]. In order to address these shortcomings, we present the results of partial melting experiments conducted at 1-2 GPa and 940 to 1100°C in an end-loaded

Voggenreiter piston cylinder apparatus using synthetic starting materials with varying H_2O (4-6 wt.%), based on the compositions of tholeiitic metabasalts from the Eoarchean Isua supracrustal belt (ISB), in southern West Greenland. ISB tholeiites typically possess higher MgO (~10-14 wt.%) and FeO*(9-12 wt.%), and lower Al_2O_3 (~8-14 wt.%) relative to modern oceanic basaltic crust [3]. These differences likely reflect a higher geothermal gradient in the Archean, enabling mantle melting to occur at greater depth [e.g., 4]. The run products of these experiments will be analysed to assess their phase assemblages and melt composition, and to constrain the magnitude of mineral-melt trace element (HSFE and REE+Y) and isotopic (Ti) fractionation during partial melting of hydrated high-Mg, low-Al metabasalts. Ultimately this experimental campaign will ascertain if partial melting of high-Mg, low-Al metabasalts is a viable mechanism to produce melt compositions resembling those of Archean TTGs.

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Partial melting and mineral-melt partitioning constraints on the genesis of lithium-rich rare-metal granites and pegmatites

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Rare-metal granites and pegmatites (RMGPs) are characterized by the enrichment of incompatible elements such as Li, Cs, Ta, Sn, W, Hf, and Rb. These critical metals, and in particular Li, are paramount for a sustainable energy transition; therefore, it is imperative to understand their origin and occurrence to improve exploration prospects. The genesis of RMGPs is often associated with late-stage melts that are the result of protracted fractional crystallization, but this mechanism fails to explain the extreme enrichment of Li (over 1000 ppm), Ta, and Nb observed in some RMGPs [1]. Recently, fluid-absent partial melting of metasediments has been proposed as a possible mechanism to produce RMGPs [2], but there is a lack of experimental data to support this. To test the viability of this mechanism, partial melting experiments were performed on hyperaluminous mica-schists and metabauxites in a piston-cylinder apparatus at 750-800°C and 700 MPa. Experiments were performed at fluid-absent conditions for up to 14 days and low degree partial melts (up to 25%) were attained. These partial melts have a peraluminous granitic composition and are enriched in elements such as Li (up to 2000 ppm) and Cs, but depleted in other rare-metals such as Ta, Hf, and Rb. The partial melts have some compositional features of RMGPs; however, they more closely resemble Sn-W granites. Consequently, these partial melts must undergo further fractionation to produce RMGPs. In order to interpret the enrichment of Li during partial melting, and how it may be further enriched during fractionation, partitioning experiments were performed in an internally-heated pressure vessel at 675°C and 300 MPa. Metaluminous to peraluminous rhyolitic samples were undercooled and crystallized for up to 26 days to acquire mineral-melt partition coefficients of Li. Experiments on the effect

of aluminousity, F, and P content, which are anomalously high in RMGPs, on the partitioning of Li are currently being investigated to further constrain rare-metal enrichment in these genetic models.

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Sulfur solubility and speciation in dacitic magmas at 0.7 GPa

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The complexities of sulfur behavior in magma are not fully understood. Sulfur (S) in silicate melts is mainly present as sulfide (S^{2-}) at reduced oxygen fugacity (fO_2), associated with various economically important metal-forming ore deposits such as cooper, gold and platinum; whereas the higher valence of sulfur – sulfate (S^{6+}) – in melts at higher fO_2 can generate SO_2 gases during volcanic eruptions which can have direct impact on local or global climate. The relationship between S^{6+}/total S and fO_2 derived from X-ray absorption near edge structure (XANES) indicates that the transition from S^{2-} to S^{6+} with increasing fO_2 occurs over a narrower interval of about 1 log unit than previously found by EPMA, i.e., FMQ +0.5 to FMQ +1.5 (FMQ = fayalite-magnetite-quartz oxygen buffer) [1]. However, it is unclear whether the transition of sulfur oxidation state in arc magma at lower crustal level is dependent on melt composition and pressure. We performed piston-cylinder experiments on sulfur-saturated, hydrous dacitic melt at 0.7 GPa and 950°C using various fO_2 solid-state buffers (Co-CoO, Ni-NiO, NiPd-NiO, Re-ReO_2 and hematite-magnetite). The activity of Fe is further constrained by Pt-Fe solution model [2] which a Pt wire was placed in inner capsule for Fe-bearing experiments. The maximum solubility of sulfur in the melt is strongly influenced by the amount of sulfide (i.e., as pyrrhotite in Fe-bearing experiments, or cobalt or nickel sulfide in Fe-free experiments) and sulfate (i.e., anhydrite) in the experimental run products. The amount of sulfur dissolved in the melt range from 68±11 to 1328±20 ppm with increasing fO_2. We find that there is no significant difference in sulfur solubility between the iron-bearing and iron-free melts, indicating the number of non-bridging oxygen atoms per tetrahedron (NBO/T) is the main controlling factor. The hydrous dacitic glasses were anaylzed by S K-edge XANES at ESRF (Grenoble, France) to determine sulfur oxidation states. These data will be combined with literature data to investigate the melt composition and pressure effects on sulfide-sulfate transition.

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Pressure-induced smooth structural evolution in a terrestrial magma ocean

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Structure and properties of terrestrial magma oceans control the co-evolution of the core, mantle and atmosphere of the early Earth, but are poorly understood because discrepancies remain between experiments and theoretical calculations. Here we combine acoustic velocity measurements and ab initio simulations on pyrolite glass/melt with a silicate Earth-like composition. In the complex system, we find a gradual increase of sound velocity with increasing pressure. Through ab initio simulations, this is explicable by the transition from four- to six-fold coordinated Si occurring over the entire mantle regime. These results are at odds with recent X-ray diffraction measurements, which show an abrupt change in Si-O coordination at 35 GPa. It is however consistent with recent high-pressure data, where Ni partitioning between molten metal and silicate exhibits a similar gradual change with pressure. Unlike amorphous silica, smooth structural evolution in a multicomponent system implies progressive changes in magma ocean properties with depth, such as density, element partitioning and transport properties, which, when incorporated into magma ocean models, may improve our understanding of early history of the Earth and other rocky planets.

Microseismicity and acoustic emissions during pyroxene-ilmenite transformation in $MgGeO_3$

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Deep earthquakes (depth > 60 km) comprise ~25% of all earthquakes and occur almost exclusively in subducting slabs. Like shallow earthquakes they exhibit double-couple sources, indicative of slip on a plane. The presence of earthquakes deeper than ~60 km is widely ascribed to phase transitions since brittle failure, the dominant mechanism in shallow earth- quakes, should be suppressed by pressure at greater depths. At intermediate depths (60 < d < 300 km) the number of earthquakes decrease with depth and dehydration embrittlement of the wet subducting slab is widely accepted as the driving mechanism for seismogenesis.

Following a minimum in the number of earthquakes around 300 km depth, the number of earthquakes increases to a maximum about 600 km depth. Below ~600 km, the number of earthquakes decreases rapidly with no events deeper than ~700 km depth. At these great depths the earthquake occurrence is generally ascribed to phase changes in the dominant mantle mineral, olivine. Metastable olivine is assumed to remain in the cold core of the subducting slab to depths greater than 600 km. Earthquakes at these depths then occur by transformational faulting or thermal runaway as the olivine transforms to higher pressure polymorphs. However, in the depth range 500-650 km there are other phase changes that could be seismogenic; candidates include Ca-garnet → Ca-perovskite,

wadsleyite → ringwoodite and enstatite → majorite / ilmenite.

We have performed experiments and observe microseismicity (or acoustic emissions) during the pyroxene-ilmenite transformation in $MgGeO_3$. Experiments are performed in a 6-8 Walker-type multi-anvil with the six receivers mounted on the back on of the tungsten carbide anvils. Background levels of acoustic emissions are observed at all temperatures. But between 750 and 850°C large events occur around the pressure of the phase transition after which there are few events. The proximity of the large events to the phase transition supports the hypothesis that the Acoustic Emissions are caused by pyroxene undergoing transformational weakening.

If pyroxene in the subducting slab is retained into the transition-zone it may provide a better explanation for the depth distribution of deep earthquakes than the olivine polymorphs.

Silicon vapor species at very reducing conditions: Applications to Mercury’s mysterious hollows

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The surface of Mercury is characteristically O-poor (fO$_2$ estimates ranging from IW-3 to -7) and S-rich (up to 6 wt.%), with extensive graphite deposits that are potentially remnants of an early graphite floatation crust. S and C deposits are likely contributors to ancient and modern volatile movement on the planet’s surface. In particular, sublimation and redeposition of sulfides in Mercury’s intense solar wind environment has been proposed as a mechanism for the creation of Mercury’s hollows, flat-floored depressions which are abundant on slopes with equator-facing aspects. Given Mercury’s extremely reducing nature, constraining which sulfide minerals may contribute to this process is non-trivial using terrestrial datasets. We are carrying out a series of novel vapor degassing and deposition experiments on Mercury magma analogs in evacuated silica glass tubes at low pressure (< 1 atm) and high temperature (> 1300°C) to test the hypothesis that Si is an important volatile species under highly reducing conditions. Silicon metal was used to buffer experiments to the Si-SiO_2 buffer, representing the most reducing end of Mercury’s fO$_2$ range. Mercury magma analog starting material powder and silicon metal were loaded into a graphite capsule placed inside of a ~55 cm-long silica glass tube, which was then attached to a vacuum pump and sealed. The tube was then run for 1 hour at > 1300°C in a vertical tube furnace, where the sample was in the furnace hot spot and the top of the tube extended ~17 cm above the top of the furnace resulting in a thermal gradient from > 1300°C to ambient room temperature along the tube length. The experiment was quenched by placing the hot end of the tube in water. Confocal Raman spectroscopy was used to identify deposits along the tube walls without breaking the tube open, necessary to preserve any air-sensitive deposits. The tube was then broken open, and deposits were analyzed using EDS on the electron microprobe. Several deposits were identified by both Raman and EDS that are consistent with SiS_2 crystals. New experiments are now being carried out using sapphire glass tubes, pre-glassed S-bearing starting materials, and Fe-Si metal buffers appropriate in composition to metal alloys expected within Mercury magmas. These tests will indicate whether Si moves from the melt in a vapor phase and whether bonded S and Si species in the melt will react to form an SiS_2 vapor. XANES measurements on glasses and SiS_2 powder standard are being performed to identify if Si and S bond within the melt structure. Results will indicate whether Si is an important volatile species on highly reducing planetary bodies.

Origin of δD signatures of mantle xenoliths: evidence from diffusion experiments performed with xenolith pieces

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Several studies have reported depleted values for the hydrogen isotope signatures of mantle xenoliths [1-3]. The deep origin of these depleted values has been questioned. We performed hydrogen-deuterium diffusion experiments in cubic pieces of natural xenolith aggregates of 1 cm^3, between 600 and 900°C and at room pressure in deuterium enriched gas. The objective was to explore the role of grain boundary diffusion in the control of isotopic exchanges during xenolith transport up to the surface.

We compared intracrystalline diffusion profiles measured in orthopyroxenes (opx) single crystals and opx located at the edge of the cubes with diffusion profiles within opx inside the cubes. The diffusion profiles in crystals inside the cubes are only slightly shorter than the ones in crystals directly in contact with the gas. In the experiments, apparent diffusion coefficients in opx inside the cubes are lower by a maximum of 0.6 log units. It suggests that the grain boundaries diffusion of hydrogen in xenoliths is at least 2.5 log units faster than intracrystalline diffusion in opx.

The results confirm that the isotopic exchange is fast enough to constantly requilibrate the δD values between the xenolith and the surrounding magma. δD depletion in pyroxenes from mantle xenoliths may be strongly influenced by late degasing prior and during eruptions.

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Experimental constraints on kamafugite mantle sources

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Earth's mantle is characterized by a heterogeneous mineralogical, chemical and isotopic composition, which represents the result of continuous melt extraction and chemical enrichment processes, mostly through subduction [1]. These modifications have led to the development of variably depleted and enriched mantle lithologies [2].

High pressure experiments have played a fundamental role in understanding the mineralogical and chemical composition of the mantle sources of igneous rocks, their solidus temperatures, and the mechanisms responsible for magma formation and evolution. However, only few of these experiments have focused on exotic lithologies, with the petrogenesis of ultrapotassic melts remaining poorly constrained. For kamafugites (kalsilite-bearing volcanic rocks), a convincing petrological model that fits their mantle compositions has not yet been found.

Here we present results of high-pressure experiments designed to better constrain the mineralogy and composition of the mantle sources of three kamafugitic magmas (Western branch of the East African Rift in Uganda, Alto Paranaiba Igneous Province in Brazil, and Intra-Apennine Province in Italy). Near-liquidus experiments on natural kamafugites (P = 2 GPa; T = 1290-1380°C) confirmed the importance of clinopyroxene and phlogopite, found as liquidus phases, in the formation of these exotic melts. The lack or scarcity of classical mantle phases such as olivine and orthopyroxene are compatible with the low silica content of the melts, while the presence of phlogopite explains the high K_2O content. Olivine occurs as a liquidus mineral only for the Brazilian kamafugites, which are characterised by lower K_2O compared to the other kamafugites. Different accessory phases, such as apatite, Fe- and Ti-rich oxides and titanite, have been found in the three kamafugitic rocks. Accessory minerals seem to be important, at least in the Ugandan and Brazilian samples, while they are less common in the Italian rocks, probably reflecting their different geochemical features (e.g., lower TiO_2 content). Variation in the amount of clinopyroxene and phlogopite, coupled with different importance of accessory phases, may explain the different geochemical compositions of the three kamafugite melts.

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Formation of polycrystalline diamonds in the Earth's mantle

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Polycrystalline diamond aggregates (framesites, boart, diamondite) are an understudied variety of mantle diamond, but can make up 20% of the production in some kimberlites, such as the Venetia kimberlite in South Africa. Their polycrystalline nature indicates rapid precipitation from carbon-oversaturated fluids and individual PDAs often contain a chemically heterogeneous suite of websteritic and peridotitic inclusions and minerals intimately intergrown with the diamond crystals. Generally, this diamond species forms in the upper mantle and has a similar suite of inclusions and mineral intergrowths as the monocrystalline diamonds [1]. However, different to silicate inclusions in monocrystalline diamonds which show almost equal abundances of eclogitic and/or peridotitic garnets and dominantly eclogitic cpx, PDAs contain dominantly websteritic garnets and/or peridotitic cpx [2]. Olivines have not yet been reported form PDAs.

We present here data on a suite of 39 samples from the Venetia kimberlite pipe in South Africa. Electron backscatter Diffraction of the diamond grains show near-random orientations, consistent with rapid crystallization from an oversaturated medium. d^{13}C values in the diamonds measured by secondary ion mass spectrometry range from -7 to -28‰ and cover the entire range for PDA from the literature. Nitrogen concentrations are between 1 and 2660 at ppm and d^{15}N values range between -4.3 to +17‰.

Detailed analysis of the sample provides evidence for a more complex growth history followed by alteration. Individual diamond crystals show complex growth zonation by cathodoluminescence imaging that can be related with the carbon and nitrogen isotopic compositions and points to growth incorporating several pulses of carbon-nitrogen fluid with distinct isotopic compositions. Most of these growth events show decoupled carbon and nitrogen systematics.

These geochemical and microstructural evidence suggests that fluid-driven redox reactions with lithospheric material occurring episodically over millions of years play a major role in freezing carbon in the subcratonic lithosphere [1-5].

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In-situ investigation of brittle failure and residual strain in rocks and minerals using 3D X-ray diffraction and microcomputed tomography

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The failure of a rock or a mineral under deviatoric macroscopic stress results from the nucleation, propagation and coalescence of multiple microfractures, which develop in response to local stress concentrations. These local stress concentrations control how and where fractures will initiate and propagate, and are thus crucial to understand the connection between microscopic and macroscopic failure. However, standard imaging techniques used in deformation experiments, like X-ray micro tomography, do not provide any information about local variations of the stress field and residual strain field after microfractures have propagated. Thus, combining standard X-ray imaging methods with X-ray diffraction could potentially bring new insights into microscopic failure mechanisms. We used 3D-Xray diffraction (3DXRD), a method developed on synchrotron X-ray sources, which allows to investigate in situ the internal structure of polycrystalline materials in three dimensions. For a given sample, 3DXRD returns the position, orientation and shape of the crystallites it is made of, and can give access to the local strain and stress state within the grains. Compared to other diffraction techniques like EBSD, 3DXRD has the advantage of requiring little preparation, thus limiting addition of new damage structure in the sample, and allows in-situ data acquisition in the volume of the sample during an experiment. We applied 3DXRD in combination with X-ray microtomography to three different rock and mineral samples that have been deformed in the brittle regime, with the aim to image grain shapes, position and stress during and after deformation. Our experiments include:

- serpentinization of olivine grains, in order to investigate the development of the serpentine mesh in 3D and find potential local stress amplification related to the volume change of reaction;
- static deformation of Fontainebleau sandstone samples in uni-axial compression until system-size failure, to investigate grain deformation and stress during loading;
- shockwave experiment with split-Hopkinson bars on a sample of Westerly granite, to detect possible residual strain resulting from the dynamic rupture.

Processing of the data allowed to map grain shapes and orientation and provides information about fracture mechanisms in the different experiments. However, further refinement is needed to correctly assess the presence of local stress concentrations and their amplitude. The goal of this presentation is to report these preliminary results and discuss the opportunities and challenges of 3DXRD for experimental petrology and investigation of natural geological samples.

Sub-solidus phase relations of FeO-rich peridotitic systems and thermodynamic parameter optimization of mantle phases: Implications for the Martian mantle

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The interpretation of seismic data from the InSight mission to Mars, with respect to its interior structure, largely depends on predicted mantle phase relations calculated using the thermodynamic model and database of [1,2] (SBL). Inspection of results of the few existing experimental studies on FeO-rich peridotitic compositions, supposedly relevant for Mars, however, shows discrepancies between modelled and observed phase relations, e.g. in the stability field of wadsleyite, or the relative proportions of ortho- and clinopyroxene as a function of pressure. It therefore seems pertinent to conduct additional experiments which can serve as basis for further refinement of the SLB databases.

We performed a series of sub-solidus multianvil experiments between 8-19 GPa on a variety of bulk compositions with different Mg/Si, Fe/Mg and Ca/Al ratios encompassing a wide range of proposed Martian bulk silicate compositions. Experiments were conducted in multi-chamber capsules with four bulk compositions run simultaneously to minimize experimental uncertainties. Run times lasted up to several days to achieve a close-to-equilibrium state. The experiments set tighter statistical contraints on the triple point of the $(Mg,Fe)_2SiO_4$ polymorphs, olivine, wadsleyite and ringwoodite and more closely reveal the systematics of the dissolution of pyroxene components into majoritic garnet. In the following step we employ a previously developed, and now updated, Bayesian algorithm [3] that permits the optimization of the SLB thermodynamic database in the light of the new experimental observations. We discuss some implications of the refined thermodynamic parameters for the seismic and geophysical properties of the Martian mantle.

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Hydrous melt partitioning in equilibrium with the lower mantle

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H_2O plays a pivotal role in generating partial melts in Earth's interior by drastically reducing the mantle solidus. The contrasting H_2O storage capacities in the Transition zone - Lower mantle minerals suggest a possibility of dehydration melting at the 660 km discontinuity [1]. Our project aims to elucidate the generation of an equilibrium melt in the MgO-SiO_2-Al_2O_3-FeO-CaO-H_2O system at the top of the lower mantle, refine the partition coefficients, and thereby constrain the composition at the onset of melting. The ultimate goal is to reconcile with geophysical anomalies reported in the lower mantle i.e. the low shear velocity zones [2].

We perform experiments using the multi-anvil apparatus at conditions near the geotherm at the top of the lower mantle (24 GPa, 1500°C). We imbibed an iterative approach [3] with a closed system of oxide mixture of a relevant starting melt composition [4] and model Pyrolite glass in predefined proportions. Their interaction synthesized a new incongruent melt coexisting with the lower mantle phases. We quantify the melt composition using *EPMA*, identify the co-existing phases with Raman spectroscopy, and image the chemical distribution using FIB-SEM. Mass balance allows us to determine the phase proportions and provisional partition coefficients. The new melt composition is introduced to the same pyrolite glass in the same conditions and the process is repeated until the partition coefficients do not vary in subsequent experiments. The philosophy is to pipette a hydrous melt in an infinite pool of lower mantle, such that it evolves over time until in equilibrium.

This method helps us monitor the melt evolution and eventually determine the absolute partition coefficients in natural lower mantle conditions. The sparse availability of robust chemical data at such extreme conditions due to experimental difficulties allows us to develop a formative fusion model on controversial volatile activity, melt chemistry and bridge the gap between contemplated geochemical and geophysical observations of the non-ubiquitous lower mantle.

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Sulfur in accessory phases as a redox monitor in volcanic systems

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The Laacher See volcanic complex (Eifel, Germany) is an extremely well-studied volcanic system in the centre of Europe [1]. Whilst the major and trace element composition of the Laacher See magma is well understood, there is less information on the volatile element concentration and the redox state of the magma.

Hauyne is a Na- and Ca-rich tectosilicate that contains several wt.% of S, but also significant amounts of Cl, and it is one of the most important mineral hosts for these elements. Furthermore, it can incorporate high concentrations of other petrogenetically relevant trace elements, and it also hosts recently discovered immiscible carbonatite melt inclusions [2].

We will present new geochemical and experimental data on the behaviour of S and other volatile elements in accessory mineral phases typical for the phonolites of the Laacher See. In this context, we will explore the stability of hauyne in a variety of silicate melts and we will also present trace element compositions of naturally occurring hauynes from the Laacher See volcanic complex. Furthermore, we will discuss how the concentrations and the speciation of volatile elements impinge on the magmatic redox history of the Laacher See complex.

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Experimentally constrained decarbonation and clast dissolution timescales in syn-eruptive magma-limestone interactions

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Magma-limestone interactions are well-known and documented at several volcanoes and probably need to be implied for all volcanoes resting on a limestone basement. Examples for such a setting include volcanic systems like Etna, Somma-Vesuvius, Colli Albani (all Italy), Merapi, Kelud (both Indonesia), Popocatepetl (Mexico) and Pacaya (Guatemala). The interaction between magma and limestones, often called carbonate assimilation, consists of 3 processes: i) the ingestion of limestones into a magmatic body (purely mechanical process), ii) the decarbonation, which describes only the release of CO_2 due to the high temperatures in magmatic systems, and iii) the dissolution of the ingested clast, which describes only the chemical dissolution of the ingested clast via diffusion or (partial) melting.

These interactions may happen on two distinctive timescales: long-term interactions, which take place in the magma chamber and last days to decades and more and short-term interactions which last seconds to hours (maybe days). The long-term interactions are well-studied from many different angles including experimentally, through gas geochemistry and through rock and mineral geochemistry. The short-term interactions instead are only studied experimentally at magma chamber conditions. For more superficial interactions (i.e., within the feeding dyke of an ongoing eruption) no data has been collected to date, even so they are evidenced in the field by the presence of limestone xenoliths within eruptive products.

Here we present the first experimental study on decarbonation and clast dissolution timescales during carbonate assimilation at atmospheric pressure. The experiments were designed to represent interactions at the second endmember of the volcanic plumbing system, Earth's surface. Within these experiments several experimental parameters were varied (e.g., temperature, magma composition, limestone composition, clast size) allowed us to identify the distinct controlling parameters of the decarbonation and clast dissolution process. While the timescale of decarbonation is mainly dependent on temperature, clast size and limestone composition, the clast dissolution process exhibits more diverse and interacting dependencies, but mainly depends on pressure and melt composition. Independent of the applied experimental constraints, the decarbonation process is a syn-eruptive process (i.e., happens in timescales between seconds to < 1 hour). This implies that magma-limestone interactions can rapidly release large quantities of CO_2 and thus alter eruptive dynamics towards a more explosive eruptive behaviour even if the interaction occurs during magma ascent within the feeding dyke of an eruption.

CO_2 diffusion in dry and hydrous leucititic melt

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Volatiles play a crucial role in the eruption dynamics of volcanoes. Volatile degassing and bubble growth upon magma ascent are controlled by the diffusivities of the volatile species that are dissolved in the silicate melt. Therefore, volatile diffusion data are crucial for understanding the eruption dynamics of volatile-rich melts.

We investigated the diffusion behavior of CO_2 in a leucititic melt from the Colli Albani Volcanic District in Italy using the diffusion couple technique. Experiments were conducted with an internally heated pressure vessel (IHPV) in the temperature range between 1200 and 1350°C at a constant pressure of 300 MPa. In order to study the influence of dissolved water on CO_2 diffusion, experiments were performed at nominally dry conditions (0.18 ± 0.03 wt.% H_2O) and at hydrous conditions (3.36 ± 0.28 wt.% H_2O). The experimental run durations were between 40 and 120 minutes and the experiments were terminated by rapid quench. CO_2 diffusion profiles in the glasses were measured via attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). The profiles were fitted with error functions from which CO_2 diffusion coefficients were obtained.

For the anhydrous and hydrous sample series, seven diffusion coefficients were determined each. CO_2 diffusivity increases exponentially with temperature for the anhydrous and hydrous melt following an Arrhenius behavior. In the experimental temperature range, dissolved H_2O has a strong accelerating effect on CO_2 diffusion. For instance, at 1200°C it increases CO_2 diffusion by almost one order of magnitude. The activation energies for CO_2 were determined to be 275 ± 47 kJ mol^{-1} for the anhydrous melt and 209 ± 58 kJ mol^{-1} for the hydrous melt.

At high magmatic temperatures above 1200°C, CO_2 diffusivity in the leucititic melt is only slightly lower than CO_2 diffusion in rhyolitic and basaltic melts. This supports the idea that CO_2 diffusion in natural melts is relatively independent from the bulk melt composition. CO_2 diffuses slower than other volatile components such as halogens and H_2O in depolymerized silicate melts. Thus, a fractionation of volatiles can occur during magma ascent and fast bubble growth. In such a case, CO_2 would be retained in the melt whereas fast diffusing species (e.g. fluorine) would be enriched in the vapor phase.

Chemical interactions between methane and iron at extreme conditions

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Compounds of planetary ices, specifically methane, and mixtures of methane and water, methane hydrates (MH), are believed to be present in a variety of planetary bodies, both within and beyond our Solar system. The presence of methane on exoplanets is regarded as a potential indicator of the presence of life and informs assessments of planetary habitability [1,2]. Consequently, the abundances of methane and methane hydrates are considered to be significant factors when modelling planetary evolution [3].

Despite this importance, the chemical behaviour of CH_4 and CH_4/H_2O in presence of other elements at the high-pressure and high-temperature (HP-HT) conditions relevant for planetary bodies is poorly understood. Possible chemical interactions between methane and methane hydrates with iron-bearing mantle silicates and iron-rich core materials might cause the formation of yet unknown compounds within the Fe-C-O-H system. An improved understanding of this system is thus crucial for the modelling of the interior composition, dynamics, and evolution of ice planets and exoplanets.

We studied the reactivity between iron and methane (as a model system) in a series of experiments performed at conditions from 10 up to 60 GPa and 1200(100)-3500(100) K in laser-heated Diamond Anvil Cells. Using in situ synchrotron single-crystal and powder X-ray diffraction (SC-XRD and PXRD), we observed that at conditions relevant for (exo)planetary interiors chemical interactions between methane and iron lead to the formation of a series of iron carbides (such as Fe_7C_3 and Fe_3C) and iron hydrides (dhcp-FeH, fcc-FeH_x). Our results imply that such compounds might form in the interiors of (exo)planets and, therefore, corroborate the necessity for further experiments to refine existing models for (exo)planetary composition and evolution.

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Iron isotopic fractionation during core formation in large terrestrial planets

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The Fe isotopic compositions of planetary mantles of differentiated inner solar system bodies exhibit a variability of which the origin is debated. The Earth and Moon have heavier-than-chondritic signatures with respect to other planetary bodies (*e.g.* Mars, Vesta) that have chondritic signatures [1]. Several processes could account for this variability, including volatile loss upon giant impacts, accretion with various degrees of nebular and post-nebular Fe loss in planetary building blocks, disproportionation of Fe^{2+} into Fe^{3+} and metallic Fe by bridgmanite crystallisation and deep mantle recycling processes. Core-mantle differentiation, as the largest mass transfer process that occurred on planets, is a potential contributor to Fe isotopic fractionation measured in planetary materials.

Changes in the structure of silicate melts and Fe-Ni alloys may have an effect on the Fe isotopic fractionation factor between them. Due to their different compressibilities, the proportion of Fe^{3+} relative to Fe^{2+} in equilibrium with metallic Fe changes with pressure, and markedly so above 7-8 GPa [2]. However, the Fe isotopic fractionation factor between molten metal and silicate has not been determined for pressures above 7.7 GPa [3], despite the fact that core formation on Earth, Mars and other terrestrial planets is thought to have taken place at significantly higher pressures. In order to quantify the influence of high-pressure core formation on the Fe isotopic variability among the terrestrial planets, we investigated the Fe isotopic fractionation between metal and silicate in the range of 2-17 GPa, and carefully studied the effect of pressure. In detail, these results contribute to clarifying the controls of core formation at high pressure on the variability of the Fe isotopic compositions observed in planetary mantles.

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Experimental equilibration and optical analysis of methane clumped isotopes relevant for hydrothermal vent settings

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Clumped isotope analysis of methane, $\Delta^{13}CH_3D$ and $\Delta^{12}CH_2D_2$, is a powerful tool for investigating the temperature and origin of hydrothermal fluids. However, the equilibration behavior of these methane isotopologues in presence of seawater is not well understood. This is exemplified by the Lost City hydrothermal vent fluids, where the $\Delta^{13}CH_3D$ values suggest methane formation temperatures of approximately 300°C, while the $\Delta^{12}CH_2D_2$ values indicate an extrusion temperature of 70 to 100°C, as measured independently at the white smoker hydrothermal vents [1].

In this study, we present an experimental and analytical setup for investigating methane in hydrothermal vent systems. Our experimental setup includes a hydrothermal Parr autoclave (50 cm^3) capable of reaching temperatures of up to 350°C and pressures of up to 200 bars, with internal leak-free stirring capabilities exceeding 800 rpm. This setup is connected to a custom-built fluid sampling and gas extraction system. We present first experimental results on methane isotopologues equilibration in a synthetic gas-seawater system with varying temperatures and seawater compositions.

We further demonstrate that clumped isotope measurements of methane with sub-permil precision can be achieved using a laser absorption method, which significantly reduces the measurement time to approximately 20 minutes relative to classical high-precision IRMS (1-2 samples/day) [2]. We present our calibration approach, which involves preparing reference gases over an activated γ-Al_2O_3 catalyst, to ensure reproducible results spanning a wide range of equilibrium temperatures and bulk isotopic compositions. Our study provides insight into the equilibration behavior of methane isotopologues and highlights the importance of the laser-based method for fluid-related geochemistry research.

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Water speciation and hydrogen isotopes in hydrous stishovite

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Stishovite, a high-pressure SiO_2 polymorph, is a main component of subducted oceanic crust at > 9 GPa and remains stable across a broad range of temperatures and pressures, spanning from the lower upper mantle to the lower mantle [1]. Its ability to store water makes it a potentially significant conveyor of water to the transition zone and lower mantle [2]. Previous multi-anvil studies have revealed that Al-free stishovite can absorb up to 3.2 wt.% water[3-5] (< 550°C, 10 GPa). A hydrogarnet substitution mechanism was suggested, wherein four H^+ replace one Si^{4+} in the tetragonal stishovite lattice. In-situ X-ray diffraction experiments on hydrous stishovite synthesized in a diamond anvil cell demonstrated a maximum of 3.5 wt.% water in stishovite, but also suspected diffusive water loss upon cell decompression, pointing to the presence of more mobile molecular water within the stishovite structure [2-6].

We produced hydrous stishovite from partially deuterated SiO_2 glass using a multi-anvil press at 450°C and 9 GPa, and then conducted ^1H NMR spectroscopy to analyze the water speciation. According to X-ray diffraction, our stishovite contained 1.5-2.0 wt.% water and led to a 0.4% unit-cell volume expansion. Although the hydrogarnet substitution mechanism cannot be ruled out by ^1H NMR, spinning sideband analysis revealed that most water must be stored as interstitial H_2O defects. The Raman spectroscopic D/H analysis of the system components suggested that deuterons preferred partitioning into the stishovite relative to coexisting water. Additionally, we present a capillary technique to recover and preserve the quenched fluid from the experimental capsule.

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Compression behavior of sintered, polycrystalline Fe-Al-bridgmanite studied in the diamond anvil cell

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Bridgmanite, the most abundant mineral in the Earth’s lower mantle, is a critical mineral for comprehending the complex dynamics and geochemistry of our planet’s interior. The crystal structure of bridgmanite allows for the substitution of iron for magnesium and aluminum for silicon in Earth’s lower mantle. This substitution results in significant changes in the crystallographic and elastic properties, including its equation of state [1,2]. Such changes affect the propagation of seismic waves [3] and result in the formation of seismic heterogeneities in the lower mantle. To explore the behavior of Fe-Al bearing bridgmanite, we pre-synthesized polycrystalline samples of bridgmanite with variable compositions using a large volume press at Bayreuth Geoinstitut (Bayreuth, Germany). The compression behavior was studied utilizing the diamond anvil cell (DAC) in combination with Synchrotron X-ray diffraction at the Extreme Conditions Beamline P02.2 Petra III at the German Electron Synchrotron facility, DESY (Hamburg, Germany). We will present and discuss preliminary results on compression behavior of pre-synthesized Fe-Al-bridgmanite measured at pressures from 10-75 GPa. Our results contribute to our understanding of the crystallographic and elastic properties and their implications for the dynamics and evolution of the Earth’s interior.

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The elastic properties of the Martian mantle

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Determinations of the seismic wave velocity structure of the Martian interior are becoming increasingly available from the SEIS seismometer on the NASA InSight lander. The interpretation of such data relies crucially on the ability to model the mineralogy and seismic velocities of the Martian interior in order to test plausible compositions and temperature gradients. The amount of iron present in Martian rocks, which is significantly higher than that observed in terrestrial settings, is expected to be the major cause of differences in the seismic signature of the Martian mantle with respect to the Earth.

The Martian mantle is dominated by $(Mg,Fe)_2SiO_4$ olivine at the top and by its high-pressure polymorphs wadsleyite and ringwoodite at the bottom. Analyses of olivine samples in the Gale crater of Mars by the Curiosity rover revealed an Fe content spanning from 0.5 to 0.8 atoms per formula unit (apfu). However, the elastic properties of olivine and ringwoodite with such compositions, as well as those of their Fe_2SiO_4 end-mebmers fayalite and ahrensite, are not tightly constrained. As a result, current mineral physics models of density and seismic velocities of the Martian mantle are subject to uncertainties that are higher than necessary.

In this study, high quality single-crystals of $Mg_{1.44}Fe_{0.56}SiO_4$ olivine and $Mg_{1.4}Fe_{0.6}SiO_4$ ringwoodite have been synthesised in a multi anvil apparatus and characterised using single-crystal X-ray diffraction, electron microprobe analysis and Mössbauer spectroscopy. Simultaneous Brillouin scattering measurements and single-crystal X-ray diffraction have been performed at high-pressure and room temperature in order to determine the elastic tensor of Martian olivine and ringwoodite compositions in a self-consistent manner, without having to rely on the use of a secondary pressure standards or previously determined pressure-volume equations of state. The elastic tensor at room temperature has been determined up to 11 GPa for olivine and up to 20 GPa for ringwoodite. Olivine is elastically anisotropic at room pressure and such anisotropy decreases only slightly with increasing pressure remaining very similar to the anisotropy determined for the forsterite end-member. On the contrary, ringwoodite appears elastically anisotropic at room pressure with a variation of v_S and v_P of ~ 400 m/s between minima and maxima. Such variation, however, decreases rapidly with increasing pressure reaching a value below 100 m/s already at 11 GPa. Moreover, whereas v_P increases rapidly with pressure, the maxima of the shear acoustic velocity remain practically constant, suggesting a very shallow slope of the shear modulus of ringwoodite with pressure. Further Brillouin measurements are being performed at the moment in order to constrain the elastic tensor of these minerals at high-pressures and high-temperature and the results will also be presented.

Thermodynamics, phase stability and melting relations of $MgSiO_3$ pyroxene polymorphs: new insights from ab initio calculations

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Pyroxene minerals are key to understanding the structure and composition of Earth and other rocky exoplanets interiors. Nevertheless, the full details of the $MgSiO_3$ phase diagram still remain unclear, in particular in the high temperature region. Protoenstatite (PEn) is one of the high temperature forms of $MgSiO_3$ pyroxenes, having stability range from 1200 to 1800K at ambient pressure. Its importance has been recognized by many authors, in fact PEn is regarded as a precursor phase of low-clinoenstatite (LP-CEn)/orthoenstatite (OEn) intergrowths in some cometary samples and in calcium-aluminum-rich inclusions (CAIs) from CV3 chondrites [1,2]. Moreover, PEn is the liquidus phase of pyroxene in the MgO-SiO_2 binary system. Nevertheless, very little is known about its thermodynamics, phase relations with other $MgSiO_3$ polymorphs and melting relations. This is due for the most part to its unquenchable nature, meaning that even if PEn can be synthetized at high temperature conditions, it doesn’t preserve as a metastable phase at ambient conditions since it rapidly reverts either to OEn, or into LP-Cen (very much like HP-clinoenstatite). The impossibility to perform measurements on samples of PEn prevents to obtain information on its thermodynamic properties, which are fundamental for the investigation of phase equilibria and melting relations. In that sense, ab initio DFT calculations based on quantum-mechanical theory are one of the most reliable methods available to obtain information on thermodynamics and phase relations of minerals at planetary conditions. We present a DFT based ab initio B3LYP computational study on $MgSiO_3$ PEn. All its relevant thermophysical and thermodynamic properties (e.g. isobaric heat capacity, vibrational entropy, thermal expansion, EoS) have been calculated in the framework of the quasi-harmonic approximation (QHA) by a full phonon dispersion calculation. We thus obtained original insights on PEn thermodynamics, as well as a complete set of both internally and physically consistent thermodynamic properties that are in good agreement with the few experimental data available. Computed properties have been tested by predicting relevant phase equilibria involving PEn up to melting conditions, in particular the OEn – PEn phase transition. The P-T location of the phase boundary and its Clapeyron slope (dP/dT = 2.04 MPa/K) are consistent with previous pyston-cylinder experiments [3,4]. Theoretical modelling of the melting curve of PEn in the $MgSiO_3$ phase diagram reveals a change of the melting behavior from incongruent to congruent before the onset of the solid-state OEn – PEn phase transition.

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Kinetic aspects of major and trace element partitioning between olivine and basaltic melt

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Olivine is one of the most important mineral phases in naturally cooled basaltic rocks. Its morphology and composition are controlled by the cooling kinetics, and the mechanisms controlling the crystal growth impact the partitioning of elements. Major elements composing a mineral usually affect the thermodynamic environment, while trace elements are sensitive to thermodynamic conditions and act as passive tracers of the chemical reactions occurring in the system without influencing the bulk reactions themselves [1]. Therefore, cations partitioning between two phases may document on the crystallization conditions of rocks.

Disequilibrium experiments were designed to explore i) the partitioning of major and trace elements between olivine and basaltic melt during solidification, and ii) cation substitution and the mechanisms of charge balance controlling their entrance in the crystal lattice. The effect of undercooling ($-\Delta T$) and cooling rate (CR) were tested on a Hawaiian tholeiitic basalt melted at 1 atm and QFM-2 oxygen fugacity. Experiments started from a superliquidus temperature of 1250°C and were cooled at the rates of 4, 20, and 60°C/h to the final temperature of 1175 ($-\Delta T$ = 35°C) and 1125°C ($-\Delta T$ = 85°C). Results show that the olivine texture shifts from euhedral (i.e. polyhedral texture) to anhedral (i.e. dendritic texture) as function of the undercooling during rapid crystal growth. Therefore, these morphologies indicate equilibrium at $-\Delta T$ = 35°C and strong disequilibrium at $-\Delta T$ = 85°C, also verified by the determination of the Fe-Mg exchange between olivine and melt. Low $-\Delta T$ experiments show bulk chemical equilibrium, while local equilibrium occurs at higher $-\Delta T$. The forsterite content decreases as CR increases and a diffusive boundary layer develops in the melt next to the crystal interface. Nonetheless, here is established a local equilibrium highlighted by the near-equilibrium incorporation of Mg, Fe, Mn, and Ca. At the T-site, Ti incorporation is controlled by a homovalent substitution ($\mathrm{TSi^{4+}}$) → ($\mathrm{TTi^{4+}}$), while heterovalent substitutions occur for Al and P, following ($\mathrm{MMg^{2+}}$, $\mathrm{TSi^{4+}}$) → ($\mathrm{MAl^{3+}}$, $\mathrm{TAl^{3+}}$), and (2 $\mathrm{TSi^{4+}}$) → ($\mathrm{TP^{5+}}$, $\mathrm{TAl^{3+}}$). Although Cr is an octahedrally coordinated cation, it shows the same behaviour as cations entering in the T-site. In fact, Cr is incorporated in the olivine lattice by forming a coupled substitution with a tetrahedrally coordinated cation ($\mathrm{MMg^{2+}}$, $\mathrm{TSi^{4+}}$) → ($\mathrm{MCr^{3+}}$, $\mathrm{TAl^{3+}}$). To preserve the charge balance, disequilibrium incorporation of minor elements is governed by the same mechanisms that occur under local equilibrium crystallization at the crystal-melt interface.

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Oxygen-enhanced magma generation in the Earth

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Oxygen, the most abundant element in the Earth, is distributed heterogeneously in the Earth's mantle and crust. Recently, we showed that oxygen abundance has a significant effect on magma generation at 1 atm [1,2]. Here, we experimentally determined the melting behaviour of a mid-ocean ridge basalt (MORB) composition and of natural peridotite KLB-1 at 2 GPa under buffered low and high oxygen fugacity (fO_2) conditions. Results indicate that MORB liquidus and solidus decrease by up to 180°C and the KLB-1 solidus drops by ~135°C as oxygen fugacity increases by ~1.5 log units at 2 GPa. This implies that oxidation of Earth's upper mantle can trigger the generation of large volumes of magma. Upward transport of proposed oxygen-enriched reservoirs in the deeper mantle can induce melting, increases in magma volume and increases in the oxygen fugacity of gases emitted from such magma. This provides a novel chemical, instead of thermal, mechanism for the formation of Large Igneous Provinces.

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Development of an artificial magma chamber in a one-atmosphere box furnace

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Upon conducting experimental research on crystal settling and related processes of cumulate formation, a necessity came to construct an efficient setup suitable for conditions up to 1400°C in a one-atmosphere box furnace, while avoiding the use of noble metal equipment. The novel setup [1] utilizes two commercially available materials and can be customized to sample or furnace size with few limitations and negligible requirements on material cost. Furthermore, the design allows easy extraction of samples from the capsule in one piece, making them eligible for textural analysis.

The setup is constructed of a graphite capsule, which acts as a sample container, and an outer fireclay shell providing heat resistant protective shield. The presence of fireclay blocks the graphite from direct contact with surrounding oxygen-containing atmosphere and therefore effectively prevents its ignition. The setup can be reliably used in temperature conditions below the heat tolerance limit of the commercial fireclay, commonly ~1400°C, and for run durations of up to 36 hours. Moreover, the presence of graphite buffers the oxygen fugacity inside the container to strongly reducing values ($\log fO_2$ values lower than -8.7 for 1400°C at 1 bar). The main advantage of our setup lies in the combination of easily accessible and low-cost materials with durability, versatile use, and easy production in larger quantities. The method is especially useful for studies of igneous textures and kinetics, but also has the potential for effective preparation of synthetic materials.

The method has been successfully employed during a study of magmatic suspensions, focused on mechanics of crystal settling and subsequent textural equilibration of mafic cumulates. The capsule served as an artificial magma chamber, where the suspension could have developed similarly to natural conditions. Following the quench, the run products were subjected to full-scale textural analysis in order to decipher the processes which took place during cumulate formation and equilibration.

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A new model of radiative thermal conductivity of olivine

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The thermal conductivity of olivine controls the thermal evolution of subducting slabs and thus phase transitions and associated devolatilization reactions. Two principal microscopic heat transport mechanisms contribute to the total thermal conductivity of olivine in the mantle: the lattice and the radiative mechanisms, which are both functions of pressure, temperature, and composition. Yet, most numerical models of slab heat up assume a constant value of lattice thermal conductivity of ~3 W/m/K and ignore the radiative component. The radiative thermal conductivity of olivine is determined by its absorption coefficient (opacity) in the infrared (IR) spectral range at high pressure-temperature conditions. Here we report on optical measurements of the olivine absorption coefficient up to 10 GPa and 1300 K. Our results suggest that the radiative thermal conductivity of olivine in subducting slabs may be as high as the lattice component (up to ~3 W/m/K), suggesting a more rapid devolatilization of subducting slabs. More generally, future numerical models of slabs thermal evolution must account for both lattice and radiative components.

Scapolites behavior at non-ambient (P,T)-conditions: the case of an intermediate scapolite

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Scapolites are a group of open-framework aluminosilicates with general formula $M_4T_{12}O_{24}A$, where M are monovalent or divalent cations (usually Na, Ca and minor K), T are trivalent or tetravalent cations (mostly Al and Si) in tetrahedral coordination, and A are anionic elements or groups such as Cl, CO_3 and SO_4. Samples with a composition closer to the $Na_4Al_3Si_9O_{24}Cl$ and $Ca_4Al_6Si_6O_{24}CO_3$ end-members are usually reported to crystallize with a structure described in the *I*4/*m* space group, whereas intermediate members are reported to show a $P4_2/n$ symmetry. Scapolites are usually formed under metamorphic conditions in the presence of fluids, but are also reported as constituents of upper mantle xenoliths [1,2]. Scapolites form a complex non-binary solid solution as a function of the (NaCl)-($CaCO_3$)-($CaSO_4$) substitutions, which couples with Al-Si re-arrangements [3,4]. The variable crystal chemistry of these minerals influences their elastic and structural response to pressure and temperature variations and, consequently, their stability fields. In this study, we have investigated the behavior of an intermediate scapolite of the composition $(Na_{1.86}Ca_{1.86}K_{0.23}Fe_{0.01})(Al_{4.36}Si_{7.64})O_{24}[Cl_{0.48}(CO_3)_{0.48}(SO_4)_{0.01}]$ and its unusual symmetry *I*4/*m*, by means of in situ X-ray and neutron diffraction at high-T (from -100 to +1000°C), high-P (up to 17.8 GPa) and combined high-T and P (up to 650°C and 16 GPa). Experimental data show that the unusual *I*-centered lattice is always preserved, whereas a phase transition towards a triclinic polymorph was found to occur at 9-10 GPa, with a modest influence from temperature. The deformation mechanisms, acting at the atomic scale, that lead to the structural instability and phase transition have been described on the basis of a series of single-crystal structure refinements. A comparison with data from literature allows to model the elastic response of scapolites as a function of their crystal chemistry, whereas a model of the thermo-elastic behavior is less straightforward on the basis of the available data, suggesting that a thorough re-investigation of the thermal behavior of the complex scapolite solid solution is desirable.

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In-situ spectroscopy as a key to unlock the properties of high P-T fluids

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High-pressure high-temperature (PT) fluids that form through the devolatilization of rocks and magmas display a wide range of composition and properties depending on their source and depth of formation. High concentrations of Cl, S, F, phosphate or carbonate, as well as changing volumetric properties often make them much better solutes than pure H_2O and thus key actors of the chemical transfer between different reservoirs. Yet, their high PT composition and properties are difficult to assess based on natural samples that are both scarce and prone to chemical reequilibration. Experimental investigation through conventional 'quenched methods' is also challenging due to back reactions from high P-T to room conditions.

In-situ spectroscopy has thus established itself as the only direct approach to investigate the composition and properties of geological fluids directly at the high P-T conditions relevant for the study of magmatic or metamorphic processes. In the last 20-30 years, it has for instance been successfully used to identify new volatile and metallic species in ore-forming fluids [1-3] and determine the PVTX properties or transport capacity of lower crustal and subduction zone fluids [4-7]. The sum of these

experiments has and continues to help in building new thermodynamic models that are adapted to simulate fluid-rock-magma interaction in hot and pressurized environments [8].
In this talk, I wish to present the technical challenges encountered to study hydrothermal, magmatic or subduction zone fluids via in-situ spectroscopy. Those include the choice of apparatus that can generate variably extreme conditions (low P-T, high T but moderate P, high P but moderate T, etc.), the choice of adequate 'transparent' windows for different analytical techniques, and detection limits associated with each technic. After brief examples of how we can use hydrothermal diamond-anvil cells and autoclaves to assess the properties of subduction zone and ore-forming fluids, I will focus on the development of a novel IHPV that enables in-situ Raman and X-ray absorption (XAS) spectroscopy measurements to 600-1200°C and 2kbar and opens new opportunities to study the fate of volatiles and metals during magmatic degassing.

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Evolution of carbonatite and silicate melts stable at the same pressure and temperature conditions in the mantle

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Carbonatite melts can be generated and migrate through the astenosphere and lithosphere, causing metassomatism [1], where they can evolve in to carbonate-silicate magmas by reacting with the mantle [2]. Experimental studies suggest that some silicate melts primary composition like kimberlite can form by carbonated melt that reacts with the lithosphere and evolves carbonate-silicate melts [3], during the consume of the mantle, a carbonate-silicate melt can undergo an immiscibility event that creates two liquids, one carbonatitic and another silicatic [4]. In more detail, Na-dolomitic melts are considered to react with the shallow mantle, transforming lherzolite or hazburgite in to wherlite by consuming orthopyroxene and generating sodic clinopyroxene [1]. In this experimental petrology study we sought to determine primitive melt compositions of ultramafic magmas derived from carbonate-silicate melts and its phase relations in the presence of water in mantelic conditions, with alkalis content, in addition, determine the amount of silica and carbon this melts can dissolve and its implications for carbon budget in deep earth and its transportation in mantelic environments. Two mixtures (C-K 10/90 and C-K 30/70) with different carbonatite and kimberlitic components proportions were prepared, loaded in an Au-Pd capsule and processed in toroidal types press under varying conditions (4 to 6 GPa, 1200-1300°C), the experiments were analyzed using SEM-EDS for semi-quantitative investigation, EMPA for quantitative compositions determination and Raman spectroscopy for phases confirmation. 9 experiments were made, preliminary results showed the stability of calcic-magnesian carbonate-silicate melts in equilibrium with wherlitic mineral compositions in both mixtures under litospheric conditions (4GPa, 1200°C), where increasing temperature leads the C-K 10/90 melt to increases silica content and trend to lamprophyre compositions, while the C-K 30/70 melt decreases in silica and maintains calcium and magnesium rich carbonatitic composition. At 4 GPa both proportion experiments show melts as separated phases and as melt inclusions with different geochemical signatures in olivines. The study remains in data interpretation phase as off this submission.

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H_2O degassing experiments of the lower Laacher See Phonolite

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The Laacher See volcano is one of the youngest volcanoes in Germany with its last eruption 13,006±9 years BP [1]. About 6.3 km^3 of phonolitic magma was explosively erupted by phreatomagmatic and plinian eruptions in less than 10 days [2]. The eruption behavior of such volcanic systems is determined by the phase separation mechanism of H_2O fluid from the supersaturated hydrous silicate melt, caused by pressure decrease of the magma. The number of fluid vesicles per unit volume of silicate melt (VND) is a standard parameter used to quantify the efficiency of fluid-melt separation and thus the acceleration of magma ascent. Two important homogeneous vesicle formation mechanisms are established in the investigation and evaluation of the degassing behavior of silicate melt systems. According to the classical nucleation theory, the VND increases strongly with decompression rate [3] and is therefore a proper parameter for quantifying ascent rate. Recently and specifically for phonolitic melts, the process of spinodal decomposition has been demonstrated, which manifests in the independence of VND from the decompression rate [4].

To characterize the degassing behavior of the lower Laacher See composition, systematic decompression experiments were conducted in the internally heated pressure vessel. The melts were hydrated with 5.7 or 5.0 wt.% H_2O at 200 MPa and 1523K for 96 h and then continuously decompressed at 1323K with

0.064-1.7 MPa/s to final pressures between 110 MPa and 40 MPa. By reaching the final pressure, the samples were rapidly quenched to room temperature to preserve the vesicle textures and the residual H_2O contents in the melts and to minimize vesicle shrinkage until the glass transition temperature was reached. The VNDs and the spatial distribution of the vesicles, as well as the H_2O contents in the decompressed melts were analyzed with quantitative BSE image analysis, transmission light microscopy, and FTIR-spectroscopy.

Upon reaching sufficient supersaturation pressure, all samples exhibit homogeneously dispersed vesicles in the sample center, with vesicle sizes ranging from 2 to 13 µm in diameter. Preliminary results indicate that VND is independent of decompression rate at all decompression rates. Irrespective of the decompression rate, high logVNDs of 4.5 to 5.5 mm^{-3} are observed. These observations are consistent with that of Allabar and Nowak [4], who determined a logVND of ~5.2 mm^{-3} for hydrous phonolitic melt of the AD 79 Vesuvius white pumice composition. From this, a trend emerges that at least for hydrated phonolitic melt, spinodal decomposition plays a crucial role in the degassing behavior of the melt and thus in the explosive eruption behavior of the volcanic systems.

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The stability of cinnabar (HgS) and its liquid structure at HP-T: implications for the mobilization of Hg during magmatic events

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Mantle-derived primitive melts are the main carriers towards the Earth's surface of both volatiles (e.g., CO_2, H_2O, SO_2) and trace elements some of which are widely employed as geochemical tracers of magmatic processes. Among the trace elements, magmatic Hg is of particular interest since in the last decade it has been widely used as geochemical marker in the sedimentary record for Large Igneous Provinces (LIPs), which have been considered the major cause for Phanerozoic mass extinctions [1]. To date, however, no experimental studies have addressed the mechanism of Hg mobilization from the mantle source to the atmosphere. Only few geochemical studies on both meteorites and peridotite xenoliths exist that indicate sulfide minerals as the main hosts of Hg.

In this study, we investigated 1) the equation of state and melting behavior of cinnabar (HgS) up to ~ 6 GPa between 1200 and 1300°C and 2) the atomic liquid structure up to 1600°C.

Cinnabar crystals with a negligible amount of quartz were selected from the MUST collection (Sapienza University of Rome, Italy) and used as starting material. The experiments were performed by the VX5 Paris-Edinburgh press combined with angle dispersive X-ray diffraction at beamline 13-ID-C (GSECARS) of the Advanced Photon

Source, Argonne National Lab (Chicago, USA; [2]). The incident monochromatic radiation at ~42 keV was double-focused, allowing structural measurements of liquids to be performed at high temperature and pressure over 5 to 10 minutes.

In contrast to previous literature data reporting sublimation at high T and room P, we successfully observed melting of cinnabar at HP-T. Preliminary results shed light on different compression mechanisms upon increasing pressure at different temperatures both in the intermediate-range ordering (i.e., the structure factor, S(q)) and in the local structure (i.e., pair distribution factor, G(r)) of the liquid with respect to available data referred to liquid Hg and FeS [3,4].

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A general approach to quantify phase equilibria and silicate mineral stability in calc-alkaline basaltic systems

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Despite recent developments, the influence of chemical and physical parameters on magmatic phase equilibria still requires further research to understand the formation and evolution of igneous rocks. As the "in-situ" study of magmatic processes is only possible to a limited extent at active volcanoes, igneous petrology predominantly relies on the analysis and interpretation of solidified magmatic products and their crystal cargo. As a consequence, a huge variety of petrological tools has been developed over the last years that have been widely applied to plutonic and volcanic rocks to reconstruct magmatic processes (e.g. thermobarometers). However, resultant data are frequently of only limited validity due to significant uncertainties. Moreover, such models are often interdependent meaning that the derivation of individual parameters is challenging, which further complicates their application to natural rocks.

The prediction of phase equilibria is particularly complex for calc-alkaline systems, because water and oxygen fugacity vary over wide ranges. This contribution is an attempt to fill this gap by providing new experimental data exploring systematically the effects of temperature, pressure, magma composition, H_2O, and fO_2 on phase equilibria in calc-alkaline basaltic systems. We extended existing high-pressure (400-900 MPa) experimental datasets on a high-Mg basalt from the Adamello Batholith (Italy) and a high-Al basalt from the Cascades (U.S.) to upper crustal pressures. Crystallisation experiments were run in internally heated pressure vessels (IHPV) at 200 and 400 MPa and varying H_2O contents (0-9 wt.%) with fO_2 conditions buffered between NNO+1 and NNO+2.3.

Beside changes in mineral assemblages, we established the role of crystallisation parameters on silicate mineral chemistry (e.g. for olivine, clinopyroxene, orthopyroxene, and plagioclase). We combined our results with high-quality experimental data from literature to formulate empirical mineral saturation models for olivine, plagioclase, and clinopyroxene predicting the saturation of these phases as a function of bulk system composition, pressure, temperature, H_2O, and fO_2. Furthermore, employing our data compilation, we test existing mineral-based thermobarometers to provide some general insight on the limitations of these petrological tools and present some recommendations on their application to natural rocks.

Anelasticity of HCP magnesium alloy as an analogy for the inner-core

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Once believed to be a homogeneous sphere, the complex attenuation of body waves in the inner-core reveals a complex anisotropic structure which varies laterally and vertically. Seismic waves passing through the inner-core attenuate at rates greater than predicted by geometric spreading and much of this attenuation is inferred to be a result of intrinsic anelastic properties. However, current models of the inner-core assumed the Earth is almost perfectly elastic, and have been unsuccessful in satisfying all geophysical and experimental observations. There is limited existing literature on anelasticity in hexagonal close-packed (HCP) metals, where present it is typically at frequencies too large to be comparable with seismic waves. Anelastic dissipation is predicted to be present in most materials below their yield strength, as a time-dependant, mechanically recoverable response which results in a phase lag between stress and strain. Despite its significance relatively little is known about the atomistic processes that control anelasticity. Iron in the solid inner-core is believed to be HCP, diluted with ~10% nickel and a few percent unknown light elements. HCP iron is only stable above 12 GPa making experiments difficult. Therefore using the magnesium alloy, AZ31, as a low pressure analogue, we performed dynamic mechanical analysis (DMA) under high temperature conditions. DMA applies sinusoidal strains to samples at frequencies between 0.1 to 100 Hz and measures the repose of the samples. The inverse quality factor was calculated from the phase lag between stress and strain, characterising dissipation. These results show that the AZ31 HCP alloy is anelastic at seismic frequencies. Microstructural evolution was monitored using EBSD to infer potential anelastic accommodation mechanisms. Gaining an understanding of anelasticity and anelastic accommodation mechanisms in HCP metals enables improved modelling of the inner-core from seismic data, graining new insights into its properties and behaviour.

Experimental constraints on the conditions of formation of ferropericlase inclusions in diamonds

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Ferropericlase, (Mg,Fe)O is the second most abundant mineral in the Earth's lower mantle and is found in ~50% of superdeep diamonds where often it shows evidence of exsolution of a spinel ferrite phase ($M^{2+}Fe^{3+}{}_2O_4$). In order to understand both the conditions at which the ferropericlase inclusions formed and those at which the spinel-ferrite exsolution developed, several experiments

were performed both at room and at high pressures up to 30 GPa, with starting materials composed of mixtures of ferropericlase having different Fe^{2+} contents plus hematite. Pt metal also was added to the starting materials to act as oxygen fugacity sensor. Several of the recovered ferropericlase samples contain nanocrystalline topotaxial exsolutions of spinel-ferrite which have been carefully characterized by means of transmission electron spectroscopy. Such type of exsolutions are present even in ferropericlase crystals which are in equilibrium with high-pressure Fe,Mg-oxide phases. These exsolutions have a characteristic magnetic signal in the Mössbauer spectra and their Fe^{3+}/Fe_{tot} ratio can be recombined with that still present in the quenched ferropericlase in order to obtain an estimate of the Fe^{3+} content present in ferropericlase at high-pressure and high-temperature. The results have been used to construct a thermodynamic model for determining the Fe^{3+}/Fe_{tot} ratio of ferropericlase as a function of composition, pressure, temperature and oxygen fugacity. The Fe^{3+}/Fe_{tot} ratio of ferropericlase in equilibrium with spinel ferrite increases slightly with pressure. Above 10 GPa, however, when the coexisting phases are either $[Fe^{2+}, Mg]_2Fe^{3+}{}_2O_5$ or $[Fe^{2+}, Mg]_3Fe^{3+}{}_2O_6$, the Fe^{3+}/Fe_{tot} ratio in ferropericlase declines rapidly. This suggests that ferropericlase inclusions in diamonds with Fe^{3+}/Fe_{tot} ratios larger than 0.1 have unlikely originated in the Earth’s lower mantle.

Basaltic andesite derived by mantle melting beneath Kluchevskoy volcano, Kamchatka

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It is commonly accepted that starting point for subduction zone magmatism is partial melting of mantle wedge peridotite fluxed by fluids derived from the subducted slab. Although Mg-rich basalt is one of the most common products of this type of mantle melting, a variety of other mantle-derived primitive arc magmas, ranging in composition from high-Mg andesite to picrite, has been recognised based on geochemistry and experimental petrology [e.g. 1]. This variety reflects changes in the thermal state of the underlying mantle wedge and the supply of water from the slab. Understanding source depth of primitive magmas has implications for thermal modelling of subduction zones and interpretation of geophysical data.

Several strategies can be utilized to constrain the depth from which a given magma was sourced. Here we use experiments to determine the point of multiple saturation on the liquidus of an erupted magma. An experimentally-constrained multiple saturation point defines the pressure and temperature at which the erupted melt could be extracted from a polymineralic source rock, such as mantle peridotite.

Kluchevskoy is one of the most active volcanos on Earth, yielding roughly biannual eruptions of predominantly basaltic andesite magmas. This compositional consistency of erupted magmas suggests buffering of the magma composition either by mantle or crustal lithology. To explore the conditions of magma generation beneath Kluchevskoy

we used inverse experimental approach to constrain multiple saturation point on the liquidus surface of high-MgO basaltic andesite (KLU-96-03, [2]).
Equilibrium piston-cylinder experiments were carried out between 0.5 and 1.0 GPa under hydrous (3 and 6 wt.% H_2O) conditions at DNNO+1. We show that high-MgO basaltic andesite is multiply saturated with lherzolite assemblage (ol (Fo_{90}) + cpx + opx + Cr-spinel) close to its liquidous (melt fraction ≥ 90) at 0.60±0.05 GPa (23±2 km depth) and 1220-1240°C. Thus, experimental results indicate that high-MgO basaltic andesite was produced by partial melting of peridotite source and a primary, undifferentiated magma. These results are in a good agreement with geophysical studies of Kluchevskoy that show magmas are supplied directly from a reservoir at a depth of 25-30 km through a nearly vertical pipe-like conduit [3]. These results provide a tight constraint on the thermal structure of the mantle wedge beneath Kluchevskoy. The mantle wedge temperature obtained in these experiments are higher than typical temperatures used for thermal models [e.g. 4] suggesting that upwelling asthenosphere might directly impinge the Moho in a similar fashion to mid-ocean ridges.

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Effect of iron on the elastic behavior of mantle monosulfide solid solution

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Monosulfide solid solution (mss), with a metal-to-sulfur ratio of 1:1, is a significant sulfide phase in the upper mantle and commonly hosts elements such as Fe, Ni, Cu, and Co. It forms wide solid solutions and is unstable in all compositions in crustal environments, as evidenced by paragenetic assemblages in mantle rocks, meteorites, and inclusions in diamonds (i.e. pyrrothite, pentlandite, chalcopyrite). However, high-pressure and high-temperature (HP/HT) synthesis can stabilize the end-member of this solid solution. In this study, we report on the HP/HT synthesis (multianvil press, 5 GPa, 750°C) of Fe-Cu mss (Fe0.8Cu0.2S) and Ni-Cu mss (Ni0.8Cu0.2S) and their characterization using electron microprobe and single crystal diffraction (laboratories at the Department of Earth Sciences, University of Milano). We then investigate the compressibility of these two synthetic minerals using diamond anvil cell and synchrotron X-ray radiation up to 15 GPa with He as a pressure transmitting medium. Our results indicate that Fe-bearing mss exhibits an elastic anomaly, with an increase in compressibility up to around 6 GPa and significant volume contraction, likely due to high to low spin electronic transition in Fe. Similar anomalies are also detected in natural pyrrothite. In contrast, Ni-bearing mss (Fe-free system) does not exhibit such anomaly. These findings demonstrate that sulfides, particularly Fe-bearing mss, exhibit electronic transitions detectable within an accessible P-T range. Further research is needed to determine the exact P-T bracketing of this electronic transition and its implications for the thermodynamic stability and magnetic properties of these materials at planetary conditions.

The oxidation state of copper in silicate melts

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Copper is one of the most critical elements in enabling green technologies. Copper is redox variable and may occur as Cu^0, Cu^+, and Cu^{2+} in the Earth's crust. The oxidation state will affect its partitioning between coexisting minerals, melts and fluids and hence its behaviour in magmatic processes. To investigate how the oxidation state varies, copper bearing silicate glasses were quenched from 23 melt compositions (21 synthetic CaO-Na_2O-K_2O-MgO-Al_2O_3-SiO_2 compositions, an Fe-bearing synthetic basalt and an Fe-bearing synthetic andesite) equilibrated at oxygen fugacities (fO_2), expressed in log units relative to the fayalite-magnetite-quartz (FMQ) buffer, ranging from -0.7 to 14, temperatures from 900 to 1500°C and pressures from 0 to 2.5 GPa. Cu *K*-edge X-ray absorption near edge structure spectra were recorded from the glasses and a pre-edge feature was found to scale with the proportion of Cu^+. Cu^+/Cu_{Tot} (where $Cu_{Tot} = Cu^+ + Cu^{2+}$) was quantified by fitting the intensity of the pre-edge feature as a function of fO_2 to the thermodynamically expected relationship. Cu^+/Cu_{Tot} was found to only weakly depend on melt composition, with more basic melts (e.g., a basalt rather than a granite) preferentially stabilising Cu^{2+}. Increasing temperature stabilises Cu^+, while increasing pressure had little effect on Cu^+/Cu_{Tot} in basaltic melts but preferentially stabilised Cu^{2+} in granitic melts. Cu^+/Cu_{Tot} can be predicted in silicate melts by the empirical equation:

$$\log(Cu^{2+}/Cu^{+}) = 0.25(\Delta FMQ + 8.58 - 25050/T + 940P/T - 0.02P) - 4.73 + 5400/T + 1.99*\Lambda + (280P - 90P^2)$$

where T is temperature in K, P is pressure in GPa and Λ the optical basicity of the composition. The effects of fO_2, melt composition, temperature and pressure on Cu^+/Cu_{Tot} indicate that Cu^+ will be the dominant oxidation state in terrestrial silicate melts.

Latent heat as a probe for binary phase diagrams

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Multi component, high pressure (P) and temperature (T) phase diagrams, are a fundamental tool to understand the processes taking place in planetary interiors. In metallic Fe-bearing systems, the first phase to crystallize when cooling, and its properties relative to the remaining liquid, controls the dynamic of planetary cores, with important implications for magnetic field generation. Numerous studies have been dedicated to the study of metallic alloys at high pressure and high temperature, using a variety of experimental apparatuses and analytical techniques. However, for pressures above about 25 GPa, the intrinsic limitations of the laser heated diamond anvil cell technique have resulted in widely diverging results and often give access only to solidus temperatures. Recently, pulsed joule heating calorimetry at the microsecond scale, coupled with a new system for temperature measure based on a photomultiplier tube array, has produced outstanding results to identify the melting curves of Pt and Fe. Using latent heat plateaus as a thermodynamic criterion to identify melting has been demonstrated to be a reliable technique [1], and the very short time scale of each pulse prevents damage of the sample. This new approach to measure temperatures works across a wide range of temperatures and with extreme precision (reported error of +/- 40K at 80 GPa, instead of the average +/- 150K for standard laser heating experiments).

Here we report the application of this novel technique to binary Fe-bearing alloys. We will present data collected on two compositions with different carbon content in the binary Fe-C system and in a pressure range between ambient and 60 GPa. Our preliminary results display the existence of different features in the temperature-time plots. In some cases, plateau-like features are observed, while in others only changes in the steepness of the curve. Double plateau-like features in some temperature-time plots are also observed. The temperatures of the observed features were often consistent with those predicted for the Fe-C phase diagram by Lord et al. [2]. We hypothesize a dependency of the observed features on the composition of the starting material. Additionally, using a thermodynamic criterion to detect melting might provide the possibility of identifying both the solidus and the liquids temperatures, hence the observation of double plateau-like features in the same curve. If our hypotheses are confirmed, this novel approach would permit mapping melting phase relations of metallic alloys at extreme conditions with unprecedented precision.

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Development of new methods to track magma degassing and fluid fluxing in complex magmatic systems: The study of heavy halogens

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Magma degassing and fluid fluxing within trans-crustal magma reservoirs play an important role in the transport of volatile elements and ore metals. Tracking the migration of magmatic fluids within such systems is challenging, yet important for the understanding of magmatic-hydrothermal ore genesis and volcanic degassing.

We aim to develop new geochemical tools to track magma degassing and fluid fluxing over a broad melt composition range. We hypothesize that halogen ratios may be useful for this purpose because previous studies have found that the fluid/melt partition coefficients ($D^{f/m}$) of halogens significantly increase with increasing halogenide ion radius [1-3]. However, the data available on Br and I partitioning is limited; therefore, we are experimentally studying the $D^{f/m}$ of halogens as a function of melt composition, pressure, and fluid salinity.

The experiments realized so far were conducted at T = 785°C and P = 150 to 500

MPa. We used synthetic peralkaline, metaluminous and peraluminous haplogranitic starting glasses and starting fluids with 7 different salinities. The experiments were performed in rapid-quench externally heated René 41 and Molybdenum-Hafnium Carbide (MHC) pressure vessel apparatuses, as well as an end-loaded piston cylinder apparatus with a 19.05 mm diameter assembly.

Halogen concentrations in the run product glasses were determined by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the University of Geneva and will shortly be confirmed using Secondary Ion Mass Spectrometry (SIMS) at the SwissSIMS facility. The concentration of halogens in the equilibrium fluids was then estimated by mass balance calculation allowing us to determine the $D^{f/m}$ for Cl, Br and I as a function of fluid salinity, confining pressure and melt composition. In average, the $D^{f/m}$ of Br and I are 3 and 5 times higher than that of Cl, respectively. The $D^{f/m}$ of all three studied halogens increases by a factor of 3 to 8 with fluid salinity increasing from 0.5 to 32 molal. Moreover, the effect of pressure on the $D^{f/m}$ of halogens depends on the salinity of the fluid phase. With increasing pressure at low-fluid salinities, all three halogens partition stronger towards the fluid phase, but the opposite trend was observed at high-fluid salinities. This difference can be rationalized by taking the much lower compressibility of high-salinity fluids into account. Overall, our results up to date indicate that I/Cl and Br/Cl ratios in the silicate melt will decrease during progressive magma degassing, with the I/Cl ratio being more sensitive and thus more applicable during the early stages of magma degassing, and Br/Cl being well-suited to address crystallization-driven degassing in more crystalline/felsic systems. The I/Cl ratios may serve as a sensitive indicator of fluid fluxing.

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The electron diffraction pattern of a quenched davemaoite at ambient conditions. The volume at ambient pressure

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The precise volumes of high-pressure minerals at ambient pressure (V_0) are important for quantitative discussions in mineral physics. The recovered high-pressure samples are used for the further physical and chemical measurements, even though they are metastable at ambient conditions. Calcium-rich perovskite, davemaoite (Dvm) is often unquenchable to ambient conditions, but a small amount of Dvm was identified by X-ray diffraction and nuclear magnetic resonance (NMR) spectroscopy in samples recovered from 15 GPa and 1500°C [1]. In the recovered Dvm, the existence of the reflections could not be indexed with the cubic unit cell, indicating that the symmetry of the Dvm is lower than cubic [2]. To clarify the mechanisms of the presence of Dvm at ambient conditions, we investigate recoverable Dvm and its symmetry at the sub-micrometre scale by using conventional transmission electron microscopy (TEM). We present for the first time a selected area electron diffraction

(SAED) pattern of Dvm coexisting with Al, Fe-bearing bridgmanite (Bdm).

A high-pressure assemblage of Dvm and Bdm phases was synthesized at 40 GPa and 2000°C for 24 hrs, by using a Kawai-type multianvil apparatus. A thin TEM foil of the recovered sample was prepared with a focused ion milling machine. In bright-field TEM images, submicrometric-sized crystalline Dvm domains exist within an amorphized domain transformed from the precursor of a Dvm grain. From the SAED pattern of Dvm, we have confirmed that the space group (S.G.) of $Pm\bar{3}m$ and evaluated the lattice parameter of ***a*** (cubic) = 0.356 nm (V_0 = 45.12 Å^3). The obtained lattice parameter of Dvm is comparable with the literature data that the lattice parameters at 0 GPa were estimated as ***a*** = 0.3572 nm (V_0 = 45.576 Å^3) [3] and 0.358 nm (V_0 = 45.88 Å^3) [4]. The lattice parameter of Dvm, 0.356 nm in the present study is larger than 0.351 nm, calculated from a half of ***c*** (orthorhombic) = 0.702 nm in the coexisting Bdm (S.G., *Pbnm*), based on the relation that 1/2 ***c*** (orthorhombic) = ***a*** (cubic) in the orthorhombic perovskite structure. The mechanisms to prevent the complete amorphization of Dvm on the decompression should be explained from the microtextures displaying a remaining crystalline domain of Dvm at the core part and amorphous domains at the rim. The significant volume expansion due to the amorphization of Dvm induces static stress which prevents the complete amorphization, as the same mechanism as the reported in the presence of bridgmanite in meteorites [5].

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Silicon partitioning between iron-rich metal and silicate melt: new constraints from aerodynamic laser levitation furnace experiments

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The partitioning of light elements (e.g., Si, C, H, etc.) between silicate melts and iron metal alloys as a function of pressure and temperature is a critical constraint in defining the compositional evolution of planetary interiors. While there are a significant number of experimental studies in the literature [e.g., 1-3, and references therein] that examine the various influences of oxygen fugacity, temperature, pressure, and composition on the metal-melt partitioning of silicon, it is difficult to disentangle the effects of each variable due to the nominally independent parameters (e.g., pressure, temperature, composition) being collinear. To better test for the independent effects of pressure, temperature, and melt composition on the partitioning of silicon between iron alloy and silicate melt, new high temperature (1800-2500°C), rapid quench (~700°C/s) aerodynamic levitation laser-heating experiments in the Fe-Si-Mg-O (En_{65}-Fa_5-

Si_3-Fe_{27}) system were conducted. This high temperature, low pressure method is ideal for these experiments because it eliminates the metal container as a sink for elements of interest to partition into, and it has a rapid quench rate that minimizes potential exsolution of silicon from the metal phase during quench cooling. Given the short run times of the levitation experiments (30-60 seconds), a time series at a lower temperature (1700°C) in a vertical gas-mixing muffle tube furnace was also conducted to assess equilibrium times of the bulk composition. All successful runs were imaged using back-scatter electron imaging and analyzed for phase composition using a JEOL 8530F field emission microprobe. These new data were added to a comprehensive and internally consistent data set created from published experiments, and subsequently modeled using parameters designed to minimize collinearity (e.g., optical basicity is used as a proxy for melt composition). High collinearity is found in the data set however between temperature and oxygen fugacity, precluding any model that contains both as nominally independent variables. The resulting model demonstrates a statistically significant effect of pressure, temperature, and melt composition on the partitioning of silicon in Fe-rich metal, which has implications for the formation of planetary cores in rocky planets and provides important constraints on potential bulk core compositions.

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Development of internal pressure standards for in-house elastic wave velocity measurements

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Laboratory wave velocity measurements constitute a powerful tool to determine the equations of state (EoS) of mantle minerals and to better understand the complex structure of the Earth's mantle. Ultrasonic interferometry has been adapted to a range of large-volume presses in recent years: Griggs apparatus [1], piston-cylinder presses [2], Paris-Edinburgh cells [3] and more generally multi-anvil presses (whether Kawai-type, DIA-type, D-DIA type or 6-ram Hall-type). Typically, a $LiNbO_3$ piezoelectric crystal (transducer) is attached to the back of an anvil and is used to simultaneously send compressional (P-) and shear (S-) waves that travel from the anvil to the sample through an alumina buffer rod (BR). Due to acoustic impedance contrasts between materials, elastic waves are reflected along interfaces, producing echoes that return to the piezoelectric crystal. The transducer acts not only as an emitter but also as a receiver, it thus produces electric pulses for each reflected echo that is captured. The time difference between two successive echoes gives the two-way travel time of elastic waves within materials of interest.

An accurate determination of pressure is necessary to analyse and extrapolate the collected data. Ultrasonic interferometry is thus essentially used in combination with synchrotron radiation, enabling the in-situ determination of pressure and sample height from X-ray diffraction (XRD) and radiography. These equations of state, if well known, can also be used the other way around, to expand the use of acoustic techniques to in-house experiments and to develop internal pressure standards.

Previous attempts calibrated the travel times of P- and S-wave through the alumina BR of certain assemblies [4]. This parametrization is, however, limited to identical assemblies. Here, we present a novel travel time cross-calibration method, using P- and S-wave travel times within a reference material of known EoS that would replace a backing plate at the rear of the sample. This technique simultaneously determines pressure and the length of the reference material; however, it requires a thermocouple to determine temperature. To confirm the validity of this method, X-ray diffraction and radiography as well as P- and S-wave travel times were collected on a San Carlos-like olivine sample (P61B, DESY). Pressures and sample length determined using the classical X-ray techniques and the new travel time cross-calibration, are compared and show excellent agreement. This novel method not only allows continuous in-situ pressure determination during in-house experiments, but also provides the potential to conduct in-situ phase relation studies, given that phase transformations greatly impact travel times.

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Experimental constraints on Fe isotope fractionation between magnetite and silicate melt at high pressure and high temperature

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Correct interpretation of isotopic variations of heavy (non-traditional) elements observed in natural specimens requires a firm knowledge of the isotope fractionation factors between minerals and melts. Thanks to the advent of multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) it is now possible to detect minor differences of heavy isotope compositions in specimens that equilibrated at high pressure and high temperature (HP-HT). Reliable fractionation factors, on the other hand, can be determined by analyzing natural specimens that formed under very well constrained conditions, which are not very common, or by theoretical calculations, which have a number of complications. Alternatively, laboratory experiments routinely employed in experimental petrology can be used to synthesize mineral and melts in a controlled environment at HP-HT, which, in principle, can be analyzed for their isotopic composition to investigate isotope fractionation. However, given the many complexities that characterize these experiments, experimentally determined isotope fractionation factors remain scarce.

In this study we conducted a series of HP-HT experiments to provide a calibration of Fe isotope fractionation between magnetite and silicate melt. Iron was chosen, among other heavy elements, given its wide use as chemical tracer of the formation and differentiation of Earth. Magnetite, on the other hand, was targeted as the mineral phase in equilibrium with a silicate melt due to its key role in magmatic evolution. Magnetite-melt pairs were equilibrated at 1 GPa and 800°C and at different oxygen fugacities (FMQ ± 2) using a piston cylinder apparatus, for several days. Care was taken to ensure that isotopic equilibrium was reached, and Fe loss avoided in the experiments.

Mineral and melt pairs synthesized at HP-HT were recovered at room conditions and efforts were put in order to develop a protocol to obtain near-pure separates of each phase. Once obtained, mineral and melt separates were digested in acid, purified to separate Fe via chromatography and their Fe isotope compositions were determined by MC-ICP-MS.

The experimentally determined Fe isotope fractionation factors between magnetite and silicate melt indicate some degree of covariation with the conditions investigated in this study. The new data will be discussed in the context of Fe isotope variations in natural samples, namely to understand the conditions (e.g., redox state) at which particular igneous processes occur.

The effect of capsule material on near-liquidus phase relations of Fe-rich anhydrous basalts

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The development of the piston-cylinder in early 1960s has permitted the acquisition of physical and chemical data under various pressures, temperatures and fugacities relevant to the crust and upper mantle, owing to large sample volumes and its time-integrated run stability. However, in complex silicate systems, chemical exchange between the sample, capsule and assemblage may occur, potentially compromising the results. Ideally, the capsule should approximate a closed system, chemically inert with respect to the sample, as well as easy to work with and weldable.

The objective of this study is to compare the effect of different capsule materials on phase relations of Fe-bearing anhydrous basalts. Experiments were done in a ¾” piston cylinder at 1180°C and 1210°C, 0.8 GPa. Each experiments contained four capsules of the following configurations: Ir, Pt, or AuPd, C+Pt, Mo+Pt, Fe+Pt, Re+Pt. To investigate fO_2, we determined the Fe^{3+}/Fe^{2+} of quenched glasses using the pre-edge feature of Fe K-edge XANES spectra. The near-liquidus 1210°C series shows limited crystallization (0-20%). Samples in Pt, Ir, AuPd, C+Pt, Mo+Pt and Fe+Pt capsules crystallized plagioclase (An_{97-99}) while the experiment in the Re+Pt capsule did not crystallize any phase. Iridium and Mo+Pt crystallized pyroxenes ($En_{76}Fs_{21}$) with plagioclase. Olivine is present in Mo+Pt (Fo_{78}), Fe+Pt (Fo_{67}) and Ir (Fo_{79}). The $K_D^{Fetot-Mg}$ between olivine and melt is 0.29 ± 0.001 for samples in Ir capsules, which compares to 0.32 ± 0.005 for Mo+Pt capsules. The 1180°C series crystallized plagioclase (An_{80-99}), olivine (Fo_{64-86}) and zoned pyroxene in all capsule configurations. In pure Pt and AuPd an accessory (< 1%) spinel phase is present. The crystal sizes are much smaller compared to the 1210°C runs and experiments have a higher overall crystallinity. The $K_D{}^{Fetot-Mg}{}_{ol-melt}$ ranges from 0.27 ± 0.005 for the experiment in the Re+Pt capsule to 0.32 ± 0.03 for Mo+Pt.

Samples show variable degrees of iron loss, which is expected in Pt (4.8 ± 0.3 wt.% at 1180°C and 1.19±0.6 at 1210°C), but also in Mo+Pt (3.7±0.6 wt.% at 1180°C and 1.9 ± 0.9 wt.% at 1210°C) and C+Pt (3.5±0.6 wt.%

for 1180°C and 3.6 ±0.1 wt.% for 1210°C), the latter likely due to cracks in the graphite capsule. Capsules with minimal or no iron loss are AuPd, Ir, and Re+Pt. The $Fe^{3+}/\sum Fe$ of the glasses were quantified relative to a calibration using MORB glasses [1]. $Fe^{3+}/\sum Fe$ for the 1210ºC runs range from 0.08-0.33 (typically ±0.03), the highest value for Pt which has the largest Fe-loss.

From this study, Pt is (as expected) not suited for Fe-bearing anhydrous melts. Mo+Pt, Fe+Pt and C+Pt cause significant reduction of the sample charge, and Mo and Fe strongly interact with melt, while AuPd, Ir and Re+Pt limits the Fe loss from the silicate melt and introduce the least modification to the chemical system.

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Experimental determination of the rate of fluid flow through mantle rocks

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Subduction-related fluids are known to be involved in arc melting and source metasomatism [e.g. 1,2] but the nature of fluid flow processes that allow transport from the subducting slab to the mantle wedge are poorly understood. The nature of these processes has implications for the geochemistry of the fluids, as pervasive flow can leach elements from much larger volumes of the slab compared to channelized flow [3]. The transport timescales are also important because if these are too slow, fluids will tend to be subducted with the slab rather than released into the overlying mantle [3].

In order to evaluate the mechanisms and time scales of fluid transport in subducting slabs, multi-anvil experiments were performed at 2.5 GPa and 500-1000°C to examine the rate of fluid flow through upper mantle minerals. A hot-pressed olivine or orthopyroxene core is sandwiched between a fluid source of aluminium hydroxide $Al(OH)_3$ or serpentinite and a fluid sink of MgO. The experiments are performed for timescale of 6-144 h. At the experimental conditions, the fluid source dehydrates, inducing an overpressure and resulting in a fluid flow through the dense sintered core. The fluid can then be captured in the MgO fluid sink on the other side of the core through the formation of brucite ($Mg(OH)_2$). This method allows the rate of water transport through the bulk sample, including along the grain boundaries, to be determined.

It is possible for water to move through the olivine and pyroxene using an $Al(OH)_3$ water source, whereas this is possible only for olivine on similar experimental timescales when serpentine is used as the source. We interpreted this to imply that the fluid overpressure, which is much higher in the case of $Al(OH)_3$, plays a role in the rate of transport. None the less, the rate of fluid flow is slow, with diffusivities of 1.7×10^{-11} m^2/s and 1.3×10^{-12} m^2/s at 500°C for olivine and orthopyroxene, respectively. Therefore, even though large overpressures were produced, only processes with rates similar to those expected for grain boundary diffusion of water seem to be in operation at these conditions. When these diffusivities are extrapolated to grain sizes of the upper mantle (~1 mm), it allows for a water transport of only 2.4 m and 0.6 m in a million years, which is far too slow to allow transport of water into the overlying mantle wedge.

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The *f*O_2 range of sulfur redox transition in slab-derived aqueous fluids: A synthetic fluid inclusion study

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Slab-derived fluids that metasomatize the mantle wedge at convergent plate margins may carry significant amounts of sulfur and Fe^{3+} and potentially increase the average oxidation state of the mantle wedge and derivative arc magmas. Though previous experiments have addressed the transfer of these constituents by slab-derived melts, little data exists for slab-derived aqueous fluids, which may be a more common medium of mass transfer in many subduction zones. This is in a large part due to the challenge of experimentally investigating such non-quenchable fluids at the relevant P-T conditions and controlled *f*O_2.

Our aim was to experimentally determine the oxygen fugacity range at which the sulfide-sulfate transition happens in aqueous fluids at P = 2.6 GPa and T = 700-900°C. To sample the fluid at these conditions after the attainment of redox equilibrium, we used the synthetic fluid inclusion (SFI) technique. The experiments were conducted in a newly-designed compact end-loaded piston cylinder apparatus (Strecon AS) with a twin hydraulic cylinder press. We used a 14 mm bore diameter WC pressure vessel with a low-friction pressure assembly of BN-MgO-NaCl. We used a double capsule design with redox buffer assemblages of Ni-NiO, Re-ReO_2 or MnO-Mn_3O_4 in the external capsule. The internal capsule was loaded with aqueous sulfuric acid solution and an intact quartz cylinder. During the experiment, the S-bearing fluid was equilibrated with the oxygen fugacity buffer, then trapped as SFIs in a quartz cylinder, which was fractured in situ during the experiment by briefly crossing the quartz-coesite transition pressure [1]. The concentrations of various S species in the SFI were investigated by Raman spectroscopy at ambient conditions after terminating the experiment, because the average oxidation state of the S within the SFI cannot change significantly during the quenching of the experiment.

The Ni-NiO buffered run products show that the S in the fluid was predominantly present in reduced form as H_2S. The SFIs from the Re-ReO_2 buffered runs contain S in the form of SO_4^{2-}, H_2S and elemental S daughter mineral. The presence of the latter indicates that reduced and oxidized S species coexisted at experimental P-T conditions and comproportionated to form elemental S upon quenching. Mass balance calculations suggest that most of the S was present in reduced form at the experimental P-T conditions in the Re-ReO_2-buffered experiments. Our results show that the sulfide-sulfate redox transition in aqueous fluids shifts to lower *f*O_2 with increasing pressure, because previous experiments at P = 150 MPa and T = 800°C found the predominance of oxidized S species (SO_2 and SO_4^{2-}) at the *f*O_2 of the Re-ReO_2 buffer [2]. These results are consistent with those of Matjuschkin et al. [3], who found the sulfide-sulfate transition in silicate melts shifting to higher *f*O_2 with increasing pressure.

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Ocean Island Basalts in the upper mantle: Multiply saturated volatile-bearing melts from 3 to 7 GPa

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Ocean Island Basalts (OIBs) are deep-rooted mantle melts providing a unique source of information about the Earth's interior. However, erupted compositions are not necessarily parental OIB compositions, as the primary melts may be modified by entrainment and assimilation when traversing the lithosphere, by fractional crystallization, and by degassing. Melt inclusions assert the presence of volatiles, including considerable CO_2 in OIBs [1]. The carbon surfacing in OIBs is likely related to subduction-initiated redox cycling [2], unstable carbonate (as melt or fluid) redox-freezes above deep subducting slabs to form C^0 enriched domains. In upwellings, the C^0 in these domains will convert to CO_2 and trigger redox melting at depths of ~250 km [3]. Melt formation then extracts H from NAMs [4], combined, these processes lead to CO_2 and H_2O-bearing deep melts.

We use multi-anvil experiments to investigate OIB primary melts and their evolution down the asthenosphere. Employing a reverse method, we force volatile-bearing primitive OIBs into multiple saturation with peridotite from 3 to 7 GPa at adiabatic temperatures, iteratively adapting mantle mineral fractions and melt compositions such that the initial melt equilibrates with all four mantle silicates. The 3 GPa melt is then used at 4 GPa, and so on. The carbon-saturated experiments include a peridotitic (KLB-1) [5] and a basaltic or basanitic melt component. The latter are primitive average compositions from shield stage Hawaii and the Cape Verdes (compiled from GEOROC) representing tholeiitic and alkaline endmember OIBs. Starting volatile contents of the melt are 5 wt.% CO_2 and 1 wt.% H_2O [1]. A layered starting arrangement ensures large melt pools allowing large-area microbeam analysis of the unquenchable liquids.

Olivine, low- and high-Ca pyroxene, and garnet saturation was obtained at all pressure steps. Already at 3 GPa, 1380°C, Hawaii and Cape Verde become very similar, with 39 wt.% SiO_2, 8 wt.% Al_2O_3, 17 wt.% MgO, 6 wt.% CO_2, and 1.3 wt.% H_2O. With increasing pressure SiO_2 and Al_2O_3 decrease (to a few wt.% at 7 GPa), and MgO, CaO, Na_2O, K_2O, P_2O_5, CO_2, and H_2O increase with pressure. At 7 GPa and 1410°C, both melts have (d)evolved to coincide with primary kimberlite melts [5]. Therefore, we propose a kimberlitic composition as a precursor for various OIBs. Melt composition differences at the surface can then be explained by differing chemical separation depths; these could, at most, correspond to the lithosphere-asthenosphere boundary, the likely transition from porous to channelled/fracture flow. The depth of the last equilibration with the mantle hence governs the primitive mantle melt and hence formation of the different OIB series.

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The Fe(Ni)-C-N phase diagram at 10 GPa – Implications for nitrogen and carbon storage in the deep mantle

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The concentrations of nitrogen, the seventh most abundant element in the solar system, in Earth's various reservoirs are intensely debated. Although nitrogen makes up about 78% of Earth's atmosphere, it is depleted on Earth by an order of magnitude compared to other volatiles such as carbon, water, and most noble gases [1]. In addition to the potential storage of N in the Earth's core and its degassing during accretion processes [2], N could also be present in (hidden) reservoirs in the Earth's deep mantle. Evidence for Fe-C-N species in the reduced mantle [3] are inclusions of Fe_2N, Fe_3N, Fe_7C_3, and $Fe_9(N_{0.8}C_{0.2})_4$ in deep mantle diamonds from Rio Soriso, Brazil [4].

To understand the deep nitrogen cycle and the formation of deep diamond inclusions, we studied the Fe-N-C-(Ni) system experimentally at 10 GPa and 1000-1400°C using a walker-type multi-anvil press. We developed a method to measure N and C by electron microprobe (EMPA) using metals, synthetic carbides and nitrides as standards. We compare C/N derived by EMPA with transmission electron microscopy-electron energy loss spectrometry (TEM-EELS) results. We also characterized the synthesized nitrides and carbides by TEM diffraction methods. Data shows, that subsolidus Fe-nitrides, carbonitrides and carbides are stable at ambient deep mantle pressures and at fO_2 conditions around the iron-wustite equilibrium. However, melting temperatures in the Fe-N-C system at 10 GPa are < 1250°C and thus significantly lower than the adiabat. This suggests that inclusions in deep diamonds were either trapped as melts and recrystallized during exhumation, or that they were included as solids and are perhaps related to fluid and N-rich cold subduction processes.

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The stability of tuite [γ-$Ca_3(PO_4)_2$] in a peridotitic bulk composition and its significance for the deep Earth phosphorus cycle

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Dehydration of subducted oceanic crust allows phosphorus to be transported into the mantle wedge by fluids or melts. This phosphorus is then either incorporated into silicate phases, especially garnet and olivine and/or forms apatite. The phosphorus-enriched mantel wedge peridotite may then be carried along with the subducted slab into the deep mantle. Once apatite reaches its upper P-stability limit, the anhydrous Ca-phosphate tuite forms. While the role of Ca-phosphates in the global phosphorus cycle is well understood for the crust and shallow upper mantle, this is not the case for the deep silicate Earth near and below 660 km depth.

In this study, we investigated the P-T stability, phase relations, and compositional evolution of tuite in a peridotitic bulk composition at P-T conditions of the upper to lower mantle transition. For this purpose, multianvil experiments were performed at 15 to 25 GPa and 1600 to 2000°C. The starting material was a synthetic peridotite based on the composition of a moderately fertile spinel lherzolite. This peridotite was doped with 3% synthetic β-$Ca_3(PO_4)_2$, 1% of a trace element mix containing a range of HFSE, LILE, and REEs, and approximately 2200 µg/g each of Br and Cl.

Coexisting phases stable within the P-T range studied include tuite, majoritic garnet, ringwoodite, forsterite, clinoenstatite, bridgmanite, davemaoite, ferropericlase, and melt. Tuite breaks down between 1700 and 1750°C at 20 to 25 GPa and between 1750 and 1800°C at 15 GPa, resulting in a negative slope for the tuite-out reaction.

At pressure beyond the stability limit of apatite, the main phosphorus carriers in a typical peridotite are tuite and/or garnet depending on the phosphorus content of the bulk. With increasing depth, the modal amount of Ca-phosphates decreases due to progressive phosphate-to-silicate P transfer, leading to phosphorus contents of up to 1.79 wt.% P_2O_5 in majoritic garnet at 1700°C and 20 GPa. When majoritic garnet reaches its upper P stability limit, tuite remains the only phase that contains significant phosphorus under subsolidus conditions, whereas bridgmanite and davemaoite contain negligible phosphorus (<60 µg/g and <100 µg/g, respectively), even when buffered by tuite.

NanoExtrem2: Nano-focus end-station for experiments at ID27 at ESRF

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In the framework of the BMBF-funded 'Nanoextrem' project, research groups of the Universities of Potsdam and Cologne contributed to constructing an end station of ID27 high-pressure beamline for nano-focused X-ray diffraction (XRD), fluorescence (XRF), and imaging (XRI) at the ESRF, Grenoble. A second BMBF-funded project, 'Nanoextrem2', will expand the experimental possibilities by adding a high-resolution X-ray emission (XES) spectrometer and pulsed laser heating to the beamline.

Setting up an end station for in situ XRD, XRF, XRI and XES at extreme conditions will allow investigating samples in the field of high-pressure materials and solid state physics in an unprecedented manner, and the addition of XES spectroscopy will further extend these extreme conditions research capabilities.

The end station allows for different focusing schemes by Kirkpatrick-Baez (KB) mirror systems (covering an energy range of 15 to 60 keV) arranged to form either a nano focus setup, a laser-heating setup, a micro focus arrangement for spatial flexibility and heavy load setups. A Soller slit system was developed and implemented to reduce the Compton scattering of complex sample environments.

Two highlights of the setup have been aleady characterized : (i) the focusing of the nano-beam (available in the energy range between 15 and 25 keV) to 300 × 300 nm; (ii) the gain of a factor 70 in flux obtained using a nano-focused pink beam instead of the monochromatized microbeam (FWHM for pink and monochromatic beam is 0.8 µm × 0.8µm at 0.3738 Å).

As an example, we present performance parameters and results from high-pressure XRD experiments on hydrous and anhydrous SiO_2 glasses up to 40 GPa. We discuss pressure induced structural changes in the SiO_2-H_2O system and show first results of a laser-heating experiment up to 4000K performed to study the structures of the respective melts.

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Investigating crystallization history in synthetic trachybasalts using electron backscatter diffraction

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Small differences in magma composition can strongly affect the crystallization history and microstructure of igneous rocks.

Here we present results of crystallisation experiments carried out in a piston cylinder apparatus at constant pressure of 4 kbar. Three synthetic trachybasaltic starting glasses were used, with different minor elements composition as follows: Glass 1 - different transition metals and REE elements added (total of 1 wt.% dopants); Glass 2 - doped only with Cr_2O_3 (0.5 wt.%); Glass 3 - undoped. The major element compositions of Glasses 2 and 3 are almost identical, and similar to Glass 1. Experiments using doped and undoped compositions were carried out under anhydrous and hydrous conditions (nominally 0 and 2 wt.% H_2O, respectively). After 30 minutes of superheating at 1300°C the samples were cooled at a rate of 80°C/min to the final resting temperature ranging between 1150°C and 1050°C. These temperatures correspond to nominal undercooling ($\Delta T = T_{liq} - T_{exp}$) between 60° and 160° for the anhydrous glasses and between 30° and 130° for the hydrous ones. Dwell time at the final resting T was between 5 minutes and 8 hours for different experiments.

Dendritic clinopyroxene (Cpx) is the main crystal phase, comprising up to 50 vol% of the samples. Spinel crystals (Spl) comprise 3 to 5 vol%. Spl crystals from Glass 1 are mainly Titanomagnetite (Tmt), homogenously distributed through the sample, often decorating Cpx crystals and rarely found isolated in the glass. Occasionally, they surround a Cr-oxide at the centre of a Cpx rosette (i.e., radially arranged dendritic Cpx). Spl crystals from Glass 2 show Cr-rich cores and Ti-rich rims. They can be found embedded in larger Cpx crystals, but also isolated in the glass, or forming clusters of Spl crystals comprising > 100 grains. Spl crystals from Glass 3 are Tmt, and always decorate Cpx edges or tips. Cpx crystals with size of 1 - 5µm, formed during quenching, nucleate around Spl crystals isolated in the melt in the hydrous runs.
Electron Backscatter Diffraction maps have been acquired to investigate the Crystallographic Orientation Relationships (CORs) between Spl and Cpx crystals and shed light on their crystallisation order and clustering mechanism. More than 70% of Tmt crystals decorating Cpx from glasses 1 and 3 show CORs with Cpx, suggesting a process of heterogeneous nucleation on top of pre-existing Cpx. Less than 10% of Spl crystals from Glass 2 show CORs with large Cpx crystals, while 20 to 50% of the small Cpx quenched crystals around Spl grains show CORs with Spl. Spl crystals from Glass 2 runs are likely formed by homogenous nucleation before Cpx crystallization. The Cr content of trachybasaltic melts strongly affects the crystallisation order of Spl and Cpx at large ΔT, impacting the size, shape, and distribution of Spl as well as the geometry of the Cpx crystal framework developed.

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Reactive transport of carbonatite melts: constrains from ex- and in-situ high P-T experiments

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Carbonatite melts play a crucial role in the deep carbon cycle, as major carbon carriers from the deep Earth to its surface. Indeed, due to their low viscosities (<10-2 Pa.s), small wetting angles (< 30°), and large buoyancy relative to surrounding mantle rocks, these liquids are expected to form interconnected networks and to be efficiently extracted even at low melt fractions. From a chemical point of view, this connectivity along grains implies an important exchange surface that makes them highly reactive agents. Therefore, knowledge of the location, transport, and reactivity of carbonate-rich melt in the deep Earth is an important step toward understanding of deep geochemical and geodynamical processes. In this work, we performed high-pressure/high-temperature infiltration experiments in peridotite minerals powders to investigate mantle metasomatism by those unusual magmas, as well as the dynamics and morphology of carbonate melt migration. Using real-time computed tomography (CT) imaging under extreme conditions (PSICHE beamline, Synchrotron SOLEIL) and Raman plus SEM-EDS on quenched samples (Laboratoire de Géologie de Lyon), we provide insights into the kinetics of melt infiltration and reactivity. Time-lapsed CT images exhibit the diffusive dynamics of capillary flow, and the observed infiltration rates of 5.3 - 5.9 mm/h confirm the high mobility of carbonate liquids relative to silicate ones. Chemical reactivity along specific grains, corresponding to matrix wherlitization, was also observed at a time scale comparable with the melt flow and was further investigated to address the interplay between chemical reactions and melt transport physics.

The role of fO_2 in the evolution of basaltic arc magmas: Bridging the geochemical and experimental discrepancies

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The role of fO_2 on olivine-clinopyroxene (ol-cpx) cotectic melt evolution in arc systems remains relatively unexplored, despite theoretical and experimental work suggesting its importance. The theoretical basis of our approach can be explained with the difference of liquidus temperatures between the olivine and clinopyroxene Fe-Mg end-members: the difference in liquidus temperature between forsterite and diopside is ca. 500°C, whereas the difference between fayalite and ferrobustamite ($CaFeSi_2O_6$ pyroxenoid) is about 20°C (at 1 atm; [1,2]). Hence, an increase in fO_2 and/or effective xMg (i.e., $Mg/(Mg^{+}Fe^{2+})$) would result in an increase of the normative cpx component of ol-cpx-cotectic melts. We experimentally tested the relative roles of xMg and fO_2 in basaltic arc magma evolution to tackle inconsistencies between the natural arc rock record and previous high-pressure (e.g., > 5 kbar) experimental results since the latter show lower normative cpx (i.e., higher Alumina Saturation Index - ASI) for a given SiO_2 content.

We used a multicomponent basaltic composition representative of mafic arc magmas. We synthesised three starting materials, based on a near-primary ol-tholeiite, with xMg of 0.5, 0.6, and 0.7. We conducted H_2O-saturated crystallisation experiments, between 1010 and 1100°C, from QFM to QFM+3, at 0.2 GPa in an internally heated pressure vessel equipped with a Shaw membrane using an Ar-H_2 pressure medium to buffer fO_2 conditions. The fO_2 was additionally monitored with CoPd redox sensors [3].

Our experiments show an expansion of the cpx stability field with decreasing xMg, in agreement with the working hypothesis. Oxygen fugacity affects melt evolution in two significant ways. The early saturation of magnetite-rich spinel (sp) at high fO_2 (ΔQFM > 2) leads to SiO_2 enrichment of residual liquids, with an increased cpx component for a given SiO2 content compared to more reducing conditions. Second, sp-undersaturated, ol-cpx cotectic melts show a higher cpx component (i.e., lower ASI) at QFM+1 compared to QFM, for a given SiO_2 content. Additionally, we observe higher proportions of ol relative to cpx (i.e., lower ASI increase with differentiation) at higher fO_2. This is attributed to the increase of the effective xMg at higher fO_2.

Our experiments confirm that fO_2 is a critical variable in the SiO_2-ASI evolution of arc magmas, due to the combined effects of the expansion of the ol stability field relative to cpx, and the increased sp stability at higher fO_2. These results reconcile field, geochemical and experimental observations on arc magmas and reinforce the hypothesis that basic to intermediate arc magmas are more oxidised than previously calculated [4].

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High temperature liquid-liquid silicate immiscibility experiments in the systems SiO_2-MO (M = Ca, Mg, Sr), SiO_2-X_2O_3 (X = La, Sm) and SiO_2-Nb_2O_5

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Immiscibility is thought to play an important role in driving magmatic differentiation in natural silicate liquids. Although debated, it has been invoked to account for the Daly gap [1], but also in the formation of anorthosite complexes, volcanic rocks on Earth and other planetary bodies (e.g., the Moon), granitoids and layered intrusions. However, the study of silicate liquid-liquid immiscibility is complicated due to the scarcity of natural settings in which immiscibility is preserved, notwithstanding the very high temperatures needed to study binary SiO_2-MO or SiO_2-X_2O_3 systems experimentally. As a consequence, experimental data on the extent of the liquid-liquid silicate immiscibility field in most binary systems and the associated thermodynamic mixing properties remain either completely unknown or are very limited. To resolve this shortfall, we have studied silicate liquid immiscibility in seven SiO_2 - metal oxide binary systems in Mo capsules, under an Ar-atmosphere and controlled $f(O_2)$ by using a custom-built high temperature furnace (Petroceramics, Milan, Italy; the only one of its kind). Quenched samples were analyzed by WDS (EPMA) for compositional analysis and under the SEM for textural characterisation, as well as for secondary compositional verification by EDS.

The acquired data were fit using a sub-regular solution model [2-4] to determine temperature-independent interaction (Margules) parameters for the liquid phases and thus determine the heats of mixing and activity coefficients of the melt oxide components. The liquidus, metastable liquidus and spinodal for all systems are modelled and compared to existing models.

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Diffusion of major and trace elements in plagioclase

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Chemical zoning is common in plagioclase and provides insight to the magmatic history and to time scales of magmatic processes. The wide range of diffusion coefficients in plagioclase allows access to information about processes with extremely long timescales via sluggish NaSi-CaAl interdiffusion and intermediate to short timescales via relatively mobile trace elements (e.g. Mg, Sr, Li). All studies so far have assumed anorthite content to be constant when looking at trace element diffusion in natural plagioclase. However, as outlined by Costa et al. [1], the chemical potential of trace elements depends on the anorthite content which may have strong impact on the development of trace element profiles in zoned plagioclase. However, experiments by Liu & Yund [2], suggest this assumption may not necessarily hold under water saturated conditions.

In this study, diffusion of major and trace elements in plagioclase was studied using homogeneous natural plagioclase single crystals. Thin films were deposited from synthetic plagioclase glasses on top of plagioclase crystals using pulsed laser deposition. Trace element diffusion experiments were conducted at 850-1150°C and 1 atm (1 atm gas mixing furnace) as well as 200 MPa (internally heated pressure vessel, IHPV). Experiments designed to constrain the effect of water on NaSi-CaAl interdiffusion were run in IHPVs, with the addition of hydrous rhyolitic glasses to control water fugacity during experiments. Trace element diffusion was analyzed using TOF-SIMS, EPMA and fs-LA-MC-ICP-MS depth measurements, while NaSi-CaAl interdiffusion was measured via TOF-SIMS and EDX (EDX measurements were carried out on lamellae cut as a cross sections between thin film and crystal using a FIB-SEM).

First results for Mg and Sr diffusion are in good agreement with literature. While we were not able to resolve diffusion profiles using fs-LA-MC-ICP-MS depth measurements, we have shown this method can be used to calibrate TOF-SIMS intensities for trace elements in thin film and the crystal, allowing correction without the need of additional matrix matched standards. Preliminary results for NaSi-CaAl interdiffusion also show that the applied analytical methods are suitable for resolving NaSi-CaAl interdiffusion profiles and allow a distinctively more accurate determination of diffusion coefficients than was previously the case. Furthermore, our results indicate diffusion under hydrous (not water saturated) conditions to be faster than literature for dry conditions and significantly slower than diffusivity under water saturated conditions.

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Experimental re-assessment of Li diffusion in plagioclase

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Within the last 20 years, lithium has become an important element in diffusion chronometry. Due to its extremely fast diffusion and strong isotope fractionation compared to other elements, lithium is particularly suitable for tracking short-lived processes (e.g. final ascent of magma), which are not accessible with slower diffusing elements. Because of the ubiquitous chemical zoning in plagioclase and its wide stability in magmatic systems, plagioclase is one of the main target minerals for diffusion chronometry. So far all studies have used the Li diffusion data of Giletti & Shanahan (1997), who conducted experiments at 1 atm between 200-850°C. In view of the deviation observed by Audétat et al. [1] from the data of Giletti & Shanahan [2] at high temperatures, a re-investigation of the Li diffusion coefficients in plagioclase is necessary.

We performed diffusion couple experiments between plagioclase single crystals (oligoclase and labradorite) and synthetic glasses of plagioclase composition enriched with 100 ppm Li. Experiments were run in rapid-heat / rapid-quench CSPVs and IHPVs. Experimental conditions comprised a temperature range of 400-1100°C and a pressure range of 0.1-400 MPa with timescales between 0.5 h and 168 h. Samples were analyzed using fs-LA-MC-ICP-MS and TOF-SIMS measurements. Our results show Li diffusion at 200 MPa to be slower by more than one order of magnitude compared to Giletti & Shanahan [2]. These findings have significant implications for time scales derived from natural Li diffusion profiles in plagioclase, resulting in considerably longer time scales than previously assumed.

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The origin of melilitites: preliminary results on melting of carbonated wehrlites

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Melilitites are ultramafic magmas characterized by normative Ca_2SiO_4, larnite. Liquids compositionally close to melilitites were experimentally reproduced from carbonated lherzolites in alkali and iron-free model systems at 3.2-3.3 GPa, approx. 1500°C [1], at relatively high melt proportions. In complex compositions, MORB-eclogite derived, carbonated, partial melts reacted with a fertile peridotite were proposed at the origin of melilitites [2]. The experimental reconstruction of phase relationships along a join olivine melilitite - carbonate revealed that at 3 GPa, clinopyroxene and olivine or garnet are stable on the liquidus [3], suggesting that carbonated wehrlites are potential sources for the genesis of melilitites.

Here, we explore phase relationships on the high pressure melting of a model wehrlite, initially composed of a mechanical mixture of San Carlos olivine, diopside, aegirine, dolomite, rutile and kyanite. Starting materials were loaded in graphite capsules, inserted in sealed platinum capsules. Vitreous carbon spheres and synthetic diamond grains were adopted for liquid traps. Preliminary experimental results show that at 3 GPa the solidus is located at temperatures lower than 1200°C. A thick, orthopyroxene-rich layer, with polygonal microstructure, forms at contact with aggregates resulting from quenched liquids, both at 1200°C and 1400°C. Estimates of liquid composition are broadly melilititic.

Currently available experiments suggest that the solidus is controlled by the reaction dolomite + olivine + clinopyroxene = orthopyroxene + liquid, as suggested in [4]. This is feasible only if the liquid composition is located on the CaO-rich side of the plane diopside-forsterite-dolomite in the model system $CaO-MgO-SiO_2-CO_2$, i.e. on the normative larnite (akermanite) portion of the tetrahedron.

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Experimental investigation of the role of sulfur in highly reduced silicate glasses and melts

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Elucidating sulfur speciation and bonding at the atomic scale is required to understand transport properties in S-bearing melts such as diffusivity, viscosity, and electrical conductivity at high temperature and pressure. These properties are fundamental to modeling the evolution of terrestrial planets and moons. Despite several investigations of sulfur speciation in glasses formed by temperature-quenching of their melts, questions remain regarding the structural role of S and its effect on transport properties under highly reducing conditions such as S-rich lava on Mercury.

Here, we report a laboratory study of sulfur in silicate glasses formed by quenching of melts at 1573-1673K synthesized in evacuated silica tubes under highly reducing conditions (Delta IW=-5.8 and -6.4, with IW the iron-wüstite oxygen fugacity buffer). The compositions reproduce the silicate portion of enstatite chondrites, representative of the northern volcanic plains at the surface of Mercury. Major cations in the silicate glasses included Al, Mg, Ca, Na, and K; S was varied from 0 to ~5 wt.%. The samples were characterized with impedance spectroscopy performed at 2 and 4 GPa and from 475 up to 1738K using a multi-anvil press and the 4-electrode technique, ^{29}Si MAS NMR spectroscopy, Raman spectroscopy, and electron microscopy.

We observe that conductivity generally increases with the S content of the glass, though no systematic correlation is observed. Electrical activation energy E_a below the glass transition temperature ranges from 0.56 to 1.10 eV, in agreement with sodium being the main charge carrier in all samples. The glass transition is located at 650-750K based on impedance measurements. Above Tg, E_a decreases (0.35-0.68 eV) and the conductivities of the samples are comparable (~5-8.10^{-3} S/m) until 973K. At T > 1600K, the melt fraction is 50-70% and melt conductivity varies from 0.8 to 2.4 S/m, with the melt containing 5 wt.% S being the most conductive. ^{29}Si NMR results reveal that a portion of S bonds with silicon by substitution for oxygen, as previously observed in Na_2S-SiO_2 glasses [1], affecting slightly the degree of polymerization of the glass. This result is in accord with a study on viscosity of S-bearing melts [2]. Raman spectra show that some S is isolated from the glass-network structure and combines with divalent cations, $Ca^{2+}$and Mg^{2+}, to form sulfide clusters in the glass, consistent with previous work [3]. Our results also indicate that CaS and MgS are not as strong network modifiers as CaO and MgO. Our spectroscopic measurements do not reveal direct interactions between sulfur and sodium, which is consistent with only a moderate effect of S on conductivity. This study not only illuminates the role of sulfur in highly reduced complex silicate glasses and melts, but also exemplifies a multi-disciplinary approach that would be useful for the investigation of other geomaterials.

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High temperature equilibrium sulphur isotope fractionation between melt and sulphide from experiments using a dynamic 1-atm gas-mixing furnace

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The sulphur isotope fractionation factor is a critical parameter describing the evolution of sulphur concentration and isotopes in a natural magmatic system. However, currently available values are tied to analogue systems and models. By conducting laboratory experiments, an effort has been made to establish a model for sulphur isotope fractionation in a magma with sulphides. To this end, a new and safe gas-mixing furnace using the gas mixture CO-CO_2-SO_2 has been designed to control the fO_2 and fS_2 conditions at temperatures up to 1600°C [1]. The instrument can dynamically change the fO_2 within the furnace at a maximum rate of 2 log unit min^{-1}. This allows for the simulation of dynamic processes occurring in nature, such as volcanic degassing. Experiments were carried out using ~Fo_{90} crystals as capsules with basalt powder and 99.99% Fe powder as the starting materials. A dominant proportion of sulphur in this system is acquired from the gas. A constant change of 1 log unit in fO_2 and fS_2 over 4 hours shows that the system remains in a continuous equilibrium, illustrating that this rate of change in this system does not upset the equilibrium. This suggests that for potential kinetic isotope fractionation to occur, the change in fO_2 and fS_2 must be more significant and/or faster, perhaps by an order of magnitude. The result implies that kinetic isotopic fractionation potentially occurs on short timescales, such as degassing during magma ascent, but not magma chamber crystallization. Equilibrium experiments were carried out under fO_2 conditions ranging from -8.5 to -11.1 (ΔQFM -0.65 to -3.27) and fS_2 conditions ranging from -1.1 to -1.8 at 1200-1400°C. The samples were analysed for their major element compositions using an EPMA and $\delta^{34}S$ using a Secondary Ion Mass Spectrometer (SIMS). Time-series experiments demonstrate that the system reaches equilibrium, both in terms of major element and sulphur isotope composition, within 8 hours. Hence, the length of all experiments was fixed to be 8 hours. From over 25 equilibrium experiments at arbitrarily determined conditions and temperatures of 1200-1400°C, the fractionation observed is significant and follows a trend, i.e., the higher the fO_2 and lower the temperature, the larger the fractionation is. At 1300°C, the fractionation ($\Delta^{34}S$melt-sulphide) is as high as 4.36±0.47‰ for an fO_2 of -9 (ΔQFM -1.79) and tends to 0 at an fO_2 of -10.71 (ΔQFM -3.49). This fractionation is significantly greater than what is predicted by analogue models [2]. Our experimentally determined equilibrium sulphur fractionation model could explain the evolution of $\delta^{34}S$ from -1 to +5.6‰ observed among the lower crustal cumulates of the Talkeetna arc [3], in which sulphide precipitation under oxidising conditions raises the $\delta^{34}S$ of the magma. Thus, $\delta^{34}S$ trends in cumulates may be an indicator of magmatic redox condition.

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Effect of pressure on trace element activity coefficients in metal-silicate systems

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The partitioning of trace elements between metal and silicate melts serves as the foundation for understanding the differentiation of a planetary body into a metallic core and silicate mantle. Element activity influences metal-silicate partitioning behavior. Activity coefficients are directly dependent on composition and temperature, and can be indirectly dependent on oxygen fugacity and pressure. Distinguishing the effect of pressure from other variables on the activity coefficients and partitioning is important for understanding the chemical evolution of different planetary bodies during differentiation. In this study, we investigated the influence of pressure on the activity coefficients of Cu, Mo, Pd, Pt, As, Sb, and Bi in Fe-Si metallic liquids. All of these elements exhibit moderate to high activity coefficients in Fe-Si liquids at low pressure, which significantly controls their metal-silicate partitioning behavior. Identifying whether this strong dependence persists at higher pressures is critical to modeling and understanding the chemical consequences of core formation. New experiments at 10 GPa were used to derive activity coefficients for these metals which can be compared to activity coefficients determined at 1 GPa.

Experiments were conducted at 10 GPa and 2373K using a 10/5 assembly in the 880-ton multi-anvil press at NASA Johnson Space Center. The standard 10/5 COMPRES assembly was slightly modified to accommodate a sample capsule machined from single-crystal MgO that minimizes melt percolation out of the sample volume during the experiment. Experiment starting materials were comprised of 70 wt.% Knippa basalt and 30 wt.% metal. The metal mixture (~85 wt.% Fe) was created by adding the elements of interest (Cu, Mo, Pd, Pt, As, Sb, Bi) to Fe metal powder. Varied amounts of Si metal (0-10 wt.% Si) were added to the metal-silicate mixtures to generate a systematic series of starting materials.

For each element, an epsilon interaction parameter in Fe-Si liquid was derived from the results of our 0-10 wt.% Si metal series. To investigate whether pressure influences the trace element activity coefficients in the 1-10 GPa pressure range, we compared our results at 10 GPa to those at 1-4 GPa [1-3]. Our results can also be directly compared to interaction parameters for Au, P, V, Mn, Ga, Zn, Cd, Sn, W, Pb, and Nb previously determined at 10 GPa and 2373K following the same methods [4]. Combined, this suite of interaction parameters will directly inform metal-silicate partitioning between 1 and 10 GPa, and assess whether these values can be extrapolated to modeling differentiation processes at pressures >10 GPa.

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Lunar impact melt crystallization produces reflectance spectra dominated by clinopyroxene signatures: Implications for the origin of pink spinel anorthosite

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Magma-wallrock interaction and impact melt crystallization are the two leading hypotheses for the formation of orbitally detected lunar “pink” spinel anorthosite (PSA) [1-3]. Distinguishing among hypotheses is complicated because both require mixing of anorthositic crust and MgO-rich ultramafic components. Models for PSA formation need to account for either the thermodynamic hurdles of crustal assimilation, or the size of impactor and composition of target material needed to generate spinel during crater and basin formation. Determining whether the energy source is endogenic or exogenic is important for understanding the thermal and chemical evolution of the lunar crust.

Here we test the impact melt hypothesis by performing controlled cooling experiments on two hypothetical impact melt compositions. The compositions represent mixing of ultramafic magma and anorthositic crust in molar ratios of approximately 50:50 and 25:75. Synthetic crystallized assemblages were prepared for chemical analysis and bidirectional reflectance spectroscopy in the visible to near-infrared wavelengths. All crystallization experiments contained plagioclase, olivine, and clinopyroxene, but trace amounts of spinel were only observed in the 50:50 mix. The experimental spinel is similar to the compositions inferred from remote observations. However, the high-Ca pyroxene in our experimental assemblages (9-18 wt.%) resulted in 1 and 2 µm absorption band center positions consistent with synthetic clinopyroxene. The clinopyroxene absorptions are present regardless of specific mineral modes and the presence of either olivine or spinel. These results suggest that impact melt crystallization will produce clinopyroxene-bearing lithologies, the presence of which masks spectral contributions from coexisting spinel and olivine. Assuming that the trace amounts of spinel observed in our experiments could be concentrated and isolated from the mafic silicates by convection or density settling in the impact melt sheet, the spinel-rich areas would still be proximally associated with the remaining silicate-dominated assemblage exhibiting strong clinopyroxene spectral signatures.

We conclude that impact melting of the lunar crust can explain rare cases of PSA in association with clinopyroxene. Previous investigations of magma-wallrock interactions [2] demonstrate that small plagioclase-contaminated regions of an ultramafic intrusion can concentrate spinel whereas larger portions of the same intrusion remain relatively uncontaminated and yield olivine and orthopyroxene, consistent with the more common occurrence of PSAs in association with orthopyroxene ± olivine in the remote sensing database (e.g., Moscoviense Basin) [4].

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Amphibole stability, water storage in the mantle, and the nature of the lithosphere-asthenosphere boundary

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Amphibole could potentially be an important host of water in the upper mantle. Moreover, the decomposition of amphibole has been invoked as a possible cause of the lithosphere-asthenosphere boundary. However, amphibole stability has been experimentally studied mostly under water-saturated conditions, which are unrealistic for most of the mantle that may contain only traces of water. Experiments with low nominal water contents yielded controversial results and were hampered by problems in controlling water activity. We have solved this problem with a novel experimental approach. We carried out piston cylinder experiments from 900 to 1350°C and 2 to 4.5 GPa using a peridotitic composition coexisting with an excess H_2O-N_2 fluid phase. The dilution by inert N_2 was used to precisely control water fugacity to values realistic for the upper mantle. Numerous reversed experiments were carried out to circumvent problems with the metastable formation of amphibole. Our data show a dual effect of water fugacity on the stability of amphibole. With decreasing water activity, the stability field is simultaneously displaced to lower pressures, and expanded to higher temperatures. This behavior is due to two different decomposition reactions with dehydration involving only solid phases at low temperature, but melting at high temperature. Along a continental geotherm, amphibole will never be stable for typical upper mantle water contents. However, for a mantle containing 150-200 ppm of water, traces of amphibole may form in a narrow pressure interval along an oceanic geotherm. Here, amphibole may contribute significantly to bulk water storage, although most of the water still resides in nominally anhydrous minerals. However, even if amphibole is stable in a restricted depth range, it cannot account for the lithosphere-asthenosphere boundary, since decomposition proceeds through a solid-state reaction and does not involve melting for realistic mantle water contents.

Experimental determination of equilibrium iron stable isotope fractionation between metal and troilite

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Iron metal and troilite co-exist abundantly in many meteorite groups, including ordinary chondrites and iron meteorites [1,2]. Stable isotope systematics between metal and sulfide phases in these meteorites are affected by kinetic effects. The equilibrium stable isotope composition of Fe between metal and troilite is therefore difficult to obtain from natural materials.

Here, we present results from Fe metal equilibrium sulfidation experiments in evacuated silica glass tubes at 600 to 1200°C. Iron metal and Fe-Ni metal pellets were placed in graphite cups that were loaded in SiO_2 glass ampules with elemental S at a molar ratio of Fe(+Ni)/S = 4. The glass ampules were evacuated to ~10^{-5} bar and sealed with a H_2-O_2 flame. The glass ampules (~4 cm long) were suspended in the hot zone of a vertical tube furnace for up to 260 h. The experiments were mounted in epoxy resin and imaged by SEM. The two distinct phases, Fe and FeS, were analyzed in-situ for their δ^{56}Fe and δ^{57}Fe compositions with a high mass resolution MC-ICP-MS (Thermo Scientific Neptune Plus). The materials were ablated using a Spectra-Physics Solstice femtosecond laser ablation system at the institute of Mineralogy, Leibniz University Hannover, see [3] for analytical details. A second set of experiments were run at identical conditions. However, the sulfide and metal phases were separated physically, digested and analyzed for their δ^{56}Fe and δ^{57}Fe compositions in solution with a Neptune Plus MC-ICP-MS at the institute of Mineralogy, University Münster.

At 600-900°C the sulfidation reaction occurred in the solid state, and at 1000, 1100 and 1200°C we observe Fe and FeS melts. We insured isotopic equilibration by running experiments with different durations. At 600°C and 71h we observed kinetic fractionation effects, whereas after 260 h the sulfide coating was isotopically homogeneous. The sulfide phase was troilite, confirmed by X-ray diffraction (XRD) at the institute of Mineralogy, University of Münster. The FeS is systematically isotopically heavier compared to the Fe metal in all experiments, and the overall isotopic fractionation decreases with increasing temperature from 600 to 1200°C. At 600°C $\Delta^{56}Fe_{Fe\text{-}FeS} = -0.68 \pm 0.11$‰ (determined by in-situ measurements). However, a comparison of the experimental results with δ^{56}Fe data from ordinary [1] and iron [2] meteorites shows the opposite fractionation trend. In the meteorites the FeS is always isotopically lighter compared to the Fe metal. We suggest that this is due to kinetic fractionation effects that occur during cooling of the Fe-FeS melts and between the solidified phases in the meteorites, whereas our quenched experiments retained the equilibrium δ^{56}Fe fractionation.

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Initial fractional crystallisation of a full Martian magma ocean

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The InSight mission to Mars and its seismic recordings from the SEIS instrument have revealed unprecedented details on the planet's interior, in particular its liquid core size (1830 km) [1]. Yet, the most recent interpretations of the data suggest that this radius includes not only metal but also a (partially) liquid silicate layer on top of the metallic core [2]. If such a putative layer exists then its origin may be related to the solidification of a primordial Martian magma ocean (MMO).

Knowledge of the crystallisation of this magma ocean is therefore required to place tighter constraints on the early evolution of Mars. In this study, we perform fractional crystallisation experiments of the MMO on a Yoshizaki & McDonough [3] bulk composition using a multianvil apparatus. We aim at studying the liquidus temperature and phase relations along the liquid line of descent starting at the present-day estimate for the core-mantle boundary pressure of ~19 GPa. At this pressure, majorite is the liquidus phase, followed by minor amounts of ferropericlase down temperature. Fractionating out a majorite cumulate layer of ~330 km, which corresponds to 12% total crystallisation, yields a residual melt composition (or new starting material) depleted in Al_2O_3 and Cr_2O_3 and slightly enriched in FeO relative to the initial bulk. The next fractionation step at 15 GPa still has majorite on the liquidus but is closely followed by a $(MgO,FeO)_2SiO_2$ phase. Subsequent fractionation steps will determine the pressure range of olivine as dominant cumulate phase until Mg/Si ratios are sufficiently low to stabilise pyroxenes. Once pyroxenes dominate the liquids phase assemblage, fractional crystallisation becomes analogue to the lunar magma ocean, for which cotectic phase relations are well understood [4], and can be used to predict the low pressure crystallisation of the MMO. We discuss chemistry and density relations between minerals and melts and evaluate the likelihood of buoyant cumulate layers, and whether late stage MMO products, when re-entrained into the deep mantle, may serve as plausible explanation for the current seismic observations.

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Quartz under stress: Raman calibration and applications to geobarometry of metamorphic inclusions

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An experimental calibration of the three major Raman peaks of quartz with hydrostatic pressure and uniaxial differential stress is presented, and implications for their use in geobarometry based on Raman spectroscopy of quartz inclusions is discussed. The position of 206 cm^{-1} peak depends only on hydrostatic pressure P, and its pressure dependence is recalibrated with a peak fitting procedure that is more adequate for Raman barometry than previous calibrations. The position of the 128 and 464 cm^{-1} peaks depends on P and also on differential stress σ, which can be determined from the position of these two peaks knowing hydrostatic pressure from the position of the 206 cm^{-1} peak. The results obtained here are different from those inferred previously from first-principles calculations. The present calibration provides direct relationships between Raman shifts and stress, with a simple formulation of residual pressure and differential stress assuming uniaxial stress along the c-axis of quartz inclusions. It is tested on data from experimental and natural inclusions. Residual pressures from the present calibration are similar within uncertainties to those obtained with previous experimental calibration within uncertainties, and experimental inclusions yield residual pressures consistent with synthesis pressure. Inconsistent residual differential stresses are obtained from the 128 and 464 cm^{-1} peaks on some experimental inclusions, providing a criterion for identifying inclusions under complex stress conditions that are not appropriate for geobarometry. Recent data on natural inclusions show self-consistent differential stress, consistent with the assumption of major stress along symmetry axis of the inclusion crystals and with values expected from elastic models. The average pressure values from the 128 and 464 cm^{-1} peaks is similar to the residual pressure from the 206 cm^{-1} peak that depends only on hydrostatic pressure. It can be used to obtain pressure when the 206 cm^{-1} peak position cannot be used due to interference with host mineral peaks. Using the 128 and 464 cm^{-1}

peaks alone, or averaging either 128 and 206 or 206 and 464 cm^{-1} peaks can induce systematic bias in the residual pressure determination. Applications of the present results to natural inclusions suggest that combined determination of residual pressure and differential stress may be used both for barometry and thermometry pending further calibration.

Hydrogen diffusion in hydrous minerals: revised closure temperatures for isotopic exchange during fluid-rock interactions

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Interactions between aqueous fluids and rocks occur in a broad range of contexts ranging from hydrothermal alteration to regional metamorphism on Earth and parent body metamorphism in meteorites. Tracking these processes and understanding their reaction kinetics require a precise knowledge of the diffusion of water in rocks, and of isotope fractionation in major hydrous minerals. Deuterium-hydrogen exchange between amphibole (tremolite), vesuvianite minerals and deuterated gas (D_2) was experimentally investigated in a furnace over the temperature range of 400-550°C at ambient pressure. D/(D+H) ratios in exchanged mineral grains were mapped using Raman spectroscopy. Deuterium-hydrogen exchange proceeded by deuterium-hydrogen lattice diffusion, and also along cleavage in amphibole. Arrhenius relations for deuterium-hydrogen lattice-diffusion coefficients were derived from the new dataset. Values of activation energy (E) is 198±11 (1s) kJ/mol and $\log D_0$ -3.0±0.8 are obtained for vesuvianite, and 133±13 kJ/mol, and -9.2±0.9 for tremolite. Activation energy for tremolite is a minimum value and is likely higher and similar to those in the range 170-200 kJ/mol inferred for antigorite, chlorite and vesuvianite using similar methods. Diffusion coefficients obtained with bulk isotopic analysis for amphiboles and epidote-zoisite are much higher and display lower apparent activation energy (<80 kJ/mol) than those inferred from spatially resolved diffusion profiles obtained using punctual methods (Raman, NanoSIMS). Overestimation of diffusion coefficients by bulk analysis is attributed to unverified assumptions on grain size for minerals presenting easy cleavage (amphiboles, epidote, ...) that decrease effective grain size and increase surface for diffusive exchange during the experiments. Minerals like vesuvianite and tourmaline that have no cleavage planes show low diffusion coefficients from both spatially resolved and bulk analytical methods. Extrapolation of these new diffusion laws to low temperatures yields closure temperature of hydrogen isotope diffusion in hydrous minerals that are much higher than previously estimated. Hydrous minerals may thus retain information on relatively high temperature metamorphism on parent bodies of carbonaceous chondrites, and could display hydrogen isotope zoning in terrestrial rocks that may record the history of metamorphic fluid interactions and volcanic eruptions.

The variation with pressure of the elastic tensor of $Na_{0.62}Mg_{0.19}Fe^{2+}_{0.174}Al_{1.20}Si_{0.70}Fe^{3+}_{0.08}O_4$ calcium-ferrite type phase

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The calcium-ferrite-type phase (CF) is anticipated to be the dominant Al-bearing phase in MORB compositions throughout most of the Earth's lower mantle. As a major phase, it can affect the seismic signature of subducting slabs at these conditions. To date, however, the elastic properties of this phase have been determined only for simple compositions which are not representative of those which can be encountered in MORB. Therefore, such data poorly constrains mineral physics models for the comparison with seismic observations. Here, we present the single-crystal elastic properties and acoustic velocities of a Fe-bearing CF-type phase with a composition more relevant for MORB, obtained by means of simultaneous Brillouin scattering and X-ray diffraction measurements. The elastic tensor was determined at eight different pressures up to 26 GPa at room temperature.

The CF-phase is highly anisotropic at room pressure, especially in the compressional velocities, and such anisotropy decreases with increasing pressure. The *c* axis was found to be the stiffest ($M_{c,0}$ = 757(5) GPa), whereas the *a* and *b* axes have similar compressibility ($M_{a,0}$ = 557(5) GPa and $M_{b,0}$ = 488(5) GPa).

A second order Birch-Murnaghan equation of state was used to fit the pressure-volume data determined by X-ray diffraction. The resulting room pressure unit-cell volume, V_0, and bulk modulus, K_{T0}, are 242.18(5) $Å^3$ and 199(1) GPa, respectively. Both volume and unit-cell lattice parameters are in agreement with the trends established in previous static compression studies on CF of various compositions. The elastic moduli and acoustic velocities were found to be lower than reported in previous computational and experimental studies. This suggests that the presence of Fe decreases the acoustic wave velocities of this phase significantly and therefore needs to be taken into account in mineral physics models describing the seismic properties of subducting slabs in the lower mantle.

Alkali feldspar - aqueous alkali chloride equilibria at nominally supercritical conditions

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Although K-Na exchange among alkali feldspars and alkali chloride aqueous solution as an important hydrothermal geochemical process has been the focus of many experimental studies [e.g. 1], accurate equilibrium constants are lacking for a wide range of temperature and pressure. Namely, equilibrium constants were derived from experiments at elevated concentrations for which the activity coefficients were unknown, potentially leading to serious, unrecognized errors [2]. We performed new experiments at temperatures of 400 and 450°C and pressures equivalent to a pure water density of about 0.3 and 0.5 g cm^{-3} and concentrations from 13 down to 10^{-4} molal. At the very dilute concentrations, activity coefficients approach unity as evidenced by constant K/Na ratios in the equilibrated solutions from 10^{-2} to 10^{-4} molal. The resulting equilibrium constants differ significantly from those by Lagache & Weisbrod [1] that were derived from high-concentration solutions; for example, at 450°C and 0.3 g cm^{-3} water density, our equilibrium K/Na ratio (0.04) is about 75% lower than the 0.173 of Lagache & Weisbrod [1]. Our data obtained so far also demonstrate a significant pressure effect, in contrast to literature [1] that considered the equilibrium constants as independent of pressure. Finally, using on the new, improved equilibrium constants, the activity coefficient ratios of K/Na can be extracted over the wide range of experimental concentration range from 10^{-4} to 13 molal.

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Exploring planetary interiors with X-ray absorption spectroscopy

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A major challenge for “Deep Planetary Interiors” studies resides in probing the properties of geological samples simultaneously under relevant high P/T conditions, under their natural chemical complexity and under high degrees of dilution (down to ppm). Synchrotron X-ray radiation has been a key tool for these types of studies, but because of the extreme difficulties and technical limitations previous investigations have often focused only on simplified chemical systems and/or on elemental concentrations exceeding by far those in nature.

The two refurbished energy-scanning X-ray absorption beamlines BM23 and ID24-DCM (Double-crystal-monochromator) at the ESRF-EBS (Extremely Brilliant Source), operating since 2021/2023, offer now unprecedented opportunities for this type of research. Indeed, these instruments provide the technology to overcome previous limitations, as they feature simultaneously an unprecedented high flux (up to 10^{12} ph/sec), improved beam focusing capabilities (down to 0.7×0.7 µm^2), state-of-the-arte experimental stations (laser/resistive heated DAC) and multi-detection systems for XAS, XRF, XES and XRD (Van Hamos, quick EXAFS – 1sec/spectrum, single and multi-element SSD, Pilatus 1M).

I will demonstrate on recent examples the capabilities of these instruments to study: (1) the distribution behaviour, incorporation mechanisms and valence states of a large range of important geochemical marker elements down to the ppm, (2) to monitor the structural and chemical changes in amorphous materials (silicate and metallic melts), and (3) to identify pressure-induced electronic changes, such as spin-transitions. I will provide an outlook on the implications of these new measurements for our understanding of very complex geological phenomena, such as the chronology of planetary accretion stages, the genesis of their magnetic fields, the long-term interaction between the atmosphere and the interior of a planet, and oxidation state variations of silicate mantles over geological time.

Cr incorporation in post-spinel Mg-Fe^{3+} oxides

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The occurrence of high-pressure Mg-Fe-oxides in meteorites [1] and magnesiochromite inclusions in diamond [2] open the possibility that such phases can be used as petrogenetic indicators. However, the corresponding phase relations must be known in order to establish quantitative constraints. The initial focus of our study was on the stability of $Mg_3Cr_2O_6$ and solid solutions involving Cr-Fe^{3+} exchange, with an extension to other stoichiometries. Experiments were performed at 1100-1500°C and 14-20 GPa in a multi-anvil press. Starting materials were stoichiometric mixtures of pre-synthesised $MgCr_2O_4$ and MgO. The originally anticipated “O_6” phase was not observed at any pressure in the endmember composition, with the assemblage $Mg_2Cr_2O_5$ + MgO always being stable. At 20 GPa a $MgCr_2O_4$ phase with the Ca-titanite structure also appeared, consistent with the work of [3].

Further we experimentally studied the $Mg_3Cr_2O_6$ – $Mg_3Fe^{3+}{}_2O_6$ binary by adding different proportions of $MgFe_2O_4$ to the starting mixture. Again, no “O_6” phase was found to be stable. Instead, we find $Mg_2(Fe,Cr)_2O_5$ solid solutions coexisting with MgO. Solid solution appears to be complete across the $Mg_2Cr_2O_5$ – $Mg_2Fe^{3+}{}_2O_5$ binary even though the two endmembers have somewhat different crystal structures (*Pbma* vs. *Cmcm*). In fact, molar volumes appear to vary linearly across the join. The transition between the two crystal structures must lie near the 50%-50% composition.

The unit cell parameter of the coexisting periclase exhibits a distinct variation as a function of Cr content, as well as the temperature and pressure of the experiment. From EPMA, up to 25 wt.% Cr_2O_3 (i.e. ~0.16 cpfu Cr) can be incorporated in periclase at high temperatures (i.e. 1400°C at 14 GPa), with less present at lower temperatures and higher pressures.

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An experimental study of storage conditions beneath Krafla Central Volcano (Iceland) and the importance of oxygen fugacity

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Rhyolite accounts for about 10% of Iceland's volcanic products, providing insights into silicic magmatism in basalt-dominated oceanic settings. However, the phase relations and storage conditions (P-T-fO$_2$-XH$_2$O) of these magmas are poorly understood due to a lack of experimental studies on Fe-rich but Ca- and K-poor rhyolites such as the rift zone rhyolites of Iceland. To address this, we used an Internally Heated Pressure Vessel (IHPV) to conduct phase equilibria experiments on rhyolite from Krafla volcano. Because rhyolite magma was unexpectedly encountered at shallow depth (2.1 km) during recent drilling of the IDDP-1 geothermal well, Krafla represents an opportune target for this work, providing a unique opportunity to compare experimental results with natural phase assemblages where pressure conditions are known a priori. Preliminary results show good agreement between the phase assemblages and mineral compositions of the natural Krafla rhyolites and our experimental samples at 850-875°C and 50 MPa, including the presence of augite at low (1-3 vol%) crystallinity and presence of fayalite at fO$_2$ < ΔNNO = -2. Our results imply that relatively hot (> 800-850°C) and shallow (≤ ~50 MPa) storage conditions are typical of most rift-related Icelandic rhyolites, and are consistent with the view that the low to moderate H$_2$O contents of on-rift rhyolites reflect H$_2$O saturation at low pressures. They also highlight an especially strong influence of fO$_2$ on the stability of ferromagesian phases in these magmas, reflecting their Fe-rich melt compositions (~3 wt.% FeO^T). Our experiments offer new perspectives on the enigmatic origins of Iceland's rift zone rhyolites, and provide important temperature and fO$_2$ constraints that support developing plans to study the active IDDP-1 magma body via targeted drilling.

Nitrogen solubility in bridgmanite

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Experimental studies on nitrogen solubility in the upper mantle and transition zone minerals [e.g. 1,2], have shown that the mantle has the potential to store more nitrogen than the atmosphere, which was traditionally regarded as the main N reservoir on our planet. Despite this, our knowledge of nitrogen solubility in lower mantle phases is still very limited. Previous data suggest that bridgmanite, lower mantle's main constituent, may dissolve only little nitrogen, i.e. 20 ppm at 24 GPa and 1600°C for an Al-free composition [2].

In this study, we conducted systematic multi-anvil experiments using aluminous bridgmanite compositions (ranging from 0 to 7 wt.% Al$_2$O$_3$) in a pressure and temperature interval ranging from 24 to 33 GPa and 1600 to 1800°C. Experiments were designed to crystallize bridgmanite from an oxide

mixture in the presence of an excess N-rich fluid phase and metallic Fe to buffer oxygen fugacity close to the iron-wustite buffer (Fe-FeO), realistic for the lower mantle. Nitrogen was introduced as ^{15}N-enriched ammonium nitrate ($^{15}NH_4{}^{15}NO_3$) to allow a reliable distinction of the sample signal from atmospheric contamination during analyses. After experiments, samples were studied by Raman spectroscopy for phase identification and by electron microprobe for major element composition. Nitrogen concentrations were measured by SIMS (Secondary Ion Mass Spectrometry).

Our data show that both pressure and temperature have a limited influence on N solubility in bridgmanite. However, introducing Al can enhance N dissolution by more than one order of magnitude, with a maximum of solubility near 4 wt.% of Al_2O_3, followed by a decrease at higher Al contents. This behavior may reflect the transition between two competing Al dissolution mechanisms in bridgmanite [e.g. 3]: At low Al contents, the oxygen vacancy mechanism prevails, while the charge coupled substitution mechanism, which requires two Al^{3+} to be close to each other, becomes dominant at higher Al contents. In the oxygen vacancy mechanism, Al^{3+} substitutes for Si^{4+}, charge compensated by oxygen vacancies. N^{3-}, possibly in protonated form as NH^{2-}, may then enter these vacancies. On the other hand, as the main Al dissolution mechanism shifts towards the charge coupled substitution, where 2 Al^{3+} substitute for Mg^{2+} + Si^{4+}, it becomes more difficult to introduce N, consistent with the decrease in N solubility observed for Al_2O_3 contents above 4 wt.%.

These results suggest that the nitrogen storage capacity of the lower mantle is even larger than previously thought and most of the nitrogen on our planet may have been retained in the lower mantle during magma ocean crystallization. This may imply that the "subchondritic N/C ratio of the Earth" [e.g. 4] only reflects an under-sampling of the lower mantle, while the real bulk Earth N/C ratio may very well be similar to the chondritic value.

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Novel ammonia hydrates in the mid-mantle layers of icy (exo)planets

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Ices of water (H_2O) and ammonia (NH_3), and their mixtures thereof, are major components in the interiors of Solar ice giants and likely thousands of newly discovered mini-Neptune exoplanets. These ices can display ionic and superionic behavior at extreme conditions (> 10 GPa and 900K) that can account for the unusual magnetic field detected for instance in Neptune [1-3]. Understanding the structure and physical properties of hot compressed ices at relevant conditions is thus key to accurately model the internal structure and dynamics of large icy bodies. Experimental studies over the last two decades have largely focused on pure H_2O and NH_3 ices, while the behaviour of ice phases in the binary system still remains poorly understood. It is currently unknown whether planetary conditions could stabilize other ammonia hydrates than the well-known low temperature stoichiometric forms - ammonia dihydrate (ADH, $NH_3:H_2O = 1:2$), ammonia monohydrate (AMH, $NH_3:H_2O$ = 1:1) and ammonia hemihydrate (AHH, $NH_3:H_2O = 2:1$) [4].

Here we investigate the high P-T behaviour of ice phases in the NH_3-H_2O system using a combination of resistively heated dynamic diamond anvil cells (RhdDAC) and double-sided laser-heated diamond anvil cells (LHDAC) experiments and synchrotron X-ray diffraction. An H_2O-rich ammonia mixture with 32 wt.% NH_3 ($NH_3:H_2O = 1:2$) was chosen as a starting material to approach their cosmo-chemical abundance, $NH_3:H_2O$ = 1:7. Samples were pressurized at room temperature to form a mixture of ice VII and NH_3-rich ammonia hemihydrate (AHH-II)before the high temperature experiments. Our time-resolved high P-T X-ray diffraction studies result in the identification of several phase transitions in the ammonia hemihydrate phase up to 26 GPa, and 800K. Above this temperature, a novel ammonia hydrate phase with body-centered cubic (bcc) crystal structure forms by the reaction of H_2O ice and the high pressure AHH phase. The new phase carries more H_2O than any of the known ammonia hydrates as estimated from linear mixing of NH_3 and H_2O (Ice VII) phase volumes. Ultimately, we will discuss the implications of these findings for the structure and dynamic of mantle layers in icy planetary bodies in comparison with the available geophysical observations [2,3].

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Influence of grain size on the high-pressure elasticity of sintered polycrystalline Mg_2SiO_4 forsterite

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The geological evolution of our planet is tightly linked to deep geodynamic processes, which, themselves, are governed by the physical and chemical properties of the Earth's mantle. Our current understanding of the thermo-chemical structure of the Earth's mantle largely relies on the interpretation of the seismic observables. Accurate interpretations of these observations, and hence a quantitative understanding of deep geodynamical processes, require experimental constraints on the elasticity of polycrystalline mantle materials at relevant pressure conditions. Previous high-pressure experimental studies have shown that polycrystalline materials exhibit an elastic behavior that deviates from that predicted based on single-crystal properties. Yet, the underlying reasons, including the effects of grain size in polycrystalline mantle materials remain poorly understood [1,2].

Here, the compression behavior of six sintered polycrystalline forsterite samples, having different average grain sizes (d_{ave}) ranging from 0.17 μm to 6 μm, was investigated by synchrotron X-ray diffraction experiments at the Extreme Conditions Beamline at PETRA III/DESY up to 19 GPa in a diamond-anvil cell. Our static compression experimental results are complemented by direct elasticity measurements of the sample with $d_{ave} = 0.17$ µm to pressures of 24 GPa using the Brillouin spectroscopy system at the University of Oxford. We will discuss the effects of grain size on the high-pressure elasticity of sintered forsterite, and discuss our findings in regard to the interpretation of geophysical observables.

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Experimental insights into the formation and geochemistry of high potassium dacitic domes in northern Chile

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The formation and geochemistry of dacitic domes in the Central Volcanic Zone of the Andes (CVZA) have been the subject of scientific interest for decades [1,2]. However, a comprehensive understanding of the processes and factors that control their formation and evolution remains elusive. This study presents a multi-faceted approach that combines experimental petrology with mineralogical and geochemical analyses of samples from three high potassium dacitic domes in northern Chile, Chillahuita, Chac-Inca, and Cerro Pabellon.

The experimental petrology component of the study involved pressure, temperature, and oxygen fugacity-controlled experiments using a starting material of a representative sample for each dome. The experimental results were used to constrain the conditions that favor the formation of high potassium dacitic melts and the crystallization of specific mineral phases. The experimental results were then contrasted with the natural rock samples to evaluate the applicability of the experimental results to natural systems. The mineralogical and geochemical analyses involved scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) to identify and quantify the mineral phases and their chemical compositions in the natural and experimental rock samples. The results show that the studied domes comprise a complex assemblage of minerals, including plagioclase, amphibole, biotite, and magnetite, as common phases, and ilmenite, apatite, and quartz as minor phases. In addition, the percentage of each mineral phase and texture varied between the domes, reflecting differences in their magmatic evolution and eruption history.

The geochemical and experimental analyses revealed that the high potassium dacitic domes bear calcic amphiboles characterized by a low Al_2O_3 content and plagioclases with higher An concentration than other dacitic lavas (e.g., Pinatubo, [3]; San Pedro, [4]) suggesting that they are a result of a mixture of processes (i.e., magma mingling, fractional crystallization and assimilation of crustal rocks). The experimental results also suggest that low temperatures (<850°C), moderate pressures (around 2-3 kb), and oxidizing conditions prevailed during the formation of high potassium dacitic melts, prior to eruption.

Overall, the results of this study contribute to a better understanding of the processes and factors that control the formation and evolution of high potassium dacitic domes in the CVZA and highlight the importance of combining experimental and analytical techniques to achieve a comprehensive understanding of magmatic systems.

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Quantification of water in amphiboles by Raman microspectrometry

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Confocal Raman microspectroscopy has been used to quantify water incorporated as hydroxyl (OH^-) into the structure of kaersutitic amphiboles synthesized in a piston-cylinder apparatus at upper-mantle conditions (1.4 GPa and 1015-1050°C). The Raman spectrum of amphibole (i.e., shape and relative intensities of the bands) varies significantly depending on the orientation of the crystal lattice with respect to the polarization plane of the laser source, with the most intense peaks occurring at 228, 665 and 750 cm^{-1} (silicate network) and between 3600 and 3750 cm^{-1} (OH region). The method used for water quantification adopts a statistical approach similar to that described in [1-3] for quantitative spectroscopic measurements in anisotropic crystals. Measurements were made on a large number of amphibole grains differently oriented in two dimensions, were averaged, and the area of the water band was then converted to water contents using the calibration lines defined by kaersutitic amphibole standards with known water contents previously determined by CHNS elemental analysis.

The method was used to investigate the effect of chlorine on water incorporation by the oxo-substitution mechanism in magmatic amphiboles (0.93-1.50 wt.% H_2O) that crystallized in equilibrium with trachy-andesitic melts (2.20-5.03 wt.% H_2O) [4]. Our results show a positive correlation between the Cl content of amphibole (0.18-0.88 wt.%) and the partition coefficient of water between amphibole and glass (${}^{Amph/L}D_{H2O}$ ranging from 0.29 to 0.52). This effect is ascribed to the incorporation of Cl at the anion site $O(3)$ that influences the oxo-substitution mechanism by impeding the entrance of Ti^{4+} at the $M(1)$ sites and thus preventing amphibole dehydrogenation. Our findings reveal that at mantle depths the occurrence of Cl in the system increases the stability of a more hydrogenated amphibole, thus capable of incorporating higher amounts of water.

We highlight the high potential of Raman microspectroscopy as a versatile, non-destructive analytical technique for water quantification in hydrous minerals at high spatial resolution down to the micrometer scale, suitable for studying samples with polyphasic composition and/or small volumes, including those recovered from high-pressure experiments or tiny valuable samples.

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MORB, OIB (+carbonatites), kimberlites: Surface expressions of the same incipient mantle melting?

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Despite its ubiquitous parenthood to several major magmatic series, incipient mantle melting in deep rooted upwellings remains poorly understood. The forward melting approach suffers from very small melt fractions and hard-to-control trace volatiles, and is biased by the choice of incompatible element concentrations. Furthermore, non-peridotitic sources may yield a momentary glimpse of incipient melt composition, but any upward migration will unavoidably lead to equilibration with an average mantle composition, a hybrid source combination not easily mirrored in experiments.

Thus, it is time to turn the question around and ask - for any primitive erupted melt - which melt compositions are parental to them at incipient melting depths. These depths are readily defined as those of redox melting, i.e. when diamond oxidizes to CO_2 upon demise of the Fe^{3+}-rich majorite component in garnet (~ 6-9 GPa). The experimental strategy then consists of saturating primitive surface melts - including appropriate amounts of CO_2 and H_2O - with the four mantle phases, at adiabatic or super-adiabatic temperatures. We have done so for a primitive kimberlite, average OIB, MORB and a carbonatite at 7 GPa, 1480 and 1630°C, maintaining saturation in C^0 (for an adequate fO_2) and using 10-1 wt.% CO_2 and uniformly 1-2 wt.% H_2O.

The result are rather similar kimberlitic melts at 7 GPa, with 18-25 wt.% SiO_2, <2 wt.% Al_2O_3 and high MgO. Conceptually, the four majors SiO_2-Al_2O_3-(Mg,Fe)O-CaO are controlled by the four mantle phases, while Na and K partition with cpx. Similarly, H is controlled by partitioning with olivine and the pyroxenes, leaving only Ti and P to bulk composition (or mantle heterogeneities). Mantle carbon content is then simply in control of the degree of melting, as all melts have 15-25 wt.% CO_2. Of course, this reasoning remains qualitative and melts are not identical (as not rigorously buffered), but nevertheless, all become kimberlitic at 7 GPa.

Upon rise within deeply rooted upwellings, porous flow likely leads to equilibration with the surrounding mantle and melts become lamproitic, melilititic, basanitic and finally basaltic with decreasing pressure. This is consistent with extraction of primary melts from the lithosphere-asthenosphere boundary, kimberlites from 200-250 km below cratons, melilitites at craton edges, basanites in ocean islands with comparatively deep oceanic lithosphere and basalts above thin lithosphere, where overstepping of the dry solidus leads to very large melt fractions and MORBs. Modifications in the lithosphere are and should not be negated, but are not necessary to understand the various asthenosphere-derived melts. At the same time, it can be shown that carbonatites origin from alkali-basanitic parents, direct mantle melting remaining largely a myth.

Ion dissociation in water under supercritical conditions: A molecular perspective on linear density models for equilibrium constants

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The volumetric properties of solutes diverge strongly towards infinity at the critical point (CP) of water. This makes the pressure and temperature conditions near the CP a major challenge for thermodynamic modelling of fluid properties. Linear density models for predicting equilibrium constants offer a promising basis for future models as they may allow to bypass the direct treatment of the anomalous properties near the CP [1]. However, the experimentally derived linearity between the logarithm of the water density ($\log(\varrho_w)$) and the logarithm of equilibrium constants ($\log(K)$) is purely empirical and requires validation. In previous classical molecular dynamics studies, enhanced sampling methods were used to investigate the dissociation of NaCl in supercritical water [2]. With this approach, the linearity between $\log(K)$ and $\log(\varrho_w)$ could not be confirmed.

Here, we perform classical MD simulations and follow an alternative approach for validating the linearity between $\log(K)$ and $\log(\varrho_w)$. Using NaCl and the 400°C isotherm as an example, we can discuss our results in the context of previous experimental and theoretical studies. The approach used is based on the determination of the volumetric solute and solvent properties underlying $\log(K)$, i.e., the reaction volume and the compressibility of the solvent. Our results confirm the constant $\log(K)$ vs. $\log(\rho_w)$ relation in the experimentally investigated density range between ~0.3 g/cm^3 and ~0.8 g/cm^3. Furthermore, we show that $\log(K)$ levels off at densities below ~0.3 g/cm^3 and forms an s-shaped curve with the significantly lower values calculated for vapor-like densities, which is consistent with the theoretical predictions of Pitzer [3].

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Molecular properties of hydrous $MgCO_3$ melt studied by ab-initio molecular dynamics simulations

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Understanding how water affects the molecular structure of carbonate melts is crucial to assess their function as metasomatizing agents and conveyors for the transport of carbon and incompatible elements in the deep Earth. It has been shown, that the solubility of water in carbonate melts is particularly high at high pressure (P), reaching contents of up to 16 wt.% at 900°C and 2 GPa [1]. However, the form in which water is dissolved in the structure of carbonate melts is not well understood [2]. Results of in-situ Raman experiments [3] are in contradiction to theoretical expectations based, among other things, on the increased solubility of incompatible elements in hydrous carbonate melts [4].

The elusive picture of the chemical speciation in hydrous carbonate melts calls for further insights using complementary approaches. Here we meet this need with the help of ab-initio molecular dynamics (AIMD) simulations, which provide a powerful tool for studying chemical systems from a computational perspective. We investigate the molecular properties of $MgCO_3$ melt containing 10 wt.% H_2O at conditions up to 1765 K and ~2 GPa. We report on the chemical equilibria controlling the dissolution of H_2O in the carbonate melt and discuss our results in the context of previous experimental and theoretical studies. Furthermore, we show that H diffuses the fastest of all elements, with self-diffusion coefficients up to three times higher than those of Mg. We discuss the molecular process underlying this rapid H-diffusion and implications for the electrical conductivity of hydrous carbonate melts.

Simulations were performed on the JUWELS supercomputer at Jülich Supercomputing Centre (JSC).

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Cr incorporation in post-spinel Fe^{2+}-Fe^{3+} oxides

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Chromite is generally a minor constituent of many ultramafic and mafic rocks, including mantle peridotite and it also occurs as inclusions in diamond. In addition, the chromitites of the Luobusa ophiolite in Tibet contain traces of diamond and coesite, suggesting a potential origin in the deep mantle [1]. High-pressure polymorphs of chromite have also been found in meteorites [2]. Thus, Cr-rich Fe-oxides can be of great importance for constraining extraterrestrial and deep Earth conditions and processes. However, the P-T stability of Cr-bearing high-pressure phases is not completely known. Although the $Fe_2Cr_2O_5$ endmember composition is known to be stable between 13 and 20 GPa [3], there is no information on the stability of $Fe_3Cr_2O_6$.

We performed multi-anvil high-pressure experiments over a pressure range of 12 to 20 GPa and a temperature range of 1200 to 1500°C to investigate phase relations in the system Cr-Fe^{2+}-Fe^{3+}-O. Starting materials comprising $FeCr_2O_4$, Fe_3O_4 and Fe° and having $Fe^{2+}{}_3Cr_2O_6$ or $Fe^{2+}{}_3(Cr,Fe^{3+})_2O_6$ stoichiometries were employed.

We find the $Fe_3Cr_2O_6$ endmember composition to be unstable over the entire range of pressure and temperature studied, the stable assemblage being $Fe^{2+}{}_2Cr_2O_5$ + wüstite. In the search for an O_6-structured phase across the Fe_5O_6 – $Fe_3Cr_2O_6$ binary, we found only a maximum of 0.11 cations Cr per formula unit (cpfu) could be accommodated in Fe_5O_6 (i.e. ~5 mol% $Fe_3Cr_2O_6$). In contrast, a complete Cr-Fe^{3+} solid solution series is observed in the O_5 phase. This is in spite of the fact that the two endmembers have somewhat different crystal structures: Fe_4O_5 and $Fe_2Cr_2O_5$ belong to space groups *Cmcm* and *Pbam*, respectively. The transition between the two structures occurs at ~50% Fe_4O_5 – 50% $Fe_2Cr_2O_5$. However, molar volumes exhibit essentially linear behavior across the join.

Furthermore, we observe a variation in the lattice parameter of wüstite, suggesting not only Fe^{3+} incorporation, but also Cr into the FexO structure as a function of P, T, and bulk composition. EPMA analysis indicates 2 to 9 wt.% Cr_2O_3 in wüstite, further contributing to its non-stoichiometric composition.

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Stress-driven phase reactions of fayalite olivine to ringwoodite under mantle conditions

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The Earth's mantle is a dynamic system due to its constant convection, and consequently large regions of the mantle are not under isostatic conditions. Magnesium-rich forsterite olivine (α) constitutes most of Earth’s mantle, and the pressures where forsterite transforms to its high-pressure polymorphs, modified-spinel structured wadsleyite (β-spinel) and spinel structured ringwoodite (γ-spinel), correspond to the depths of major seismic discontinuities. These large discontinuities show depth variations up to 10s of kilometres, which have been attributed to variations in temperature, kinetics, or composition. None of which can explain all the observations. However, much of our understanding between the relationship of olivine phase transitions and mantle structures have been conducted under isostatic conditions. Here we perform preliminary experiments on fayalite olivine (Fa_{100}) to understand if a simpler mechanism, stress, driven by the dynamic pressure environments in the mantle, can account of large variations in olivine phase transitions to account for variations in seismic discontinuities. Fayalite olivine was selected over forsterite since it undergoes a simple phase transition from a $\alpha \rightarrow \gamma$ without a β-spinel structured polymorph, and up to 10 GPa lower than forsterite allowing for experiments to be conducted in a large volume 18/11 cell. We conducted a series of experiments using a multi-anvil apparatus with four capsules, with three containing internal Al_2O_3 pistons to simulate strain under mantle conditions and one capsule without applied stress. Experiments were performed at 6 GPa at 1200°C and held for various durations to capture the $\alpha \rightarrow \gamma$ reaction at different applied stresses. We will be presenting results on how different applied stress conditions effect the transformation of fayalite olivine to ringwoodite compared to stress-free isostatic conditions. The results from these experiments can be extrapolated to multiple natural conditions, including the phase reactions that occur in the transition zone under stress, through to shock metamorphism of fayalite to ringwoodite in meteorites.

The eastern Australian leucitite chain: assessing hotspot-continental lithosphere interactions

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Most of our knowledge of the relationship between volcanism and hotspots comes from oceanic volcanic chains where rock types vary from tholeiites to alkaline basalts. Hotspot-associated rocks erupted on thick continental lithosphere include types not usually represented in oceanic chains, which results from complicated interactions with the continental lithosphere. Lack of knowledge of hotspot-continental lithosphere interactions hinders the identification of ancient continental hotspot tracks. In eastern Australia, one-third of the Earth’s longest continental hotspot track, the ~2,000-km-long Cosgrove Track, consists solely of unusual leucitites [1]. The leucitites have low SiO_2 (43.3-48.3 wt.%), high K_2O (3.9-7.7 wt.%) and TiO_2 (3.4-5.9 wt.%) contents with K_2O/Na_2O up to 11.4 [2]. In addition, the depth of lithosphere-asthenosphere boundary (LAB) had been imaged well by body-wave tomography. This reveals that surface outcrops of the leucitites are regularly associated with depressions and slopes of the LAB topography at ~120-140 km indicating the leucitites are linked with hotspot–continental lithosphere interaction [1].
Identifying the source lithology is the key to unveiling details of these interaction processes. Phlogopite has been invoked as an important source mineral for ultrapotassic rocks, but all experimental melts derived from phlogopite peridotite and phlogopite clinopyroxenites are distinct in composition from the eastern Australian leucitites, particularly in CaO and Al_2O_3 contents. We experimentally melted a garnet phlogopite websterite at 3.0 and 4.0 GPa and found that the melts show remarked resemblance to the eastern Australian leucitites in SiO_2, TiO_2, Al_2O_3, CaO, K_2O and MgO contents. Modelled trace element contents based on the experimentally derived melting reaction also match the those of the leucitites, suggesting that garnet phlogopite websterite is the most likely source lithology of the eastern Australian leucitites. This interpretation also agrees with the ~130 km lithospheric resistivity anomalies beneath the 3 outcrops of the leucitites [3]. Additionally, modelling shows that only a young formation age of the source garnet phlogopite websterite can reconcile the Sr-Nd isotopes of the leucitites. Given that hydrous alkaline melt interacting with peridotite forms garnet phlogopite websterite, and high mobility of melt at 4.0-6.0 GPa, we propose a hotspot-lithosphere interaction model which successfully explains the spatial relationship of the leucitites to LAB topography and lithospheric resistivity anomalies: the passage of a hotspot from thick to thinner lithosphere where ponded melt results in garnet phlogopite websterite under thinner parts of the lithosphere, and this garnet phlogopite websterite is remelted by the passage of the same hotspot shortly afterwards, generating the surface leucitites.

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Electrical conductivity for hydrothermal conditions: in-situ measurements with saline fluid

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We are developing methodologies to probe the in-situ electrical conductivity of porous samples with salt solutions.

We develop diverse protocols to measure electrical conductivities from room to hydrothermal conditions. We work on granite from Kakkonda (well WD-1a) and Pontgibaud borehole samples (Peyrouses 1). For salt solution, we used a various quantity of NaCl (0.02 wt.% to 20 wt.%) in demineralized water. When sample are hydrated, there are always saturated.

First data were collected at room temperature and atmospheric pressure for rock cores with different sizes. We are able to measure dry sample and hydrated samples with various salinity contents and these data are compared to porosity and permeability constraints.

Under pressure and temperature, we have different protocols that are deployed in the Paterson press. One with copper jacket and coaxial design for temperature up to 600°C and 2 kbar. We have the possibilities to make measurements on dry sample or pre-hydrated sample.

Another protocol is used for lower temperature (up to 300°C) and 1 kbar. We perform measurement with Teflon jacket and electrode on top and bottom of the sample. We can measure electrical conductivity on dry or pre-hydrated samples. With this protocol, the advantage is the possibility to inject fluid during the experiment under temperature and pressure and to control fluid pressures.

Melt evolution in primitive silicate-carbonatite systems

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Many carbonatite rocks occur as plutonic rocks, often associated with an abundance of peralkaline, Si-undersaturated rocks like syenites, nephelinites or ijolites in larger intrusive complexes. Despite their rarity, carbonatites and associated rocks constitute the main resource for rare earth elements. However, since carbonatites are prone to alteration, their formation and enrichment mechanisms remain elusive.

This work investigates the mineral and melt evolution in a primitive silicate-carbonatite system in order to complement previous studies focusing primarily either on strongly simplified or more evolved systems like the Oldoinyo Lengai. The silicate starting glass was synthesised according to melt inclusion compositions in perovskite from the Kola Alkaline Province and doped with a wide range of rare metals. Half of the experimental samples were nominally dry, the other half contained 5 wt.% H_2O, while CO_2 contents varied between 0 and 20 wt.%. Experiments were then conducted in an internally heated pressure vessel at 200 MPa and temperatures between 1000°C and 1100°C and at different oxygen fugacities.

Primitive silicate-carbonatite compositions corresponding to natural systems yield a complex melt and mineral assembly with an abundance of different phases. In nominally dry systems, all CO_2-free experiments lead to more evolved silicate melts, meaning melts containing increased amounts of SiO_2 and alkalis, by fractionating Ca-rich phases like monticellite, melilite and larnite. Liquid immiscibility occurs exclusively under oxidising conditions in CO_2-bearing systems via fractionation of melilite, perovskite and iron oxide. Contrastingly, under more reduced conditions, CO_2-bearing experiments produce melts with a primitive carbonatitic composition, meaning Ca-rich and poor in alkalis. They form directly from the silicate starting glass due to heavy crystallisation of biotite, perovskite and melilite, therefore evading liquid immiscibility. Introducing water into the system suppresses crystallisation, which leads to relatively minor changes in melt composition compared to the starting glass. Further experimentation in a broader temperature range could help resolve trends for water-bearing systems.

Diffusion and kinetic isotope fractionation of Li and B in pegmatitic systems

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Pegmatites are potentially Li-rich ore deposits that may facilitate the transition towards a more renewable energy oriented society. These magmatic rocks are often associated with highly fractionated granites and can be highly enriched in fluxes (e.g. Li, B, P, F). Fluxes likely play a key role in pegmatite genesis by lowering their crystallization temperature, nucleation rates, melt polymerization and viscosity and increasing diffusion rates [1]. There are many models for the formation of rare-element pegmatites, however, the mechanisms leading to strong metal enrichment are yet poorly constrained.

In this experimental study, Li and B diffusion coefficients were determined in flux-rich pegmatitic melts. For this purpose, a synthetic pegmatitic melt was used that is based on a rhyolitic composition with high amounts of added fluxes. Diffusion couple experiments were performed at 100 MPa in a rapid-heat/rapid-quench cold-seal pressure vessel (650-940°C) and in an internally-heated pressure vessel (1000-1250°C). One half of the diffusion couple was enriched in either Li_2O (1.8 wt.%) or B_2O_3 (2.6 wt.%), while the other half did not contain the studied element.

Li diffusion is coupled to an interdiffusive exchange with Na, while the other elements are immobile on the experimental time scales (1-30 min). B is likely involved in multicomponent diffusion with the other elements. However, due to the small concentration of B relative to the abundance of major elements, the diffusion of the other elements taking part in multicomponent diffusion is not resolvable. The diffusion of Li occurs at rates that are orders of magnitude higher than for B. While Li diffusion rates seem to be insensitive to the melt composition in dry aluminosilicate melts, B diffusion strongly depends on melt composition and is mainly controlled by melt viscosity. Fluxing elements alone do not enhance the diffusivity and lower the activation energy for Li diffusion in the same way as observed for H_2O [e.g. 2].

Chemical diffusion also results in isotope fractionation, as light isotopes generally diffuse faster than heavier ones. For Li and B this effect results in an enrichment of 6Li and 10B toward the interface of the Li- and B-free glass, while on the other side of the diffusion couple the Li- and B-rich glass becomes enriched in the heavier isotopes 7Li and 11B, respectively. This isotope fractionation can be modelled using an isotope fractionation factor 'β' of 0.20 for Li and < 0.05 for B.

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Monohydrocalcite-rich incrustation as an indicator of geochemical conditions in waters associated with hard coal mining

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In the Czech part of the Upper Silesian Coal Basin, highly mineralized mine waters and waters from draining coal dumps cause the distinct formation of incrustations close to watercourse areas [1]. By using X-ray powder microdiffraction, incrustations emerging from the drains of hard coal heaps were identified as a carbonate system with the dominant mineral monohydrocalcite and subsidiary aragonite, calcite and gypsum. The newly formed minerals were studied by other techniques such as LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry), EPMA (Electron Probe Microanalysis) and Raman spectroscopy with the primary objective of detecting any trace elements entering the structure. The formation of the monohydrocalcite was simulated in the laboratory. Crystallization from the solution sampled at the water source was compared with other previously reported synthesis methods [2,3].

Monohydrocalcite is a naturally occurring rare mineral that primarily forms in recent sediments in salt lakes, and not much is known about its origin related to hard coal mining. This specific mineral has been studied for its potential use in the remediation of toxic anions [4], which in terms of pollutants detected by LA-ICP-MS, is supported by our new data. Natural occurrences show that some impurities stabilize the formation of monohydrocalcite, and according to failed synthetic laboratory experiments, these conditions must be met; otherwise, aragonite or calcite will be formed. Together with the chemical analyses of the water, a comprehensive picture can be obtained of which elements migrate within this system, which are sorbed within the incrustation and what specific environmental conditions (such as temperature, pH, etc.) are needed for this system to function.

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The use of Knudsen Effusion Mass Spectrometry in the determination of activities of trace components in silicate melts

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The group 13 elements Ga and In are overabundant in Bulk Silicate Earth (BSE) when compared to lithophile elements of similar 50% nebular condensation temperature T_c^{50}. To understand whether evaporation from silicate melts provides a more accurate description of volatility during the later stages of planetary accretion, namely, at higher temperatures and more oxidising conditions than in the solar nebula, the activities of $GaO_{1.5}$ and $InO_{1.5}$ and knowledge of their gaseous species in and above silicate melts are required. To this end, we doped anorthite-diopside (An-Di) eutectic glasses with ~1000 and ~10000 ppm of Ga and In and determined their equilibrium partial pressures above the silicate liquid by Knudsen Effusion Mass Spectrometry (KEMS) using Ir cells at 1550-1700K over the $\log(fO_2)$ range ΔIW+6 to ΔIW+9 (IW = iron-wüstite buffer). We detect Ga^0 and In^0 as the dominant vapour species and determine activity coefficients of $\gamma(GaO_{1.5})$ = 0.036(6) at 1700K and of $\gamma(InO_{1.5})$ = 0.017(12) at 1674K. Comparing these with the activity coefficients of $BO_{1.5}$ and $AlO_{1.5}$ in silicate melts, we find a decreasing trend in activity coefficients of melt oxide components down group 13. Using these activity coefficients, we calculate partial pressures of Ga and In, together with the similarly volatile elements K and Zn as a function of temperature and fO_2 and show that their relative volatilities from basaltic melts differ from those predicted from their 50% condensation temperatures, T_c^{50}. This substantiates the view that the abundances of volatiles in BSE, such as Ga and In, may have been set by evaporation from silicate melts under oxidising conditions at later stages of planetary accretion. Moreover, chondrules likely never underwent significant evaporation during melting and their volatile-depleted nature is likely inherited from the earliest solid condensates.

Segregation and extraction of late magmatic melt in mushes: experimental approach at high pressure

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In recent years the crustal mush, defined as volcanic structures formed by a high crystalline content and silicate liquid, has been gradually replaced the traditional idea of a magma chamber. However, the physical mechanisms that could lead to the segregation and melt extraction in a network of interconnected crystals within the volcanic mush are still poorly understood. In this study, simple shear deformation experiments were performed in order to investigate the deformation structures developed, how force chains propagate within a crustal mush and how the morphology of the crystals can affect the dynamics of mushes. An internally heated pressure vessel was used to synthesise starting materials with haplotonalitic composition (SiO_2: 68.9 wt.%, Al_2O_3: 19.6 wt.%, Na_2O: 8.0 wt.%, CaO: 3.5 wt.%, plus water). During the syntheses, the pressure remained constant (P = 300 MPa), while the temperature ranged between 1000°C and 790°C. We created hydrous (3 wt.% H_2O) mushes composed of euhedral plagioclases crystals with different aspect ratio (R = 2 or 4), and various crystal content (f: 0.52-0.85), exploring the boundary of the expected extraction windows phase. We performed torsion experiments in a Paterson HP-HT apparatus, with strain rates ($\dot{y}$) vary from $1.0x10^{-5}$ s^{-1} to $2.0x10^{-3}$ s^{-1} and a finite strain (γ) ranging between 0.5 and 2.0. Using the SEM and EBSD techniques, we were able to carry out the quantitative structural analysis, including shape-preferred orientation (SPO), crystallographic-preferred orientation (CPO) and crystal interaction (CI). Depending on the aspect ratio, the samples show different behaviour after deformation: samples with an aspect ratio of 4 show strain localisation expressed by shear bands; samples with an aspect ratio of 2 do not show any strain localization, but they have 2 orientation domains, with an inclination ±65° and ±30°. For this series of experiments, none of our samples show melt migration. We are currently working on a high crystal content series of experiments (f: 0.70-0.85) to achieve the melt migration. We conclude that: 1) the localization of the deformation in magmatic mushes is strongly influenced by the morphology of the crystals, which may favour stress propagation on the crystalline network in a homogeneous or localised way, 2) high crystal content experiments are needed to investigate the melt migration in volcanic mushes.

Experimental observation of lithium partitioning in a three-phase system: melt-gas-plagioclase

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There is growing interest in understanding the behavior of lithium (Li) in volcanic systems. Recent studies have shown that Li diffusion in melt depends on dissolved water concentration [1,2] and demonstrates that in a two-phase system, composed of silicate melt and gas bubbles, Li behavior is dependent on the dynamics of decompression-related degassing [3,4]. However, these preliminary studies involved simplified one- or two-phase systems, but natural magmas are often three-phased systems, composed of coexisting liquid, gas, and minerals. Furthermore, few studies have examined Li partitioning between melt and crystallizing minerals. This would provide key starting conditions for modeling Li behavior in natural systems, where the focus is on the final products of a volcanic eruption, without having a complete constraint of Li evolution through the magmatic conduit.

In this study, we experimentally investigate Li partitioning in a three-phase system, namely a hydrous rhyolitic melt forming plagioclase crystals and gas bubbles during storage and decompression. Cold-seal pressure vessel experiments were carried out using synthetic rhyolite glass powder with an initial water content of 3.5 wt.% and Li concentration of ~100 µg/g. The capsules were held at constant initial pressure (150 MPa) and temperature (850°C) for five days to trigger plagioclase formation. One of the three runs was immediately quenched after dwelling in order to define the dynamics of crystallization and to assess the starting conditions prior to the decompression-degassing process. For the remaining two runs, after the five-day dwell, pressure was continuously decreased with decompression rates of 0.12 and 0.06 MPa/s, triggering bubble nucleation and growth. The two decompression experiments were quenched at a final pressure of 70 MPa.

In the dwell experiment, plagioclase crystals formed with an average size of ~15 µm. The bubble size and distribution are heterogenous, as the crystals acted as nucleation sites for gas bubbles and formed prior to the decompression process. Upcoming SIMS analyses of H_2O, Li and its isotopes are being performed to explore the bubble/melt and crystal/melt interface. A first evaluation of Li partitioning between melt, crystals, and volatiles will be presented along with a discussion of how these data can be used in models of Li behavior in complex natural systems.

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Positive thermal Raman shifts in silicates

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In real crystals, increased temperature normally has a lowering effect on the frequencies of Raman-active vibrational modes. Here we show positive thermal Raman shifts in a variety of silicate minerals, and discuss how this property can be used for a fruitful shake-hands between mineralogy and materials science.

Influence of crystallization on magmatic degassing and eruptive dynamics

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Gas escaping from the magmatic column significantly impacts the eruptive dynamics of silicic volcanoes. According to a recent study [1], outgassing probably occurs several kilometers deeper in the magmatic column than previously believed (several hundreds of meters below the surface). When crystal content reaches 40 to 70 vol%, bubble channeling takes place causing early outgassing [2]. This specific crystal concentration ought to enable the magma to become permeable at lower starting gas contents (more than 15 vol% bulk porosity).

We propose to model this phenomenon and the evolution of bubble coalescence and channelization regarding crystal size and gas content using synthetic magmas (haplogranit, alumina crystals, and water) using decompression experiments in internally-heated autoclave. The bubbles are created thanks to high-rate decompression of a hydrous melt in order to have a homogeneous nucleation in the sample. In these experiments, we propose to test the influence of crystal size and crystal content on the permeability in a gas-poor mixture.

Preliminary results suggest the presence of permeability at 10% bulk porosity for a bulk crystal content of 50 vol%. Surprisingly, our results suggest that one of the most important parameters for the formation of permeability in gas-poor magma is the number density of bubbles. High BND seems prone to enhance bubble coalescence and channelization. The decompression rate can experimentally control the BND [3]. Therefore, we will try to change the BND in our future sample by extending the decompression time from 4-5 minutes to 40 minutes to determine if the different samples show various behavior from one case to another. Based on our preliminary results and assumptions on the future samples, the role and process of nucleation are then to be considered seriously in the problematic of channelization and further in magmatic degassing.

One of our hypotheses is that crystals serve as a framework for the coalescence of bubbles and, to an extent, their channelization and the permeability of our samples. To test this hypothesis, we need to compare samples with different sizes of crystals (50 µm, 300 µm, mix of both) to determine if the bubbles' behavior might control that parameter. These experiments were designed to mimic the natural occurrence of phenocrysts, microlite, and a mix of both. Also, we performed experiments with different amounts of crystals (70% bulk, 50% bulk, and no crystals) to constrain the importance of crystal contents in the coalescence process.

The parametrized behavior of bubble coalescence and permeability at low gas volume fraction and high crystal fraction will then be integrated into large-scale numerical model to predict the evolution of degassing in magmatic columns.

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Experimental constraints on the phase equilibria of mafic, alkaline magmas

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Alkaline magmas, characterized by high K_2O and Na_2O, encompass a wide range of compositional diversity, and occur at a variety of settings, including continental rifts, ocean-islands and arc-settings. The onset of crystallization of feldspathoids is one of the most obvious mineralogical features marking the boundary between silica-saturated and undersaturated alkaline magmas. However, the boundary between the stability fields of plagioclase and the feldspathoids in the compositional space of alkali basalts, and the effects of P, T, volatiles and fO_2 on the evolution of residual liquids during progressive cooling and crystallization are poorly defined.

This initial study examines the dry phase equilibria and liquid lines of descent of mafic alkaline magmas, with the aim of understanding how they might differentiate in shallow crustal storage regions. Five primitive (9.3-11.1 wt.% MgO) and four evolved (5.0-5.6 wt.% MgO) alkaline samples, from Fogo (Cape Verde), Terceira (Azores), Tristan da Cunha, Nyamulagira (Democratic Republic of the Congo; DRC) and Nyiragongo (DRC) were used as starting compositions. Two series of equilibrium crystallization experiments were performed in a gas mixing furnace (CO-CO_2) at 1 atm. Experiments using primitive starting compositions were performed in the temperature range 1220-1100°C, while those using evolved starting compositions were in the range 1170-1050°C. Oxygen fugacity in alkali magmas varies substantially and we therefore performed our experiments at fugacities corresponding to the fayalite-magnetite-quartz (FMQ) buffer, FMQ+1.5 and FMQ+3.

Saturated phases in the primitive samples include olivine + spinel + clinopyroxene ± plagioclase ± magnetite ± ilmenite. Evolved samples saturate spinel ± olivine ± clinopyroxene ± plagioclase ± nepheline ± magnetite ± ilmenite. In both series of experiments, increased fO_2 enhances the stability of spinel, which is the liquidus phase across all compositions under oxidising conditions. Experiments at higher fO_2 have lower melt fraction, due to the earlier crystallisation of clinopyroxene (primitive samples: FMQ: 1130-1150°C, FMQ+3: 1150-1170°C; evolved samples: FMQ: 1080-1110°C, FMQ+1.5: 1110-1120°C) ± plagioclase (primitive samples: FMQ:1110-1140°C, FMQ+3: 1130-1150°C; evolved samples: FMQ: 1070-1090°C, FMQ+1.5: 1090-1140°C), alongside spinel and Fe-Ti oxides. Melt CaO content and plagioclase anorthite content reflect increased clinopyroxene stability, falling with increasing fO_2 at constant temperature. Alkali rich phases are absent in primitive samples, meaning melt Na_2O and K_2O content increases steadily across all fO_2 conditions. These experiments, in addition to ongoing experiments on evolved compositions, demonstrate that greater fO_2 promotes a greater degree of melt evolution, and less alkali rich liquid lines of descent. Subsequent work will explore the effect of pressure and volatiles on feldspar and feldspathoid stability, and the evolution of alkaline magmas.

Carbon mobility in slab-fluids and implications for mantle metasomatism by carbon-saturated COH fluid

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COH fluids have a crucial role in a variety of geological processes in subduction zones, where carbon-bearing aqueous fluids released from the down going slab infiltrate the overlying mantle wedge and trigger partial melting and arc volcanism. Graphite has been traditionally considered a refractory sink of carbon in the subducting slabs. Nonetheless, recent experimental studies suggest that the presence of different carbon forms (e.g., crystalline graphite, glassy carbon) modifies COH fluid properties, and results in enhanced mass transport capacity for major elements such as Si and Mg, through complexation with inorganic and organic C-bearing ligands [see 1]. A quantitative understanding of the effect of carbon-saturated COH fluids is, however, still lacking because the speciation of carbon and major solutes in the fluids, and hence their transport mechanisms, have not been identified yet. This is mainly due to the scarcity of experimental data on mineral solubility in complex COH fluids at conditions relevant to subduction zones.

Here we present preliminary results on the solubility of reduced carbon in aqueous fluids that mimic fluids released by dehydrating slabs in fore to back-arc settings. The solubility of crystalline graphite/glassy carbon was determined by in situ observations of the complete dissolution of samples up to 2 GPa and 700°C while the speciation of the fluids was monitored by Raman spectroscopy. Our results constrain the mutual solubility of carbon and silica in natural slab fluids and provide new constraints for metasomatism in the mantle wedge by solute-rich COH fluids. The retrieved experimental data represent a significant step forward in the study of deep carbon and clarify the role of organic/inorganic carbon complexes in the transport of solutes at high-pressure conditions.

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Experimental redox dissolution of carbonaceous matter at 1 GPa, 550°C and its implications for COH fluid production in forearc subduction zones

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Biogenic carbonaceous matter (CM) is the main carrier of organic carbon into the subduction zones. Its redox dissolution occurring along with slab dehydration contributes to the production of COH fluids that are involved in mantle wedge metasomatism and in the production of volcanic arc gaseous emissions, which can ultimately affect the Earth's climate. To assess how and to which extent organic carbon is recycled into the mantle it is first necessary to recognize the processes that are able to extract it from CM. A complication in this estimate arises from the fact that CM is an heterogenous material, in that it can have various degrees of crystallinity and proportions of sp^2 and sp^3 hybridized C atoms, it can assume different textures and contain significant amounts of H, heteroatoms (especially O) and oxygenated functional groups (OFGs).

To investigate the role of these features in the redox dissolution of CM in water, we conducted a series of short (1h) experiments on a piston-cylinder apparatus at 550°C and 1 GPa, with fO_2 buffered from ΔFMQ ≈ +4 to −7 using the double capsule technique. Most reducing conditions, which rely on H_2–H_2O equilibrium, were attained by a novel buffering strategy that exploits the thermolysis of ammonia borane to produce free hydrogen in the fluid. As reactants we used ultrapure water and synthetic analogues of CM characterized by peculiar structural, textural and compositional features, i.e., graphite (crystalline C(sp^2); O < 1 at%), mesoporous carbon (poorly ordered sp^2 C with a mesoporous texture; O < 1 at%; OFGs ~2%), glass-like and Vulcan® carbon (disordered sp^2-rich C; C(sp^3) < 30 at%; up to ~8 at% O; OFGs < 30 at%), graphite oxide (partly ordered C(sp^3); C(sp^2) < 2 at%; O ~31 at%; OFGs ~41 at%).

Graphite and mesoporous carbon show very low solubility in water ($CM_{dissolved}$ < 0.4%);

graphite oxide reacts more extensively at all redox conditions ($CM_{dissolved}$ > 2%); glass-like and Vulcan® carbon are more soluble at extreme redox conditions ($CM_{dissolved}$ ~ 1% at ΔFMQ ≈ +4 and > 1% at ΔFMQ ≈ –7). Carbon dioxide is the dominant volatile carbon species in the fluid with some exceptions: for graphite at ΔFMQ ≈ +0.3, –5, mesoporous carbon at ΔFMQ ≈ +4, 0, –5 and Vulcan® carbon at ΔFMQ ≈ 0 CO is the most abundant volatile C species; CH_4 prevails at ΔFMQ ≈ –7 for all carbon forms, graphite oxide excluded.

Thus, low crystallinity, high content of C(*sp^3*), O and OFGs contribute to increase CM solubility. Hydrogen adsorption seems to reduce graphite and mesoporous carbon reactivity at ΔFMQ ≈ –5 and –7, probably because of passivation of active sites; a similar process likely hinders methane formation at ΔFMQ ≈ –5, where a pure CH_4 fluid would be expected from thermodynamics. Carbon monoxide is a reaction intermediate whose production is probably accompanied by the formation of H- and O-bearing surface complexes. High contents of oxygen heteroatoms and OFGs in CM seem to catalyze CO_2 release.

These results indicate that immature CM (poorly crystalline, C(*sp^3*)- and O-rich) is more prone to dissolution at the onset of dehydration reactions in forearcs and can buffer the fluids to rather oxidizing conditions; therefore, immature CM may give a fundamental contribution to the shallow organic carbon flux. Moreover, the relatively high stability of H- and O-bearing functional groups may be associated with a previously neglected flux of hydrogen and oxygen associated with CM subduction.

H_2O and CO_2 metasomatism at the lithosphere-asthenosphere boundary and its evolution

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One of the main effects that small amounts of volatiles, such as water and carbon, can have on the mantle is the considerable melting point depression [e.g. 1], this is a common effect in all experiments involving volatiles in their composition when compared to dry experiments. In addition, it is commonly understood that CO_2 expands the stability of orthopyroxene and garnet [e.g. 2], generating melts that are more depleted in silica and aluminum, and richer in magnesium and calcium. However, it is essential to consider the proportion of water and carbon present in the experiments. Depending on this proportion the reaction products can be quite different in the carbonated hydrous peridotite experiments. Besides that, the balance and variation in the number of alkalis will also bring mixed results in different pressure and temperature conditions. We performed experiments that simulate the lithosphere-asthenosphere boundary in subcontinental crustal thinning environments through two pressure conditions: 2.5 GPa and 4.5 GPa. All experiments were made with two compositions layer per capsule, while the variable parameters were only the temperature and pressure. The compositions are representative of a depleted lithosphere (NHD-peridotite) and a fertile pyrolite with 30% of eclogite (MPY peridotite + GA1 eclogite). Amounts of 0.8 wt.% water were added to the depleted NHD-peridotite and

0.75 wt.% CO_2 was added to the enriched asthenosphere composition. The results show melts highly enriched in silica and aluminum and poor in magnesium when compared with the same conditions in carbonated peridotite and as well as in experiments with higher ratios of CO_2 to H_2O [3]. Final residual minerals are formed by olivine and clinopyroxene. Thus, these conditions provide expansion of olivine and augite stability and garnet and orthopyroxene instability. In this context, the CO_2 is quite insoluble in the melt, which rapidly releases in both low and high pressures in moderate to high temperatures. In a low degree of melting the CO_2 is only dissolved in the melt, whereas the H_2O creates stable hydrated phases such as amphibole and phlogopite. These experiments contribute to a better understanding of the geodynamics of C-O-H fluids in mantle metasomatic environments.

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Effects of the iron spin crossover on the compressibility of iron-enriched ferropericlase with relevance to Ultra Low Velocity Zones

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$(Mg_{1-x}Fe_x)O$ ferropericlase is the second most abundant mineral in Earth's lower mantle. Ferrous iron in ferropericlase undergoes a change in electronic spin state at pressures of the lower mantle. The compressibility of ferropericlase is enhanced across the pressure range corresponding to the iron spin state crossover. This leads to a marked decrease of compressional wave velocities, with wide-ranging implications for the interpretation of seismic observations in the lower mantle. The onset pressure and, hence, depth of the spin crossover, however, depend on the iron content of ferropericlase. The amount of iron incorporated into the ferropericlase structure can vary substantially depending on depth and location in the mantle. In the shallow lower mantle ferropericlase has an iron content of about 20% (i.e. $x = 0.2$), but this may increase to 35% with depth, e.g. due to spin-crossover induced changes in iron partitioning between ferropericlase and bridgmanite [1]. Ferropericlase may even have iron contents of > 80% in iron-enriched regions near the core-mantle boundary, which has been suggested as an explanation for the strongly reduced wave velocities observed in Ultra-Low Velocity Zones (ULVZs) [2]. The effects of the spin crossover on the compressional wave velocity of ferropericlase must be considered in any attempt to infer mantle properties from seismic observables, including investigating the origin of ULVZs. However, the effects of iron content on the spin crossover-induced bulk modulus softening have not been measured systematically.

Here, we investigated the effect of iron content on the compression behaviour of ferropericlase using continuous compression experiments in the Diamond Anvil Cell, in combination with time-resolved synchrotron X-ray diffraction measurements at beamline P02.2 (PETRAIII, DESY) [3]. Pressure-volume curves of $(Mg_{1-x}Fe_x)O$ with $x = 0.2$-

0.8 were measured up to 135 GPa. The quasi-continuous pressure-coverage of our data allows us to map out the spin crossover-induced bulk modulus softening as a function of iron content. We will discuss the implications of our findings for the interpretation of lower mantle seismic observables.

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Water-dependent alkali trace element diffusion (Li, Rb, Cs) in silicic melts

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The study of magmatic processes like recharge and fluid exsolution is critical for understanding the evolution of the Earth's crust. Trace element diffusion is a powerful tool for tracking such processes, but its dependence on melt water content is not well understood. Previous studies have also been limited by their use of water-free melts, which may not accurately represent natural magmatic systems. To address these issues, we investigate the diffusion of alkali trace elements in different types of rhyolite as a function of water content.

For the diffusion couples, homogenous hydrous glass cylinders with 1-8 wt.% H_2O were produced from trace element-doped and undoped powdered glass. Diffusion experiments were conducted between 720-1100°C and 1 to 7 kbar for 5-25 min using gas pressure vessels and a piston cylinder apparatus. The diffusion profiles were analyzed by LA-ICPMS and evaluated by a Monte Carlo iterative fitting procedure for full error propagation. At a given experimental temperature, measured logD values increase linearly with melt water content, with one order of magnitude increase for Li, two orders for Rb, and three orders for Cs from driest (1 wt.%) to wettest (8 wt.%) experiment, due to a linear decrease in activation energies. Variations in major element composition only have a minor effect.

We illustrate the effect of differential diffusion in hydrous silicic magmas on their trace element budget by coupling our data to a two-phase mechanical model of channelized fluid transport in magmatic systems. Our results demonstrate that quantifying water-dependent diffusivities can provide an important tool to track the exsolution, mass, and rate of fluid transport within long-lived shallow mushy magma reservoirs in the Earth's crust. These findings are essential for advancing our understanding of the role of kinetics in magmatic processes.

Isotopic exchange among graphitic carbon, calcium carbonate and CO_2: The link between subducted marine sediments and volcanic arc emissions

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Ocean sediments consist mainly of calcium carbonate and organic matter (phytoplankton debris). Once subducted, some carbon is removed from the slab and returns to the atmosphere as CO_2 in arc magmas. Its isotopic signature is thought to reflect the bulk fraction of inorganic (carbonate) and organic (graphitic) carbon in the sedimentary source. Tumiati et al. [1] challenged this assumption by experimentally investigating model sediments composed of ^{13}C-$CaCO_3$ + ^{12}C-graphite interacting with water at pressure, temperature and redox conditions of an average slab-mantle interface beneath arcs. We demonstrated that oxidation of graphite is the main process controlling the production of CO_2, while CO_2derived from carbonate decomposition/dissolution is negligible. The isotopic composition of CO_2 reflects therefore the CO_2/$CaCO_3$ rather than the bulk graphite/$CaCO_3$ (i.e., organic/inorganic carbon) fraction. Tumiati et al. [1] also provided a mathematical model to predict the arc CO_2 isotopic signature on the basis of the fluid-rock ratios and of the redox state in force in its subarc source. In order to test the model in a carbonate + graphite system characterized by natural isotopic compositions, we replicated the experiments using dried cultured coccolithophores instead of marked compounds. Coccolithophores, which constitute the best part of open ocean sediments above calcite compensation depth, are able to provide at the same time calcium carbonate (coccoliths) and organic matter (cell material), which become aragonite and graphitic carbon, respectively, at the run conditions of 3 GPa and 700°C. We demonstrated that the model published by Tumiati et al. [1] fits well the new experimental data, and it confirms to be valid to predict the isotopic composition of CO_2 emitted by arc volcanism even for low amount of graphite < 1 wt.%, which is the assumed to be the average abundance in marine sediments.

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High-P phase relations of Al-bearing magnetite: Implications for terrestrial and extraterrestrial samples

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Over the last decade, accessory phases like iron oxide spinels and their respective post-spinel phases have attracted more and more attention since their occurrences as inclusion in diamond or in extraterrestrial samples provide information to constrain their depths of origin or the P-T conditions during a shock event [e.g. 1,2]. For instance, magnetite occurs as exotic non-ultramafic inclusions in diamond, either as a discrete grain or associated with other phases such as wüstite, metallic Fe, hematite, or pyrrhotite [e.g. 2,3]. Since such magnetite is reported to have an almost pure end-member composition, it can be assumed that it either formed at pressures up to 10 GPa or, if particular microstructures are observed, that it formed as a breakdown product from a high-pressure precursor phase (e.g. Fe_4O_5 or Fe_5O_6). However, current information about high-P-T phase relations is mostly restricted to spinel end-member compositions so that the interpretation of natural samples forming solid solutions is often hampered by uncertainties in the actual phase relations. For instance, some magnetite samples are reported to contain Al [e.g. 3,4], which could affect the high-P-T stability of this phase.

Thus, we experimentally investigated the phase relations of Al-bearing magnetite ($Fe^{2+}(Fe^{3+},Al)_2O_4$) between 8-22 GPa and 1000-1600°C using a multi-anvil press. Analysis of run products demonstrate that the spinel-structured phase is stable only up to ~10 GPa at 1100-1400°C, irrespective of the amount of hercynite ($FeAl_2O_4$) component present in the starting composition (20, 40 or 60 mol%). At higher pressures, the assemblage $Fe_2(Fe,Al)_2O_5$ + $(Al,Fe)_2O_3$ becomes stable over the P-T range of 11-20 GPa and 1200-1550°C. Depending on T, the assemblage $Fe_3(Fe,Al)_4O_9$ + $(Al,Fe)_2O_3$ or a hp-$Fe(Fe,Al)_2O_4$ polymorph becomes stable at $P \geq 18$ GPa. While $Fe_2(Fe,Al)_2O_5$ and $Fe_3(Fe,Al)_4O_9$ are recoverable phases, the hp-polymorph is unquenchable, yielding a defect-bearing spinel-phase with numerous twin lamellae and with notably less Al content than the initial starting bulk composition. While complete solid solution exists between magnetite and hercynite at low P, all post-spinel phases have only very limited Al solubility with up to ~0.1 cpfu Al in hp-O_4, ~0.3 cpfu in $Fe_2(Fe,Al)_2O_5$ and ~0.4 cpfu in $Fe_3(Fe,Al)_4O_9$. The remaining Al available stabilizes an additional $(Al,Fe)_2O_3$ phase. The phase relations remain essentially the same in Al-richer bulk compositions, with just different proportions of $(Al,Fe)_2O_3$ appearing in the assemblage. The co-existence of both hematite- and corundum-rich solid solutions in a number of experiments indicates that the miscibility gap across the rhombohedral oxide join established at low-pressures persists up to at least 20 GPa.

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The viscosity of volcanic melts: current knowledge, challenges, and future directions

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Magma viscosity is the key physical property that governs magma transport and eruptive style of volcanoes. The viscosity of magma is dramatically influenced by the composition and temperature of the melt phase, as well as the presence of bubbles and crystals, albeit to a lesser extent.

While several studies over the last four decades have measured the viscosity of volcanic melts as a function of composition and temperature, recent research has revealed that the formation of nanosized crystals of Fe-Ti-oxides, known as nanolites, during viscosity measurements can heavily affect the accurate determination of the pure melt viscosity. In particular, the crystallization of nanolites significantly increases the viscosity of volcanic melts due to still unclear changes in the chemical composition of the melt, subsequently affecting the reliability of the resulting empirical models based virtually on nanolite-bearing viscosity data.

To overcome this challenge, we propose a new multipronged methodology that combines conventional viscometry with differential scanning calorimetry, transmission electron microscopy imaging, Brillouin, and Raman spectroscopy. The results show that the viscosity of our melts prone to nanocrystallization during viscosity measurements at eruptive conditions is lower than the predictions of commonly employed empirical models. Our findings have implications for the numerical modeling of magma ascent and thereby predictions of volcanic scenarios from the probabilistic point of view.

Rheological behaviour in melts and magmas induced by crystallization and strain rate

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The two main parameters which are of importance to model the rheological properties of crystallizing magmatic systems and which are poorly investigated so far, are crystallization and strain rates. This study highlights the rheological variation of partly crystallised systems undergoing shear deformation. Etna basaltic glass previously synthesized, from natural basaltic rock powder, at 1400°C, was used to perform 0.1, 1 and 10 s^{-1} shear rate controlled experiment at temperature of 1150°C by using wide-gap concentric cylinder viscometry. Nine experiments were run and samples were collected after 3, 6 and 9 h. The experiment with the highest shear rate (10 s^{-1}) showed a brittle failure when viscosity reached the value of approximately 2.86 log (Pa·s) after ca. 1150 s. The viscosity measured at a shear stress of 7244 Pa possibly corresponds to the brittle failure in our partly crystallised system at these conditions. Brittle failure was observed after 20300 s when applying a shear rate of 1 s^{-1} (3.48 log Pa·s) and 22230 s when applying a shear rate of 0.1 s^{-1} (4.35 log Pa·s). The response of the partly crystallised Etna basalt to different deformation rates results in shear thinning behaviour pointing to an increase in viscosity as shear rate decreases as reported above. The shear thinning effect is also evident for others partly crystallized systems under variable shear rate [1] and should be taken into account when considering magmatic processes. Since there are difficulties in comparing experimental data gained using different methodologies, we focus mainly on data obtained with the concentric cylinder technique. This highlights the fact that a general experimental protocol is needed in order to compare and model viscosity data to predict the dynamic rheological evolution for volcanic rocks.

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Time-resolved X-ray diffraction during continuous compression of MgO using dynamic Diamond Anvil Cells

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MgO periclase is an important end member of $(Mg_x,Fe_{1-x})O$ ferropericlase in Earth's lower mantle. Understanding the elastic behavior of MgO at high pressures is essential to quantify the physical properties of Earth's lower mantle. MgO is also a well-studied reference material. Both static compression experiments with relatively small strain rates and shock experiments with extremely large strain rates have been performed to constrain the compression behavior of MgO under contrasting regimes of strain rates [e.g., 1-3].

Here, we report time-resolved continuous compression experiments using a dynamic diamond-anvil cell (dDAC) on MgO powder. Experiments have been performed at the Extreme Conditions Beamline P02.2 at PETRA III/DESY (Hamburg, Germany) employing compression rate up to 1.6 GPa/s. Additional cyclic loading experiments have been conducted at the highest pressures. Our experimental approach generates quasi-continuous volume-pressure curves, recording hundreds of X-ray diffraction patterns in a single experimental run, either in a pressure ramp or during pressure oscillations. This unprecedented resolution of data coverage allows us to explore and discuss the compressibility and the stress state of MgO at intermediate compression rates and to assess the potential effects of varying strain rates and stress states on the compression behavior.

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Experimental constraints on the formation of Hongge Fe-Ti oxide-mineralized layered intrusion, SW China

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The Hongge layered intrusion in Southwest China hosts the largest Fe-Ti-V oxide deposit in the world. It is formed by three lithological zones, including a lower (±amphibole) olivine clinopyroxenite zone, middle magnetite clinopyroxenite zone with massive ore layers, and upper gabbro zone. Previous studies proposed that the parental magma of Hongge layered intrusion is similar in composition to the coeval high-Ti ferrobasalts of the Emeishan large igneous province. However, due to limited experimental data on crystallization/differentiation of high-Ti ferrobasaltic systems, its formation processes, especially the ore mineralization processes, are still controversial. To understand crystallization processes in Hongge layered intrusion, we conducted a series of experiments in internally heated pressure vessels with a high-Ti ferrobasaltic parental composition. The experiments were run in a temperature range from 1200 to 950°C, at 100 and 300 MPa, and with different water activities ($a\mathrm{H_2O}$ = 0 to 1). Since crystallization of Fe-Ti oxides is sensitive to oxygen fugacity ($f\mathrm{O_2}$), both oxidizing and reducing conditions (ΔFMQ+3.3 and ΔFMQ+1 at $a\mathrm{H_2O}$ = 1) were applied. Experimental results show that magnetite/chromite is always the liquidus phase under all the experimental conditions, followed by olivine, clinopyroxene, ilmenite/hematite, plagioclase, apatite, and amphibole, which matches well with the observations from Hongge natural samples. The natural mineral compositions could be reproduced in the experimental products. Oxygen fugacity mainly influences the oxide species and olivine stability field in our system, while pressure variations control the stabilities of all silicate phases. High water content in the melts can suppress the crystallization of plagioclase. Based on the experimental results, we can use the obtained phase relations to constrain the crystallization conditions of Hongge layered intrusion.

The Hongge parental magma started to crystallize at relatively reducing and hydrous conditions. As a result of the crystallization of olivine and clinopyroxene in the early stage, forming a lower olivine clinopyroxenite zone, the oxygen fugacity in the residual magma increased, leading to the co-crystallization of magnetite and clinopyroxene in the middle zone. In the late stage, temperature decreases lead to the crystallization of clinopyroxene and plagioclase, forming the upper gabbro zone. It is worth noting that a stability field in which only magnetite and ilmenite were stable (without silicate phase) was not observed in our experiments. Thus, to explain the formation of massive (magnetite + ilmenite) ores in Hongge layered intrusion, other essential processes are required, such as magma mixing or subsolidus hydrothermal reworking.

Effect of water on the carbonate glass transition temperature

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Quantification of carbonate glass properties is required to better constrain the ascend dynamics of mantle-derived carbonate melts as well as the chemical interaction between low-viscous, highly mobile carbonate melts and the Earth lithosphere. When compared to the list of well-studied multi-component silicate melt systems for their physico-chemical properties, carbonate systems remain to date only poorly constrained, which ultimately relates to the poorly glass forming nature of most carbonate melt systems. In order to determine the effect of water on the carbonate melt properties, we performed the first calorimetric measurements of the glass transition temperatures of hydrous carbonate melts using a near eutectic K_2CO_3 - $MgCO_3$ composition with various quantities of dissolved H_2O in the carbonate melt. Calorimetric measurements of the glass transition temperatures of hydrous carbonate melts, quenched at 1.0 GPa to transparent and crystal-free glasses, were performed by high-sensitivity differential-scanning-calorimetry. Glasses were analyzed for bulk water content before and after measuring the glass transition temperature. The glass transition temperatures as a function of the water content range from 240-250°C at nominally anhydrous conditions to less than 100°C in presence of >10 wt.% H_2O. Through a generalized Gordon-Taylor analysis, the determined interaction parameters indicate strong specific molecular interactions between water and the carbonates in the glassy state.

Diamond formation during interaction between peridotite and metasediment or eclogite: Coupled redox equilibria without involvement of iron

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Redox freezing has been proposed as a mechanism for diamond formation in the deeper upper mantle with heterogeneous redox states, where migrating carbonate melts encounter more reducing domains and react to form diamond [1]. Carbonate reduction is balanced by the oxidation of Fe-Ni alloy present in the reduced domains. However, the small amount of available alloy in peridotite limits the effectiveness of such a process [2]. We have undertaken experiments to explore other potential redox reactions without Fe that simulate the reduction of carbonate-bearing lithologies in a mélange environment with strong redox gradients [3].

Experiments employed simple compositions that were Fe-free proxies for peridotite (forsterite) and either carbonated metasediment or eclogite ($CaCO_3$+SiO_2+Al_2O_3, $MgCO_3$+SiO_2 ±Al_2O_3 or MgO+$CaCO_3$+SiO_2+Al_2O_3 mixes). A graphite disc separated the two layers to limit mechanical mixing. Runs were made at 10 GPa and 1200-1500°C to assure unambiguous formation of diamond upon reduction of carbonate.

The redox contrast between the two layers caused metasomatic reactions, with magnesite and low-Ca pyroxene forming within the forsterite layer and simultaneously, carbonate decomposed in the metasediment/eclogite layer adjacent to the graphite disc. Diamond crystallized in the metasediment layer and formed a monomineralic layer at the interface with the graphite disc due to carbonate reduction. On the “peridotite” side, dissolution and carbonation of graphite occurred, with no diamond observed at the contact with the graphite. Limited melt migration from the metasediment/eclogite layer produced a series of well-defined metasomatic zones in the peridotite, leading to Ca-metasomatism and wehrlitization.

We document simultaneous carbonation of peridotite and decarbonation of juxtaposed metasediment or eclogite, even in Fe-free bulk compositions. Thus, in a heterogeneous mantle, there are further possibilities to form diamonds by redox reactions in addition to those coupled to changes in Fe^{3+}/Fe^{2+}. The resulting diamond content of the metasedimentary/eclogitic domains depends on the original carbonate concentration, and therefore, the occurrence of diamond-rich metasediment and eclogite lithologies is not unexpected.

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Melting deep Mercury’s mantle constrained by high pressure-temperature experiments

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The compositional diversity of volcanic rocks revealed by NASA’s MESSENGER at the surface of Mercury has been interpreted to result from partial melting of a heterogenous sulfur-rich Mercurian mantle. However, melting relations and the composition of partial melts for iron-free and sodium-rich mantle, together with the effect of sulfur as a key volatile, have not yet been studied in detail. In this study we present results from high-pressure and high-temperature experiments on the mineralogical and geochemical evolution of the mantle residue and melting products of primitive deep Mercury’s mantle with two starting compositions differing by their Mg/Si ratios. Both compositions have sulfur added as FeS. Experiments were conducted using a multi-anvil press under reduced conditions (by controlling the Si/SiO_2 ratio of the starting composition) at pressures of 3 and 5 GPa.

The residual mantle of Mercury with the lower Mg/Si ratio of 1.02 contains olivine + orthopyroxene above ~15 wt.% melting at 3 and 5 GPa, and olivine disappears at melting over ~30 wt.% at 5 GPa. The Mercurian mantle with the Mg/Si of 1.35 contains olivine + orthopyroxene in the residue above ~15 wt.% melting at 3 and 5 GPa, and olivine only when the melting degree is over ~50 wt.%. Our experiments also show that the majority of chemical composition of the

High-Magnesium region (HMR) can result from ~ 25±15 wt.% melting of a deep primitive mantle. Further work will enable us to evaluate the compositional diversity of the mantle that is needed to explain the broad range of surface lavas.

The effect of pressure on partitioning of trace elements between sulfide liquid and silicate melt at 0.5-2.5 Gpa

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Sulfide melt plays an important role in controlling the behavior of many trace elements during magmatic evolution, during ore formation, and possibly during terrestrial core formation. Although the partitioning of trace elements between silicate and sulfide melts had been investigated by a number of authors, Kiseeva & Wood [1,2] showed that the data for many elements could be best represented by exchange reactions involving FeS (in sulfide) FeO (in silicate) and the corresponding components of the trace element of concern. They thus developed equations to express partition coefficients of Ag, Cd, Co, Cr, Cu, Ga, Ge, In, Mn, Ni, Pb, Sb, Ti, Tl, V, and Zn in terms of the FeO content of the silicate and the major element concentrations in the sulfide

$$LogD_M^{sulph/sil} = A + \frac{B}{T} + \frac{n}{2}Log[FeO]_{corr} + \frac{1673}{T}[\varepsilon_{MS_{n/2}}^{FeO}Log(1 - x_{FeO}) + \varepsilon_{MS_{n/2}}^{NiS}Log(1 - x_{NiS}) + \varepsilon_{MS_{n/2}}^{CuS_{0.5}}Log(1 - x_{CuS_{0.5}})]$$

Although these equations were fitted to data over the temperature range of 1300-1700°C, all experiments were performed at 1.5 GPa and the potential effects of pressure were not accounted for. To better understand the role of pressure, we determined the partition coefficients of Cu, Ga, In, Tl, Pb, Ag, Zn, Cr, V, Co, Sb, Ge, Cd, Se, Te, Sn, and As between sulfide liquid and anhydrous basaltic liquid in a piston-cylinder apparatus at pressures of 0.5-2.5 GPa and temperatures of 1300-1700°C under reduced conditions. We compared the measured $D^{sulfide/silicate\ liquid}$ values with those predicted from the empirical equation of Kiseeva and Wood [2], the results show that increasing pressure reduces the partition coefficients of Ga, Ge, Zn, Sb, Ge, In, Tl, V, Cr, As and increases D_{Te}. The partition coefficients of Cu, Ag, Pb, Se, Sn, and Co are virtually independent of pressure.

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Melting point depression of Fe in the presence of silica from 20 to 80 GPa

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Accurate knowledge of melting curves of iron and iron alloys is crucial for understanding planetary cores. For decades, different experimental studies have identified different melting temperatures of iron at high pressures. Possible reasons for the discrepancies include ambiguous melting criteria, and undiagnosed chemical reactions. Recently, pulsed Joule heating calorimetry on the microsecond timescale has been developed to solve the problem of ambiguous melting criteria. The method has been used to reproducibly identify the latent heat of melting and freezing of platinum and iron up to megabar pressure within ± 50K precision in diamond anvil cells (DACs) [1,2]. In those studies, potassium chlorite (KCl) serve as the thermal insulator and pressure medium. Silica is also a commonly used thermal insulator due to its low thermal conductivity [3]. In this study, we document a substantial melting point depression (~ 400K), observed up to 80 GPa, occurring only when loading the iron in the amorphous silica or quartz pressure medium. We hypothesize that a reaction or contamination of the pure iron sample occurs on the microsecond timescale at near melting temperatures. It is possible that iron and silica react to form iron oxide and an iron-silicon-oxygen alloy with a much lower melting point than pure iron [4]. Contaminations, for example, from residual water in the silica cannot be ruled out, although we fired it at 1000°C in the furnace before loading it in the DACs. Future work includes X-ray diffraction and chemical analysis of samples decompressed to ambient pressure.

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Niobium solubility in carbonate melt: an experimental approach

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This study investigates the solubility of pyrochlore and crystallization of niobium-bearing solids in carbonate melt using an experimental approach. Pyrochlore, $(Na,Ca)(Nb,Ta,Ti)_2O_6(O,F,OH)$, is a common accessory mineral in carbonatites and a main carrier of niobium, which is one of the critical elements essential to modern society. It remains a matter of debate whether the mineralization of pyrochlore in carbonatites occurs as magmatic or hydrothermal process. This study provides new insights into understanding the behavior of pyrochlore and niobium in these tricky magmatic systems.

Dissolution and crystallization experiments respectively using pyrochlore and niobium oxides mixed with synthetic carbonate melts of several compositions have been conducted. Experiments at temperatures of 875°C/950°C/1025°C and pressure of 1 kbar under oxidizing condition were performed using an IHPV (internally heated pressure vessel). The dissolution experiments were carried out in the melts of $Na_2Ca(CO_3)_2$-$Ca(OH)F$ and $NaCa(CO_3)_{1.5}$-$Ca(OH)_2$ systems. Starting materials for crystallization experiments are mixtures of $CaCO_3$-Na_2CO_3-$Ca(OH)_2$ with a range of fluorine contents (0/1/3/7.5 wt.% F), where the Na/Ca ratio is

fixed as 0.5 and the CO_2/OH ratio is fixed as 0.75. The run products were examined by scanning electron microscopy (SEM). The pyrochlore solubility in carbonate melts was measured by means of electron microprobe analyzes (EPMA) and LA-ICP MS.
In this study, results show that the solubility of pyrochlore is dependent on carbonate melt compositions and has a positive correlation with temperature. At 875°C, the average niobium contents of melts were 0.72 and 1.46 wt.% in the $Na_2Ca(CO_3)_2$-Ca(OH)F system and $NaCa(CO_3)_{1.5}$-$Ca(OH)_2$ system. At higher temperatures, i.e. 1050°C, pyrochlore solubility (Ksp) is higher than 3.55 wt.%. SEM and electron microprobe data indicate that the main run products of the crystallization experiments are pyrochlore and fersmite ($CaNb_2O_6$). Additional results revealed the influence of other HFSE elements such as Si, P and Ti on niobium solubility in carbonate melts. We will finally present experimentally determined trace element partition coefficients (D) between crystallized minerals and carbonate melts.

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The formation of diverse mineral assemblages in the deep sub-cratonic mantle lithosphere by melt-peridotite redox reactions

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The thick mantle lithosphere beneath cratons is refractory and is stabilized by its buoyancy relative to the underlying convecting, asthenospheric mantle. Xenoliths brought to the surface by kimberlite magmas indicate that the deeper cratonic lithospheric mantle consists of originally strongly reduced peridotite that has been enriched and oxidised by metasomatic melts from the asthenosphere. These low-silica, incipient melts are likely CO_2 and H_2O-bearing and react with wall rocks, forming an enriched, mineralogically diverse, oxidised zone near the base of the lithosphere, which may be a source region for some diamonds.
We describe high pressure experiments in which we simulate redox and metasomatic reactions in the lower cratonic lithospheric mantle. We reacted synthetic oxidised, hydrous carbonate-rich melts with compositions determined in previous high pressure experimental studies, with reduced, depleted synthetic peridotite at 5 GPa pressure, using Fe-capsules to buffer experimental oxygen fugacities to near the near iron-wüstite (IW) buffer. The redox contrast between H_2O+CO_2-bearing melts and reduced peridotite/Fe in the experimental samples led to formation of complex, layered, mineral assemblages, as follows:

Redox-freezing layer: Oxidised, carbonate-rich, hydrous melts migrated into reduced peridotite, formed graphite and replaced orthopyroxene in peridotite by clinopyroxene.
Redox fractionation layer: Melt evolved to a hydrous, carbon-poor composition which dissolved clinopyroxene, garnet and orthopyroxene from the peridotite layer overlying the redox freezing zone, forming a dunite layer with compositionally zoned olivine.
Hybridization layer: Residual melt in the redox fractionation layer became enriched in alkali components and H_2O and then froze near the top of the capsules, forming a strongly metasomatised layer with abundant alkali-rich hydrous phases, mineral assemblages akin to the MARID xenolith suite.
These redox reaction experiments demonstrate that mineral assemblages known to exist in the cratonic lithosphere, may be explained by reaction of oxidized melts with reduced, depleted peridotites in conditions corresponding to those of the cratonic roots. The experiments may explain the formation of lithospheric diamonds, phlogopite and alkali-amphibole bearing rocks, anomalously iron-rich dunites, and garnets and clinopyroxenes with compositions akin to hybrid pyroxenitic rocks.

Measuring and parameterizing the room-pressure viscosity of ultramafic melts

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In order to study the room-pressure viscosity of peridotite melts, ultramafic glasses were synthesized within a broad compositional landscape (SiO_2 between 34 and 45 mol%, FeO_{tot} between 0 and 12 mol%, H_2O between 0 and 12 mol%), using aerodynamic levitation coupled to laser heating for anhydrous samples and a rapid-quenching multi-anvil technique for hydrous ones. An unconventional experimental approach was subsequently developed and optimized to circumvent the poor glass stability and small size of the samples, combining classical micropenetration viscometry with (flash) calorimetry and Brillouin spectroscopy. The results reveal a marked influence of FeO_{tot} and H_2O on glass transition temperature and melt fragility; due to the exotic composition of the melts, existing viscosity models perform rather poorly in predicting the compositional dependence of these properties. Providing an improved model for the room-pressure viscosity of peridotite melts as a function of water content, we demonstrate the untapped potential of exploring the flow behaviour of

compositional extremes coupling Brillouin spectroscopy to more traditional viscometry and (flash) calorimetry.

Crystal/melt trace element partitioning for the main groundmass phases of kimberlites

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Kimberlites are volatile-rich (CO_2, H_2O) and ultrapotassic volcanic rocks that originate from deep asthenospheric mantle sources (6-10 GPa [1]), making them the main carrier of diamonds. Primary kimberlite melts are modified en route to the surface by various processes (entrainment and assimilation of mantle and crustal materials, fractional crystallization, volatile degassing, and alteration during or emplacement). Thus, natural kimberlites generally do not correspond to true melt compositions. Experiments on kimberlite melts have defined mineral saturation assemblages in model kimberlite melts at high pressures, varying from garnetite to garnet-bearing harzburgite or lherzolite. The main object of this study is to obtain partition coefficients of fluid-soluble elements, including Na, between key minerals (olivine, perovskite, apatite) and silicate-carbonate (kimberlite) melts. The goal is to reconstruct the ephemeral elements in kimberlitic melts from partition coefficients.

We performed experiments on an average primary kimberlite melt composition from compiled literature data. We subtracted 30% of olivine from this composition and added variable amounts of Na_2O, CO_2, and H_2O, plus a mix of trace elements. Experiments were conducted at 3 GPa and 1150-1350°C, representing likely conditions of partial kimberlite crystallization during ascent. The experiments were run in a ¾" piston-cylinder apparatus using 4 mm C+Pt double capsules, where graphite + CO_2^{melt} impose the appropriate f_{O2} close to the CCO buffer. Experimental phases and quenched melt were measured by EPMA and LA-ICP-MS to determine mineral-melt partition coefficients.

Mineral assemblages on bulk with 3 wt.% Na_2O, Mg# 85, 17 wt.% CO_2, 5 wt.% H_2O consist of olivine + spinel at 1300°C, clinopyroxene + perovskite ± phlogopite at 1250°C, and apatite at 1150°C. Olivine (Fo_{87-90}) is present in all experiments as the most abundant phase. The melt composition decreases in SiO_2, FeO_T and MgO with decreasing temperature (1300-1150°C), but increases in CaO, total volatiles (CO_2 and H_2O), Na_2O and K_2O. The crystallization of cpx in the experiments results from the increased CaO content in the melt and relative high crystallization pressure, while cpx is absent in natural kimberlites, monticellite being the only stable Ca-silicate phase. The melt composition of our experiments does not correspond to the primary melt composition of kimberlites due to the low pressure (3 GPa), literature data from carbonated peridotite melting indicates a pressure range of 5-10 GPa for kimberlitic melts [2]. However, the main magmatic phases of kimberlites crystallize at our conditions. Trace element partitioning between pvk, olivine, or apatite and a close-to-kimberlitic melt was measured and gave insights into the trace element composition of kimberlite melts at various stages.

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Magmatic differentiation and silicate liquid immiscibility in large igneous provinces

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Large igneous provinces (LIPs) represent the largest volcanic episodes on Earth. The lavas are usually classified into high-Ti and low-Ti in LIPs [1], which often form economically critical Fe-Ti oxide ores in layered intrusions via mechanisms that remain debated: density-driven sorting during fractionation or accumulation from separated Fe-rich melts formed by liquid immiscibility [2]. To understand the processes controlling the differentiation of high-Ti and low-Ti basalts that account for the geochemistry variability and the ore formation, we performed stepwise equilibrium crystallization experiments at atmospheric pressure to quantify the influences of starting composition and oxygen fugacity (fO_2) on phase stability, phase compositions, and in particular the onset of silicate liquid immiscibility during cooling [2]. Both types of magma crystallize similar phase assemblages at QFM (quartz-fayalite-magnetite thermodynamic equilibrium) and QFM+2: olivine, clinopyroxene, plagioclase, Fe-Ti oxides, and whitlockite. Tridymite crystallizes late in experiments at QFM+2. The starting composition exerts a strong influence on phase and melt compositions. High CaO and Al_2O_3 contents in the melt favor the early crystallization of plagioclase and enhance FeO enrichment before Fe-Ti oxide saturation. fO_2 affects the composition and stability of Fe-Ti oxides therefore may promote melt differentiation into the calc-alkaline field at high fO_2.

Silicate liquid immiscibility producing Fe-rich globules in equilibrium Si-rich melts was observed in both types of magma at high and low fO_2 conditions. Fe depletion caused by Fe-Ti oxide saturation does not hamper the development of immiscibility. Combined with the published experiments, we propose a new parameterization to map the binodal surface in temperature-composition space that successfully fits the two-liquid field in experiments and natural immiscible compositions. Our results indicate that Fe-Ti oxide ores in layered intrusions associated with LIPs form by the segregation of Fe-rich melts and/or the accumulation of early crystallized Fe-Ti oxides during fractionation.

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Subducted slabs induced high heat flux at the core-mantle boundary

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Despite growing evidence suggesting chemically distinct regions and partial melting at the core-mantle boundary (CMB) throughout Earth's history, current heat-flow models assume a homogeneous thermal boundary layer. To understand the probable thermal response of bridgmanite to subducted slab, we measured the thermal diffusivity of mid-ocean ridge basalt (MORB)-bearing olivine polycrystalline as an analogy. Our results show a sharp increase in thermal conductivity with an addition of 0.1 vol.% MORB, followed by a systematic decrease with increasing MORB. When the infection point of 1.2 - 5 vol.% is exceeded, thermal conductivity jumps again with 10 vol.% MORB. If it were the case at the CMB, MORB introduced by subducted slab and scattered by mantle flow may have led to a lateral variation of heat flux. It results in plume clusters with varying scales, which either grows into superplume with mobile plume root or vanishes when MORB is drained to the inflection point.

Influence of disorder and Fe-content on the properties of ankerite

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Carbonates are the most important C-bearing minerals and key phases in the Earth's carbon cycle. Under subduction conditions, the occurrence of phase transitions [e.g., 1-4] stabilizes the carbonates structure, increasing their potentiality to store C into the deep Earth. The crystal-chemical features of carbonates, e.g. the nature and distribution of the cation present in the structure, influence their stability at non-ambient conditions. Ankerite is an interesting carbonate mineral, where the Mg-Fe substitution is not complete and is limited to $Ca(Mg_{1-x}Fe_x)CO_3$ with $0 \leq x \leq 0.7$.

The present research is devoted to the study of the influence of both cation disorder and Fe content on the mineral physics of ankerite. Ex-situ disordering and Fe-enrichment experiments in ankerite were performed by means of the piston-cylinder technique at the Bayerisches Geoinstitut (Bayreuth, Germany) and at the HP-HT lab at the University of Pisa (Italy). The experimental run products were characterized by means of a multidisciplinary approach, coupling Scanning Electron Microscopy, Electron Microprobe Analysis, ambient pressure (P) and high pressure (HP) Single Crystal X-ray Diffraction (SC-XRD) both in-house and at ESRF synchrotron facility (Grenoble, France).

Experimental conditions were P = 3 GPa and T = 25 - 1000°C. Disordering experiments were carried out on natural ankerites (space group *R*-3) with different Fe-content (0.3 - 0.7 a.p.f.u.); complete disorder (space group *R*-3*c*) was achieved at T conditions varying with the Fe content. As for the study of the Fe-enrichment in ankerite structure, both natural and disordered samples were used in 1:1 mixture with Fe-oxalate, as Fe-bearing phase.

Ankerites with both ordered and disordered structures were subjected to HP SC-XRD data collection, ranging from ambient pressure up to 24 GPa, to investigate the occurrence of phase transitions and in order to derive the Equation of States (EoS) for the analyzed samples.

Results showed that ordered ankerite undergoes phase transition, between 12 and

14 GPa, to ankerite-II that has the same crystal structure as dolomite-II [1,2,4]; whereas, disordered ankerite, in analogy with dolomite [1,2], is stable in the investigated P range. As for compressibility analysis, data were treated by means of a 3rd order Birch-Murnaghan EoS and both ordered and disordered ankerites show similar behavior with K_0 = 94(2) and 99(2) GPa, and K' = 3.7(5) and 2.7(1), respectively. On the contrary, ankerite-II EoS data show a larger K' value with respect to the low-pressure polymorph, suggesting a steep increase in stiffness after the phase transition.

Results also pointed out that disordered ankerite at HP might be enriched in Fe with respect to the naturally occurring ordered structures. This hypothesis sheds light to the open questions related to the Fe enrichment in the lower mantle and gives to ankerite the role of Fe-bearing phase in the Earth's interior.

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