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Plastic deformation of aluminous stishovite and implications for mantle heterogeneities

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Information on the elasticity and plasticity of candidate minerals in the Earth's interior assists in understanding mantle flow and the underlying geodynamic processes at depth when compared with seismic observations. Seismic signals from mid-mantle depths of ~800 to 1850 km show negative shear wave anomalies of 2 to 6% in the vicinity of subduction zones [e.g. 1-4], including a new discontinuity at ~1000 km [5]. A possible explanation for these anomalies could be the presence of remnant unmixed basaltic crust, where shear softening accompanies the transformation of stishovite (rutile structure) to post-stishovite (CaCl2 structure) under pressure [7]. However, additional information on the physical properties of deformed stishovite due to mantle flow is required to understand the origin of seismic anomalies and mantle heterogeneities.

Here we present results from plastic deformation experiments on aluminium-bearing stishovite containing 5 wt% Al_2O_3 up to 37 GPa along different isotherms between 873 and 1473 K. Experiments were conducted using synchrotron radial x-ray diffraction at PETRA III beamline P02.2. The samples were loaded in x-ray transparent boron gaskets in a Mao-Bell-type diamond anvil cell [6]. Our preliminary data shows that the lattice strain supported by the sample is comparable to that of pure SiO_2-stishovite and that differences in the strength arise from the effect of aluminium in the elastic properties [7]. Implications of these results and the effect of textures on the seismic velocities will be presented to discuss mantle deformation and heterogeneities.

[1] Le Stunff et al. 1995: Science 270, 74
[2] Kaneshima and Helffrich 1999: Science 283, 18888
[3] Vinnik et al. 2010: Geophys. Res. Lett. 37, L24302
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Control of oxygen fugacity in rapid-quench molybdenum-hafnium carbide pressure vessel assemblies: method and verification

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Oxygen fugacity (f_{O2}) is a fundamental variable affecting phase equilibrium. Externally-heated pressure vessels typically use redox buffer assemblages for controlling f_{O2}. However, these do not allow fine enough resolution; for example, most arc magmas fall between the f_{O2} imposed by the neighboring Ni-NiO and Re-ReO$_2$ buffer assemblages and so does the transition of S^{2-} to S^{6+}. Hydrogen gas mixed into Ar pressure medium can impose desired f_{O2} conditions in capsules containing hydrous phase assemblages. A thermodynamic calculation procedure is proposed to estimate the amount of H_2 to be initially admixed into the Ar pressure medium to yield the desired f_{O2} at run conditions. This was verified by CoPd alloy redox sensor experiments to be accurate within ±0.3 log unit f_{O2} for the P-T range of 900-1070 °C and 94-206 MPa. However, hydrogen is known to diffuse through the pressure vessel's walls at high T resulting in increasing f_{O2}. Therefore, we constrained the hydrogen permeability of the Molybdenum-Hafnium-Carbide (MHC) alloy as a function of T by directly monitoring H_2 loss in experiments with pure H_2 loaded into the vessel at ~0.8 MPa initial pressure. The such-obtained permeability values can be used to estimate the rate of H_2 loss in any MHC vessel configuration and were confirmed by time series redox sensor experiments at elevated P. In our setup at T=1000 °C, f_{O2} increases about 0.36 log units/day, and this value approximately doubles for every 100 °C increase in T. This rate is 3-4 times smaller than that reported by Shea and Hammer (2013). This is most likely because they used filler rods which reduced the mass of H_2 in the vessel, and thus increased the rate of f_{H2} drop. Therefore, we propose that H_2 addition to the Ar pressure medium is an effective way to accurately impose f_{O2} in many experiments where only relatively short times are required to attain equilibrium.

Shea T. and Hammer E.J. (2013) American Mineralogist, 98, 1285-1296.

Bubble shrinkage in experimentally decompressed Vesuvius melt

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Bubble nucleation and growth are the fundamental mechanisms that control melt degassing during volcanic eruptions. In order to study the degassing behavior of Vesuvius melt (VAD79), decompression experiments were performed in an internally heated argon pressure vessel. After hydration the samples were decompressed at 1323 K (super-liquidus) with 0.17 MPa/s to final pressures (P_{final}) between 110 MPa and 60 MPa and isobarically quenched. Bubble number densities (BND) and porosities were determined with transmitted light microscopy and BSE image analysis.

In experiments decompressed to P $\leq$ 100 MPa, homogeneously distributed bubbles are observed with a BND of ~10^5 mm^{-3}. BNDs are constant down to 60 MPa with narrow size distributions and glass porosity increases up to 20 %. However, glass porosity does not reflect melt porosity due to bubble shrinkage during cooling, which is caused by (1) the decrease of molar volume (V_m) of H_2O (EOS, Marxer et al. 2015) and (2) resorption of H_2O from fluid bubbles into the melt, driven by increasing H_2O solubility with decreasing temperature (McIntosh et al. 2014). Nevertheless, melt porosity can be estimated: Considering decompression rate and the BND, H_2O diffusivity calculations indicate near-equilibrium H_2O contents adjusted prior to quench, resulting in melt porosities up to 37 %.

To explain the difference between equilibrium and glass porosity, contributions from both shrinkage processes are required. However, to resolve the mutual influence and individual contribution of EOS- and resorption shrinkage, computational modeling and in-situ experiments are needed. This is especially important for "post mortem" analyzed decompression experiments. Modeling of bubble shrinkage processes is in progress in collaboration with Jason Coumans and Ed Llewellin (Durham University).

Marxer H et al. (2015) J Volc Geotherm Res 297: 109-124
McIntosh et al. (2014) EPSL 401: 1-11
Schmidt and Behrens (2008) Chem. Geol. 256: 259-268

Spinodal decomposition of hydrous Vesuvius melt triggering explosive volcanism

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The starting point of explosive volcanic eruptions is determined by the phase separation of an H_2O fluid from a supersaturated hydrous silicate melt. The number of fluid vesicles per unit volume of silicate melt (VND) is a basic property that controls the efficiency of fluid-melt separation, ascent velocity and finally explosive fragmentation of magma. To simulate magma ascent, decompression experiments were performed with hydrous silicate melt using phonolitic AD79 Vesuvius white pumice composition. After hydration with 5.3 wt% H_2O, the melts were continuously decompressed with rates between 0.024 and 1.7 MPa/s. At final pressures, samples were isobarically quenched. VND and porosity were determined with transmitted optical microscopy and quantitative BSE image analysis using 2D to 3D transformation.

Nucleation theory is commonly used to quantify magma ascent velocity during volcanic eruptions using VND of volcanic ejecta. Here we report a high VND of 10^5 mm^{-3} with a previously unknown independency of decompression rate that contrasts nucleation theory. Instead of nucleation being the initial phase separation mechanism, we suggest that analogue to organic polymeric systems (Tanaka et al. 1990) decompression induced H_2O-silicate melt phase separation is caused by spinodal decomposition at the limit of thermodynamic stability. Irrespective of magma ascent velocity, spinodal decomposition leads immediately to a high VND. Even at low decompression rates, this phase separation mechanism inevitably causes rapid degassing that initiates abrupt decrease in density and abrupt acceleration of magma ascent required for explosive volcanic eruptions.

Tanaka, H et al. (1990) Phys. Rev. Lett, 65, 3136-3139.

Large oxygen excess in the primitive mantle could be the source of the Great Oxygenation Event

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Before the Archean to Proterozoic Transition (APT) the tectonic regime was dominated by microplates floating on a low viscosity mantle. Such a regime restricted chemical exchange between the shallow and deeper mantle reservoirs. After the APT, a more global convection regime led to deep subduction of slabs. We propose that the improved vertical mixing of the mantle favoured the release to the Earth's surface of an oxygen excess initially trapped in the deep mantle. This excess built up when the primordial lower mantle was left with a high $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio ($\#Fe^{3+}$), after metallic iron segregated down into the core. Our synchrotron-based in situ experiments suggest a primordial Fe^{3+} excess of ~20 % for the mantle iron. By comparison with the $\#Fe^{3+}$ of the present mantle, this Fe^{3+} excess would correspond to 500-1000 times the O_2 content in the Earth's atmosphere. The tectonic transition greatly facilitated the ascent of oxidised lower mantle material towards the Earth's surface, inducing a continuous arrival of O_2 at the Earth's surface and into the atmosphere.

Tracking the evolution of basalt to phonolite magmas at Tenerife: an experimental approach

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To improve hazard assessment in volcanic environments it is necessary to have accurate information concerning 1) the structure of the plumbing system (depth/s of magma/s ponding); and 2) the conditions (P, T, f volatiles) and mechanisms (crystal fractionation, magma mixing, assimilation) for generating evolved compositions (ie, phonolites, rhyolites) susceptible of developing a highly explosive volcanic activity. The combination of all this information provides strong constraints on the feeding system, which can be used to predict the type of magma and the type of seismic/gas-signal once the magma rises from the source/storage level/s towards the surface. In this work, we have performed crystallization experiments on representative basaltic and phonotephritic samples from Tenerife (Canary Islands, Spain), with the aim to determine the liquid line of descent (LLD) and the conditions at which phonolitic magmas are generated. Explored conditions cover T (1150-900 ºC), P (400-50 MPa) and oxygen fugacities (f_{O2} ~NNO+1.5) that encompass those previously determined for Tenerife magmas. In comparison, a large X_{H2O} range (from 1 to nominally dry conditions) has been explored since the amount of dissolved H_2O in parental mafic magmas is to date poorly constrained. Our preliminary results support crystal fractionation as the main mechanism to generate the LLD of Tenerife magmas. They show that water-poor conditions (< 3wt%), P (>250 MPa) and f_{O2} of NNO-NN-0.5 are necessary to reproduce the mineral assemblage and the LLD characteristic of Tenerife rocks. Such information, when combined with those gained on storage conditions of phonolitic melts, points towards a multi-stage plumbing system where evolved liquids generated at depth (> 8-9km) migrate to shallow levels (<5km), where they finally pond and erupt. This information will improve the hazard assessment at Tenerife during future episodes of unrest.

Chemical interaction of iron with diamond anvils in pulsed and continuous wave laser heated diamond anvil cells

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Laser heating inside a diamond anvil cell is the main approach in order to reach the necessary pressure and temperature conditions to study iron melting. However, several factors can influence the accuracy of the melting curve measurements. If a chemical reaction occurs on this surface, it may dramatically affect the results, as it becomes uncertain if the measured temperature relates to the material under investigation, or to the products of the undesired chemical reaction. Pulsed laser heating is a technique that minimizes heating time of the sample and is therefore thought to improve the chemical stability of the system. However, there has not been so far direct comparison between pulsed laser heating and continuous wave heating under the same sample conditions.

Using X-ray Absorption Near Edge Structure spectroscopy, Synchrotron Mössbauer Source spectroscopy, and Synchrotron X-ray diffraction, we examine the effect of chemical interaction between the iron sample and the carbon of the diamond anvils during laser heating, that would lead in the formation of iron carbides or the solution of carbon in iron. Such a process is a common occurrence during melting experiments and it is unwanted since it can significantly affect the estimated melting temperature. In order to investigate the influence of the sample's chemical environment, similar iron samples were loaded inside different diamond anvil cells with different materials as pressure media - neon, argon, potassium, and sodium chloride.

It was found that indications of chemical reactions could be observed independently of the heating technique applied. There were cases when a reaction was occurring almost immediately, after only a few seconds of heating at moderate temperatures, depending mainly on the sample geometry and environment inside the diamond anvil cell.

Late magmatic transfers and strain localization under high shear stresses: Insight from HP-HT experiments

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The transfer and emplacement dynamics of highly crystalised (c > ~0.6) magmas are mostly dependent on the interconnected crystal-framework controlling the tortuosity of the residual melt flow and capable of transmitting deviatoric high stresses. Crystal fraction, size distribution, and strain rate control the development of crystal fabrics and strain localisation. How localised structures potentially promote the transfer of residual gas and melts in hardly moveable late magmatic mushes is a critical question that remains largely undocumented.

We present high temperature (650° to 750 °C) and high pressure (P = 300 MPa) deformation experiments on both natural and synthetic dioritic, hydrous (3 wt% H_2O) suspensions with markedly euhedral anisometric crystals (0.43 > c > 1) submitted to simple shear. Quantitative structural analysis, including grain shape fabric, clusters formation, and shear zones geometry, were performed by 2D SEM imagery and by 3D high resolution X-ray Computed Tomography.

Crystal fraction c< ~0.75 exhibit a glomeroporphyritic texture compose of a mixed population of isolated grains and clusters of touching grains. Development of clusters induces a dramatic increase in tortuosity of melt flow leading to a significant increase of the apparent viscosities of the shear-thinning suspensions.

At c > ~0.75, a modification of the mechanical behaviour is evidenced with a nearly solid like behaviour associated with a dramatic change of the microstructures. Strain localisation leads to the development of S/C' like structures progressively replaced by tensions gashes and Riedel cataclastic shears when approaching the full crystallization stage. Residual melt, and fluids when present, migrate from compressive regions to transtensive zones favouring potential outgassing and residual melt escape at near-solidus conditions.

Our results stress the importance of strain localisation structures for residual fluids and melt transfers in magmatic suspensions submitted to high stress.

Rapid growth of plagioclase: implications for conduit processes in basaltic Plinian eruptions

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Rock textures of volcanic products record the evolution of the conditions and processes that lead to their formation. Particularly, time is a paramount variable in volcanic processes because it is intimately linked with equilibrium vs disequilibrium processes. During magma ascent in volcanic conduits, crystallization is controlled by degassing and cooling. The study of crystallization kinetics allows us to determine the disequilibrium conditions that affect the dynamics of magma in a conduit. This has strong implications for volcanic hazard. For the first time we performed real-time 4D (3D plus time) crystallisation kinetics experiments, through fast synchrotron X-ray microtomography, in order to quantify plagioclase crystallization kinetics in basaltic magma. The experiments were performed at Diamond Light Source (beamline I12), Harwell, UK. For these experiments we used small cylindrical chips of Etna 2001 basaltic glass, which were heated in-situ in the Alice furnace up to 1250 °C for 30 minutes. After the initial annealing period, crystallisation was induced by decreasing temperature isobarically from 1250 °C to 1170 °C, 1150 °C and 1100 °C, and then holding at the final temperature for 4 h. After this step, final cooling rates of 0.4 °C/s and 0.2 °C/s simulate rapid cooling scenarios due to fast magma ascent within the conduit and outside the vent during a Plinian eruption. Preliminary results indicate rapid crystal growth of plagioclase of ~5×10^{-4} cm/sec, meaning that plagioclase can reach 500 µm of length in 90 seconds. These are the first data ever produced on plagioclase crystallisation of basaltic magma in 4D. Crystallization kinetics of basaltic Plinian eruptions are fundamental to constrain better the timescales of magma chamber-conduit processes, triggering and ascent. This is extremely important in improving our capacity to predict eruptions and mitigate volcanic hazard.

Effects of crystallization time on trace elements partitioning between alkali feldspars and trachytic melts

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We present new experimental data on partition coefficients for major and trace elements between alkali feldspar and trachytic melt. The experiments were conducted with piston cylinder at 500 MPa and 870-890 °C. We investigate through short disequilibrium and long near-equilibrium experiments the influence of time on the partitioning of trace elements during crystallization. Our data show that Ba and Sr behave compatible, their partition coefficients are influenced by orthoclase (Or) content, experimental time and growth rate. The high field strength elements (HFSE) and rare earth elements (except Eu) are strongly incompatible, but alkali feldspar efficiently fractionates light rare earth elements (LREE) from heavy rare earth elements (HREE).

The crystallization experiments reveal a strong influence of disequilibrium crystal growth on the partitioning behaviour of Ba and Sr. In particular, short-duration experiments show that alkali feldspar crystals can grow extremely fast after nucleation. Rapid growth promotes less selectivity in partitioning of compatible trace elements (e.g., Ba and Sr), which can enter into the crystal lattice. This produces partition coefficients of compatible elements higher than those obtained through long-duration experiments, in which growth is slower and more selective. Our results indicate that besides crystal-chemical effects (lattice strain energy), the substitution mechanisms of Ba and Sr in alkali feldspar are strongly influenced by crystal growth kinetics. This implies that partition coefficients of Ba and Sr can be determinant in establishing timescales of crystallization processes under pre- and syn- eruptive conditions. The application of our results to alkali feldspar's crystallization, in rocks from Campi Flegrei, constrain the magma residence time to a maximum of 6 days under disequilbrium conditions and to a minimum of 9 days upon reaching of the equilibrium conditions.

Reduced sulfur control on cadmium mobility in natural and industrial aqueous environments

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Cadmium is highly toxic metal with strong affinity for reduced sulfur. Formation of S-bearing aqueous complexes and their role in Cd transport and precipitation are thus of major interest for both environmental and ore deposit research. The present study is aimed at quantifying the stability of cadmium hydrosulfide complexes as a function of temperature from solubility measurements of well crystalline synthetic greenockite CdS(s) together with revision of the thermodynamic properties of CdS(s). These new data are crucial for modeling Cd behavior in hydrothermal systems, improving ore prospecting and safe treatment technologies, storage of Cd wastes, and assessing Cd bioavailability in modern and paleo aqueous environments.

Our new solubility measurements of greenockite CdS(s) at $25 - 80$ °C allow revision of the standard thermodynamic properties of CdS(s). We recommend $\Delta G_0 298.15 = -151.5 \pm 0.3$ kJ mol^{-1}, $\Delta H_0 298.15 = -155.0 \pm 0.3$ kJ mol^{-1} and 72.18 ± 0.26 J mol^{-1} K^{-1}. We do not recommend values commonly selected in thermodynamic handbooks (e.g., [1]) because they overestimate the CdS solubility by several orders of magnitude.

Our new solubility measurements in H2S-rich aqueous solutions at near-neutral pH allow to estimate, for the first time, the effect of temperature on the $Cd(HS)n2-n$ (n = 1-4) complexes stability. Surprisingly, Cd-HS species are more important than previously believed. Thus, for example, in H_2S-NaCl-H_2O model solutions at near neutral pH and 3.5wt% of NaCl, the Cd-HS complexes are the major Cd species at ≥ 10-6 m H_2S at 5-25°C (deep anoxic marine environments), or at ≥ 10-4m H_2S at 150 °C (some ore-forming hydrothermal systems).

[1] Robie and Hemingway (1995) U. S. Geol. Surv. Bull. 2131.

In situ XAS-HERFD experimental study of zinc transport by hydrothermal fluids

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Zinc is a common and abundant metal in natural and industrial aqueous solutions containing chlorine and sulfur ligands. Numerous studies at ambient T-P agree that dissolved zinc forms complexes with these ligands. However, the existing literature data on these complexes properties at high T-P are contradictory and do not allow quantitative modeling of Zn transport and precipitation at hydrothermal conditions. The identity, structure and thermodynamic stability of the dominant Zn complexes at high T-P remain uncertain. The goal of our study is quantify Zn-Cl and Zn-S complexes up to 450 °C by X-ray Absorption spectroscopy (XAS) and high energy resolution fluorescence detection (HERFD) via crystal analyzers on BM16 at ESRF (Grenoble, France).

In Cl-bearing solutions, our XAS-HERFD data demonstrate that in hydrothermal fluids at temperatures above 300°C $ZnCl_4^{2-}$ is less important than previously thought. For example, at 300°C this highly charged zinc complex becomes predominant at Cl concentrations above 4m and not 1m as proposed by recent thermodynamic studies [1, 2]. To measure Zn speciation in S-bearing solutions we used thiosulfate solutions in equilibrium with sphalerite ZnS(s). At T above 200 °C the thiosulfate becomes unstable and decomposes to SO_4^{2-}, $H_2S0(aq)/HS^-$ and other intermediate-valence S species such as S^{3-} [3]. In highly concentrated solution (3m S), dissolved Zn is surrounded by 3.5 ± 0.5 S atoms at 2.33 ± 0.01 Å as found from EXAFS modeling. Due to the fact that hydrosulfide HS^- and S^{3-} are the major reduced S species in such solution at 350 °C, the question is open to assign this Zn species to the trigonal planar $Zn(HS)^{3-}$, tetrahedral $Zn(HS)_4^{2-}$ or $Zn(HS)_2S^{3-}$. The work is in progress to derive a consistent set of structures and thermodynamic properties of Zn aqueous species operating at high T-P.

[1] Akinfiev and Tagirov (2014) Geochem. Int. 52, 197;
[2] Mei et al. (2015) GCA 150, 265;
[3] Pokrovski&Dubessy (2015) EPSL 411, 298.

Experimental phase equilibria of primitive high-K magmas from the Colima Graben, Mexico

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Monogenetic activity of the Colima Graben, Mexican Volcanic Belt, is characterised by geochemical diversity and ubiquitous high-Mg magmas, the most primitive cones having shoshonitic affinity. This magmatic diversity has been explained either by different contributions from two subducted slabs or by a heterogeneous mantle source. Thus, the primitive magmatism in the Colima Graben provides an ideal case study to discuss the role of the mantle wedge in producing high-K subducted-related primitive magmas.

We have designed an experimental approach aiming at establishing whether Colima Graben high-K basaltic magmas are multiple-saturated at mantle wedge conditions. A phenocryst poor sample enhanced in most of the features of the alkaline-magmatism was chosen as a starting material. We estimated its petrological variables, T (1327-1358 °C), P (1-3GPa) and f_{O2} (ΔQFM+3), and used MELTS calculations to explore for multiple saturation. The MELTS models show that a multiple-saturation is thermodynamically feasible at ~2GPa, but also show that the H_2O and f_{O2} values can change the phases that saturate the system. Phlogopite, clinopyroxene and olivine are saturated at 4wt% H_2O, conversely, at 2wt% H_2O only clinopyroxene and olivine are present. Orthopyroxene in the latter case is favoured by slightly more reduced condition (NNO).

We assess the MELTS calculations using experiments in a piston-cylinder apparatus with synthetic materials under controlled H_2O and f_{O2} conditions. The first results are broadly consistent with the thermodynamic modelling at 1 GPa. However, at greater pressure the phlogopite exhibits an extended stability field. The experiments suggest a potential multiple-saturation point with phlogopite within a pyroxenite (cpx+opx) or a fertile peridotite (cpx+opx+ol) assemblage. Our results will be used to place some constraints on the nature of the mantle source of high-K magmas.

Bulk modulus of Fe-rich olivines

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A good knowledge of the physical properties of olivine, one of the most abundant minerals in the mantles of terrestrial planets, is essential to understand and model planetary interiors. Because the accepted average composition of Earth's mantle olivine is around $[Fe_{0.1},Mg_{0.9}]_2SiO_4$, Fe-rich olivines have received relatively little attention. The goal of this study is to obtain equations of state (EoS) of olivines with different compositions (Fe%: 40, 60, 80, 100) to constrain the effect of Fe content on their elastic properties.

Our specimens were synthesized from nanosize powders of elementary oxides mixed with the proper stoichiometries and reacted at room pressure and 1000 °C under controlled atmosphere (close to IW buffer). The fully reacted powders were then sintered using Spark Plasma Sintering to minimize the porosity of our samples. The resulting aggregates have fairly homogeneous grain sizes from about 300 nm to 2 microns depending on their Fe content. High-pressure high-temperature experiments coupled with synchrotron X-ray diffraction and X-radiographic imaging were conducted using the DIA apparatus at the X17B2 beamline at NSLS (Brookhaven, NY, USA). We also performed ultrasonic interferometry measurements in order to obtain P- and S-wave travel times using the DIASCoPE setup at X17B2. In situ measurements of sample densities, lengths and travel times yield P and S-wave velocities. These data give a direct measurement of the elastic bulk and shear moduli at all conditions of the experiment.

Our presentation will focus on results obtained at room temperature. The bulk modulus was calculated by two methods: 1. by fitting a Birch-Murnaghan EoS with NaCl as pressure standard, 2. by using the ultrasonic acoustic velocity measurements. This will allow to compare different methods but most importantly to discuss the effect of deviatoric stress on our results.

Lead diffusion in CaTiO₃: A combined study using Rutherford Backscattering and ToF-SIMS

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For the first time, we present experimental data on the diffusivity of Pb in $CaTiO_3$ perovskite, which is commonly used for dating of kimberlites and carbonatites. Experiments were performed on oriented synthetic and natural $CaTiO_3$ single crystals. The Pb-source was either a laser deposited $(Ca_{0.83}Pb_{0.07})Ti_{1.05}O_3$ thin film or a $(Ca_{0.9}Pb_{0.1})TiO_3$ powder reservoir. The crystals were annealed in a high-temperature furnace between 736 and 1135 °C and for durations from 2 to 283 hours. The diffusion profiles were measured with Rutherford backscattering and time-of-flight secondary ion mass spectrometry. The concentration profiles, extracted from the thin film and powder source experiments, are in agreement. We found that diffusion coefficients are a function of the Pb concentration, best expressed by using two diffusion coefficients for high and low Pb concentrations. Thus, the diffusion profiles were fitted using a concentration dependent diffusion coefficient, and the diffusion equation has been solved with an explicit finite difference algorithm. The cross over between the two diffusion regimes is sharp, with a steep gradient at the diffusion interface and a shallow low concentration tail penetrating deeper into the crystal. Pb diffuses slower at concentrations between 7 and 0.6 wt.% and 1.6 to 2.6 log units faster below ~ 0.5 wt.% Pb. The activation energies obtained from the present data set are used to calculate the closure temperature for Pb in $CaTiO_3$, which is mandatory for the correct interpretation of radiometric ages and Pb zonation patterns.

Behavior of sulfur during core-mantle differentiation of the Earth

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Differentiation of the Earth to form its metallic core and silicate mantle is the most important chemical fractionation of the Earth's history. All elements have been distributed between the mantle and the core following their respective chemical affinity for silicate or iron. This is modeled through the partition coefficient of the element i (Di) which is a function of variables such as pressure (P), temperature (T) and chemical composition of both metal and silicate phases. Sulfur is a powerful element when it comes to understand processes that happened during the formation and differentiation of the Earth. Being both volatile and siderophile, it can provide important constraints on the delivery of volatile elements to the Earth and on the conditions of core formation. Several models have been proposed in the past few years to best explain the abundance of sulfur in the BSE, leading to different and sometimes contradictory conclusions ([2], [3]). Recently, two papers containing high P-T partition coefficient for sulfur were published ([4], [5]). In the present study, we combined all pertinent data published in the literature to develop a simple model of sulfur partitioning as a function of P, T, silicate composition and oxygen abundance in the core. Including about 100 experimental results and covering a wide range of physical and chemical conditions, we propose new regression parameters that allow sulfur partitioning to be modeled reliably. These parameters have been included in a state of the art multi-stage core formation model that is coupled with N-body accretion simulations ([1], [6]). We will present the first results in this meeting.

[1] Rubie et al. (2015) Icarus 248, 89-108
[2] Tsuno et al. (2011) PEPI 185, 1-12
[3] Boujibar et al. (2014) EPSL 391, 42-54
[4] Suer et al. (2017) EPSL 469, 84-97
[5] Blanchard et al. (2017) GPL 5, 1-5
[6] Rubie et al. (2016) Science 353 (6304) 1141-1144

Iron redox equilibria in hydrous basaltic melts and Fe^{2+}-Mg exchange between olivine and melt

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The exchange of Fe^{2+} and Mg between olivine and melt, defined as $K_{d\ Fe-Mg} = (Fe_{ol}/Fe_{melt})\cdot(Mg_{melt}/Mg_{ol})$, is one of the most widely used parameters in petrology, for example in fractionation modelling of basaltic magmas and corrections for post-entrapment crystallisation of melt inclusions. In their seminal work Roeder & Emslie (1970) showed that at atmospheric pressure $K_{d\ Fe-Mg}$ is remarkably constant (0.30) over a wide range of temperature and melt composition. There have been many subsequent studies of olivine-melt equilibrium to refine the canonical value and establish if Fe-Mg exchange is sensitive to P-T-X-f_{O2}. The latter parameter is especially relevant given its fundamental control on the availability of Fe^{2+} in the melt (and hence $K_{d\ Fe-Mg}$) and the difficulty of determining Fe^{2+}/Fe^{3+} microanalytically.

We synthesised olivine-saturated basaltic glasses with variable H_2O (0 to 7 wt%), over a wide range of f_{O2} (iron-wüstite to air), P (0 to 13 kbar), and T (1025 to 1300 °C). Fe^{3+}/Fe_{tot} (in the range 0 to 0.93) was determined by Fe K-edge XANES and/or microMössbauer; H_2O and CO_2 were determined by SIMS. We show that Fe^{2+}/Fe^{3+} is consistent with the algorithm of Kress & Carmichael (1991) and insensitive to dissolved H_2O. Using our data, in conjunction with published (anhydrous) experimental data with independently measured Fe^{2+}/Fe^{3+}, we show that for basaltic melts over the studied conditions, and Fo_{65-98} olivine, $K_{d\ Fe-Mg}$ has a constant value of 0.316±0.001. This provides not only a robust tool modeling for hydrous and anhydrous basaltic magmas, but also a means to determine f_{O2} in experiments that lack external redox buffering, via the relationship $Fe^{3+}/Fe_{tot} = 0.316 - K_{dobs}$, where K_{dobs} is the measured experimental $K_{d\ Fe-Mg}$ with all iron as Fe^{2+}. The f_{O2} can then be recovered from Kress and Carmichael (1991) for the measured melt composition at the experimental P-T.

High-pressure single-crystal structural analysis of $AlSiO_3OH$ Phase Egg

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In this study we present the first single-crystal high pressure X-ray diffraction data on $AlSiO_3OH$ Phase Egg. Synchrotron X-ray diffraction was performed on a high quality single-crystal of $AlSiO_3OH$ Phase Egg in a diamond-anvil cell to a maximum pressure of 23.3 GPa. Aluminosilicate phases such as $AlSiO_3OH$ Phase Egg are considered to play an important role in Earth's deep water cycle, therefore knowledge of their high pressure properties are important parameter to constrain thermodynamic models. Phase Egg has a monoclinic $P2_1/n$ structure consisting of silicon and aluminum octahedra. At pressures below 15 GPa, the Si octahedron is distorted due to a much longer Si-O4 bond length with respect to the other five. With increasing pressure this bond distance decreases much more rapidly than the others and this process results in the formation of a more regular SiO_6 octahedron. This has a major effect on the compressibility of the b-axis along which the Si-O4 bond distance mainly lays and on the behavior of the beta angle which, after a fast decrease up to 15 GPa, remains then unchanged at a values of about 97.8° up to the maximum pressure reached. The bulk compressibility was fitted using a third order Birch-Murnaghan equation of state resulting in the following parameter: $V_0 = 214.1(2)$ Å³, $K_0 = 153(8)$ GPa and $K_0' = 8.6(13)$. This study suggests larger K_0' values than those reported in earlier powder diffraction studies.

Water incorporation in transition zone minerals, Wadsleyite and Ringwoodite: A study using ERDA (Elastic recoil Detection Analysis)

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The transition zone is potentially an important water reservoir within the Earth. Indeed, transition zone minerals, namely wadsleyite and ringwoodite, can contain up to 3.2 wt% H_2O by weight. In recent years, we have been working on extending the capabilities of measurements of water in minerals using other techniques than Fourier Transform Infrared spectroscopy (FTIR) like Raman spectroscopy that allows the use of very small probing beams under reflection geometry, but also ERDA (Elastic Recoil detection Analysis, Bureau et al., 2009; Withers et al., 2012) that allows quantification without the use of any standards. The main problem of using FTIR on wadsleyite and ringwoodite is that these phases are often too absorbing to allow proper quantification of water. Also, whenever working on realistic, i.e. complex, compositions, samples end up having small grain sizes that are difficult to deal with FTIR when the samples are polyphasic.

Thanks to ERDA, we calibrate the Raman spectroscopy for quantifying water in wadsleyite and ringwoodite. We will also discuss the incorporation mechanisms of H in both phases.

Rheology of primitive alkaline basalts: constraints on the pre-eruptive system of Campi Flegrei (Naples, Italy)

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The knowledge of the rheology of magmas at high pressure and temperature is of fundamental importance to model their mobility, ascent rate and volcanic activity at surface. In this study, we determined the viscosity and the atomic structure of the nominally anhydrous APR16 alkali basalt representative of the least-evolved magmas of Phlegrean Volcanic District (Phlegrean Fields, Italy; Bonechi et al., 2017). The sample is a lithic fragment belonging to the Solchiaro hydromagmatic tuff of Procida island, characterized by a porphyritic texture (P.I. 12% volume) with phenocrysts of olivine (Fo85-80), occasionally hosting Cr-spinel grains (Cr# ~0.50), and clinopyroxene (Wo46-48 En46-31 Fs6-23), and a groundmass made of olivine, clinopyroxene, plagioclase (An79-52), Ti-magnetite (Usp4.1-4.4). The APR16 has [Mg/(Mg+Fe)] 0.66, 49 wt% SiO_2, 4.4 wt% of total alkali (Na_2O+K_2O) and ~12 wt% of CaO. The anhydrous glass was prepared at Bayerisches Geoinstitut by using a gas-mixing furnace. The rock powder was melted at 1400 °C for 15 minutes at atmospheric pressure and oxygen fugacity buffered at Nickel-Nickel Oxide level using a CO/CO_2 gas mixture. The viscosity of glassy APR16 was determined by the in situ falling sphere technique at P of 0.7-2.5 GPa and T of 1335-1700°C using the Paris-Edinburgh press available at the 16BMB beamline at the Advanced Photon Source (Argonne National Lab, Illinois, USA). The falling velocity of the Pt probing spheres was measured by X-ray imaging using a high-speed camera recording 500 frames per second. In addition, analyses of the melt structure were performed by using multi-angle energy dispersive X-ray diffraction technique. Preliminary data show the viscosity being in the range of 0.1-1 Pa·s at the target P and T. These viscosity values can be used to model the mobility and ascent velocity of primitive alkali basalts considered to be parental magmas at Campi Flegrei with important implications for the volcanic hazard of the area over time.

Equilibrium fractionation of chromium isotopes between chromites and silicate melts

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The redox condition of the Earth's interior is an essential parameter that controls the chemical behaviour of elements during geological processes. The study of redox sensitive elements, such as Fe or Cr, has helped us understand the way the Earth evolved through time. Recently, the use of stable isotopes to study changes in redox conditions has also been proposed. In this study, we investigate the influence of the redox conditions on the partitioning of Cr isotopes between chromites and a silicate melt in a 1 atm furnace.

Two sets of experiments were performed. In the first set of experiments, a Cr-free melt was equilibrated with natural chromite grains, and in the second set of experiments, chromites were crystallised from a Cr-doped silicate melt. Both sets of experiments were run for 7 days.

Microprobe analyses of the ~100 μm chromite grains from the first set of experiments show that they are zoned in Cr, suggesting that full equilibrium was not obtained between the two studied phases. The chromite grains for the second set of experiments are much smaller (2-3 μm) which suggest that isotope equilibrium was obtained. Large Cr isotope variations were found in both melts and chromites. The Cr isotopic compositions of the melt are always lighter than the chromite grains. Furthermore, melts that equilibrated at high fO2 are isotopically lighter than the melts equilibrated under more reduced conditions.

This contribution shows that Cr isotopes are fractionated between chromite grains and silicate melts and that this fractionation increases with oxygen fugacity. This corroborates the observation made that Cr isotopes are fractionated during fractional crystallisation of natural systems and supports the view that Cr isotopes could be used as a redox proxy.

Mantle modification via pyroxenite-peridotite reaction: an experimental study at 2 GPa

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Interactions between peridotite and pyroxenite-derived melts at deep mantle levels are thought to enhance mantle heterogeneity producing hybrid rocks (i.e. refertilized peridotite, secondary-type pyroxenite). The resulting veined mantle has been diffusely invoked as a suitable source of oceanic basalts. We experimentally investigated the reaction between a fertile lherzolite and partial melts produced by a mantle pyroxenite at 2 GPa. Melting behavior of garnet websterite Px-1 [1] has been firstly derived. Px-1 starts to melt just below 1280 °C, and up to 1350 °C it produces MgO-rich basaltic andesites. Garnet and clinopyroxene are progressively consumed by melting (at 1330 and 1380 °C, respectively); orthopyroxene is the liquidus phase and is completely exhausted at 1400 °C.

We perform piston cylinder reaction experiments by juxtaposing pyroxenite Px-1 on a powdered fertile lherzolite, previously synthesized at the same P-T conditions of reaction experiments. This allows a direct comparison between the modal and mineral compositions in the fertile lherzolite and in the peridotite modified by reaction with pyroxenite-derived melt. At 1300 and 1350°C, partially molten pyroxenite interacts with the subsolidus lherzolite producing a thin (about 50-100 μm) orthopyroxene-rich reaction zone at the pyroxenite-peridotite interface. Chemical profiles along the capsules show that X_{Mg} in pyroxenes decreases across the pyroxenite-peridotite boundary, with intermediate values in the reaction zone. At 1300°C, residual pyroxenite is more depleted in Fe than after partial melting alone, at the same temperature, and this inhibits the stability of residual garnet. Remarkably, in the subsolidus lherzolite spinel records X_{Mg} and X_{Cr} decrease and TiO_2 increase going toward the molten pyroxenite, with spinel X_{Cr} variation increasing with temperature. Similar chemical gradients are observed in some natural pyroxenite-peridotite sequences.

[1] Sobolev A. et al. (2007): Science 316, 412-417

Segregation of alkali metals Na, Rb and Cs with sulfides into planetary cores: implications for volatile depletion in planetary mantles

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Planetary mantles are depleted in volatile elements due to the high temperatures involved during accretion. Volatile siderophile elements are depleted in mantles through both processes of volatilization and core segregation. It is therefore usual to consider volatile lithophile elements to isolate the effect of volatile depletion. Previous studies showed that K and Na have significant affinities with Fe sulfides, especially when sulfides are enriched in oxygen. On the other hand, several models of Earth's accretion suggested that core segregation could have involved chemical equilibria between magma ocean and Fe-sulfide liquid. It is therefore important to understand the behavior of elements that are traditionally considered as lithophile during sulfide segregation into planetary cores. Using multi anvil and piston cylinder apparatuses, we investigated the distribution of alkali metals Na, Cs and Rb between Fe-sulfide and silicate liquids between 1 and 8 GPa and 1700 to 1900 °C. We found that oxygen in sulfide enhances their partition coefficients by two orders of magnitude when it is increased to 13 wt%. We used these experimental data to obtain expressions that predict their partitioning as a function of temperature and chemical composition. Core segregation of Earth, Mars and asteroid Vesta was then modeled, assuming that part of accreted planetary embryos contained a Fe-sulfide layer between core and mantle. For Earth, we also considered a differentiation model with an exsolving sulfide "matte" from a crystallizing magma ocean. We found that alkalis fractionation in Martian and Vesta's mantles could be explained by their partitioning into sulfides that ultimately entered the cores. Terrestrial abundances of alkali metals cannot be explained by both models involving sulfides. Therefore, in oxidized planetary bodies such as Mars and Vesta, Na, Rb and Cs have likely been depleted in mantles due to both processes of volatilization and core segregation.

Nitrogen solubility and speciation in silicate melts

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Nitrogen isotopes are key tracers to investigate the origin of volatiles of planetary bodies because $^{15}N/^{14}N$ ratios show outstanding variability across the Solar System [Füri and Marty, 2015]. Therefore, a quantitative understanding of nitrogen incorporation into different materials (melt, minerals, metal) is necessary to constrain the volatile evolution of planetary objects. However, only a few data on nitrogen solubility and behavior in silicate melts are available today. In this study, we investigate the nitrogen solubility in silicate melts as a function of the oxygen fugacity (f_{O2}) and chemical composition (i.e., NBO/T) using a one atmosphere, high temperature equilibration system under controlled nitrogen and oxygen partial pressures. Different melt compositions were investigated: basaltic (CMAS), rhyolitic, ordinary and enstatite chondrites chondrule mesostases. The oxygen fugacity was varied from IW-8 to IW. The nitrogen content of the quenched run products was determined by CO_2 laser-extraction, static-mass spectrometry (VG-5400) and by secondary ionization mass spectrometry (SIMS). Our new results demonstrate that the nitrogen concentration increases linearly (from 1144.3 to 3252.8 ppm at IW-8) in silicate glasses with increasing melt polymerization (NBO/T) (from 0.206 to 0.494). Step-wise heating mass-spectrometry analyses reveal that nitrogen cannot be extracted from the glass at temperatures below 1000 °C. Consistently, Raman spectroscopy results suggest that nitrogen is chemically incorporated into silica network by forming Si-N complexes in silicate glasses. More data are being acquired to investigate the combined effects of the oxygen fugacity and melt composition on the nitrogen solubility and speciation. These results are key for constraining the nitrogen incorporation into and release from silicate melts and glasses, and, ultimately, for improving our understanding of the nitrogen signature of planetary objects.

Phase relations of Fe₄N at high pressure and temperature determined in a laser-heated diamond anvil cell

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The nature of the light elements in the Earth core is an ongoing debate [1]. Sulfur, silicon, oxygen, carbon and hydrogen are widely accepted candidates. However, nitrogen is also an abundant element in the solar system and is known to be siderophile, rendering it another potential candidate. For instance, some iron meteorites contain up to 1 wt % of nitrogen suggesting that the iron core of planetary bodies could be a significant reservoir of nitrogen in the solar system and could have provided substantial amount of nitrogen to the Earth during its accretion [2]. As such it is believed that significant proportion of nitrogen has been stored in the deep Earth because reducing and high-pressure conditions stabilize nitrides and enhance the solubility of nitrogen into metallic iron rendering nitrogen compatible with the Earth's core [3, 4].

Despite the possible presence of Fe-N alloys in the Earth's core, the phase relations of the Fe-N system under high pressure and temperature remain poorly constrained. Previous high pressure and temperature experiments investigated the phase relations in the system Fe_3N-Fe_4N to 30 GPa [5] and in the system Fe_7N_3 to 150 GPa [6]. In those studies, the stability relations in Fe_4N (the most iron-rich compound) were not well constrained. In this study, we examine the phase relations in Fe_4N up to 65 GPa and 2200 K using synchrotron in-situ X-ray diffraction (XRD) in a laser-heated diamond cell. The in-situ experiments were conducted at I15, Diamond Light Source. We will show the XRD data and discuss the stability of Fe_4N and its implications for Earth's core.

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Volatile exchange coefficients between apatite and silicate melt; new data for carbon

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We present the first measurements of carbon partitioning between apatite and silicate melt, demonstrating the way it competes with hydroxyl and halogens in the apatite structure. Melt compositions range from haplobasaltic andesite to trachyte and kimberlites at 0.1-1 GPa and 1250 °C. Volatiles, major and some trace elements were analysed by EMPA and/or secondary ion mass spectrometry (SIMS) using a newly developed set of apatite standards. Distribution coefficients for OH-halogen exchange are generally similar to previous studies, but we identify a significant log-linear relationship with temperature, while the effects of pressure and melt composition are minimal. In halogen-free experiments very high carbon contents (up to 2.65 wt% as CO_2) are observed in apatite. Stoichiometry calculations and infrared spectra indicate that carbon is mainly incorporated onto the channel volatile site in these experiments, as carbonate. However, in halogen-bearing experiments, concentrations are significantly lower for a given melt carbon content and in this case, the carbonate tends to be forced into the phosphate site whilst the channel site is filled by the more ideal sized F then Cl and OH. These new constraints on exchange coefficients will enable quantitative modelling of apatite-volatile exchange in igneous systems, in particular for H_2O-CO_2 systematics during deep early stage degassing which can be difficult to investigate by traditional melt inclusion methods. We present examples to show how it is possible to use natural magmatic apatite to trace volatile behaviour during magmatic differentiation and degassing and potentially the separation of brines during mineralisation processes.

Apatite and titanite as a proxy of magma evolution?
What is experimental work telling us?

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The magmatic record has evolved through geological time from Tonalite Tronjhemite Granodiorite (TTG) in the Archean toward typical arc magma compositions (BADR) observable at the present day. The Archean-Proterozoic transition is marked by the appearance of sanukitoids, which have been found on every continent. This shift in composition has been interpreted by some as reflecting major geodynamic changes and, in particular, the appearance of sanukitoids has been linked to the onset of subduction-driven plate tectonics.

However, there are remaining fundamental questions about the conditions of the early Earth as its record is extremely sparse (e.g. composition of the crust, geodynamic regime). For example, recent studies are still debating the composition of the early Earth crust: felsic or mafic? The processes leading to the differentiation of the crust during the early Earth need, therefore, to be better characterized. New tools are required to provide further insights on Earth evolution via the petrogenetic analysis of the Archean-Hadean record and the transition to the post-Archaean. Trace element geochemistry of accessory phases can give additional information about the petrogenesis and the sources of their host rocks. In this contribution, we present new geochemical data on accessory phases (titanite, apatite, zircon) from a compilation of granitoids through geological time: TTG's, sanukitoids and BADR from a variety of settings. We demonstrate that trace element analysis and detailed petrographic work on these phases can give direct access to petrogenesis of the host magmas and are good proxy for magmas evolution. In this contribution, we will discuss our results in the light of available experimental data for those phases and we will try to emphasize the limitations of the available dataset.

High-pressure elasticity of polycrystalline stishovite and seismic scattering in Earth's lower mantle

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Geochemical and geophysical evidence points to deep cycling of crustal materials in Earth's mantle. Seismic scattering in the lower mantle has been attributed to the presence of subducted oceanic crust based on low sound wave velocities of the high-pressure silica polymorph stishovite. According to theoretical predictions, the sound wave velocities of stishovite are expected to decrease substantially in the vicinity of the ferroelastic tetragonal-to-orthorhombic phase transition due to elastic softening of the shear modulus. Direct measurements of stishovite sound wave velocities, however, have been limited to low pressures, non-hydrostatic conditions, or discrete crystallographic directions. We performed high-pressure X-ray diffraction and Brillouin spectroscopy experiments on sintered stishovite polycrystals up to pressures of 73 GPa and 60 GPa, respectively. Circular disks were cut from a double-sided polished thin section of a stishovite polycrystal using a focused ion beam and compressed in diamond anvil cells using neon as pressure-transmitting medium. The volume compression curve of the stishovite polycrystal indicates a drop in bulk modulus at the transition pressure. In contrast, shear wave velocities follow a smooth increase across the phase transition. Our results on sintered polycrystalline stishovite differ clearly from those of previous compression experiments on single-crystalline or powdered samples that did not show a reduction in bulk modulus. Furthermore, the absence of shear modulus softening questions the commonly established link between shear wave scattering and stishovite-bearing materials in the lower mantle. We tentatively attribute these differences to the complex elastic response of sintered polycrystals that might serve as a bound for the behavior of real mantle rocks. By modelling seismic properties of basalt and pyrolite, we evaluate the seismic scattering potential and detectability of subducted oceanic crust in Earth's lower mantle.

Growth and Dissolution of Diamonds in the Lithosphere

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Natural diamonds contain mineral and fluid inclusions which preserve information about diamond growth conditions. Replicating the growth of inclusion-bearing diamonds in the laboratory is therefore an efficient diagnostic tool to constrain the conditions of diamond formation in the Earth's lithosphere (Bureau et al., 2012; 2016). Experiments were performed using multi-anvil presses at BGI, Bayreuth and LMV, Clermont-Ferrand at conditions relevant for the lithosphere: 7 GPa, 1300-1400 °C for a few hours (4 to 32 hrs). As starting materials we used mixtures of powders of carbonates, natural lherzolite or MORB, water, graphite and diamonds seeds, all loaded in sealed platinum capsules. Results showed that inclusion bearing diamonds were formed in hydrous-carbonate-silicate fluids through carbonate reduction processes. This means that all lithospheric diamonds: monocrystalline, cloudy fibrous or from ultra-high metamorphism are formed from the same parent fluids. Results also evidenced that, depending on the redox of the experiment, for similar pressures and temperatures, diamond can be dissolved in the same hydrous-carbonate-silicate "parent" fluids. This may explain the common features of resorption observed in lithospheric monocrystalline diamonds, possibly mantle-derived and not only due to kimberlite-induced resorption during ascent, in agreement with recent studies on natural diamonds (Fedortchouk and Zhang, 2011). This places also constrains on the redox conditions necessary for diamond growth in the lithosphere.

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H. Bureau, et al. (2012) Geochimica et Cosmochimica Acta, 77, 202-214.
Y. Fedortchouk and Z. Zhang (2011) The Canadian Mineralogist, Vol. 49, pp. 707-719

The partitioning of molybdenum stable isotopes into sulfide and the potential affects of core formation

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Experimental work suggests that the core contains a significant proportion of sulfide, added during the final stages of accretion [1], and under reduced conditions this sulfide can potentially incorporate substantial quantities of refractory lithophile elements [including the REE and Th-U; 2]. Better understanding of the fractionation of siderophile element stable isotopes may help contrain the conditions and chemical consequences of core-mantle differentiation in planetary embryos. Previous experimental work has shown that at equilibrium at 1600 ºC, the $\delta98/95Mo$ ratio of silicate is $0.12 \pm 0.02‰$ heavier than that of metal [3]. However, the extent to which Mo isotopes fractionate during silicate-sulfide and metal-sulfide segregation, is so far unexplored.

Here we present results of grapahite capsule, piston cylinder experiments that have been conducted at 1400ºC and at a range of oxygen fugacities, from logFeO -0.7 to +1.5 to constrain the paritioning of Mo isotopes between silicate melt and sulfide. The results show that the silicate has a $\delta98/95Mo$ that is $0.25 \pm 0.05‰$ heavier than that of sulfide, which is independent of the oxygen fugacity conditions.

Measurements of three iron meteorties (Gibeon and Muonionalusta (IAB) and Toluca (IVA)) that contain cosexisting sulfide and metal have been used to quantify partitioning between these phases. Heavy Mo istopes consistently partion into the metal, with the $\delta98/95Mo$ of the metal 0.35‰ to 0.55‰ heavier than in the coexisting sulfide phase. Taken together, these results suggest that removal of sulfide to the core of the Earth and other planets will leave a heavy residual silicate mantle, if sulfide removal was late then this may have set the composition of planetary mantles [4].

[1] Wade et al. GCA 85, 58 (2012)
[2] Wohlers & Wood, Nature 520, 337 (2015)
[3] Hin et al. EPSL 379, 38 (2013)
[4] Burkhardt et al., EPSL 391, 201 (2014)

The effect of P_2O_5 on unmixing of basaltic melts

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A series of phosphorus-bearing glasses with concentrations up to 8 mol% P_2O_5 was synthesized to investigate the effect of phosphorus on the unmixing of basaltic melts and the ferrous to total iron ratio. The "Champagne" glass composition of the Wishstone Class rocks found in Gusev Crater on Mars was chosen as the base composition. Our glasses were synthesized in a 1 atm furnace in a temperature range between 1523 and 1573 K. The glass composition was determined by electron microprobe analysis and μXRF. The viscosity of the melts was determined in the range 10^9 to 10^{13} Pa.s using micropenetration viscometry. Heat capacity was determined using differential scanning calorimetry. Glass structure was investigated by Raman spectroscopy and electron microscopy and Fe speciation was investigated using a wet chemical technique for colorimetric ferrous iron determination. The addition of phosphorus to the melt causes strong structural changes and results in an increase in Fe^{2+}/Fe_{tot} as well as viscosity. Despite apparent depolymerization of the melt structure due to increasing the amount of network modifying iron, viscosity increases by approximately 4 log units with the addition of P_2O_5; up to a maximum around 6 mol% P_2O_5. Viscosity decreases with further addition of phosphorus (>6 mol% P_2O_5) to the melt. According to Raman spectra, phosphorus enters the melt network as orthophosphate (PO_4^{3-}) species, which is shown by intense Raman bands around 950 cm^{-1} as described in earlier studies. The melts with higher phosphorus content unmix into two separate melts, presumably into a phosphate- and a silicate-rich melt, as observed by two glass transition peaks in the heat capacity data. This phase separation is shown in backscattered electron micrographs where the second melt phase appears as spheres with an average diameter of 50 to 100 nm. Our research shows that increasing phosphorus concentration in the melt enhances phase separation in natural basaltic melts.

Experimental Investigation of the Interaction of Saline Fluids with the Lithospheric Mantle

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Saline (i.e., Cl-rich) fluids potentially play an important role as metasomatic agents in the lithospheric mantle. Natural evidence for such fluids exists as inclusions within natural diamonds [1,2] and within groundmass minerals in kimberlites [3,4]. Previous experimental studies have investigated melting relations in the chloride-carbonate-silicate system [5], but a systematic experimental study of how saline fluids react with the lithospheric mantle is lacking.

Here, we present reaction experiments between a saline fluid and different mantle lithologies (peridotite and eclogite) at conditions corresponding to the base of the cratonic lithosphere. Experiments were performed at pressures of 4-5 GPa and temperatures of 1050-1200 °C at the Institute for Mineralogy, WWU Münster, Germany, using a 1000 t Walker-type multi-anvil apparatus with a ceramic 18/12 assembly. Starting materials were prepared from powders of high purity oxides, carbonates, hydroxides, and halogen compounds. The fluid mixture was placed at the bottom of the Au-Pd capsule and covered by the mantle rock mixture.

Preliminary results show that reactions between saline fluid + lherzolite at ca. 4 GPa and 1200 °C lead to extensive melting in the presence of a free fluid phase. The residual peridotite is harzburgitic, consisting mainly of olivine and garnet. Pyroxenes are only observed as rare inclusions within garnet. Towards the colder end of the capsule chromite spinels appear. These are followed by a zone of Si- and Cr-rich melt phase and a zone enriched in mica. These preliminary results need to be substantiated with further experiments, including repeat experiments (i.e., without saline fluid), further experiments at lower temperatures (i.e., at lower degrees of melting), and experiments with different bulk rock compositions.

[1] Izraeli et al. (2001) EPSL
[2] Weiss et al (2015) Nature
[3] Kamenetsky et al (2004) Geology
[4] Abersteiner et al (2017) Chemical Geology
[5] Safonov et al (2007) EPSL

The high pressure solubility of CO_2 and H_2O in granitic melts: an experimental study with centrifuging piston-cylinder

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CO_2 and H_2O are the most important volatiles involved in subduction and crustal melting. However, there is a paucity of data regarding the solubility of CO_2 and H_2O in granite melts at > 0.5 GPa as relevant for subduction zones. This is due to the non-quenchability of such melts and the consequent difficulty in analyzing the experimental products. To overcome this hurdle, we used the centrifuging piston-cylinder, effectively separating the fluid and melt phases. The starting mixture was a granitic composition with all FeO substituted by CoO, to avoid the $Fe^{+2} + CO_2$ - Fe^{+3}-graphite redox couple, which would change the volatile composition of the system. Carbon dioxide was introduced through $CaCO_3$, Na_2CO_3, and K_2CO_3, H_2O through $Al(OH)_3$ and when necessary as liquid using a micro-syringe. Starting materials were sealed in $Au_{80}Pd_{20}$ capsules (4.0 mm O.D.) and experiments conducted at 1300 °C and 1.3-1.7 GPa, using a 14-mm non end-loaded piston-cylinder mounted on a centrifuge exposing the sample to 1000 g. Experiments were quenched after 4-6 hours and capsules recovered. The fluid completely accumulated at the gravitational top of the capsule forming a beautiful meniscus. Capsules were analyzed either by weight-and-loss technique using a newly constructed cooling stage (at ETH Zürich), or by quadrupole mass spectrometry (QMS, at Università di Milano). Subsequently, glasses were extracted from the capsules and characterized with Scanning Electron Microscope (SEM). Dissolved CO_2 was determined with a LECO elemental analyzer, whereas dissolved H_2O was analyzed with Karl-Fischer Titration (KFT). Results show that (1) the centrifuge is extremely effective in separating the two phases, (2) both weight-loss and QMS techniques are accurate in characterizing the volatile phase, and (3) the concentration of CO_2 dissolved in glass ranges between 0.4 and 2.0 wt.%, whereas that of H_2O is $\leq$ 7.4 wt.%, rather low for a pressure of ~1.5 GPa.

Looking for potential fluid-mobile elements reservoirs in the lithosphere: preliminary results from experimental studies

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The recycling of volatile and incompatible elements through the entire Earth's history is one of the most important processes for the chemical evolution of the lithosphere. In particular, some fluid-mobile elements (FME: e.g., Sb, As) were demonstrated to be good geochemical tracers able to unravel geological processes where fluid-mediated mass transfer occurs. Despite olivine and pyroxene represent the most abundant mineral phases in the lower crust and upper mantle, the development of amphibole from a precursor hydrous melt or by metasomatic processes replacing pyroxene may play a key role in these reservoirs. The partitioning behavior of FME between amphibole, clinopyroxene, olivine and melt is still poorly constrained. This hampers to model the transport of these elements in the mantle wedge and to constrain if these elements can be stored in the upper mantle or in the deep crust.

In order to better constrain the partitioning of As and Sb between amphibole, clinopyroxene and melt, we carried out hydrous partitioning experiments at P-T conditions of the lower continental crust (1.4 GPa and 1075-1015 °C) considering an alkali-basalt as starting material. Given the multiple oxidation state of As and Sb different buffer techniques (hematite-magnetite, graphite and iron-wustite) were used. At all run conditions, Ti-pargasites and kaersutite either as individual crystals or replacing former pyroxenes crystallized in equilibrium with the melt.

Trace and FMEs were determined by LA-ICP-MS techniques in melt, pyroxenes and amphiboles. Preliminary results show that amphibole has better capability to incorporate As and Sb with respect to pyroxene and glass (amph/lDAs up to 2.6 and amph/lDSb up to 1.3). This ability seems redox-dependent.

Our first results highlight the capability of amphibole to trap FME in the lower crust and upper mantle becoming thus an important potential reservoir for the cycling and re-cycling of these elements in the Earth system.

Ti as Mercury's core formation tracer: evidence for negligible FeS layer

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Geophysical and geochemical measurements by MESSENGER have refined our understanding of the internal structure and geological history of Mercury. Nevertheless, some important questions remain unresolved, particularly regarding the structure of Mercury's core, which may contain a $\leq$ 200 km-thick external FeS layer. Here, we compare MESSENGER data with experimentally constrained geochemical models to evaluate the presence of such a layer and estimate its likely thickness.

We conducted equilibrium experiments in a multi-anvil apparatus at 5 GPa, 1640-1850°C, and under highly reducing conditions (IW-1 to -6), to reproduce Mercury's core-mantle equilibration. The intrinsic oxygen fugacity of Mercury mantle has recently been estimated to IW-5.4 $\pm$ 0.4. In these conditions Ti is chalcophile, but not siderophile. However its metal/silicate partitioning is not negligible. Therefore we use Ti as a tracer for the potential formation of a FeS layer in Mercury.

We construct a single-step model for Mercury's core formation using Ti partitioning data. The main structure of the planet is imposed by geophysical constraints: the metallic core is ~2020 km in diameter, while the outer solid shell is 420 km thick and consists of the crust, mantle, and a potential FeS layer at the core-mantle boundary with a thickness between 0 and 200 km. We also consider the possibility of a liquid FeS layer, localized in the outer part of the core. In both scenarios the best match between Mercury data and our models corresponds to no (0 km) FeS layer. Considering all uncertainties, a FeS layer would probably be less than 20 km thick and certainly not thicker than 70 km. Considering no FeS extraction, the model reproduces the slightly subchondritic Ti/Al of the bulk silicate Mercury. This subchondritic ratio can thus be explained by the selective extraction of Ti by the metallic core.

Concentration-dependent diffusion of trace elements in olivine

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Quantification of diffusion rates of trace elements in olivine is necessary for applications in diffusion chronometry, evaluation of closure temperatures, and for melt / fluid inclusion studies. Experimentally determined diffusion coefficients of trace elements (e.g. Al, Li, H, REE that have a different charge from those of the regular structural constituents) are complex (e.g. H, Li, and Al), or different studies yield controversially different results (e.g. REE, [1] vs. [2]), with rates varying by over four orders of magnitude. In order to address this problem, we have carried out experiments to study diffusion of REE in olivine where the concentration gradients were varied systematically. Thin films of a nominally olivine composition doped with different amounts of Lu, Eu and Ce (100, 1000, 10000, and 50000 μg/g) or of a basaltic composition doped with the same elements (300 μg/g) were deposited on oriented and polished single crystals of San Carlos olivine by pulsed laser deposition. These were annealed under controlled f_{O2} in a gas-mixing furnace at 800 - 1300 °C. Concentration profiles were measured using Rutherford backscattering spectroscopy (RBS) and secondary ion mass spectrometry (SIMS). Results from RBS and SIMS are consistent with each other, although at the lower doping levels profile measurements were possible only with SIMS. The concentration profiles show two different gradients, indicating a slower diffusion rate at high concentrations and a faster diffusion rate at lower concentrations. A concentration-dependent diffusion model where diffusion rates converge to a high value at low concentrations and a low value at high concentrations quantitatively describes the profile shapes, with the results being consistent with data from [2] and [1], respectively, resolving the controversy.

[1] Cherniak 2010, Am Mineral 95:362-368
[2] Spandler and O'Neill 2010, Contrib Mineral Petrol 159:791-818.

Experimental determination of the storage conditions and fractionation path of the Pavin trachyandesite (Massif Central, France)

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We examine phase-equilibrium conditions for a representative trachyandesite (~58 wt% SiO_2, 9-10 wt% alkalis) taken from the Pavin volcano, a maar-like explosive crater belonging to a small group of youngest volcanoes in the Massif Central, with the aim of (1) constraining the storage conditions of the Pavin trachyandesite and (2) investigating the conditions that could generate trachyte compositions such as those of the neighbouring Chaîne des Puys.

The Pavin pumice clasts were fused and used as starting material for the crystallization experiments whose conditions range from 850 to 1000 °C, 150 to 400 MPa, NNO +1 to +2, and X_{H2O} in between 0.6 and 1 (melt H_2O contents from 5.5 to 9.5 wt%). The natural products consist of 10-20 % of plagioclase (rim composition of An35-38), hastingite, clinopyroxene (Wo46-49.5 salite), Fe-Ti oxides (Mt67-78 and Ilm63-68), apatite as accessory phase, and cryptic biotite. Matrix glasses and glass inclusions mostly preserved in clinopyroxenes, show trachytic compositions with 64-66 wt% SiO_2 and 11.5-12.5 wt% alkalis. The H_2O contents of the glass inclusions range between 1.1 and 5.3 wt% (calibrated by-difference method).

The experimental phase assemblage and compositions that best reproduce the natural ones suggest storage of the Pavin trachyandesite at ~150-200 MPa (i.e. ~5-6 km in depth), 950-1000 °C, NNO +1.5, and melt H_2O contents of 5-6 wt% (H_2O undersaturated conditions). The trachytic residual glasses of the Pavin trachyandesite experiments and the trachytic bulk-rocks of the neighbouring Chaîne des Puys overlap in the major oxides, except for alkalis (i.e., the Pavin glasses are enriched by ~1 wt% K_2O and depleted by ~1 wt% Na_2O; which may reflect intrinsic differences attributed to distinct volcanic suites). However, the accordance of the other oxides makes it possible the generation of trachytic liquids by main fractionation of plagioclase, amphibole, and clinopyroxene from a trachyandesitic parent at upper crustal conditions.

Pressure dependence of the liquidus and solidus temperatures in the Fe-P binary system determined by in-situ ultrasonics: Implications to the solidification of Fe-P liquids in planetary cores

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We have developed a new technique for determining the liquidus and eutectic (or solidus) temperatures of Fe-light element alloys at high pressures in a multi-anvil apparatus, by studying ultrasonic wave propagation through the sample. While the onset of melting is manifested by the loss of both compressional (P-) and shear (S-) wave signals due to the scattering of sound waves by partial melts, the completion of melting is confirmed by the reappearance of the P-wave signal when the scattering due to residual crystals disappears. By applying this technique to the Fe-P binary system with three different phosphorus contents, we were able to constrain the Fe-rich portion of the phase diagram up to 7 GPa and 1733 K. Our results show that for phosphorus-poor compositions, ranging from Fe-5wt%P to the eutectic composition, the liquidus temperature exhibits a weak negative pressure dependence (dT/dP = -10.4 $K.GPa^{-1}$ for Fe-5wt%P). While for the phosphorus-richer compositions, including Fe-10wt%P and Fe_3P, the liquidus temperature increases significantly with pressure (dT/dP = 71.3 and 62.5 $K.GPa^{-1}$, respectively). This indicates a shift of the eutectic composition to lower phosphorus contents with increasing pressure. Consequently, molten metallic cores of planetary bodies with phosphorus contents ranging from Fe-5wt%P to the eutectic composition would start crystallization from the top of the core and proceed downward. Whereas, cores with phosphorus-richer compositions (Fe-10wt%P to Fe_3P) would undergo a bottom-up crystallization, resulting in a growing solid inner core.

Crystallization of the lunar magma ocean and the primordial mantle-crust differentiation of the Moon

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We present crystallization experiments on silicate melt compositions related to the lunar magma ocean (LMO) and its evolution with cooling. Our approach aims at constraining the primordial internal differentiation of the Moon into mantle and crust. We used graphite capsules in piston cylinder (1.35-0.80 GPa) and internally-heated pressure vessels (< 0.50 GPa), over 1580 to 1020 °C, and produced melt compositions using a stepwise approach that reproduces fractional crystallization. Using our new experimental dataset, we define phase equilibria and equations predicting the saturation of liquidus phases, magma temperature, and crystal/melt partitioning for major elements relevant for the crystallization of the LMO. These empirical expressions are then used in a forward model that predicts the liquid line of descent and crystallization products of a 600 km-thick magma ocean. Our results show that the effects of changes in the bulk composition on the sequence of crystallization are minor. Our experiments also show the crystallization of a silica phase at ca. 1080°C and we suggest that this phase might have contributed to the building of the lower anorthositic crust. Calculation of crustal thickness clearly shows that a thin crust similar to that revealed by GRAIL cannot have been generated through solidification of whole Moon magma ocean. We discuss the role of magma ocean depth, trapped liquid fraction (with implication for the alumina budget in the mantle and the crust), and the efficiency of plagioclase flotation in producing the thin crust. We also constrain the potential range of pyroxene compositions that could be incorporated into the crust and show that delayed crustal building during ca. 4% LMO crystallization on the nearside of the Moon may explain the dichotomy for Mg-number. Finally we show that the LMO can produce magnesian anorthosites during the first stages of plagioclase crystallization.

Towards a new biotite-based barometer for metaluminous granitoids

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The emplacement pressure of granitic plutons is arguably one of the most critical parameters required in order to reconstruct and understand the physio-chemical evolution of magmatic(-hydrothermal) systems, as well as the tectonic history (deformation, erosion, exhumation) of the terranes in which they are emplaced. Despite this, there are surprisingly few ways to quantify this pressure accurately. This is in large part due to the limited number of mineral phases present and the subsequent small number of reactions suitable for magmatic geobarometry. Either the thermodynamic variance is high (too many compositional degrees of freedom) or the phases are characterized by component exchange that is easily reset during slow cooling and/or minor degrees of hydrothermal alteration. The Al-in-hornblende geobarometer is one of the most common ways to estimate emplacement pressures of metaluminous granitoids. Few studies have proposed that biotite might also lock barometric information in its chemistry, notably the Al content (e.g., Mutch et al., 2016, Uchida et al., 2007). However, these early studies could not provide the basis for quantitative calibration of a biotite-based geobarometer.

We will present preliminary results from available and new experiments conducted with various metaluminous starting materials (ASI from 0.80 to 0.95). Experiments were conducted under near-solidus fluid-saturated conditions from 100 to 800 MPa where biotite crystallized together with a low-variance mineral assemblage. The chemical variation of biotite provides the basis to calibrate a new biotite-based geobarometer.

Measuring the viscosity of lava: an experimental approach in the field

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Viscosity is the key parameter that needs to be well constrained to model lava flow dynamics. Viscometry in the laboratory using re-melted lava at super- and sub-liquidus conditions allow parameters to be controlled and accurate measurements to be made. However, they are unable to precisely replicate natural lavas with their range of crystal and bubble contents, dissolved volatiles, and oxygen fugacity. One promising approach for quantifying lava rheology in its natural state is therefore to carry out direct field measurements by inserting a viscometer into the lava while it is flowing. Such syn-eruptive in-situ experiments are notoriously difficult to perform due to the lack of appropriate instrumentation and the difficulty of working on or near active lava flow. However, if suitable precautions are taken during measurements and post-processing of data, the results form an extremely valuable dataset that can be used to model active lava flows. This work provides: 1) a review of all rheological measurements performed in the field since the first attempt 68 years ago to the latest in 2016; 2) a detailed description of this latest experiment. For this, a unique rotational field viscometer has been refurbished, and measurements were carried out and associated with sampling on active pāhoehoe lobes at Kilauea Hawaii, in Nov. 2016. Lava viscosity was measured around 380 Pa.s at strain-rates between 1.6 and 5 s^{-1} and at 1144 °C. This result is compatible with rheological properties estimated via current physico-chemical models and from chemical and textural analyses of the quenched lava samples. However, the sensitivity of these estimates to our capacity of understanding the role of each phase present in the lava and in particular the role of deformable bubbles that is usually inaccessible in high temperature rheological laboratory measurements on natural lava, supports the need for continued field viscometry in concert with precise textural characterization.

Project PLANEX: X-ray in-situ diagnostics of materials under High Pressure and High Temperature

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In order to better understand the behavior of natural (geological) and industrial systems under high pressure and high temperature conditions (HP-HT), it has become necessary to analyze them with time resolved in-situ diagnostics to follow the systems changes in real time. Due to recent technological advances in HP-HT experimentation and improvement of in-situ diagnostics, this study under extreme conditions has become more complete and possible in real time.

In this context, the 'PLANEX' project aims at installing an in-situ HT-HP plateform for in-situ, time resolved studies of geomaterials under hydrothermal conditions (up to 2 kbars and 1200 °C) [1].

For this, several optical diagnostics (IR, Raman, and RX) will be couples with Internally Heated Pressure Vessels (IHPVs) equipped with transparent windows in the appropriate transmittance range compared to the light spectrum of the diagnostic.

In this work, we present instrumentation dedicated to X-rays diagnostics at HT-HP (IHPVs and X-rays diagnostics devices) together with first results for image, XRD and SAXS analysis obtained at room temperature and pressure but using the same optical path (Be windows, amorphous carbon container, …) as in IHTPs.

Oriented growth of metamorphic olivine under disequilibrium drained conditions

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Mechanical instabilities produced by dehydration reactions of serpentinites in subduction zones are ultimately determined by the mechanism by which fluids are drained out from the system. The microstructure of the reaction products (in particular olivine) should record draining processes and could be used to discriminate the actual draining mechanism. Yet, the experimental study of the relations between microstructure and fluid draining conditions is challenging due to the difficulty to reproduce in the laboratory the geological rates of heating, compaction, and grain growth and the associated permeability changes.

We present a set of dehydration experiments designed to investigate the microstructural effect of the anisotropic permeability on the fluid transport under drained conditions. Hollow cylinders, 11 mm-long, 7.8 mm-wide, with 3.0 mm thick walls were cored in strongly or weakly foliated antigorite-serpentinites with their long axis either parallel or normal to the foliation. Draining conditions were ensured by using porous Alumina discs at the top and the bottom of the serpentinite sample as well as a central porous Alumina cylinder passing vertically through the sample. Experiments were run in a Paterson press at 300 MPa and 730 °C. High spatial resolution EBSD maps (step size $\geq$ 200 nm) allow identifying two populations of metamorphic olivine. Both have their [001] axes randomly oriented in the former serpentinite foliation plane. Relatively large (20 μm-long) idiomorphic crystals elongated parallel to the [001] crystallographic axis (aspect ratios of ca. 3:1) crystallised preferentially with their [010] axes normal to the former foliation. Smaller crystals have mainly [100] normal to the foliation. Moreover, we observe growth of acicular olivines at high angle to nm-wide seams both within and normal to the former foliation, which we interpret as re-sealed fractures, which acted as fast pathways for fluid extraction.

Low hydrogen contents in the cores of terrestrial planets

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The accretion of planets from primordial materials and their subsequent differentiation to form a core and a mantle are fundamental questions in terrestrial and solar system. Many of the questions about the processes are still open and much debated. For example, could the presence of water during the metallic phase segregation affect the planet-accretion models?

The existing studies on the elemental metal-silicate partitioning under hydrous conditions were extended recently to a range of P, T, f_{O2} and water content (5 - 20 GPa, 2000 - 2500 K, from 1 to 5 log units below the iron-wüstite buffer, and for X_{H2O} varying from 500 ppm to 1.5 wt.%) [1].

These experimental results show that except for Fe, there is no effect of water on the partitioning of moderately siderophile elements. It allowed us to build consistent models of planetary accretion from reducing to oxidized conditions. Furthermore, for the range of water concentrations studied, there is no evidence of important hydrogen incorporation into planetary cores, thus making unlikely for hydrogen to be a major light element of the core as previsously assumed [2]. We report H metal-silicate partition coefficients of about 0.2, up to two orders of magnitude lower than reported previously, and indicative of lithophile behavior. Our results imply H content of ~60 ppm in the Earth and Martian cores [3].

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Geochemistry of olivine-hosted melt inclusions of the ~ 7 ky basanitic Montcineyre eruption, Massif Central, France

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We have investigated the geochemistry of naturally quenched olivine-hosted melt inclusions, groundmass and bulk rock lavas of the Montcineyre volcano situated in the south of the Chaîne des Puys volcanic chain (France). This monogenic volcano is part of the Pavin group volcanoes (Montcineyre, Estivadoux, Montchal, Pavin) which represent the most recent activity in metropolitan France (~7ky).

The Montcineyre eruption produced a scoria cone associated with a lava flow with silica-undersaturated basanitic composition ranging from 42 to 45 wt% SiO_2 and 4.1 to 6.6 wt% total alkali oxides. Melt inclusions were analyzed in highly magnesian olivine phenocrysts (Fo > 82.5) in order to characterize the primitive magma composition (major, volatiles and trace elements) of this particular eruption.

Melt inclusions have a basanitic composition with SiO_2 content as low as 42 wt%, MgO > 5.6 wt% and $Na_2O + K_2O$ > 5.5 wt%. Water and carbon dioxide contents were measured using Raman spectroscopy. A set of basanitic glasses with up to 2.86 wt% H_2O and 2.35 wt% CO_2 were synthesized in a piston-cylinder apparatus (at 1.5-2.2 GPa and 1325 °C) and used for calibration. Melt inclusions contain from 1.4 to 1.6 wt % H_2O and up to 7000 ppm CO_2 suggesting melt entrapment at deep conditions. Additionally, chlorine, fluorine, sulfur and trace elements abundances are determined to better understand the characteristics of the magma source beneath the Chaîne des Puys and the dynamics of the eruption.

In situ quantification of the sulfur radical species (S3(-), S2(-)) in aqueous fluids and silicate melts using a hydrothermal diamond-anvil cell (HDAC)

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Our current view of sulfur behavior in lithospheric fluids and melts, that considers sulfate, sulfide and sulfur dioxide as the main S species, was recently questioned by the findings of the radical ions S3(-) and S2(-) that may be stable across a large range of pressure (P) and temperature (T) [1,2]. These new species can only be detected at high P-T conditions as they rapidly breakdown to sulfate and sulfide in aqueous solutions upon cooling. We currently lack direct data at T above 500 °C. To fill this gap, we present new experiments in a HDAC, in an attempt to quantify in situ these species at 500-800 °C and 10-20 kbar using micro-Raman spectroscopy. We have studied thiosulfate and sulfur-bearing solutions and pyrite-pyrrhotite-albite-hematite assemblages in aqueous fluid, and aqueous fluid-silicate melt systems. We show that, when the conditions for the sulfate and sulfide coexistence are met, S3(-) and S2(-) species are systematically present in the fluid in significant amounts increasing with T. In the presence of alkaline or peralkaline silicic melts, these radicals partition largely in favor of the fluid phase. Several technical improvements have been made to preserve these very reactive S species in the experimental cell over time. The concentrations of the radical ions have been determined by comparison of their Raman peak intensities with those of standard solutions of sulfate and sulfide and ultramarine samples with known S speciation and content, and using mass balance and corrections of Raman scattering coefficients for the differences in densities, refractive indexes, and Raman signal absorbance by colored samples [3]. The results are compared with thermodynamic models [2,4] to derive the stability constants of the radical ions and estimate their abundance in lithospheric fluids.

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Generation of K-rich magmas in the metasomatised upper mantle

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Potassium-rich magmas are observed in almost all tectonic settings worldwide. While they offer an opportunity to better understand the global geochemical cycle of volatile elements, their geochemical signatures cannot be reconciled with simple peridotite melting sources and their petrogenesis is thus still under debate. Because of its ultrapotassic nature, phlogopite is a very good candidate to form K-rich magmas within the mantle. However, its stability at pressure beyond 5 GPa is poorly constrained whereas numerous studies have emphasized the peculiar role of pressure on ultrapotassic magma genesis.

Multi-anvil experiments have been performed to study phlogopite-peridotite phase relationships and low-degree melt compositions between 4 and 8 GPa. Just above the solidus, located between 1200 and 1250 °C, melts in equilibrium with residual phlogopite are silica-undersaturated and contain up to ~ 13 wt.% K_2O. Together with their perpotassic features ($K_2O/Al_2O_3 > 1$), such hydrous melts share strong affinities with lamproites, the most K-enriched lavas observed on Earth. Pressure has a strong influence on both K_2O content and K_2O/Na_2O ratio of peridotite-derived melts, up to the breakdown of phlogopite to form K-richterite around 8 GPa.

Accounting for small amounts of fluorine, phlogopite could persist above the solidus up to temperatures near of the average mantle adiabat. Consequently, volatile elements such as H and F, together with K, could be stored within the mantle even at very high temperature. In turn, the presence of F would facilitate phlogopite to remain stable in the deep mantle, implying a long-term evolution of the radiogenic Sr signature of the mantle toward enriched mantle signatures, similar to potassic lavas described worldwide.

Determination of $^{15}N/^{14}N$ ratios in reduced silicate glasses using Raman spectroscopy

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The heterogeneous distribution of nitrogen two stable isotopes ^{14}N and ^{15}N between the terrestrial reservoirs, ^{15}N-depleted mantle and the ^{15}N-enriched surface, remains poorly understood. The use of N isotopes to address possible origins of the mantle ^{15}N depletion requires constraints on the magnitude of fractionation between minerals, melts and fluids within the mantle. We have developed the analytical protocol for measuring N isotopes by Raman spectroscopy.

We present Raman spectra acquired in silicate glasses (NS4, an anorthite-diopside eutectic glass in CMAS, a haplobasalt, a haploandesite and a haplorhyolite), enriched in variable proportions of $Si_3{}^{15}N_4$ and $Si_3{}^{14}N_4$ ($^{15}N/^{14}N$: 0.004, 0.08, 0.2, 0.44 and 5.4). Glasses were synthetized at 1 GPa and 1400 °C for 6 hours in graphite capsules (to ensure reducing and graphite saturated conditions). The N content and $^{15}N/^{14}N$ molar ratios were measured by secondary ion mass spectrometry.

Raman spectra were acquired using the 457.9 nm (blue) excitation source with 9 to 23 mW on samples, allowing us to detect: CO, N_2, CH_3, CH_4, NH_3, NH_2 and OH species. We show that Raman spectroscopy has sufficient resolution to separate the ^{14}N-^{14}N (shoulder at 2325 cm^{-1} on the N_2 peak of the air), ^{14}N-^{15}N (2290 cm^{-1}) and ^{15}N-^{15}N (2250 cm^{-1}) peaks, as well as the ^{14}N-H vibration peaks from the ^{15}N-H peaks in NH_3 and NH_2, down to $^{15}N/^{14}N \geq 0.25$, even at 1000 ppm of N.

In our glasses, N_2 species are dominant below the IW buffer (IW to IW-2) at low f_{H2}, whereas at $H_2O > 2000$ ppm, NH_2 and NH_3 are the dominant N species. Boulliung et al. (abstract EMPGXVI) show that under very reducing conditions (IW-8), N forms Si-N complexes in silicate glasses, replacing non bridging O in the silicate network (N solubility increases with NBO/T). In summary, N speciation in silicate glasses is controlled by both f_{O2} and f_{H2} conditions. More results are currently being acquired to determine their effects on $^{15}N/^{14}N$ fractionations.

Argon incorporation and diffusion in polycrystalline olivine

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Argon (Ar), is a reliable tracer of geochemical heterogeneities since it is both an incompatible and volatile element, and is not easily recycled into the mantle. The $^{40}Ar/^{36}Ar$ ratio is useful to trace mantle heterogeneities since after atmospheric contamination correction, the value of this ratio is around 40 000 in MORBs and less than 10 000 in OIBs [1]. Here, we propose an alternative to large-scale models to explain the preservation of such chemical and isotopic heterogeneities by studying storage sites in mantle rocks at microscopic scale for Ar. Indeed, high temperature partitioning experiments have shown that incompatible elements are preferentially stored at grain interfaces in polycrystalline olivine [3]. For noble gases, grain boundaries as a potential storage site were experimentally demonstrated for He and Ar [4,5,6].

To investigate Ar storage and diffusion in polycrystalline olivine, polycrystalline olivine, which were experimentally doped by using orthoclase as a source of Ar, were analyzed by step heating method. The resulting diffusivities are in agreement with the diffusion parameters and correspond to the temperature range where the lattice and grain boundary diffusions are expected (for He and Ar, see [5]; for He, see [6]). The lattice diffusion parameters for Ar in olivine were determined by reinterpreted literature data and grain boundary diffusion parameters were derived from bulk diffusivities. These results predict a significant storage of Ar in grain boundaries and an enhancement of bulk diffusivities compared to lattice diffusivities. This implies that the proportion of Ar stored in grain boundaries as well as bulk diffusivities increase as the grain size decreases.

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Hydrogen partitioning between NAMs in garnet-bearing peridotite at subsolidus conditions

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Hydrogen distribution between nominally anhydrous minerals (NAMs) of a garnet-lherzolite under subsolidus conditions has been investigated. Separated NAMs from a garnet-peridotite from Patagonia (Chile) are annealed together (olivine, orthopyroxene, clinopyroxene and garnet) using a piston-cylinder at 3 GPa and 1100 °C using talc-Pyrex cell assembly for 10, 25 and 100 hours. The talc-pyrex assembly provides enough hydrogen in the system to re-equilibrate the hydrogen concentrations at high pressure. The three co-existing nominally anhydrous minerals (NAMs, i.e., olivine, orthopyroxene and clinopyroxene) were successfully analyzed using FTIR. The resulting hydrogen concentrations exceed significantly the initial hydrogen concentration by a factor of 13 for olivine and a factor of 3 for both pyroxenes. Once mineral-specific infrared calibrations are applied, the average concentrations in NAMs are 115 ± 12 ppm wt H_2O for olivine, 635 ± 75 ppm wt H_2O for orthopyroxene and 1214 ± 137 ppm wt H_2O for clinopyroxene, garnet grains are dry. Since local equilibrium seems achieved over time (for 100 hours), the calculated concentration ratios are interpreted as mineral-to-mineral hydrogen partition coefficients (i.e., Nernst's law) for a garnet-peridotite assemblage. It yields, based on mineral-specific infrared calibrations, $D_{opx/ol} = 5\pm1$, $D_{cpx/ol} = 10\pm2$, and $D_{cpx/opx} = 1.9\pm0.4$. While $D_{cpx/opx}$ is in agreement (within error) with previous results from experimental studies and concentration ratios observed in mantle-derived peridotites, the $D_{px/ol}$ from this study are significantly lower than the values reported from mantle-derived xenoliths and also at odd with several previous experimental studies where melt and/or hydrous minerals co-exists with NAMs. The results confirm the sensitivity of hydrogen incorporation in olivine regarding the amount of water-derived species (H) in the system and/or the amount of water in the co-existing silicate melt. The rapid concentration modification in mantle pyroxenes also points out that pyroxenes might not be a hydrogen recorder as reliable as previously thought.

Experimental evidence for H_2O-rich boundary-layers during the crystallization of pegmatites

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Granitic pegmatites are now considered as sources of critical and strategic elements. Their textures indicate specific crystallization conditions with possible implications on mineral/melt element partitioning. Kinetic crystallization experiments are being carried out on haplogranitic melts to explore the influences of the cooling rate ($\Delta T/\Delta t$), degree of undercooling (ΔT), liquidus and solidus temperatures (T_L and T_S) and melt H_2O content on the development of pegmatitic textures. All experiments were carried out at 2 kbar between 600 and 900 °C using both cold-seal and internally heated pressure vessels pressurized with Ar. The liquidus temperature of the studied haplogranitic composition as well as its dependency with the melt H_2O concentration was first determined from phase equilibrium experiments. The crystallization kinetics experiments followed a specific isobaric three-step time-temperature cycle. First, a pre-conditioning step at 800°C was imposed for 5 days. Second, the charge was cooled at a fixed $\Delta T/\Delta t$ to a given temperature T (= T_L - ΔT). Third, the charge was kept at T for a given duration (t). Quenching was performed under constant pressure. For H_2O-saturated conditions, pegmatitic textures marked by large euhedral or skeletal crystals and graphic intergrowths appear when supercooled melts are crystallized at T = 600°C (ΔT=120°C, $\Delta T/\Delta t$=10°C/min, t=552 hours). A 10 μm melt boundary layer enriched in SiO_2 (83 wt%) and H_2O (10 wt%) and depleted in K_2O and Na_2O (K_2O = Na_2O = 2.5 wt%) when compared to the far-field melt is present at the alkali-feldspar growth front. Rapid growth of alkali-feldspars leads to enrichment of Si and H and depletion of Na and K at the melt-crystal interface. The co-enrichment in H and Si at the interface is unexpected because H diffuses much faster than Si in granitic melts. These results stress the importance of kinetic processes in the crystallization of pegmatites.

Experimentally determined grain growth kinetics of spinel peridotite and the implications for emplacement of mantle xenoliths

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Mantle xenoliths provide rare insight into the deeper parts of Earth, their scarcity and many sources makes determining their tectonic histories challenging. Many undergo metamorphic reactions upon exhumation and leave behind textural relics of their journey, such as kelyphitic coranae found in transitional garnet to spinel peridotites. These coranae have been used to estimate uplift rates, however, the lack of reaction kinetics data in combination with geothermometry and geobarometry has limited P-T-t pathway estimates and as such an understanding of residency times and emplacement mechanisms.

We present new experimentally determined grain - growth kinetics for spinel and enstatite intergrowths, which result from the complete retrogression of garnet peridotites and intermediate metamorphic textures such as kelyphitic coronae.

Time series experiments have been conducted at UCL at 1050 - 1200 °C, starting with a fine-grained mixture of natural spinel and enstatite from a Lanzarote peridotite.

Traditional methods of grain size analysis have used homogenous grain shapes and assumptions for non-spherical grains. In our analysis, we used advanced image processing techniques to determine 2D grain morphologies. Application of a watershed segmentation scheme allows for the separation of touching grains in a quantitative approach with out the inherent biases of researcher preconceptions. Our experimental results find; an activation enthalpy for grain growth of 256±1.5 kJ/mol, initial grain sizes of 0.32±0.15 μm, grain growth exponent (n) = 2.5±1 and Log(ko) = -9.8 m^2/s. We use the grain growth kinetics to estimate uplift rates of a Lanzarote peridotite xenolith. A coarsening duration of 6000 years is derived, which is 7 m/year of uplift from 50 - 15 km. A lack of overprinting from lower pressure phases such as plagioclase suggest the xenolith was transported rapidly through the last 15 km of lithosphere before reaching the surface during the 1780 Timanfaya eruption.

Phase equilibria experiments on a leucitite from the Colli Albani volcanic district (Italy)

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The Colli Albani volcanic district is a quiescent volcano near Rome (10 km southeast, central Italy) belonging to the ultrapotassic Roman Province. This volcano was characterized by high volume explosive volcanic events induced by the interaction of low SiO_2 ultrapotassic magma with carbonate rocks, representing an anomalous high explosive behaviour of SiO_2-poor magmas on planetary scale. Highly explosive eruptions are driven by the exsolution of volatile components to a separate fluid phase. The presence of crystals facilitates the nucleation of H_2O bubbles in the magmas because of a reduction of the surface tension at the bubble crystal interface. This work is focused on the determination of mineral stability fields in ultrapotassic, SiO_2-poor, H_2O- to CO_2-dominated magmas and is intended to gain knowledge needed to study the bubble nucleation in the CO_2-dominated volcanic systems.

Crystallization experiments were performed on a synthetic leucititic melt from the Colli Albani volcano at 100, 200 and 300 MPa and at temperatures from 1000 to 1200 °C with run durations up to 15 days. Capsules were prepared with an initial mole fraction of water (X_{H2O}) of 0, 0.25, 0.50, 0.75 and 1 and run in Internally Heated Pressure Vessel (IHPV) at intrinsic redox conditions ($\log f_{O2}$ = NNO+3). Run products were analysed by microscope, electron microprobe and spectroscopic techniques.

First results show that the liquidus for the investigated system lays between 1150 and 1200 °C. In the H_2O-dominated systems, magnetite is the first crystallizing phase immediately followed by clinopyroxene. The third crystallizing phase is phlogopite appearing at 1000 °C, when the crystallization degree is above 70%. In the CO_2-dominated systems (CO_2 > 70%) the first crystallizing phases are leucite and clinopyroxene.

Experiments show that the most common natural phenocrystal assemblage (leucite, clinopyroxene and oxides) could have been formed only in CO_2 dominated systems.

The effect of water and oxygen fugacity on seismic properties of olivine

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By analogy with the effect of water on olivine rheology, it was expected that water significantly reduces seismic velocities and increases attenuation. Experimental testing of this hypothesis became possible with a sample assembly that allows water (hydroxyl) retention without the need for a buffer. The samples consisted of undoped and Ti-doped solution-gelation derived Fo90 and Fo100 olivine, as well as San Carlos olivine. These were encapsulated in Pt, as well as Ni and NiFe alloy. The samples were mechanically tested in torsion at seismic frequencies (1 – 1000 s), 200 MPa confining pressure and temperatures from 1200 – 25 ºC. FTIR spectroscopy both before and after mechanical testing showed bound hydroxyl as well as molecular water in the samples.

A surprising result is that shear modulus and attenuation are insensitive to variations in water content. Instead, the oxygen fugacity imposed by the metal capsule is the key variable. The oxygen fugacity in the interior of the samples was determined in separate experiments by analyzing the Fe content of dispersed PtFe particles in equilibrium with olivine. Fitting of the seismic data indicates a slope of the oxygen fugacity dependence of roughly 1/3.

The results imply that seismic velocities and attenuation in normal asthenospheric upper mantle are not sensitive to the presence of water. This is consistent with seismic observations from older Pacific upper mantle which can be modeled with dry, melt-free olivine, despite the geochemically inferred presence of water in the mantle. Velocities lower than expected for dry olivine for younger mantle, and particularly near ridges therefore imply the presence of melt. Above subducting slabs more oxidizing conditions may also reduce seismic velocities.

Behaviour of lithophile trace elements during the Earth's core formation

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The earliest history of the Earth was marked by accretion and core formation within about 100 Myr. While most studies constraining this episode in term of P, T and f_{O2}, etc … are based on the behaviour of siderophile elements, the impact of core formation on "non-siderophile" elements has still to be understood. We choose here to focus our work on the behaviour during Earth's core formation of elements usually describe as lithophile: Rare Earth Elements (REE), Uranium (U), Potassium (K), and Thorium (Th).

It has long been known that the Earth's mantle is more depleted in potassium (K), than CI-Chondrites, The K/U of CI-Chondrites being 6 times greater than the BSE ratio [1]. This depletion is generally ascribed to the K volatility during the early stages of planetary accretion. On the other hand, it has also been suggested that at least part of the K deficit in the mantle may be due to incorporation into the core during the segregation of an Fe-rich metallic liquid. It remains controversial, however, how much K has entered the core at the early stage of the core-segregation from a deep magma ocean, the available metal-silicate partition coefficients of K cover nearly four orders of magnitude, making the implications of the potassium content of the core uncertain [2].

REE are classified in the refractory group, and are particularly abundant in the sulphides of enstatite chondrites (100 to 1000 times the CI value) proving that these elements are not strictly lithophile under extremely reducing conditions. However by investigating experimentally the impact of Earth's core formation on the behaviour of Sm and Nd, we have shown the absence of fractionation between Sm and Nd during the segregation of the metallic phase [3]. Recently, Wohlers and Wood proposed that Nd and Sm could be fractionated in presence of a S-rich alloy phase [4].

By combining our new metal-silicate partition experiments of REE, U, K and Th with all already published data, we present here a coherent model of Earth's accretion, constraining the impact of core formation on the segregation of these elements between the different Earth's reservoirs. We will also bring new constrains on the composition on the Earth's core, by discussing the effect of S and O on the behaviour of REE, U, Th and K.

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Protoplanet compositions recorded by glass inclusions hosted in porphyritic magnesian olivines in chondrules: an experimental study

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Determining how glass inclusions in the oldest and most primitive magnesian porphyritic olivines of type 1A chondrules formed and were preserved since 4.5 Ga is crucial to understand the first steps of solar system evolution.

Some rare silica-rich glass inclusions ($69 < SiO_2 < 82$ %wt.) are described within these magnesian olivines. These glass inclusion compositions are clearly out of equilibrium with their host Mg-olivines and their presence within olivines is generally attributed to an unclear secondary process as a late interaction with nebular gases. Indeed, a magmatic origin for these Si-rich glass inclusions means that classical thermodynamic phase relations do not operate. In particular, peritectic reaction that produces low-calcium pyroxene from forsterite and a silica-rich liquid should be impeded. We performed experiments that demonstrate that Si-rich glass inclusions are actually magmatic inclusions trapped inside olivines that crystallize slowly from a magma which has a CI composition, i.e. the solar composition. The peculiar compositions of these inclusions result from combination of two factors: small volume of melt inclusions and large temperature gap between the crystallization temperature of the first phase, i.e. olivine in our experiments, and the occurrence of the second phase (pyroxene) that inhibits nucleation of this pyroxene and so peritectic reaction. Then, crystallization of olivine continues metastably on the walls of inclusion until the liquid is frozen as a glass. Therefore, we suggest that Si-rich glass inclusions could be the only reliable relicts of what were the first magmas of the solar system, exhibiting a CI, i.e. non-fractionated, composition (Faure et al., 2017).

Faure F., Tissandier L., Florentin L., Devineau K. (2017) Geochimica et Cosmochimica Acta 204, 19-31

Ionic conductivity of natural olivine

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The electrical conductivity of olivine has three major mechanisms: proton conduction (σp) due to migration of free protons within the crystal structure, small polaron conduction (σh) through the hopping of electron holes between ferric and ferrous iron, and ionic conduction (σi) by the migration of Mg vacancies. They dominate olivine conductivity at relatively low, moderate, and high temperatures, respectively. Both σp and σh have been well studied in previous studies whereas σi is poorly constrained because people had believed that the contribution of σi to mantle conduction is negligible. However, recently, Fei et al. [1] and Yoshino et al. [2] pointed out that σi might be an important conduction mechanism in the upper mantle based on Mg self-diffusion experiments and σi measurements in iron-free forsterite. In order to evaluate the contribution of σi to the conduction of iron-bearing mantle, here we systematically measured σi in natural olivine single crystals as a function pressure from 2 to 8 GPa and temperature from 1750 to 2200 K. The results show that σi[001]> σi[100]> σi[010] at <1800 K, and σi[001]> σi[010]> σi[100] at >1900 K. The activation energies for σi[001], σi[100], and σi[010] are ~220-245, 305-315, and 240-280 kJ/mol, respectively, whereas the activation volumes are ~2.4-3.0 cm^3/mol. Additionally, oxygen fugacity has relatively small effect on σi. By applying the mantle geotherm, we have σi[001]>>σi[010]≈σi[100] and σi>>σh>>σp in the asthenosphere beneath both young and old plates. Namely, σi dominates olivine conduction almost in the entire asthenosphere. The conductivity anomaly at 70-120 km depth beneath young oceanic plates interpreted from magnetotelluric data [3, 4] can be well explained by σi in olivine.

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Experiments and modeling of metal partitioning between sulfide and silicate liquids suitable for the formation of magmatic sulfide ore deposits

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A comprehensive knowledge of metal partitioning between sulfide liquid and silicate melt is essential to understand sulfide liquid enrichment in chalcophile and siderophile elements that can lead to the formation of magmatic sulfide ore deposits.

We present a new experimental set of partition coefficients ($D_{sul/sil}$) for Co, Ni, Cu, Pd, Ag, Pt and Au at crustal conditions relevant to the Noril'sk-Talnakh region (Russia). Experiments were conducted in internal heated pressure vessels at 1200 °C and 70 MPa.

The originality of these experiments is that they were done (1) using natural rocks from this region, (2) under variables f_{O2} (from FMQ-1.9 to FMQ+2.1) relevant to mantle derived magmas, (3) with metal-undoped concentrations, and (4) with a sulfide liquid created directly during the experiment.

Our results show that $D_{sul/sil}$ for Pd, Ag, Pt and Au increase with the content of the element in the sulfide liquid, showing that these elements do not follow Henry's law, in contrast to those for Co, Ni, and Cu. These $D_{sul/sil}$ can reproduce the metal contents of natural sulfides of the Noril'sk region, considering a parent magma Pd- and Pt-richer than the lavas of the region, and with the help of interactions between the masses of silicate liquid and sulfide liquid in order to enrich the latter.

$D_{sul/sil}$ variations were modeled as a function of magmatic conditions using a thermodynamic approach. This modeling allows investigating the variations of $D_{sul/sil}$ with temperature, pressure, oxygen fugacity and the compositions of both liquids and suggests that mafic magmas with the lowest temperatures and pressures and the highest oxygen fugacities are more efficient to produce enriched sulfide liquids, and create magmatic sulfide ore deposits.

The pressure-induced HS to LS transition of octahedrally coordinated Mn^{3+} in the hydrogarnet henritermierite, $Ca_3Mn_2[SiO_4]_3$-$x[O_4H_4]x$

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The importance of garnets within the Earth's mantle, the high symmetry of the garnet structure, and the manifold cation and anion substitution mechanisms make garnets an ideal model system to study pressure-induced spin-pairing transitions of 3d-transition-metal cations (Friedrich et al. 2014, 2015). Here we study the effect of water content and compare the pressure-induced spin-pairing transition of Mn^{3+} in tetragonal henritermierite $Ca_3Mn_2[SiO_4]_3$-$x[O_4H_4]x$ with that of the $Ca_3Mn_2[SiO_4]_3$ garnet with 0.2 wt % H_2O incorporated via the hydrogarnet substitution.

We used a natural henritermierite sample from the N'Chwaning II mine, Kalahari manganese ore fields, Republic of South Africa (thanks to T. Armbruster, Bern Switzerland and J. Gutzmer, Freiberg, Germany). $Ca_3Mn_2[SiO_4]3$ garnet has been synthesized at 6 GPa / 1100 °C in a multi-anvil press. We traced the spin transition with X-ray diffraction, Raman- and FTIR-spectroscopy by pressurizing the samples in diamond anvil cells at room temperature. The single-crystal X-ray diffraction data were collected at the PETRA III synchrotron facility (beamline P02.2, DESY, Hamburg, Germany, thanks to H.-P. Liermann). Compared to the water-rich henritermierite, which shows a pressure-induced spin transition in the pressure range of 55-70 GPa, $Ca_3Mn_2[SiO_4]_3$ garnet shows distinct discontinuities in the X-ray diffraction and Raman-spectroscopic data at about 50-65 GPa, which we relate to the spin-pairing transition of Mn^{3+}. Obviously the hydrogarnet substitution weakens the structure and higher pressure is needed for the spin transition compared to the nearly water-free garnet.

Friedrich, A. *et al*. (2014) Physical Review B, 90, 9.
Friedrich, A. *et al*. (2015) Physical Review B, 92, 014117.

Transmission of dislocations across olivine grain boundaries

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In the uppermost part of the upper mantle ($\leq$ 200 km of depth), olivine is believed to deform mainly by dislocation creep. In polycrystalline materials, plastic deformation progresses through the transfer of dislocations across individual grain boundaries (slip transmission). As grain boundaries may introduce obstacles for the motion of dislocations, increasing stress concentration due to dislocation pile-up in the vicinity of the grain boundaries lead to bulk mechanical hardening. Here we analyse slip transmission and the influence of the distribution of grain boundary planes in olivine (Fo50), torsion - deformed at constant stress in a Paterson triaxial apparatus. Crystal orientation and the distribution of olivine grain boundary planes were obtained from EBSD data.

Our results show that olivine deformation is mainly accommodated by dislocation creep associated with the B-type slip system. Slip transmission becomes easier as strain increases. At the highly strained region, {010} grain boundary planes are the most frequent. The {010} boundary planes are the ones where slip transfer is predicted to occur more easily. This shows that crystal alignment and slip transfer are intrinsically correlated. As deformation progresses, more grains are oriented in an easy to glide orientation, with the b planes parallel to the shear plane. This also means that slip systems of adjoining grains are closer to coincidence, characterizing a feedback process.

Carbon partitioning between metal and silicate melts – Implications for the origin and inventory of Earth's carbon

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During early accretion a lid-less magma ocean of 400-800 km depth is thought to have covered the Earth. During this stage, carbon was distributed among metal droplets in suspension, the silicate magma ocean and a hot, potentially dense atmosphere. Gravitational metal segregation then led to core formation. We performed high P-T-experiments (1.5 - 6.0 GPa, 1300 – 2000 °C) to investigate the effects of pressure, temperature, oxygen fugacity (f_{O2}) and silicate melt polymerisation (NBO/T) on the carbon partition coefficient ($D_{Cmetal/silicate}$).

Carbon concentrations of metallic and silicate melts were analyzed in-situ by secondary ionization mass spectrometry (SIMS). Raman spectra were collected from all silicate melts to identify the C-bearing species. While C in the metallic melt is roughly invariable throughout our range of conditions (5.6(7) wt.% C), that of the silicate melt strongly varies from 0.010(1) to 0.97(1) wt.%. Consequently, $D_{Cmetal/silicate}$ mainly depends on the C solubility in the silicate melt, which increases with increasing temperature, NBO/T, and f_{O2}. Experimentally determined $D_{Cmetal/silicate}$ values range from 0.035(4) to 640(49), but, because of the negative correlation of $D_{Cmetal/silicate}$ with temperature and NBO/T, relatively small partition coefficients result for realistic metal-silicate seperation conditions. Based on our experimental data we parameterized $D_{Cmetal/silicate}$ in terms of the above variables, yielding most likely values of 6-9 for conditions at the base of the magma ocean. To reproduce the modern bulk silicate Earth C content of 120-765 ppm, bulk Earth would result in 0.1-0.7 wt.% and the Earth's core to 0.4-3.0 wt.% C. Any late veneer delivery of carbon would result in lower core C contents. This study constrains C as minor in the core and provides new indications for the Earth's carbon inventory, suggesting that the primordial C reservoir in the Earth's mantle may have been set during core formation and differentiation.

X-ray absorption spectroscopy study of the chemistry of As and Au in arsenian pyrites

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In many deposits of hydrothermal origin arsenian pyrites host industrial concentrations of Au with direct correlation between Au and As contents. The aim of our study is to characterize the state of Au in arsenian pyrite by means of X-ray absorption spectroscopy. For this purpose, we synthesized Au-bearing pure and arsenian pyrites using hydrothermal technique at 300 °C/P_{sat} and 450 °C/1 kbar. This method yielded fine-grained pyrite powders with As concentration of 0-0.9 wt%, and "invisible" Au concentration ca 100 ppm independently of As content. In addition, one sample of natural pyrite (Samolazovskoe Au-porphyry deposit, Yakutia, Russia) was studied. The sample contained 300 ppm Au and 0.5 wt% As.

The Au L3-edge and As K-edge X-ray absorption spectra were recorded at BM16 FAME-UHD beamline of ESRF. The High Energy Resolution Fluorescence Detection mode was employed (HERFD-XAS) to record Au spectra. Simultaneously the Total Fluorescence Yield (TFY) As spectra were acquired. The As K-edge XANES spectra of high-temperature synthetic pyrites (450°C) and natural pyrite showed that As in the samples is in +3 oxidation state. Low-temperature (300°C) synthesis experiments produced pyrites that contained both As^{3+} and As^{5+}. The Au L3-edge HERFD XANES spectra of Au-bearing pyrites differ from the spectra of Au_2S and Au-bearing FeAsS, which suggests that Au is bound in the structures of pure and arsenian pyrites. Analysis of Au L3-edge EXAFS spectra showed that in synthetic pyrites Au is octahedrally coordinated with S atoms in As-free pyrite, and with 3S+3As atoms in arsenian pyrites. In the sample of natural arsenian pyrite Au is octahedrally coordinated with S atoms. Despite high As content, no As atoms has been detected in the first coordination sphere of Au in the sample of natural mineral. Results of the present study indicate that both As-bearing and As-free pyrites of hydrothermal origin can host important concentrations of structurally bound "invisible" Au.

Effect of starting material and temperature path on phase equilibria

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Crystallization experiments are a common method in experimental petrology to investigate liquid evolution and phase equilibria in different magmatic settings. This study investigates the effect of temperature path and method for the preparation of the starting material on experimental run products of mafic systems.

Experiments were conducted in an internally heated pressure vessel at temperatures between 1080°C and 1140°C, a pressure of 200 MPa and f_{O2} ~FMQ -2. Nominally dry starting materials were prepared 1) from oxide, carbonate and phosphate powders as fine-grained powder mixture and 2) as fused glass with identical composition (andesitic). The experimental run temperature (TF) was reached using two different temperature paths. The first path consisted in heating with a ramp of 50 K/min till a temperature 20°C below TF. TF was then reached with a ramp of 10 K/min to avoid overshooting. In a second approach, a two-step temperature path was applied where the sample was heated above the liquidus to 1200°C for two hours with a ramp of 50 K/min to melt the sample prior to crystallization. The temperature was then dropped down to TF. In both approaches TF was held for 48 h.

Run products of experiments conducted at similar P and TF conditions but different preparation methods for the starting material and/or temperature path show significant differences in mineral assemblage and phase composition. Experiments using oxide powders without overheating show Al-rich remnants of unreacted starting material, affecting the phase equilibrium. Runs with the two-step temperature path using oxide powder and those with a one-step path and pre-fused glass are in agreement with each other. While experiments using glass as starting material produce tiny crystals, which can cause analytical problems, a remarkable feature of the two-step experiments are the large, unzoned crystals (up to 0.5 mm) at similar crystallinity (~30%), enabling adequate mineral sizes for easy measurements.

Experimental halogen partitioning between mantle minerals and silicate melts: Implications for the melting of metasomatized mantle source

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Halogens are important volatile elements in the Earth's mantle [1]. However, their abundance and behavior in the different mantle reservoirs are only poorly understood. Moreover, little is known about the fractionation of these elements during mantle melting and crystallization processes. Recently, several papers were recently published focussing on halogen partitioning between major mantle minerals (olivine, pyroxene, garnet) and melts [2] but there is scant data on halogen partitioning between less abundant but nevertheless important mantle phases such as amphibole and mica [3].

In order to partially address this matter, we have conducted partitioning experiments in the systems Na_2O-K_2O-CaO-MgO-Al_2O_3-SiO_2 and Na_2O-FeO-CaO-K_2O-MgO-Al_2O_3-SiO_2-TiO_2. To all compositions we added all four halogens (F, Cl, Br, I). Experiments were run in a piston-cylinder apparatus at a pressure of 1.4 GPa and temperatures between 1015°C and 1300°C. We used four different bulk compositions in order to assess possible effects of bulk composition on the fractionation of halogens between the different phases. The experimental run products were analysed using electron microprobe techniques, using a custom made analytical protrocol following [4, 5]. Mineral/melt and mineral/mineral partition coefficients ($D_{min/melt}$) for halogens were calculated from the analytical results for amphibole, phlogopite, clinopyroxene. These values were then used in a simple melting model for phlogopite and amphibole-bearing mantle sources.

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Trace Element Partitioning in Fractionating Mid Ocean Ridge Basalts

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The chemical evolution of Mid Ocean Ridge Basalts (MORBs) is enigmatic. MORBs exhibit a wide range of major and trace element compositions due to source region heterogeneity, reactive flow in the mantle and crust, magma mixing and fractional crystallisation. The deconvolution of the chemical effects of these factors is difficult, owing to their variable and poorly understood nature. Most MOR experiments were conducted assuming equilibrium crystallisation, resulting in major and trace element trends apart from those in nature and uncertainties in geochemical modelling.

This study uses equilibrium and ca. 15-30°C steps fractional crystallisation experiments, to quantify phases abundance, major elements compositions and partition coefficients throughout crystallisation. The first synthetic glass has a primitive tholeiitic composition and is doped with an initial concentration of 20-60 ppm of 24 trace elements. At 1atm, QFM-1, the liquidus temperature is 1205°C.

Glass and solid phases are analysed by SEM, EPMA and LA-ICP-MS. Minerals saturation temperature and volume fraction of the first experimental run at 1190°C (77.0 wt% glass, 4.6 wt% Ol and 18.3 wt% Plg) are consistent with the results shown by MELTS. The measured composition of residual glass from the previous experiment is used for the next step at sub-liquidus temperature. We are currently running next experiments.

Tholeiitic immiscibility phenomena as a rock-forming mechanism is an issue of contention. If the liquid line of descent under fractional crystallisation is sufficiently divergent from that of equilibrium crystallisation, then it could mean that tholeiitic liquids enter the immiscibility zone more readily than the current petrological database infers. This study will attempt to induce immiscibility in a tholeiitic magma, to assess the role of immiscibility in the formation of silicic material in dominantly silica poor mafic systems.

Experimental evidence supporting global melt layer at the base of the Earth's upper mantle

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The globally observed low velocity layer (LVL) at mantle depths of 350-410 km has long been attributed to occurrences of partial melting. The hydrous wadsleyite-to-olivine phase transformation in the upwelling mantle across the 410-km discontinuity was proposed as the main process. This reaction induces subsequent release of free fluids due to the O-H solubility drop during the major mineral component transition. The generated melt is required to be neutrally buoyant to remain trapped above the mantle transition zone in order to explain the observed geophysical anomalies.

In this study, we experimentally reproduced the phase transformation and dehydration melting process in the upwelling mantle at relevant mantle conditions (12 GPa and up to 1400°C) and investigated the sound wave velocity during partial melting of hydrous peridotite. The measured seismic velocities reductions indicates that the globally observed Vs negative anomaly (-4%) can be explained with less than 1% of melt fraction (0.7%) in the host peridotite. The produced melt is volatile and incompatible elements rich (up to 16.5% H_2O and 33% FeO) and its estimated density (3.56-3.74 $g.cm^{-3}$) is compatible with gravitationally stable requirements. The corresponding water content in the mantle transition zone (MTZ) can be retrieved to 0.22%, which is significantly lower than literature water statured conditions.

This experimental confirmation of the presence of a melt layer at the base of the upper mantle is of significant interest for Earth volatiles and incompatibles elements budget, as this layer should be a significant mantle reservoir. It would also play an important role on mantle differentiation and material circulation. Finally, local water rich or hotter conditions in the MTZ could induce more buoyant melt able to ascent the upper mantle and represents a possible source for hotspot volcanism.

Melt-dunite interactions at 0.5 and 0.7 GPa: experimental constraints on the origin of olivine-rich troctolites

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Studies on oceanic lithosphere suggested that melt-rock reactions play a key role in the origin of olivine-rich troctolites. In order to provide experimental constraints, we performed reactive dissolution and crystallization experiments by reacting variably evolved MORBs with pre-impregnated San Carlos olivine at 1300°C and then cooling to 1150°C at constant pressure (0.5 and 0.7 GPa). Additionally, an isothermal experiment (0.7 GPa, 1250°C) provides a snapshot of olivine-melt reaction after the high-temperature step. Although high-porosity trap has been used, only limited reactive melt percolation occurred. Runs result in glass-bearing gabbro overlain by olivine-rich troctolite/dunite showing disequilibrium textures comparable with natural occurrences typically related to melt-rock reaction, e.g. embayed and resorbed subhedral olivine with lobate contacts against plagioclase and clinopyroxene, often occurring as large poikiloblasts including rounded olivines. Textural and chemical observations on olivine-rich layer suggest that interactions occurred at rather low melt/olivine ratio. We found that higher pressure further limits the extent of olivine dissolution and results in a lower high-T porosity, decreasing the final abundance of interstitial phases. Olivine dissolution and re-precipitation combined with element diffusion reset the composition of starting olivine, by lowering its X_{Mg} and NiO content as a function of melt-olivine ratio. Regardless the basalt composition, olivine X_{Mg} approaches 0.88. Melt composition affects the chemistry of interstitial minerals, that show, mostly at high pressure large compositional variability (anorthite in plagioclase, TiO_2 in clinopyroxene) as a result of local equilibrium driven by trapped melt effect. Remarkably, mineral co-variation trends (e.g. plagioclase anorthite vs. olivine X_{Mg}) match those of some natural olivine-rich troctolites settings, supporting the lead role of melt-rock reactions in their origin.

Iron isotopic fractionation in olivine-hosted melt inclusions as an indicator of mantle oxygen fugacity

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Many studies have demonstrated that arc basalts are more oxidized (FMQ -0.5 to FMQ +4) than MORB (FMQ -1.2 to ~FMQ; Carmichael, 1991; Pichavant and McDonald, 2007; Kelley and Cottrell, 2009; Kelley and Cottrell, 2012; Christie et al., 1986; Bezos and Humler, 2005; Cottrell and Kelley, 2011). However, the oxidation state of the sub arc mantle is still debated. On one hand Kelley and Cottrell (2009, 2012) suggest that the variations in the Fe^{3+}/Fe_{Tot} ratio between basaltic glasses and olivine-hosted melt inclusions from mid-ocean ridges and arcs could be explained by the sub arc mantle being more oxidized than the mantle beneath ridges. On the other hand, Mallmann and O'Neill (2009) and Lee and al. (2005, 2010) proposed the use of other f_{O2} proxies, namely V/Sc and Zn/Fe^{2+} ratios, and suggested that the oxidation state of the mantle source region of MORB cannot be distinguished from that of arc magmas. Dauphas et al., (2014) have demonstrated that the iron isotopic fractionation ($^{56}Fe/^{54}Fe$) in basaltic and rhyolitic synthetic glasses is dependent on oxygen fugacity; therefore, they proposed that this iron isotopic fractionation of glasses can be used as a proxy for the oxidation state of silicate melts. In the present study and for the first time, iron isotopic $^{56}Fe/^{54}Fe$ ratios were measured by Secondary Ion Mass Spectrometry (SIMS) in olivine-hosted melt inclusions from 6 different arcs, and OIB and MORB localities. The results obtained with this technique, along with Fe^{3+}/Fe_{Tot} ratios obtained by Raman spectroscopy and XANES on the same set of melt inclusions, will be used to constrain the oxidation state of primary magmas formed in these different geological settings. A careful evaluation of the differentiation and degassing processes and their effects on the various f_{O2} proxies will be carried out using major and volatile element compositions in order to better constrain the link between the redox state of iron in melts and that of their mantle-source regions.

The electrical conductivity of the Earth's interior deciphered by laboratory measurements on volatile-bearing melts

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Electrical conductivity is a geophysical property of the Earth's interior that is sensitive to the presence of hydrated minerals, fluids, and melts. In silicate melts, the addition of water and CO_2 enhances the electrical conductivity. The reason for this effect remains elusive, but it makes the electrical conductivity of the Earth's interior a particularly relevant probe of the deep volatile cycling.

Here, we summarize our recent work and present new data of the conductivity of hydrated silicate melts ranging from silicic to basaltic compositions. We conclude that water has a broadly similar effect for all melt compositions, that is, a linear relationship between log-conductivity and water content. In details, the effect of water is stronger for polymerized than depolymerized melts. The effect of CO_2 is markedly different since it induces a strongly non-linear effect as the melts evolves from silicate to carbonate melts. Changes in the melt structures due to CO_2 dissolution and a shift from polymerized-covalent to ionic-depolymerized melts can explain these effects.

Zones of crustal high-electrical conductivities observed in convergent settings such as subduction zones (Andes) or collision belts (Tibet) are interpreted in terms of melt storage zones. These melts must be particularly water-rich to explain the regional electrical anomalies.

In intraplate and divergent settings, CO_2-rich melts are certainly the triggers for the high conductivity that is broadly observed in the asthenosphere and in rejuvenated cratonic lithosphere. The required melt fractions and CO_2 content complies with the independent geochemical estimates.

Dry and CO_2-free melts must be electrically invisible in the Earth's interior, implying that electrical conductivity is a unique tool to track the relationships between magma and deep volatiles.

Using tracer diffusion experiments to highlight rock-mineral interactions and rock permeabilities at high pressure

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Fluid-rock interactions are central to numerous processes on Earth and in the solar system. They may have a major role on Earth plate tectonics and on its initiation. For instance, subduction zones are known as sites of intense fluid circulations. If fluid circulation in subduction zones is known from a variety of observations (high electrical conductivity zones, non-volcanic tremors and slow slip events, hydrothermal vents and mud volcanoes), mechanisms of fluid-rock interactions are still poorly constrain. For example, permeabilities of rocks under subduction high-pressure are unknown, fluid pathways, i.e. channelized or not, are still debated. One difficulty with fluid-rock interaction study is to identify them in rocks where fluid is not present anymore. One way to encompass this difficulty is to use hydrogen-isotope variations in rocks and minerals, as they provide a powerful method of documenting fluid-rock interactions in the Earth's crust, and also in experimental systems at the P-T conditions of subduction (1-3 GPa, 300-700°C).

In order to investigate in details fluid-rock interactions in subduction zone conditions, i.e. at high pressure, we reacted different high-pressure hydrous minerals with liquid D2O in a Belt apparatus in the range 1.5 to 3 GPa and from 315 to 650°C. Experimental samples were characterized both by Raman micro-spectrometry and SEM imaging in order to reveal fluid-rock interactions and fluid pathways, active at high-pressure. By combining both analytical techniques, we can build on rock porosity and permeability. Our experiments show that the tested hydrous minerals have different reactivity, porosity and permeabilities. We discuss potential implications of our experimental observations to subduction zones with an emphasis on fluid flows and fluid-rock interactions.

Combined bulk and nano-scale investigations of low melt fractions in upper mantle rocks

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While mid-ocean and intraplate volcanisms attest for the presence of melt in the upper mantle, the role and implications of partial melting is actively debated. Former experiments and calculations indicate that low fraction of either silicate or carbonate interconnected melt can account for observed electrical and seismic anomalies in the upper mantle. However, the nature, amount and distribution of low melt fractions actually produced in the upper mantle remains undetermined, as those were not investigated on undoped, naturally fertile peridotite.

We report here experiments on a natural, C- and H-bearing peridotite from Lanzarote at upper mantle conditions. In situ electrical conductivity measurement and post mortem nano-scale microcopy investigations reveal that partial melting of fertile upper mantle rocks produces very low fraction of carbonated melt (< 1 %) to low fraction of silicate melt below and above silicate solidus, respectively. Moreover, those low melt fractions are interconnected, resulting in bulk rock conductivity enhancement.

Heat transport by radiation in San Carlos olivine from high temperature infrared emittance spectroscopy

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Knowledge of thermal transport properties of mantle materials is a prerequisite to understand the thermal structure and the dynamics of the Earth's mantle. Among the processes affecting these properties at high temperature and pressure, the role of heat transfer by radiation remains controversial and poorly documented, even if it may significantly enhance the global heat transport due to its large temperature dependence. In this work, we present a new approach allowing for evaluation of optical properties of minerals at high temperature. Polarized emittance spectra were acquired on natural San Carlos olivine single crystals (Fo87) over a large spectral range (100 cm^{-1} to 7000 cm^{-1}) from room temperature to 1200K and along the three principal directions, B1u, B2u and B3u. The spectra have been fitted by a model of dielectric function that allows for determination of the absorption coefficient. At room conditions, the shape of the absorption spectra is consistent with previous investigations (e.g. Ulrich et al., PCM, 2002), in particular regarding the spectral signature of iron d-d transitions. At high temperature, a low absorption region is located between 2000 and 5000 cm^{-1}. The combined effects of broadening of multiphonons bands located at frequencies lower than 2000 cm^{-1} and d-d transition bands lead to a progressive closure of this transmission region, in agreement with previous observations (e.g. Shankland et al., JGR, 1979). The resulting contribution of radiative transport to the thermal conductivity from absorption coefficient indicates that this contribution varies between 1.05 and 1.34 $W.m^{-1}.K^{-1}$ at 1200 K, depending on polarization, which is lower than previous determinations on similar starting materials (about 1.7 $W.m^{-1}.K^{-1}$ in Shankland et al., 1979). Infrared emittance spectroscopy appears to be a powerful method for quantifying heat transfer by radiation in minerals in mantle conditions, as its capabilities can be extended to very high temperatures.

Effect of temperature and pore fluid on the electrical conductivity of basaltic rocks up to supercritical conditions

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Exploration and exploitation of deep high-temperature geothermal resources in volcanic environments require a good knowledge of the physical properties of rock reservoirs. Exploration of supercritical reservoirs (T> 375°C and Pore fluid pressure> 225 bars for pure water), whose exploitation is a long-term objective for improving power generation, suffers from the lack of laboratory data under such conditions. In particular, determination of the physical processes affecting electrical transport is a pre-requisite to interpret electromagnetic surveys that are widely used in geothermal industry.

In this work we present several results from high temperature-high pressure experiments performed in a Paterson gas pressure apparatus up to 700°C and 100 MPa and under a controlled pore pressure of 30 MPa. Rock samples coming from deep geothermal reservoirs located in Iceland have been investigated.

The electrical conductivities have been measured first under dry conditions and under saturated conditions using different fluid salinities up to seawater salinity. The conductivity of saturated rocks is dependent on the rock type (dolerites/hyaloclastites) and mineral alteration is a key parameter controlling the absolute values and the temperature dependence of electrical conductivity. In addition, it is found that the conductivity of the bulk rock is not only controlled by the conductivity of the brine, but also by the interface conductivity, which strongly increases with temperature and becomes dominant above 300°C, even for high salinity pore fluids. Above supercritical point, electrical conductivity slightly decreases and lies on the electrical conductivity of « dry » rock at temperature of about 500 to 600°C, depending on the rock type and fluid salinity. Measured electrical properties are found to be in agreement with electromagnetic surveys and downhole measurements in different Icelandic geothermal areas.

The phase composition and critical relation in the eclogite-$CaCO_3$+Na_2CO_3+K_2CO_3+H_2O system at P=4 GPa, T=1100-1300°C (experimental data)

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The phase and critical relationships was studied experimentally in the eclogite–$CaCO_3$–Na_2CO_3–K_2CO_3+H_2O system at P=4 GPa, T=1100-1300°C.

The experiments were carried out at the IEM RAS using a "anvil with hole" apparatus by quenching technique in Pt ampoules. The initial composition of the system is 70 wt.% of tholeiitic basalt, 30 wt.% of carbonates of Ca, Na and K. The source of the fluid was distilled water (~10 wt.%). The temperature was measured with a $Pt_{30}Rh/Pt_6Rh$ thermocouple, the pressure was calibrated against the quartz-coesite equilibrium curve. The accuracy of determining the temperature and pressure in the experiments is estimated at ±5°C and ±1 kbar. The duration of the experiment was from 12 to 24 hours. The polished preparations of quenching samples were analyzed on an electronic scanning microscope at the IEM RAS.

At P = 4 GPa, the solidus temperature is 1150 ± 50°C, liquidus temperature is 1275 ± 25°C. The subsolidus association is represented by Grt, Cpx, Cb. At partial melting a high-K alkaline silicate melt (L_{Sil}) forms at T=1100°C and coexisting with Cpx, Grt, Cb. With increase T up to 1200°C a carbonate melt (L_{Cb}) appears, the main mineral of the liquidus is Cpx. The immiscible L_{Sil} and L_{Cb} are stable in the range of T=1100-1250°C. In the interval T from 1250 up to 1300°C there is a "critical" point of the temperature (T_K) equilibrium of alkaline silicate and carbonate melts, at the attainment of which complete mixing is observed between L_{Sil} and L_{Cb}. At T > T_K, there is only one carbonatized silicate melt. In the results of quenching, a heterophase mixture of carbonate and silicate phases is formed, the compositions of which form a linear trend, the extreme members of which are silicate and carbonate components.

Nanoscale evidence of partial resetting of the U-Th-Pb systems in monazite due to anisotropic and incomplete replacement

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Alteration experiments on natural monazite crystals under alkali conditions at 300 to 600 °C and 200 MPa were conducted to clarify mechanisms behind incomplete resetting of U-Th-Pb geochronological systems in monazite replaced by dissolution and precipitation processes. Monazite experimental products show a replacement rim (altered domain), in which in-situ isotopic and chemical U-Th-Pb dating yields intermediate ages between the monazite standard (555 Ma) and complete experimental resetting (0 Ma). Nanoscale observations reveal that partial resetting is best explained by a nanomixture of primary (Mnz1) and secondary monazite (Mnz2) due to anisotropic replacement. At 400 °C (and 500 °C), altered domain corresponds to Mnz2 nanochannels and pore/inclusion of Si-rich amorphous material propagating through Mnz1. The anisotropic propagation of the reaction front is caused by preferentially oriented dissolution and/or fracturing at the reaction interface. At 600 °C, the Mnz2 component becomes more important in the altered domain, due to progressive textural and chemical equilibration. This leads to an apparently homogeneous rim of altered material with no pore/inclusion at the microscopic scale. However, the reaction front remains anisotropic, with a propagation of Mnz2 through Mnz1 associated with dislocations. As a result, Mnz1 relics can be found in altered domain apparently homogeneous at the microscopic scale. Another important feature is that secondary inclusions occur in the core rather than in the rim.

Because no structural Pb or Pb nanoinclusions were observed, Pb in the altered rim is attributed to the Mnz1 component. Although microanalytical techniques have the spatial resolution to date micrometer-sized rims, they are unable to resolve a nanoscale mixture of pristine and secondary monazite that could occur in altered rims formed by fluid-driven replacement, especially at low temperatures.

Experimental determination of stable Ru and S isotope fractionation between liquid metal and liquid silicate

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The abundances of highly siderophile elements (HSE, e.g. Ru) and siderophile volatile elements (SVE, e.g. S, Te) in Earth's mantle are assumed to predominantly derive from late accretion of broadly chondritic material. Yet, the behavior of some elements leaves questions open about the late veneer and Earth's core formation.

Remaining in the mantle after core formation the highly siderophile element Ru should show strong mass-dependent isotope fractionation and a different isotopic signature compared to chondrites. In case this element largely derives from the late veneer, it should show no isotope fractionation attributable to core formation. [1-3].

S isotopes from MORB show an excess of light S isotopes in the Earth's mantle relative to chondrites, which might be balanced by light S-isotopes core. This implies that accretion of the volatile element S would have occurred rather during core formation than during the late veneer [4]. However, Earth's mantle rocks show the same S/Te as carbonaceous chondrites, but S and Te have very different metal-silicate partition coefficients [4,5]. A simple possibility is, therefore, that S and Pd isotopes reflect both processes: core formation and late accretion [6].

To test these assumptions, we performed metal-silicate partitioning experiments in a piston cylinder press (1 GPa) with large volume MgO single crystal capsules at temperatures between 1200 °C and 1450 °C. With these experiments we can determine the partitioning of the elements S and Ru, as well as potential stable isotop at different temperatures and pressures. We will present recent results and implications of our piston cylinder runs.

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Metal-silicate differentiation in early accreted small bodies: constraints from tungsten (W) isotope fractionation experiments

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Planetesimals are small objects (10 to 1000 km in diameter) that accreted early in the solar system history and show a wide variety of thermal histories from simple metamorphism to complete metal-silicate differentiation. Stable isotope fractionation of siderophile elements such as W has the potential to trace processes, including metal segregation, and to constrain the physico-chemical conditions that prevailed at that time.

We performed two sets of isotope fractionation experiments of W between metal and silicate in a gas-mixing ($CO-CO_2$) vertical furnace, at different temperatures (1300°C to 1600°C), oxygen fugacity (IW to IW-6) and times (0.5 to 48 hours). In the first set, the starting silicate was a synthetic anorthite-diopside eutectic composition glass, and the starting metal a pure W wire. In the second set, the glass was doped in W and the starting metal was a W-free metallic wire (Ni or Fe).

After each experiment, metal and silicate were mechanically separated and digested in acids. Tungsten separation has been achieved using the procedure described in [1] and isotope measurements have been performed using a high resolution MC-ICPMS.

Preliminary results show evidence for strong kinetic isotope fractionation at short annealing times, with faster diffusion of light isotopes, whatever the experimental set-up. A similar mechanism has already been seen for iron and nickel isotope fractionation between silicate and metal [2, 3]. Chemical and isotopic equilibrium are not reached after 24 hours and further investigations are still in progress. These experimental data will shed light on the W stable isotope compositions of (partially) differentiated meteorites and help quantify the degree of metal-silicate equilibrium.

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The non-trivial U-Pb and Lu-Hf isotope systematics of ancient zircons from the Napier Complex (Antarctica)

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The Napier complex is an Archean crustal block located in East Antarctica that contains some of Earth's oldest rocks. This complex recorded Meso- and Neoarchean metamorphic episodes that reached among the most extreme conditions ever documented (1050-1120°C and 7-11 kbar). Consequently, Napier gneisses had their radiogenic isotope systematics such as Rb-Sr and Sm-Nd severely disturbed at the scale of whole-rocks. Metamorphic episodes were, nevertheless, recorded within zircon grains while sometimes also preserving information about original crystallization. Yet, these crystals show a complexity greater than commonly seen in ancient zircons.

The present study examined U-Pb age profiles by LA-ICP-MS and associated Lu-Hf isotope systematics by LA-MC-ICP-MS of zircon crystals from two orthogneisses of the Napier complex. The analyzed samples were originally thought to be older than 3.9 Ga. However, our study highlights the great zircon age complexity and allows the age of the orthogneisses to be reassessed at 3769 ± 35 and 3861 ± 38 Ma. These ages comfort previous interpretations stating that the oldest zircon ages are artifacts of ancient Pb mobility. Alike U-Pb ages, the Lu-Hf isotope systematics of Napier zircons are quite complex as previously noted. In one sample, a dichotomy of Lu-Hf isotope signatures clearly stands out and interpreted in conjunction with crystal textures and age patterns reveals that some crystals contain a pristine magmatic core surrounded by domains either recrystallized in closed system or neoformed from exogenous material (crustal melt). The second sample does not display a dichotomy despite ranges in Hf isotope signatures, U-Pb ages, and crystal textures that are similar to those in the first sample. Finally, the Hf isotope signatures of Napier zircons reveal that both orthogneisses formed by reworking of pre-existing enriched crust(s), perhaps Earth's primordial crust.

Experimental calibrations on Cu isotope fractionation between magmatic-hydrothermal fluid and silicate magma

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Hydrothermal-fluid is essential for magma evolution and transporting volatiles and metals in the crust and mantle. To explore the potential of Cu isotopes as a tracer of hydrothermal-fluid activity, copper isotope fractionation between Cl-bearing aqueous fluids and silicate magmas (andesite, dacite, rhyolite dacite, rhyolite, and haplogranite) were experimentally calibrated. Fluids containing 1.75 to 14 wt% Cl were mixed together with rock powders in $Au_{95}Cu_5$ alloy capsules, which were equilibrated in cold-seal pressure vessels for 7 to 13 days at 800 to 850 °C and 2 kbar. The elemental and Cu isotopic compositions of the recovered fluid and solid phases were analyzed by (LA-) ICP-MS and MC-ICP-MS, respectively. Our experimental results show that the fluid phases are consistently enriched in heavy Cu isotope (65Cu) relative to coexisting silicates, with isotope fractionation factor ($\Delta^{65}Cu_{FLUID-MELT}$) ranging from 0.09‰ to 0.69‰.

Within the experimental conditions in this study, the magnitude of Cu isotopic fractionation between fluids and silicates primarily depends on the Cu speciation in the fluids and silicate melts. At fixed Cl concentration (3.5 wt%) and temperature (850°C), $\Delta^{65}Cu_{FLUID-MELT}$ is correlated with fluid constituents caused by varying composition of starting rocks, indicating the influence of fluid components on Cu speciation in aqueous fluids. Our results indicate that the exsolved fluids have higher $\delta^{65}Cu$ than the residue magmas, which can be used as a monitor for volatile fluxing. Our data also have implications in explaining the Cu isotope anomaly of the rocks that have reacted with hydrothermal fluids. Together with previous studies on Cu isotope in the brine and vapor phases of porphyry deposits, the results in this study may be utilized for better understanding copper mineralization.

Chalcophile element partitioning between sulfide- and silicate melts

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The question when and how volatile elements were delivered to Earth is subject to intense debate [1-7]. Understanding the partitioning behavior of volatile elements that are also siderophile and/or chalcophile (S, Se, Te, Tl, Ag, Au, Cd, Bi, Pb, Sn, Cu, Ge, and In) may provide key information in this regard. This project aims to unravel whether the depletion of the siderophile volatile elements (SVE) in Earth's mantle is a core formation signature [7-10], a volatilization signature or related to a late accretion after core-mantle differentiation had largely ceased [2-3].

A special interest is laid into chalcophile element (Cu, Pb, Bi, Se, Te, S, and Ni) behavior with respect to the possible formation and late segregation of a "Hadean Matte" [9].

To examine the influence of sulfur on SVE partitioning between metal- and silicate melts, we performed experiments from sulfur free to sulfur rich melts (~ 20 wt% S). Partitioning experiments were carried out under various P-T-f_{O2} conditions with a 600 t walker-type multi-anvil press (7-18 GPa, 1700 - 2300 °C). The run products were analyzed via EMPA and Excimer laser ablation system coupled to an ICP-MS. Our preliminary partition coefficients indicate that chalcophile element concentrations in the Earth's mantle may neither be explained by core-mantle differentiation nor by late sulfur-melt segregation as "Hadean Matte".

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Temporal Evolution of Proto-Izu-Bonin-Mariana Arc Volcanism: Constraints from Statistical Analysis of Melt Inclusion Composition

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International Ocean Discovery Program (IODP) Expedition 351 "Izu-Bonin-Mariana (IBM) Arc Origins" drilled Site U1438 into volcaniclastic sediments deposited immediately after subduction initiation and inception of arc volcanism in Amami Sankaku Basin (ASB), the north-western margin of the Philippine Sea plate 52 million years ago. From the drill cores, we have recovered melt inclusions hosted in fresh silicate minerals (augite and plagioclase) and analysed their major, trace and volatile element compositions. This provides us with a record of the magmatic evolution of the proto-IBM arc between 30 and 40 Ma or the period when the arc magmatism must have matured (Brandl et al., 2017, EPSL). These melt inclusions are diverse in composition, ranging from low- to high-K series basaltic through rhyolites. The melt inclusions were recovered from volcaniclastic sediments possibly representing materials derived from different volcanic centres. To better integrate the geochemical composition of melt inclusions with the magmatic evolution of the proto-IBM arc, we performed a statistical analysis on the geochemical composition of 236 individual melt inclusions reported by Brandl et al. (2017). These melt inclusions can be grouped into seven distinct clusters that originate from (1) the transition of volcanism from high-Mg andesitic to island arc tholeiitic volcanism (frontal-arc and rear-arc volcanism) at an age interval of 35 to 38 Ma, (2) a higher S concentration in the melts due to higher f_{O2}, (3) brine assimilation of the melt, and (4) silicic volcanism. Such processes are likely to happen in other proto-arcs. An identification of subgroups of melt inclusions cannot be made by conventional graphical approach using two-dimensional diagrams, demonstrating the usefulness of introducing statistical approaches into geochemistry.

Carbonatite breakdown and acoustic emissions

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Carbonatites are magmatic rocks consisting mainly of molten carbonate. Carbonatites that form at equilibrium with the mantle have a dolomitic composition, i.e. they contain both calcium and magnesium carbonate components. Dolomitic melts are stable only above ca. 2.5 GPa (corresponding to approximately 80 km depth). At lower pressure, the carbonate components break down and CO_2 is liberated. This reaction occurs at the crossing of the so-called 'carbonate ledge'.

In order to get further insight into the processes associated with carbonate breakdown, we have monitored acoustic emission during controlled decompression at magmatic condition. The experiments were performed in a multianvil apparatus, using the 250 ton press installed on 13-BM-D beamline of GSECARS facility at the Advances Photon Source [1]. We used a setup that was designed for use at mantle conditions [2]. Pressure evolution was monitored by in-situ x-ray diffraction at high pressure and high temperature. Transducers were positioned at the back of the six anvils, in order to permit acoustic emission location and check that the source was located inside the sample. In addition, this setup allows to studying focal mechanisms. Combination with x-ray diffraction is necessary to verify that the emissions are caused by transformations occurring in the sample.

For this preliminary study, we studied decarbonation reactions both from a solid and from a melt, to compare the acoustic signals. In our first experiments in the CaO-MgO-SiO_2-CO_2 simplified system, we recorded acoustic emissions at the expected conditions during melt decompression (3 GPa - 1300 °C). Further measurements will allow for better constraining the mechanism of CO_2 production.

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Water transport in subduction zone peridotites beyond the stability of chlorite

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Hydrated ultramafic rocks play a key role in the transport of water from the surface to the mantle along subduction zones. With progressive subduction the main fluid-producing reaction is related to the well-constrained breakdown of antigorite at 600-650°C producing secondary harzburgites consisting of olivine, orthopyroxene and chlorite. The second important dehydration reaction involves chlorite, which has been much less investigated. In order to constrain this deep water cycle, two main questions arise: i) Does chlorite react to another hydrous phase along any feasible slab geotherm? ii) How much water can be retained in nominally anhydrous minerals such as olivine beyond the stability of any hydrous phase?

We have conducted piston cylinder experiments in the range of 1-6 GPa and 600-950°C to address these two questions. The maximum stability of chlorite has been investigated using a natural chlorite with Mg# of 94 and 1.38 wt% Cr_2O_3. The maximum thermal stability is reached at 2 GPa, 850°C and then there is a moderate backbend of chlorite stability to 5.6 GPa, 740°C. Above 5.6 GPa, chlorite reacts to the hydrous 11.5 Å phase and above 6 GPa, 700°C, Mg-Sursassite was found. The transition of chlorite to other hydrous phases found in this study occurs at higher temperature and lower pressure conditions than previously reported. Such conditions are potentially encountered in cold subduction zones providing an extremely efficient mechanism to transport significant amounts of water to the deeper mantle along subduction zones.

In order to constrain the amount of water that is retained in olivine beyond the stability of any hydrous phase, we performed serpentinite dehydration experiments with olivine sensor layers. The olivines recrystallised during the experiments and the water contents as well as the water substitution mechanisms have been investigated by FTIR spectroscopy. The amount of water retained in olivine after chlorite breakdown is about 50 ppm H_2O.

Zircon U/Pb dating and tectonic implication of the Erlangping back-arc unit in the Qinling orogen, central China

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The formation of the collisional orogen is generally a complex process involving multistage subduction and collision tectonism associated with numerous magma events. One of the most important orogenic belts in East Asia, the Qinling-Tongbai-Dabie-Sulu orogenic belt in central China, is an ideal place to study the formation of ancient continental margins and orogenic processes. A metavolcanic and metasedimentary complex among the belt named the Erlangping unit was suggested to record an integrated arc-backarc volcanic sequence generated by the Qinling orogenic event in Paleozoic. Therefore, the Erlangping unit is capable of unveiling the ocean-continent subduction evolution of the Paleozoic accretionary and collisional orogeny processes.

Two felsic volcanic tuffs intercalated within the back-arc basin basalts in the Erlangping unit were collected for zircon U-Pb geochronology study. Magmatic zircon grains from the two tuff samples yield average $^{206}Pb/^{238}U$ ages of 435.8 ± 4.2 Ma and 435.7 ± 3.8 Ma, respectively, suggesting that the Erlangping back-arc basin has opened during the early Silurian. Considering the arc magmatic activities associated with the subduction of the Prototethyan Ocean occurred at ca. 470-440 Ma in the Erlangping unit, we suggest that the back-arc extension was triggered by the rollback of the subducting slab. The subsequent arc magmatism located closer to the continental margin at ca. 440-400 Ma posterior to the opening of the Erlangping backarc extension, indicating a trench ward migration of the suduction front. Combining with the comprehensive study of subduction related magmatism and UHP metamorphism, our data provide crucial constraints on reconstructing the complex orogeny processes of the Qinling orogen.

The speciation of Fe and Al in bridgmanite as a function of composition and oxygen fugacity

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$(Mg,Fe)(Si,Al)O_3$ bridgmanite (brg), the dominant phase of the lower mantle, is a relatively complex solid solution due to variable valence state of Fe in the structure and the fact that Fe^{3+} and Al^{3+} can be incorporated following both a couple substitution and an oxygen vacancy mechanism. Understanding the Fe^{3+} concentration and its distribution as a function of composition and oxygen fugacity (f_{O2}) is important for (1) determining the redox state of the lower mantle, which in turn influences C-O-H fluid speciation and may have influenced the redox state of the mantle during core formation; and (2) deriving compositional models for the lower mantle that are required to derive and compare seismic velocity-depth profiles for specific lower mantle compositions. In this study, we are investigating the relationship between the $Fe^{3+}/\Sigma Fe$ content in bridgmanite and oxygen fugacity in addition to characterizing the partitioning of Fe^{3+} between the A and B sites of the brg structure as a function of bulk Fe and Al content.

Samples of $(Mg,Fe)(Si,Al)O_3$ brg were synthesized in multi-anvil runs at 25 GPa between 1973~2273 K. Different f_{O2} conditions were obtained by adding to the starting materials either Fe powder or hematite with different amount of water together with redox sensitive alloys, which allowed the f_{O2} to be calculated. In the run products Fe or Fe_4O_5 were found to coexist with brg and a wide range of f_{O2} values between IW-1 to IW+5 were achieved. The brg samples were characterized by microprobe analysis and Mossbauer or electron energy loss spectroscopy. The $Fe3+/\Sigma Fe$ ratio increases with f_{O2} and Al content. At low Al content, Fe^{3+} partitions into both A and B sites while at higher Al concentrations, Fe^{3+} prefers the A site. Both coupled and oxygen vacancy substitution mechanisms occur in the samples and by comparing the partial molar volume differences of different end members we could predict the changes in substitution mechanism expected under higher pressures.

Fe-Ni ideality during Earth's Core Formation

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The Earth's core is mainly composed of Fe-Ni alloy with a Fe/Ni ratio of ~16 (Allègre et al., 1995; Mcdonough & Sun, 1995). Since the geophysical effect of nickel content is negligible with respect to density, compressibility and sound velocities under core conditions (e.g. Kantor et al., 2007; Lin et al., 2003; Martorell et al., 2013), it is a common practice to ignore Ni when simulating or experimenting on core properties; similarly, due to the chemical similarities between iron and nickel, Fe-Ni ideality is also a prerequisite for metal-silicate partitioning experiments. However, this ideality has never been tested. A recent metal-silicate equilibration study (Elardo & Shahar, 2017) found that light Fe isotopes preferentially fractionate into the mantle in the presence of nickel during planetary core formation, but the effect for a large (hot) planet such as the Earth would not be measurable. This makes it reasonable to consider that nickel can affect the partition behavior of siderophile elements during core formation. In this study, we performed the laser-heated diamond anvil cell (LHDAC) experiments up to 93 GPa and 4500 K, to investigate the effect of Ni content (0% to 49 wt.%) in the liquid metal on the partitioning of different elements between molten silicate and liquid metal. We found that there is no measurable effect of nickel concentration on the partitioning of Cr, V, O, or Si; the Fe-Ni alloy is chemically ideal over the investigated range of Ni concentrations.

Rare Earth Elements behavior under reducing conditions, implications in the sulfide/liquid and enstatite/liquid partitioning within Enstatite Chondrites

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Oldhamite (CaS) is a key mineral for the rare earth element (REE) budget of the enstatite chondrites (EC). REE are important for tracing and dating cosmochemical processes, and a precise knowledge of their behavior in the EC formation conditions is essential. Mixtures of a natural EC (Hvittis, EL6) doped in REE and calcium or iron sulfides were placed in graphite crucibles and run in evacuated pure silica tubes at 1300C or 1400°C, and at oxygen fugacities between IW-4 and IW-6 (IW refers to the Fe-FeO equilibrium). Sulfides and quenched silicate melts have been analyzed by electron microprobe for major elements and with Laser Ablation ICPMS for trace elements. In all sulfide/melt systems we note positive anomalies for Eu and Yb partition coefficients. Our results are in agreement with literature data [Lodders et al., 1996; Dickinson et al., 1997] but provide a more complete dataset. Here positive anomalies appear to be caused by the reduction of Eu and Yb to Eu^{2+} and Yb^{2+}. X-ray Absorption Near Edge Spectroscopy (XANES) analysis confirms the presence of Yb^{2+} in the system.). XANES on Sm also shows evidence of some Sm^{2+} in the system. An in-depth study of the sulfide/melt and enstatite/melt partitioning of the anomalous elements within these experiments evidences a direct relation between the intensity of the anomaly and the oxygen fugacity of the experiment. The obtained partition coefficients cannot explain the observed high (100 to 1000 x CI) REE abundances in oldhamite in EC [Floss et al., 2003; Gannoun et al., 2011]. The negative Eu anomalies in the REE patterns of some EC are also inconsistent with the experimental data. The highly reducing character of EC being beyond doubt, the natural REE patterns cannot be explained by CaS crystallization on the liquidus, and another process must be involved.

Melt extraction, metasomatism and "refertilization" in the evolution of continental mantle

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It is commonly accepted that the major element composition of the continental lithospheric mantle has been shaped by different degrees of melt extraction from a fertile source, with variable, but generally minor, effects of post-melting metasomatism. This concept, supported by ample experimental data on peridotite melting, was recently challenged by claims that fertile mantle can alternatively form by interaction of refractory melting residues with basaltic melts, without providing adequate experimental evidence for the viability of this mechanism. Published data on chemical and Os-isotope composition of peridotite xenoliths from the Siberian craton are examined to assess these alternatives. Xenoliths from two sites (Obnazhennaya and Tok) show a broad range of compositions indicative of strong interaction of refractory mantle with basaltic and other magmatic liquids. Their modal, chemical and Os-isotope compositions are very particular (high Ca/Al, no Mg#-Al correlations, highly variable Cr, low $^{187}Os/^{188}Os$, continuous modal range from olivine-rich to low-olivine peridotites, wehrlites and websterites) and distinct from those of fertile lherzolites in off-craton xenoliths and peridotite massifs. These features argue against the concept of 'refertilization' of cratonic and other refractory peridotites by mantle-derived melts as a major mechanism to form fertile to moderately depleted lherzolites in continental lithosphere. The Obnazhennaya xenoliths represent a natural rock series produced by 'refertilization', but include no rocks equivalent in modal, major and trace element to the fertile lherzolites. This study shows that 'refertilization' yields broad, continuous ranges of modal and chemical compositions with common wehrlites and websterites that are rare among off-craton xenoliths.

Experimental determination of the pressure dependence of sulfur speciation in silicate melts

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Sulfur is a minor but ubiquitous element in magmatic systems. Being multivalent makes it a potential useful tracer of the redox state of evolving magmas. One particularity of sulfur is that different species do not coexist in any mineral phase, unlike other multivalent cations (such as Fe). The only relevant phases in which different S species can coexist are silicate melts and volatile phases. Sulfur has been shown to dissolve in silicate melts as either reduced species (sulfide, S^{2-}) or oxidized species (sulfate, S^{6+}) depending on the oxygen fugacity (f_{O2}). It is widely considered that S is entirely expressed as sulfide at f_{O2} below the FMQ buffer and as sulfate above ~FMQ+2. In between lies the sulfide-sulfate transition in the course of which the solubility of sulfur at sulfide saturation (SCSS) increases dramatically until reaching the solubility of sulfur at anhydrite saturation (SCAS). Over this narrow f_{O2} range, S dissolves in silicate melts as both S^{2-} and S^{6+}, and it is generally admitted in the literature that the transition occurs at fixed f_{O2}, independently of the intensive parameters (pressure, temperature, melt composition, H_2O concentration).

Yet, the thermodynamic model of Moretti and Baker (2008, CG) as well as recent experimental studies (Jégo et al., 2016, GCA; Matjuschkin et al., 2016, CMP) suggest that the transition would be shifted towards higher (i.e., more oxidizing) f_{O2} with increasing pressure. Therefore, we aimed to test this hypothesis by a direct method, i.e., by performing melt sulfur solubility experiments over a wide pressure range, imposing oversaturation in both sulfide and sulfate so as to target the transition, and measuring the corresponding f_{O2} with solid sensors. Melt S content and speciation were determined by EMP and Raman analyses. Results allow the pressure effect on sulfur speciation to be experimentally verified, and emphasize its importance for the redox state and metal enrichment of uprising sulfide-saturated magmas.

Storage and degassing conditions of monogenetic eruptions at Tenerife (Canary Islands, Spain): Constraints from melt inclusions and phase equilibrium experiments

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Effusive and mildly explosive mafic monogenetic volcanism has predominated over felsic eruptions during the historical and recent period (last 2000 years) at Tenerife (Canary Islands). Therefore, this type of volcanic activity is expected to occur in the near future and it is crucial to have a better understanding on storage conditions, ascent mechanism and degassing paths for this eruption style. Nevertheless, this information, along with volatile content and its behaviour, remains poorly constrained at Tenerife.

This work is focused on Arafo and Fasnia historical eruptions (1704-1705). By combining data from (1) phase equilibrium experiments on a representative Fasnia basanitic magma and (2) melt inclusions in olivines and clinopyroxenes, we aim at determining the storage conditions and the composition of the fluid phase (H_2O, CO_2, S, F and Cl) in equilibrium with the magma. Explored conditions on the Fasnia sample range from 50 to 400 MPa, 1200 to 1050°C, for X_{H2O} from 1 to 0 ("nominally dry" conditions) and a f_{O2} of ~ 1.5 log units above the Ni-NiO solid buffer. Volatile contents and chemical compositions of melt inclusions trapped in olivine and clinopyroxene phenocrysts from both eruptions have been also analysed to trace the magma ascent from its mantle source.

Results from the current work will contribute to improve knowledge on 1) storage conditions and ascent mechanism of these mafic magmas; 2) degassing paths and 3) interpretation of precursory signals (gas-emissions) prior and during this type of eruptions.

The effect of H$_2$O on relative component mobilities and microstructure development in metamorphic reaction rims

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Not only the overall thickness of a reaction rim but also its microstructure may provide important insights into the conditions and dynamics of a geological system.

Diopside + merwinite reaction rims were experimentally grown at contacts between monticellite (^{40}CaMg^{28}SiO$_4$) and isotopically labelled wollastonite (^{44}Ca^{29}SiO$_3$) at 900°C and 1.2 GPa with trace amounts of H$_2$O present. The reaction rim shows three monomineralic layers forming the sequence merwinite - diopside - merwinite. NanoSIMS analyses revealed that both, ^{44}Ca stemming from the wollastonite as well as ^{40}Ca stemming from the monticellite are distributed across the entire rim. In contrast, ^{28}Si and ^{29}Si are retained in those regions that stem from the monticellite and isotopically doped wollastonite, respectively. This indicates that solely transfer of MgO across the entire rim controlled overall rim growth rates with D(bulk,MgO;Di+Mw)=10$^{(-16.3\pm0.2)}$ m^2/s.

Formation of the rim microstructure can either be explained by a two-step model starting with the development of a cellular microstructure comprised of alternating diopside-merwinite lamellae oriented perpendicular to the original interface, which transformed into the multilayer microstructure through mobility of CaO, or by a one-step model implying that SiO$_2$ was transferred solely across the two merwinite layers.

CaO and SiO$_2$ are both notoriously immobile at very dry conditions resulting in the development of a cellular microstructure comprised of alternating diopside-merwinite lamellae (Joachim et al. 2012). The comparatively high mobility of CaO and the potential finite mobilization of SiO$_2$ in the merwinite layers, which lead to the development of the multilayer microstructure observed in this study, are ascribed to the presence of small amounts of water. The profound effect of trace amounts of water on relative component mobilities implies that rim microstructures may be used to infer the availability of water during their formation.

The interior structure of Mars: New constraints from experiments and thermodynamic modelling

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The upcoming NASA InSight mission to Mars, scheduled for launch in May 2018, will likely provide unprecedented new geophysical data on the interior of our nearest terrestrial neighbour. However, the interpretation of InSight data requires comparison with predictive models for geophysical properties such as mantle densities or seismic velocities, which are not necessarily optimised for Mars-like compositions. This work will take an interdisciplinary approach in the hopes of deriving a deeper understanding of the nature of the present day Martian mantle structure.

Using high-pressure, high-temperature multianvil experiments we will precisely determine phase transition pressures and mineral modes for a range of possible bulk silicate Mars compositions over the entire mantle depth and at various temperatures. We will employ a multi chamber capsule method, allowing all compositions of interest to be investigated simultaneously within one experiment at a given pressure and temperature. This approach avoids experimental uncertainties that would arise from running the samples consecutively. The results from these experiments form the basis for a thermodynamic optimisation to fine-tune an existing, internally consistent data base (Stixrude & Lithgow-Bertolloni 2011) using a Bayesian method. The ultimate goal of this combined experimental and thermodynamic approach is to provide a most accurate predictive tool that will be used in conjunction with data from InSight to obtain a clearer integrated picture of the interior of Mars.

Experimental study of Zn and Cu isotope fractionation: implications for the lunar core composition

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The Earth and the Moon share a genetic link, as evidenced by their near identical composition across a number of stable isotopic systems, such as Ni, Ti, Cr, W and O and in their elemental Hf/W contents. Unlike the refractory lithophile elements, however, the isotopic fractionation of more volatile elements, such as Cu, Ga and Zn, show significant variability across the two bodies. For instance, lunar mare basalts are about 1.5 per mil heavier in $^{66/64}$Zn than the estimated bulk silicate Earth. This enrichment in heavy isotopes has been attributed to volatile loss during the accretion of the Moon.

Evidence from both geochemical and geophysical models support the existence of a small metallic lunar core, comprising an inner solid- and outer, light element rich, liquid component. Separation of a metallic core from silicate melt during lunar differentiation has the potential to sequester significant amounts of Cu and Zn, without noticeable influence on lithophile volatiles such as Rb, K, Li, and Ga.

To explore this, we combine experimental results with high-precision isotopic measurements of Zn and Cu isotope fractionation factors between metallic, sulphide, and silicate melts at conditions relevant to lunar core formation. For both elements we observe resolvable isotopic fractionation, with the metallic liquids being slightly enriched in heavier isotopes relative to both the silicate melts and sulphide melt. However, sulphide melts are in turn isotopically lighter than the coexisiting silicate melt. In all experiments Zn isotopes display a smaller degree of fractionation than Cu isotopes. Overall, the isotope fractionation of both elements slightly decreases with temperature, consistent with the theory of equilibrium mass-dependent isotope fractionation.

We propose that segregation of a sulphide melt from the cooling lunar magma ocean will result in the bulk silicate Moon exhibiting heavier Zn and Cu isotope compositions than the bulk silicate Earth.

Stable isotope fractionation during degassing of silicate melts

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Loss of volatile elements from silicate magmas is a common process in igneous terrestrial rocks but the extremely depleted volatile element budget of the Moon indicates that degassing also occurs during planetary formation or as a consequence of planetary impact processes.

In order to quantify the degassing behaviour and the fractionation of stable isotopes during the degassing of several trace elements, we performed a series of experiments in 1 atm gas-mixing furnaces (University of Münster) at a range of oxygen fugacities (f_{O2}), ranging from $\log f_{O2}$ = -10 (IW, Re-wire loops) to -0.7 (air, Pt-wire loops) at temperatures between 1200°C and 1400°C.

Element concentrations in residual glasses were measured by LA-ICP-MS and EMPA at University of Münster. The quenched residual melts were found to be homogeneous with respect to element concentrations, suggesting degassing was not controlled by surface geometry or limited by diffusion of elements in the liquids. Stable isotopes of several 'non-traditional' trace elements were measured in residual quenched melts using a Thermo Neptune Plus MC-ICPMS and a Triton TIMS at the Institut für Mineralogie at the University of Münster using the double spike method. The stable isotope fractionation behaviour of each element is fit thermodynamically as a function of time, temperature and f_{O2}, and used to predict the effects of degassing on silicate melts in various geological and planetary settings.

Grain boundary diffusion of Re, Os, Pt, and Pb in olivine aggregate in presence of sulfide

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Upper mantle heterogeneity of the elements hosted by sulfide, such as Os, Pt, Pb, is controlled by the rate of grain boundary diffusion in olivine-rich mantle rocks. As a small quantity of sulfide minerals is dispersed within mantle peridotite, the diffusive homogenization through the grain boundary is the rate limiting process to exchange variable amount of trace elements hosted by sulfides, but not hosted in other silicate minerals. Specifically, highly siderophile elements are such elements hosted by sulfides but not in mantle silicate minerals. We have conducted piston cylinder experiments at 2.0 GPa and 1260 °C, designed to measure the olivine grain boundary diffusivity in presence of sulfide for Re, Os, Pt and Pb. Our results of the bulk diffusivity vary from $\sim 10^{-11}$ m^2 s^{-1} for Re and Os to $\sim 10^{-9}$ m^2 s^{-1} for Pt and Pb. These values represent the rate of exchange through a polycrystalline olivine aggregate. With consideration of the grain size and the grain boundary thickness, the grain boundary diffusion rate is deduced from the bulk diffusion values, and they range from $\sim 10^{-8}$ m^2 s^{-1} for Re and Os to 10^{-5} m^2 s^{-1} for Pt and Pb. Surprisingly, the fast values are comparable to an olivine grain boundary diffusivity for hydrogen. Applying these diffusion coefficients to upper mantle conditions, the "rule of thumb" scaling model shows that the mantle peridotite hosting Pb for one billion years must have a kilometer-size homogeneous domain of Pb abundance and isotopes, while for Re and Os, the homogeneous domain can be as small as 50 m. This suggests significant decoupling of Pb and Os isotope signatures in mantle derived materials (basalts and xenoliths) can be explained by variable extent of diffusive equilibration of sulfide grains.

The effect of trisulfur radical ion on sulfur isotope fractionation in hydrothermal systems

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The major chemical forms of sulfur have been believed to be sulfate, sulfide, and sulfur dioxide; however, the recent discoveries of the sulfur radical ions in geological fluids [1, 2] may change our vision of sulfur isotope fractionation used for tracing different natural processes. Here we studied the isotopic composition of sulfur species in aqueous S-bearing fluids at T from 300 to 450°C and P from P_{sat} to 800 bar, using a hydrothermal reactor equipped with a flexible gold cell and a rapid sampling device. The cell was loaded with $K_2S_2O_3$ aqueous solutions as a source of sulfur. Solutions of HCl and $FeCl_2$ were introduced in-situ into the cell during the experiment to create conditions favorable for the formation of sulfur radicals and pyrite precipitation. The fluid was periodically sampled into a zinc acetate solution to fix aqueous sulfide. The precipitate of ZnS was separated by centrifugation, and the remaining solution was reacted with barium acetate to precipitate barium sulfate ($BaSO_4$). Molecular S was extracted with hexane. The precipitated pyrite was recovered after experiment. GFMS measurements of sulfur isotope ratios were realized in the form of Ag_2S that was obtained by chemical treatment of zinc sulfide, barium sulfate and pyrite using HCl 6N, Thode [3] and $CrCl_2$ solutions [4]. First results indicate that isotopic equilibration between sulfate and sulfide at 300°C is rather slow, but was attained within 1 week at 450°C, in agreement with previous studies [5]. No detectable mass-independent fractionation (MIF) of ^{33}S (Cap< ±0.05‰) was found in sulfate, sulfide, native S or pyrite; in contrast some minor MIF was observed on ^{36}S (Cap=-0.5‰). Work is in progress to relate the observed isotope fractionation with detailed S aqueous speciation and natural data on pyrites and barites.

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Phase transition boundary between fcc and hcp structures in Fe-Si alloy and its implications for thermodynamics of silicon-bearing Earth's core

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The phase transition between a face-centred cubic (fcc) and hexagonal close-packed (hcp) structure in Fe-Si alloys were examined in an internally resistive heated diamond anvil cell under high-pressure (P) and -temperature (T) conditions to 71 GPa and 2000 K by in-situ synchrotron X-ray diffraction. Starting from the precisely constrained phase loop in Fe-4wt%Si, we have constructed a thermodynamic model for the phase transition. The well-known negatively nonideal mixing properties of Fe and hypothetical Si for the Fe phases at 1 bar are found to become ideal with increasing P and T. The entropy changes upon melting of the end-members Fe ($\Delta S\_Fe^{melting}$) and Si ($\Delta S\_Si^{melting}$) are fairly large, and therefore the melting temperatures of the end-members ($T\_Fe^{melting}$, $T\_Si^{melting}$) are expected to be close, to account for the reported close compositions of coexisting liquid and solid (< 1 wt%Si at P >50 GPa). As such, the melting phase loop of the Si-bearing Fe phases should be narrow and nearly temperature independent. The liquidus temperature of Fe alloy is therefore, not changed by the presence of Si at the inner core-outer core boundary, which implies that Si does not significantly affect the thermal structure of Earth's core.

Simulation of a fully fractional crystallization of the Moon: a lunar liquid line of descent

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The Moon is thought to have undergone a completely molten stage during its accretion. To understand the evolution and differentiation of this lunar magma ocean, we performed a series of consecutive liquidus experiments on the Taylor bulk composition. In these experiments, we determine the liquidus temperature, crystallize 10-20% (relative) of minerals and then step to a new bulk composition representing the residual liquid after fractionation of these minerals. Pressure is adopted to the appropriate value after each (gravitational separation) step. Crystallization starts with copious amounts of high XMg olivine, the liquidus temperature decreasing from 1900 to 1850°C at 4.5 to 3.5 GPa. Crystallization begins at the core-mantle boundary, but density calculations indicate that initial olivine may float achieving neutral buoyancy at 3.7-3.5 GPa. This leads to a stable olivine layer of several 100 km thickness at a depth of around 900 km. This layer should rapidly compact yielding two chemically separated inner and outer magma reservoirs. We hence studied the chemical evolution upon cooling in both reservoirs, the inner one crystallizing ol→opx→grt→cpx leaving 16% residual liquid at 1450°C, while the outer one has a crystallization sequence of ol→opx→Cr-sp→cpx→plag with a residual magma fraction of 16% remaining at 1160°C. Cpx with augitic composition appears at 1250°C after 60% upper reservoir fractionation, i.e. at ~230 km depth. Plagioclase appears after 70% fractionation, when the magma ocean has shallowed to ~180 km depth. Both series are presently continued with the goal to determine the melt composition leading to lunar anorthosites and the very final melt fractions.

Alternatively, if olivine has not a level of neutral buoyancy in the magma ocean (the uncertainties in the melt density calculation leading to a close call), the higher pressure portion of the Moon will accumulate olivine only and there would be no garnet forming during fractional crystallization.

Tracing Earth´s volatile delivery with tin

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The history of Earth's volatile element depletion compared to primitive chondrites is poorly understood, namely whether (1) volatile elements were delivered during the main phase of Earth's accretion, or (2) Earth accreted largely from material devoid of volatiles with late addition of volatile-rich material. The chemical and isotopic signature of volatile siderophile elements in the terrestrial mantle can thus be used to discriminate between these models, as these signatures can be affected by core-mantle differentiation. Tin is a moderately volatile and moderately siderophile element, and as such is sensitive to both core formation and volatility related processes, making it well-suited to track the history of volatile elements during Earth's formation. However, very little is known about its metal-silicate partitioning behavior, and even less is known about its isotopic behavior during such processes. High pressure and high temperature metal-silicate differentiation experiments were performed in a piston-cylinder press at 2 GPa, from 1700 to 2300 K, in order to study the partitioning behavior of Sn, including the relative influence of oxygen fugacity, metal and silicate composition, and experimental capsule material. Tin concentration in the metal and the silicate phases were analysed using a CAMECA SX5 electronic microprobe (CAMPARIS, UPMC), and isotopic results were produced using a double-spike wet chemistry approach and MC-ICPMS analysis (Neptune Plus, IPGP). Our results indicate that Sn partitioning is largely controlled by changes in temperature and oxygen fugacity, wherein siderophility markedly decreases with temperature, and these results can be used to remark on the conditions of Earth's formation. Isotopic results from the same experiments indicate that core-mantle equilibrium temperatures (~3000K) could potentially generate mantle Sn that is isotopically heavier than the core by 150-200 ppm per amu.

Kinetic isotope fractionation effects during carbon-precipitation from a CH_4-rich, progressively oxidizing COH-fluid

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In an attempt to better understand the high variability of carbon isotope distributions in natural diamond and graphite, we performed time series experiments that (involuntarily) simulate the progressive oxidization of an initially reduced, CH_4-dominated COH-fluid. Equidimensional gold capsules filled with 5 mg stearic acid have been exposed to 800°C and 2 kbar producing a reduced CH_4-rich COH-fluid together with a C0-phase. The drastic f_{H2} gradient between capsule and Ar-pressure medium in the hydrothermal vessel leads to H-loss which then causes CH_4 dissociation and hence carbon precipitation accompanied by progressive oxidation of the fluid. Solid carbon (µm-sized carbon-spheres) and gaseous run products have been analyzed with elemental analyzer and gas chromatography isotope ratio mass spectrometry for gas speciation and carbon isotope composition.

Experiments yield f_{O2}'s of IW +1.5 to CCO and fluid compositions changing from initially 84 mol% CH_4 to a pure CO_2-CO mix exactly on CCO. The unidirectional CH_4-dissociation favors the breakdown of the light isotopologue causing ^{13}C enrichment in the remaining fluid-phase. At the extreme, CH_4 results 11.4‰ heavier than C0, while at isotopic equilibrium C0 would be 2.4‰ heavier than CH_4. Rayleigh distillation modelling yields 1) a continuous depletion in ^{13}C of 4 to 5.8‰ of the C0 precipitate over the CH_4 carbon source and 2) predicts a progressive ^{13}C enrichment of the C0 precipitate that could lead to an isotope zonation within the carbon-spheres of > 10‰. Our experimental results and the slow carbon-self diffusion in graphite and diamond suggest that kinetic isotope fractionation can be significant at high-temperatures and may cause internal isotope patterns mimicking isotope patterns commonly assigned to carbon precipitation from CO_2-rich fluids or melts under isotopic equilibrium.

Magnetic hematite at depths of the Earth's transition zone

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The Earth's crust-mantle boundary (Moho discontinuity) has been traditionally considered as a fundamental boundary between the magnetic crust and the nonmagnetic mantle. Nevertheless, this assumption has been questioned recently by geophysical studies and by the identification of magnetic remanence in mantle xenoliths [1,2] which suggest deep magnetic sources. Owing to their high critical temperatures, iron oxides are the only potential sources of magnetic anomalies at mantle depths [3]. However, the lack of data on their magnetic properties at relevant pressure-temperature conditions hampers any conclusive result about the Curie depth, below which mantle temperature is too high to sustain any kind of long-range magnetic order. Here we report investigations of the magnetic transitions and critical temperatures in Fe_2O_3 polymorphs [4] to 95 GPa and 1200 K by means of Synchrotron Mössbauer Source spectroscopy [5] in laser-heated diamond anvil cells. The experiments were conducted at ID18 beamline of the ESRF. Our results demonstrate that hematite, α-Fe_2O_3, remains magnetic at the depth of the Earth's transition zones along cold or very cold subduction paths in the West Pacific region. The geophysical implications of these findings will be discussed.

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Water solubility in a martian basaltic melt at high pressures (0.5 - 1.5 GPa)

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The surface of Mars has been studied by various landed and orbital spatial missions. The Curiosity rover is currently analyzing rocks on Mars using several tools and gives us the chemical compositions of the basalts. Many igneous rocks have been detected on the surface, and basaltic rocks represent the most abundant part.

Martian basalts are different from Earth basalts since their FeO_{tot} content is about 20 wt % in average, for only 10 wt % for the Earth's basalts. Based on the analyses of Martian meteorites, the Martian mantle is thought to be strongly depleted with respect to H_2O (hundreds of ppm) and CO_2. However, the volatile budget of the Martian mantle is still debated. Currently, there is no H_2O solubility data for a Martian basaltic melt equilibrated at high pressures and temperatures.

We have conducted high pressure (0.5 - 1.5 GPa) and high temperature (> 1550 °C) experiments on a Martian basalt-like composition (15.5 wt % FeO_{tot}). These experiments were in equilibrium with an H_2O fluid phase. The preliminary results reveal that H_2O solubility is extremely low in a Fe-rich melt. At 1 GPa, 3 wt % H_2O initial, the H_2O solubility can only reach 1.5 wt %.

Our first results suggest that the FeO content appears to have a strong control onto the H_2O dissolution in a Martian basaltic melt. It also implies that this Fe-rich melt is not a good carrier of H_2O from the mantle to the surface.

On the use of experimentally derived redox sensors in olivine-hosted melt inclusions

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The study of highly primitive magmas trapped as olivine-hosted melt inclusions has allowed a better understanding of petrogenetic processes and the compositions of mantle source regions. These unique samples may also provide a means to link the redox state in primary magmas to that in their mantle source region.

Arc magmas are more oxidized than mid-ocean ridge magmas (Kelley & Cottrell, Science, 2009), likely because the mantle source region of arc magmas has been modified by oxidized and volatile-rich fluids from the subducting slab. However, whether the variations in $Fe^{3+}/\Sigma Fe$ of magmas from various environments arise owing to differences in mantle f_{O2} or to differentiation processes in the arc crust such as partial crystallization and degassing is still a matter of debate (Gaillard et al., Chem. Geol., 2016). Alongside this scientific debate, $Fe^{3+}/\Sigma Fe$ ratios in primitive melts also show discrepancies between values derived from different analytical methods (wet chemistry, XANES and Mössbauer spectroscopy) that clearly need to be resolved.

Here we combine different f_{O2} proxies in an attempt to carefully reconstruct mantle source f_{O2} from the compositions of highly primitive olivine-hosted melt inclusions from mid-ocean ridge, hot spot and arc settings. These f_{O2} proxies include $Fe^{3+}/\Sigma Fe$ measurements and trace element proxies that rely on the experimental calibration of the partitioning behavior of multivalent cations such as V, Cu and S during petrogeneitc and differentiation processes as a function of f_{O2}.

In particular we will compare f_{O2} values derived from the V oxybarometer with direct measurements of the oxidation state of Fe. A careful assessment of the differentiation and melting processes and their effects on f_{O2} proxies will be carried out in order to reveal the link between redox state in melts and that of their mantle source. This work will provide an evaluation of the robustness of the various redox sensors when applied to melt inclusions.

Dissolution-precipitation of forsterite phenocrysts in a thermal gradient and melt inclusion formation

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Primary melt inclusions are microscopic droplets of liquid that have been trapped into crystals during their growth. Magmatic inclusions may preserve the conditions of their formation, and thus are important tools for petrological and geochemical studies. However, their formation remains unclear. It has been proposed that melt inclusions result from an alternation between diffusion and interface attachment control during host crystallization, most likely due to variations of the cooling rate.

Here, we present the results of forsterite growth in a haplobasaltic melt by dissolution-precipitation under a thermal gradient (~15°/mm), but in the absence of temporal variation of temperature (no cooling). On the hotter side of the forsterite crystal, dissolution typically results in a rounded shape or an alternation of melt embayments and crystal columns. On the other (colder) side, the precipitation of forsterite develops a zigzag surface that likely results from cellular growth, sometimes trapping melt inclusions. We hence show that melt inclusions in forsterite can form at nearly constant temperature and a relatively slow rate of crystal growth.

Development of in situ techniques for the quantification of volcanic processes

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A thermo-mechanical rig (P2R) is being developed to replicate on a synchrotron the conditions of pressure (P), temperature (T), oxygen fugacity (f_{O2}) and volatile content that magmas experience during eruptions. Using synchrotron X-ray tomography (sCT), this innovative technology will allow us to directly capture and quantify the kinetics of both degassing and crystallization during ascent in the shallow conduit ($P \leq 50$ MPa, 2 km depth) every few seconds. So far, we have studied the 4D (3D plus time) crystallization of plagioclase and clinopyroxene in basaltic systems, with and without control of f_{O2} under ambient pressure. The cooling-driven crystallization experiments were performed at the I12 Diamond Light Source synchrotron beamline (United Kingdom). Two separate furnaces were used, the first used high-temperature resistance heating (Alice) for highly stable, but slowly changing thermal histories, and the second used infrared heating (Helios) for very rapid heating and quenching. Both reached temperatures of 1250 °C. The first f_{O2} controlled 4D imaging of crystal nucleation and growth, together with pressurised vesiculation results, will be presented, enabled by these technological and synchrotron imaging developments.

Ti K-EDGE XANES study on pyroxene, olivine, Fe-Ti oxides and basaltic glasses equilibrated under Lunar conditions of oxygen fugacity

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We report new X-ray absorption near edge structure (XANES) spectroscopy measurements on a wide range of minerals (pyroxene, olivine, Fe-Ti oxides) and basaltic glasses equilibrated under lunar conditions of f_{O2}. Experiments were conducted in 1 bar gas-mixing furnaces using Pt or Re wire, with temperatures between 1100 and 1300 °C and f_{O2} from IW-1.5 and IW-1.8. Run products were analysed via electron microprobe and XANES Ti K-edge spectra were acquired in fluorescence mode using a Si (111) double crystal monochromator and X-ray beam focused to 50 μm at sample position, at the SUL-X beamline of the ANKA synchrotron facility. Because crystal orientation can be a source of uncertainty, we have measured several points randomly allocated among the crystals in different experiments at the same f_{O2}. To determine Ti coordination and oxidation of state in the experiments, the 1s-3d energy shifts were used, and the lever rule between standards. Typical run products had large (> 100 μm) crystals in equilibrium with quenched silicate glass. Crystal size was controlled by the cooling ramp and the TiO_2 content of the silicate melt. Ti K-edge XANES spectra show a clear shift in energy for the absorption edge features from oxidizing to reducing conditions, for example, about 3 eV from TiO2 to Ti2O3 at the main-edge feature. Preliminary XANES data yield an average valence for Ti of 3.6, i.e., a $Ti^{3+}/\Sigma Ti$ value of 0.4 for crystalline phases under these conditions. Silicate glasses show that Ti is exclusively tetravalent. Pre-edge peak intensities also show that the coordination number of Ti varies from average V-fold in the silicate glass to VI-fold in the Fe-Ti oxides and a mixture between VI and IV-fold coordination in the pyroxenes and olivine. The maximum amount of Ti in tetrahedral coordination in the pyroxenes in our study is ca. 40 %. Our results help to better constrain the $Ti^{3+}/\Sigma Ti$ of the lunar mantle during magmatic processes.

The role of oxygen fugacity on clinopyroxene: major, minor and REE elements chemistry

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Terrestrial planets magmas have a large range of oxygen fugacity (f_{O2}). The magma f_{O2} affects the stability of Fe-bearing phases. It has a direct effect on incorporation of redox-sensitive elements (Fe^{3+}/Fe_{tot}, Cr, V, Eu^{3+}/Eu_{tot}) in the crystal lattice and indirect effect on elements exchanged with Fe (e.g. Mg, Al^{VI}) and through coupled substitutions (e.g. Al^{IV}). Fe, Cr, V concentration is high in gabbro and basalt, which are the dominant lithologies in the oceanic crust, the arc lower crust and occur on the Moon and solar system rocky planets.

We performed equilibrium, dry, O_2-buffered, 1-atm experiments on a Rum intrusion parental picritic magma in gas-mixing furnaces. We explored a f_{O2} range from NNO-4 to NNO+1 and air, at 1200 to 1110°C, evaluating the effects of oxygen fugacity and temperature only.

Clinopyroxene crystallizes from 1180°C (1190°C in air) to the solidus temperature (~1000°C), together with plagioclase (1200°C), olivine and spinel. The olivine reacts to pigeonite at high f_{O2}. The plagioclase FeO_{tot} increase and the olivine Cr^{3+} and V^{3+} decrease, with no effect of temperature. Spinel is absent under strongly reducing conditions (NNO-4) and its stability increases under oxidised conditions, while its chemistry changes from Al-Cr-rich to Fe^{3+}-rich. The clinopyroxene Fe^{3+}/Fe_{tot} strongly increases and V^{3+} and D_V strongly decrease at higher f_{O2}, with no effect of temperature. Also Cr^{3+} and D_{Cr} strongly decrease at high f_{O2} and at low temperature. The Cpx/Spl Fe^{3+}/Fe_{tot} partition coefficient strongly increases at high f_{O2}, independently of temperature. CaTs (Si = Al^{IV}) substitution is slightly higher at high f_{O2}. High Al^{IV} affects the lattice site configuration and size, allowing more REE (increased D_{REE}). However, REE and D_{REE} generally show no dependence on f_{O2}. Only exception is the multi-valence Eu^{2+}-Eu^{3+}. D_{Eu} increases under oxidized condition, showing higher compatibility of smaller REE^{3+} in clinopyroxene.

A new experimental study on multicomponent diffusion of F, Cl and OH in apatite and implications for magma ascent rate determinations

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Chemical zonings in minerals from volcanic rocks have been used to constrain timescales of pre-eruptive magmatic processes, such as magma mixing, yet rarely for those occur within short times but may control eruption styles, such as magma ascent. Recent studies show that Cl zoning in volcanic apatite varies with eruptive styles and thus may be related to ascent rate [1]. Halogen diffusivities in apatite, however, have not been thoroughly studied given only one dataset from literature. Here we report new experimental results for diffusivities of F, Cl and OH in apatite at 800-1100 °C, 1-atm and f_{O2} of WM buffer. Diffusion couples consist of two types of apatite showing distinct F-Cl-OH compositions. Two types of diffusion sources are used: powders, and thin films deposited using pulsed laser deposition method. Diffusion couples were annealed in a furnace at constant P, T and f_{O2} for a series of run durations. Concentration profiles of F and Cl were measured using electron microprobe, and OH was calculated assuming stoichiometry. Depth profiles will be measured from thin film samples using SIMS. We find that Cl profiles show uphill diffusion, indicating multicomponent diffusion of F, Cl, and OH. By using a finite difference algorithm to calculate diffusion matrix, we obtain diffusivities of F and OH at 1100 °C as ~3 (±1) 10^{-15} m^2/s and ~2 (±1) 10^{-16} m^2/s, respectively, consistent with those from literature. Despite that F and OH show isotropic diffusion, Cl diffusion is anisotropic, where its diffusivity parallel to c-axis at 1100 C is ~6 (±2) 10^{-16} m^2/s, >25 times faster than that parallel to a-axis. D_{Cl} parallel to c-axis obtained here is ~5-10 times slower than that from [2]. Using the new diffusivities, Cl zoning in apatite from Merapi deposits would give timescales of ~2-4 weeks, implying similar time periods of magma ascent before the eruption in 2006, consistent with ground deformation data from literature.

[1] Li et al., 2018, in prep
[2] Brenan, 1994.

On the origin of Mars

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The terrestrial planets are believed to have formed from primitive material sampling a broad region of the inner solar system, suggesting the presence of radial mixing during planetary accretion. Element abundances of Martian meteorites have been interpreted to resemble a genetic relationship to CI chondrites, a class of undifferentiated meteorites with refractory element ratios similar to those of the solar photosphere. However, closer examination based on isotopic constraints reveals that Mars can only contain a small proportion of CI chondrites and is more likely to be predominantly composed of ordinary and enstatite chondrites. Many isotopic mixing models attempting to reconcile isotopic characteristics for Mars, but also Earth, have been proposed, but, because of the inherent non-uniqueness of such solutions, additional independent observations are required to resolve the nature of the primary building blocks of the terrestrial planets.

In this study existing isotopic measurements of Δ^{17}O, ε^{48}Ca, ε^{50}Ti, ε^{54}Cr, ε^{62}Ni and ε^{92}Mo are used in Monte Carlo mixing models to reproduce the isotopic signature of Mars with various chondrites and differentiated achondrites. We observe $\sim 10^5$ unique mixing solutions, which are categorised into distinct clusters of mixtures using principle component analysis. The large number of solutions implies that isotopic data alone is insufficient to resolve the building blocks of Mars. Each isotopically valid mixture is converted into a core and mantle component via mass balance and the geophysical parameters mean density, mean moment of inertia and tidal response are computed and compared to observations from Mars. We discuss the entire isotopic and compositional solution space and show that Mars cannot purely consist of chondrites but that a relatively oxidised, differentiated object is additionally required to match all geochemical and geophysical constraints.

Carbon-bearing magmas in the Earth's deep interior

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Geodynamic models considering fast mantle upwelling without volatile-bearing components are inapplicable due to high melting temperatures of mantle silicates. Here, we discuss the possible nature and composition of melts in the deep upper and lower mantle, which can enhance material transport under superplumes and hot spots originating from the transition zone or from the core-mantle boundary of the Earth. We emphasize fundamental differences between melting in the petrologically important systems containing H_2O, CO_2, and with a reduced C-O-H fluid. Significant melting of subducted carbonates is expected at transition zone depths, especially if the slab stagnates above the 660 km discontinuity. Mantle melting in the presence of volatiles depends strongly on the redox state. An increase or decrease of the f_{O2} causes redox melting or freezing in defined parts of the mantle. The role of sluggish kinetics of solid-solid and even melting reactions involving carbonates in the deep mantle is also of great important. Slow reaction rates allow subducted carbonates to penetrate as deep as the core-mantle boundary. An important requirement for diapiric motion is stress-induced melting and dissolution-precipitation of fusible components at the front and rear of the plume, respectively. Carbonated or carbonatite melt is the best candidate for the fusible component of the plumes, especially for the upper mantle and transition zone. Hydrocarbon-bearing hydrous melt serves as the liquid component in mantle plumes arising from the core-mantle boundary. The conclusions are based on the recent data on melting in mantle systems with CO_2 and reduced C-O-H fluid, the stability of diamond and carbide phases, and the role of redox conditions in carbon and hydrogen cycles.

Fate of natural diamonds: from crystallization to dissolution (as evidenced by experiments)

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Precipitation of diamonds and associated minerals from the parental silicate-carbonate-carbon melts-solutions through their cooling and consolidation in the upper mantle reservoirs-chambers are bound to generate the maximum potential for diamond deposits. However the kimberlitic magmas transferring diamonds from mantle to crust are capable to dissolve them in shorter lifting period and prolonged solidification durability in the crust cumulative chambers (on the eve of formation of the explosive kimberlitic pipes).

Physico-geochemical conditions of diamond genesis have generalized as the mantle-carbonatite concept (Litvin, 2017) having been conformed to experimental results for the relevant multicomponent peridotite/eclogite-carbonate-carbon parental systems, to mineralogical analytic data for the diamond-hosted mineral inclusions of ultrabasic and basic parageneses, and to geochemical carbon isotope measurements in diamonds relating to both of the parageneses.

Experimental studies are indicative for the dissolution of metastable diamonds in carbonate-bearing kimberlitic melts as a factor for their weight loss and, correspondingly, the enrichment lowering for diamond deposits. The quantitative results are obtained at 0.15 GPa, 1200-1250°C in Ar gas-apparatus demonstrating that single crystalline diamonds have lost 3.0-4.5 wt.% for 2 h with a weak surface dissolution (conditions of kimberlite magma transfer) and 24.5-27.5 wt.% for 7-8 days with a sensible volume dissolution (conditions of cumulative chambers). By the estimations, about 20% of kimberlitic deposits have revealed as diamondiferous, but only near 2% of them are suitable for mining. It is reasonable to believe that dissolution of diamonds in the accompanying transferring kimberlitic melts may be not only partial but complete as well.

Litvin Yu.A. (2017) Genesis of Diamonds and Associated Phases. Springer, 137 p.

Geophysically resolved electrical structure may not be used to map water content in the shallow mantle

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It is widely accepted that OH groups dissolved in the crystal structure of nominally anhydrous minerals enhance strongly their electrical conductivity, as documented extensively for various materials. Olivine is the most abundant mineral in the upper mantle, and determines greatly the electrical structure and physical properties of the upper mantle. Mantle olivine usually contains trace amounts of OH groups, and quantitative work on the electrical property of OH-bearing olivine has led to the theory that, by combining experimentally-yielded data of olivine conductivity with geophysically-resolved mantle electrical structure, the OH content in the shallow mantle (above ~200 km depth) could be inferred (e.g., Karato 1990; Wang et al. 2006).

Studies on natural samples have shown that the OH content of olivine is commonly <100 ppm H_2O in the shallow mantle (e.g., Peslier et al. 2010). It has also been experimentally demonstrated that, given conditions prevailing in the shallow mantle, the OH solubility of olivine is usually <200 ppm H_2O (Yang 2015; Yang et al. 2014). Therefore, the potential OH contents of olivine in the shallow mantle are actually very low. Here, we have carried out a careful evaluation of the electrical conductivity of OH-free and OH-bearing gem-quality single crystal olivines, by looking into the data obtained by impedance spectroscopy at various pressure, temperature and redox conditions. We show that, given conditions in the shallow mantle and in particular in the zones where high electrical anomalies have been detected (e.g., with a temperature of ~1000-1350 °C), the electrical conductivity of dry olivine is always larger than, or at least comparable to, that of OH-bearing olivine with an OH content of less than ~200 ppm H_2O. This is due to the smaller activation enthalpy of proton conduction in OH-bearing olivine and its thus lower proton-dominated electrical conductivity at high temperatures when compared to dry olivine. It would therefore be hard, if not impossible, to modulate the contribution to bulk conductivity of proton conduction at shallow mantle conditions. We thus suggest that geophysically resolved electrical structure may not be used to map water content in the shallow mantle.

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Si distribution in disordered $MgAl_2O_4$ spinel

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A series of SiO_2-bearing $MgAl_2O_4$-spinels were synthesized at 1500-1650 °C and 3-6 GPa. These spinels had SiO_2 contents up to ~1.03 wt%, and showed a substitution mechanism of $Si^{4+} + Mg^{2+} = 2Al^{3+}$. Unpolarized Raman spectra were collected from well-polished single grains of these spinels, and displayed a set of Raman peaks at ~823, 856, 920 and 968 cm^{-1} which had not been observed before. Aided with the Raman features of natural SiO_2-free $MgAl_2O_4$-spinel, synthetic SiO_2-free $MgAl_2O_4$-spinel, natural quartz, synthetic coesite, synthetic stishovite and synthetic forsterite, we infer that this set of new Raman peaks should be attributed to the SiO_4 groups. The relations between the Raman intensities and SiO_2 contents of the SiO_2-bearing $MgAl_2O_4$-spinels suggest that, mainly due to the small size, Si cations primarily appear on the smaller tetrahedral sites and occur as 4-coordinated at relatively low P-T conditions; as P and T increase, most them quickly move to the larger octahedral sites and become 6-coordinated. This redistribution of some Si cations (Si-disordering) observed for the SiO_2-bearing $MgAl_2O_4$-spinels implies that similar Si-disordering might happen to the $(Mg,Fe)_2SiO_4$-spinels (ringwoodite), the major phase in the lower part of the mantle transition zone of the Earth.

Partitioning of siderophile but volatile elements during late stages of core formation

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The depletion of Earth's mantle in numerous elements as a result of accretion and core-mantle differentiation is known and heavily studied for more than four decades now. However, the siderophile but volatile elements (SVE) is one potentially important group of elements that has received considerably less attention in this context. SVE provide important information regarding the timing of volatile delivery to Earth. Though, the SVE partitioning between metal and silicate melt ($D_{metal/silicate}$) at core formation conditions remains poorly constrained.

The initial hypothesis that we are testing uses the accretion of major portions of volatile elements while the core formation was still active.

In this study we present new metal-silicate partition coefficients for a wide range of SVE (S, Se, Te, Tl, Ag, As, Au, Cd, Bi, Pb, Sn, Cu, Ge, Zn, In and Ga), as there is only scant data available for most of these elements. We focus our experimental endeavor on the effects of P, T and f_{O2} on the partitioning with systematic isobaric and isothermal experiments.

The partitioning experiments were performed using a Walker-type multi-anvil apparatus at pressures between 7 and 20 GPa and at temperatures between 1700 and 2100°C. Trace elements in experimental run products were analyzed with a Photon Machines Analyte G2 Excimer laser (193 nm) ablation system coupled to a Thermo Fisher Element 2 single-collector ICP-MS.

We present a first set of preliminary metal/silicate partition coefficients together with implications for core formation and the chemical budget of the early Earth.

Experimental investigation of Germanium isotopic fractionation during evaporation processes

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Many asteroids, protoplanets and Earth underwent episodes of melting and partial vaporisation during accretion. This observation is one basis for interpreting the degree of depletion of volatile elements relative to CI in the final budget of planetary silicate mantles.

Vaporization experiments at high temperature (1300°C) and f_{O2} from 10^{-7} (modern mantle) to 10^{-13} atm (core formation) [1] show that loss of volatile elements from a silicate melt does not follow their condensation temperature (from a nebular gas) and that germanium (Ge) is very volatile. In order to evaluate if Ge loss follows melt-vapour equilibrium or kinetic fractionation, we have performed, on the same experimental samples, measurements of Ge isotopes that are known to fractionate upon high-temperature evaporation processes [2,3]. Separate silicate phases have been chemically processed to isolate Ge for isotopic measurements by HG-MC-ICPMS ($\delta^{74/70}$Ge NIST 3120a <0.1‰ 2σ SD) (NeptunePlus, CRPG-Nancy) [4].

f_{O2} series experiments show a continuous increase in $\delta^{74/70}$Ge values, with a strong fractionation $\Delta74/70$Geend-start up to +3‰ between highly reduced samples and the starting material. The enrichment in heavy isotopes with a decrease in Ge concentration indicates Ge loss by evaporation processes from the silicate melt, according to the reaction: $GeO_2(melt) \rightarrow GeO(g) + 1/2\ O_2$. Additionnal time series isotopic data will help to quantify gas-melt isotopic equilibrium.

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The linked fate of H and C during planetary core mantle differentiation

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The volatile elements Hydrogen (H) and Carbon (C) are subjects of debates with regard to their history during the differentiation of telluric planetary bodies. We have investigated their behavior during the core segregation by determining the partition coefficient of H and C between metal and silicate at High Pressure (HP) and High Temperature (HT) and under variable f_{O2}. We performed experiments (at 1-15 GPa, 1400-2200°C and between 2 and 5.5 log units under the iron wüstite buffer) using piston cylinders and multi-anvil presses simulating equilibration between silicate melts and Fe-Ni-rich metals. The samples were analyzed by electron, ion and nuclear micro-probes. Our results showed that increasing pressure makes H more siderophile and C more lithophile. The f_{O2} dependence is important too but less essential than pressure. Thermodynamic modeling of our data combined with the literature data revealed that the decrease of siderophile nature of C with pressure is due to a gradual formation and dissolution of CH_4 in silicate melts at HP. This trapping of CH_4 in silicate melts allowed to store C in a differentiating mantle, despite its remaining siderophile nature. The dissolution of CH_4 in the silicate melts at the expense of H_2O would result in H being increasingly siderophile. The capacity of a planet or a planetary body to keep H and C in their cores would be then principally controlled by the depth of its magma ocean. The core of the smallest planetary bodies must retain most of the C whereas H would remain in the magma ocean and/or be lost in space. The core of the biggest planets, like Earth, could store both H and C but HP-HT equilibration should enable the mantle to retain a significant part of H and C essentially in the CH_4 form. Finally, during the cooling of the magma, the CH_4 would degas. A deep magma ocean, as expected on large planetary bodies would produce C and H-rich planetary surfaces, and might enable H-C-rich primitive atmosphere like on Earth.

Quantifying cooling rates in magmatic systems – application of the Mg-in-plagioclase and Ca-in-olivine diffusion chronometers on the Skaergaard intrusion

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Quantifying the rate of temperature (T) changes of rocks during geological processes provides insights into energy transfer processes on Earth. Different mechanisms of heat exchange leave behind different patterns of cooling rates through a given T-interval, and mapping cooling rates in natural rocks provides the possibility to identify the dominant process of heat removal. Cooling rates can be obtained by diffusion chronometers, which are based on the exchange of elements between different coexisting minerals in a rock.

Layered intrusions such as the Skaergaard intrusion have been used as natural laboratories for computational studies in transport theory, e.g. in a seminal study Norton & Taylor (1979) developed a numerical model of interaction between the crystallizing Skaergaard pluton and the circulating fluid. To test this model, we apply the Mg-in-pl and the Ca-in-ol diffusion chronometers to obtain quantitative cooling rates on samples covering the stratigraphic section of the Skaergaard intrusion. These tools are based on the sub-solidus diffusive exchange of Mg between pl and cpx, and Ca between ol and cpx, respectively.

The Mg-in-pl diffusion chronometer was calibrated in the compositional range of gabbroic rocks from the lower oceanic crust (i.e. for pl with X_{An} ~0.5-0.8 and $a(SiO_2)$ constraint by the coexistence of Fo + En, or the existence of free SiO_2). Thus, new experiments are required to check if this calibration is applicable for some of the plutonic rocks of the Skaergaard intrusion, which exhibit An-poor pl and Fe-rich ol and cpx. Additionally, as both the partition and diffusion coefficient in this model are a function of $a(SiO_2)$, experiments covering Fe-rich cpx and Ab-rich pl compositions need to be conducted to constrain $a(SiO_2)$ under these conditions and to broaden the applicability of the diffusion chronometer to determine cooling rates for the whole stratigraphic section of the Skaergaard intrusion.

Experimental investigation of strain localization in two-phase plagioclase-orthopyroxene assemblages

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The current view of the strength of the lithosphere is based on extrapolation of strength envelopes derived from laboratory experiments. As a natural starting point, the deformation of monomineralic material has been considered for understanding the lithosphere behavior. Nevertheless, the layers constituting the lithosphere are better described as two-phase aggregates. Here we present rock deformation experiments from two Griggs-type deformation laboratories. Deformation experiments have been performed on two-phase assemblages of plagioclase (Plg: An 60) + pyroxene (Fe- and Mg-Opx), representative of the lower crust. Shear experiments have been performed at constant displacement rate of ~10^{-8} m.s^{-1}, at temperatures of T=800 to 900°C and confining pressures of Pc=1.0 GPa. The microstructures show major differences between Plg+Fe-Opx and Plg+Mg-Opx deformation experiments. The assemblage of Plg+Fe-Opx shows abundant reaction products, while the Plg+Mg-Opx assemblage is close to equilibrium and does not react. In the assemblage of Plg+Fe-Opx the reaction products (amphibole: Amp, clinopyroxene: Cpx and more albitic Plg) occur only at 850°C and 900°C and are completely absent at 800°C. At 900°C these reactions occur pervasively throughout the sample, without localizing the deformation. However, at 850°C the volume of reaction products is smaller and the syn-kinematic products (Amp and Cpx) occur preferentially in a network of shear bands localizing the deformation. The Plg+Mg-Opx assemblage showing no reaction is dominated by brittle deformation. The mechanical data indicate that the reacting assemblages are significantly weaker than the one that does not react. In addition, reacting samples show pronounced strain weakening after initial peak stress, suggesting that the weakening behavior is related to the reaction progress. Conversely, the coincidence of reaction zones with the deformed domains indicates that reaction is strongly accelerated by the deformation.

Electrical conductivity of Fe-S alloys at high pressure and high temperature: Implications for Mercury's weak and long-lived magnetic field

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The planet Mercury currently exhibits an intrinsic magnetic field with a strength representing 1.1% that of the Earth's magnetic field. In this study, we investigate the electrical and thermal conductivities of Fe-S alloys at high pressure and temperature, with the aim of understanding how Mercury sustains its weak dynamo. Our results indicate that electrical conductivity of Fe-S alloys at 1500 K is about 10^3 S/m, two orders of magnitude lower than the previously assumed value for dynamo calculations. The low electrical conductivity of convecting fluids increases ohmic dissipation, reducing the power available to drive the dynamo. The low thermal conductivity of Fe-S suggests that the heat extraction from Mercury's core is a highly inefficient process. The low heat flow at the core-mantle boundary prevents the Mercurian core from rapid solidification, sustaining a long-lived intrinsic dynamo potentially operating since ~ 3.9 Ga.

Storage conditions of the mafic and silicic magmas at Cotopaxi, Ecuador

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The 2015 reactivation of the Cotopaxi volcano urges us to understand the complex eruptive dynamics of Cotopaxi for better management of a potential major crisis in the near future. Cotopaxi has commonly transitioned from andesitic eruptions of strombolian style (lava flows and scoria ballistics) or nuées ardentes (pyroclastic flows and ash falls) to highly explosive rhyolitic ignimbrites (pumiceous pyroclastic flows), which entail drastically different risks. To better interpret geophysical and geochemical signals, Cotopaxi magma storage conditions were determined via existing phase-equilibrium experiments that used starting materials chemically close to the Cotopaxi andesites and rhyolites. The results suggest that Cotopaxi's most mafic andesites (last erupted products) can be stored over a large range of depth from ~7 km to ≥16 km below the summit (pressure from ~200 to ≥400 MPa), 1000 °C, NNO +2, and contain 4.5–6.0±0.7 wt% H_2O dissolved in the melt in equilibrium with ~30–40% phenocrysts of plagioclase, two pyroxenes, and Fe-Ti oxides. These mafic andesites sometimes evolve towards more silicic andesites by cooling to 950 °C. Rhyolitic magmas are stored at 200–300 MPa (i.e. ~7–11 km below the summit), 750 °C, NNO +2, and contain ~6–8 wt% H_2O dissolved in a nearly aphyric melt (<5% phenocrysts of plagioclase, biotite, and Fe-Ti oxides). Although the andesites produce the rhyolitic magmas by fractional crystallization, the Cotopaxi eruptive history suggests reactivation of either reservoir at distinct times, likely reflecting flux or time fluctuations during deep magma recharge.

Water quantification by Raman spectroscopy: quantitative approach on dispersion and uncertainties: Cases of olivine and wadsleyite

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Olivine and its polymorphs are the major mineral phases of the upper mantle. Although nominally anhydrous, olivine can incorporate up to 1% weight water, and wadsleyite up to 3.5%. This water content is known to influence many properties of the Earth's mantle. Many analytical techniques allow determining the mineral's water content, such as FTIR, ERDA, nanoSIMS, and Raman spectroscopy. The first two will give precise results, but will either require large single crystals (FTIR and ERDA), or saturate quickly at high water content. SIMS requires well-characterized standards, and both ERDA and SIMS are heavy methods relying on large facilities. Raman spectroscopy allows punctual measurement (spot size under 5µm) of any water content down to 100 ppm, requiring only one polished surface. Experimental samples produced in multi-anvil press very fine-grained and fragile, making Raman spectroscopy more suitable to avoid sample loss. Water content of a sample can be obtained by measuring many randomly oriented crystals supposed to store the same quantity of water. These measurements show a large dispersion due to the crystal anisotropy, which can be mistaken for an uncertainty. An olivine single crystal measured along the crystallographic axes with polarized Raman has a total variation of $+53$ -33% (1σ) after complete data treatment, and a wadsleyite single crystal $+42$ -30%.

Although such huge data dispersion seems to make this method unsuitable for precise quantification, this study shows that most of this dispersion is induced by the crystal anisotropy alone, and thereby can be used as an anisotropy-sampling indicator, allowing to calculate what the real analytical errors of the methods are. Uncertainty sources have been identified, quantified, and used in a 3D model to understand their effect on water quantification with Raman spectroscopy. Knowing this, the parameters affecting water solubility, today blurred in the uncertainties, could be understood more accurately.

Polybaric Fractional Crystallisation of Arc Magmas - An Experimental Study

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Despite a still ongoing debate, differentiation of primary calc-alkaline liquids by fractional crystallisation is now generally accepted as one of the main driving mechanism controlling the compositional evolution of arc magmas. However, previous experimental studies failed to reproduce the predominantly metaluminous natural rock record by lower crustal crystal fractionation. At high pressures, experimental liquids rather evolve towards peraluminous compositions. The absence of abundant cumulates in the upper crust does not support the alternative scenario of major differentiation at low pressure conditions. Therefore, we propose an alternative process, namely polybaric fractional crystallisation, inferring that arc magmas differentiate progressively by crystal fractionation upon ascent through the crust. This hypothesis is tested through a series of experiments along several P-T ascent trajectories with continuously decreasing temperatures and pressures. Phase equilibria data, chemical compositions of stable mineral phases, liquid lines of descent as well as the evolution of crystal/melt ratios will provide crucial information to improve our understanding of the evolution of the calc-alkaline magmatic series and clarify if fractional crystallisation can be considered as a major process in the differentiation of mantle derived magmas at convergent plate boundaries. Our first experimental results support theoretical considerations on the effect of decreasing crystallisation pressure on mineral phase equilibria: the olivine-clinopyroxene cotectic curve is shifted towards more Cpx-rich compositions (equivalent to a destabilisation of clinopyroxene) rendering residual melts more metaluminous and, therefore, circumventing a rapid evolution of liquid lines of descent towards and into the peraluminous compositional field.

A thermodynamic model with CO_2 and H_2O for the lithosphere-asthenosphere boundary beneath thick continental roots

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The lithosphere-asthenosphere boundary (LAB) is a prominent feature of Earth?s plate tectonic engine. Its depth typically changes through time and is not directly measurable. Therefore, petrophysical models are used to circumvent this technical obstacle concerning the LAB on the modern Earth. For example, indirect petrological evidence is obtained from cratonic mantle-derived xenoliths through the application of phase equilibria thermobarometry. This approach has critical limitations such as xenoliths typically representing samples from above the LAB and often being metasomatically altered. An alternative to estimate the LAB depth in an area of interest is to involve the composition of the melts that brought the mantle xenoliths to Earth's surface, assuming that these melts last equilibrated with peridotite near the LAB. Here, we improve our previous thermodynamics-based model of melting in CO_2-H_2O-bearing peridotite under upper mantle conditions (Massuyeau et al., 2015 Chem Geol), utilizing available experiments for mantle-derived melt compositions down to 300 km depth. This model provides a new petrological tool to predict the last pressure of equilibration of uncontaminated magmatic kimberlites based on their chemical composition. The study is based on a quality compilation of major element compositions for worldwide magmatic kimberlites (Tappe et al., 2017 EPSL), corrected for degassing effects and potential olivine xenocryst accumulation. We determine the LAB depth in relation to the different cratonic regions, and compare these findings with results obtained from thermobarometry on mantle-derived xenoliths. This allows for tracking LAB evolution through space and time for different regions (e.g. Kaapvaal, Slave). Finally, we present first results on the ongoing calibration of a partitioning model for the REE between clinopyroxene/garnet and CO_2-H_2O-bearing melts, which provides further constraints on the physicochemical nature of the continental/oceanic LAB.

Methane-bearing fluids in the upper mantle: an experimental approach

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We present a new experimental approach for the control of fluid speciation at strongly reduced oxygen fugacity conditions. The presentation will give a summary of the main pitfalls of earlier designs and technical aspects related to achievement of reduced f_{O2} conditions and maintenance of constant fluid equilibrium during the run. Experimental design is suitable for studying of CH_4-rich fluid compositions at f_{O2} below graphite saturation in solid media apparatuses having a cell volume of $>200mm^3$ (piston cylinder, belt apparatus, large volume multi-anvil press). Test runs were performed at f_{O2}~IW+0.5 buffered conditions, T<1300°C and 5 GPa and demonstrate that for these conditions the fluid consists mainly of CH_4 and higher hydrocarbons like C_2H_6. The f_{O2} was monitored using an IrFe-redox sensor. No water was detected, but H_2 was found to have been present in the fluid. Our results are inconsistent with most published fluid speciation models. It is apparent that fluids with significant CH_4 contents are likely to be stable at mantle conditions recorded by some natural samples.

Peridotite melting and the effect of pressure on Ni partitioning between olivine and silicate liquid

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Sobolev et al. observed a correlation between the trace element concentrations in olivine phenocrysts (principally, Ni and Mn) and thickness of the lithosphere on which they were erupted [1]. A wide range of geochemical scenarios may be able to explain this observation: the mantle may have interacted with the Ni-rich core; the trace element concentrations may reflect presence of recycled crust, eclogite, in the mantle; or the variations may result from melting of peridotite at different temperatures and pressures [2]. Determining which, if any, of these hypotheses is responsible for the observed variation requires accurate partitioning data.

Many experiments have been conducted to elucidate how elements partition themselves between olivine and co-existing silicate melt. These experiments show that temperature (T), pressure (P), and the composition of the silicate liquid affect the observed partition coefficient; however, unambiguously disentangling the effects of these variables is difficult.

To resolve the conflation of T, P and compositional effects we turned to metal (met)-silicate melt (sil) partitioning experiments. Our isothermal experiments show that P has a strong effect on the partitioning of Ni between Fe-rich metal and silicate melt, in line with previous observations [3]. Assuming the pressure dependence of Ni-Fe, metal-silicate melt exchange is driven primarily by the changing activities in the silicate melt, we can approximate the effect of pressure on Ni-Mg, olivine-silicate melt exchange as measured by [2]. We predict that the P- effect contributes significantly to the observed systematics between 1 atm and 3 GPa [2] such that the correlations observed by [1] between lithosphere thickness and Ni content can be explained by the effects of pressure and temperature on peridotite melting.

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Halogen volatility from silicate melts

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The Earth, the Moon and other bodies in our solar system (e.g., Vesta) are depleted in volatile elements [e.g., 1]. The causes of these depletions, however, are uncertain: did the Earth form as a volatile-free body only to have a volatile-rich component added towards the end of accretion (a kind of late-volatile veneer)[2], or was the process of partial melting and vaporization on proto-planets responsible for the depletion of volatile elements observed on the Earth [3]?

In an attempt to answer these questions we measured the volatile behavior of the halogens (F, Cl, Br, and I) from a silicate melt at fixed temperature and oxygen fugacity. To do this, we performed experiments in a furnace where a crucible of melt was constantly stirred, thereby minimizing the role of diffusion. Calculations suggest the gas species of metallic volatile elements above a silicate melt are generally atomic gases (i.e., Na0) [4]. Thus, one would expect, and indeed it is observed [3] that the volatilities of these metallic components increase with decreasing oxygen fugacity. We find that non-metallic halogens, on the other hand, are more volatile at higher oxygen fugacities; for example at 1300°C a one hour experiment run one log unit below the NNO buffer, retained ~ 10% of the Cl, whereas an experiment run at the same temperature, and duration but run at an oxygen fugacity 5 log units below the NNO buffer retained ~80% of its Cl. This volatile trend is consistent with the inference that the halogens exist as anions in the silicate melt and volatilize to monatomic or dimeric gases, F, Cl2 etc. It is also consistent with the relative abundances [5] of the halogens having been established by melting and vaporization on planetary precursors.

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The stability of hydrous phases beyond antigorite breakdown for a magnetite-bearing natural serpentinite between 6.5 and 11 GPa

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Despite the relatively dry character of upper and lower mantle, the recent discovery of hydrous ringwoodite trapped in diamond has highlighted the possibility of hydration of the transition zone. This water could be transferred by hydrous minerals in subducting slabs. Thanks to numerous experimental investigations in the MgO-SiO_2-H_2O simplified system, the role of antigorite as a significant water carrier in the mantle, is well established. Its destabilization produces high pressure hydrous minerals (clinohumite, 10Å phase, chondrodite and the Dense Hydrous Magnesium Silicates: DHMS - phase A, phase E, phase D). However, recent studies in more complex chemical systems brought attention on the potential of new intermediate pressure hydrous minerals (such as the HAPY phase, Mg-Sursassite, the 11.5Å and 23.5Å phases and the HySo phase) in transporting water in the slab.

Phase relations in a natural serpentinite composition containing 5 wt.% of magnetite have been investigated using a multi-anvil apparatus between 6.5-11 GPa and 400-850°C. Post-antigorite hydrous phase assemblages comprise the DHMS phase A (11.3 wt.% H_2O) and aluminous phase E (Al-PhE, 11.9 wt.% H_2O). In addition, a ferromagnesian hydrous silicate (11.1 wt.% H_2O) identified as balangeroite $(Mg,Fe)_{42}Si_{16}O_{54}(OH)_{40}$, typically described in low pressure natural serpentinite was found coexisting with Al-PhE between 650 and 700°C at 8 GPa. Phase E stability is extended to lower pressures (8 GPa) than previously reported in simple chemical systems. The reaction Al-PhE = Grt + Ol + H2O is constrained between 750-800°C at 8 GPa as the terminal boundary between hydrous mineral assemblages and nominally anhydrous assemblages. Despite a relatively good agreement on water budgets compared to previous studies, phase assemblages and relationships in the natural serpentinite composition suggests important discrepancies with previously established phase diagrams.

The origin of high-Ca plagioclase: Combining experiments, natural observations and phase petrology

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The origin of high-Ca plagioclase in subduction related volcanic and plutonic rocks remains enigmatic. Refractory melts, diffusion-reaction processes occurring between ascending melts and gabbroic wall rocks, and re-melting of pre-existing crust are all considered to be plausible scenarios. It is well known that Ca/Na, ASI, H_2O and pressure control the composition of liquidus plagioclase. However, the role and relative importance of each is still debated. This controversy inspired me to compile existing experimental data (~1100 runs) carried out on wide range of basaltic compositions at variable P-T-H_2O-f_{O2}.

The experimental data suggest that plagioclase with An>90 crystallises only at H_2O-saturated or near-saturated conditions over a narrow range of P-T, 2 - 5 kbar and 1020-1100 ºC. However, the lack of high-P (>5 kbar) and high-T (>950 ºC) experiments with elevated initial H_2O content make it difficult to preclude stability of calcic plagioclase above 5 kbar.

The Lesser Antilles volcanic arc is an excellent case study to explore this possibility. High-Ca plagioclase with An≤96 is found in low-MgO basalts and basaltic andesites, and up to An100 in xenoliths. Experiments were performed at 5 and 7 kbars on high-Al basalt from St Kitts with Ca/Na=6, and initial H_2O ~ 5 wt.%. The aim of the study was obtaining plagioclase with An>90 and generating the most common assemblages and chemical compositions of lavas and xenolith from Lesser Antilles.

Based on this study, it is suggested that plagioclase with An ≤ 96 in equilibrium with olivine + clinopyroxene ± orthopyroxene ± amphibole assemblages can be generated between 1.5-5.0 kbar and 1100 - 950 ºC by high-Al and low-Mg basalts with H_2O close to saturation values. Exceptionally calcic plagioclase (An>96) cannot be ascribed to any explored P-T-H_2O. Rather, it could be the result of re-melting of pre-existing gabbroic residues by ascending melts. The involvement of exotic, highly refractory calcic melt is unlikely.

Investigations of high pressure transformation microstructures using multigrain crystallography

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Multigrain crystallography (MGC) allows characterizing hundreds of crystals in a polycrystalline material. This technique has also been adapted for Diamond Anvil Cell (DAC) high pressure experiments [1-3] and simulations have show that the method allows to index up to 500 grains with a theoretical resolution of 0.02° in grain orientation [4].

MGC is particularly efficient for the study of phase transformation microsctructures [5,6]. During displacive transformations, newly formed grains can keep a memory of the orientation and size of the parent grains. The microstructure o fthe newly formed phase is hence inherited from that of the parent phase. During reconstructive transformation, on the other hand, the microstructure memory is erased and the newly formed phase microstructure is not directly related to that of the parent phase.

In recent years, our group in Lille, in coordination with ESRF, combined high pressure / high temperature experiments in the resistively-heated or laser-heated DAC in order to study such processes in deep Earth minerals. For instance, we studied the perovskite to post-perovskite transformation in $NaCoF_3$ and its effect on grain sizes and grain orientations, with important implications to our understanding of the Earth's D'' layer.

In this presentation, we will present the method of multigrain crystalloraphy in the DAC and its potential for deep Earth mineral physics.

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Textures and microtextures of low degree crustal melts

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Partial melting experiments were conducted to investigate the origin of evolved magmas such as rare metal granites enriched in Li, Sn, Nb, Ta and W (RMG). One model for the origin of Variscan RMG involves low degree of partial melting of crustal protoliths. To test this model, aH_2O and temperature were adjusted to simulate the generation of low degree partial melts (<15%). Both undeformed (isotropic) and deformed (pure shear) experiments were performed to investigate the influence of deformation on melting texture and melt composition. Two different protoliths were selected as starting materials: a paragneiss (bi, pl, qz, ky, gt, fk, mu) and an orthogneiss (mu, pl fk, qz, bi) both from the metamorphic series of La Dronne (Limousin, FMC) and containing variable concentrations of metals (especially Sn and W). Microcores (plurimillimetric) cut perpendicular to the natural cleavage and sealed into gold capsules were melted at 800°C and 4kbars for 2 weeks in an internally heated vessel pressurized with an Ar-H_2 mixture (initial pH_2 = 6 bars) to control the f_{O2}. No water was added to the capsule and partial melting proceeded by dehydration melting. Experimental charges were quenched isobarically and one was deformed in torsion in a Paterson press at 800°C and 3kbars. Textures in both deformed and underformed reacted cores were imaged by SEM and Xray CT. Degrees of melting were calculated from 2D image processing. Compositions of glasses, major phases and newly formed minerals were determined by electron microprobe. Results show degrees of melting of ~8% for the paragneiss and ~12% for the orthogneiss. The melt distribution differs between the 2 samples. In the orthogneiss the melt is heterogeneously distributed and occurs preferentially associated with muscovite reaction zones. In the paragneiss, melt forms a continuous network at grain boundaries. Glass have subhomogeneous compositions close to peraluminous granites. Trace metal analysis are in progress.

Experimental determination of H$_2$O solubility in basalt at upper mantle conditions

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The solubility of H$_2$O in silicate melts has been studied extensively at pressures up to ~500 MPa – conditions relevant for understanding magmatic processes in crustal reservoirs. At upper mantle conditions, however, the solubility of H$_2$O in basaltic melt is poorly constrained due to the difficulty associated with reliably quenching silicate melts containing greater than ~10 wt% dissolved H$_2$O. To overcome this limitation, we developed a new experimental approach that relies on the use of secondary ion mass spectrometry to measure the concentration of H dissolved in olivine and using it as a proxy for the concentration of H$_2$O in the co-existing basaltic melt. The solubility of H$_2$O in the melt is determined by performing a series of experiments at a single pressure and temperature with increasing amounts of liquid H$_2$O added to each charge. The point at which the concentration of H in the olivine first becomes independent of the amount of liquid H$_2$O added to the charge indicates its solubility in the melt. Experiments were conducted by packing basalt powder into capsules fabricated from San Carlos olivine, which were then pressure-sealed inside Ni outer capsules. Our experimental results indicate that at 1000 MPa and 1200 °C, the solubility of H$_2$O in basaltic melt is 20.6 ± 0.9 wt% (2σ). This concentration is considerably higher than predicted by most solubility models but defines a linear relationship between H$_2$O fugacity and the square of molar H$_2$O solubility when combined with solubility data from lower pressure experiments. Further, our solubility determination agrees with melting point depression determined experimentally by Grove et al (2006) for the H$_2$O-saturated peridotite solidus at 1000 MPa. Melting point depression calculations were used to estimate H$_2$O solubility in basalt along the experimentally determined H$_2$O-saturated peridotite solidus. The results suggest that a linear relationship between H$_2$O fugacity and the square of molar solubility exists up to ~1300 MPa, where there is an inflection point and solubility begins to increase less strongly with increasing H$_2$O fugacity.

Quantitative determination of iron oxidation states in minerals using electron energy-loss near-edge structure spectroscopy: a geochemical application of Fe L2,3-edge ELNES revisited

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Ferric iron in bridgmanite (Brdg) has been under spotlight since we acquired reasonable probes such as Mössbaur spectroscopy, x-ray absorption spectroscopy and electron energy loss spectroscopy (EELS) to evaluate it. The crystal chemistry of Brdg can be largely controlled by the behaviour of trivalent cations of aluminium and ferric iron in the ABO$_3$ orthorhombic perovskite structure. The nature of the charge balance determines the influence on physical and chemical properties of Brdg. Fe L2,3-edge ELNES is a powerful tool to determine ferric / ferrous iron ratios in iron-bearing minerals coexisting at the submicron scale. The pioneer studies of the ELNES were mainly performed by using dedicated scanning transmission electron microscopy (STEM) and conventional transmission electron microscopy with a parallel electron energy loss spectrometry system. In the previous system a core-loss spectrum and corresponding low-loss spectrum from the same area are acquired separately in time on a single array photodiode detector. On the contrary, in our new system they can be acquired simultaneously with independent exposure times onto different domains of 2 dimension CCD detector. It incurs a negligible increase in the exposure time per spectrum. The new system can provide new capabilities such as better precision in energy scale of the Fe L2,3-edge ELNES. In this work we revisit a quantitative determination of iron oxidation states in minerals by using a new EELS system with a dual spectra mode. At first, we performed Fe L-edge ELNES of an orthopyroxene containing ferric iron in STEM-EELS mode. The energy resolution of averaged zero-loss peaks is 0.71(1) eV at full width at half maximum in the total measuring time of 50-150 sec. The measured energy values of the Fe L2,3-edge peaks are fit to those of high-spin six coordinated iron in the literature. The differences are within the value of selected energy dispersion, 0.05 eV per channel. We present Fe L2,3-edge ELNES of Brdg.

On the cooling of a deep mushy mantle

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In its early evolution, the Earth mantle likely experienced several episodes of complete melting enhanced by giant impact heating, short-lived radionuclides heating and viscous dissipation during the metal/silicate separation. After a first stage of rapid and significant crystallization (Magma Ocean stage), the mantle cooling is slowed down because of the rheological transition that occurs at a critical melt fraction of 40-50%. From this transition, the early mantle follows up its cooling from the bottom up to the surface while 10-100 km thick thermal boundary layers form above and below this reservoir (Mushy stage). Once the mantle becomes fully solidified, large-scale geodynamical coupling may eventually arise resulting in global convection and modern tectonics.

We have developed numerical models to monitor the thermo-chemical evolution of a cooling and crystallizing mushy mantle from an initially partially molten mantle. For this purpose, we use a 1D approach accounting for turbulent convective heat transfer. Our numerical model benchmarked with analytical solutions solves the heat equation in spherical geometry. This model also integrates recent and strong experimental constraints from mineral physics such as adiabatic temperature profiles and liquidus/solidus up 140 GPa for different mantle compositions.

Our preliminary results show that the mushy mantle cooling is strongly dependent on the thermal boundary layer thickness. Thick thermal boundary layers favor slow mantle cooling, inefficient heat exchanges at the core-mantle boundary and persistent molten reservoirs located below the thick shallow conductive layer. Thin thermal boundary layers enhance rapid core and mantle cooling but prevent molten layers from remaining in the upper mantle during geological time-scales. In this presentation, we will illustrate these processes and discuss the global deep consequences of this early cooling event.

X-ray Absorption Spectroscopic investigation of the Ca and Mg environments in CO_2-bearing silicate glasses

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Recent investigation showed that the CO_2 solubility in silicate melts is strongly affected by the #Mg (Mg/Mg+Ca). CO_2 solubility is decreasing with increasing #Mg implying that CO_2 molecules dissolves in the vicinity of Ca atoms to form CO_3^{2-} molecular groups. We have investigated several CO2-bearing (1.5 to 17.2 wt.%) silicate glasses using X-ray Absorption Spectroscopy (XAS) at the Mg and Ca K-edge absorption threshold in order to determine the exact molecular surrounding of Mg^{2+} and Ca^{2+} cations. Analyses of the Mg XANES region (peak positions and deconvolution) show that the Mg environment is not affected by the presence of CO_2 dissolved as CO_3^{2-} groups regardless of the CO_2 content. The Mg K-edge EXAFS simulations and XANES modelling show that the average Mg-O distance is close to 2Å and the average Mg coordination is close to 6.

On the contrary, the Ca XANES peak main resonance assigned to the 1s → n p transitions is negatively correlated with the CO_2 content and changes from 4051.4 to 4050.8 eV in between 0 and 17.2 wt.% CO_2. The Ca EXAFS simulations showed that Ca-O average distance is longer (>2.5Å) than the Mg-O distance. Furthermore, we observed that the average Ca-O distance and the Ca coordination number are positively correlated with the CO2 content: Ca-O changes from 2.5 to 2.7Å and Ca coordination number from 8 to 12 for CO_2 content changing from 0 to 17.2 wt.%.

Results suggest that CO_3^{2-} groups are dissolved in the vicinity of Ca^{2+} cations and not in the surrounding of Mg^{2+} cations which remains unaffected by CO_2 dissolution. This difference is ascribed to the tighter structural environments of Mg^{2+}. The gradual change in the Ca coordination number suggests that several CO_3^{2-} molecular are likely to be present in the surrounding of Ca^{2+} cations which could have major implications for the CO_2 diffusive behaviour or even carbonate liquid immiscibility.

2D and 3D quantification of olivine growth rates in a Hawaiian basalt: an experimental approach

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Olivine texture and morphology inform petrogenetic understanding of numerous rock types. However, olivine growth rates are not well constrained for terrestrial basalt compositions and the only experimental data available to date is from Jambon et al. (1992), who crystallized small olivine crystals (≤ 50 μm) in melt inclusions. The small size of crystals coupled with difficulties in estimating the dimensions of complex 3D skeletal crystals in a 2D section, imply substantial uncertainty in the growth-rate data. We performed crystallization experiments at 1-atm using a parental Kīlauea tholeiitic composition. Our starting material consists in 1820 CE glassy, weakly olivine-phyric (<4 vol.%) pyroclasts with a relatively primitive bulk composition (11.4 wt.% MgO, with an equilibrium olivine composition Fo85.5) (Garcia et al. 2003). Olivine phase equilibria and f_{O2} conditions are also well constrained for Kīlauea magmas (Rhodes & Vollinger 2005; Helz et al. 2017). Modeling crystallization of this sample using MELTS at 1 atm and a range of f_{O2} shows that olivine is the only crystallizing phase for an undercooling up to $\Delta T \sim 130°C$.

We carried out experiments with undercooling ΔT between 10 and 60°C, with durations at the final conditions from 45 minutes to 96 hours. We estimate the rates at which olivine grows in natural basalts as a function of undercooling in three different ways: (1) by 2D measurement of different morphologies; this method is has the disadvantage that the variety of crystal sizes and intersection effects in the charges induces important variations in the growth rates of olivine; (2) using mass-balance calculations from chemical analysis of the glass; Chemical analyzes show that olivine growth rates follow the same trend with time regardless of undercooling; (3) in three dimensions using X-ray micro-computed tomography. Growth rates calculated exceed $\sim 10^{-7}$ m/s at $\Delta T=60°C$, and phenocryst-size skeletal olivine can form in less than 1 hour.

Volatile solubility and molecular structure of kimberlite melts

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Kimberlitic melts have the deepest origin of all terrestrial magmas. They are generated by low degree partial melting of carbonated mantle peridotite, may be widespread in the upper mantle and might originally contain up to 40 wt% volatiles (CO_2 + H_2O). The solubility laws of volatiles, and their effect on the molecular structure of kimberlite melts however have never been resolved. We report the result of mix CO_2-H_2O solubility experiment successfully producing quenched volatile-bearing and volatile-free kimberlitic glass. We further investigated these glasses by FTIR, Raman and NMR spectroscopy. Our results show that kimberlite melts can retain extremely large quantities of volatiles up until the very last few kilometres of ascent before releasing them into the gas phase at a near instantaneous rate. This strongly non-linear solubility behaviour, unlike that of any other melt, can readily explains the peculiar morphology of kimberlite pipes and the depth of their root zone. Our spectroscopic investigations suggest that CO_2 has a strong effect on the melt degree of polymerisation, hinting to a major influence of CO_2 on the melt physical and transport properties.

The oxidation state of the deep Earth: Fe^{2+}/Fe^{3+}-ratios of high pressure garnets and pyroxenes

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The iron oxidation state in upper mantle minerals is frequently used as a proxy for the Earth upper mantle's redox conditions. Over the last few years, several experimental studies showed that high pressure garnet and pyroxene as well as bridgmanite incorporate increasing amounts of ferric iron at higher pressures, despite reducing conditions and redox equilibrium with iron metal [1,2]. Consequently, the Earth's mantle was modeled to be metal saturated at depths greater than ~250 km. The aim of this study is to refine this model and to establish experimentally ferric iron – f_{O2} relationships for pyroxenes and majoritic garnets at relevant pressures, temperatures and chemical compositions. High-pressure experiments at 10 GPa with a synthetic lherzolite composition were performed in a 600 ton Walker-type multi anvil apparatus at Münster University with a natural total Fe content of 8 wt% at different oxygen fugacities between ~FMQ and iron-wustite equilibria. Run products were first characterized by SEM and EPMA. We then employed two distinct methods to quantify Fe^{2+}/Fe^{3+} with high spatial resolution, TEM-EELS [3] (Zeiss LIBRA 200 FE in Münster with 0.7 eV energy resolution) and the EPMA flank method at Frankfurt University [4]. Preliminary results show a positive correlation of f_{O2} and ferric iron content of mantle minerals and confirm the observation of significant ferric iron contents in pyroxenes and garnets despite low f_{O2}. EELS and flank method results agree well within uncertainties. Further results and implications for the redox state of the deep mantle will be presented at the meeting.

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3D chemical characterization of melting at lower mantle conditions in the laser heated diamond anvil cell

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Laser-heated diamond anvil cell (LH-DAC) is a unique tool to achieve the static pressure and temperature conditions up to the deepest settings of the Earth. However, the small volume of the sample in contact with diamonds in LH-DAC produces large temperature gradient during the experiments. Therefore, the interpretation of results in these experiments depends on our understanding of this tool and the effect of temperature gradient on the resulting microstructure.

In this study, San Carlos olivine was loaded into DAC to make 3 samples at 45 GPa. Then, the samples were molten with laser heating for 1, 3 and 6 minutes. Half of the heated volume in each sample was sliced by focused ion beam (FIB) with the slice thickness of 50-150 nm. Images and energy dispersive X-ray (EDX) spectroscopy maps were acquired from each slice by scanning electron microscope (SEM). Then, the EDX maps were used to reconstruct the 3D phase distribution in the molten zone. The other half of the sample was used to make a thin section with FIB for analytical transmission electron microscope (TEM) investigations.

3D reconstruction of SEM EDX maps shows three main regions in all samples which correspond to ferropericlase (Fp) shell surrounding the molten volume, bridgmanite (Brg) region inside the Fp shell, and an Fe-rich core in the center. TEM analysis shows the presence of Fp grains in the Brg region. The results indicate that by increasing the heating time in the LH-DAC experiment, the temperature profile becomes narrower while keeping the constant peak temperature in the center. Thus, the solidification starts with Fp shell as the first liquidus phase and continues toward the center of heating following the cotectic valley of $FeO-MgO-SiO_2$ ternary phase diagram where Brg and Fp crystallize from the melt. Therefore, the core shrinks by increasing the time and becomes richer in Fe. The phases forming closer to the center are also richer in Fe due to the effect of fractional crystallization.

Rare Earth Elements fractionation in alkaline magma: an experimental approach

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Carbonatite and alkaline magmas are often associated and constitute the principal deposits of REE. Several studies suggested that the economic enrichment of those magmas is related to hydrothermal and supergene processes which remobilized the REE, but little is known about magmatic processes potentially responsible for a pre-enrichment.

The principal aim of the study is to reproduce, by high pressure and high temperature experiments, crystal fractionation and immiscibility between carbonatite and alkaline silica-undersaturated magmas to evaluate the petrological parameters ruling REE-enrichment during alkaline magma differentiation.

Previous experimental studies on trace element partitioning between carbonate and silicate melts have shown that carbonate melt REE-enrichments can vary by two order of magnitude. Such variations have not yet been linked to any experimental and petrological parameters. Therefore, there is a need for new experimental data on REE partition coefficients between carbonatite and alkaline magma at suitable pressure and temperature.

The experiments were conducted in internally heated pressure vessels and piston-cylinder at crustal and mantle conditions. The experimental charges were observed and analysed for the composition of both liquids and crystal phases with electron microprobe, and LA-ICP-MS for REE concentration. Finally, we calculated carbonate/silicate melts and crystal/melts REE partition coefficients.

Our results confirmed the large variation of REE partitioning, from minor to massive enrichment into carbonate melts (up to 40 times more). In fact we found that this variation is explained by a perfect correlation between REE and Ca partition coefficients, for all experimental conditions. Thus only Ca-dominated carbonatite in coexistence with alkaline magma are highly enriched in REE.

Based on REE-Ca partitioning correlation and on silicate melt composition, a predictive modelling has been made to assess carbonatite REE enrichments.

Carbon solubility in silicate under reducing conditions and the Implications for Mercury

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Mercury is the smallest planet of our Solar system and also the closest to the Sun. It is characterized by a very large core (70 vol.% of the planet) and its surface is highly depleted in FeO. These features have been interpreted as an evidence for primary differentiation of Mercury under very reducing conditions (IW-5±2; with IW being the iron-wüstite equilibrium). The primordial crust of Mercury may have been made up of graphite and would have formed by graphite flotation during solidification of a magma ocean. Recent neutron spectroscopy measurements in deep craters by the MESSENGER spacecraft show abundant C concentration (1-3 wt%) interpreted as relict from a primordial graphite crust. In order to model the formation of such a crust and to estimate its likely primordial thickness, carbon solubility data at graphite saturation are needed. Recently published data between IW and IW-4 show that the C content of the metal decreases continuously as the oxygen fugacity conditions become more reducing. The behaviour of C in the silicate melt is however more complicated and may significantly change as a function of the speciation of C in the silicate melt (methane or carbonate). New SIMS measurements at conditions between IW and IW-9 will be presented. We will show how extremely reducing conditions affect carbon solubility at graphite saturation. These new results will then be used to model the formation of Mercury's primary crust.

Study of primitive olivine-hosted melt inclusions from the Ecuadorian arc

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We present geochemical data from primitive olivine-hosted melt inclusions (Fo82-89) selected from the most primitive lavas (Mg#>60) of the Ecuadorian Arc belonging to Puñalica and Sangay volcanoes. Melt inclusions (MI) from both volcanoes are mostly Ne-normative and volatile-rich (F, Cl, S) and only Sangay MI are Ca-rich (up to 16 wt.% and $CaO/Al_2O_3<1$). Sangay and Puñalica melt inclusions display trace element patterns typical of arc-related magmatism, namely a negative anomaly in Nb and Ta and enrichment in LILE and LREE. We deciphered the source lithologies and the metasomatic agents for both volcanoes. Major elements (e.g. Al_2O_3 wt. %) and variable La/Yb point to a garnet-bearing peridotite as the sources of Puñalica MI. Prior to partial melting, the source of Puñalica MI was metasomatized by slab-derived melts associated to the Grijalva Fracture Zone (GFZ) characterized by high volatiles (e.g. F, Cl), low Ba/Th, Sr/Th and high Th/La. Based on major and volatile elements (high F/Cl), the source of Sangay MI is explained by mixing between amphibole-bearing clinopyroxenite and peridotite-derived melts. The slab component added to the source of Sangay MI is interpreted as an aqueous fluid with higher Ba/Th, Sr/Th and lower Th/La than Puñalica MI. We conclude that (1) the hydrous-siliceous melts derived from the slab are present at least until the southern boundary of the young oceanic crust including the Carnegie Ridge, and that (2) the slab metasomatic agent coming from the older slab to the south of GFZ is dominated by an aqueous fluid.

Basaltic magmatism's biased record of mantle chemistry

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The chemistry of erupted magmas provides our main window into the composition of Earth's convecting mantle. However, magmatic differentiation in the crust can impose significant biases on our picture of mantle chemistry. Here we investigate how the capacity of basaltic magmas to survive crustal processing is affected by the major and volatile element compositions they inherit from their mantle sources. By performing internally heated pressure vessel experiments on analogues of primitive melts derived from lithologically distinct sources under realistic storage conditions (300 MPa, 1140-1260 °C), we show that enriched melts from recycled and potentially pyroxenitic sources retain higher melt fractions during cooling than depleted melts from lherzolitic sources. In ocean island settings, variations in magmatic water (H_2O) content may also impart biases: hydrous magmas are more likely to survive than their anhydrous equivalents. Hence, the melts most likely to survive differentiation and contribute to erupted magma mixtures are more H_2O and incompatible-element enriched than average mantle melts, biasing the record of basaltic magmatism towards hydrous and enriched mantle sources. This can explain why mid-ocean ridge basalts often show anomalous over-enrichments during differentiation and indicates that their cargoes of anorthitic plagioclase are remnants of depleted, lherzolite-derived melts.

Metal-silicate segregation in early-accreted bodies of the Solar System: insights from interfacial energies, connectivity and 3D microtomography

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Meteorites preserve a record of accretion and evolution of primitive bodies in the early Solar System. The study of primitive achondrites indicates that metal-silicate segregation occurred in bodies that reached temperatures high enough to partially melt both metal and silicate. Liquids have to form interconnected networks to segregate, thus the determination of the interconnection threshold is of prime importance. This parameter is a function of composition, interfacial energy and proportion of each phase, thus difficult to predict in multi-phase systems of natural complexity.

To provide relevant constraints, experiments have been performed using a three-phase system consisting of forsterite, silicate melt and nickel, in a controlled atmosphere furnace (1440-1470°C, $\log(f_{O2})$=-8.5). First of all, we find that high magnification of SEM images (x3000) is essential for accurate measurement of dihedral angles and the associated interfacial energies. Besides, the relationships between these energies vary with the composition of the metal-rich phase (i.e. S-content), leading to different equilibrium geometries and thus, varying interconnection thresholds. However porosity is present in these experimental charges and may have an influence on the organization and dynamics observed. Piston-cylinder experiments have been conducted (1500°C, 0.8 GPa) to check these effects. Comparison indicates that porosity has a major effect on the 3D organization of the system and possible time-dependent changes. Porosity can either decrease the interconnection threshold or form channels along which liquid nickel may flow, depending on the degree of connectivity of the crystalline matrix. Quantification of the interconnection threshold of nickel is in progress using piston-cylinder experiments.

Experimental study of the Ultra High T metamorphism of a restitic metapelitic granulite: role of a previous partial melting event on the UHT metamorphism and influence of the redox state

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The origin of UHT metamorphism prevailing in the continental crust is still matter of debate. Partial melting probably plays a key role. UHT metamorphism occurs at temperatures above the fluid-absent melting of most crustal rocks. Partial melting is an endothermic process that consumes heat and buffers the temperature at around 750-850°C. Thus, partial melting prevents a fertile crust to attain UHT. Conversely, UHT conditions can be more easily reached upon refractory / restitic rocks and occur preferentially in terranes that underwent previous partial melting event and melt loss.

The Gruf complex (Lepontine Alps) is a field area that confirms this scenario; it is one of the rare occurrences of Eocene UHT metamorphism in the world. This complex previously suffered the post Hercynian high-thermal regime responsible for the widespread formation of granulites in the Austro-alpine domain and Southern Alps. We propose that the typical UHT parageneses of the Gruf complex crystallized from refractory/restitic lithologies. The refractory character was acquired through fluid-absent melting reactions during the post Hercynian metamorphic event, while UHT conditions were reached during the Alpine cycle.

The typical mineral assemblage diagnostic of UHT metamorphism Spr + Qtz is sometimes replaced by the Spl + Qz assemblage under similar P-T conditions. The reason for this dichotomy is not yet understood.

In order to bring new elements to this discussion, we conducted experiments in an internally-heated pressure vessel on a metapelitic granulite from the Ivrea zone composed of Q-Grt-Sil-Kf±Pl±Bt±Rt. This rock is representative of a component of the lower crust after melt extraction. It would represent a restite associated with the process of differentiation of the crust.

The P and T intervals considered during these experiments were 0.3-0.8GPa and 950-1050°C; their duration lasted 7 or 13 days. Between 0.8-0.6 GPa, the paragenesis is Spr-Opx-Sil-Qz-TiMag-Melt (and Grt at T < 950°C) for the long-time experiments. For the short-duration experiments (same, P, T, and X), the paragenesis is Spl-Qz-Sil-TiMag-Melt. We interpret the change of paragenesis to a change from reducing (short-duration) to more oxidizing conditions (long-duration) due to progressive loss of hydrogen during the experiments at very high temperatures. At 0.3GPa, the stable assemblage is Spl-Qz-TiMag-Ilm-Melt-Crd and/or Osm and Grt at T>900°C, whatever the duration of the experiment.

In conclusion, our experiments show that UHT conditions applied to a restite from the lower crust produce typical parageneses of UHT metamorphism. They also suggest that Spl-Qz assemblages are indicative of reducing conditions while Spr-Qz assemblages prevail under more oxidised conditions.

Experimental determination of the hydrogen storage capacity of olivine in the subducting slab and the mantle wedge

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Subduction causes the largest chemical recycling system on Earth. A significant reservoir after complete slab dehydration corresponds to nominally anhydrous minerals where hydrogen is incorporated as complex defects in the mineral structure at the level of ppm of equivalent H_2O. Transient fluid saturated conditions in the mantle occur in two important settings: [1] in the subducting slab during dehydration reactions (from ca. 5 GPa/600 °C to 3GPa/800 °C) and [2] in the mantle wedge (P > 3 GPa, T= 900-1050 °C). The extrapolation of current solubility laws to these two settings is uncertain. Here, we report new subsolidus experiments to constrain the maximum H solubility in olivine at conditions relevant for subduction settings.

The P and T sensitivity of the two most important hydrous defects in mantle olivine involving Si-vacancies (associated to titanium [TiChu-PD] or pure Si-vacancies [Si]) was investigated in a fluid-saturated natural peridotite from 0.5 to 6 GPa (ca. 20-200 km) in a temperature range from 750 to 1050 °C using piston cylinder apparatuses. Water contents in olivine were monitored in sandwich experiments with a fertile serpentine layer in the middle and olivine sensor layers at the border. Textures and mineral compositions provide evidence that olivine completely recrystallized during the week-long experiments allowing to formulate a site-specific water solubility law. [TiChu-PD] is the most relevant defect for the shallow upper mantle (P ≤ 3 GPa, i.e. ≤ 100 km). Water content in both defects decreases significantly at the onset of hydrous melting. Chlorite dehydration in the partially hydrated slab is roughly parallel to the isopleth of 50 ± 20 ppm wt. H_2O. Hydrous defects are dominated by [Si] under the relevant conditions for the mantle wedge affected by fluids coming from the slab dehydration. At 1.5 and 5.5 km from the slab surface the storage capacity of the mantle wedge ranges from 100 to 900 and 400 to 2,000 ppm wt. H_2O respectively.

Variations in $Fe^{3+}/\Sigma Fe$ ratios in sediment-derived silicic melts at sub-arc depths

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Island arc basalts (IAB) typically show a higher $Fe^{3+}/\Sigma Fe$ ratio compared to that of ocean island basalts and mid-ocean ridge basalts [1-4]. It is argued that the sub-arc mantle is globally more oxidized than the depleted mantle [1-4]. Fe^{3+} enrichment in IABs was suggested to be caused by metasomatic agents expelled from the slab and percolating through the mantle wedge [3]. Prime candidates for these are sediment-derived melts for two reasons: firstly, Fe3+/ΣFe is typically high in subducted sediments (~0.82; [5]); secondly, Fe^{3+} is much more mobile in silicate melts than in aqueous fluids [3]. Previous experimental studies [6,7] were carried out mostly on $Fe^{3+}/\Sigma Fe$ ratios in silicate melts at P < 1 GPa conditions. Data at higher pressures remain scarce.

Using piston-cylinder apparatus, we have run melting experiments on a synthetic sediment composition close to GLOSS-II [8] at 2.5-3.0 GPa and 1600°C. A large range of oxygen fugacities has been explored, from reduced (~FMQ-2) to very oxidized conditions (~FMQ+4) while variable H_2O contents (0-10 wt%) were added. Metaluminous silicic glasses were analysed using electron microprobe, FTIR and Mössbauer spectroscopy. To facilitate the latter, ~20% of the total Fe content of the starting bulk was added as [57]Fe.

This study is a first step in constraining the redox state of Fe in silicate melts expelled from slab lithologies during subduction at 2.5-3.0 GPa and in assessing the efficiency of these melts to transfer of Fe^{3+} from the slab to the wedge.

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Acoustic velocities across the olivine – wadsleyite – ringwoodite transitions and the seismic signature of the 410 km mantle discontinuity

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The phase changes of olivine $(Mg,Fe)_2SiO_4$ to its high pressure polymorphs, wadsleyite and ringwoodite, have long been associated with the seismic discontinuities observed at 410 and 520 km depth in the Earth's mantle. The position and thickness of these discontinuities potentially provide basic constraints on the temperature, chemical composition and water content of the mantle. A common practice is to infer these properties by comparing seismic observations with modeled velocities from equilibrium phase relations and elastic moduli of the individual phases. Here, we propose to directly measure the evolution of velocities across the olivine phase changes in order to investigate the transient, i.e. time-dependent, processes of the transformation.

We developed an experimental method that combines in situ X-ray diffraction and ultrasonic interferometry to follow the elastic wave velocities as a function of reaction progress, with a time resolution of ~ 30 s. The experiments were carried out on the 1000 t multi-anvil press of the ID-13D beamline of the APS synchrotron (Chicago, USA). Samples were sintered polycrystalline powders of olivine with $X_{Fe}=0.10$ and $X_{Fe}=0.52$ composition, that have been reacted in the stability field of wadsleyite or ringwoodite at 7-12 GPa and 1000-1200 K. Measurements show an unexpected decrease in shear waves velocity at the onset of reaction, followed by a steady increase that correlates with the percentage of transformation. This velocity anomaly is coupled with an increase in attenuation as observed from amplitudes of S-waves echoes. We interpret this softening at the early stage of transformation as the result of the presence of an intermediate spinelloid phase, as observed in the pseudo-martensitic reaction mechanism, and discuss the implication on the structure and sharpness of 410 km discontinuity.

Toward 4D X-ray imaging under extremes conditions

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Upon the last decade, many efforts have focused on the implementation of the in situ 3D tomography technique towards high pressure and temperature conditions, using either dedicated DACs or large-volume presses. For instance, the RoToPEc device is a static high-pressure press where the opposed anvils rotate under load up to ~ 10 GPa for a full 360° acquisition of CT scans [1]. It has been successfully applied to study the evolution of microstructure, phase distribution, strain state and volume changes of materials under extreme P-T-stress conditions [2, 3]. With the advent of high brilliance, high-energy and spatially coherent synchrotron X-ray beams, as well as continuous development of high efficiency fast detectors and algorithms, the next challenge is to explore the time dimension. Here, we will present recent development of high-speed X-ray tomography using a pink beam through a standard PE press and algebraic reconstruction technique allowing complete high-resolution tomograms to be acquired in the minute to second range. This provides the opportunity to perform near real-time four dimensional imaging for the characterization of dynamic phenomena in geosciences or materials science. The potentialities of this new equipment will be illustrated by the case study of the migration of carbonate melts through a solid silicate matrix under the conditions of the Earth's mantle.

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Carbon Isotope Fractionation between CO$_2$ and Carbonate Melt

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Ab initio calculations on carbon isotope partitioning in the CO2-carbonate system yield a decidedly non-linear fractionation behaviour between 500 and 1000°C [1,2]. However, only limited experimental data are available that test this prediction [2,3] and isotope fractionation experiments involving carbonate melts have not been reported yet.

With this study we present our results on carbon isotope partitioning for the CO$_2$ - carbonatite pair. For this purpose, we equilibrated Na,K,Ca,Mg - carbonate blends with CO$_2$ at 500 to 1100°C, atmospheric pressure. Experiments were conducted in vertical gas mixing furnaces under a continuous stream of pure CO$_2$. The carbonate starting materials are composed of various binary mixes of Na_2CO_3, $CaCO_3$, K_2CO_3, and $MgCO_3$ in eutectic proportions to assure batch melting. Starting materials (carbonates and CO$_2$) as well as run products were characterized for $\delta^{13}C$ using a GasBench II (Carbonates) and a HP 8610 gas chromatograph (CO$_2$) connected to a ThermoFisher Delta V isotope ratio mass spectrometer (IRMS).

Our first results suggest a rapid isotope exchange rate between CO$_2$ and carbonate melt, i.e. isotopic equilibration within hours and as to be expected a much faster attainment of isotope equilibrium relative to the solid-state system. Carbon isotope fractionation amounts to 3.21 - 1.14 ‰ at 850 - 1000°C, respectively, with CO$_2$ being always isotopically heavier. The results appear in good agreement with previous experimental and theoretical studies on calcite, suggesting that the binding environment in the CO$_3$-groups of calcite and carbonate melt are similar enough to not cause any differences in isotope fractionation.

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Linking H$_2$ concentration and redox state (f_{H2} and f_{O2}) in H$_2$O-H$_2$-NaCl fluids

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Hydrothermal processes such as serpentinization involve complex H$_2$-rich fluid mixtures whose thermodynamic properties are poorly known. One parameter that needs to be better constrained is the molal activity coefficient of H$_2$ dissolved in the fluid ($\gamma H_2(aq)$). Knowledge of this parameter is critical to link the H2 molality (mH$_2$(aq), commonly measured in hydrothermal fluids) and the H$_2$ fugacity ($f_{H2}(v)$, one redox parameter) by using:

$$f_{H2}(v) = \gamma H_2(aq) . mH_2(aq) . K$$

where K denotes the equilibrium constant for the reaction:

$$H_2(aq) = H_2(v) \text{ (Rn1)}$$
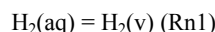
It is commonly assumed that $\gamma H_2(aq) \equiv \gamma CO_2(aq)$ at the same T. However the few determinations of $\gamma H_2(aq)$ suggest a complex dependence with P$_{Tot}$, T and mNaCl [1], and so systematic data are needed. In this study we have developed an experimental setup allowing $\gamma H_2(aq)$ to be determined in H$_2$O-H$_2$-NaCl fluids at T = 250 to 450°C and P$_{Tot}$ = 20 to 50 MPa. The experiments are performed in large-volume Dickson-Seyfried bombs fitted with an $Au_{20}Pd_{80}$ (wt.%) H$_2$ permeable membrane for in situ f_{H2} monitoring and allowing fluid sampling and mH$_2$(aq) determination by gas chromatography. With K for reaction (Rn1) known from thermodynamic data, $\gamma H_2(aq)$ can be determined.

For the pure H$_2$O-H$_2$ system, our $\gamma H_2(aq)$ values are close to 1 (1.1 at 250°C and 1.0 at 300°C; 50 MPa), confirming the validity of our experimental setup. In experiments performed with NaCl (3.2 wt.%), first measurements show, as expected, an increase of $\gamma H_2(aq)$ with T. At 30 MPa, $\gamma H_2(aq) = 2.1$ (at 250°C) and 2.9 (at 300°C); at 50 MPa, $\gamma H_2(aq) = 1.1$ (250°C) and 2.2 (300°C). Those preliminary results also confirm the strong dependence of $\gamma H_2(aq)$ with P$_{Tot}$ [1]. Furthermore, the measured $\gamma H_2(aq)$ are significantly > 1. This implies that, for a given mH2(aq), the f_{H2} of H$_2$O-H$_2$-NaCl fluids will be higher and so the f_{O2} lower (more reducing conditions) than expected.

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The effect of redox on the viscosity of halogen-bearing basaltic melts

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The viscosity of halogen-bearing basalt (MORB) was studied as function of the oxygen fugacity from log f_{O2} -0.7 to -9.0. The melts with different Fe^{2+}/Fe_{total} were synthesized in a 1 atm gas mixing furnace at 1473 K using a CO_2/H_2 mixture. All samples were quenched with a rate of 200 K/min. The high viscosity measurements were performed by micropenetration techniques in the range of $10^{8.5}$-$10^{13.5}$ Pa.s and the Fe^{2+}/Fe_{total} was determined by wet chemistry and colorimetric methods. The effect of f_{O2} on the iron speciation results in an increase from 0.16 to 0.82 in Fe^{2+}/Fe_{total} due to decreasing in log f_{O2} from -0.7 to -9. This is an increase of network modifier Fe2+ accompanied by a 0.5 log unit decrease in viscosity at 700°C. The addition of halogens to the present peralkaline melts synthesized in air results in a 0.05 increase in Fe^{2+}/Fe_{total} for 1.0 mol% Cl and a 0.05 decrease for 1.3 mol% F by a constant oxygen fugacity. Previous investigations have demonstrated that the addition of Cl to peralkaline melts synthesized in air resulted in an increase in Fe^{2+}/Fe_{total}, whereas the addition of F as well as (Cl + F) resulted in a decrease in Fe^{2+}/Fe_{total}. The chlorine-bearing melts synthesized in air show a decrease in viscosity by 0.5 log unit due to the addition of 2.8 mol% Cl and the addition of 7.7 mol% F to the present basalt results in a decrease in viscosity by 1.5 log unit. The increase of Fe^{2+}/Fe_{total} due to decreasing of f_{O2} in the halogen-free basalt results in a decrease in the viscosity by 0.5 log unit. This effect is enhanced by a further 0.5 log unit due to the addition of Cl, F as well as (Cl + F). Thus, the viscosity of basaltic magmas is not only a function of composition and temperature but also oxygen fugacity, halogen content and melt structure.

The impact of sulfur on the transfer of platinoids by geological fluids

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A remarkable feature of the geochemistry of platinum group elements (PGE) is their intimate association with reduced sulfur. Current models of PGE deposit formation are focused on the magmatic stage at which PGE are concentrated with Fe-Cu sulfide minerals and melts; however, there is growing evidence of PGE (re)mobilization by aqueous fluids in various geological settings ([1] and references therein). Yet, existing data on aqueous chloride, sulfate, and hydroxide PGE complexes yield far too small metal contents (<ppb) in fluids from most geological settings to account for such fluid-phase mobility [2], thus calling upon an important role of the sulfide and, potentially, trisulfur ion ligands in PGE transport.

To gain quantitative insight into the role of S-bearing fluids in the fate of PGE, here we combined solubility measurements, in-situ X-ray absorption spectroscopy (XAS), and physical-chemical modeling based on recent advances of our knowledge of S speciation in crustal fluids [3,4]. Our results demonstrate enhanced solubility of Pt both in reduced (HS-/H_2S) and oxidized (H_2S/SO_4/S^{3-}) model hydrothermal solutions over a wide pH range (4-7), attaining values of 100s ppm Pt, which is ~5 orders of magnitude above the Pt average lithospheric abundance. Furthermore, XAS spectra reveal significant differences between HS-bearing (pH>6) and S3-bearing (pH<5) solutions, demonstrating, for the first time, the existence of Pt species with the trisulfur ion, similar to those recently proposed for gold [5].

Thus, our new data imply a potentially important (but largely underestimated so far) contribution of S-bearing hydrothermal fluids in PGE transfer and accumulation in the Earth's crust.

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Unraveling the formation of economic tungsten deposits in the Earth's crust in hydrous fluids: Solubility of scheelite ($CaWO_4$) in supercritical fluids in the system H-O-Cl-F

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Tungsten (W) is a so-called "strategic technology metal" which is of great economic importance due to its applications in hard materials, filaments, electrodes, satellites or similar technological equipment. W products are mainly (>80%) supplied by Chinese producers and future W shortages have been projected by the EU due to insufficient exploration for W. Therefore, W has been added to the EU list of "critical metals". To possibly aid future exploration for W, one needs to better understand the formation of W-rich deposits in the Earth's crust.

It is well known that W mineralization occurs in the Earth's crust and enrichment of W is due to interaction of supercritical hydrothermal fluids with crustal rocks. Main W-rich minerals in such hydrothermal ore deposits are scheelite ($CaWO_4$) or wolframite (($Fe,Mn)WO_4$). In order to model mineral mobility in fluids or precipitation of W ores, one needs a thorough understanding of mineral solubilities as a function of P, T and fluid composition. However, there is overall scant experimental data on W-mineral solubilities in high-P and high-T crustal hydrothermal fluids. Moreover, previous results from quench-experiments resulted in conflicting experimental evidence for W speciation in hydrothermal fluids.

Here, we present results of an in-situ EXAFS study on scheelite ($CaWO_4$) solubility and W speciation in supercritical fluids at conditions relevant to ore formation in Earth's crust. Experiments were performed at BM30-FAME at ESRF (France) at T between 30-600°C at a pressure of 600 bar, using a dedicated high-temperature high-pressure autoclave. XAS measurements were performed in transmission and fluorescence geometry on heating -dissolution cycles of CaW04 in H_2O solutions with HCl or HF (0.01 m to 5.0 molal).

Preliminary results that scheelite solubility depends on temperature and fluid composition. Final results will be presented during the conference.

OH-defect incorporation in quartz in granitic systems at 1-5 kbar

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Quartz is the second most abundant rock-forming mineral in the Earth's crust and occurs as a main phase in igneous, metamorphic and sedimentary rocks. Quartz incorporates trace elements (e.g. H, Li, Al, B, and Fe) in the crystal structure depending on the formation conditions in different geological environments. In this experimental study we focus on OH-defect incorporation in quartz from granites over a pressure/temperature range realistic for the emplacement of granitic melts in the upper crust. Piston cylinder and internally heated pressure vessel synthesis experiments were performed in the water saturated granitic system at 1 – 5 kbar and 600 – 950 °C. A mixture of natural granite doped with additional quartz powder and 12 – 18 wt% H_2O was used as starting material. Successful runs consisted of a free aqueous fluid, amorphous quench material and quartz crystals that were successively analysed by FTIR spectroscopy. Crystal homogeneity was verified by FTIR-imaging of one particular crystal. IR absorption bands can be assigned to specific OH-defects and discriminated qualitatively and quantitatively. Preliminary results show: 1) the AlOH band triplet around 3310, 3380 and 3430 cm^{-1} is the dominating absorption feature in all spectra, 2) the LiOH-defect band at 3470-3480 cm^{-1} increases strongly with pressure, 3) the total OH-defect content increases with pressure in the range of 3 kbar (125 wt ppm H_2O) to 4.5 kbar (500 wt ppm H_2O), which is in contrast to a recent experimental study in a similar system between 5 to 20 kbar, where decreasing OH-defect contents with increasing pressure were observed. Thus, the current data suggest the existence of a maximum in OH-defects in quartz between 4 and 5 kbar. These new findings underline the high potential of OH-defect content in quartz to be used as petrogenetic indicator.

Water pumping induced by shear localization during high-pressure experiment

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Strain localisation commonly affects naturally deformed rocks of the crust and mantle. In the ductile regime, this gives rise to shear zones where the deformation of fine-grained phases involves creep cavitation and possible fluid pumping to occur with strong implications for geological processes. However, as some dilatancy are expected during creep cavitation, it remains challenging for these mechanisms to be relevant at high pressure, typically when differential stresses are far below the lithostatic pressure, i.e., below the Goetze criterion. Based on ion probe analyzes, we here document the water content of a fine-grained (1-2 μm) olivine matrix deformed experimentally in presence of water added (1330 ppm) and coarse-grained (> 100 μm) diopside (30 %). The experiments were carried out at 1.2 GPa, 900 °C and a differential stress of maximum 0.9 GPa. They also gave rise to pronounced sample-scale strain localisation within a narrow shear zone (~ 50 μm thick), giving the opportunity to probe across a post-mortem strain gradient. Through data interpolation, our ion probe dataset reveals high water concentration – higher than initially added (> 2000 ppm) – where strain has been localized. Furthermore, based on high-resolution measurements of olivine grain size, we show that water content does not follow the trend of the expected porosity related to grain size reduction. Instead, we document a deficit of water in the low-strain region and an excess of water in the high-strain zone. Together with evidence of Zener-stroh cracking and other cavitation, these features indicate the presence of strain-induced cavities where water has been pumped and trapped as fluid inclusions. This definitely supports creep cavitation to occur at high pressure below the Goetze criterion, suggesting that related fluid pumping may persist at great depths despite increasing pressure.

Evaporative Iron Loss During One-Atmosphere Gas-Mixing Experiments

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Iron loss to the sample container presents a well-known challenge for experimentalists studying Fe-rich systems. In one-atmosphere gas-mixing furnace experiments, the experimental charge is often suspended in a vertical tube furnace on a metal loop. Platinum wire is commonly used, however Pt in contact with silicate melt will extract Fe to form Pt-Fe alloys [1]. An alternative to Pt, Re wire minimizes Fe-loss in experiments conducted at reducing oxygen fugacities [2].

Using the Re wire loop technique, we performed experiments on ultramafic glass compositions with oxygen fugacities ranging from f_{O2} = IW-1 to IW+2. We measured the Fe isotopic composition of each experimental sample, Re loop, and starting material. We observed Fe isotopic fractionation between the sample and Re wire, similar to that observed previously for Pt wire [3]. However, isotopic mass balance for Fe between the wire and sample requires a reservoir for light Fe isotopes that is not accounted for by the analyzed materials. We have identified this missing reservoir as Fe vapor, i.e. there is evaporative loss of FeO during the experiment.

Though Fe loss has been previously assumed as loss via diffusion into the Re metal container, we have determined that evaporation is the main mechanism of Fe loss. Considering both the thermodynamics of FeO vaporization and the Fe isotopic mass balance of our experiment parts, we have quantified the amount of Fe in each experimental reservoir (sample, wire, gas). We find that Fe-loss to the Re wire accounts for 3-36% of the total Fe-loss, while evaporative Fe-loss accounts for 64-97%. At lower f_{O2} we observe an increase in the Fe-loss through Fe-Re alloy formation, consistent with previous studies [2], as well as an increase in the total amount of vaporized FeO, suggesting there is an f_{O2} control on the evaporative process.

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The breakup of liquid iron diapirs within the magma ocean

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The latest stages of planetary accretion probably involved large impacts between differentiated bodies and large scale melting events. The energy brought by giant impacts could be added to the energy associated with the accretionary energy and with the radioactive heating caused by the decay of short-lived radio-elements (^{26}Al and ^{60}Fe). These early heat sources may have caused the formation of deep magma oceans where the iron brought by the impactors can sink and eventually fragment. A subsequent metal/silicate separation can occur via negative diapirism and contributes to core formation. Yet the process of liquid iron segregation within a magma ocean remains poorly known. We perform numerical simulations using COMSOL Multiphysics to model the sinking dynamics of an initially spherical iron liquid diapir within a molten silicate phase. We use a 2D cylindrical axisymmetric computational domain. We vary the viscosity of the silicates in the range of 0.05 Pa.s to 100 Pa.s and the initial radius of iron diapir in the range of 1mm to 100mm. Our numerical models constrain the morphology of the iron flow, the potential exchange surface between the iron and the silicate phases, the characteristic sinking time and the iron fragmentation modes that depend on the dimensionless Weber number. Our models show that the fragmentation of the liquid iron occurs falling a sinking distance equal to 4-8 times its initial radius. We show that increasing the viscosity of the silicate phase relative to the iron viscosity prevents oscillations of the iron phase and limits the exchange surface between the iron and the silicate phases. Oppositely, increasing the initial radius of the iron diapir enhances its deformation and increases its exchange surface with the silicates.

Raman imaging D/H diffusion in experiments

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The interactions of fluids and rocks are studied and quantified using isotopic compositions. Quantitative interpretation relies on obtaining reliable diffusion coefficients. In order to measure D/H exchange kinetics, we reacted various rocks and minerals with liquid D_2O at high pressure and high temperature in a Belt apparatus in the range 1.5 to 3.0 GPa and from 315°C to 540°C, and also at room pressure in Ar-D_2 atmosphere. Samples are then analyzed by Raman micro-spectrometry, from which D/(D+H) maps are calculated, in order to quantify the exchanges between hydrogen (H) from the hydroxyl (OH) groups and deuterium (D) from the deuterated water or gas. Results on antigorite, chlorite, amphiboles, and Ca-rich hydrous silicates will be discussed and compared with forme studies. High activation energies suggest that D/H diffusion may be less rapid at low (>400°C) than previously extrapolated from higher temperatures experiments.

Refinement and Application of Calcic Amphibole Thermobarometry for Volcanic Rocks

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Amphibole plays a crucial role in the study of several earth and planetary processes. One of its most common application is thermobarometry, especially for volcanic systems. However, many amphibole models require the input of the melt composition which is not always available in volcanic products (e.g. partially crystallized melts or devitrified glasses). By contrast, the model of Ridolfi & Renzulli (2012), valid for Mg-rich calcic amphiboles in equilibrium with calcalkaline or alkaline melts across a wide P-T range, presents the advantage to be a single-phase application with relatively low errors (P±12 %; T±23 °C). This model relies on an empirical procedure to estimate the best P value obtained from a series of barometric equations obtained through multivariate linear regression of experimental data. Once P is constrained, the model can be used to estimate T, f_{O2} and melt composition by other equations.

In order to refine this single-phase model and understand its limitations and the extent of its use, we have performed a series of experiments in P-T ranges of 120-630 MPa and 730-1045°C. Our results show that this method can be confidently used whenever amphibole crystallization occurs at equilibrium conditions. By contrast, its application to amphiboles crystallized during kinetic (e.g., cooling) experiments could result in large P overestimations (up to 200%).

We present case studies and methodological suggestions for detecting compositional and textural features of volcanic amphiboles crystallized at equilibrium conditions, hence optimizing the accuracy of crystallization P (and depth) determination. Finally, we show that the depth-T conditions of amphibole equilibrium crystallization are consistent with those of independent methods, such as seismic tomography, pre-eruptive seismicity and other thermobarometric methods for characterizing magma chambers.

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Rapid segregation of carbonate melts from subducting slabs

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Carbon is recycled into the mantle via subduction and released through volcanic outgassing, but an important fraction of C is retained at depth [1]. Partial melting of subducted lithologies produce alkaline (Na, K) carbonate melts that infiltrate the mantle wedge [2]. These melts are linked to the source regions of diamond-bearing kimberlites and act as effective metasomatic agent due to their excellent wetting properties [3,4]. Although the petrogenesis of carbonate melts has been studied for decades, their physical properties remain largely unknown. The density is of particular interest due to its influence on percolation, ascent rate and buoyancy relations with surrounding rocks.

Here we report in-situ density measurements of alkaline carbonates at crustal and upper mantle conditions using synchrotron X-ray absorption in a Paris-Edinburgh press at beamline Psiché (Synchrotron Soleil). Experiments were conducted on samples along the $CaCO_3$-K_2CO_3 and $MgCO_3$-K_2CO_3 joins up to 2.9 GPa and 2018 K. The molten stage of the sample was confirmed by angular X-ray diffraction prior to the density measurements. The results show melt densities lower compared to any known liquid/solid under these conditions. The density data were fitted to a third-order Birch-Murnaghan equation of state to derive a robust model for these liquids at upper mantle and lower crust conditions. Combined with available data [5] on the viscosity, the melt mobility could be determined as a function of depth. It will be shown that the separation velocity of the alkali carbonate melts is fast enough to trigger formation of vertical dykes, in which the melt can travel at ultra-high rates back to the surface.

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Stability of carbon and sulfur-rich metals in the deep Earth's mantle

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It is widely accepted that Earth's deep mantle is highly reducing, and consequently Fe-rich metals are stable in the rocks deep inside the Earth [1-3]. However, it has recently been suggested that metal melts could also be stable in the deep Earth which may be the major host for light elements like carbon and sulfur [4]. This hypothesis is strongly supported by recently performed analyses of metal, carbide and metal melt inclusions found in large diamonds like Cullinan, Constellation, and Koh-i-Noor [5]. As it is well known that alloying and incorporation of light elements can significantly change melting temperatures, it is vital to determine melting temperatures and the sub-melting phase diagram of the Fe-Ni-S-C system at relevant P-T condition in order to understand the possible formation of metal melts and diamonds. Up to now melting temperatures were based on quench experiments whose textures were generally difficult to interpret. We studied the Fe-Ni-S-C system at high-pressures and high-temperatures by in-situ XRD to derive subsolidus phase diagrams and the Clapeyron slope of solidus and liquidus to understand the nature of the reduced species at depth. We performed four successful experiments at ID06 LVP at ESRF Grenoble, two runs at 10 and 19 GPa respectively. We studied two different compositions with varying Fe/Ni and (Fe,Ni)/S ratios at each pressure and collected diffraction patterns continuously during heating from room T to superliquidus conditions. Run pressures were calculated from EOS of Fe metal, Ni metal and MgO; temperatures were calculated from the thermal EOS of MgO.

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Experimental study of Halogens partitioning between apatite, fluid and silicate melts

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Volcanic activity is responsible for the constitution of our atmosphere during geological times. In the atmosphere halogens (Cl, F) are present in trace amounts but are relatively abundant in volcanic gases. They have repeatedly proved to be major precursors of volcanic crises.

In magmatic rocks, Cl and F are main constituents of apatite, whose crystallisation thus controls halogens behavior during magma evolution. Thus apatite can be used as a geochemical tool as it allows to record the fugacity of key volatile species.

In order to shed further light on apatite-melt halogens equilibria, we have performed experiments of Cl and F partitioning between a rhyodacitic melt, an aqueous halogenated fluid and apatite. The experimental charges have been synthetized using internally heated pressure vessels at different pressures (50-200 MPa), temperatures (800-1100°C), oxygen fugacities (from NNO-1 to NNO+2), and Cl contents in fluid (up to 15 wt% equivalent (Na-K)Cl). CO_2 has been added at different amounts to understand its impact on Cl partitioning.

Experimental charges were analyzed by SEM, EPMA and Raman spectroscopy. Our first results show that the Cl content of apatite, melt and fluid is dependent on pressure, temperature, compositions of magma and of the added fluid. In particular, with increasing Cl content of the starting fluid, a positive correlation between the content of Cl in apatite and that of melt is systematically observed, as well as between fluid and melt (Cl in apatite: 0.2 to 2.5 wt%, Cl in melt: 0 to 1 wt%). From these results, a solubility model of Cl (and F) in rhyodacite will be created from the experimental data. We are performing similar experiments on phonolitic, trachybasaltic and basaltic compositions. Then, in situ experiments will be realized in transparent autoclave connected to a Raman spectrometer in order to determine the fluid composition in equilibrium with the melt and the conditions of salt (Na-K)Cl saturation in silicate melts.

Density changes in hydrous oceanic crust subducted to the Earth's transition zone obtained by in situ x-ray diffraction

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This study refines the densities of hydrous eclogite up to the transition zone, the deeper behaviour having been described recently [1], and accounts for the effect of all compositional changes along subduction paths using state-of-the-art in situ x-ray diffraction measurements.

We conducted experiments using an average altered oceanic basalt GA2 [2] + 3 wt.% H_2O from 3 up to 22 GPa at subsolidus conditions along a subduction path using the large volume press at ID06, ESRF. We analysed major and minor elements of phase compositions by microprobe.

Our experiments yield eclogites of garnet [GA] + clinopyroxene [CPX] + Ir ± coesite/stishovite ± phengite ± lawsonite ± vapour. As in previous studies [e.g. 3], the increased dissolution of CPX into GA causes the rise in GA/CPX ratios towards greater mantle depths. Similar to Irifune et al. [3], the determined lattice volume of eclogitic GA at ambient pressure increases with increasing pressure and recovered GAs from highest pressures are least dense. The GA/CPX proportion is largest contributor to the observed eclogitic density on the geotherm.

Eclogite is ~3-6 % denser than mantle models [4] up to 12 GPa, which develops into a zero-density contrast above 12 GPa in the transition zone. Our estimations of the bulk sound velocity and seismic parameters using Anderson's model [5] are consistent with ultrasound data by Kono et al. [6] and the seismic description of IASP91 [4] over the full pressure range studied.

The outcomes clarify the influence on density and buoyancy changes caused by the recycling of oceanic crust as part of the subducting slab in Earth's deep convecting mantle.

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Helium in the Earth's core

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The Earth formed through the accretion of numerous planetesimals that were already differentiated into a metallic core and silicate mantle. During impact each planetesimal core will sink rapidly to the Earth's proto core, mixing and equilibrating with the silicate mantle, but isotope data and modeling indicate that complete equilibration is highly unlikely (Dahl and Stevenson 2010; Rudge et al. 2010). Therefore, the He content of Earth's core could have been set by metal-silicate equilibration in planetesimals, rather than in a terrestrial magma ocean. Here we determined He partitioning between liquid metal and solid silicate during percolative core formation at the conditions expected to prevail in planetesimals. We performed seven experiments at 1 GPa using a conventional solid-media piston-cylinder apparatus and Pt-graphite capsules with an outer diameter of 4 mm. Starting materials were 1:5 mixtures of submillimeter-size olivine fragments from the Admire pallasite and powdered iron-sulphide with a composition of $Fe_{0.705}S_{0.295}$ corresponding to the eutectic composition at 1 GPa. Five experiments were conducted at 1200 °C and two experiments were conducted at 1450 °C. This was above the eutectic of FeS and below the solidus of olivine so that FeS was melted and olivine remained solid. The experiments lasted from 2 hours to 6 days and were quenched. Helium and Ne isotopic concentrations were measured in the run products using a compressor-source magnetic sector field mass spectrometer (Baur 1999). Results indicated that He behaves as a moderately siderophile element during percolative core formation. Hence, the Earth's core may contain substantially more primordial He than previously considered (e.g., Bouhifd et al. 2013). The high $^3He/^4He$ ratios in ocean island basalts therefore represent the last vestiges of metal-silicate disequilibrium in a magma ocean preserved from the time of Earth's formation.

Experimental constraints on trace element mobility in subduction zone fluids

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Trace element abundances in arc magmas can give useful information on subduction zone processes. Typical features such as the relative enrichment of Rb and Ba and the negative Nb-Ta anomaly, may suggest a transport by aqueous fluids from the subducting slab to the mantle wedge. On the other hand, some studies argue that fluid transport is too inefficient to explain the trace element enrichment observed in arc magmas (e.g. [1]) and propose hydrous melts as the main agent of mantle metasomatization.

However, a series of piston cylinder experiments conducted at 4 GPa and 800 °C show that the addition of Cl enhances trace elements solubilities in fluids equilibrated with eclogitic minerals. Fluid salinities ranging from pure water to 10 wt. % NaCl were investigated. Quenched fluids were sampled with the diamond trap method, which allows analyzing the frozen fluid and the fluid components that precipitate upon quenching together using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). LA-ICP-MS analyses were also performed on the solid phases to determine fluid/mineral partition coefficients.

The results indicate that the fluid/mineral partition coefficient of Large-Ion Lithophile Elements (LILE) may increase by up to two orders of magnitude for fluid salinities typical of subduction zones. Enhanced partitioning into the fluid was also observed for the Rare Earth Elements (REE), with the light REE partitioning preferentially into the fluid for high salinities. On the other hand, the behavior of High-Field Strength Elements (HFSE) is less affected by Cl. The presence of Cl therefore tends to enhance the characteristic negative Nb-Ta anomaly of arc magmas. Overall, the preliminary data obtained in this study suggest that in most cases, Cl-bearing aqueous fluids are likely the mobile phase responsible for metasomatism and melting in the mantle wedge.

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Time-resolved X-ray diffraction study of the spin crossover of (MgFe)O under dynamic compression

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(Mg,Fe)O ferropericlase, the second most abundant mineral in Earth's lower mantle, undergoes a change of electronic spin state at pressures of about 50 GPa. Previous works show that this spin transition leads to a marked decrease of compressional and bulk sound velocities in ferropericlase with implications for the interpretation of seismic observations in the lower mantle. The reduction of wave velocities is a consequence of the decreased bulk modulus of the ferropericlase across the spin transition. Previous experiments to measure the bulk modulus softening of (Mg,Fe)O have been done by direct sound wave velocity measurements at very high frequencies (GHz) using Brillouin Scattering, Impulsive Light Scattering or Inelastic x-ray scattering or have relied on indirect inferences from static compression experiments combined with x-ray diffraction. Here we present a time-resolved x-ray diffraction study of (MgFe)O across the spin transition employing a piezo-driven (dynamic) Diamond Anvil Cell (dDAC) in combination with very sensitive GaAs LAMBDA detectors implemented at the Extreme Conditions Beamline, PETRA III, DESY. Two different types of compression experiments have been carried out at room temperature across the spin transition: (1) Compression paths with different compression rates ranging from 0.01 GPa/s to 100 TPa/s have been conducted in order to determine a possible compression rate dependence of the spin transition; (2) compression paths have been designed that contain sinusoidal oscillations in order to simulate a propagating compressional seismic wave and directly quantify the bulk modulus at seismic frequencies (~1Hz). In our experiments, up to 2000 diffraction images per second have been collected to follow the spin crossover with splendid resolution. Results of both experimental approaches will be presented.

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Shear anisotropy in textured carbonates and the detection of carbonated regions in subducting slabs

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Constraining the amount of carbon that is reintroduced into the mantle via subduction is a critical parameter to quantify the deep carbon cycle [1]. Carbonates are the main hosts of carbon in subducted oceanic crust and their stability to lower mantle depths has been documented by experiments and thermodynamic models [2,3]. A better knowledge of their physical properties (seismic velocities and anisotropy) is thus required for the detection of carbonated lithologies by geophysical methods and to constrain carbon recycling at depth. Previous sound velocity measurements in Mg-Fe carbonates concluded that the seismic contrast between carbonated and non-carbonated lithologies is within the resolution of seismic methods [4,5], although it could be enhanced further by velocity anomalies associated to spin transitions in Fe^{2+} in Fe-bearing carbonates [6]. Alternatively, the large shear anisotropy displayed by carbonates (35%) is likely the best diagnostic feature to identify carbonated regions at depth [4], but the effect of textures on the propagation of seismic waves remains unknown. We present results from plastic deformation studies on Mg-Ca-Fe carbonates (magnesite, dolomite and ferromagnesite) conducted to lower mantle pressures in a diamond anvil cell by radial X-ray diffraction. The results show the development of strong textures upon compression that preserve anisotropy in the deformed polycrystalline aggregates. Specifically, we will discuss the observed slip systems active in axial compression and the effect of textures on the propagation of shear waves, as well as the detectability of carbonated regions at depth.

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Experimental determination of the H$_2$O-undersaturated peridotite solidus from 1.0 to 2.5 GPa using olivine sphere hygrometers

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The oceanic upper mantle contains ~50-200 ppm H_2O dissolved in nominally anhydrous minerals. This strongly influences the solidus temperature of peridotite and, thereby, the depth at which partial melting begins beneath oceanic spreading centers. An experimental determination of the H_2O-undersaturated peridotite solidus is, therefore, a prerequisite for understanding the relationship between the depth at which partial melting begins and mantle potential temperature. This presents two experimental challenges: characterizing the concentration of H_2O dissolved in the peridotite and identifying the presence of a small amount of partial melt. These challenges can be overcome by using spheres of San Carlos olivine, a few hundred microns in diameter, as hygrometers. Rapid volume diffusion of H equilibrates the spheres with the H_2O fugacity imposed by the peridotite within a few hours. Crossing the peridotite solidus is marked by a decrease in the H_2O concentration of the olivine spheres due to its incompatible behavior during partial melting. As isobaric partial melting proceeds with increasing temperature, H_2O is progressively sequestered in the melt and the concentration of H_2O in the San Carlos olivine spheres systematically decreases. We used this approach to experimentally determine the peridotite solidus at 1.0 to 2.5 GPa. Results from secondary ion mass spectrometry analyses of the olivine spheres indicates that the charges consistently contain ~140 ppm H_2O - within the range appropriate for the ambient oceanic upper mantle. On the basis of these experimental results, reverse cryoscopic calculations were used to estimate the temperature of the 0 ppm H_2O (anhydrous) peridotite solidus between 0.8 and 2.8 GPa. Our results demonstrate that the 0 ppm H_2O peridotite solidus is hotter than existing estimates. Our results also suggest a smaller range of potential temperatures for the ambient oceanic upper mantle and a smaller thermal anomaly for mantle plumes.

Single-crystal elasticity of iron-rich phase E

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Water plays a key role for the dynamics of subduction zones. A quantitative estimation of the deep water cycle is needed to understand both earthquake triggering processes and volcanic activities in subduction zones. Water can reach the top of the lower mantle through the formation of Dense Hydrous Magnesium Silicate (DHMS) phases, a group of hydrous phases that have been found to be stable in cold subducted slabs. Phase E (R-3m) is a DHMS stable over a wide P-T range and a likely constituent of subducted slabs. Due to its low bulk modulus and density, phase E might be detectable in seismic observations on subduction zones. In this study, we performed single-crystal Brillouin scattering measurements at ambient conditions in several crystallographic directions on two iron-rich phase E samples. The samples have been characterized by means of electron microprobe and Mössbauer spectroscopy to determine chemical composition and $Fe^{3+}/\Sigma Fe$ ratio, respectively. Single-crystal X-ray diffraction experiments have been performed for structure determination. The resulting dataset of experimental data has been used to constrain the full elastic tensor through least-squares fitting of the Christoffel equation. Our measurements are the first direct determination of the single-crystal elastic tensor of phase E. We find a bulk modulus of 95.7(4) GPa, consistent with previous determinations by high-pressure x-ray diffraction. The Hill average of the shear modulus is 59.4(1) GPa. Based on the here-measured data, phase E will show average compressional and shear wave velocities of 7.59(2) and 4.43(1) km/s at ambient conditions. At room pressure, elastic wave velocities of phase E will therefore be ~18 % slower as compared to hydrous wadsleyite indicating that even minor amounts of phase E might distinctly reduce seismic wave speeds. However, high-P and -T experiments are needed to quantify elastic wave velocities of phase E at conditions of the deep upper mantle.

Experimental determination of H_2O and CO_2 sulubilities in ultrapotassic melts

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Dissolved H_2O and CO_2 in silicate magmas affect the density, viscosity and the phase equilibria of these systems, thus influencing their evolutionary history as well as their eruptive behaviour. Solubility data are still missing for ultrapotassic compositions, characteristic products of some of the most dangerous active volcanic areas in the world: e.g. Mt Somma-Vesuvius and the Colli Albani volcanic district.

In this study, experiments were conducted to determine H_2O and CO_2 solubilities on end-member compositions of the Italian ultrapotassic suite: a phonolitic melt from the 79 a.D. eruption of the Vesuvius and a leucititic melt from the Pozzolane Rosse eruption of the Colli Albani Volcanoes. Synthetic analogues of the natural melts were prepared and inserted in AuPd capsules with distilled water and $Ag_2C_2O_4$ as sources for H_2O and CO_2, respectively.

Experiments were performed in an internally heated pressure vessel at 1250°C, intrinsic redox conditions ($\log f_{O_2}$= NNO+3) and pressures of 100-300MPa in order to bring H_2O and CO_2 in the melts in equilibrium with H_2O-CO_2 fluids with varying mole fraction of water (X_{H2O}) of 0, 0.2, 0.4, 0.6, 0.8 and 1.

The composition of the fluid-phase was determined by a weight-loss method. The volatile content in the quenched glasses was obtained by FTIR spectroscopy. An accurate calibration of the absorption coefficients of the water-related and carbon-related IR bands was performed. Bulk volatile contents in pure H_2O and CO_2 samples were also analysed by Thermogravimetry and Carbon-Sulfur Analyser.

First results show that the solubility of water is similar in both leucititic and phonolitic melts, increasing with pressure from 3.78 wt% and 3.62 wt% at 100 MPa to 7.07 wt% and 7.37 wt% at 300 MPa, respectively. However, a significant difference in CO_2 solubility was found between the leucititic and phonolitic melts, increasing with pressure from 1733 ppm(wt%) and 577 ppm(wt%) at 100 MPa to 8443 ppm(wt%) and 1795 ppm(wt%) respectively.

Assessing the initial volatile content of melt inclusions by 3D Raman imaging of hosted bubbles

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The style, dynamics and intensity of volcanic eruptions are controlled by the volatile content of magmas [1]. Reliable modelling of volcanic processes and magma ascent rates is based on correct assessment of the original volatile budget of primitive magmas. Phenocryst-hosted melt inclusions record the volatiles contents of the magma at the time of inclusion entrapment. Melt inclusions often contain a bubble that forms due to pressure drop and cooling during magma ascent and eruption [2, 3]. Recent studies have showed that up to 40-90% of the CO_2 initially contained in the inclusion is sequestered inside bubbles [4]. In addition to a fluid phase, bubbles often contain solid phases crystallized on the inclusion bubble wall, which are mainly carbonates and sulfates precipitated from the fluid. Preliminary investigations carried out using Raman spectroscopy indicate that the volume of these solid phases relative to the fluid phase may be important [5]. This implies that their contribution to the original magma volatile (CO_2 and SO_2) budget needs to be assessed for correct estimation of inclusion entrapment conditions, depth of magmatic chambers and original volatile contents of magma sources.

In this study, we present a method to identify the different phases filling inclusion-hosted bubbles and to quantify the volume of the solid phases using 3D Raman imaging. The method is applied to the study of olivine-hosted glass inclusions of basanitic and basaltic compositions erupted from different volcanoes. The accuracy and the limits of the method are examined by performing both inclusion homogenization experiments and 3D Raman imaging of bubbles in silicate glasses synthesized in the laboratory.

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Why natural monazite never becomes amorphous: experimental evidence for alpha self-healing

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Monazite, a common accessory rare-earth orthophosphate mineral in the continental crust widely used in U-Pb geochronology, holds promise for (U-Th)/He thermochronology, and for the immobilization of Pu and minor actinides (MA) coming from spent nuclear fuel reprocessing. Previous results obtained on natural and plutonium-doped monazite have demonstrated the ability of this structure to maintain a crystalline state despite high radiation damage levels. However, the low critical temperature (180°C), above which amorphization cannot be achieved in natural monazite under ion irradiation, does not explain this old and unsolved paradox: why do natural monazites, independent of their geological history, remain crystalline even when they did not experience any thermal event that could heal the defects? This is what the present study aims to address. Synthetic polycrystals of $LaPO_4$-monazite were irradiated sequentially and simultaneously with alpha particles (He) and gold (Au) ions. The use of Au^{2+} ions at 1.5 MeV allows the simulation of the nuclear energy loss of the recoil nucleus and He^+ ions at 160 keV simulate the electronic energy loss of the alpha-particle released in alpha-decay. In situ irradiation experiments were performed at room temperature conditions on the JANNuS-Orsay/SCALP platform, which couples two accelerators with a Transmission Electron Microscope. Our results demonstrate experimentally for the first time in monazite, the existence of the defect recovery mechanism, called alpha-healing, acting in this structure due to electronic energy loss of alpha particles, which explains the absence of amorphization in natural monazite samples. This mechanism is critically important for monazite geo and thermochronology and to design and predictively model the long-term behavior of ceramic matrices for nuclear waste conditioning.

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Influence of pressure on distribution of Rare-Earth Elements between silicate and salt melts in the granite system with the maximum Fluorine concentration

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The distribution of rare-earth elements, Y and Sc between the aluminosilicate (L) and salt aluminofluoride (LF) melts in the Li-bearing granite system with high contents of fluorine has been experimentally studied. In the investigated Si-Al-Na-K-Li-F-H-O system the phase equilibrium of the aluminosilicate (L) and aluminofluoride salt (LF) melts is stably reproduced at the temperature of 800 °C , pressure of 1 and 2 kbar and a water content from 2.5 to 15 weight %. Among the main components of Na, Li, Al and F are predominantly distributed into the fluoride phase, and K, Si and O - into the silicate phase. Phase relationships and the contents of the main components and F in the solid products of the experiments were studied with the help of the electron microscope and microprobe Superprobe JSM-6480 LV and Superprobe JXA-8230. An analysis of the contents of rare-earth elements and Li in quenched melts and fluids was carried out by mass spectrometry ICP-MS2000 instrument (apparatus of the Lomonosov Moscow State University). It was shown that REE, Y and Sc with large partition coefficients Kp (LF / L) are distributed in favor of the fluorine- and lithium-rich melt, as compared to a silicate melt (which agrees with the known data [1,2]), and with larger Kp (LF / Fl) in comparison with the aqueous fluid (Fl).

When studying the distribution of REE, Y, and Sc between coexisting aluminosilicate and salt melts, it was found that the behavior of REE, Y, and Sc essentially depends on pressure. The partition coefficients of REE Kp (LF / L) decrease by a factor of 5-10 with a pressure increase from 1 to 2 kbar. The partition coefficients between the melts decrease monotonically from light to heavy REE, both at 1 and at 2 kbar, forming a small maximum by Gd, i.e. when going from light to heavy REE. There is an increase in Kp (LF / L) with an increase in the water content in the system from 2.5 to 15 weight %. Thus, the rare earth elements proved to be much more sensitive to the processes occurring in the system than the main components. For the first time, a clear effect of REE partitioning between immiscible silicate and salt melts is found, depending on the pressure and water content of the system.

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Mechanisms for the development of phosphorus and aluminum zoning in olivine: lessons from crystallization experiments

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Phosphorus and aluminum are present in magmatic ferromagnesian olivine typically as trace elements (<0.1 wt.%). Their spatial distribution in single olivine crystals has generated considerable interest since Milman-Barris et al. (2008) revealed the striking fine-scale, intricate enrichment patterns that both elements can display within samples from various geological settings (Ocean Intraplate Basalt, Mid-Ocean Ridge Basalt, Komatiites, Arc Andesites, and Meteorites). These zoning patterns are interpreted as blueprints of rapid olivine crystallization, where intrinsic factors (e.g. changing growth rates) rather than external forcings (e.g. repeated magma mixing) lead to strong variations in incorporation of P or Al. These findings forced petrologists to reassess canonical ideas about the formation of phenocrysts and the interpretation of element zoning in olivine: phenocrysts do not necessarily form via concentric addition of growth layers (i.e. the 'tree ring' model), but by skeletal growth. The mechanism(s) for incorporation of higher concentrations of P or Al in olivine are still largely unidentified. Two end-member models are usually proposed: the 'boundary layer' model (BL) and the 'growth entrapment' (GE) model. In both cases, the growth rates required to form large boundary layers or preserve trapped concentration anomalies are very high, at least 10^{-7} m/s. By coupling simple crystallization experiments involving a Hawaiian basalt with numerical simulations of diffusion-controlled growth, we tackle three questions: (1) Are P and Al zoning patterns consistent with a model of skeletal growth for phenocryst-sized olivine? (2) What are the degrees of undercooling and growth rates required to produce skeletal growth and its P-Al zoning blueprint? (3) How are P and Al incorporated into olivine (BL/GE models, or …something else?) and what are the implications for equilibrium vs disequilibrium trace element partitioning?

Viscosity of carbonated melts: the effect of volatiles (CO_2, H_2O) at HP and HT

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The presence of melts in the first part of upper mantle is image by many geophysical studies. The nature of these melts is referring by different petrological and experimental studies that show a melt rich in volatiles, principally in CO2. To apprehend the deep carbon cycle, the first necessity is to know the mobility of these melts, like the viscosity. As a function of geodynamical context, the temperature and the pressure change, therefore different carbonated melts are produce. In this study, we investigate different SiO_2/CO_2/H_2O content in melt to determine their influences on the viscosity.

To investigate the viscosity, the experiment is making in ESRF in Grenoble. We produce in-situ measurements in Paris Edinburg cell with falling sphere viscometry experiments. Experiments are produce between 1 and 3 GPa and liquid temperature of sample.

One result show a viscosity of 0.15 Pa.s for 20wt% of CO^2. It is one order of magnitude more viscous than dolomite [1] and average 5 times less viscous than basalt [2]. Primarily results obtain in ESRF show a no linear effect of SiO_2/CO_2 content. Volatiles have an effect on viscosity and this has implication on melt migration in the mantle, so on the deep carbon cycle.

[1] Sakamaki et al., Nature Geosciences 6, 1041-1044 (2013)
[2] Kono et al., Nat. Commun. (2014)

Radium partition coefficients during basalt fractionation at Mt. Hekla comparison of empirical and experimental approaches

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Estimating time scales of magmatic processes from U-series disequilibrium requires understanding of elemental partitioning of the short-lived nuclides between solid, melt and fluid phases. During fractional crystallization of basalt, partition coefficients (D) of both U and Th can be considered close to nought, whereas those of Ra and Pb are known to be partially incorporated in plagioclase while sulphide will readily accommodate Pb.

Historical eruptions at Hekla volcano, Iceland, terminate with the production of basaltic icelandite (i.e. iron-rich bas. andesite of the tholeiitic magma suite) of uniform composition (SiO2 ~54 wt%; Th ~4.5 ppm). The basaltic icelandite is formed by fractional crystallization of basaltic melt, which composition is represented by the Recent lavas of the Hekla volcanic system. In such a simple case, the bulk D_{Ra} between fractionating crystal assemblage and melt can be empirically estimated from the Rayleigh law by assuming negligible DTh. On a log Ra vs log Th diagram, Hekla basalt and basaltic icelandite are strongly correlated with a linear regression coefficient of 0.99. The slope is equal to (1- D_{Ra}) that yields bulk radium partition coefficient of 0.09. The fractionating mineral assemblage forming the basaltic icelandite (melt fraction of 37%) from a typical Hekla basalt is composed of plagioclase (41%), which composition is labrodorite (An60), augite (34%), FeTi-oxides (17%) and olivine (8%). If Ra is only distributed between melt and plagioclase, the DRa between plagioclase and melt is simply equal to 0.09/0.41, or 0.22.

Recently, Fabbrizio et al. (2009) measured D_{Ra} between melt and four different plagioclase compositions. A linear interpolation of D_{Ra} between a bytownite (An80) and an andesine (An34) yields a value of 0.2 for An66 labrodorite (Hekla basalt) and 0.3 for An55 (Hekla bas. icl.). The experimental determination of D_{Ra} between plagioclase and melt is thus in perfect agreement with that determined empirically.

High pressure / high temperature PLANEX's platform for in situ Raman and IR spectroscopy studies

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In order to better understand complex volcanic and geothermal processes as well as to improve related thermodynamic models, it is necessary to acquire experimental data in situ, in real extreme conditions. Consequently, the main goal of PLANEX project is the development of a high pressure – high temperature analytical platform that allows to measure in situ thermal/physical/structural/chemical properties of various molten silicates and salts, hydrous fluids and gases. This research axis, based on vibrational spectroscopy: Raman scattering and Infrared emissivity, appears as a crucial part of the Planex's platform. These complementary spectroscopic techniques allow us to determine - as a function of temperature, pressure and time - the structural and dynamics modifications of main silicate network (50-1200 cm^{-1}) and of various (volatile) species such as H_2O, CO_2, etc. (1200-6000 cm^{-1}). Moreover, they provide the opportunity to determine the sample temperature and to track nucleation and crystallisation processes.

In order to record Raman and IR emissivity spectra up to 1200°C and 2000 bar, the high resolution, wide spectral range spectrometers are coupled to the so called transparent Internally Heated Pressure Vessels (IHPVs) equipped with three windows offering transparency to the desired electromagnetic radiation. The actual design based on sapphire windows and inner sapphire sample container allows to record the spectroscopic data from UV till 5 µm. This design is especially well adapted for Raman scattering using 355 nm and 532 nm excitation wavelengths. However, it is rather limited for IR emissivity measurements since it does not allow to reach the middle and far Infrared regions. Our current efforts to expand the IR spectral range through the research on new window/container materials will be presented. Finally, the high potential of this vibrational spectroscopy platform to study/simulate various natural and industrial materials/processes is discussed.

An experimental study on the effects of melt composition and temperature on sulfur redox state and solubility in silicate melts

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We have determined the redox state and concentration of sulfur dissolved in silicate melts for a series of melt compositions ranging from Fe-rich basalt to dacite to constrain the relative proportions of S^{2-} and S^{6+} present in natural magmas. Silicate melts were equilibrated in CO-CO_2-SO_2 gas mixtures at 1300°C and 1 bar under oxygen fugacities (f_{O2}) ranging from -1.67 to +1.60 log units relative to the Fayalite-Magnetite-Quartz (FMQ) buffer. The S^{6+}/S^{2-} of our experimental run products were determined using S K-edge X-ray Absorption Near-Edge Spectroscopy (XANES) and by Secondary Ion Mass Spectrometry (SIMS).

The S redox state in each melt undergoes an abrupt transformation from S^{2-} to S^{6+} with increasing f_{O2}, which is shifted ~0.2 log units higher in f_{O2} as melt FeO increases from ~9 wt% to ~18 wt%. As S^{2-} concentrations at constant f_{O2}/f_{S2} are consistently greater in more FeO-rich melts, the compositional effect on speciation may be explained by a negative dependence of S^{2-} activity on FeO concentration. The S^{6+}/S^{2-} of our samples show a linear relationship with Fe^{3+}/Fe^{2+} and follow the equilibrium FeS + $8FeO_{1.5}$ = 8FeO + $FeSO_4$, indicating that the redox couples for Fe and S can be directly related. Using thermodynamic data to model the effect of temperature on Fe-S equilibrium yields excellent agreement between our results and those from previous experimental studies done at lower temperatures.

We used our results to demonstrate how relatively small changes in f_{O2} can result in the suppression of sulfide saturation and can be used to explain the differences in the chalcophile element abundances between MORB and arc basalts. We also illustrate how our results can be used to assess the effects of electron transfer between Fe and S on quenching of natural glasses. Considering glasses from Mauna Kea, Hawaii we calculate an increase in Fe^{3+}/Fe_{Total} of approximately 0.05 during quenching which results in a calculated f_{O2} of ~0.8 log units higher than the true value.

Melting of felsic crust at mantle depth: implications for orogenic ultrapotassic magmatism

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The phase and melting relations in subducted felsic crust were investigated experimentally from 2.0 to 4.5 GPa and 675 to 1000°C. Starting material was a slightly peraluminous metagranite from the Dora Maira Massif, Western Alps. Fluid-present experiments produced a dominant paragenesis of coesite/quartz–phengite–clinopyroxene–K-feldspar/K-cymrite±garnet coexisting with a hydrous silicate melt/supercritical liquid at run conditions. A glass is present up to 4 GPa, whereas at higher pressures, solute-rich, non-quenchable fluid was present. Melt compositions range from granitic to quartz-syenitic. Alkalinity and K/Na increase with pressure due to increasing compatibility of Na in coexisting clinopyroxene. Many experiments contain small amounts allanite, apatite and zircon. Solubility of accessory phases increases with increasing pressure, as melt compositions become more alkaline. Allanite strongly controls the LREE–Th budget and causes high Th/La of up to ~2 in coexisting melts. High Th/La is a typical feature of ultrapotassic rocks, such as the lamproites of the Alpine–Himalayan belt, for instance. These magmas originate from melting of lithospheric mantle during post-collisional extension that has been contaminated during a previous stage of subduction. This work shows that high-pressure silicate liquids released from subducted felsic crust already have many major and trace element features typical for these ultrapotassic rocks.

The signature of syn-eruptive gas emissions at Piton de la Fournaise volcano (La Réunion island) during 2014-2015 activity

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The study of degassing processes in a volcanic system is crucial to constrain its internal structure, its eruptive dynamics and also it has implications on forecasting the type of volcanic activity (Woods & Huppert, 2003). The aim of this study was to perform the first systematic characterization of the syn-eruptive gas emissions of Piton de la Fournaise (PdF, Réunion Island) and to put new constraints on the storage and ascent conditions of magma feeding the intense phase of activity in 2014-2015.

Gas emissions were studied during the 2014-2015 eruptions by measuring in situ the ratios between the main volatile components (H_2O, CO_2, SO_2 and H_2S), using a portable Multi-GAS device. The equipment integrates an InfraRed Spectrometer for CO_2, a hygrometer for H_2O, two electrochemical sensors for SO_2 and H_2S, plus temperature and pressure sensors.

We quantified molar ratios H_2O/CO_2, CO_2/SO_2 and H_2O/SO_2 in plumes and fumaroles, which ranged between 3.85 - 1239, 0.1 - 487, and 4.65 - 83262, respectively. Data representing plume emissions were constrained by filtering the dataset for SO_2 concentrations higher than 10 ppm. We considered data with SO_2 lower than 10 ppm as affected by significant dilution by mixing with air and/or scattered emissions by the lava field and fumarolic areas. Comparison with degassing models (Di Muro et al., 2015, Whitam et al., 2012; Burgisser et al., 2015) demonstrated that the analysed gas originated mainly from shallow (< 1 km) and differentiated magmas, mixed with only a minor contribution (< 10%) of deeper inputs (> 2 km).

Comparing our dataset with previous analyses performed in 2010, before a long-lasting eruptive quiescence (2010-2014), we confirmed the extensive degassing and differentiation of magmas during a phase of prolonged inactivity.

Further studies will be completed by long-term gas monitoring during the future eruptions at PdF. This will allow us to understand and forecast the future evolution of its volcanic activity.

The behaviour of Nitrogen during Earth's accretion and core-mantle differentiation

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Nitrogen is a key constituent of our atmosphere and forms the basis of life, but its early distribution between Earth reservoirs is not well constrained. We investigate nitrogen partitioning between metal and silicate melts as relevant for core segregation during the accretion of planetesimals into the Earth.

N-partitioning coefficients were determined over a wide range of temperatures (1250-2000°C), pressures (1.5-5.5 GPa) and oxygen fugacities (IW-5 to IW). Centrifuging piston cylinders were used to equilibrate and then gravitationally separate metal-silicate melt pairs, which were then each bulk analysed. The two quenched melts were cut apart mechanically, cleaned at the outside and their N concentrations then analysed by an elemental analyser. Separation of the two melts is also necessary to avoid micro nugget contamination in the silicate melt at reducing conditions < IW-2.

Complete segregation of the two melts was reached within 1-3 hours at 1000g and 1600-1250°C. The applied double capsule technique with a welded outer Pt or Ir and an inner graphite capsule minimizes N-loss compared to single non-metallic capsules, where >80% of the N disappears into the assembly.

We were able to determine a D_N metal melt/silicate melt of 13±0.3 at IW-1 decreasing to 2.0±0.2 at IW-5 (1250°C, 1.5 GPa), N partitioning into the core forming metal. Increasing pressure shows minor effect on N, while increasing temperature dramatically lowers the $DN_{m/s}$ down to 0.5±0.15 at IW-4. During early core formation N was hence mildly incompatible in the metal. The results suggest that under magma ocean conditions (>2000°C and f_{O2}~IW-2.5), N-partition coefficients were within a factor 2 of unity, thus N did not partition into the core, which in turn should contain negligible quantities of N.

Melting relations of multicomponent diamond-forming MgO-FeO-SiO_2-$(Na,Ca,K)CO_3$ system of the Earth's transition zone (experiments at 20 GPa)

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The main minerals of primary inclusions in the transition zone derived diamonds are represented by wadsleite and ringwoodite (high pressure ploymorphs of olivine $(Mg,Fe)_2SiO_4$), majorite garnet, magnesiowustite $(Fe,Mg)O$, stishovite SiO_2 and carbonates of Na, Mg, Fe, Ca and K. Therefore, the experimental study is focused onto melting relations of the diamond-forming oxide-silicate-carbomate system MgO-FeO-SiO_2-$(Na,Ca,K)CO_3$ are of the direct interest for the genesis of diamond and associated minerals.

Experimental studies of the melting phase relations were carried out at 20 GPa, which corresponded to the stability conditions of ringwoodite (which is stable in the interval of 18-24 GPa at depths of 520-660 km). It has been established that Mg-Fe solid solutions of ringwoodite $(Mg,Fe)_2SiO_4$ are unstable with increasing iron content of diamond-forming melts. As a result of the reactional interaction with melts, ringwood is disproportionated to stishovite and wustite. This is a sign of a non-variant peritectic reaction ringwoodite + melt = magnesiowustite + stishovite. As a result of this reaction, ringwoodite disappears out the phase composition of the system with formation of uni-variant association of magnesiowustite + stishovite + melt. With a decrease in temperature two stishovite-containing subsolidus assemblages are formed: (1) ringwoodite $(Mg,Fe)_2SiO_4$ + stishovite SiO_2 + ferropericlase-magnesiowustite solid solutions $(MgO/FeO{\leftrightarrow}FeO/MgO)$ and (2) magnesiowustite $(Fe,Mg)O$ + stishovite SiO_2. A partial metasomatic interaction of the Ca-carbonate and silicate components was observed with the formation of $CaSiO_3$. The experimental results are consistent with the natural data for primary inclusions in the transition zone derived diamonds.

Tin mobilization and transport in magmatic-hydrothermal fluids and the formation of Sn(-W) deposits in the Earth's crust

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Tin is a highly demanded industrial metal, although the processes that affect its transport and precipitation of the ore mineral cassiterite (SnO_2) are still poorly understood. Tin-deposits are associated with peraluminous granites where Chlorine-bearing acidic fluids are the key in the transport of tin to the surface where the deposition of SnO_2 is probably controlled by an increase in oxygen fugacity (Wilson & Eugster, 1990). The goal of this investigation was to determine the solubility of cassiterite as well as the structure and stability of the dominant Sn aqueous species by XAS (X-Ray Absorption Spectroscopy) at the BM30b Fame beamline at the ESRF synchrotron.

The XAS measurements were performed over a broad range of P-T conditions (20 – 1000 bar and 30 – 500 °C), fluid compositions and redox state. The investigated fluid compositions represent a natural magmatic fluid and vary in salinity concentrations (2 m - 5 m NaCl) at acidic conditions (0.1 – 1 m HCl). A piece of quartz and a piece of SnO_2 were added as representative silica and Sn sources, and buffer assemblages where used to control oxygen fugacity. The XAS measurements at the Sn K-edge (29.19 keV) were conducted in the FAME autoclave (Testemale et al., 2005). At the the desired P-T condition, the dissolution of cassiterite was monitored by the fluorescence signal of Sn until equilibrium conditions were achieved before the collections of the XAS spectra to determine Sn solubility and the structure of the dominant aqueous complexes.

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Coesite and stishovite as carrier of OH and other light elements during ultra high-pressure metamorphism of continental crust

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The high-pressure silica polymorphs coesite and stishovite were synthesized under water saturated conditions from a natural granitic composition doped with Li and B. Experiment were performed in a multi-anvil apparatus between 4 and 9.1 GPa and 900 and 950°C, realistic for the ultra-high-pressure metamorphic units of a subducting continental crust. Run products consisted of coesite/stishovite + kyanite ± phengite ± omphacite, and quench material. Silica polymorphs were analyzed by infrared spectroscopy, electron microprobe and secondary ion mass spectrometry (SIMS). No hydrous defects were observed in coesite synthesized at 4 GPa, whereas coesite grown at higher pressures revealed a triplet of infrared absorptions bands at 3575, 3523 and 3459 cm^{-1}, and other minor bands. The triplet at 3575, 3523 and 3459 cm^{-1} is strongly correlated to the aluminum content suggesting an assignment as AlOH-defects. Stishovite displays one dominant band at 3111 cm^{-1} with a shoulder at 3150 cm^{-1}, and a minor band at 2667 cm^{-1}, probably all associated to AlOH-defects. BOH-defects were not observed in stishovite, and LiOH-defects were neither observed in coesite nor stishovite, in accord to the very low concentrations of Li in coesite and B and Li in stishovite. The total amount of water increases with pressure and with metal impurity concentrations. The increase in OH-defects in coesite and stishovite with pressure (from <10 to 380 wt ppm water from the quartz/coesite transition to the stishovite field) contrasts the negative pressure trend of water in quartz within the quartz stability field (from 70 to 40 wt ppm) observed previously (Frigo et al. 2016) from the same starting material, revealing an incorporation minimum of OH in silica polymorphs around the quartz/coesite phase transition. Therefore, silica polymorphs alone cannot serve as carrier for water to great depth, and need an accompanying hydrous phase such as phengite in order to bridge the OH-depression between 3 and 5 GPa.

Yttrium speciation in aqueous brines under subduction zone conditions: Ab-initio molecular dynamics simulation and free energy exploration

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The rare-earth-elements (REE) fractionation patterns are used in geochemistry to characterize geological processes, especially of subduction-related magmatism. Experimental data show that the REE signature of high-grade metamorphic rocks is modulated by the presence of aqueous fluids (1). The mobility of REE is controlled by the capacity of an aqueous fluid to host elements in form of solute species. The formation of such species depends on the present of ligands such as F^- or CO_3^{2-}.

So far, many REE speciation models for higher temperature, T, and pressure, P, conditions rely on extrapolation from thermodynamic data at ambient conditions (2). In some cases, the available high P/T experimental results show large deviation from these extrapolations (3), which underlines the necessity to study thermodynamic properties at the relevant conditions.

Here, first-principles molecular dynamics simulations in combination with thermodynamic integration (TI) (4) are used to derive equilibrium constants of dissociation reactions of different Y-Cl species. To understand the behavior of HREE in subduction fluids with high salinity we use a simulation box, which contains 84 H_2O, 1 $YCl3$ and 3 NaCl. We can show in accordance to experimental data (5) that $YCl(H_2O)_7^2 + YCl_2(H_2O)6^+$ are the main stable Y-Cl aqueous species at ambient conditions. At high temperature and pressure conditions the complexation of Y with Cl increases and we find five different stable complexes. Finally, we interpolate the stability constants derived from TI and provide thermodynamic data over the P/T range of a subducting slab.

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Fractionation experiments of primitive shoshonitic magmas at 8 kbar

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Very limited information is available on the differentiation paths of potassic magmas ascending from mantle depth differentiating in crustal magma chambers on their way towards shallow levels to form shoshonitic intrusive and extrusive bodies.

In this study we perform a set of equilibrium and fractional crystallization experiments on primitive trachytic basalts simulating possible ascend paths through the continental crust. The initial starting composition corresponds to a trachytic basalt dyke associated with the Triassic shoshonitic Monzoni intrusion in the Dolomites (Northern Italy).

To date, we conducted a set of equilibrium crystallization experiments in piston cylinder apparatus starting above the liquidus temperature delimited 1100°C at 8 kbar. The goal is to constrain conditions of magma segregation (pressure, temperature) from the cumulate mush in the lower crust via multiple saturation assemblages on or close to the liquidus. Subsequent experiments consist of both, polybaric equilibrium and fractional crystallization experiments to trace the liquid line of descent as well as to determine crucial trace element partition coefficients to tighter constrain geochemical modeling of the magma evolution. These experiments are directly linked with intermediate to evolved magmatic products (trachytes to rhyolites) in the Triassic Alpine complexes forming the initial pulse of voluminous more mafic magma extrusions and represent a volcanic counterpart of the plutonic complexes of Predazzo and Monzoni.

Densities of metals at high pressure using X-ray absorption method with diamond anvil cell

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To understand compressional and elastic properties of the planetary cores, densities of Fe-alloys are required to be measured in a wide pressure range. In this study, we performed density measurements of solid metals (Fe, Ga, In) using X-ray absorption method with a diamond anvil cell (DAC). Density measurements were performed at BL10XU and BL22XU beamlines, SPring-8 synchrotron facility. Incident and transmitted X-ray intensities were measured using ion-chamber or photo diode detectors to obtain the sample densities based on the Beer-Lambert law. We used a Re gasket with 2-3 multiple holes and placed sample metals and a reference material (KBr or NaCl) in each hole. Mass absorption coefficients of the samples were referred from the national standard database. The sample densities were also obtained from X-ray diffraction measurement to crosscheck the density. In some experiments, externally-heated DAC was used to obtained the density at high temperatures (~500 K). Measured densities of the sample metals from X-ray absorption up to 19 GPa are well consistent with the densities from X-ray diffraction within error bars. The density differences between X-ray absorption and diffraction methods are in the range of 0.3–2.2 %.

Stress evolution and associated microstructure during transient creep of olivine at 1000-1200 °C

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As the major constituent of Earth's upper mantle, olivine largely determines its physical properties. In the past, deformation experiments were usually run until steady state or to a common value of finite strain. Additionally, few studies were performed on polycrystalline aggregates at low to intermediate temperatures (< 1100 °C). For the first time, we study the mechanical response and correlated microstructure as a function of incremental finite strains. Deformation was conducted in uniaxial compression in a gas-medium deformation apparatus at temperatures of 1000 and 1200°C, at strain rates of 10^{-6} s^{-1} to 10^{-5} s^{-1} and under 300 MPa of confining pressure. Finite strains range from 0.1 to 8.6 % and corresponding differential stresses range from 71 to 1073 MPa. Grain sizes obtained from electron backscatter diffraction maps range from 1.8 to 2.3 μm, with no significant change in between samples. Likewise, the texture and texture strength, grain shape and aspect ratio, density of geometrically necessary dislocations, grain orientation spread, subgrain boundary spacing and misorientation do not change significantly as a function of finite strain, stress or temperature. Transmission electron microscopy shows grain boundaries acting as low activity sites for dislocation nucleation. Even during early mechanical steady state, plasticity seems not to affect grains in unfavorable orientations. We find no confirmation of dislocation entanglements or increasing dislocation densities being the reason for strain hardening during transient creep. This suggests other mechanisms affecting the strength of deformed olivine, such as grain boundaries acting as agent of deformation or as dislocation sources. At last, extrapolated to strain rates of the mantle (e.g. 10^{-14} s^{-1}), olivine-rich rocks show a strength of 0.5 to 1 GPa at temperatures of 1000 °C and below, matching the requirements of a not so soft lithospheric mantle, able to upkeep large orogens for millions of years.

Local and global thermodynamic analysis of hydromagmatism

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Hydromagmatism results from explosive interactions between magma and non-juvenile waters, featuring, in particular, hydrothermal, phreatomagmatic or surtseyan volcanism. This type of volcanism is commonly addressed through a global thermodynamic analysis, which evidences the key control of the water/magma ratio on the eruptive intensity. This work revisits current methods by considering possible thermodynamic pressure-temperature pathways and by taking into account the irreversibility of steam expansion. Thermodynamics of magma-water interactions are also discussed at the microscopic scale, demonstrating the interest to consider the coupling between thermal and mechanical properties of magma-water systems and the multicyclic succession of discrete thermohydraulic events against the magma-water interface. In particular, this study shows how the magmatic mechanical energy can be maximized in porous and wetted environments typical of peperites. Local thermodynamic models yield good estimates of the energy magnitude of hydrovolcanic eruptions. An application example is given, using the bulk mass of magmatic tephra and their textural properties as input parameters.

Thermal equation of state of solid Fe_3S and its implications for Earth's core

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Seismic study of the Earth's core reveals that the density of the core is less than that of pure iron at the relevant conditions. The density deficit of the core is most easily explained by the addition of light elements to the core such as silicon, sulphur, oxygen, carbon, and hydrogen. Identification of the light elements in the core provides important constraints on the origin and evolution of the solid Earth as the dissolution of those elements into core melt depends on the core formation processes. Despite over 60 years of research history, the light element budget of the Earth's core is yet to be accurately defined. Among the possible candidates, sulphur is among the top three strongest candidates. Sulphurs siderophilic nature means it bonds readily with molten iron, which is likely to have occurred during planetary differentiation. Sulphur also has a relatively depleted character in the mantle when compared to chondritic material, which can be explained by sulphur being sequestered in the core. Meteorites that have been suggested to represent the cores of planetesimals/proto-planets also show relatively high sulphur contents.

In this study, we construct a thermal equation of state for Fe_3S, which is the most iron-rich sulphide, to compute its density at the inner core conditions. Existing EoS for Fe_3S were based on compression experiments up to 200 GPa at 300 K or simultaneous high-P-T experiments up to 80 GPa and 2500 K. In the present study, we conducted In-situ X-ray diffraction (XRD) experiments on Fe_3S under simultaneous high-P-T conditions to 110 GPa and 2500 K in a laser-heated diamond anvil cell. In-situ X-ray diffraction experiments were performed at the BL10 XU, SPring-8. We will show the P-V-T data and will discuss the density of solid Fe_3S in the inner core.

An experimental model for the fluid-rock interaction at the slab-mantle interface: measured composition of subduction-related fluids in the presence of graphite/organic carbon, carbonates and silicates

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Subduction of the oceanic lithosphere and its sedimentary cover is accompanied by devolatilization processes, which provide an efficient way to recycle volatiles back to the mantle wedge and, ultimately, to the Earth's surface. CO_2 removal through dissolution of carbonates and graphite/organic carbon occurring in altered oceanic lithosphere and its sedimentary cover has been suggested by thermodynamic models but the experimental data base remains very sparse. For instance, graphite has been considered to represent a refractory sink of carbon in the subducting slab, owing to its lower solubility in aqueous fluids and melts compared to carbonates. However, recent experimental studies [1] suggest that the silica component derived from the dissolution of either olivine or quartz/coesite [2], even in absence of carbonates, controls the composition of deep COH fluids in equilibrium with graphite, in particular enhancing their CO_2 content when compared to SiO_2-free systems and producing fluids characterised by 8.1E+05 ppm CO_2 at 3 GPa and 800°C.

We present experimental data on the composition of COH fluids produced during the interaction between water and carbon-bearing phases (graphite, amorphous carbon, calcite) at pressures up to 3 GPa and temperatures of 700-800°C, retrieved by quantitative analyses performed through quadrupole mass spectrometry [3]. Experimental results will stress the importance of dissolution processes especially in cold subduction zones, where subsolidus conditions prevail.

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Phase relations between $(Mg,Fe)_2Fe_2O_5$ and Mg-Fe silicates like garnet and phase B

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Post-spinel phases with the M_4O_5 stoichiometry have been recently reported in a number of simple oxide systems, including $(Mg,Fe)_2Fe_2O_5$ [e.g.1, 2]. However, it is unclear whether $(Mg,Fe)_2Fe_2O_5$ can occur in a peridotitic bulk composition. Therefore, this study aimed to explore the phase relations involving $(Mg,Fe)_2Fe_2O_5$ and Mg-Fe silicates at deep mantle conditions. Multi-anvil experiments were performed at 14-20 GPa and 1100-1400 °C using two different starting mixtures: i) $MgFe_2O_4$ + Mg_2SiO_4 and ii) $MgSiO_3$ + Fe_2O_3. Run products were analysed by EPMA, XRD, Raman and TEM.

Our experiments demonstrate that (i) $(Mg,Fe)_2Fe_2O_5$ does not incorporate Si into its structure, consistent with previous studies [e.g. 3, 4] and (ii) $(Mg,Fe)_2Fe_2O_5$ can not only coexist with olivine, wadsleyite or ringwoodite [3], but also with majoritic garnet or Fe^{3+}-bearing phase B [5]. Garnet has a composition of 82 mol% $(Mg,Fe)_4Si_4O_{12}$ and 18 mol% $(Mg,Fe)_3Fe_2Si_3O_{12}$. The stabilization of phase B in our "dry" experiments was surprising. A possible explanation is the additional incorporation of Fe^{3+}. EPMA and EDX measurements in the TEM gave a composition of $Mg_{11.17(4)}Fe_{1.04(6)}Si_{3.79(3)}O_{21}H_2$ and Fe-L ELNES analyses yielded a $Fe^{3+}/\Sigma Fe = \sim 0.41(4)$, confirming that significant Fe^{3+} entered the structure via the charge-balanced substitution: $Si^{4+} + Mg^{2+} = 2Fe^{3+}$. Evaluation of Mg-$Fe^{2+}$ partitioning between $(Mg,Fe)_2Fe_2O_5$ and the silicate phases indicates that the O5-phase always has the highest preference for Fe^{2+}. Solid solutions involving different 2+ and 3+ cations has the potential to expand the stability of the O5-phase over a wide range of P, T and oxygen fugacity relevant to the deep upper mantle and transition zone.

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[2] Ishii et al. (2014) Am Min 99: 1788-1797
[3] Woodland et al. (2013) Contrib Min Petrol 166: 1677-1686
[4] Bindi et al. (2016) Phys Chem Min 43: 103-110
[5] Uenver-Thiele et al. (2018) Contrib Min Petrol 173: 20

The behaviour of C- and S- bearing species in shrinkage bubbles before and after melt inclusion homogenisation: insight from Raman spectroscopy

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Melt inclusions are considered excellent proxies for magma at depth due to their closed-system behaviour following entrapment in the host crystal. Post-entrapment modifications, however, are unavoidable and can lead to significant changes in the glass composition. Homogenisation, or re-heating experiments, is a common technique to restore crystallized melt inclusions to their primary vitreous composition. Given that the inclusions are not overheated and do no decrepitate during the experiments, the effect on volatile contents has been assumed to be minor but poorly investigated. To address this knowledge gap, we focus our work on crystallized melt inclusions from the Garibaldi Volcanic Belt in Western Canada. As the current literature states, 40-90 % of the total CO_2 is found in the shrinkage bubble of the inclusion [1]. Therefore, we used Raman spectroscopy to investigate the changes in fluid (CO_2) and solid phases filling the bubbles before and after homogenisation. Our data show that prior to homogenisation, the bubble is rich in Fe sulphides and oxides as well as hydrated carbonates and sulphates. Following reheating, the hydrated phases disappear and are replaced with copper sulphides and carbonates, while Fe sulphides and oxides remain. Additionally, the density of total CO_2 in the bubble increases after homogenisation, suggesting a diffusion of CO_2 from the melt into the bubble. These results pose significant implications for volatile concentrations following homogenisation as there is a clear partitioning of elements not only between the melt and bubble, but within the bubble phases itself.

Implication of water phase condition on the K-, Nitrogen, Ca- and La- smectite-muscovite transition under high pressure and application for subduction processes

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The lithospheric mantle is depleted in incompatible elements and nearly anhydrous. However, in subduction zones, smectite is one of the most important minerals that could bring together volatiles elements and trace elements into the mantle promoting re-hydration and trace element enrichment. However, in order to be considered efficient, smectite must resit to pressure and temperature or must transform into other phases able to bring such elements to the mantle. Our group is developing phase diagrams under high pressure and temperature (HPHT) in K+-, nitrogen-(NH^{4+}), Ca^{+2}- and La-doped smectite in order to understand the smectite-illite/muscovite-feldspar/hollandite transformation. Current results shows that La-smectite is stable under pressures of 2.5GPa, 4.0 and 7.7GPa at temperatures up to 250°C, ~300°C and 350°C, respectively, above which they transform into a La-muscovite-like structure, being irreversible in such conditions. K^-, NH^{4+}- smectite, however, are stables at temperatures around 250° C, independently of any pressure. Above this, they transforms into a I/S structure before changing into a muscovite structure at ~450°, 350° and ~300°C, under 2.5, 4.0 and 7.7GPa, respectively. These results show that pressure does not affect the stability of K- and NH^{4+}- smectite, which remain stable up to 250°C under pressures up to 7.7GPa. On the other hand, higher pressures enlarge smoothly the La-smectite stability field in a very limited extension. Transformation of La-smectite into muscovite occurs directly, but K- and NH^{4+}-smectite transformation occurs via I/S structure. La-smectite/muscovite transformation coincides perfectly with high pressure water/ice transformation. However, K- and NH^{4+}-smectite does not have such straightforward influence, due to the existence of the I/S stability field. We are investigating these systems at higher pressure conditions.

Physical properties of synthetic magnesian calcites

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Calcite-magnesite is an important solid-solution both in the Earth's interior and in the biosphere. Yet, the properties of magnesian calcites are poorly known. Nineteen syntheses of magnesian calcites covering the range 0-50 mol% $MgCO_3$ (2% and 5% intervals in the ranges 0-30, 30-50, respectively) have been carried out in piston-cylinder apparatus, at high pressure and temperature (1-1.5 GPa, 1000-1100 °C, for 96h) in large volume gold capsules. Marbles with 200 μm large euhedral crystal of magnesian calcite were obtained. Crystal compositions were checked with the electron microprobe. Synchrotron XRD, FTIR, and μ-Raman measurements were performed on the synthetic products. Most data series show correlations with limited dispersion between peak positions, peak widths and magnesium contents. The most surprising result is that data plot along the calcite-dolomite line, not along calcite-magnesite. This and other patterns indicate that there is more magnesium ordering in the solid-solution than previously thought, in agreement with the presence of a superlattice in dolomite. Biogenic magnesian calcites systematically depart from their inorganic counterparts. Organic matter present in biogenic calcites is probably responsible from these singularities. Organic matter often seen as foreign material trapped in the crystalline structure is, on the contrary, part of the crystal structure itself, making biominerals archetypes of organic/inorganic nanocomposites.

Experimental melting of ortho- and paragneiss under fluid-present conditions: melt compositions (major and trace elements) and implications for granite genesis

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In recent works, fluid-present melting in the crust is commonly invoked to explain some petrological features regarding anatexis and granite genesis. However there is still a little known on the implication of fluid-present melting on the composition of melt. We realised a set of melting experiments using two natural gneisses an orthogneiss and a paragneiss as starting material. Both sources were crushed and sieved (80 to 100 μm). Experiments were realised in internally heated pressure vessel under controlled fO2 at 4 kb and at 800 and 850°C for 8 and 15 days respectively. In addition to fluid-absent experiments (i.e. no fluids added), 10 wt% of fluids with variable compositions $(x(H_2O)=H_2O/(H_2O+CO_2))$ have been added to starting material. Results have been analysed using electron microprobe and LA-ICP-MS.

Melt fraction increases with 1) temperature; 2) source composition and 3) with $x(H_2O)$. Melt composition is strictly peraluminous and slightly more ferromagnesian from the paragneiss than from the orthogneiss. Major elements in melt are mostly controlled by the composition of the source and the pressure and temperature of melting. Fluid-present melting has only a limited effect on major element contents. In regard of trace element, rock source has a clear control of trace elements in melts. In the same way, the fluid regime of melting affects trace element in the melt. Yet, relation between trace elements and melt fraction is not obvious.

As a consequence melt composition, in our experiments, do not respect the principles of batch melting. On the contrary, melt composition is controlled by the stoichiometry of the melting reaction. In that sense, melt composition depends on the proportions and compositions of mineral involved in the melting reaction, either as reactant or as product (i.e. peritectic phases). While fluid-present melting significantly affects melt productivity it appears to have only a limited effect on melt composition compare to fluid-absent melting.

Evidence for Carbon-rich cores in asteroids and terrestrial planets

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The light element compositions of planetary and asteroidal cores play a significant role in setting the resultant Hf/W ratios of their silicate Mantles. During core formation the metal/silicate partitioning behaviour of W, a moderately siderophile element of 6+ valence, is dominated by the prevailing oxygen fugacity of core formation. Additionally, W exhibits strong positive interactions with S in the metallic phase, resulting in siderophile W partitioning much less strongly into the metallic liquid if the core is S-rich. The large, S rich core of Mars coupled with the high FeO content of the mantle (~18wt% FeO) results in bulk silicate Mars having low Hf/W ratios of ~5. In contrast the Earth, with lower FeO content in the mantle (8wt% FeO), and higher pressures of metal/silicate equilibration, exhibits Hf/W contents of ~25.

Vesta is enigmatic. It has an oxidised mantle with a Mars-like FeO content, whilst its small size means that peak pressures of metal-silicate equilibration are very low. This makes the elevated, Earth-like, Hf/W ratio of 19 surprising and leads to the obvious question - how can W be so strongly partitioned into Vesta's core? The presence of cosmochemically abundant carbon during Vesta's differentiation is a likely explanation. Carbon dramatically increases the siderophile behaviour of W. The implication is that Vesta's Hf/W can only be explained if its core is carbon rich and W is preferentially partitioned into the metallic phase. Hence we show that to explain the mantle abundances of W in silicate Mars and Vesta, light element core contents must be dramatically different.

Rheological weakening of orthopyroxene and the impacts on asthenosphere rheology and the Lehmann seismic discontinuity

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Pyroxenes constitute up to 40% by volume in the upper mantle and should impose significant influences on the rheological behavior of the asthenospheric mantle. Here we report high-pressure, high-temperature deformation experiments on polycrystalline orthoenstatite (OEn). Natural crystals with an average composition of En89Fs10Wo1 with ~4 wt% Al_2O_3 were ground into powders with grain size ~25-35 microns. The powders were sintered at 3 GPa and 1273 K for 4 h, to form polycrystalline "rocks".

Creep experiments were conducted in the D-DIA apparatus at beamline 13-BM-D of the Advanced Photon Source, at 1273-1473 K and up to 8 GPa, with strain rates between 4×10^{-6} and 4×10^{-5} s^{-1}. Ni foils were attached to the samples as strain markers and to help constrain oxygen fugacity. Up to 4.5 GPa, the quasi-steady-state stress-strain data can be fitted quite well with a power-law rheology yielding a stress exponent n=3.85 and an activation volume V*=13 cc/mol. EBSD shows that the (100) poles are generally aligned with the shortening (axial) direction, while the (001) poles tend to be normal to that direction, consistent with previous results that [001](100) slip system dominates deformation in OEn. Above 4.5 GPa, OEn exhibits an unexpected pressure-induced rheological weakening, with a strongly negative apparent V*. EBSD on samples recovered from above 6 GPa reveals that (001) poles form additional well-defined maxima, suggesting new slip directions in the (001) plane. We postulate that the new "slip directions" are activated when OEn is compressed close to a high-pressure structure under differential stress and that the pressure-induced rheological weakening is due to an incipient response prior to the transition. Such a weakening behavior is expected to have profound impact on the nature of the asthenosphere. The high-pressure phase transition in OEn, together with weakened pre-transition rheology, may also be a main contributor to the Lehmann seismic discontinuity.

Clinopyroxene dissolution: A melt inclusion study

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Pyroxene is an important receptacle of trace elements in chondrules and the outer layers of dusty planets, and its dissolution is thus key in the production and chemical diversity of melts. We performed heating experiments on clinopyroxene microcrysts within plagioclase-hosted melt inclusions from Ardoukoba (Assal Lake, Djibuti) by using a Linkam TS1500 heating stage to track their textural evolution and measure their dissolution rates.

Our first results indicate that for a heating event starting at $10 - 60$ °C below the liquidus and rising at 130°C/min, the integrated rates of dissolution range from $1.58 \times 10^{-9} - 2.53 \times 10^{-7}$ m/s, consistent with previous measurements in closed vessels and gas-mixing furnaces. Barring local effects in the melt, the decrease in crystal size seems to remain linear over time, indicating that dissolution was not limited by diffusion. The habit of clinopyroxene crystals evolved from euhedral, skeletal, or dendritic to rounded, and the crystal faces usually regressed at similar rates, showcasing isotropic dissolution. We observed several cases of crystal segmentation, with the starting crystal breaking into smaller parts at advanced stages of dissolution. These results will be useful in recognizing the dissolution textures of clinopyroxene and estimating the timescales of crustal contamination and xenolith survival in magmas.

Properties of magmas at depth from SiO_2 local structure measured using X-ray Raman spectroscopy

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Melt properties at high pressure are crucial to model the evolution of the deep part of the Earth formation and evolution. SiO_2 is the main component of silicate melts in the Earth's deep mantle and controls their network structure and physical properties with pressure. Knowledge of the short-range atomic and electronic structure in melts brings important constraints about their compressibility and viscosity at depth. We measured the O K-edge and the Si L2,3-edge in silica up to 110 GPa using X-ray Raman scattering spectroscopy, with a striking match to calculated spectra of the quenched high-pressure melt based on structures from molecular dynamics simulations. Our data show two major discontinuities at high pressure that are related to coordination changes. Between 20 and 27 GPa, at the transition zone (660 km), 4-fold coordinated Si species are converted into a mixture of 5-fold and 6-fold coordinated Si species. Between 60 and 70 GPa, in the lower mantle, a further transition marks the decrease of 5-fold Si species with 6-fold Si becoming dominant above 70 GPa without crossing-over the 6-fold references stishovite and $CaCl_2$ phases up to at least 110 GPa. These two discontinuities are found at the same pressures where changes in compressibility and density occur, measured on the same SiO_2 glass [1]. The changes of coordination and density measured on SiO_2 may have direct influence on the properties of silicate melts at depth with changes in viscosity and partitioning of elements at such pressures. Higher coordination than 6 only takes place beyond 140 GPa corroborating Brillouin scattering measurements in agreement with our results with a further increase in density at such pressure. Silicate melts containing network modifier elements may potentially densify at a lower pressure making magmas neutrally buoyant at the depth of the core-mantle boundary.

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Halogen volatility in the early solar system

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When considering volatility during planetary formation elements are generally classified according to the temperature at which they would condense from a gas of solar composition at 10-4 bar total pressure (Lodders, 2003) with the most volatile elements having the lowest condensation temperatures. When abundances relative to solar composition are plotted against condensation temperature there is, for lithophile elements, a volatility trend of decreasing abundance with decreasing temperature. The halogens do not fit this trend well, however with relative abundances (normalised to Mg=1) (Clay et al., 2017) in silicate Earth of ~0.2 for F and ~0.08 for Cl, Br and I, while the condensation temperature for Cl (954K) is greater than for F (739K) and much greater than those for Br (546K) and I (535K).

The behaviour of Cl is particularly important because it is abundant in the solar system and it forms stable gaseous complexes with many volatile elements of interest (Ga, Ge, Tl, Na, Cs, In, Li for example). When Cl condenses, so do many of these other elements. We have repeated the condensation calculations, however and find that Cl, Br and I should all condense at about 400K and that Lodders'(2003) result for Cl is probably based on an old inaccurate experimental determination of sodalite stability.

The revised abundances of the halogens (Clay et al., 2017) imply that these elements were actually much less volatile than elements of similar condensation temperature (e.g Tl) during planetary formation. Our volatility experiments (Matzen, this meeting) are consistent with this conclusion and suggest that melting and partial vaporisation were important influences on the establishment of the halogen contents of silicate Earth.

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Sulfur Solubility in Silico-Carbonate Melts at High Pressures

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Sulfides are common minor phases in the Earth's mantle and their influence on trace elements, including Pb, Re and PGEs can be profound. The S content at sulfide saturation (SCSS) in mafic magmas has been extensively studied [1], but there are only limited data for carbonatitic melts. One reason is that silico-carbonate melts produce diverse quench textures [2]. Another reason is the "nugget" problem, where suspended sulfide droplets make true analysis of S difficult.

We present an experimental method to overcome these problems for systems with immiscible sulfide and carbonate melts at mantle pressures and report the first data on the SCSS for Ca–Mg silico-carbonate melts. We rely on the different wetting properties of sulfide and carbonate liquids in a porous matrix. A mixture of carbonates and FeS was loaded into an olivine container and sealed in a Pt capsule (+ graphite). During the experiments at 5-10.5 GPa and 1400-1600°C, the silico-carbonate melt migrates through fine fractures in the olivine, but filters out suspended sulfide droplets.

Sulfide melts have a composition ~ $Fe_{0.9}Ni_{0.1}S$, while the silico-carbonate melt is dominantly a Ca–Mg–Fe carbonatite. Three kinds of melt pools occur: melts next to the sulfide globules yield high S contents with much scatter (0.1–0.3 wt % S). Small melt pockets within the olivine container and larger melt pools between the olivine and Pt capsule yield lower S contents and less scatter (~0.04–0.12 wt% S) even though the major-element composition is identical in all three situations. We consider that 0.03–0.1 wt% S can be dissolved in silico-carbonate melts in equilibrium with graphite at 1400–1600°C, which is ~2x lower than observed for basalt [1]. S solubility is strongly correlated with FeO content and less sensitive to P and T. The small fractions of silico-carbonate melt produced in the mantle will not significantly affect the sulfide budget.

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Precursor phenomenon in phase transition from tetragonal to cubic phases in ZrO_2, HfO_2, $BaTiO_3$ and $PbTiO_3$

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High-temperature X-ray diffraction experiments of ZrO_2 and HfO_2 powders were performed using a container less aerodynamic levitation technique up to melting points. A two-dimensional IP detector was used for data collection and their integrated one-dimensional X-ray profiles were analyzed by the Rietveld method. The lattice constants, thermal expansions and c/a rations for tetragonal phases were refined. The c/a ratios in the tetragonal phases decrease remarkably above 2500 K and this is considered as a precursor phenomenon for the transition. No clear lattice volume changes were observed at the transition points from the tetragonal phases to the cubic phases. We therefore propose that the phase boundary between the tetragonal phase and the cubic phase in ZrO_2 and HfO_2 systems does not show a negative slope in P-T phase diagram.

Single-crystal X-ray diffraction studies of $PbTiO_3$ and BaTiO3 perovskite were carried out in the wide temperature range 298–928 K [1,2]. Transitions from tetragonal to cubic phases have been revealed at 753 and 413 K in $PbTiO_3$ and $BaTiO_3$, respectively. The deviation from the linear changes in Debye-Waller factors and bonding distances in the tetragonal $PbTiO_3$ phases can be interpreted as a precursor phenomenon before the phase transition. In $PbTiO_3$, temperature factor Ueq values for Pb and Ti are continuously changing with increasing temperature. The estimated values of Debye temperature Θ_D for Pb and Ti are 154 and 467 K in tetragonal $PbTiO_3$ phase and decrease 22% in the high temperature phase. Effective potentials for Pb and Ti in $PbTiO_3$ change significantly and become soft after the phase transition.

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Nitrogen solubility in the deep mantle and the origin of nitrogen on Earth

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Several geological observations suggest that nitrogen is either depleted on Earth relative to other volatiles or a major nitrogen reservoir has to exist within Earth's interior. Nitrogen exchange between such a deep reservoir and the atmosphere may have caused fluctuations of bulk atmospheric pressure in the geologic past, which may have affected both paleo-climate and habitability.

We studied nitrogen solubility in transition zone and lower mantle minerals (ringwoodite, wadsleyite, bridgmanite and Ca-silicate perovskite). Experiments were carried out with a multi-anvil apparatus at 14-24 GPa and 1100-1800 °C. Minerals were synthesized coexisting with a ^{15}N-doped nitrogen-rich fluid at the Fe-FeO buffer. Nitrogen concentrations were quantified by SIMS. Observed nitrogen (^{15}N) solubilities in wadsleyite and ringwoodite were typically in the range of 10-250 µg/g. High temperature strongly enhanced nitrogen dissolution. Nitrogen solubilities in bridgmanite and Ca-silicate perovskite were about 20 µg/g and 30 µg/g, respectively, indicating that lower mantle minerals dissolve less nitrogen than transition zone minerals.

Nitrogen contents in Fe-rich metal coexisting with the mineral phases were also measured. Nitrogen solubility in metal increases with pressure and decreases with temperature, with a maximum value of nearly 1 wt. %. These data show that that the mantle can store at least 33 times the mass of nitrogen presently residing in the Earth's atmosphere. Combining these results with data on nitrogen solubility in silicate melts from the literature, the partitioning of nitrogen during magma ocean crystallization can be modeled. Such a model suggests that if the magma ocean coexisted with a primordial atmosphere having a nitrogen partial pressure of just a few bars, several times the mass of nitrogen in the present atmosphere must have been trapped in the mantle. Therefore, it is plausible that most of the nitrogen on Earth still resides in a deep reservoir.

High-pressure phase transitions of natural chromitite from the Tibetan ophiolite

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The podiform chromitites in the Tibetan ophiolites has been thought experienced metamorphism corresponding to pressures about the top of mantle transition zone (MTZ). However, very little is known about phase relations of natural podiform chromitite in the MTZ, as well as the implications for processes related to formation of the ultra-high pressure (UHP) chromite. Here, an experimental study is presented to constrain the phase relations of natural podiform chromitite at pressures and temperatures of 11–18 GPa and 1400–1600 $^{\circ}$C. A nodular chromitite sample (T97-C1) from Luobusha, Tibet, was used as the starting material in this study. The sample is composed mainly of chromite (~85 vol.%) + olivine (~10 vol.%), and contains some altered serpentine (~5 vol.%). The experimental results show that the chromitite transforms into phase assemblages composed of chromite + eskolaite + garnet for pressures at the base of the upper mantle (~11–13 GPa), and chromite + eskolaite + garnet + MC-phase at the top of the MTZ (~14–16 GPa). Chromitite is replaced by a $CaTi_2O_4$-structured phase + eskolaite + garnet in the middle of the MTZ (~> 17 GPa). The MC-phase has an average composition of about $A_2^{2+}(A_{0.2}^{2+}B_{0.8}^{3+}C_{0.3}^{4+})O_4$ or $A_2^{2+}(B_{0.8}^{3+}C_{0.4}^{4+})O_4$ (where A=Mg^{2+} + Fe^{2+} + Ni^{2+}, B=Cr^{3+} + Al^{3+}, C=Si^{4+}), with a cubic space group of *Fd3m*, and represents a solid solution between chromite and olivine, but retains the same crystal structure of chromite. Therefore, it is suggested that the MC-phase should be a new post-spinel phase. The identification of the MC-phase in a natural chromitite system is significant for understanding the post-spinel phase family, and the incorporation of Mg and Cr minerals in the MTZ, and helps constrain related geological processes in major collision zones.

The influence of potassium on the carbon-carbonate equilibrium and the melting of harzburgitic mantle

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Equilibrium between carbon and carbonate in harzburgites can be written as:
enstatite + magnesite = olivine + graphite/diamond + O_2 (EMOG/D), which also defines the oxygen fugacity (f_{O2}) at a given P and T. Replacing magnesite with a carbonate melt shifts f_{O2} down by lowering carbonate activity by dilution with silicate components [1]. Although alkalis generally occur in low concentrations in the mantle they can lower the solidus of mantle assemblages [2] and may also influence the f_{O2} at which carbon and carbonate coexist.

To test how K affects the position of the carbon-carbonate equilibrium in T-f_{O2} space, melting experiments of carbonated harzburgite were carried out at 1200-1500°C and 5.5GPa. The starting material was a mixture of natural ol and opx separates and synthetic carbonates (molar opx:carbonate:ol ratio=3:2:1) [1]. The carbonates were 4:1 molar mixtures of $MgCO_3$ and K_2CO_3. The mixture was packed into a graphite container and welded into a Re-lined Pt capsule. A trace of Ir was also added as an Ir-Fe redox sensor to measure f_{O2} [1,3].

Our experiments suggest the solidus of K-bearing, carbonated harzburgite lies somewhat below 1200°C, in accordance with previous results [2]. Interpreting primary and quench features of the carbonate phase(s) is not always straight forward. Although the obtained compositions exhibited some degree of heterogeneity, the melts evolve towards more SiO_2-rich compositions with increasing temperature. The f_{O2} values calculated from the Ir-Fe sensor are up to 1log unit below the K-free EMOG equilibrium. This shift is mostly due to coexisting ol and opx becoming Mg-richer when coexisting with K-bearing carbonate melt, driving the redox equilibrium to lower f_{O2}. These results may help to explain the discrepancy between the low f_{O2}'s observed for mantle xenoliths containing diamond with carbonate inclusions.

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