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# Carbon mobilisation in the shallow Mariana subduction zone: insights from IODP Exp. 366

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Deep-rooted serpentinite mud volcanism in the Mariana forearc allows unique insight into dynamic processes and element cycles in the shallow portions of a subduction zone. IODP (International Ocean Discovery Program) Expedition 366 drilled and cored three of these mud volcanoes.

Recovered materials include mafic rock fragments enclosed in a serpentinite mud matrix. Titaniferous augite in these clasts is diagnostic of alkali basalt, implying an ocean island provenance. This result is in line with the composition of larger rock clasts that can be assigned to recycled Pacific Plate seamounts (Fryer et al., 2017, doi: 10.14379/iodp.pr.366.2017). The recovered samples are altered to prehnite–pumpellyite and blueschist facies mineral assemblages, indicating peak pressure/temperature conditions consistent with the estimated slab depth of $\sim$19 km.

Distinct veins generations crosscut the clasts and comprise i) silicate-only, ii) carbonate–silicate, or iii) carbonate–sulfate vein types. The most abundant vein minerals are pectolite, aragonite, calcite, and prehnite. Late nesquehonite veins are present in some samples. Carbonate 87Sr/86Sr values of $\sim$0.705 indicate precipitation from fluids released from the subducted slab rather than being of seawater origin. Carbon isotopes ($\delta$13C = -0.6 to 3.3‰ VPDB) suggest an abiogenic source of carbon while O isotopes ($\delta$18O = 20.1 to 23.5‰ VSMOW) indicate precipitation at $\sim$40–60°C, based on an estimated $\delta$18Ofluid of -2‰.

Mineral assemblages in the veins point to precipitation during water–rock interactions in rock-dominated systems. The lack of deformation suggests that they most likely formed away from the décollement, possibly within the mud volcano conduits. Fluids from which the vein phases precipitated contained C, Ca, Na, Sr, Ba, and S. Some of these elements (notably C and Sr) have most likely been derived from the subducted plate. The carbon may have been released during compaction of sediments, and subsequent release of pore waters and inorganic sedimentary compounds, or derived from decarbonation of carbonate in the ocean crust. Our data support the hypothesis that carbon mobilisation in the forearc of subduction zones is occurring and show that this process may happen shallow in the system at low metamorphic grades. Trapping of carbon in low-temperature vein mineralisations is a previously unidentified sink inside the forearc lithosphere, implying that only part of the carbon escapes to the seafloor.

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# Thermodynamics of aqueous species at high pressures: constraints from mineral solubilities on applicability of equations of state

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Aqueous fluids and their solutes play fundamental role in geochemical mass transport over multiple spatial and temporal scales in settings ranging from diffuse devolatilization to focused fluid flow. Understanding macroscopic mineral-fluid interaction or reaction mechanisms at atomic level requires thermodynamic equations of state and data for aqueous species applicable over wide range of pressure-temperature conditions and solute concentrations. Recent advances in calibration of electrostatic permittivity of water [1] have allowed extrapolation of thermodynamic models and data from hydrothermal conditions to extreme temperatures and pressures [2,3]. Here we evaluate the extrapolation behavior and accuracy of the Helgeson-Kirkham-Flowers (HKF) model by comparing predictive calculations with experimental solubilities of representative rock-forming minerals – quartz, corundum and calcite. The thermodynamic properties of neutral species (e.g., $H_4SiO_4$, $H_6Si_2O_7$) are implicitly nearly insensitive to dielectric constant of the aqueous solvent. Calibrations of the thermodynamic properties at hydrothermal conditions [4,5] yield discrepant quartz and corundum solubilities at temperatures above 500 $^o$C or pressures exceeding 0.6 GPa, as a result of universal correlations between the HKF parameters. By contrast, thermodynamic calibrations at high-pressure conditions [1] reproduce experimental solubilities but at the expense of extrapolation stability. Fluids involving highly charged species such as carbonate ions require accurate calibration of the dielectric constant of water above 550 $^o$C, but predicted solubilities remain one order of magnitude lower above 650 $^o$C and 0.6 GPa than experimental determination. Overall, the HKF model offers moderate versatility when the universal correlations among its parameters are removed, but it does not achieve continuous accuracy from low- to very high-PT conditions. These drawbacks are implicit in the model's functional form that was designed to reproduce strong departures in infinite dilution properties near the conventional and sub-ambient critical point of water while ignoring the compressibility of the solute's hydration sphere. We will introduce several universal constraints, which dictate functional forms of new equations of state for aqueous solutes and their applicability to a wide range of crustal and mantle conditions: ($i$) Gibbs-Duhem consistency, which propagates pure solvent properties to those of infinitely dilute species, and (*ii*) internal continuity between infinite-dilution and pure-liquid standard state to cover supercritical water-silicate systems. Exploratory calibration of a five-parameter equation of state results in superior accuracy and interpolability between ambient conditions and 1100 $^o$C and 2.0 GPa.

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# Highly oxidizing fluids generated during serpentinite breakdown in subduction zones (invited)

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In subduction zones, the dehydration of serpentinites is a major process responsible for the transfer of water from the slab to the mantle wedge. Serpentinites are also an important host of volatiles (e.g. sulfur, fluorine, chlorine) such that their dehydration also leads to the modification of the mantle wedge and arc magmas compositions by fluids enriched in these volatiles. In this context, constraining the evolution of serpentinite redox state is a key to obtain a better understanding of the nature and composition of slab-derived fluids and fluid/rock interactions in subduction zones. These processes play a fundamental role in governing metasomatic processes taking place in the mantle wedge as well as magma genesis and magma degassing processes and will also affect the stability of redox sensitive phases (e.g. carbonates, sulfides), the mantle wedge solidus and the properties of the resulting melts.

The aim of my work is to constrain the behaviour and mobility of redox sensitive elements, in particular iron, in serpentinites from their formation at the ridge to their devolatilization during prograde metamorphism in subduction zones. To address this, I have selected samples from the Western Alps (Italia and France) and Sierra Nevada (Spain) ophiolitic complexes. These remnants of the oceanic lithosphere have preserved different stages of serpentinization and deserpentinization: from oceanic serpentinization and the formation of lizardite and chrysotile assemblages, to the prograde destabilization of oceanic serpentine into antigorite, from greenschist to blueschist facies, and finally the dehydration of antigorite into olivine-orthopyroxene-chlorite assemblages at eclogite facies. I have combined iron K-edge $\mu$-XANES and magnetic measurements, as well as the use of theoretical chemical mass transfer calculations to predict the redox state of fluids generated during serpentinite dehydration. The results demonstrate that serpentinite devolatilization produces highly oxidized fluids in subduction zones and can contribute to the oxidization of the sub-arc mantle wedge. This provides some of the first direct constraints on the redox state of serpentinites-derived fluids in subduction environment.

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# Pressure estimates from fluid and solid inclusions in minerals from UHPM rocks

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Mineral inclusions entrapped in UHPM rocks can provide fundamental information about geological processes such as subduction. When a host-inclusion pair is exhumed from depth to the Earth's surface, a non-lithostatic pressure ($P_{inc}$) is developed in the inclusion because of the contrast in their elastic properties (Angel et al., 2015). If correctly interpreted, $P_{inc}$,allows the stress conditions at entrapment ($P_{trap}$) to be estimated.

For solid inclusions, the back-calculation of the $P_{trap}$ requires the change in the volume of the cavity upon changes of external P and T to be accounted for. Therefore, the calculation does not rely on isochors but on isomekes, that are lines in P-T space along which the relative change in volume for the host and the inclusion are equal, but not constant. The current solution incorporates isotropic non-linear elasticity (Angel et al., 2017), and has been extended to include non-simple geometries of the system (e.g. faceting of the inclusion or proximity to external surfaces of the host, Mazzucchelli et al., 2018).

This approach could in principle be extended to fluid inclusions in UHPM rocks, that have the advantage of being elastically isotropic. Classical thermobarometric analysis of fluid inclusions relies on the assumption that the cavity does not change its volume upon exhumation implying that the host is infinitely rigid, a situation that is never met in reality.

For a water-rich fluid inclusion entrapped at the metamorphic peak for Dora Maira Massif (4.3GPa and 730°C) that did not suffer stretching or decreptation, using an isochor for the fluid we would calculate a $P_{inc}$ of 1.49 GPa at room temperature. If the host mineral is a stiff pyrope garnet and the effect of volumetric expansion of the host ($\Delta V/V=0.00702$) is included, the final $P_{inc}$ decreases to 1.32 GPa. Further, if the host is softer quartz the volumetric expansion is much larger ($\Delta V/V=0.06586$) and it decreases the final $P_{inc}$ on the fluid to 0.84 GPa. However, the $P_{trap}$ for natural fluid inclusions can be estimated quantitatively only if the composition, and thus the exact equation of state of the fluid, is known at any P and T condition.

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# The Metasomatic Influence of Silicic HDF on the Sub Continental Lithospheric Mantle

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The mantle beneath cratons (the sub-continental mantle lithosphere, SCML) is characterized by a complex history involving melting followed by fluid metasomatism. These fluids are responsible for shaping the mineralogy and rheology of the mantle as well as being the source from which diamonds are formed. Fluids found as inclusions in diamonds (high-density fluids, HDF) are thought to be the metasomatic agents. Latest models demonstrated a connection between experimental fluids and melts and HDF end members. It was suggested that alkali-rich hydrous fluids, originated from the dehydration of the subducting slab, interact with the mantle and initiate melting to form the silicic HDFs. Despite its important role in mantle processes, the interaction of volatile-bearing fluids, in general, and silicic HDF, in particular, with harzburgitic lithologies beneath cratons was only rarely investigated experimentally.

This study examines the interaction of silicic fluids with harzburgite at pressures of 3-6 GPa and temperatures of 800-1100°C, conditions relevant for metasomatism of the SCLM. This study will enable us to further investigate the fluids' role in the metasomatic processes, will shed light on the metasomatic changes in the harzburgite, and on the stability of metasomatic phases in the cratonic mantle. $H_2O$- and $CO_2$-bearing silicic fluids, similar to those found in diamonds, are mixed with a primitive harzburgite at high-pressure and temperature in order to evaluate the compositions of the equilibrated fluids and the metasomatic mineral assemblage. The experiments are performed in a rocking multi-anvil apparatus using a diamond-trap setup. The compositions of the fluid and melt phases are determined using the cryogenic LA-ICP-MS technique and the QTS technique. Using these innovative methods, we can directly measure the fluid compositions in the system. The minerals' composition is determined using EPMA.

The fluids in this study are alkali-rich, containing 45-50 wt% $H_2O$ and 25-30 wt% $CO_2$. With increasing temperature, the melts were found to contain 15-23 wt% $H_2O$ and 14 wt% $CO_2$. The results so far indicate the location of the solidus to be between 900 and 1000oC at 3 GPa and between 1000-1100oC at 4-5 GPa. The solidus found in this study is similar to previously determined solidi for lherzolite+$H_2O$ and lherzolite+$H_2O$+$CO_2$ systems. The near solidus fluid and melt compositions differ from the silicic HDF starting composition, but similar to low-Mg carbonatitic HDF fluids.

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# The Aqueous Solubility Of Rhodochrosite In Subduction Zones

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Carbon is transported to the deep Earth predominantly by the subduction of carbonate minerals. These represent the most stable and abundant carbon bearing solids down to depths of at least 200 km (6 GPa) [1]. While high pressure-temperature (P-T) experiments extend the stability of carbonates in different structures to depths of at least 2,500 km (>100 GPa) [2,3], the enhanced solubility of carbonates in high P-T aqueous fluids [4,5] instead advocates for their efficient recycling back to the atmosphere through dissolution in slab fluids, transfer to the mantle wedge and consequent volcanic outgassing [6–9]. Here, we have determined the aqueous solubility of rhodochrosite ($MnCO_3$) at subduction zone conditions (<8 GPa, <500°C). $Mn^{2+}$ ion concentrations have been measured by synchrotron X-ray fluorescence (SXRF) spectroscopy coupled with the diamond anvil cell (DAC) at the European Synchrotron Radiation Facility. Complementary aqueous carbonate speciation data have been collected by Raman spectroscopy coupled with the DAC at the University of Cambridge. Together, both methods give a full picture of the aqueous geochemistry of the fluids in equilibrium with carbonates, directly at the high P-T conditions characteristic of subduction zones and the overlying mantle wedge.

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# Thermodynamic investigations of redox state in subduction zone fluids (invited)

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The redox state and speciation of subduction zone fluids determines the capacity of these fluids to oxidise the sub-arc mantle, and extent to which the deep Earth could be oxidized by the addition of dehydrated subducted material. Oxidised sub-arc mantle is critical to many genetic models for the formation of arc-related ore deposits, and the redox evolution of the deep Earth is fundamental to our understanding of temporal change in geological processes. In spite of this importance, there is no consensus on the redox state of these fluids. Subducted ultramafic rocks, in particular, have the capacity to produce oxidized fluids via changes to the stability of magnetite and sulfide minerals. Magnetite produced by serpentinisation carries redox budget in the form of ferric iron, and it has been proposed that this redox budget is transferred to oxidized sulfur species dissolved in subduction zone fluids, and onwards to the sub-arc mantle.

THERMOCALC simulations of high pressure-low temperature metamorphism of ultramafic rocks replicate observed mineral assemblages but, rather than predicting release of oxidized species, predict release of methane and hydrogen sulfide. Loss of these reduced species results in a small increase in the redox budget of the subducting slab, and infiltration of such fluids into the sub-arc mantle would not produce oxidation. However, there are limitations to these models that require careful consideration, and these will be presented and discussed.

An alternative approach, that circumvents some of the limitations inherent in the THERMOCALC calculations, but imposes others, is to compare the predictions of activity-activity diagrams in the system Ni-Fe-O-H-S to oxide-sulfide-alloy assemblages in subducted ultramafic rocks. Application of this approach to serpentinised ultramafic rocks from supra-subduction zone mantle in New Caledonia, from high pressure-low temperature rocks from the Zermatt-Saas ophiolite, and to rocks from different tectonic settings in Alpine Corsica, reveal that fluids sufficiently reducing to stabilize awaruite, and sufficiently oxidizing to stabilize pyrite are found in different settings.

It is concluded that subduction of ultramafic rocks can produce either reducing or oxidizing fluids, depending on factors that include, but are not limited to, geodynamic setting of the protolith, the extent of open system fluid interactions, and the proximity of contrasting lithologies.

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# COH-fluid driven carbonation of serpentinites and spinel peridotites within the forearc region of the mantle wedge and in the subducting slab

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Carbonation of serpentinite and spinel peridotite in the forearc region of the mantle wedge in subduction zones and within the subducting slab by $CO_2$-bearing aqueous fluids released during subduction were investigated in this study. We show that this process is potentially an efficient mechanism to sequester $CO_2$ in the mantle wedge and subducting slab, which may have important implications for estimates of the carbon fluxes into the deep earth.

Piston cylinder experiments were performed using natural, powdered antigorite with $CO_2$+$H_2O$ fluids at 1 and 2 GPa and temperatures ranging from 550 ℃ to 750 ℃. The equilibrium fluid compositions were measured by piercing the capsules recovered from piston cylinder experiments and introducing the released fluid into a gas chromatograph. The resulting mineral assemblages and fluid compositions were compared with the results of thermodynamic modelling of the antigorite-$CO_2$-$H_2O$ system. Additional piston cylinder experiments were performed at 1.5-2.5 GPa and 375-700 ℃ using cylindrical samples cored from natural serpentinite and spinel peridotite in the presence of COH-fluids. These experiments include a time series and aimed to simulate fluid-rock interactions allowing investigation of fluid flow mechanisms and reaction rates. We compare our experimental results with field observations of large scale carbonation of subducted ultramafic rocks within the Western European Alps.

In the experiments using powdered serpentinite, the formation of magnesite + chlorite together with quartz, quartz + talc or talc with progressive carbonation was observed at 1-2 GPa and 500-650 °C. In the experiments using serpentinite cores, textural evidence shows enhanced fluid migration along fractures and the percolation of the reaction interface with time (and progressing reaction) from the core's surface towards the center of the core. This forms distinct and sharp boundaries between zones of quartz + magnesite and talc + magnesite. Clear distinguishable reaction zones and similar mineral assemblages were also formed in the pseudomorphic replacement of primary phases in the peridotite core experiments. Carbonation occurs rapidly even in experimental samples with natural grain sizes, textures and foliation of the serpentinite and peridotite cores. For example, ∼5 wt%, ∼20 wt%, ∼60 wt% and ∼75 wt% of the original serpentinite-core is replaced by magnesite and talc after 12 h, 24 h, 96 h and 192 h at 2 GPa and 600 ℃. The findings of our study have important implications for estimating the deep Earth's carbon fluxes as the mantle wedge may become, over time, a significant reservoir for carbon. Additionally, carbonation of ultramafic rocks within the subducting slab may contribute to C-transfer to the deeper mantle.

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# Molecular modeling approaches to element speciation in aqueous fluids (invited)

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Aqueous fluids are key agents in subduction zone processes. They do not only change the physical properties of rocks but they are also able to dissolve and transport mineral components. They are released or absorbed during mineral reactions. A starting point for understanding the role of fluids in fluid-rock interactions is to investigate their molecular structure, especially the formation of various solute species, at relevant thermodynamic conditions. Joint experimental and numerical modeling efforts are required to reveal the full complexity of fluid speciation up to high temperatures and pressures. Here, we discuss different approaches for predicting thermodynamic properties of aqueous fluids from first principles simulations. By combining ab initio molecular dynamics simulations with advanced sampling methods such as thermodynamic integration or metadynamics we derive, e.g., species stability constants or acidity constants. The methodology is illustrated by examples of our recent studies of beryllium and yttrium speciation in fluorine- and chlorine-rich fluids. Finally, we discuss the reliability of present thermodynamic models of these systems and how first-principles simulations can help to improve them considerably, especially at high temperatures and pressures.

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# Fluid release and seismicity at a transition between oceanic and continental subduction

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The Western Hellenic subduction zone is characterized by a transition from oceanic to continental subduction. In the southern oceanic portion of the system, abundant seismicity reaches intermediate depths of 100-190 km, while the northern continental portion rarely exhibits deep earthquakes. Our study aims to investigate how this oceanic-continental transition affects fluid release and related seismicity along strike. To address this question, we present results from local earthquake tomography and double-difference relocation in conjunction with high-resolution seismic images across western Greece. Our results show that, in the south, earthquake distribution and seismic velocities are consistent with the presence of a hydrated subducted crust that undergoes eclogitization and dehydration at ~100 km depth. Below the arc, the fluids released from the slab are fluxed into the mantle wedge and cause partial melting. Below the oceanic-continental transition, released fluids appear instead to rise updip along the slab and flux into the overriding crust, where they precipitate silica. To the north, our results are consistent with subduction of dry metastable crust, where the absence of fluids causes subduction to take place nearly aseismically.

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# Stability of oxidized iron species and the redox budget of slab-derived fluids

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The high oxidation state of subduction zone magmas compared to magmas from other locations might result from the influx of oxidized fluid from the subducted oceanic plate into the mantle wedge. However, the nature of the chemical agent(s) and the mechanism responsible for the transfer of the oxidized signature from the slab to the mantle wedge remains poorly understood. In this contribution, we will discuss the oxidizing capacity of slab-derived fluids in the light of experimental results of the solubility and speciation of iron in high-pressure fluids that mimic the slab flux.

Iron-bearing mineral assemblages were equilibrated with chlorinated aqueous fluids and hydrous granitic melts at different oxygen fugacities relevant for the present day crust/mantle. The distribution and stability of oxidized iron species were monitored up to 2.5 GPa and 800 C by XANES measurements in diamond anvil cells. The results illustrate the role of coordination chemistry involving halogen and polymerized species in the stability of oxidized iron in the fluids. The concentration of Fe3+ in the fluids progressively decreases as temperature increases, regardless of fluid composition and pressure. This implies that the fluid capacity to transport Fe3+ at high temperature may be limited, even at the redox conditions relevant for the present day crust and mantle. With the new experimental results, we place constrains on the oxidizing capacity of Fe-bearing metasomatic fluids and discuss the transfer of the oxidizing signature and the conditions for the genesis of oxidized arc magmas.

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# Fluids in subduction-zone rocks

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It is now ascertained that fluids are essential to metamorphism. Early seminal work1 shows that without fluids rocks do not react and preserve metastable on a long-term. This is relevant to subduction zones, where fluids affect properties and physical-chemical behaviour of large rock volumes inside the colliding plates. Importantly, fluids affect rock deformation, seismicity and mass transfer in slabs, in the subduction interface and in the mantle wedge. In the last two decades, efforts have been done to identify fluids in eclogite-facies rocks, their migration pathways and interaction with rocks.

Subduction of variably oxidized, volatile- and incompatible element-rich oceanic lithosphere is accompanied by dehydration and decarbonation reactions of various rock types at different P-T conditions. Emphasis has been placed on serpentinized oceanic and fore-arc mantle as volatile and fluid-mobile element repositories, whose dehydration leads to melting of the sub-arc mantle wedge. Devolatilization is frequently accompanied by fluid drainage in vein networks allowing fluid escape from slabs. Veins provide a wealth of information on fluid mobility and composition. Recent work shows that subduction fluid mobility occurs during short-lived pulses (200 years)2. Moreover, fluid production and drainage in veins is driven by fine-scale chemical heterogeneities. The resultant fluid pressure variations at specific microsites force the fluid flow to organize into vein networks at scales ranging from $\mu$m to metres3.

HP-UHP veins and rock-forming minerals trap inclusions of coexisting subduction fluids. Omphacite- and olivine-bearing veins in Alpine eclogite and serpentinite host brine inclusions formed by recycling of seawater trapped during the oceanic alteration of rocks4. The analysis of fluid-related inclusions in de-serpentinized metaperidotite unexpectedly revealed abundant halogens and fluid-mobile elements concentrations in the fluid. This fluid, as probably most subduction fluids, transfers to the mantle a hybrid component (serpentine + sediment) uptaken by the original serpentinite by interacting with sediment-derived fluids in the subduction zone. The aqueous fluids released by dehydrating slab lithologies also promote decarbonation or carbonate dissolution in associated sediments, producing COH fluids that can precipitate microdiamond (or graphite) and carbonate5. Slab fluids are reactive with the supra-subduction mantle: the interaction leads to formation of pyroxenite layers that filter the uprising slab melt/fluid to produce solute-rich mobile aqueous fluids. Possible consequence of such reactions is that the mantle overlying the slabs is heterogeneous in composition and veined. Hence, while hydrous melt and/or silicate-rich fluids are important for scavenging incompatible elements from the slab, they may not be the agents transferring the subduction signature to melting region of the subarc mantle wedge. Much work is still necessary to define the physical and chemical process attending rock dehydration, carbonate dissolution, fluid/rock interactions, and to define the potential of subduction fluids in affecting the composition and redox of mantle wedge rocks.

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# Metasomatism of UHP garnet peridotites by crustal-derived fluids in subduction zone setting reflected by solid inclusions and chemical zoning in garnet

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Garnet peridotites occur in spatial association with eclogites and diamond-bearing gneisses in an ultrahigh-pressure (UHP) complex within the Saxothuringian basement of the northern Bohemian Massif, European Variscan belt. The crustal and mantle rocks have a common subduction history as reflected by similar peak P-T conditions (c. 5 GPa and in excess of 1100°C) and petrological data. This rock assemblage thus provides unique material to study subduction-zone processes including fluid-mediated material transfer.

Garnets from peridotites contain primary multiphase solid solutions (MSI) concentrated at their $\approx$ 200-300 $\mu$m thick rim. These MSI are polygonal, equant to elongated, reaching up to 40 $\mu$m in size, and they are dominated by carbonates (dolomite±magnesite), amphibole and Ba-rich mica (Ba-rich phlogopite to kinoshitalite). Minor phases involve graphite, spinel, thorianite, apatite and pentlandite. Garnets from lherzolite show large chemically homogeneous core and approximately 100-500 $\mu$m wide rim with retrograde zoning features, i.e. Fe increase and Mg as well as XMg decrease. Trace element zoning patterns are distinct from those of major elements. Apart from Mn and Ti (+Nb), which continuously increase from garnet core to rim, other trace elements show rather flat zoning profiles in the core and marked changes in concentrations at the MSI-bearing rim. These involve increase in Th, U, Y+REE (and Mn) and drop in Zr, Hf, Nb, Ta and Ti. In contrast to major elements (Fe, Mg) with high diffusivities in garnet, which are prone to reequilibration upon cooling, the less diffusive trace elements can preserve the growth patterns. We suggest that trace element concentration profiles at the MSI-bearing garnet rims reflect change in composition of the growth environment characterized by high Th, U, and REE, as also reflected by presence of thorianite (Th, U) and REE-bearing Cl-apatite within the MSI. Enrichment in LILE (Ba, K, Sr: kinoshitalite, carbonates, amphibole, apatite) and volatiles ($H_2O$, $CO_2$, $Cl > F$) in the MSI provide additional evidence for fluid-mediated element transport from subducting crustal slab into the overlying mantle wedge. Our findings are compatible with evidence for cryptic metasomatism with respect to Th, U and LREE documented by bulk rock chemical data (Medaris et al., 2015). At given context, the elements could be mobilized by supercritical liquids produced by dehydration melting of the associated UHP-UHT metasediments which are efficient carriers of all trace elements in question. Major element bulk composition of the MSI in a lherzolite sample, however, is not uniform: although the XMg, MgO/FeO, $MgO/SiO_2$ and $SiO_2/Al2O_3$ ratios are similar, CaO contents are variable: this is also reflected in different proportions of carbonates. Rehomogenization experiments on the MSI will allow constraining the nature of the transport media (fluids/melts/supercritical fluids) as well as element sources.

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# Primary spinel+chlorite inclusions in mantle garnet formed at UHP: implications for the crust-to-mantle redox budget

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Multiphase inclusions represent microenvironments where the interaction between fluid and host mineral is preserved during the rock geological path. Under its peculiar chemical-physical constraints, the entrapped solute-rich fluid might follow a crystallisation mechanism which is not predictable through simple equilibrium arguments. By the modelling of solid-solution equilibrium and the application of principles of mass conservation, we demonstrate that cavities in mantle garnet filled with slab-derived fluids can re-equilibrate to a pyrope + spinel + chlorite assemblage at the same high P-T of their formation. The basis of this occurrence is a dissolution-reprecipitation mechanism, triggered by a dilute, non-equilibrated slab fluid.

A case study of supra-subduction mantle affected by metasomatism from crust-derived fluid phases is the Maowu Ultramafic Complex (China) deriving from harzburgite precursors metasomatised at $\sim$ 4 GPa, 750-800°C by a silica- and incompatible trace element-rich fluid phase [1,2]. This metasomatism produced poikilitic orthopyroxene and inclusion-rich garnet porphyroblasts. Solid multiphase primary micro-inclusions in garnet display negative crystal shapes and infilling minerals (spinel, ±orthopyroxene, amphiboles, chlorite, ± talc, ± mica) occur with constant modal proportions, indicating that they derive from trapped solute-rich aqueous fluids. A single-crystal X-ray diffraction experiment performed by synchrotron radiation at Diamond Light Source [3] demonstrated the epitaxial relationship between spinel and garnet and between some hydrous minerals. Moreover, FT-IR hyper spectral imaging analyses and micro-Raman spectroscopy, together with X-ray microtomography performed on single inclusions, indicate that liquid water is still preserved at least in some inclusions. The Fe3+ concentration of the micron-sized precipitates of the multiphase inclusions has been measured for the first time using EELS on a TEM to investigate the redox budget of these fluid phase. Results indicate that spinel contains up to 12% of Fe3+, amphibole about 30%, while in chlorite and phlogopite may reach 70%. The Fe3+ fraction of the host garnet is equal to that measured in spinel as also confirmed by Flank Method EPMA measurements.

Oxygen mass balance, performed both on the Maowu hybrid orthopyroxenite and on metasomatised supra-subduction garnet peridotites, indicate that the excess of oxygen ($nO_2$) is the same (10 mol m-3). An oxygen mass balance of the crust- derived fluids also indicates that the fluid precipitates are more oxidised than the host rock, reaching up to 400 mol m-3 of $nO_2$. This suggests that even after their interaction with the metasomatic orthopyroxenites, the residual fluid phases could be potentially carrier of oxidised components when escaping the slab-mantle interface.

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# High pressure melting of phengite-bearing eclogite: evidence for multiple slab-derived melt/fluid-mantle interaction during HP and HT metamorphism of grt-peridotites of Monte Duria (Central Alps, N Italy)

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The Monte Duria area is located in the southern part of the Adula Nappe on the north-eastern side of the Como Lake (N Italy). Garnet/chlorite peridotites were found within Bt-rich migmatitic gneiss or in direct contact with amphibole-bearing migmatites containing boudins of variably granulitised eclogites. The contact between mafic and ultramafic rocks is marked by the occurrence of a metasomatic rim composed by tremolite and dispersed round-shaped chlorite aggregates. The occurrence of lobes and cusps structures and Qtz+Pl+Kf+Bt leucosomes in eclogites provide evidence for partial melting of these rocks.

Petrographic and mineral chemical data indicate that peridotites and associated eclogites experienced a HP metamorphic peak followed by a granulitic overprint during their exhumation path. Peridotites and associated eclogites reached the eclogitic peak at $\approx 2.8$ GPa and $\approx 730 \pm 20$ °C whereas P-T estimates on symplectitic assemblages replacing HP minerals in both mafic and ultramafic rocks yielded conditions of 0.8-1.2 GPa and 850 °C (Tumiati et al. 2018).

The micostructural evidence of Qtz+Pl+Kf+Bt pockets in eclogites support the field evidence of a partial melting event. Eclogites display a HP assemblage formed by Grt+Ky+Omp+Kf, suggesting that a former phengite was completely consumed by the reaction $\mathrm{Phe+Cpx+SiO_2 = Grt+Ky+Kfs+Melt}$, further indicating that melting occurred at HP conditions. At this stage a clinopyroxenite reaction front probably results from a Ca-rich mafic silicate melt - peridotite interaction. Therefore, we suggest that tremolite-rich metasomatic rim probably represents a former grt-clinopyroxenite reaction front subsequently retrogressed under green-schist facies conditions through the reaction $\mathrm{Cpx+Opx+Grt+H_2O = Tr+Chl}$.

Bulk rock trace element analyses of peridotites show REE content slightly lower than DM with a fractionation characterised by LREE enrichment (La/NdN = 2.4) indicating that these rocks record an interaction with a silicate melt. A similar REE pattern is also displayed by eclogites, but the nature of such an imprint is likely inherited by a cumulitic gabbro protolith. The metasomatic rim shows REE concentrations slightly higher than DM with a LREE enrichment and a slight Eu negative anomaly. This pattern broadly resembles the trace elements composition of pyroxenites from other localities of eastern Europe (i.e. Gföhl Moldanubian Nappe), interpreted as the product of infiltration of slab-derived melts in the overlying lithospheric wedge (Medaris et al., 2006). The trace elements patterns of peridotites, metasomatic rim, and associated eclogites all show also an enrichment in fluid-mobile elements, such as Cs, Rb, Ba and K, and an high U/Th ratio suggesting that a subsequent fluid-assisted metasomatic event affected both mafic and ultramafic rocks under granulite or amphibolite facies conditions.

The Monte Duria area represents a unique case study where mafic melt - peridotite interaction occurs at high pressure and relatively high temperature in the Adula Nappe complex. The melt-rock interaction recorded by the Monte Duria peridotites could thus represent a proxy for the crust-to mantle mass transfer at great depths in “warm” subduction environments.

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Exploring new frontiers in fluids processes in subduction zones

# The role of volatiles in subduction zone metasomatism and melting: An experimental perspective

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Fluid-mediated metasomatism and melting in subduction zones play a key role in the geochemical evolution of the Earth's mantle and crust. Dehydration of the subducting hydrated and altered oceanic lithosphere release $H_2O$-$CO_2$-rich fluids into the overlying mantle wedge. Melting of the metasomatized mantle wedge is the source of Island arc lavas. Despite the obvious role of volatiles in subduction zones, relatively little is known about the high-pressure dehydration and melting relations of mantle rocks in the presence of $H_2O \pm CO_2$.

Experiments on both basaltic and peridotitic compositions were performed on a rocking multi-anvil apparatus using the diamond trap setup. The compositions of the volatile-bearing fluid and melt phases were measured using the cryogenic LA-ICP-MS (for the cation content) and QTS (for the $H_2O$ and $CO_2$ content) techniques. The minerals compositions were determined by EMPA.

The solidus of eclogite+$H_2O$ system is located between 850 and 900oC at 4 GPa and between 1000 and 1050oC at 5 GPa. The solidus of the eclogite-$H_2O$-$CO_2$ system at 4 GPa is ~150°C higher. The difference in the solidus temperature of the two systems narrows as pressure increases, eventually resulting in a similar location of the second critical endpoint between 5 and 6 GPa and 1050oC. Differences in solidus location are most probably due to differences in alkali and $H_2O$ content.

The $H_2O$-bearing alkali-rich peridotite solidus is located between 900 and 1000oC at 4 GPa and between 1000 and 1100oC at 5-6 GPa. Addition of 1 wt% $CO_2$ does not affect the solidus location. Increasing the amount of $CO_2$ to 5 wt% in the bulk peridotite lowers the solidus by about 100oC.

The near solidus $H_2O \pm CO_2$-bearing fluids and melts interacting with both eclogite and peridotite rocks studied here are similar to intermediate compositions along the array spanned between low-Mg carbonatitic high-density fluids and hydrous-silicic ones that are found in microinclusions in diamonds. Changes in the $H_2O/CO_2$ ratios in the bulk rock results in different location along the array. With increasing temperature, the $H_2O$-$CO_2$-bearing melts approach type II kimberlites.

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# Barian mica in multiphase solid inclusions from orogenic garnet peridotites as indicator of composition of subduction-zone fluids

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Chemical composition of barian mica in multiphase solid inclusions (MSI) enclosed in garnet from mantle-derived UHP garnet peridotite (Saxothurian basement of the northern Bohemian Massif) has been used to describe its crystallization medium. Barian mica in MSI from lherzolite forms anhedral grains, which are intimately intergrown with other associated minerals (amphibole, magnesite, dolomite, spinel and graphite). In harzburgite, barian mica commonly occurs at the rim of MSI around central dolomite. Its chemical composition corresponds to Ba-rich phlogopite to kinoshitalite. Beside Ba (0.24-0.67 apfu) and K (0.22-0.59 apfu), minor Na (0.1-1.0 wt. % $Na_2O$) and Sr ($\leq$ 0.27 wt. % SrO) fill the interlayer site. Micas are enriched not only in Mg (1.83-2.48 apfu with $X_{Mg}$ ratio $\sim$ 0.85-0.95) but also in Cr (0.03-0.43 apfu), which along with minor Fe (0.11-0.36 apfu) and Ti (0-0.11 apfu) and traces of Ni (0.1-0.3 wt. % NiO) enters octahedral sites. All barian micas are characterized by high Cl (0.04-0.34 apfu) and very low F ($\leq$0.03 apfu). Substitution vector involving Ba in the I-site and describing observed chemical variability can be expressed as $BaFe^{IV}AlClK_{-1}Mg_{-1}Si_{-1}(OH)_{-1}$. Minor amount of Cr and $^{VI}$Al enters octahedral sites following substitution trend $^{VI}(Cr,Al)_2^{VI}(Mg,Fe)_{-3}$ towards chromphyllite and muscovite. Chemistry of the barian mica from MSI studied (high Cr, $X_{Mg}$, Cl > F, low Mn, Ti) differs from the composition of other trioctahedral barian micas described typically from crustal magmatic (potassic and alkaline) or metamorphosed rocks (marbles, skarns, Fe,Mn deposits) enriched in barium.

Textural relations and chemical composition indicates crystallization of barian mica together with other minerals in MSI from fluids trapped during garnet growth. The unusual chemical composition of barian mica reflects mixing of two distinct sources. The internal source represents the host peridotite and garnet, providing Mg, Fe, Al, Cr, (+Ni). Externally sourced, crustal-derived subduction-zone fluids supplied Ba (+Sr), K and Cl > F. At UHP-UHT conditions recorded by the associated diamond-bearing metasediments (c. 5 GPa at $\geq$ 1100°C), located above the second critical point in pelitic system, solute-rich supercritical fluids with properties of hydrous melt are produced. These are efficient carriers of elements into the suprasubduction mantle peridotite. UHP peridotites can thus represent another typical environment, still overlooked, that allows formation of Ba-rich phlogopite to kinoshitalite. Its presence and chemical composition itself provide evidence for mantle metasomatism by crustal-derived fluids in subduction zone setting.

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Exploring new frontiers in fluids processes in subduction zones

# Metal mobilization and transport in magmatic-hydrothermal fluids

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High pressure fluids are major vectors for mass transfer at crustal and mantle depths, where they are involved in processes leading to ore enrichment and mass recycling. The poor understanding of the atomic-scale mechanims that controls the mobilization and transport of elements at relevant conditions, however, limits the quantitative modelling of these processes. Here we present experiments using X-ray absorption spectroscopy XAS at high pressure to monitor the chemical composition, the molecular structure and thermodynamic quantities for high-pressure fluids. Specifically, we investigate the pressure, temperature and redox controls on the dissolution of ore mineral cassiterite ($SnO_2$) and the transport of tin in hydrothermal settings.

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. At 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. We will discuss the speciation of tin and the controls on the transport and precipitation of cassiterite $SnO_2$ in high pressure fluids.

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# Redox processes and the role of carbon-bearing volatiles rom the slab-mantle interface to the mantle wedge

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The valence of carbon is governed by the oxidation state of the host system. The subducted oceanic lithosphere contains considerable amounts of iron so that Fe3+/Fe2+ equilibria in mineral assemblages are able to buffer the $fO_2$ and the valence of carbon. Alternatively, carbon itself can be a carrier of redox budget when transferred from the slab to the mantle, prompting the oxidation of the sub-arc mantle. Also, the oxidation of sedimentary carbonaceous matter to $CO_2$ in the slab could consume the available redox budget. Therefore, the correct use of intensive and extensive variables to define the slab-to-mantle redox budget by C-bearing fluids is of primary importance when considering different fluid/rock ratios. Fluid-mediated processes at the slab–mantle interface can be investigated also experimentally. The presence of $CO_2$ (or CH4 at highly reduced conditions) in aqueous COH fluids in peridotitic systems affects the positions of carbonation/decarbonation reactions and of the solidus. Some methods to produce and analyse COH fluid-saturated experiments in model systems are introduced, together with the measurement of experimental COH fluids composition in terms of volatiles and dissolved
solutes. The role of COH fluids in the stability of hydrous and carbonate minerals is discussed comparing experimental results with thermodynamic models.

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# Experimental determination of forsterite, enstatite and magnesite solubilities in graphite-saturated and redox-buffered high-pressure COH fluids (invited)

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Subduction zone fluids are able to mobilize and transport significant amounts of dissolved species resulting from fluid-rock interactions at high pressure. Experimental data, thermodynamic models and natural samples provide evidence for silicate solutes and dissolved carbon species in deep fluids, although the effect of carbon on mantle minerals solubility is still poorly constrained.

We experimentally investigated the dissolution of forsterite, enstatite and magnesite in graphite-saturated COH fluids synthesized using a rocking piston cylinder apparatus at pressures from 1.0 to 2.1 GPa and temperatures from 700 to 1200 °C. Synthetic forsterite, enstatite, and nearly pure natural magnesite were used as starting materials. Redox conditions were buffered by Ni–NiO–$H_2O$ ($\Delta$FMQ = -0.21 to -1.01), employing a double-capsule setting. Fluids, binary $H_2O$–$CO_2$ mixtures at the $P$, $T$, and $fO_2$ conditions investigated, were generated from graphite, oxalic acid anhydrous ($H_2C_2O_4$) and water. Their dissolved solute loads were analyzed through an improved version of the cryogenic technique, which takes into account the complexities associated with the presence of $CO_2$-bearing fluids. The experimental data show that forsterite + enstatite solubility in $H_2O$–$CO_2$ fluids is higher compared to pure water, both in terms of dissolved silica ($m\text{SiO}_2 = 1.24$ mol/kg$_{H2O}$ vs. $m\text{SiO}_2 = 0.22$ mol/kg$_{H2O}$ at $P = 1$ GPa, $T = 800$ °C) and magnesia ($m\text{MgO} = 1.08$ mol/kg$_{H2O}$ vs. $m\text{MgO} = 0.28$ mol/kg$_{H2O}$) probably due to the formation of organic C–Mg–Si complexes.

Our experimental results show that at low temperature conditions a graphite saturated $H_2O$–$CO_2$ fluid interacting with a simplified model mantle composition, characterized by low MgO/$SiO_2$ ratios, would lead to the formation of significant amounts of enstatite if solute concentrations are equal, while at higher temperatures these fluid, characterized by MgO/$SiO_2$ ratios comparable with that of olivine, would be less effective in metasomatizing the surrounding rocks. However, the molality of COH fluids increases with pressure and temperature, and quintuplicates with respect to the carbon-free aqueous fluids. Therefore, the amount of fluid required to metasomatize the mantle decreases in the presence of carbon at high $P$–$T$ conditions. COH fluids are thus effective carriers of C, Mg and Si in the mantle wedge up to shallowest level of the upper mantle.

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# Physical factors that control fluid migration pathways in the mantle wedge

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Arc volcanism is mainly generated by the addition of hydrous fluids that trigger flux melting in the hot region of the mantle wedge. While thermo-petrological models predict the release of aqueous fluids from the subducting slab over a wide depth range, arc volcanoes are observed only in a relatively narrow region which lies ∼100±30 km above the top of the slab, suggesting the existence of some mechanism that focuses fluids and/or melts beneath the arcs. To assess the physical factors that exert a first-order control on fluid migration (FM) pathways through the mantle wedge, we use numerical 2D Darcy's-Stokes flow models (TerraFERMA and SubFUSc).

Recent FM models have suggested that spatial variations in mantle shear viscosity and permeability are critical factors that control FM pathways in the mantle wedge [Wilson et al., 2014; Cerpa et al., 2017]. In particular, the relatively small grain size predicted by the models near the tip of the corner flow leads to the trap of fluids released beneath the forearc and their down-dip drag towards by mantle solid flow. Once they reach the sub-arc region, the fluids start to migrate upwards [Wada and Behn, 2015; Cerpa et al., 2017]. Using such models we have explored the effects of the magnitude of fluid influx from the slab, the fluid viscosity and the density of the fluid on FM pathways. By applying uniform fluid properties in the model, we find that fluid influx and fluid viscosity may play a key role in defining fluid pathways while fluid density plays a secondary role. When a temperature-dependent fluid viscosity is applied, models predict greater entrapment of shallow and relatively cool fluids by the down-going mantle, promoting their arc-ward transport. On another hand, we observe that some of the fluids released at post-arc depths are also focused towards the sub-arc region by the mantle incoming flow. Yet, most of those fluids tend to focus beneath the back-arc and may trigger melting of distal parts of the mantle wedge.

Whether such distal melts form rear-arc volcanoes or are also focused towards the arc cannot be addressed by current models, as they do not account for mantle melting. Indeed, variations in water and silica content, affect fluid properties; the large jumps in fluid composition expected in the partial melting region may affect the paths of melts. To quantify this effect, we plan to use the Subduction Framework Utilising Scientific Computing (SubFUSc) code. This new code uses a fully-coupled mathematical framework in which melting is computed assuming local thermodynamic equilibrium and a parameterized, three-components phase diagram.

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# Numerical subduction zones: advances in geodynamic and geochemical modeling

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Subduction zones are a challenge to model numerically. Over long periods of time the system can be modeled as a viscously deforming single, solid phase with a cold down-going slab driving deformation in the hotter mantle wedge. As the slab descends it releases aqueous fluids, which migrate into and across the wedge. This happens on time-scales much faster than the solid deformation but may still influence it. The aqueous fluids cause flux melting in the wedge and, ultimately, arc volcanism. Modeling these processes requires a multi-phase description that incorporates chemical reactions between the phases, including de- and re-hydration of the solid, melting and freezing, and fluid and solid compositional changes. Even a simple single-phase model of the thermal structure is computationally expensive, requiring large amounts of resolution, but fully-coupled multi-phase models are additionally highly non-linear, requiring robust solution strategies to even converge.

Despite these challenges even single-phase thermal models have done much to advance our understanding of the dynamics and chemistry of subduction. For example, assuming chemical equilibrium and initial compositions, modeled slab temperature and pressure have been mapped onto phase diagrams to give the depths of aqueous fluid release. These maps have been used to place bounds on subduction zone fluid budgets and explain the locations of intra-slab earthquakes. They have also provided the starting point for more complicated, though not yet fully-coupled, multi-phase models that include the dynamics of the aqueous fluids. These have demonstrated potential focussing mechanisms that explain the offset between the locations of fluid release along the slab and melting beneath the arc. However, other significant discrepancies remain and much work remains to be done advancing these models further.

We aim to present an overview of published geodynamic subduction zone models – from single-phase thermal models to those that have started to include multi-phase interactions. We will discuss the geochemical observations that these models can be used to explain and the remaining discrepancies between them. Finally, as much of the geochemistry in these models relies on equilibrium assumptions we will mention some ongoing work aimed at including a more complete dynamic geochemical description using disequilibrium thermodynamics.

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# Recycling Bromine in subduction zones: New insights from X-ray absorption measurements on fluids, melts and glasses.

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Volatiles fluxes in subduction zones play a critical role in the Earth's chemical evolution, contributing not only to the hydrous melting of the mantle wedge and development of arc volcanism, but also to the composition of our atmosphere. While halogens are minor volatiles compare to $H_2O$ and $CO_2$, their ability to complex with other elements makes them key agents of the chemical transfer in subduction zones. Furthermore, they are important tracers of magmatic and degassing processes and provide insights about subsurface magma movement and eruption likelihood in volcanic arcs [1]. Amongst all halogens, bromine is of further interest as its volcanic degassing has been found, through the formation of BrO in volcanic plumes, to be significantly more effective in ozone destruction than more abundant Cl [2].

A better understanding (and consequent modelling) of Br and other halogens fluxes from the subducting slab to the mantle wedge, volcanic arc and ultimately the atmosphere requires an improved understanding of the mechanisms behind their incorporation in fluids and melts. Here, we combined in situ X-ray absorption (XAS) measurements on high P-T fluids and melts in diamond anvil cells to high-energy resolution fluorescence detected (HERFD) XAS on silicate glasses to constrain Br speciation over a wide range of P-T conditions and compositions. Especially, investigated melt and glass compositions include natural basalt, andesite, rhyodacite [3] and haplogranite so as to provide an improved view of structural controls on Br incorporation in silicate melts. The structural information derived from XANES and EXAFS analysis, compared to existing constraints on Br fluid-melt partitioning [4,5,6], is used to explain Br transfer from the subducting slab to volcanic arc.

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# Lawsonite-rich veins and layers as records of fluid flow and element cycling in subducted oceanic crust

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Lawsonite is an abundant hydrous mineral in subducted oceanic crust and sediments and is an important carrier of water (∼ 11 wt.%) and trace elements (REE, U, Th, Sr, Pb) into the mantle. Despite its widespread stability at the high-pressure/low-temperature conditions of subduction, it is rarely preserved in the geologic record, particularly in eclogite. Therefore, scarce fresh lawsonite eclogites in which the composition of lawsonite can be directly determined are important geochemical archives of fluid-mediated processes during subduction. Of particular interest are lawsonite-rich veins and layers that may represent former fluid pathways and that may record element mobility related to fluid-rock interaction during subduction and/or incipient exhumation.

In the Sivrihisar (Turkey) subduction complex, lawsonite-rich veins and layers (∼30% to nearly 100% lawsonite) are preserved along mafic pod margins, where lawsonite eclogite has been partially transformed to lawsonite blueschist. To understand the petrogenesis of these lawsonite-rich assemblages, we conducted a petrographic and geochemical study of a representative lawsonite-rich layer hosted at the margin of a meter-scale lawsonite eclogite pod. Bulk rock and mineral major and trace element analyses were conducted along a transect consisting of the lawsonite-rich layer (Lws + Grt + Ph), its glaucophane-rich margin (Gln + Grt + Lws + Ph + Rt), and the lawsonite eclogite host at varying distances from the lawsonite-rich layer (∼ 1 – 2 cm away and > 10 cm away).

Bulk rock geochemistry indicates that the lawsonite eclogite protolith was MORB that experienced interactions with (meta)sedimentary rocks before or during the crystallization of high-pressure phases such as lawsonite and rutile. Integrated major and trace element composition and zoning in garnet and thermobarometric results, including Zr-in-rutile thermometry, indicate that the lawsonite + garnet + phengite layer and its associated glaucophane-rich margin formed at or near peak eclogite-facies metamorphism (2.4 ± 0.1 GPa, 550°C) as a result of fluid-mediated processes that scavenged P, Sr, Pb, Y, Mn, HFSE, and REE from the eclogite immediately adjacent to the vein (∼1 – 2 cm away). Mass balance calculations also suggest the addition of LILE and transition metals to the pod margin; these elements were likely supplied from a source external to the mafic pod, such as serpentinites. Fluid-rock interaction along the eclogite pod margin may have also driven changes in $fO_2$, as omphacite, glaucophane, lawsonite, and phengite from the pod margin record core-to-rim increases in Fe3+. We propose that the transformation of eclogite to blueschist along the pod margin occurred as a result of changes in the bulk chemistry imparted during fluid-rock interactions.

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# Reduction and abiotic synthesis of hydrocarbons in subduction zones: widespread or anecdotal?

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The understanding of the speciation of C in subduction zone aqueous fluids is undergoing extensive reconsiderations, some of which challenge common paradigms on the nature and composition of geological fluids at these conditions. Redox is a fundamental parameter because it can govern fluid-rock equilibria and the evolution and speciations of redox-sensitive volatile elements. When dealing with slab-forming rocks, great variations in $fO_2$ have to be expected based on the geology (i.e. pre- and syn-subduction evolution) of single lithological domains, and fluid moving through slab-forming lithologic can experience significant variations over small scales. Most works dealing with the fluid speciation at these conditions typically refers to oxidized species only, most notable $CO_2$. However, recent works have demonstrated that extremely reducing fluid-rock processes can exist in subducting slabs and lead to abiotic genesis of hydrocarbons. Nevertheless, these conditions have been documented only in isolated localities so far, questioning the significance of these processes at meaningful scales. The goal of this study is to consider a series of common geological conditions at subduction zones where reducing conditions are expected and confirmed by past and new natural observations, and to show that these conditions can be spatially and volumetrically relevant to subduction zone fluid-rock budgets. The direct implication of this is the the possibility to produce and transport hydrocarbon compounds of abiotic origin over large scales, as well as the possibility for these reduced fluid compounds to mobilize elements of interest.

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# An Integrated Thermodynamic and Dynamic Approach to Modeling High Temperature Fluid Interaction in the Mantle Wedge

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Melting in the mantle wedge beneath volcanic arcs is generally considered to be driven by fluids extracted from the down-going plate. However, how these fluids are transferred to the hot mantle wedge is largely unknown. Attempts to model this process have been challenged by the strong coupling between fluid-rock reaction and transport dynamics which means that neither the dynamics nor the chemical evolution can be considered in isolation. Here we present a new computationally tractable framework, based on the concepts of non-equilibrium thermodynamics, that holistically integrates thermodynamics and fluid dynamics. We apply this framework to model the interaction of high temperature super-critical fluids with the mantle wedge in the $Mg_2SiO_4$-$SiO_2$-$H_2O$ and $Mg_2SiO_4$-$SiO_2$-$K_2O$ subsystems. The model employs a thermodynamically consistent generalization of the viscous two-phase flow equations that allows for multiple solid and liquid phases. By rephrasing the thermodynamics in terms of a set of independent reactions, and using chemical affinity of each reaction as a scalar measure of disequilibrium, we avoid having to do computationally expensive free-energy minimization on the fly. Thermodynamic models are only required to return thermodynamic quantities including chemical potential, specific entropy, density and heat capacity. The coupled evolution of phase proportion, fluid composition, fluid and bulk solid velocity fields and temperature can then be tracked at reduced computational cost. We use this model to explore the effects of fluid composition, the extent of local chemical disequilibrium and temperature gradient on flow focusing and the resulting evolution of fluid composition. This work is part of the ENKI project which is developing computational thermodynamics tools which support the development and calibration of thermodynamic models and the integration of these models into fluid dynamics codes. We will describe the ongoing development of the computational infrastructure which will allow the approach outlined here to be extended to more complex systems to support future study of fluid-rock interactions in subduction zones.

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# Microdiamond and Moissanite Inclusions in Garnets from Pohorje Mountains, Eastern Alps, Slovenia

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Natural microdiamonds and moissanite (SiC) can form during the orogenic events under ultrahigh-pressure metamorphic conditions (UHP), when parts of Earth's crust are subducted to extreme depths. So far, such processes were identified only in few places on the Earth, and therefore, represent unique opportunity to study the evolution of the Earth's deep interior. An important discovery of microdiamonds and moissanite was reported from Pohorje (Slovenia), where they occurred as single or polyphase inclusions in garnets. Metasedimentary rocks from Pohorje are predominantly gneisses representing parts of the Austroalpine metamorphic units of the E-Alps. During Cretaceous orogeny (ca. 95–92 Ma) continental crustal rocks were subducted to the mantle depths (below 100 km) and metamorphosed at pressures exceeding 3.5 GPa and temperatures 800–850 °C.

Microstructural and phase analysis of the inclusions as well as detailed elemental analysis of host garnets were carried out combining several analytical techniques: optical microscope in plane polarized transmitted light, electron probe microanalysis (EPMA) with wavelength-dispersive x-ray spectrometry (WDS) and field-emission scanning microscope (FEG-SEM) with energy-dispersive x-ray spectroscopy (EDS). Micro-Raman analysis revealed sharp, first order diamond bands sometimes accompanied by graphite bands implying that transformation of diamond back to graphite occurred. To study the chemical and crystallographic relationship between microdiamonds and co-inclusions, advanced techniques of transmission electron microscopy (TEM) were applied, which included high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), combined with EDS and electron energy-loss spectroscopy (EELS). To prepare electron transparent TEM lamellae selectively a dual-beam Focused Ion Beam/SEM (FIB/SEM) was employed.

Detailed study of TEM lamellae, which was cross-sectioned from the highly faceted inclusion body located within the host garnet crystal matrix, revealed rich and rather complex internal structure. Namely, the negative crystal facets of the main inclusion body were typically decorated with up to 1 $\mu$m thick amorphous layer, reflecting the general garnet composition with slight variations in Fe/Ca content. Within these layers, ELNES analysis revealed the presence of a 28–30 nm thick layer of amorphous carbon. The very last section of this layer corresponds to composition of $SiO_2$. Within the inclusion, besides diamond and moissanite alumosilicate mineral with pronounced layered structure, iron sulfides and chlorine were identified under TEM and $CO_2$ and CH4 using Raman. Moissanite is found as single crystal or composed from numerous highly textured nano-crystals with the average size of 10 nm. Moissanite inclusions were found embedded inside the amorphous crust implying that moissanite crystalized well before the deposition of the amorphous layer.

From the microstructural, crystallographic and chemical observations so far we can deduce, that polyphase inclusions in diamond bearing garnets from Pohorje most probably crystallized from reduced supercritical fluids. Based on layered interface structure of the host mineral multiphase process of crystallization is possible. The presence of microdiamonds and moissanite in rocks from Pohorje demonstrates that these parts of the E-Alps were the most deeply subducted parts of the Austroalpine units of the Alps, and were subsequently exhumed back to the surface without complete breakdown of UHP mineral phases, allowing an opportunity to study them in-situ.

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# Brine-like fluids in the lithospheric mantle beneath the Styrian Basin – a fluid inclusion study

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Fluid inclusions in amphibole-bearing mantle xenoliths from the Miocene extensional Carpathian-Pannonian region (CPR), located within the Alps-Carpathians-Dinarides system, have been the subject of this study. The Styrian Basin lies at the westernmost part of the CPR. Beneath the basin subducted slab is suspected [1] and subduction-related volcanism was active in the Miocene. The subcontinental lithospheric mantle (SCLM) here might therefore be considered to have been affected by subduction related fluids/melts. Plio-Pleistocene alkali basalts sampled the SCLM in the form of mantle xenoliths. Fluid inclusions enclosed in the mantle xenoliths provide a particular opportunity to better understand behavior of subduction related fluids in a former mantle wedge environment.

We present mineral chemistry and fluid inclusion data from amphibole-rich (±phlogopite, ±apatite) peridotite xenoliths. Primary, two and three phase fluid inclusions (liquid + solid ± vapor at room temperature) were found in amphiboles. The inclusions consist mainly of high-density $CO_2$ inclusions (> 1 g/cm$^3$) and minor amount of $H_2O$, $N_2$ and $H_2S$ was also detected in the fluid phase using Raman microspectroscopy. Raman mapping and focused ion beam (FIB-SEM) techniques allowed the characterization of solid phases in the inclusions. The amphibole hosted fluid inclusions display a highly complex phase assemblage of Na-bearing minerals like alkali-hydrocarbonates (nahcolite, dawsonite) and sulfate (thenardite). These phases are interpreted as post-entrapment precipitates of an alkaline volatile-rich fluid. Based on the volumetric ratio of the solid phases, we estimated that the fluid phase could have contained Na up to 250 ppm and S up to 450 ppm. Considering that chlorine-rich apatites are often co-precipitated with the host amphiboles, such elements as Na, Cl and S in the $CO_2$-rich $H_2O$-bearing fluids are probably signs of brine origin.

The fluid inclusions highly likely represent a residual fluid-rich phase from which the metasomatic mantle sections might have formed. Our study agrees with previous studies [2] [3] that, besides dominant $CO_2$, significant amount of other volatiles (H, N, S) and sodium can be present, which could have migrated through the SCLM. The source of these volatiles under the studied area could be a subducted slab. Dehydration of a subducting slab can cause the migration of brine-like fluids into the above lying mantle wedge. In the Styrian Basin the Eocene Penninic slab can be the source of these fluids (e.g. [1]), which caused the formation of the metasomatic assemblage, also enclosing the residual fluid phase. This fluid migration event could have caused also the extensive annealing of the SCLM [4].

With this study, we are able to provide input data for theoretical and experimental works on subduction zone fluids from natural samples, and also provide valuable information on the survival of subduction-related metasomatic fingerprints in the subcontinental lithospheric mantle.

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# Fluid-rock interaction in the ultramafic-mafic association of Cabo Ortegal Complex (NW-Spain)

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During subduction of oceanic lithosphere dehydration of the slab induce generation of fluids which cause significant geochemical changes on the overlying subcontinental lithospheric mantle. Characterizing fluids, occurring in volatile-bearing minerals and as fluid inclusions, provides a key to understand fluid-rock interactions in subduction zones.

Fluid inclusions, which can be preserved in high-pressure mafic and ultramafic rocks give direct evidence on the composition and behaviors of fluid phases occurring in such geodynamic environment. Mafic-ultramafic assemblages exposed at surface provide an excellent opportunity to study in situ physical and chemical features of the lithospheric mantle. Orogenic peridotites, including HP and UHP ultramafic bodies, serve as a potential source of information on the origin, migration, transportation and reactions of fluids/melts in suprasubduction mantle wedges [1]. Major examples for such regions in Europe are the Central and Western Alps (Alpe Arami, Cima di Gagnone, Ulten, Dora Maira, Monviso), the WGR in the Scandinavian Caledonides and the European Variscan belt [2] [3]. The Cabo Ortegal Complex is part of the Variscan belt of Europe, which represents fragments of variably subducted continental and oceanic lithosphere that were obducted onto the Gondwana edge during Variscan orogeny [4]. In the Cabo Ortegal Complex of NW Spain besides high-pressure granulites, eclogites and gneisses, ultramafic mantle rocks are also outcropped and and cover an area of tens of km2 [5]. The ultrabasic domains with an arc-root lithospheric mantle origin consist of abundant pyroxenites associated with harzburgites, dunites and chromitites [6].

Our study summarizes features of the secondary fluid inclusions in pyroxenites bodies hosted in ultramafic massifs of Cabo Ortegal Complex.

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# Stability of serpentinite-hosted ophicarbonate during subduction metamorphism and antigorite dehydration

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Dehydration reactions play a critical role in the release of carbon in subduction zones because they supply fluids that trigger decarbonation reactions and carry dissolved carbon into the overlying mantle wedge, with implications for the long-term carbon balance between Earth′s mantle, crust, and atmosphere throughout Earth's history [1]. Natural case studies of the impact of fluids generated by serpentinite dehydration on carbon mobility are rare. Here we show meta-ophicarbonate lenses within prograde Chl-harzburgites in the Almirez ultramafic massifs (Betic Cordillera, S. Spain) that record high-pressure subduction metamorphism of an oceanic, serpentinite-hosted ophicalcite protolith. They occur in a portion of mantle subducted to conditions beyond the high-pressure breakdown of antigorite, providing an unprecedented insight into the stability of carbonates during subduction metamorphism and serpentinite dehydration. These meta-ophicarbonates are composed of a high-grade assemblage of olivine, Ti-clinohumite, diopside, chlorite, dolomite, calcite, Cr-bearing magnetite and rare aragonite inclusions. Thermodynamic modelling indicates that they reached the same peak metamorphic conditions as the host Chl-harzburgites (1.7 – 1.9 GPa; 680 °C; $XCO_2 < 0.008$), and therefore experienced high fluid-fluxes produced by breakdown of antigorite in the host rock. Despite the high capacity of antigorite dehydration fluids to mobilize carbon, the ophicarbonate retains high amounts of carbonate (40 – 45 vol% dolomite and calcite), suggesting limited fluid infiltration and that the fluid composition remained rock-buffered. Likewise, stable isotope compositions of carbonate ($\delta$18O = 13 – 17 ‰ V-SMOW and $\delta$13C = –0.5 to –1.7 ‰ V-PDB) do not indicate a major fluid-induced decarbonation. We use the recent implementation of the Deep Earth Water model in Perple_X [2,3] to calculate aqueous speciation and total carbon solubility and mass transfer in high-P serpentinite dehydration fluids as a function of ophicarbonate composition, the integrated flux of serpentinite-derived fluids and the thermal regime of the subduction zone. The modeling results and the preservation of the meta-ophicarbonates at Almirez beyond the antigorite stability indicate that even in high-flux regimes such as during deserpentinization, mineral dissolution and decarbonation are largely governed by local equilibrium between infiltrating fluid and the rock composition. We show that carbon release from serpentinite-hosted ophicarbonates is predicted to be limited in any thermal subduction regime. Therefore, despite their relatively low contribution to the carbon budget of modern subducting slabs, subduction of ophicarbonates may represent a significant carbon flux pathway beyond sub-arc depths.

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# Numerical modelling of porosity and fluid escape structures in subduction zones (invited)

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Water is brought down into the Earth through subduction zones mostly in the form of hydrous minerals. This water is released again by dehydration reactions that are triggered by elevated temperature in the subduction zone at depth. The released water needs to find a way to flow out of the rock as the volume increase due to the water release is too large to be accommodated. Porosity estimates on such rocks reveal that porosity is extremely low, in principle inhibiting efficient flow of fluid. Yet there must be an efficient way of transporting the fluid out of the rock and bringing it up to the surface. Rough estimates of the global water budget indicate that if this was not the case, the oceans would be drained within several millions of years. Geophysical imaging above subduction zones also reveal that large scale fluid transport does occur. Here I present developments in numerical modelling methods to gain insight into this problem.

The focus lies on several aspects of the initial stages of fluid release: the problem of porosity generation, and the possible ways of reaching pore connectivity in the initial stages enhancing the fluid transport. The main aspects are treated with a numerical model that solves for fluid pressure, mineral and rock density evolution, and porosity evolution coupled to local thermodynamic equilibrium. Methods of computation involve the generation of large pre-computed thermodynamic data to use in a local equilibrium transport model. The advantage of this approximation method over traditional reaction-based approaches is that most sophisticated solution models for solids and fluids can be treated more easily.

One of the interesting aspects is that with including solid solution models, fluid release occurs gradually in divariant fields in pressure-temperature space. This results in a spatially varying porosity and fluid pressure distribution already at the millimetre scale that is largely dominated by the intrinsic chemical heterogeneities in hydrous minerals such as antigorite and brucite, which occur never as perfectly pure phases in nature. The occurrence of near pure olivine veins in dehydrated serpentinite is further enhanced by involving mass transport into the model. During this process, fluid flow transport also become more effective, thus showing that mass transport further contributes to the efficiency of fluid release from subduction zones.

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# Material Transport in Subduction Zones: Not all Flow is Fluids (invited)

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Magmas produced along convergent plate margins show geochemical evidence for the contribution to their source of components derived from the subducting slab. The magma source lies in the wedge-shaped region of the mantle between the down-going and the overriding plates. Much discussion has focussed on the mode of transport of the slab-derived components from various sources within the subducting slab to the magma-source region in the mantle wedge. Hydrous fluids and silicate melts have classically been favoured as the major vehicles of long-distance material transport in this context. However, more recently models that include mixing at the slab-mantle interface followed by solid-state diapirism have been developed [1].

Metamorphic dehydration of slab-materials is the process by which the hydrated oceanic crust (including sediments and serpentinites) is transformed into relatively dry high-pressure rocks. This releases hydrous fluids (or silicate melts) that carry solutes from their original sources within the slab to the slab-mantle interface [2]. Detailed field studies in terrains with exhumed high-pressure rocks have produced evidence for transport of fluids along short-lived channels that act as transport pathways over distances beyond the scale of the outcrop and possibly across the entire thickness of the subducted crust [3]. However, fieldwork has also revealed evidence for intense mechanical mixing at the slab-mantle interface between solid crustal components of the slab and the overlying ultramafic mantle [1, 4]. Advective and diffusive metasomatism controls the chemical and mineralogical alteration of this mélange material. Any buoyant fluids that are produced in the slab have to migrate into this dynamic reaction zone from where they can either progress into the overlying mantle or be guided upwards parallel to the slab-mantle interface toward the trench.

Fluids therefore play a key role in the formation of the mélange zone at the slab-mantle interface and in its enrichment in fluid-mobile elements. However, it is not clear what their role is in connecting the mélange zones (or the slab itself) to the source region of arc magmas. Proponents of long-distance fluid-transport envisage the formation of arc magmas by melting of the mantle wedge that is metasomatized by slab-derived fluids and/or melts. However, a recent geochemical meta-data study including all available data for volcanic rocks from eight global oceanic arcs demonstrated that any such model is incompatible with the observed geochemical data [5].

In contrast, the mélange-diapir model is in agreement with the observed geochemical compositions in all investigated arcs [5]. Diapiric up-rise of buoyant mélange material into the hot corner of the mantle wedge has been identified in analogue and high-resolution numerical experiments and provides a mechanism to transport the characteristic slab signature from the slab-mantle interface into the source region of arc magmas. Long-distance material transport from the slab surface to the arc-magma source region, thus, likely operates in the form of solid diapirs, not hydrous fluids or melts.

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# Internally consistent database for oxygen isotope fractionation in minerals: theory and application to high-pressure metamorphic rocks (Sesia Zone, Italy)

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Stable isotopes are important tools for a wide range of applications in Earth sciences as the oxygen isotopic signature of minerals records the physical and chemical conditions of equilibration. Oxygen isotope fractionation between minerals has often been used for thermometry, but also to investigate samples that experienced fluid-rock interactions. The petrological interpretation of oxygen isotope data requires the knowledge of equilibrium fractionation between two phases and its evolution with temperature. A few well-documented compilations of fractionation factors are available in the literature, but they are either restricted to small chemical systems or based on different methods making the data not consistent with each other. In this study, we report the first internally consistent database for oxygen fractionation that includes fractionation factors for most major and accessory phases and a pure $H_2O$ fluid phase. This database has been derived simultaneously using a least square regression technique based on a large dataset of experimental, theoretical and natural data from the literature. All the constraints for a given phase contributed to the refinement of its fractionation properties making the final database internally consistent.

This database can be applied in a general thermodynamic framework to model the evolution of $\delta$18O in minerals through their metamorphic history. For a given a bulk rock composition, the mineral assemblage, modes and compositions can be predicted along any P-T path using Gibbs free energy minimizations. If the $\delta$18O of one phase or phase zone is known, it is possible to recalculate the $\delta$18O of the other phases of the equilibrium assemblage as well as the bulk $\delta$18O. In situ oxygen isotopes analysis performed by ion microprobe allows the isotopic composition of mineral zones to be resolved and to be related to mineral textures reconcilable with typical growth zoning, but also resorption, replacement or any other fluid-driven process.

This strategy was applied to investigate metamorphic and metasomatic evolution of high-pressure (HP) rocks from the Sesia Zone in the Western Alps. This succession of accreted continental fragments consists of poly-metamorphic and mono-metamorphic lithologies such as metagranitois, metasediments, and mafic and felsic boudins, that record different pre-Alpine histories and different P-T-t path during Alpine orogenic cycle. Several lines of evidence support the presence of fluid at HP and the modelling of its $\delta$18O is critical to reconstruct fluid sources and pathways through the crust during subduction. Different metasediments from the Eclogitic Micaschist Complex, contain relics of pre-Alpine garnet that shows systematically higher $\delta$18O values with respect to Alpine rims. However, fluid replacement textures do not necessarily imply a change in $\delta$18O values, as observed in garnet from the Ivozio mafic complex. This suggests that the metasediments experienced significant input of external fluids changing the $\delta$18O bulk composition between the Permian high temperature stage and the HP evolution, while the fluid-related textures in Ivozio must be related to no change in fluid isotopic composition.

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# Thermodynamic modeling of deep Earth fluid-rock interactions

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I will first lay out the need for theoretical thermodynamic modeling and how it can be used to help address interesting deep Earth problems, as well as being extremely useful as a tool to aid in the planning and interpretation of experimental studies at high temperatures and pressures. Next, I will focus on the basis for calculating the standard Gibbs free energies of aqueous species as functions of temperature and pressure. This treatment includes a summary of how to make estimations even when experimental data are lacking. The calculated standard state free energies give us standard state thermodynamic activities. In turn, these activities are linked to measurable concentrations by activity coefficients. A summary of current approaches to the estimation of aqueous activity coefficients will be described, including approximations that enable the treatment of mixed volatile and multi-solute fluids. Finally, examples will be discussed of the application of all of the above to place subduction zone fluid-rock interactions on a forward modelling basis. The examples include the following: models of the importance of organic species with oxidation states of carbon ranging from -4 to +4 coexisting in subduction zone fluids at pressures greater than about 30 kb; prediction of the variable speciation of nitrogen in subduction zone fluids and implications for the origin of the Earth's atmosphere; a new theory for the formation of diamond by pH drop at constant redox conditions; and a model for the breakdown of antigorite in subduction zones leading to the generation of highly oxidizing fluids. Additional applications have focused on predictions of rock solubility and pH changes in metasomatic fluids, the use of theoretical modeling to interpret solubility and speciation experiments, and comparisons with the predictions of ab initio molecular dynamics for aqueous complexing reactions. The results of all these examples illustrate the need for obtaining a fundamental understanding of aqueous complexation between ions, and ions and neutral species, in subduction zone fluids. Such an understanding can only come about by integration of the results of experimental solubility and speciation studies with thermodynamic and ab initio molecular dynamic modelling studies that can be iteratively compared with the results of petrologic and field studies of subduction zone rocks.

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# Sources and speciation of sulphur and carbon in the subduction zone mélange

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Subduction zones impose a major control on the geochemical cycling between the surficial and internal reservoirs of the Earth. Subduction of pelagic sediments and altered oceanic lithosphere returns water, C, S, B, and numerous other volatiles to Earth's mantle. The recycling of these species and in particular the release of oxidizing sulphate- and carbonate-bearing fluids modifies the redox state of the mantle and controls the chemistry of arc volcanoes through the ascent of fluids from the slab into the sub-arc mantle, where they ultimately control the formation of arc-related porphyry deposits. Yet, the mechanisms of sulphur and carbon cycling within subduction zones are still unclear, in part because data are typically derived from arc volcanoes where fluid compositions are modified during transport through the mantle wedge. To better understand sulphur and carbon fluxes within subduction complexes, we analyzed the carbon and sulfur geochemistry of exhumed mafic and ultramafic samples from Syros, Greece. In particular, we use the redox-sensitive element sulphur – abundant in altered oceanic lithosphere as both oxidized (sulphate) and reduced (sulphide) phase – to track fluid sources and redox conditions, and to infer mechanisms of element redistribution in the subduction channel mélange. Comparison of isotopic data with major and trace element compositions indicates seawater-alteration and subsequent chemical exchange with a sediment-derived fluid within the subduction zone channel. We show that small bodies of detached slab material are subject to metasomatic processes during exhumation, in contrast to large sequences of obducted ophiolitic sections that retain their seafloor alteration signatures. Furthermore, our results document limited sulphur fluxes within the subduction zone channel, and that the mélange matrix does not serve as an important conduit for sulphur transfer in subduction zones.

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# $Vp/Vs$ ratio of the subducting oceanic Nazca plate & implications for fluid processes

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Precise measurements of seismic P and S wave arrival times of local earthquakes are used to determine the P- to S-wave velocity ratio, $Vp/Vs$, within the oceanic mantle of the Nazca plate at $\sim 21^\circ\ S$. Compared to the well-known seismic tomography method, the here applied approach is more sensitive to the local structure of the earthquake sources.

We find a particularly high value of $Vp/Vs \sim 2.0$ at around 50 kilometres depth which is not explicable by a simple solid lithology, but calls for the presence of fluid filled pore space and deep hydration of the oceanic mantle.

We consider the petrology of the subducting oceanic mantle, compute elastic rock properties, model the effect of fluid-filled pores and quantify the effect of anisotropy to predict the P- to S-wave velocity ratio in the given subduction system.

Our conclusion is that the observed elevated P- to S-wave velocity ratio is in agreement with a vein- or crack-like geometry of the pore space and a relatively small value for the pore volume (less than $1\%$). The veins are probably interconnected and build a compliant network which provides an efficient pathway for slab dehydration. This concept is coherent with previous observations from field surveys and results from laboratory experiments and thermodynamic modeling.

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# Fast dehydration-related intraslab fluid-flow events: implications for pore fluid pressure fluctuations at the plate interface

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A better understanding of the subduction zone fluid cycle and its chemical-mechanical feedback requires in-depth knowledge of how fluids flow within and out of the descending slabs. Relicts of fluid-flow systems in exhumed rocks of fossil subduction zones allow for identification of the general relationships between dehydration reactions, fluid pathway formation, the dimensions and timescales of distinct fluid flow events; all of which are required for quantitative models for fluid-induced subduction zone processes. Two types of garnet-quartz-phengite veins can be distinguished in an eclogite-facies mélange block from the Pouébo Eclogite Mélange, New Caledonia. These veins record synmetamorphic internal fluid release by mineral breakdown reactions (type I veins), and infiltration of an external fluid (type II veins) with associated formation of a reaction halo. The dehydration and fluid migration documented by the type I veins likely occurred on a timescale of $10^5$-$10^6$ years, based on average subduction rates and metamorphic conditions required for mineral dehydration and fluid flow. In order to quantify the timeframe of fluid-rock interaction between the external fluid and the wall-rock, we have applied Li-isotope chronometry. This approach is based on bulk-diffusion modeling with the advantage that Li represents a trace-element in the solid and the fluid. Lithium fluid-solid exchange has been controlled by dissolution-precipitation processes, and Li transport occurred exclusively in the fluid. A continuous profile was sampled perpendicular to a type II vein including material from the vein, the reaction selvage and the immediate host rock. Additional drill cores were taken from parts of the outcrop that most likely remained completely unaffected by fluid infiltration-induced alteration. Different Li concentrations in the internal and external fluid reservoirs produced a distinct diffusion profile of decreasing Li concentration and increasing $\delta^7$Li as the reaction front propagated into the host-rock. Li-chronometric constraints indicate that fluid-rock interaction related to the formation of the type II veins had been completed in the order of 1 to 4 months ($0.150^{+0.14}_{-0.08}$years). The short-lived, pulse-like character of this process is in accordance with the notion that fluid flow related to oceanic crust dehydration at the blueschist-to-eclogite transition contributes to or even dominates episodic pore fluid pressure increases at the plate interface, which may trigger slip events reported from many subduction zones.

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# Solubility of Aragonite in Aqueous Fluids

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Carbonate dissolution in subduction zone fluids is critical to the carbon budget in subduction zones. Depending on the solubility of carbonate minerals in aqueous fluids, the subducting lithosphere may be either strongly depleted and the mantle metasomatized if the solubility is high, as recently suggested by natural samples or transport carbon deeper into the Earth's mantle if the solubility is low enough. Dissolution of carbonate minerals strongly depends on pressure and temperature as well as on the chemistry of the fluid, leading to a highly variable speciation of aqueous carbon.

Thanks to recent advances in theoretical aqueous geochemistry, combined experimental and theoretical efforts now allow the investigation of speciation and solubility of carbonate minerals in aqueous fluids at PT conditions higher than previously feasible. In this study, we present new in situ X-ray fluorescence measurements of aragonite dissolution up to 5 GPa and 500°C and the subsequent thermodynamic model of aragonite solubility in aqueous fluids thanks to the Deep Earth Water model. The amount of dissolved aragonite in the fluid was calculated from challenging and unprecedented measurements of the Ca fluorescence K-lines at low-energy. Experiments were performed at the ESRF, beamline ID27 using a dedicated design of an externally-heated diamond anvil cell and an incident high-flux and highly focused monochromatic X-Ray beam at 20 keV. The results show a spectacular multimolar solubility of aragonite at HP-HT in water, further enhanced in presence of NaCl and silica in the solution.

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# Novel isotope tracers of slab-derived fluids

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Subduction zones are the main site of volatile element transfer between the downgoing plate, the overriding mantle wedge and the Earth's deep interior. The breakdown of serpentine minerals within the downgoing slab and the fluids released play a fundamental role in volatile cycling as well as the redox evolution of the sub-arc mantle. Constraining subduction-related serpentinite devolatilisation is essential in order to better understand of the nature and composition of slab-derived fluids and fluid/rock interactions.

Iron and Zn stable isotopes are recently-established geochemical tracers can trace fluid composition and speciation as isotope partitioning is driven by changes in oxidation state, coordination, and bonding environment. In the case of serpentinite devolatilisation, Fe isotope fractionation should reflect changes in Fe redox state and the formation of chloride and sulfide complexes; Zn isotope fractionation should be sensitive to complexation with carbonate, sulfide and sulfate anions.

This study involved targeting samples from Western Alps ophiolite complexes, interpreted as remnants of serpentinized oceanic lithosphere metamorphosed and devolatilized during subduction. A striking negative correlation is present between bulk serpentinite Fe isotope composition and proportion of ferric iron, with the highest grade samples displaying the heaviest Fe isotope compositions and proportion of oxidised iron. The same samples also display a corresponding variation in Zn isotopes, with the highest grade samples displaying isotopically light compositions. The negative correlation between Fe and Zn isotopes and decrease in ferric iron content can explained by serpentinite sulfide breakdown and the release of fluids enriched in isotopically light Fe and heavy Zn sulfate complexes. The migration of these highly oxidizing sulfate-bearing fluids from the slab to the slab-mantle interface or mantle wedge has important implications for the redox evolution of the sub-arc mantle and the transport of metals from the subducting slab. Our results also demonstrate that novel stable isotopes can be used as probes to study the nature of slab fluids and to trace volatile transfer, with potential future applications for both sulfur and carbon subduction cycles.

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# HSE concentrations and highly radiogenic Os isotopic signature in orogenic lamproites from the Bohemian Massif: implications for subduction-related metasomatism of the sub-continental lithospheric mantle

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Lamproites are peralkaline, ultrapotassic and perpotassic mantle-derived rocks with low contents of Ca, Al and Na, high K/Al ratios, and extremely high concentrations of many incompatible elements (e.g., Ba, Zr, Ti). They form numerous dykes along the eastern termination of the Moldanubian and Saxothuringian zones of the Variscan Bohemian Massif (BM), with presumed emplacement age of 330 Ma (Krmíček et al., 2016). We focus our study on their highly siderophile elements (HSE: Os, Ir, Ru, Pt, Pd, Re) concentrations and Re–Os isotopic system, as opposed to previous studies, which focused on their whole-rock geochemical composition and various lithophile and chalcophile isotopic systems.

The lamproites from BM show significant depletion in HSE, namely Pt and Ru, compared to the only other available full dataset for archetypal lamproite (Kimberley block, Australia; Graham et al., 1999). On the other hand, when considering only Re and Os, elements for which multiple studies exist, our values (0.001–0.029 ppb and 0.002–0.106 ppb respectively) are consistent with other orogenic lamproites worldwide (eg. Prelević et al., 2014 and references therein). Compared to other mantle derived melts, all HSE abundances are well below the values of both OIB and continental flood basalts (Gannoun et al., 2016).

High-precision TIMS analysis revealed highly variable $^{187}$Os/$^{188}$Os$_{(330Ma)}$ ratios, ranging between 0.1627–0.6311 ($\gamma$Os $\sim$ 30–406). No significant difference between samples from different geological unts was observed. These values are best explained by variabe crustal contamination of the sub-continental lithospheric mantle source of the studied lamproites. Given their low Os concentrations, addition of small to moderate amounts of crustal material with highly radiogenic Os isotopic signature could result in the observed $^{187}$Os/$^{188}$Os values. This conclusion is further substantiated by previously published whole-rock trace element and Sr–Nd–Pb–Li isotopic data (Krmíček et al., 2016), suggesting the presence of metasomatizing metasomatised (and regionaly contrasting) crustal material component in the mantle source of lamproitic melts.

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