

Carbon mobility by hydrous carbonate liquids at subduction zones

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More than half a gigaton of CO₂ per year is recycled in the Earth interior at convergent margins. At least 40% of this CO₂ returns to the atmosphere via igneous activity at subduction zones. Experimental and thermodynamic modelling of phase relationships at high pressure indicate that decarbonation or carbonate dissolution in fluids account for only a portion of CO₂ released, and that dry carbonate melts are feasible only if thermal relaxation occurs in a subduction environment.

The subducted oceanic crust includes a range of gabbroic rocks, altered on rifts and transforms, with large amounts of An-rich plagioclase. It has been shown that epidote disappearance with pressure depend on the normative anorthite content of the bulk composition considered; we therefore expect that altered gabbros might display a much wider pressure range where epidote persists, potentially affecting the location and the nature of volatiles release.

New experimental data from 3.7 to 4.6 GPa, 750 °C to 1000 °C are intended to unravel the effect of variable bulk and volatile compositions in model eclogites, enriched in the normative anorthite component (An₃₇ and An₄₅). Experiments are performed in piston cylinder apparatus and multianvil machine, using both single and, buffered, double capsule techniques.

Garnet, clinopyroxene and coesite form in all syntheses. Lawsonite was found to persist at 3.7 GPa, 750 °C, with both dolomite and magnesite; at 3.8 GPa, 775-800 °C, fluid saturated conditions, epidote coexists with kyanite, dolomite and magnesite. The anhydrous assemblage garnet, omphacite, aragonite, kyanite is found at 4.2 GPa, 850 °C. At 900 °C, fluid-rich conditions, a silicate fluid/melt of granitoid composition, a carbonatitic melt and Na-carbonate are observed upon quenching. Close to fluid-saturation, 3.8-4.2 GPa, 870 - 900 °C, garnet and Na-rich clinopyroxene coexist with a carbonatitic liquid, Mg-calcite/dolomite and aragonite. The carbonatitic melt is enriched in Ca compared to liquids previously obtained in dry carbonated experiments.

Sandwich experiments, at variable volatile content and variable CO₂:H₂O ratio, have been designed to demonstrate attainment of equilibrium and to challenge the suggested supercritical nature of the carbonate liquid produced. H₂O strongly depresses liquidus surface for Ca-rich carbonates allowing the generation of liquids efficiently scavenging volatiles, Ca and Si from the slab.

Hydrous silicate carbonate liquids are therefore feasible if a H₂O source is provided along a relatively warm subducting path. Such source may correspond to fluids flushed from the dehydrating serpentinized lithosphere or to an internal source, i.e. epidote. In warm subduction zones, the possibility of extracting hydrous carbonatitic liquids from a variety of gabbroic rocks offers new scenarios on the metasomatic processes in the lithospheric wedge of subduction zones and a new mechanism for recycling carbon. Such liquids are expected to be extremely reactive in a percolated mantle wedge, where they generate carbonate pyroxenites, a fertile CO₂ source for magmatism at subduction zones.

Keywords: carbonate, subduction, carbon, water

H/D isotope salt effects in electrolyte-bearing aqueous solutions: In situ experiments at supercritical conditions

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Equilibrium involving two-phase fluid flow (vapor and brine) describes the evolution of halogen-enriched magmatic systems and defines the relative distribution and chemical composition of the immiscible ionic vapor and brine endmembers. The stable hydrogen and oxygen isotope composition of these phases is often used to describe evolution pathways and to determine the source of hydrothermal crustal fluids and volatile emissions from arc volcanoes. For example, the exchange and fractionation of hydrogen isotopes between H-bearing volatiles (e.g. H₂, CH₄, hydrocarbons, H₂O) in open-system Rayleigh distillation processes associated with magmatic degassing in subduction zones is critical to understanding the isotopic composition of evolved magmatic fluids, and the overall mantle-crust cycling of water and reduced C-O-H volatiles.

Experiments have shown that the presence of water affects the distribution of H- and D-bearing C-O-H species, inducing substantial changes in the isotope composition of C-O-H volatiles even at lower crust/mantle conditions (>600 °C) (1,2). Thus, isotope fractionation effects in magmatic fluids depart significantly from the traditional statistical mechanics models that calculate isotope fractionations assuming ideal-gas conditions. Such effects have also been shown to be prominent in the presence of dissolved ions that control the dielectric properties of the supercritical fluids and the structure of water (3,4). Key hypothesis is that the solvation mechanisms and the solubility of neutral species (e.g. H₂, CH₄) are greatly affected under conditions of elevated ionic strength in electrolyte-concentrated aqueous solutions ('salting-out'). For the H₂O-NaCl system, in particular, experimental studies have shown that low-salinity vapors are D-enriched relative to brines, with the extent of D/H fractionation being dependent of the density of the vapor phase (Fig. 1a) (review in (5)).

Here, we present a series of hydrothermal diamond anvil cell experiments that assess the partitioning of D and H between coexisting magmatic vapors and brine in-situ and in real-time by Raman vibrational spectroscopy (Fig. 1b). These HDAC experiments have been conducted in Na-bearing and Mg-bearing H₂O and D₂O solutions that reached the supercritical phase (homogeneous fluid) at temperatures and pressures exceeding 900 °C and 2 GPa, respectively. However, when lower temperatures were approached (e.g. 600-450 °C), phase separation effects were induced allowing for the formation of a volumetrically abundant vapor phase coexisting with a conjugated brine endmember. The effect of Na⁺ on the speciation and structure of the H₂O and D₂O was monitored in-situ and in real time. Our data suggest for the dominant presence of NaOD_(aq) (and MgOD_{2(aq)}) neutral aqueous species in the vapor, consistent with the 'salting out' effects imposed by highly ionic brine (liquid) phase. Enhanced stability of Na-OD relative to Na-OH neutral species can explain the D/H enrichment of low-salinity vapors sampled from low-pressure hydrothermal experiments (Fig. 1a).

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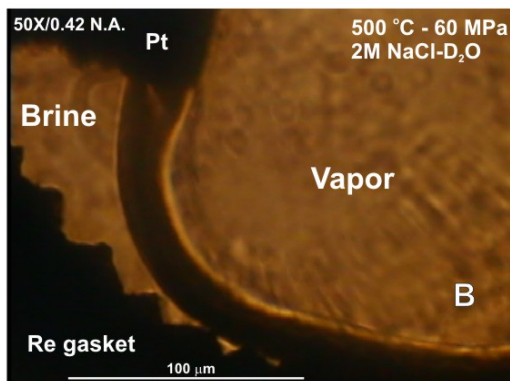
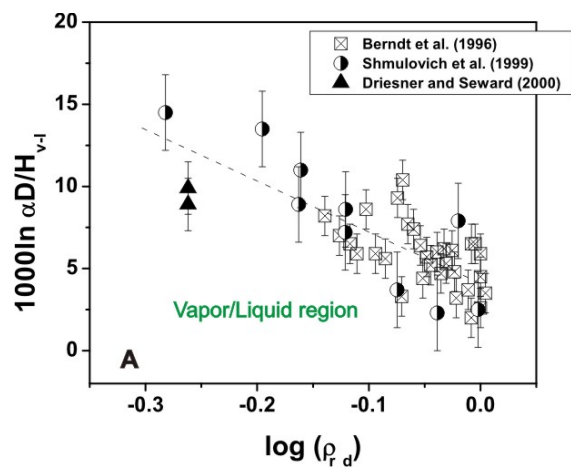
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Keywords: subduction zone, supercritical fluids, hydrogen isotope systematics, vapor, brine, hydrothermal diamond anvil cell

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IMAGING FLUIDS AND FLUID REACTIONS IN SUBDUCTION ZONES

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Water is recycled to the Earth's interior at subduction zones, and a large portion of the subducting fluid is mobilised at depths shallower than 150 km. Seismological and magneto-telluric methods are potential tools for imaging fluid circulation when combined with petrophysical models. Measurements of the physical properties of hydrous phases allow refining fluid circulation in the mantle wedge from geophysical data.

In the cold (<700 degree C) melt-free fore-arc mantle wedge above the subducting slab, serpentinisation is caused by the release of large amounts of hydrous fluids in the cold mantle above the dehydrating subducting plate. Low seismic velocities in the wedge give a time-integrated image of extensive hydration and serpentinisation within the stability of serpentine below 700 degree C. Using elastic properties, the amount of serpentinization is calculated to reach 50-100% in hot subductions, while it is below 10% in cold subduction. This amount corresponds to a time-integrated reaction of water-rich fluids originated from the dehydrating slab with the overlying mantle wedge.

Electromagnetic profiles of the mantle wedge reveal high electrical-conductivity bodies. In hot areas of the mantle wedge (>700 degree C), water released by dehydration of the slab induces melting of the mantle under volcanic arcs, explaining the observed high conductivities. In the cold wedge (<700 degree C), high conductivities in electromagnetic profiles provide "instantaneous" images of fluid circulation.

Small fractions (ca. 1% in volume) of connective high-salinity fluids account for the highest observed conductivities. Modelling shows that low-salinity fluids (<0.1 m) released by slab dehydration can evolve towards high-salinity (>1 m) fluids during progressive serpentinisation in the wedge. These fluids can mix with arc magmas at depths to produce high-chlorine melt inclusions in arc lavas.

Electrical conductivities up to 1 S.m^{-1} are observed in the hydrated wedge of the hot subductions (Ryukyu, Kyushu, Cascadia), while moderate conductivities are observed in the cold subductions (N-E Japan, Bolivia), reflecting low fluid flow in the cold wedge of the latter. This is consistent with the seismic observations of extensive shallow serpentinisation in hot subduction zones, while serpentinisation is sluggish in cold subduction zones.

Keywords: Fluids, Subduction

Intergranular fluid compositions in mantle xenoliths inferred from direct observation of crystal surfaces

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Recent geophysical observations of the Earth's interior indicate the presence of aqueous fluids in the uppermost mantle. However, direct observations of these fluids, apart from fluid inclusions observed in xenoliths and the phenocrysts of volcanic rocks, are rare; hence, the characteristics of intergranular fluids, such as volume fraction, chemical composition, and connectivity, are poorly understood. To calculate these parameters, we investigated the geometry of "dimples" (Watson and Brenan, 1987[1]) on the grain boundaries of mantle xenoliths. The dimples can be used to interpret the fossil pore fluid parameters since they retain the shape of the intergranular fluids. We estimated the compositions of intergranular fluids by analyzing the pore dihedral angles and combining them with the pressure (P) and temperature (T) conditions of the xenoliths.

We collected spinel peridotite xenolith samples from San Carlos (AZ, USA), Bullen-merri (Victoria, AU), Girona (Spain), Lanzarote Island (Canary Islands), and Ichinomegata (NE Japan) localities. Based on the relationship between the forsterite content of olivine and the chromium number of spinel, the samples from San Carlos, Bullen-merri, and Ichinomegata were classified as fertile peridotites, while the samples from Girona and Lanzarote were classified as depleted peridotites.

We observed dimples on the olivine surfaces of all the samples, and measured their three-dimensional shapes using a multi-angle SEM (Keyence VHX-1000). The lherzolite xenoliths from Bullen-merri, Lanzarote Island, and Ichinomegata contained plenty of dimples, while dimples were rare in the samples from San Carlos. The average dihedral angles of the intergranular fluids were 89°, 68°, and 82° for the Bullen-merri, Lanzarote island, Ichinomegata samples, respectively. The equilibrium P-T conditions obtained on the basis of two-pyroxene thermobarometry (Putirka, 2008[2]) or two-pyroxene geothermometry (Wells, 1977[3]) were 12.3 kbar/1130°C, 10.4 kbar/1020°C, 7.6 kbar/1100°C, 6-10 kbar/1113°C, and 6.5 kbar/861°C for the San Carlos, Bullen-merri, Girona, Lanzarote Island, and Ichinomegata samples, respectively. The obtained CO₂ mole fraction of the fluids was nearly zero (pure H₂O) for the Lanzarote and Ichinomegata samples, and 0.9 for the Bullen-merri sample.

The obtained P-T conditions of the lherzolite samples were hotter than the geothermal gradients of their respective areas and were located just below the solidus (Green et al., 2010[4]) in saturation with each fluid composition estimated from the dimple geometry. This suggests that these mantle xenoliths should not be sampled randomly from the conduit wall of the magma halfway between the mantle and surface, but from just above the partially molten region, which possibly has some genetic relation with the host basaltic magmas.

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Keywords: mantle xenolith, pore fluid, dihedral angle, 3D measurement

Dehydration of chlorite and formation of a new hydrous phase

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Subducting slabs are supplying water into the deep mantle, so the stabilities of hydrous minerals under high pressure and high temperature are important issue to clarify the water transportation mechanism into deeper part of the Earth's mantle. Dense hydrous magnesium silicates (DHMS) have been well constrained in the MgO-SiO₂-H₂O system, while few researches have been done in the MgO-SiO₂-H₂O-Al₂O₃ system under relatively high pressure (i.e. higher than 6 GPa). Previously we have reported the existence of a new aluminum-bearing hydrous phase named 23A phase, which shows a quite unique structure among the mantle minerals in having an extraordinarily long c axis (~23Å). This new hydrous phase can be stable as deep as the lower part of upper mantle. Here we conducted high pressure and high temperature experiments on the decomposition of natural chlorite. At 6 GPa 700°C, we found the coexistence of chlorite, pyrope and Mg-surssasite, while at 7 GPa and 800°C the chlorite decomposes into 23A phase plus pyrope, chondrodite and fluid. The discovery of 23A phase in the chlorite composition extends the stability region of hydrous phases in the subducting slabs, and may also open a new field on studying the structure of hydrous phases under high pressure. This 23A phase may play an important role in transporting water into the deep Earth along the subducting slabs.

Keywords: chlorite, new hydrous phase, subduction, high pressure and high temperature

Concentration dependence of water diffusion in silica glass at water pressure of 50 bar

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Water is the most abundant component in volcanic gas in subduction zones, and its bubble nucleation and growth have strong influences on magmatisms, such as silicate melt properties and a volcanic eruption style. Diffusion of water in silicate melts is one of the controlling factors of the bubble growth in magma, and it is thus important to be clarified to understand the mechanism of volcanisms in subduction zones.

Water diffusivity in silicate melt is known to depend on its own concentration (e.g., Wakabayashi and Tomozawa, 1989; Doremus, 2000; Zhang and Behrens, 2000; Okumura and Nakashima, 2004). However, the diffusion mechanism that is responsible for the observed water concentration dependence has not yet been fully understood. In this study, we carried out diffusion experiments of water in SiO₂ glass at 650-850 degree C and water vapor pressure of 50 bar in order to understand the mechanisms of water diffusion in silicate melt. We used SiO₂ glass because it allows us to consider only the water concentration dependence of water diffusion without any other compositional effects (e.g., NBO/T).

A SiO₂ glass chip was enclosed in a silica glass tube with pure water corresponding to a water vapor pressure of 50 bar at experimental temperatures. The sealed glass tube was heated in a box furnace over the range from 650 to 850 degree C for 25 and 40 hours. Diffusion profiles of ¹H and ³⁰Si were measured on the cross section of a run product with the ion microprobe (Cameca ims-6f at Hokkaido University) using a Cs⁺ primary beam (20 nA and 20 micron in diameter). Negatively charged ions of ¹H and ³⁰Si were counted for 2 sec. and 1 sec. respectively, with a 5-micron step. An electron gun was used for electrostatic charge compensation. Glasses with known water contents were used for conversion of secondary ion counts (¹H/³⁰Si) to the water content in the samples.

The surface concentration of water in run products ranged from 0.25 to 0.35 wt%. The concentration profiles of water from the surface, especially at the low concentration region, cannot be simply explained by previously proposed diffusion models, where the diffusion coefficient of water is proportional simply to the water concentration or to a relative abundance of molecular water to the total dissolved water and an empirical exponential function of total water content. The concentration profiles obtained in this study show much stronger water-concentration dependence compared with previous studies.

We explain this stronger water concentration dependence of water diffusion in SiO₂ glass as follows: (1) The main diffusion species is molecular H₂O, and its relative abundance to OH groups decreases with lowering the water content in the glass; (2) The number of pathways available for diffusion is controlled by the number of non-bridging oxygen that is determined by the concentration of OH groups. Because the diffusion coefficient of water is proportional to the above factors (the relative abundance of molecular water and the number of pathways for diffusion) and both depend on the total water content in the glass, the water-concentration dependence of water diffusion is larger than the previous models proposed for rhyolite glasses.

The smaller water-concentration dependence observed for water diffusion in other silicate glasses can be attributed to the little dependence of non-bridging oxygen concentration on water contents because it is controlled extrinsically by other network modifier cations.

Keywords: water, diffusion, silica glass, diffusion model

Behavior of water, major and trace elements in subduction zone magmatism

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I present a forward model perspective on the behavior of water mixed with major and trace elements in the slab fluxes and in the magmas from subduction zones. Arc Basalt Simulator version 4 (ABS4: Kimura J.-I. et al. (2014) Diverse magmatic effects of subducting a hot slab in SW Japan: results from forward modeling. G3, doi:10.1002/2013GC005132) is a forward model calculating element mass balance in the slab dehydration/melting and melting of the wedge mantle peridotite by fluxing of the slab fluid/melt to estimate element abundances in the primary arc magmas, such as basalt, high-Mg andesite, and adakite. Mass balance of water is considered together with major and trace elements, and Sr-Nd-Hf-Pb isotopes in the numerical model. Once element mass balance between the source materials (slab sediment, altered oceanic crust, and peridotite, and mantle wedge peridotite) and a primary arc magma is established, source conditions including (1) depth of the slab dehydration/melting, (2) contributions of slab fluxes, (3) slab flux fraction in the mantle, (4) depth and temperature of mantle melting, and (5) degree of melting of mantle, and (6) element abundance including water in the primary basalt can be estimated. I will present the results of ABS4 analyses on the SW Japan and the NE Japan subduction zone magmas representing hot-young and old-cold subduction cases, respectively, with the special emphasis in water contents in the primary magmas.

Keywords: subduction zone, magma, water, major element, trace element, numerical model

Phase diagrams for $\text{CaCO}_3 + \text{H}_2\text{O}$ and their bearing on the genesis of carbonate melts

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Phase transformations in the system CaCO_3 and $\text{CaCO}_3 + \text{H}_2\text{O}$ have been of primary concern for Earth scientists since early XIX century. Sir J. Hall performed the first investigations in this system in 1798 and pursued various attempts at defining de-carbonation reactions and melting of calcite with water in externally heated gun barrels, successfully performing the first high pressure experiments in geoscience.

Despite two centuries passed, experimental results on phase transformations in CaCO_3 are still contradictory. Discrepancy between ex-situ and in-situ determination of the reaction calcite = aragonite is in the order of 3 GPa at 1200 °C. Experimental data on melting of calcite with an aqueous fluid differ by 300 °C. Uncertainties on the phase diagram for CaCO_3 and $\text{CaCO}_3 + \text{H}_2\text{O}$ have profound consequences in predicting the fate of altered oceanic crust and of metasedimentary materials re-introduced in the mantle at subduction zones.

Multianvil experiments were performed at 4.2 GPa on model bulk compositions in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O-CO}_2$, obtained from natural calcite, Al(OH)_3 and silica. Stoichiometric proportions are intended to produce at run conditions kyanite + CaCO_3 + a fluid or/and a melt. Al_2SiO_5 saturation prevents the formation of portlandite and offers a basis for modelling melting of impure marbles. Furthermore the usage of Al(OH)_3 in the starting material allows an accurate control of H_2O added, fixed at 10 wt% in the present study. This amount is expected to produce H_2O -undersaturated melts, on the basis of solubility data determined at low pressure.

Aragonite + kyanite + fluid, and minor lawsonite form at 700 °C, replaced by zoisite at 800 °. At 850 ° and 900 ° a complex sequence of quenching textural features is observed; "chains" and dendrites of CaCO_3 grow nucleating from liquid-solid interface; they are followed by growth of Si-Al-bearing fibres; finally spheres of silica precipitate from the residual fluid exsolved from the liquid carbonate phase. Excess silica is required to prevent the formation of corundum.

Estimates of liquid ? solid proportions, retrieved by image analysis, at known bulk H_2O content, along with the solid ? pore volume proportions in the liquid region of the run charge provide constraints for H_2O solubility in CaCO_3 liquid. Chemographic analysis support the occurrence of a single hydrous silicate carbonate liquid at large $\text{CaCO}_3\text{:H}_2\text{O}$ ratios.

The model system investigated here, and the minimum temperatures of melting found, represent the upper bound of the formation of hydrous Ca-carbonate melts able to metasomatise the mantle at subduction zone environments. Alkali may further promote the generation of Ca-carbonate liquids at lower temperatures.

Keywords: calcite, mixed fluids, carbonate liquids, subduction

C-O-H volatiles, redox variation and hydrogen isotope fractionation in silicate-COH systems in subduction zones

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The structural behavior of volatiles in silicate-C-O-H melts and fluids aids in characterization of element partitioning and as well as isotope fractionation (e. g., D/H recycling) in subduction zones. In order to characterize this behavior, experiments were conducted in-situ to 900 °C and 1.6 GPa under reducing and oxidizing conditions. Vibrational spectroscopy (infrared and Raman) was employed for structural characterization and for determination of hydrogen isotope partitioning within and between haploandesitic melts and fluids in alkali aluminosilicate-COH systems.

Under oxidizing conditions, melt and fluid comprise CO₂, CO₃-groups, HCO₃-groups, H₂O, and silicate components. The abundance ratios, CO₃/CO₂ and CO₃/HCO₃, decreases with increasing temperature and pressure with ΔH -values for the exchange equilibria between -15 and -25 kJ/mol. The abundance ratio, CO₃/silicate, also decreases with increasing temperature and pressure. Hydrogen isotope exchange within coexisting fluids and melts yields ΔH -values near 14 and 34 kJ/mol, respectively, which results in $\Delta H = -25$ kJ/mol for D/H exchange between coexisting fluid and melt. Lack of spectroscopic resolution precluded determination of D/H behavior in the bicarbonate (HCO₃) species.

Under reducing conditions (near that to the iron-wustite oxygen fugacity buffer), melt and fluid comprise molecular CH₄, CH₃-groups, H₂, OH-groups, and H₂O. Hydrogen isotope exchange within fluids and melts yields ΔH near -5 and -1 kJ/mol, respectively with a ΔH -value for D/H exchange between coexisting fluid and melt of -4kJ/mol. The D/H exchange between CH₄ and CD₄ species results in ΔH near 40 kJ/mol, whereas the ΔH -value is near -4 kJ/mol under oxidizing conditions where ²H-values average near -6 kJ/mol for D/H exchange between hydrous melt and silicate-saturated aqueous fluid.

The redox-dependent D/H-behavior reflects species-dependent bond strengths. Therefore, D/H fractionation between C-O-H volatiles, released during subduction, and both residual subducting materials, and overlying mantle wedge likely will vary with depth. Somewhat analogous pressure-dependence can be seen in olivine/melt transition metal partition coefficients, which may vary by as much as 100% simply by transforming carbon-speciation from methane-rich to carbon dioxide-rich and, therefore-likely depend on depth in subduction zones. This variation depth dependence partly is because subduction zone redox conditions vary with depth and partly because the solubility of C-O-H volatiles in silicate melts and of silicate in coexisting fluid are pressure-dependent.

Keywords: melt structure, COH volatiles, spectroscopy, isotope fractionation, high-pressure experiments

Deep slab structure, dehydration and the Changbai intraplate volcanism

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We obtained a new 3-D P-wave tomography model down to 800 km depth beneath NE Asia by assembling a large number of arrival-time data of local, regional and teleseismic events recorded by ~2500 seismic stations in Japan, China and South Korea. The data from a portable seismic network (NECESSArray) in NE China are also collected and used. Our updated model shows a sharper image of the volcanism-related asthenospheric upwelling and the stagnant Pacific slab in the mantle transition zone (MTZ) beneath the Changbai intraplate volcano. The main findings are summarized as follow.

(1) Relative travel-time residuals of teleseismic events alone are not able to recover the flat stagnant slab in the MTZ, and a slab gap in the MTZ beneath the Changbai volcano imaged by relative travel-time tomography is an artifact.

(2) The low-velocity anomaly in the big mantle wedge (BMW) becomes the most prominent near the hinge of the stagnant slab, which is located slightly east of the Changbai volcano and may reflect focused hot upwelling in the BMW. This low-velocity feature coincides with the depression of both 410-km and 660-km discontinuities and a cluster of very deep earthquakes (>500 km depth) in the Pacific slab.

(3) Besides the deep dehydration of hydrous minerals within the stagnant slab, additional fluids released through deep-earthquake faulting and a stronger mantle flow circulation near the hinge of the Pacific slab have made Changbai the largest and most active intraplate volcano in NE Asia.

(4) The BMW origin of the Changbai volcanism agrees well with other geophysical, geochemical and numerical-modeling studies.

Keywords: Northeast Asia, Changbai volcano, Pacific plate, slab dehydration, deep earthquakes

Hydrogen isotope fractionation between melts and aqueous fluid: Implications for magmatic processes

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The δD of silicate glass inclusions trapped in minerals is an important tool in geochemistry because it provides information on the δD of deep fluids, and, therefore, on the water cycle between the atmosphere, the hydrosphere and the lithosphere. Such understanding relies on the knowledge of the D/H isotopic fractionation values between aqueous fluids, melts, and minerals at temperature and pressure conditions relevant to the interior of the Earth. Significant D/H isotopic fractionation between silicate melts and aqueous fluids were reported at hundreds of MPa and °C by using in situ measurements in hydrothermal diamond anvil cell (HDAC)[1] However, available datasets are focused on fluids and melts with D/H ratios close to unity. The relevance of such data for natural processes D/H ratios in the ‰ range may not always be clear because the a role of bulk D/H ratio of the system was not assessed. To address such concerns, the effect of the bulk D/H ratio on hydrogen isotopes partitioning between water-saturated silicate melts and coexisting silicate-saturated aqueous fluids has been determined in the $Na_2O-Al_2O_3-SiO_2-H_2O$ system. To this end, in situ Raman spectroscopy measurements were performed on fluids and melts with D/H ratios from 0.05 up to 2.67 at equilibrium in a HDAC, in the 300 - 800°C and 200 - 1500 MPa temperature (T) and pressure (P) range, respectively.

In the P-T range studied, the D/H ratios of fluids barely change with temperature (in average $\Delta H_{fluid} = 0.47 \pm 1.15$ kJ/mol). In contrast, the D/H ratios of coexisting melts display strong dependence on temperature (in average $\Delta H_{melt} = 7.18 \pm 1.27$ kJ/mol). The temperature-dependence of the D/H fractionation factor between melt and fluid ($\alpha_{melt-fluid} = D/H_{melt} / D/H_{fluid}$) is similar in all the experiments and can be written:

$$\ln(\alpha_{melt-fluid}) = -747 (\pm 75) \cdot T^{-1} + 0.65 (\pm 0.10) .$$

The $\alpha_{melt-fluid}$ is independent of the bulk D/H ratio of the melt + fluid system.

Therefore, experimental determination of $\alpha_{melt-fluid}$ using D-enriched fluids can be applied to natural systems. As a result, hydrogen isotope fractionation between silicate melts and aqueous fluids probably affect the δD values recorded in the geochemical observables such as the melt inclusions (MIs). Such knowledge alters the present understanding of the water cycle in subduction zones. Indeed, it has been assumed that the δD composition of MIs trapped in crystals in back-arc basalts represents the δD composition of the slab fluids present in the mantle wedge. This interpretation was based on the hypothesis that no fractionation occurs between the slab fluids and the deep magma. However, the present data leave this hypothesis open to question, and indicate that D and H likely fractionated between the slab fluids and the back-arc magma. Although these data do not allow a definitive quantification of the effect because of the simple chemical composition we used, they demonstrate the necessity of a more complete understanding of H and D fractionation processes between silicate melts and aqueous fluids. Such processes may have a direct impact on δD of the various isotopic reservoirs in subduction zones, and therefore influence our understanding of the water cycle in such a geological context.

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Keywords: Experiment, vibrational spectroscopy, hydrogen isotope fractionation, melt-fluid equilibria

Experimental study on the origin of the D/H fractionation between silicate melts and aqueous fluids at HT/HP conditions

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Subduction zones are open paths for the exchange of volatile elements between the geosphere and the atmo-, hydro- and biospheres on Earth. Water is present in the subducting slab as hydrated minerals and is released at high pressure (P) and temperature (T) during the subduction. This results in a hydrated mantle wedge, and eventually promotes volcanism in the fore-arc and back-arc regions. The water cycle can be tracked by measuring the δD of various geochemical observables. In particular, δD measured in melt inclusions trapped in crystals in back-arc magmas may reflect the δD of the slab fluids. From those values, it may be possible to assess the amount of water released from the slab to the mantle wedge by using mass balance models. However, this relies on knowledge of how D and H fractionate between silicate melts and aqueous fluids at high P and T. Results from in situ experiments of silicate-H₂O systems in a Hydrothermal Diamond Anvil Cell (HDAC) show that $1000 \ln (\alpha_{melt-fluid} = [D/H]_{melt}/[D/H]_{fluid})$ values can reach -100 ‰ at 1073 K and ~1 GPa, conditions similar to those at the onset of fluid-saturated melting in subduction settings. Such values are high, particularly when compared to those observed in minerals: for instance, the $1000 \ln (\alpha_{phlogopite-fluid})$ is about 7 ‰ at 1073 K. Considering that, the origin of such fractionation appears surprising. One explanation may be that, in addition to the zero-point energy contribution that usually drive equilibrium isotopic fractionation, D/H intramolecular fractionation within silicate melts may promote D/H exchange between coexisting aqueous fluids and silicate melts. Such effect is suggested by recent results from ²H and ¹H MAS NMR of Na₂Si₄O₉ quenched melts equilibrated with various amounts of (D_xH_(1-x))₂O (x = D/[D+H]) at 1673 K and 1.5 GPa, which show differences in the partitioning of D and H in the structure of the melts at their glass transition temperature.

To address this problem, we studied how the O-H and O-D bond strengths change with temperature and pressure in aqueous fluids and silicate melts for a series of HDAC experiments performed with aluminosilicate melts coexisting with fluids with various H₂O-D₂O mixtures. We also examined the local environments of H and D with ²H and ¹H Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy in M₂Si₄O₉ glasses (M = Li, Na or K) with 1, 3 and 6 wt% of pure H₂O or pure D₂O, and with 3 wt% of a H₂O-D₂O mixture.

Comparison of the in situ Raman spectroscopic signals assigned to O-H and O-D stretching vibrations in fluids and melts at given P-T shows significant differences in the distribution of O-H and O-D bond distances and thus strengths between melts and fluids. These differences are correlated with the observed fractionation. They may be related to the fact that water can reside as molecules (H₂O_{mol}) or as OH groups bonded to the ionic structure of the melt, the two species presenting differences in O-H bond strength. Such effect might be enhanced by an intramolecular fractionation of D and H that occurs in the melt. Indeed, comparison of ²H and ¹H MAS NMR spectra of the M₂Si₄O₉ glasses shows that D and H populate the same environments, but H is more concentrated in an environment with an oxygen-oxygen distance around 295 pm. Therefore, D and H do not have the same distribution within the structure of melts at their glass transition temperature. This may arise from a volume effect and/or from an isotopic effect on the equilibrium H₂O_{mol} + OD \rightleftharpoons D₂O_{mol} + OH. In any case, this effect, in turn, can explain the large fractionation factors observed in the HDAC experiments. They may also lead to large δD variations in subduction zone processes, which makes use of δD to trace water cycling more complex.

Keywords: hydrogen isotopes, silicate melt, silicate glass, NMR spectroscopy, Raman spectroscopy, HDAC in situ experiments