Grain Boundaries: A possible water reservoir in the Earth Mantle?

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Summary

The Earth is a wet planet, where water is recycled from the mantle to the surface and back again. The mantle is generally too hot for the stability of hydrous minerals and too cold to store water within significant melt sheets. Therefore, the current paradigm in geosciences is that water resides and moves only through point defects in nominally anhydrous minerals such as olivine, pyroxene and garnet. We challenge this view and present the first high-resolution synchrotron images of higher dimensional defect structures within olivine ($(\text{Mg, Fe})_2\text{SiO}_4$) revealing a strong variation of water content at all length scales. Within single grains water is principally located in “wet spots” around 2-dimensional defects such as grain boundaries and cracks. These wet spots are micrometer size clouds of water, located within point defects in the olivine crystalline lattice, around 2-D defects with less than nanometre size opening. The water is not found in the 2-D defects themselves. Our analysis has three major ramifications: 1) it shows water rich spots around monomineralic and interphase boundaries in the lithospheric mantle giving the last snapshot of fracture prior to xenolith eruption; 2) it unravels “cryptic metasomatism” as a fast fluid pathway into the lithospheric crust; 3) it calls for a fundamental reassessment of the dynamics of water transfer within the lithospheric mantle and the buoyant subduction below, suggested in the studied area. Storage and transfer of water along grain boundaries within nominally anhydrous minerals provides an intermediate reservoir for the dynamic planetary water cycle.

43 **Introduction**

44 Amongst terrestrial planets the Earth appears to be the only known planet to have
 45 developed stable plate tectonics as a means to get rid of its heat. The emergence of plate
 46 tectonics out of mantle convection appears to rely intrinsically on the capacity to
 47 develop extremely weak faults in the top 100km of the planet. These faults have a
 48 memory of at least several hundred millions of years. It is an open question, however,
 49 what weakens these faults, i.e. what lubricates plate tectonics. Model simulations
 50 suggest that this could be due to the effect of water on mantle rheology (*Regenauer-Lieb*
 51 et al., 2001). The basic underlying phenomenon was first discovered in the laboratory
 52 and dubbed hydrolytic weakening (*Griggs*, 1967) and commonly attributed to the
 53 existence of hydrogen in point defects. However, the exact mechanism remains obscure
 54 because point defects cannot be seen directly. Thus dynamic estimates of OH- defect
 55 mobility rely on atomistic computer simulation techniques (*Wright and Catlow*, 1994).
 56 Such atomistic modelling was also used to investigate the transfer of water through line
 57 defects (*Heggie*, 1992). Heggie argued that water does not only diffuse, but it can be
 58 pumped along dislocations, enhanced through the action of deformation. Such
 59 deformation enhanced transfer of water through the lithosphere would be exactly what
 60 is needed to explain the subduction initiation paradox. It could turn an oceanic plate –
 61 which is chemically a melt extraction product hence presumably of dry composition
 62 (*Hirth and Kohlstedt*, 1996) - locally into a wet plate, thereby bringing it close to the
 63 necessary failure condition through hydrolytic weakening (*Regenauer-Lieb*, 2006).
 64 However, it is well known that water, on a geological time scale, cannot penetrate into
 65 the dry oceanic plate through point defect diffusion. This has clearly been shown
 66 through coupled hydrogen and temperature diffusion calculations (*Regenauer-Lieb* and

Kohl, 2003). The paradigm of point defects as a means of diffusive water transfer may apply to the deeper mantle but it is definitely inadequate for explaining the transfer of water through the lithosphere. A direct proof of more efficient mechanism through higher dimensional defects such as creep fracture in the upper mantle (Ghandi and Ashby, 1979) or through super diffusion along dislocations (Heggie, 1992) is however lacking. This is exactly the problem we set out to analyze in this paper and we report the first direct evidence that water is controlled by 2-dimensional defects.

A principal problem with the exploration of the effect of water on higher dimensions than point defects is the inability to detect water on 2-dimensional defects such as grain boundaries and cracks. The difficulties in quantifying primary water content towards grain boundaries and cracks in natural mantle samples, such as xenoliths, are twofold. Firstly, water may be lost (or added) during entrainment in the erupting host lava, and secondly, the sensitivity and/or the spatial resolution for measuring water towards grain boundaries are insufficient with conventional methods.

We have overcome the first problem by examining interphase and monomineralic grain boundaries within the centre of olivine crystals. Fourier transformed infrared spectroscopy (FT-IR) is inherently very sensitive to structurally incorporated hydrogen, affecting the infrared spectra through the absorption intensity and wave number of hydroxyl bands. Such hydrogen incorporation is colloquially termed water. Conventional IR-microscopes have an unfavourable trade-off between the brilliance of the IR-source and the size of the analyzed spot. To overcome the second problem, measurements have been performed using the ANKA synchrotron at the Forschungszentrum Karlsruhe, Germany, which provides high-brilliance, diffraction-limited IR edge-radiation from its 2.5 GeV, 200 mA beam. Complementary studies of

the samples were performed using optical- and scanning electron microscopy, conoscopy, geothermobarometry and thermodynamic calculations.

Our analyses were stimulated by earlier circumstantial evidence that suggested, potential of significant water storage towards grain boundaries (*Hiraga et al., 2004*).

These authors noted a strong partitioning of incompatible elements, such as Ca and Al, towards monomineralic grain boundaries thus indicating the passage of water. *Hiraga et*

al. postulated that a volatile-rich fluid phase or low-viscosity melt infiltrates formerly fluid-free rocks and selectively dissolves and precipitates incompatible elements

preferentially towards grain boundaries. Moreover, direct evidence for anomalous heterogeneous distribution of water in olivine has been detected using TEM methods

(*Kishina and Wirth, 2002*). Nanometre size inclusions of hydrous olivine ($\text{Mg, FeSiO}_4\text{H}_2$) in samples of natural mantle olivine were suggested to be formed through

exsolution of initially OH- bearing point defects. Due to the diffraction limit such inclusions would be invisible for infrared methods; however, one could argue that the

water content could still be measured in an integrated way. On the other hand, visible micrometer size inclusions are conventionally avoided by standard FT-IR

measurements. Consequently, their contribution to the water content in olivine is not taken into account. Due to this technical limitation, there is a gap in understanding the

role of water in intermediate scales between the nanometre up to 0.4nm and tens of micrometer scale.

At nanometre level, indirect measurements of water mobility through point defects in olivine samples are relatively well understood through a series of hydrothermal

annealing experiments (*Kohlstedt et al., 1996; Kohlstedt and Mackwell, 1998*). These experiments imply that water diffusion occurs by two principal processes causing

different anisotropic OH stretching behaviour in the IR spectra: first metastable hydrogen diffusion in the presence of Fe, followed by equilibrium diffusion of all defect species for all cases (*Kohlstedt and Mackwell, 1998*). These diffusion mechanisms are characteristic for natural olivine samples with low $a\text{SiO}_2$ (*Matveev et al., 2005; Nakamura and Schmalzried, 1983*) recognized by OH-stretching bands between 3430 and 3630 cm^{-1} .

Analytical methods

About 150 olivine grains were handpicked and selected under a binocular microscope. We selected totally inclusion-free olivine grains and olivine grains, which show inclusions of Cr-spinel and/or cracks. The grains were then embedded in water free epoxy resin and polished on both surfaces in parafine to avoid any contamination with molecular water. The crystallographic orientation (Bxa, Bxo, or optical normal configurations) was determined by using a petrographic microscope. The thickness of the analysed doubly polished sections varies between 226 and 263 μm . The Beer-Lambert law was used to calculate the water content from the FT-IR spectra. An absorption coefficient of 0.188 was used to determine the water content in forsteritic olivine grains (*Bell et al., 2003*). The sum of all areas beneath the OH peaks in all 3 directions (α , β , γ) were added and normalized to 1 cm.

We focus on cracks and mineral inclusions such as spinel. Inclusions from the centre of the grains are selected. These fully embedded inclusions and cracks were selected to avoid any interference from surface cracks or intersections with the polished surfaces of the olivine grain.

The host olivine and the fully embedded cracks and mineral inclusions were investigated with FT-IR in transmitted-light mode. IR absorption spectra in the range from 600 to 10000 cm^{-1} were acquired at the infrared beamline of the ANKA synchrotron with incident light polarized along a , b and c axes using a Bruker IFS 66v/S spectrometer coupled to an IRscopeII microscope with a 36x, 0.5 N.A. Schwarzschild objective and a liquid-N₂ cooled MCT detector. To check the quality of the olivine samples they were measured first with the internal thermal Globar source using an aperture of 50 μm . The spectral region of interest for this study is the OH stretching range around 3500 cm^{-1} . We exploited the brilliance advantage (photon flux per unit source area into unit emission angle) of synchrotron light compared to conventional sources, which allows much higher measurement beam intensity through small sample areas. In addition to the single-spot measurements the synchrotron infrared light of ANKA was used to analyze large number of overlapping spots using a step size of 2 μm and an aperture of 6 μm diameter in a grid pattern accessed by an automated X-Y stage.

The geothermobarometry assessment, TWQ, is based on ion-exchange and net transfer thermometers and barometers using internally consistent thermodynamic data sets by multi-equilibrium calculations (*Berman, 1991*).

The Gibbs free energy minimizer PerPleX (*Connolly, 2005*) was applied to the thermodynamic datasets in order to build the P-T pseudosection of the existing phases equilibrated under the P-T conditions in the source area of the xenolith material.

Samples and analysis

Our samples are typical garnet and Cr-spinel bearing lherzolites collected from the Colorado plateau, where the upper mantle has been suggested to be enriched in water through the effect of subduction (*Humphreys et al., 2003; English et al., 2003*). Olivine crystals extracted from these samples are typical mantle olivine with Fo₉₀, 3000ppm Ni while Ti contents are below detection limits, also in contact with Cr-spinel inclusions. The single crystals vary between 1400-2700 micrometers in size and contain visible inclusions of clinopyroxene, Cr-spinel and cracks in nm scale.

First, in order to determine the temperature and pressure (P - T) conditions at which the olivine crystals have equilibrated, geothermobarometry and silica/periclase activity estimates have been performed (*Berman, 1991; Berman and Aranovich, 1996*). P - T calculations of the olivine-orthopyroxene-clinopyroxene-garnet pairs indicate equilibrium pressures of ~ 4.8 GPa and temperatures of $\sim 1200^\circ\text{C}$ (indicated by the circle in Fig. 1). The resulting silica activity at these P - T conditions is approximately $a_{\text{SiO}_2}=0.2$ and the periclase activity is $\sim a_{\text{MgO}}=0.16$. Following the arguments set out earlier on silica undersaturated conditions, this should lead in the presence of water to a detectable OH-stretching bands between 3430 and 3630 cm^{-1} , as indeed measured in the samples (Fig. 3).

Second, in order to determine the phase equilibrium of the whole bulk rock chemistry of the system, thermodynamic calculations have been performed using the Gibbs free energy minimization code, PERPLEX (*Connolly, 1995*), assuming a Cr-bearing peridotitic mantle composition under a wide range of P - T conditions (*Ehrenberg, 1982*). Calculations predict that the conditions derived from geothermobarometry are in a central location of a large P - T equilibrium domain for the olivine-orthopyroxene-

clinopyroxene-garnet-Cr-spinel pairs (Fig. 1). These results are in good agreement with polarized microscopic analyses, which indicate no stress fields/shadows in the surrounding olivine crystal. Both analyzed ($X_{\text{Mg}} = 0.75$) and calculated ($X_{\text{Mg}} = 0.70 - 0.80$) spinel compositions are similar. Therefore, the Cr-spinel inclusions are in equilibrium with the hosting olivine and their origin is cogenetic.

A problem in calculating the OH content in olivine is that during the entrainment of the xenolith, within the ascending magma, the rapid decrease in pressure leads to a decrease in water fugacity. We assess the extent of this problem by measuring, using synchrotron based FT-IR, the core-rim variation in olivine to determine decrease or increase of OH in all three crystallographic directions (α , β , γ) (Demouchy et al., 2006). Our results show an increase of OH from the olivine core towards the rim (Fig. 2). Analyses of the rim show complexity of OH-fluxes restricted to the grain boundary. The hump in the fast alpha grain boundary diffusion profile suggests at least two distinct pulses (Fig. 2). The fact that water apparently entered the system as a grain boundary fluid is opposite to the normal xenolith extraction trend, where the minerals - melt contact during eruption leads to a net hydrogen loss on the grain boundaries, owing to the higher solubility of water in the melt phase (Demouchy et al., 2006; Peslier and Luhr, 2006). The grain boundaries of our samples record rapid, multistage, metasomatic OH-incorporation or OH-loss events during or preceding the eruption; the uplift history will be discussed in a forthcoming contribution.

Here, we focus on defects within the core of the sample, far away from the grain boundaries, capturing a clear image of dynamic processes at the xenolith source region. The spectra show no peaks above, 3650 cm^{-1} , which implies the absence of hydrous minerals such as serpentine, talc or other hydrous silicates (Sykes et al., 1994; Kishina et

al., 2001; *Kohlstedt et al.*, 1996). Single-spot benchtop IR measurements of olivine grains show that all olivine absorbance spectra are similar to the typical olivine spectra from previous studies (*Bell et al.*, 2003; *Rossmann*, 1996; *Bell et al.*, 2004; *Berry et al.*, 2005).

We first map the core of an olivine with no visible inclusions, expecting a homogeneous distribution of hydrogen by using synchrotron based FT-IR. The mapped area of 40 x 40 micrometer ($1600 \mu\text{m}^2$) has roughly the same size as the resolution of a single benchtop measurement, using the Globar source of normal FT-IR equipment ($1960 \mu\text{m}^2$). The average water content is $138 \pm 10 \text{ ppm}$ (Fig. 3), which is similar to the observed water content in mantle olivine reported in previous work (*Bell and Rossmann*, 1992). However, the water content is not homogenous and shows small perturbations up to 148 ppm (Fig. 3, inset). These water perturbations are smaller than the maximum resolution. They may correspond to structurally bound water in a variety of defects: 1) line defects or 2) very low angle misorientations within groups of defects including metastable hydrous phases 3) nanoscale inclusions, e.g. hydrous olivine $(\text{Mg,Fe})\text{SiO}_4\text{H}_2$ or Cr-spinel. Indeed, most olivine samples of the field area contain small inclusions of Cr-spinel and/or clinopyroxene forming isolated grain boundaries within the olivine single crystal (*Bell and Rossmann*, 1992).

While the effect of line defects and groups of such defects are still below the resolution limit of the synchrotron FT-IR method, larger Cr-spinel inclusions and macroscopic cracks offer an ideal target for analysis of water content around higher dimensional defect structures. In order to avoid contamination from the above described grain boundary effects, only fully embedded Cr-spinel inclusions in olivine were analyzed far

away from any other grain boundaries. Inclusions within the 250 μm thick, doubly polished crystal wafers vary between 2-8 micrometer in size. The amount of water in olivine increases dramatically upon approaching the grain boundary between olivine and embedded Cr-spinel and form halos of about 40 μm in diameter (Fig. 4, inset). The increase of water towards the grain boundary leads also to a minor change in the olivine composition ($X_{\text{Mg}} = \sim 0.89$). Although the horizontal spatial resolution of the measurement is high, we cannot avoid smearing through the focal depth of the sample. The high spatial resolution of the maps therefore record spatial gradients, representing local variations in water content. We record a peak of water close to the centre of the Cr-spinel inclusion. The water concentration in the studied Cr-spinel inclusion is below the detection limit of the synchrotron based FT-IR and therefore any interference with Fe^{2+} in the Cr-spinel and the olivine can be avoided.

Furthermore, measurements of other sections and different focal depth shows, that the water is located in the olivine crystalline lattice near the grain boundary and not within the Cr-spinel grain. Away from the inclusion the typical water content is ~ 140 ppm (Fig. 4). An area of 200-440 ppm water content is recorded up to 15 μm away from the embedded water-free Cr-spinel inclusion (Fig. 4). On the inclusion itself, the water content rises significantly up to values of ~ 800 ppm. The measured hydrogen peak is located on the silica dislocation/vacancy and shows the typical maximum at 3572cm^{-1} , which is indicative for an increase of water in olivine towards to the grain boundary (Fig. 5).

We also analyse using optical microscopy and infrared spectroscopy totally embedded micro cracks of up to 0.4nm width in olivine and record a comparable increase of water content towards an embedded micro-crack (Fig. 6). Note that the crack has a sub-micron

size opening and is defined as a monomineralic grain boundary however, the water content increases continuously towards the crack to reach 1000 ppm. There is no visible break towards the crack. The increase of hydrogen towards the crack, and the position of the hydrogen peak at 3572cm^{-1} , suggests that the hydrogen is incorporated in the crystalline lattice of olivine and not in the crack.

Implications for water in 2-dimensional defects

We have presented here a new method for estimating water content in nominally anhydrous minerals, particularly applied to olivine. We have shown that for all three defect species, i.e. cracks, grain boundaries and Cr-spinel- inclusions the water content increases systematically by factor of 5-10 towards to the defect. Similarly, the defects are all surrounded by halos of water with a pattern of OH- point defect diffusion with increasing degree of complexity from cracks to inclusion to grain-boundary. For the case of cracks and spinel inclusion, the diffusion profiles follow the 3-D shape of the defects. The similarity of the OH- diffusion profiles around cracks and Cr-spinel inclusions suggests that water is not structurally bound but indeed progressed through point defect diffusion after microcracking of the sample, thus allowing an assessment of the timing of the damage event. While many more fluid pulses may have preceded the uplift our measurement only records a snapshot of the last pulse of the metasomatic fluid access. This last pulse has prepared conditions for the first uplift phase of the xenolith. Taking conservative estimates of equilibrium OH-diffusion (*Kohlstedt and Mackwell, 1998*) the diffusion profiles can be reconciled with a residence time of less than 10 hours after access of the aqueous fluid to the source region.

We can constrain the P-T conditions for water access further through the stability of hydrous minerals in Fig. 1. The absence of hydrous amphibole either suggests that the uplift was faster than the kinetics of amphibole formation or, that the first uplift phase stalled above 36 kbar (higher than the TrTsPg stability field in Fig. 1) followed by a second uplift through the hydrous Antigorite Atg stability field. The uplift path will be presented in closer details in a forthcoming contribution.

We suggest that our results resolve the first visible snapshot of fluid transfer responsible for the process of cryptic mantle metasomatism, described for similar temperature and pressure conditions in many xenolith suites (*Witt-Eickschen et al.*, 1993). Although the widespread existence of cryptic enrichment of the mantle is well documented the mechanism of enrichment is not fully understood. The common suggestion is that access of a low viscosity, low density, fluid phase causes cryptically enriched mantle, seen in its light Rare Earth Element content. Our observations suggest that the fluid is transferred through both grain boundaries and intracrystalline cracks.

We postulate that the inhomogeneous distribution of water content also applies to larger scale grain boundaries and cracks than those measured here. Water along grain boundaries may have a significant influence on the damage of the mantle source region possibly causing ductile/creep fracture and leading to earthquakes and eruptions (*Ghandi and Ashby*, 1979). Another interesting aspect, which will need to be investigated in future studies is the potential interaction of point and 2-dimensional defect through dislocations (*Heggie*, 1992). Such dynamics would lead to significant transport of water during solid-state deformation with important implications for metasomatism and chemical buoyancy.

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Figure captions

Figure 1: Phase equilibria computed for ultramafic bulk composition. Mineral abbreviations are: O, olivine; Opx, orthopyroxene; Cpx, clinopyroxene; Gt, garnet; CrSp, Cr-spinel; esk, eskolite; knorr, knorringite; ab, albite; Atg, antigorite; A-phase, a-phase; Chl, chlorite; B, brucite; TrTsPg, amphibole. The computations account for the oxides: SiO₂, Al₂O₃, Cr₂O₃, FeO, MgO, CaO, Na₂O, H₂O. The shading shows the variance of the different phase fields. The stability field of Gt-CrSp-O-Opx-Cpx is stippled.

Figure 2: Core rim relationship in olivine shows the increase of H in all three crystallographic directions (α , β , γ). Our results shows an increase of H from olivine core towards to the rim. These indicates an addition of H during the eruption (rim) and give the amount (core) of H added to the crystal in the mantle.

Figure 3: Single measurements of olivine grains. The FT-IR spectra were produced using a synchrotron and show the OH vibration stretching bands in α , β , γ directions for the studied olivine sample HS1. The local resolution is 2 micron. The sample was normalized to 1 cm thickness and the calculated water content normalized in ppm H₂O by weight is 138 by using Beer-Lambert law. Inset shows the 3D-map of the same optical inclusion free area of olivine crystal HS1, 40 x 40 micron in size. The water content is ~140 ppm H₂O by weight (blue).

Figure 4: 2D and 3D maps of H₂O content increasing towards a totally embedded Cr-spinel inclusion in olivine (sample HS1). The Cr-spinel inclusion varies in size between 5-8 micron (white area). The H₂O content increases towards the Cr-spinel inclusion significantly up to values of about 800 ppm.

Figure 5: The measured hydrogen peak is located on the silica vacancy and shows the typical peak at 3572 cm⁻¹.

Figure 6: We assess the effect of 2D defects on water content within olivine through mapping totally embedded micro cracks in olivine (sample HS1). The continuous increase of OH concentration towards an embedded micro crack is clearly seen. Note, that the crack itself has sub-nanometre scale opening. It is thus invisible for FT-IR measurements. Since we detect an increase in OH-concentration up 15 µm away from the crack we conclude that the water is located in point defects around the crack and not within the crack itself.

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