



## Evidence of dehydration in peridotites from Eifel Volcanic Field and estimates of the rate of magma ascent



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### ABSTRACT

We report major element compositions and water contents in upper mantle minerals from peridotites transported by silica undersaturated, mafic alkaline lavas from three volcanoes Rockeskyllerkopf, Dreiser Weiher, and Meerfelder Maar of the Eifel Volcanic Field (West Germany). The hydrogen concentrations (expressed in ppm wt. H<sub>2</sub>O) obtained from unpolarized and polarized Fourier transform infrared (FTIR) spectroscopy give water contents for olivine, enstatite and diopside of ~6 ppm wt. H<sub>2</sub>O, ~200 ppm wt. H<sub>2</sub>O and ~285 ppm wt. H<sub>2</sub>O, respectively. The hydrogen concentration in individual olivine grains is strongly heterogeneous whereas that in pyroxenes is homogeneous. Profiles measured across crystallographically oriented single-crystals of olivine using polarized infrared radiation reveal hydrogen depleted rims that are interpreted to be due to partial dehydration by ionic diffusion during the ascent of the xenolith to the surface. Using experimentally obtained diffusion coefficients for hydrogen in olivine at high temperature and high pressure, we estimate that the duration of the dehydration for the spinel-bearing xenoliths is limited to a few hours yielding rates of magma ascent from 3 ms<sup>-1</sup> to 12 ms<sup>-1</sup>. Our study suggests that the water contents of the upper mantle based solely on measurements of mantle-derived olivine, when concentration is not homogeneous, underestimate the true water content of the equilibrated uppermost mantle and that pyroxenes are a better proxy to constrain uppermost mantle water contents.

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### 1. Introduction

'Water' occurs within two different forms in the deep Earth: as hydrous minerals such as serpentine, amphibole, and lawsonite in subduction zones, and as hydrogen trapped in atomic defects and bonded to silicate oxygen in nominally anhydrous minerals (NAMs). These NAMs, which may contain hundreds of parts per million hydrogen atoms, can be found in both the crust (e.g., quartz, Aines and Rossman, 1984; Rossman, 1988) and also in the Earth's mantle (e.g. olivine, pyroxenes and garnet, Beran and Putnis, 1983; Bell and Rossman, 1992). The NAMs represent an important deep reservoir and as such, are an important component of the deep water cycle. In order to understand this reservoir, hydrogen solubility (Bell and Rossman, 1992), also known as water storage capacity (Hirschmann et al., 2005) must be quantified. In addition, the hydrogen content of natural samples must be defined to better constrain both the nature of interactions between the atmosphere/hydrosphere and the mantle and the rates and mechanisms of degassing magma, whether past or present, during its passage through the mantle and crust.

Studies of basaltic lavas have shown that silicate melts (e.g. quenched glasses) may contain a significant amount of water; of the order of a few

ppm wt. H<sub>2</sub>O (Michael, 1988; Jambon and Zimmermann, 1990) in various forms (H<sub>2</sub>O, H<sub>2</sub>, OH<sup>-</sup>). Crustal minerals such as quartz and feldspar may contain up to 1400 ppm wt. H<sub>2</sub>O (Griggs and Blacic, 1965; Aines and Rossman, 1984; Johnson and Rossman, 2003) and mantle-derived minerals such as olivine, orthopyroxene, garnet and clinopyroxene may contain as much as several hundred ppm of water by weight (e.g., Miller et al., 1987; Rossman and Smyth, 1990; Bell and Rossman, 1992; Ingrin and Skogby, 2000; Peslier et al., 2002; Demouchy et al., 2006; Li et al., 2008). Several authors have suggested that Earth's mantle may contain hydrogen concentrations equivalent to 3 to 11 times the ocean mass (Smyth, 1987; Bolfan-Casanova, 2005; Marty, 2012).

Olivine is particularly important in understanding the water budget of the mantle since it is the most abundant phase in the upper mantle (60–80% in volume). Hydrogen (H) in olivine may occupy three different atomic sites: (1) a metallic site in the octahedron, (Mg<sup>2+</sup>, Fe<sup>2+</sup> or Fe<sup>3+</sup>), and/or (2) a silicon site, replacing partially Si<sup>4+</sup> in tetrahedron, and/or (3) an interstitial site (Kohlstedt et al., 1996; Karato, 2006).

In addition to its importance in the deep water cycle, the presence of H in NAMs significantly affects the physical and chemical properties of mantle minerals and thus of mantle rocks. For instance, the presence of H can decrease the strength and velocity of seismic waves and increase major element diffusivities and electrical conductivity in NAMs (Mackwell et al., 1985; Goldsmith, 1987; Karato, 1990; Costa and Chakraborty, 2004; Hier-Majumder et al., 2004; Jacobsen et al., 2004;

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Demouchy et al., 2007; Demouchy et al., 2012; Yoshino et al., 2012). Addition of hydrogen to NAMs also decreases the solidus temperature of the mantle, increasing the degree of partial melting, and thus changing the composition of the magma produced (Kushiro, 1972; Gaetani et al., 1993). Hydrogen incorporation in NAMs is strongly affected by pressure, water and oxygen fugacity, temperature and mineral composition (Bali et al., 2008; Férot and Bolfan-Casanova, 2012).

Despite the recent studies referred to above, the origin, concentration, and ultimate fate of hydrogen in mantle minerals is still poorly constrained. In particular, the mechanism of mantle degassing is a key factor in terrestrial mantle geodynamics and there is a significant need for improvement in our understanding of how magmatic systems interact with and help to drive degassing of NAMs.

During melting, hydrogen is partitioned into the melt phase from NAMs. Mantle xenoliths in the rising magma may lose hydrogen during chemical interactions with the undersaturated melt during decompression. Since this loss will be via diffusion, due to decreasing pressure and thus decreasing water fugacity (from 2 GPa to room pressure, Pitzer and Sterner, 1994; Férot and Bolfan-Casanova, 2012), hydrogen concentrations in minerals such as olivine and pyroxene may provide a valuable new indicator of deep magma ascent rates. It will extend the current range of compositions beyond that for which ascent estimates have been so far established e.g., Spera (1984), Hawkesworth et al. (2000), Tepley et al. (2000), Costa and Dungan (2005), Humphreys et al. (2008), Mackenzie and Canil (2008), and Hamada et al. (2011). Since this H diffusion will occur regardless of whether or not there is chemical interdiffusion of Fe and Mg between the minerals and melt e.g. Shaw and Klugel (2002), it is a particularly valuable recorder of the ascent of mantle xenoliths and their entraining magma.

We must also consider a complex system in which H loss by diffusion may be linked to the final water vapor exsolution from a volatile-rich melt (H<sub>2</sub>O, but also potentially CO<sub>2</sub>) transporting mantle xenoliths toward the surface. In this case the duration of dehydration may reflect transport only in the upper crustal section rather than the total ascent time from the source of the mantle xenoliths. In both cases, dehydration profiles provide a unique insight into magma transport and eruption.

Hydrogen is an incompatible element (Dixon et al., 2002; Koga et al., 2003; Aubaud et al., 2004; Bell et al., 2004), which diffuses extremely rapidly (Mackwell and Kohlstedt, 1990). The diffusivity of H in olivine and pyroxenes, constrained by experimental studies at high pressures and high temperatures, is of the order of 10<sup>-10</sup> to 10<sup>-12</sup> m<sup>2</sup> s<sup>-1</sup> at 1100 °C (Kohlstedt and Mackwell, 1999; Stalder and Skogby, 2003; Demouchy and Mackwell, 2006) which is approximately six orders of magnitude faster than Fe–Mg interdiffusion in olivine (Chakraborty, 1997). Such rapid diffusivities imply that H concentrations in olivine in peridotite xenoliths will show significant variations over the hours to days that it takes for such xenoliths to reach surface (Demouchy, 2004; Demouchy et al., 2006) and that the observed H concentrations in mantle xenolith olivine are not representative of the concentration in the mantle source. Combining information on hydrogen diffusion with the depth to the source of xenoliths allows a calculation of the minimum ascent rate of magma. In cases where ascent is extremely rapid, i.e. a few hours or days, there may not be sufficient time to develop a measurable Fe–Mg interdiffusion profile in olivine. For such cases, the H diffusion approach allows a greater level of accuracy in quantification of ascent rates than is currently possible using major element zonation.

This study focuses on determining the concentration and distribution of hydrogen (H) in peridotite xenoliths from the Eifel Volcanic Field (Germany) to discuss the role of water in determining the rate of magma ascent. In addition, the effect of H on the electrical conductivity recorded under Eifel will be discussed.

## 2. Geological context

The Eifel Volcanic Field is part of the Central European Volcanic Province, which is associated with the development of Tertiary

intracontinental rifts (Wilson and Downes, 1991). Quaternary volcanism in the Eifel accompanied the uplift of the Rhenish Massif beginning at 0.8 Ma; the last known eruption was at 11 ka (Zolitschka et al., 1995). Tomography studies as well as receiver function and seismic anisotropy analysis indicate abnormal seismic velocities between 50–60 km and 410 km depth which have been interpreted to result from a narrow thermal plume in the asthenosphere below the Eifel (Ritter et al., 2001; Keyser et al., 2002). In addition, the receiver function images show a thinning of the lithosphere placing the Moho between 25 and 28 km beneath the Eifel Volcanic Field (Budweg et al., 2006).

Eifel volcanism comprises 250 eruptive centers spread over 600 km<sup>2</sup> (Fig. 1). The average time between eruptions is 2875 years, assuming monogenetic volcanism; though Shaw et al. (2010) have shown that individual volcanic centers can have multiple events separated by tens to hundreds of thousands of years. Two distinct areas can be defined: the West and the East Eifel volcanic fields. Each domain was developed on both sides of the zone of maximum uplift. The volcanoes of the West Eifel sit atop the highest parts of the Rhenish Massif, while the lavas of the East Eifel were erupted in the Neuwied Basin. In each area the early eruptions are characterized by potassic basanites followed by more evolved and sodic lava (Mertes and Schmincke, 1985). Volcanoes are mainly cinder and tuff cones and maars with tuff rings whose formation is partially governed by magma–water interaction resulting in phreatomagmatic eruptions. The presence of gas fumaroles with carbon dioxide, sulfur and methane, as well as weak volcanic earthquakes show that magmatic activity in Eifel is nowadays dormant, but not ended (Schmincke, 2007).

The West Eifel field shows a clear trend NW–SE in both the distribution of volcanoes and age of volcanism (Schmincke et al., 1983). The volcanic activity of this field was developed initially near Ormont, and then volcanism has migrated to the SE after a stagnant period in the uplift of the Rhenish massif. The frequency of volcanic eruption has decreased during the last 100,000 years (Nowell et al., 2006).

The samples analyzed in this study are peridotite xenoliths brought up by three volcanoes in the West Eifel Volcanic Field: Meerfelder Maar, Dreiser Weiher, and Rockeskyllerkopf (Fig. 1). Dreiser Weiher is a maar where xenoliths are abundant in the tuff cone. The host lava is part of the sodi-potassic olivine nephelinite and basanite suite (Mertes and Schmincke, 1985). Meerfelder Maar is part of the largest group of maars and cinder cones in the extreme south of the West Eifel. Peridotite xenoliths were collected from tephra deposits in a quarry on the west side of Meerfelder Maar. Quartzofeldspathic xenoliths, rich in glass and vesicles are also found among the laminated deposits of scoria, together with clinopyroxenites (Shaw and Eyzaguirre, 2000), and glimmerite xenoliths with large grains (> 5 mm) of phlogopite and amphibole. Based on magmatic cumulate xenoliths (mostly dunite), the magma reservoir of Meerfelder Maar was located at a depth of ~14 km (Shaw, 2003). Studies based on Fe–Mg interdiffusion in these magmatic olivines have shown that they recorded at depth a magma arrival between 1 and 3 years before the eruption. Two suites of mantle clinopyroxenites recorded two other events of a few days (1–8) and also only 3 h before the eruption (Shaw, 2003) based as well on Fe–Mg interdiffusion data. The last event is interpreted as recording the volcano eruption and it also represents the time required for xenolith transport from the peridotite source to the surface, it yields a rise rate of 4.2 ms<sup>-1</sup> (Shaw, 2003).

Several studies of the evolution of the lithospheric mantle beneath the West Eifel used specimens from Dreiser Weiher and Meerfelder Maar. In the xenoliths studied, two distinct episodes of metasomatism have been identified: a Hercynian event that formed titanium-poor amphibole, phlogopite and clinopyroxene and a second event, dating from the Quaternary, which formed Ti-rich amphibole veins, clinopyroxene and phlogopite. In the case of xenoliths derived from greater depth, the second event resulted in development of clinopyroxene veins (Witt-Eickschen and Kramm, 1998; Witt-Eickschen et al., 2003).

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