The distribution of volatile elements in the Earth's mantle

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INTRODUCTION

Hydrogen is the most abundant volatile elements in the Earth's mantle and even when present in trace amounts can strongly influence the geochemical and geophysical properties of rocks such as their melting temperature (Green, 1973), rheology (Hirth & Kohlstedt, 2004), electrical conductivity and diffusivity (Bolfan-Casanova, 2005). Therefore, understanding the behavior and distribution of H in the Earth's mantle is fundamental to modeling its geodynamic processes and evolution.

Because of its importance, the presence of H in mantle rocks, particularly from the cratonic lithosphere, have been extensively studied in the past decades (see *e.g.*, Aines & Rossman, 1984; Moine et al., 2020) to constrain how H_2O is stored in the mantle. These studies showed that nominally anhydrous minerals (NAMs) can host large amounts of H_2O, with potentially important effects in the long-term stability of cratons (Peslier et al., 2010). However, it was suggested by Doucet et al. (2014) that most of the H_2O content measured in NAMs from the cratonic lithosphere may be the result of metasomatic enrichment and of H_2O loss during kimberlite eruption and therefore might not reflect the pristine H_2O content of the cratonic lithospheric mantle.

Recently, attention has shifted to NAM inclusions in diamonds as an alternative method to investigate the H_2O content of the mantle (see *e.g.*, Matveev & Stachel, 2009; Novella et al., 2015) since diamonds shield the inclusions from interactions with the surrounding environment, and therefore preserve the NAMs in the state they were in the deep lithospheric mantle. Moreover diamonds, being a product of metasomatic reactions, can also be an important source of information regarding metasomatic fluids in the mantle. Most of the available studies that investigated the H_2O content of diamond-hosted NAM inclusions report low H_2O contents, in strong contrast with the studies performed on minerals from mantle xenoliths. However, as of today, studies on the H_2O content of diamond-hosted NAM inclusions are relatively scarce and focused mostly on olivine, preventing a solid, global interpretation of H_2O in the lithospheric mantle to be produced.

In addition, in order to properly understand and model the behavior of H_2O in the Earth's mantle, the presence of C cannot be ignored, as it is the second most abundant volatile element in the mantle and has been shown to strongly influence the behavior of H_2O by lowering its solubility in minerals (see *e.g.*, Yang et al., 2014 and Guo et al., 2020). An important effect C can have on the behavior of H_2O in the mantle during melting is lowering its mineral/melt partition coefficient ($D_{H_2O}^{min/melt}$), which would stabilize silicate melts at lower temperatures than expected in C-free systems. However, only a single study investigated the effect of C (specifically CO_2) on (Sokol et al., 2013) and was limited to olivine at high pressures, where the authors were forced to estimate the H_2O content of the melt in equilibrium with olivine.

The aim of this thesis is to provide new information and constraints on the behavior and distribution of both H_2O and C in the Earth's mantle. This is done by following two approaches: *i*) studying a large set of NAM inclusions in diamonds from different kimberlites ad cratons for their H_2O and trace elements content in order to investigate the H_2O content of the cratonic lithosphere as well as the nature of diamond-forming fluids; and *ii*) performing a series of high-pressure and high-temperature experiments on hydrous and hydrous carbonated basaltic systems to explore the effects of CO_2 on the clinopyroxene/melt H_2O partition coefficient.

MATERIALS AND METHODS

Samples

A set of 118 diamond-hosted NAM inclusions (more than the entire current available literature) from the Kaapvaal, Zimbabwe, Siberian, Tanzanian and North Australian cratons were investigated for their H_2O content. The inclusions are mostly clinopyroxenes and garnets together with a small number of olivine and orthopyroxenes and were hosted inside lithospheric diamonds. Four garnet inclusions among the 118 total were already extracted from their diamond hosts.

Afterwards, seven more inclusions were extracted from their diamond hosts to analyse them again and validate the results obtained from within the diamonds and to measure their trace elements concentration.

Experimental methods

High-pressure and high-temperature experiments were conducted using a ½ inch end-loaded piston cylinder apparatus at 2 GPa and 1200°C at Laboratoire Magmas & Volcans (LMV, Université Clermont Auvergne, Clermont-Ferrand, France). The starting composition was prepared by mixing high-purity oxides, carbonates, hydroxides and synthetic mineral powders to obtain a basaltic composition with amounts of H_2O from 4 to 6 wt.% and of CO_2 ranging from 0 to 2 wt.%. The experimental assembly consisted of a $Au_{80}Pd_{20}$ cell, cushable MgO spacers, a straight graphite heater, a pyrex tube, a NaCl cell wrapped in Teflon sheet and a type C thermocouple.

Analytical methods

The diamond-hosted inclusions were identified using Raman spectroscopy and single crystal X-ray diffraction (SC-XRD) at the Dipartimento di Geoscienze (Università di Padova, Padova, Italy). For Raman spectroscopy a Witec alph 300R confocal Raman micro-spectrometer with a wavelength of 532 nm and a laser power between 5 and 20 mW was used, for SC-XRD a Rigaku Oxford Diffraction SuperNova diffractometer with a Dectris Pilatus 200K detector was employed with Mo Kα radiation.

The composition of synthetic products was measured using a Cameca SXFive-TACTIS electron microprobe at LMV, while the composition of the extracted NAM inclusions was measured using a TESCAN SOLARIS Field-Emission SEM equipped with a Ultim max 65 silicon drift EDS at the Dipartimento di Geoscienze (Padova).

The trace element concentration of NAM inclusions was measured by LA-ICPMS at the Gemological Institute of America (GIA), New York, USA). The spectrometer uses an ESI 193 nm ArF excimer laser ablation system coupled to an Agilent 8900 QQQ ICPMS via He carrier gas. The analytes were ^{27}Al, ^{29}Si, ^{47}Ti, ^{61}Ni, ^{71}Ga, ^{89}Y, ^{93}Nb, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{160}Er, ^{169}Tm, ^{172}Yb, ^{175}Lu.

X-ray computed tomography was performed on diamonds to ascertain no fractures were present that connected the inclusions to the surface of the diamond and to precisely calculate the thickness of the inclusions still enclosed in the diamonds needed for H_2O quantification using FTIR spectroscopy. The measurements were done using a RX Solutions EasyTom equipped with an X-ray tube with a LaB6 cathod and a Varian PaxScan 2520DX imager at LMV.

The H_2O content of the synthetic clinopyroxenes and melts, as well as that of natural diamond-hosted inclusions,+ was measured using FTIR spectroscopy. A Bruker Vertex 70 spectrometer with a Hyperion microscope at LMV and a Thermo Scientific Nicolet iN10 at the Dipartimento di Geoscienze (Padova) were used. The H_2O content was calculated using absorption coefficients from Withers et al. (2012) for olivine, Bell et al. (1995) for orthopyroxene, peridotitic clinopyroxenes and garnets and Koch-Müller et al. (2007) for eclogitic clinopyroxenes. FTIR spectroscopy was also employed to measure the N content and aggregation state of the diamonds hosting the NAM inclusions.

RESULTS

NAM inclusions in diamonds

The analyzed inclusions span a range of H_2O contents going from below the FTIR detection limit up to 550 ppm wt. H_2O, with low H_2O contents observed mainly in olivine, orthopyroxene and garnet, and higher H_2O

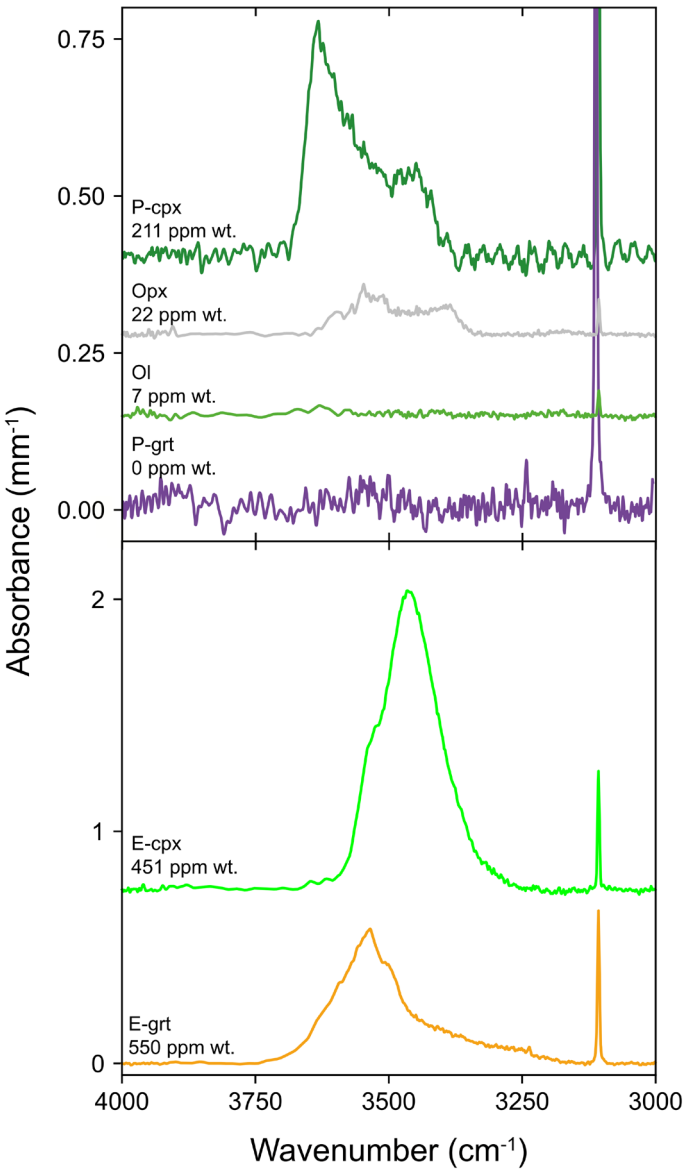

Figure 1 *Representative baseline-corrected FTIR spectra normalized to a thickness of 1 mm for each phase studied as a diamond hosted inclusion.*

contents recorded in clinopyroxene (Fig. 1). Three eclogitic garnets are outlier as they show H_2O contents > 100 ppm wt., with sample Grt_E_4 from Udachnaya (Siberian craton, Russia) showing the highest H_2O concentration of this dataset at 550 ppm wt. Repeated measurements performed after extraction of some of the inclusions from the host diamonds allowed validation of the H_2O contents obtained from the inclusions still enclosed in diamond.

Trace elements concentration measured in the extracted NAM inclusions (a total of three eclogitic clinopyroxene, four eclogitic garnets, two peridotitic clinopyroxenes and two peridotitic garnets) were normalized to CI carbonaceous chondrite (McDonouh & Sun, 1995; Fig. 2). The resulting normalized LREE patterns are similar to those observed in other diamond-hosted mineral inclusions (see *e.g.*, Stachel et al., 2022). Eclogitic clinopyroxene (except for sample KFB65P25) show a positive slope in the LREE peaking at Na-Sm and then a progressive decrease in the concentration in the MREE and HREE. Eclogitic garnets show a normalized REE pattern characterized by a positive slope in the LREE and a plateau in the MREE and HREE. Peridotitic clinopyroxenes show an overall negative slope from the LREE to the HREE, and peridotitic garnets show the classic sinusoidal pattern in the REE.

High-pressure high-temperature experiments

Experimental runs resulted always in large omphacitic clinopyroxenes in equilibrium with large pools of hydrous and hydrous-carbonated basaltic-andesitic melt. The H_2O and CO_2 content of the melts ranged from 5.18 to 6.97 wt.% and from 0.18 to 2.59 wt.%, respectively. The omphacitic clinopyroxenes showed high amounts of Al^{3+} in tetrahedral coordination ($^{IV}Al^{3+}$) from 0.15 to 0.21 apfu. Given the well-known effect of $^{IV}Al^{3+}$ in promoting H_2O incorporation in clinopyroxenes (see O'Leary et al., 2010), only those experiments where the resulting clinopyroxenes had the same $^{IV}Al^{3+}$ within error were considered here. The H_2O content of clinopyroxenes as measured with FTIR ranges from 869 to 1950 ppm wt.

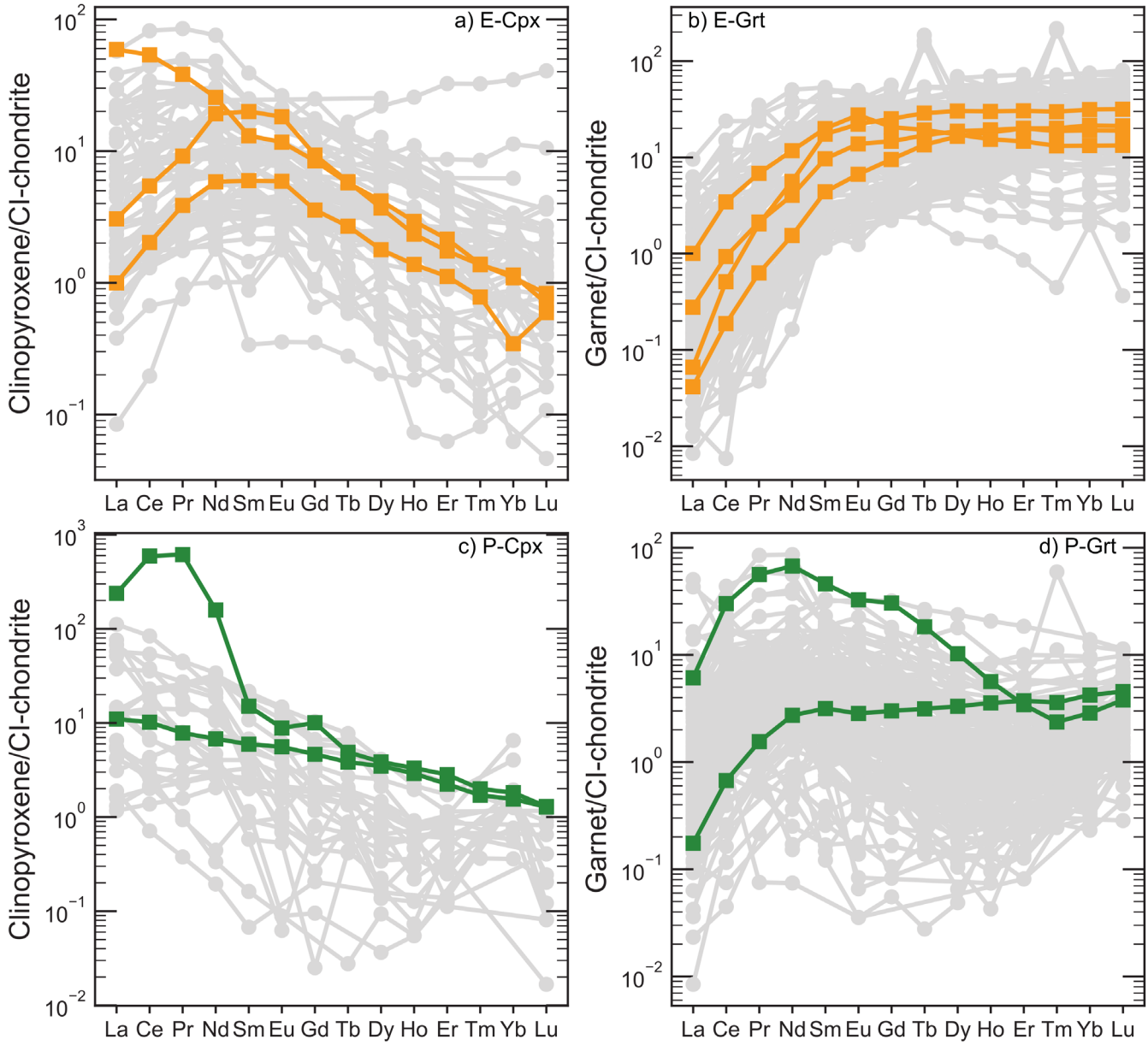

Figure 2 *CI-chondrite normalized rare earth elements patterns for the clinopyroxene and garnet inclusions investigated in this study. The grey patterns in the back represent data from inclusions in diamonds from Stachel et al. (2022).*

DISCUSSION

The H_2O content of diamond-hosted NAM inclusions

The highest H_2O contents in diamond-hosted inclusions are observed in eclogitic minerals, like for xenoliths, and the lowest H_2O contents are observed in peridotitic garnet and olivines, in agreement with the trends observed in xenoliths. Diamond-hosted NAM inclusions however show H_2O contents that are markedly lower than their counterparts from xenoliths, regardless of the mineral and paragenesis (Fig. 3). This difference is attributed to the effect of metasomatic alteration subsequent to diamond formation that enriched the xenoliths in H_2O as suggested by Doucet et al. (2014).

In order to address the source of H_2O in diamond-hosted NAM inclusions a diffusion model of H in olivine, clinopyroxene, orthopyroxene and garnets at the conditions of diamond formation was developed using diffusion coefficients from Demouchy et al. (2016), Hercule & Ingrin (1999), Demers-Roberge et al. (2021), and Reynes et al. (2018) and assuming the minerals to be infinite slabs with initial H_2O content of 0 ppm wt. and a thickness of 500 µm (more than was is observed in diamond-hosted inclusions to obtain conservative estimates of diffusion times). Results from these models show extremely fast re-equilibration of the H_2O content of a NAM with a H_2O-bearing fluid, with the longest time required being less than seven day for garnet and with other minerals generally requiring less than 24 hours (Fig. 4). In this regard, given the fact that diamonds precipitate from fluid phases in the mantle, although the precise timescale of diamond formation is unknown, it is unlikely that a diamond will form in the timespan of minutes or hours, and in this regard it is most likely that the H_2O content of diamond-hosted NAM inclusions reflects the H_2O content of the diamond-forming fluid rather than that of the per-existing cratonic lithosphere.

If this is the case, given the very low H_2O content of diamond-hosted NAM inclusions and the extremely fast equilibration times of H at the conditions of diamond formation, diamonds must form fluid phases with very low H_2O concentrations/activites. Assuming the diamond-forming fluid to be a hydrous-carbonated silicate melt, and using mineral/melt H_2O partition coefficients calculated in high-pressure and high-temperature experiments (Aubaud et al., 2008; Novella et al., 2014) with the H_2O concentrations measured in this work, the melt responsible for diamond formation should have ≤ 1.5 wt.% H_2O, in stark contrast with previous suggestions that diamonds should form from H_2O-rich fluids (*e.g.*, Shirey et al., 2013).

The nature of diamond-forming fluids

By comparing the H_2O content measured in diamond-hosted NAM inclusions and in NAMs from xenoliths with their trace elements concentrations it is possible to obtain some information about the nature of the diamond-forming fluids and of metasomatic fluids in the mantle in general.

Comparison of the LREE and H_2O contents reveals two very clear trends in both eclogitic clinopyroxenes and garnets, both in inclusions and in xenoliths. One of these trends shows an association of very low LREE concentrations together with high H_2O contents, the other shows low to moderate H_2O contents coupled with high LREE concentrations instead.

The high-H_2O trend can possibly be associated with H_2O-rich fluids generated by deserpentinization reactions in subducting slabs (Aulbach et al., 2020) which can also precipitate diamonds and remove LREE from coexisting minerals. The low-H_2O trend on the other hand can be associated with the action of H_2O-poor carbonatitic melts, which could precipitate diamonds and which are rich in LREE.

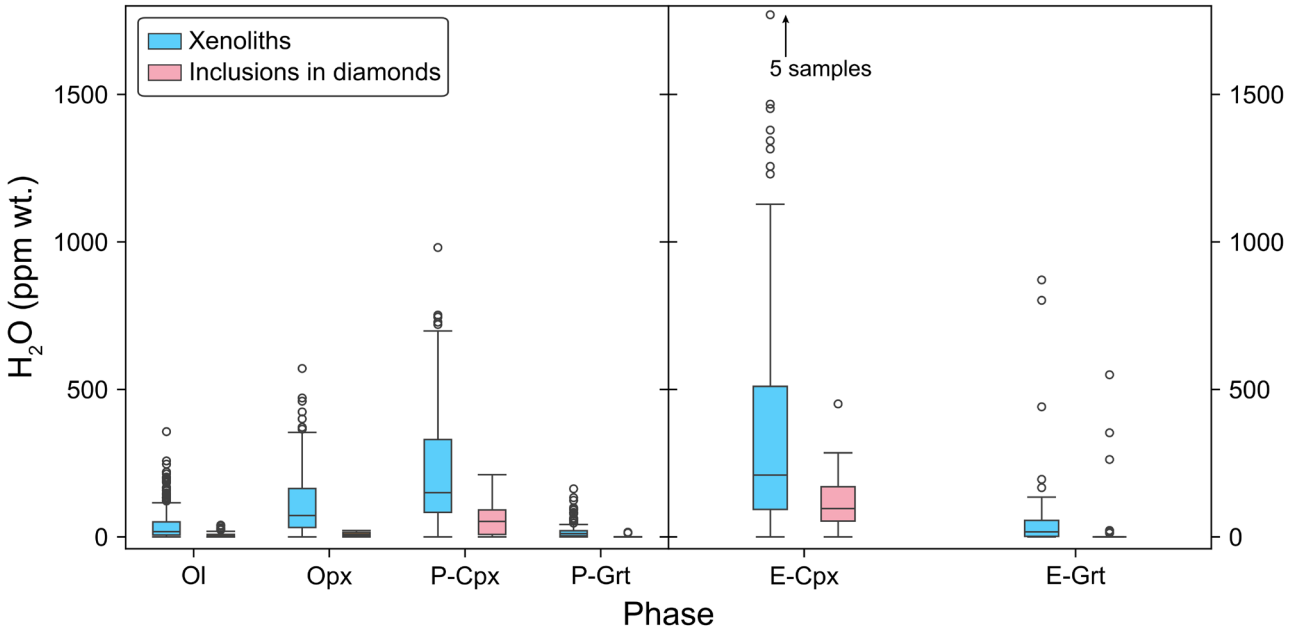

Figure 3 *Boxplot of the H2O content measured in minerals in xenoliths (> 1700 samples from a worldwide database) and in inclusions in diamonds (left and right, respectively). For clarity, the vertical axis was cut leaving five samples outside of the plot.*

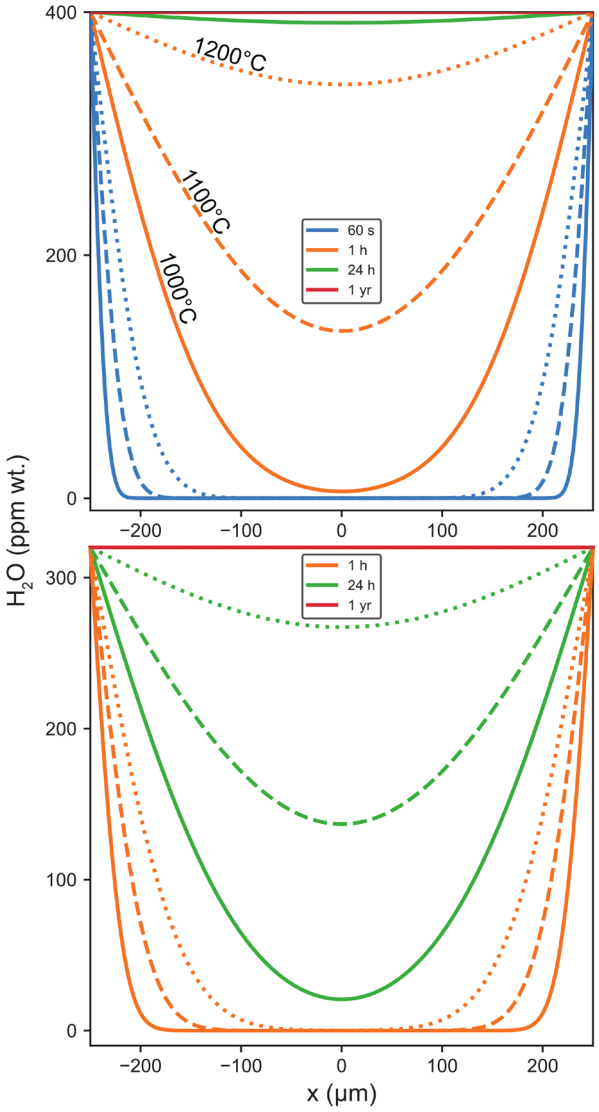

Figure 4 Diffusion profiles of H at different times and temperatures for olivine (top) and garnet (bottom). Clinopyroxene and orthopyroxene show even shorter equilibration times and therefore are not shown here.

The effect of CO_2 on clinopyroxene/melt H_2O partitioning

From the H_2O content of clinopyroxene and melt $D_{H_2O}^{cpx/melt}$ was calculated as a function of the XCO_2 (= CO_2/[CO_2 + H_2O]) of the system. The effect of CO_2 on $D_{H_2O}^{cpx/melt}$ is clearly noticeable as, with increasing XCO_2, $D_{H_2O}^{cpx/melt}$ decreases of a factor of two, from ~0.03 to ~0.015 (Fig. 5). These results are in agreement with the observations made on olivine by Sokol et al. (2013). The $D_{H_2O}^{cpx/melt}$ as a function of XCO_2 was fitted using a negative power law to obtain for the first time an empirical calibration of the effect CO_2 has on $D_{H_2O}^{cpx/melt}$. The resulting relation is $D_{H_2O}^{cpx/melt} = 0.0123 * XCO_2^{-0.237}$.

This effect of CO_2 on the clinopyroxene/melt H_2O partition coefficient results in H_2O behaving more incompatibly in the presence of CO_2, leading to the dehydration melting occurring at temperatures lower than those expected in CO_2-free systems. Moreover, the presence of CO_2 will cause minerals in equilibrium with a hydrous-carbonated melt to host less H_2O than would be expected if a CO_2-free melt was present.

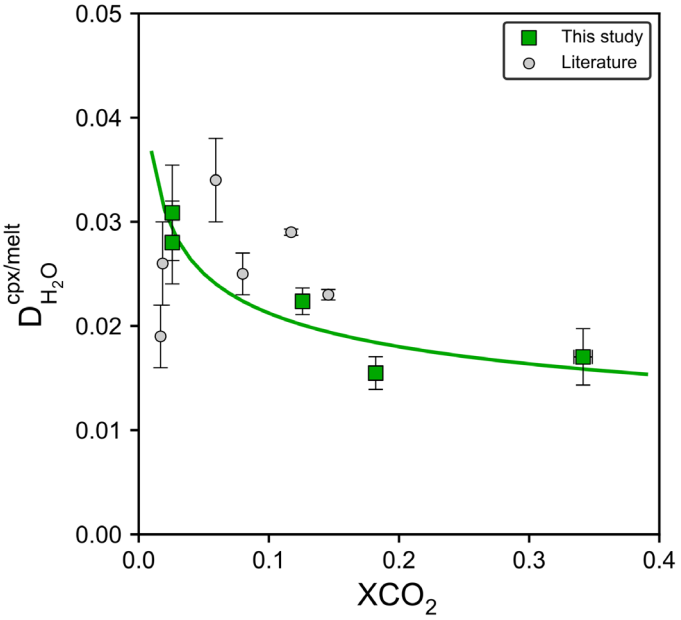

Figure 5 $D_{H_2O}^{cpx/melt}$ as a function of XCO_2 of the system. The solid green line represents the empirical fit of the data. The grey circles are nominally carbon-free data from the literature corrected for their real XCO_2 using the CO_2 concentration reported in the melt in the original manuscripts (Aubaud et al., 2004; Hauri et al., 2006; O'Leary et al., 2010).

CONCLUSIONS / FINAL REMARKS

In this study, a large number of diamond-hosted NAM inclusions were analyzed for their H_2O content, significantly expanding the presently available database. The results of these analyses showed that diamond-hosted inclusions are drier compared to their xenolithic analogues. This, coupled with the results of H diffusion modeling and the study of trace elements in NAM inclusions suggests that diamonds form from fluids that are either H_2O-rich and LREE-poor, or from carbonatitic melts with low H_2O activity and high LREE concentrations.

Moreover, the study of the effect of CO_2 on $D_{H_2O}^{cpx/melt}$ showed that, in the presence of CO_2, H_2O will behave more incompatibly and could potentially lead to dehydration melting taking place deeper in the mantle, with profound implications for mantle differentiation and for the mobilization of volatile elements. In addition, the decrease of the H_2O partition coefficient caused by the presence of CO_2 could also in part explain the lower H_2O concentrations observed in diamond-hosted NAM inclusions compared to xenoliths. It is reasonable to assume that diamonds form from a C-rich fluid, in this scenario, NAMs will equilibrate the this C-rich fluid during diamond formation, resulting in a low $D_{H_2O}^{cpx/melt}$, which causes minerals to incorporate lower amounts of H_2O compared to a scenario in which they equilibrate with a similar fluid, but will lower C concentrations, such in the case of normal mantle xenoliths, which exhibit higher H_2O contents.

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