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Argon storage and diffusion in Earth’s upper mantle

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Abstract

In this study, fine-grained polycrystalline olivine was doped in static conditions with argon at high pressure (0.30 ± 0.01 GPa) and high temperature (1050 ± 25 °C) during 24 h in a Paterson press, and was then analysed using a step-heating extraction protocol coupled with noble gas spectrometry to investigate argon storage and diffusivity in Earth’s upper mantle rocks. Our results show that a single diffusion mechanism controlled argon diffusion in our samples during the step heating experiments. The effective diffusion in olivine has a low activation energy implying that diffusivity is governed by combined argon diffusion in grain boundaries and lattice. Unfortunately, the grain boundaries were not fully emptied at the end of the step heating experiments. Mean values of lattice diffusion parameters were obtained from our results and by reprocessing literature data \( (Ea = 166 ± 44 \text{ kJ/mol}^{\text{-1}} \text{ and } D_0 = 10^{-7.04 ± 1.13} \text{ m}^2\text{s}^{\text{-1}}) \) and grain boundary diffusion parameters were determined from our data \( (Ea = 22 ± 5 \text{ kJ/mol}^{\text{-1}} \text{ and } D_0 = 10^{-12.87 ± 0.3} \text{ m}^2\text{s}^{\text{-1}}) \). Isotopic diffusivity ratios are constant and close to the values determined by Graham’s law in the C- (bulk diffusion dominated by grain boundary diffusion) and A-regimes (bulk diffusion controlled by grain boundary and lattice diffusion in proportion to the segregation of Ar between those sites), but vary in the B-regime (bulk diffusion controlled by both grain boundary and lattice diffusion in a complex manner), implying a higher isotopic fractionation in this kinetic regime. Extrapolation to typical mantle grain sizes implies that around 22 % of the argon in the upper mantle can be stored at grain boundaries and effective diffusion is mostly in the A-regime, suggesting a low isotopic fractionation and diffusivities faster than lattice diffusivities alone. The consideration of grain boundaries as a potential Ar storage site can modify equilibrium during partial melting and can significantly enrich a liquid during fluid percolation. The grain size dependence of Ar storage and diffusivity highlights the underestimated role of grain boundaries in upper mantle,
especially in zones of reduced grain size (via dynamic recrystallization) possibly followed by fluid percolation and/or partial melting, such as in subduction zones or below oceanic ridges.

1. Introduction

The degassing of primitive volatile isotopes at mid-oceanic ridges such as $^3$He (e.g., Lupton & Craig, 1975; Farley et al., 1995; Bianchi et al., 2010) implies that primordial volatiles have been stored in the mantle since Earth’s core-mantle differentiation, and are still degassing into the atmosphere. Furthermore, the chemical and isotopic dichotomy between mid-ocean ridge basalts (MORBs) and ocean island basalts (OIBs) indicates the chemical heterogeneity of the mantle despite large-scale convection: a deep reservoir that is rich in primordial isotopes and volatile elements is sampled only by OIBs (e.g., Hofmann et al., 1978; Hofmann & Hart, 1978; White, 1985; Zindler & Hart, 1986; Farley et al., 1992; Hart et al., 1992; Hanan & Graham, 1996; Hofmann, 2003).

Argon (Ar), as other noble gases, is a reliable tracer of geochemical heterogeneities since it is (i) both a strongly incompatible and volatile element, and (ii) not easily recycled into the mantle, except perhaps via cold subduction zones (e.g., Staudacher & Allègre, 1988; Moreira & Raquin, 2007; Smye et al., 2017). Argon has three stable isotopes: two primordial isotopes ($^{38}$Ar and $^{36}$Ar) and one radiogenic isotope ($^{40}$Ar) produced by the radioactive decay of $^{40}$K with a negligible part of primordial $^{40}$Ar. The K-Ar system is used to constrain the degassing of the Earth’s mantle and the $^{40}$Ar/$^{36}$Ar ratio is a reliable tracer of mantle heterogeneities because after correction for atmospheric contamination (by using the $^{20}$Ne/$^{22}$Ne isotopic ratio, e.g., Zhang, 2014), the value of this ratio is around $40\,000$ in MORBs (e.g., Burnard et al., 1997; Raquin et al., 2008) and less than $10\,000$ in OIBs (e.g., Fisher, 1983; Hiyagon et al., 1992; Honda et al., 1993; Moreira et al., 1995; Valbracht et al., 1997; Sarda et al., 2000; Trieloff et al., 2000, 2002; Honda & Woodhead, 2005; Hopp & Trieloff, 2005; Raquin & Moreira, 2009; Mukhopadhyay, 2012). These values suggest an OIB source that is enriched in
primordial isotopes and less degassed compared to the MORB source. Furthermore, the $^{38}\text{Ar}/^{36}\text{Ar}$ ratio can be used to trace the origins of volatiles in the mantle. The whole-mantle value $^{38}\text{Ar}/^{36}\text{Ar} = 0.188$ implies a primordial signature significantly different from the solar composition ($^{38}\text{Ar}/^{36}\text{Ar} = 0.1818 \pm 0.0002$; e.g., Meshik et al., 2007) and may indicate a chondritic origin for primordial argon (Moreira, 2013), as is the case for xenon (Caracausi et al., 2016). This primordial isotopic signature may have been inherited from the Earth’s building blocks and preserved in the deep mantle since its differentiation, 4.5 Ga. To explain the preservation of volatiles and primordial isotopic compositions in the OIB source, several geochemical models (layered or not) have proposed an isolated OIB mantle reservoir despite the expected convection of the entire mantle, including: (i) the two-layer mantle model (e.g., Allègre, 1987), (ii) the basal magma ocean model (Labrosse et al., 2007), and (iii) models involving a hidden reservoir as the OIB source, such as the D″ layer (Coltice et al., 2011) or outer-core material (a liquid or a solid phase) that could be incorporated in mantle plumes during their formation (Porcelli & Halliday, 2001; Bouhifd et al., 2013).

In this study, we propose an alternative to such large-scale models to explain the preservation of chemical and isotopic heterogeneities in the mantle by identifying and studying microscopic Ar storage sites in mantle rocks. Indeed, high-temperature partitioning experiments have shown that incompatible elements are preferentially stored at grain interfaces in polycrystalline olivine (Hiraga et al., 2003, 2004, 2007), as recently confirmed for grain boundaries (Bachhav et al., 2015) and along mineral dislocations (Piazolo et al., 2016) by atom probe tomography performed on natural samples. The storage of noble gases along grain boundaries implies that the storage capacity of mantle materials depends on grain size, as is the case for helium in fine-grained lithologies (Kurz et al., 2009; Recanati et al., 2012). Moreover, the segregation of an element between grain boundaries and mineral lattices influences its transport through the polycrystalline material depending on the diffusion regime.
This influence has been studied in several studies by modelling grain boundary diffusion (Lee, 1995; Dohmen & Chakraborty, 2003; Maier, 2004; Mantisi et al., 2017), and by experimental quantification (e.g., Joesten, 1991; Herzig et al., 1993; Farver & Yund, 1996, 1998; Mishin & Herzig, 1999; Herzig & Divinski, 2003; Van Orman et al., 2003; Herzig & Mishin, 2005; Hayden & Watson, 2007; McCaig et al., 2007). However, only a few ionic diffusivities are available for silicates: OH\(^-\) (Lasaga, 1986), O (Farver & Yund, 1991, 1992, 1995; Joesten, 1991; Shimojuku et al., 2009), H (Demouchy, 2010a, 2010b), Mg (Farver et al., 1994), Mg-Fe (Dohmen, 2008) and Si (Farver & Yund, 2000a, b; Shimojuku et al., 2009). For He and Ar, grain boundary storage and its influence on diffusion have been investigated in experimentally doped polycrystalline olivine, mimicking mantle conditions (Burnard et al., 2015; Delon et al., 2018). These studies have shown that a significant amount of He and Ar can be stored at grain boundaries, increasing their bulk diffusivities in fine-grained olivine-rich rocks at low temperature (< 900 °C) compared to lattice diffusion alone.

By applying these results to the upper mantle, these studies have determined that the amount of He stored at grain boundaries increases with reduced grain size, reaching 22 % of the total He content at a grain size of 1 mm. These results imply increased bulk diffusivities when accounting for grain boundary diffusion, even at typical mantle grain sizes of 1-7 mm (e.g., Hiraga et al., 2010), reaching the maximum value of grain boundary diffusivities at smaller grain sizes (≤ 100 μm). In this study, we report new data on Ar distribution and diffusion in polycrystalline olivine and constrain Ar storage and mobility in Earth’s upper mantle.

2. Materials and methods

We followed a two-step experimental protocol: first, olivine powder was sintered to obtain dense polycrystalline olivine with clean, dry, melt-free grain boundaries; then the
starting materials were doped with noble gases at high pressure (HP) and high temperature (HT) using uraninite and orthoclase as the He and Ar sources, respectively. The doped polycrystalline olivine samples were analyzed by step heating coupled with a noble gas mass spectrometer. Helium analyses of the three samples produced and analyzed (RDPC1, RDPP1, and RDPP1-2) were reported in Delon et al. (2018); here we report Ar analyses of the same samples. A brief description of the experimental protocol with respect to Ar is reported below; for further details see Delon et al. (2018).

2.1. Starting material

Inclusion-free, gem-like, and hydrogen-poor San Carlos olivines (Mg$_{0.904}$Fe$_{0.092}$Ni$_{0.0035}$Cr$_{0.0003}$SiO$_4$) were carefully selected and then crushed and sieved to obtain powders of different grain sizes. Powder grain sizes were analyzed using a Helos BF laser diffraction granulometer with a He-Ne red laser. Powders were introduced into a water tank and agitated before being sent to the R5 (measurement range of 2.5-875 µm, focal depth of 500 mm) or R2 lens (measurement range of 0.25-87.5 µm, focal depth of 50 mm) for laser diffraction analysis. The same analysis was performed a second time after 60 s of sonication in the water tank to avoid grain agglomeration. The resulting olivine grain size ranges were 0.5-100 µm (average around 14 µm) for RDPC1, and 0.3-80 µm (average around 14 µm) for RDPP1.

Once characterized, the olivine powders were sintered: RDPP1 at 0.30 ± 0.01 GPa and 1225 ± 25 °C for 5 hours in a gas-medium HP-HT apparatus (Paterson press; Paterson, 1990) at Geosciences Montpellier (GM, University of Montpellier, France), and RDPC1 at 1.00 ± 0.02 GPa and 1275 ± 1 °C for 72 h with a piston cylinder apparatus at the Laboratoire Magmas et Volcans (LMV, Université Clermont Auvergne, Clermont-Ferrand, France). The recovered polycrystalline olivine samples were then hand-polished and cut into slices, prisms,
or cubes as the starting materials for the doping experiments. The experimental assemblies and the different sintering conditions are reported in Table 1.

The texture and grain size of the polycrystalline olivine samples were characterized after the sintering experiment by scanning electron microscopy (SEM), electron backscatter diffraction (EBSD). SEM imaging and EBSD analyses were performed at Geosciences Montpellier with a CamScan X500FE CrystalProbe, and with a 15 kV accelerating voltage, 3.5 nA beam current and a working distance of 20 mm under low vacuum conditions (5 Pa of gaseous nitrogen). Samples were embedded in a 1-inch epoxy plug and regularly polished before a final chemo-mechanical polish with a colloidal silica suspension required for EBSD. Then, samples were surrounded by copper-carbon conductive tape. EBSD maps were acquired with a step size of 0.2 to 4 µm (for further details on the data treatment, see Demouchy et al., 2011, 2014 or Thieme et al., 2018).

2.2. Doping at high pressure

The starting materials were doped at temperature (T) of 1060 ± 25 °C and 0.30 ± 0.01 GPa during 24 h in the presence of an Ar source (orthoclase from Madagascar, chemical composition detailed in Arnaud & Kelley, 1997) using the Paterson press at Geosciences Montpellier. The doping experiment was carefully developed to mimic sub-solidus mantle conditions for natural, polycrystalline, and texturally equilibrated olivine at low noble gas partial pressure. After doping, the polycrystalline olivines were cut into mm-sized cubes to ensure no residual doping material (orthoclase) was present during the subsequent noble gas analyses and that the sample size is large enough compare to grain size to average out the competing mechanisms. Thus, contamination by Ar with an atmospheric ratio can only occur during the doping experiment at high pressure and high temperature (i.e., high Ar fugacity), then coming from the pressure medium of the HP-HT apparatus (Ar gas vessel). Indeed, mm-
sized cubes are poorly affected by atmospheric contamination due to their low surface to volume ratio (Protin et al., 2016). The doping conditions are reproduced in Table 1 and the assembly in Fig. 1. To constrain the potential grain size variations during the doping experiment, we calculate the diffusion length of silicon (Si) by using the Si diffusion coefficient in dry (Dohmen et al., 2002) and wet olivine (Costa & Chakraborty, 2008) at the conditions of the doping experiment (24h and 1060 °C). This diffusion length is 0.20 nm in dry olivine and 23 nm in wet olivine. Since the grain size variation does not exceed these diffusion lengths, we can conclude that it is very minor during the doping experiment.

After doping, olivine microstructures were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) at Unité Matériaux et Transformations (UMET, University of Lille, France). Doubly polished thin sections (30 µm thick) were ion milled at 5 kV under a low beam angle of 15° to reach electron transparency. The thin foils were then covered by a thin layer of carbon before characterization using a Philips CM30 microscope operating at 300 kV and a FEI® Tecnai G2-20 twin microscope operating at 200 kV for TEM analyses, and a FEI Titan® Themis 300 operating at 300 kV for HR-TEM analyses.

2.3. Noble gas analyses
Analyses of argon were performed using a noble gas mass spectrometer and following a step heating protocol. Analytical protocol is identical to Delon et al. (2018). The samples were annealed at different temperatures (400 to 1200 °C) and the extracted amount of gas was analyzed to get the Ar molar quantity released at each heating step. Then, the fractional gas loss ($F$) from the sample at each step was calculated by dividing the molar quantity by the initial total amount of Ar in the sample. It yields the diffusion coefficient $D$ as a function of
the square of the radius of the diffusion domain \(a\), following the equations (e.g., Crank, 1975; Fechtig & Kalbitzer, 1966; McDougall & Harrison, 1999):

\[
\frac{D}{a^2} = \frac{\pi}{36} \frac{(P_1^2 - P_2^2)}{(t_1 - t_2)} \quad \text{for } F < 0.10 \quad ,
\]

\[
\frac{D}{a^2} = \frac{1}{(t_1 - t_2)} \left[ \frac{1}{3} (F_2 - F_1) + \frac{2}{\pi} \left( \sqrt{1 - \frac{\pi}{3} F_2} - \sqrt{1 - \frac{\pi}{3} F_1} \right) \right] \quad \text{for } 0.10 < F < 0.85 \quad ,
\]

\[
\frac{D}{a^2} = \frac{1}{\pi^2(t_2 - t_1) \ln \left( \frac{1 - F_1}{1 - F_2} \right)} \quad \text{for } F > 0.85 \quad ,
\]

where \(t_1\) and \(t_2\) are the respective extraction durations and \(F_1\) and \(F_2\) the respective cumulative fractional gas losses at the beginning and at end of each step. The diffusion coefficients \(D\) (or \(D/a^2\) ratio when the value of \(a\) is unknown) are obtained as a function of \(1/T\), and used to extract the diffusion parameters: (i) the activation energy \(E_a\) and (ii) the pre-exponential factor \(D_0\) (or \(D_0/a^2\) if \(a\) unknown). Noble gas analyses were achieved at Centre de Recherches Pétrographiques et Géochimiques (CRPG, Université de Lorraine, Nancy, France) using a Helix MC Plus mass spectrometer calibrated using aliquots (≈ 0.3 cc) of an in-house Ar standard with known molar quantities of \(^{40}\text{Ar}\), \(^{38}\text{Ar}\), and \(^{36}\text{Ar}\). The \(^{40}\text{Ar}\) signal was collected on a faraday cup coupled with a \(10^{11} \Omega\) amplifier, and the \(^{38}\text{Ar}\) and \(^{36}\text{Ar}\) signals were measured simultaneously on an electron multiplier CDD. For each standard run, the sensitivity of the mass spectrometer was calculated and used to measure an unknown molar quantity from an analysis. About 5 mg of doped olivine sample was placed in a container above a Nicrofer® alloy tube (inner diameter 13 mm), heated by a radiative external furnace. Blank measurements of the empty tube were performed at each temperature step for the first sample; and for others, only 5 blanks (between 0 and 1200 °C) were analyzed leading to the same results. The sample was then placed at the bottom of the tube by dropping it from the container. At each temperature step between 400 ± 1 and 1200 ± 1 °C, the temperature was increased by 25 or 50 °C and held for 15 to 30 min. Individual step sequences are reported in Table 1. The extracted gases were analyzed and background and blank corrections were
performed at each analysis. External error was calculated based on the sensitivities of each standard, and is less than 4% per measurement, leading to a maximum external error of ±0.02 on the resulting $\log(D/a^2)$ value. The samples were crushed in a vacuum and the extracted gases analyzed prior to step heating analyses to investigate the amount of Ar stored in intergranular porosity. The extracted Ar accounted for less than 10% of the total Ar in the samples, ensuring that no Ar stored in porosity was analyzed in the subsequent step heating analyses.

After the final heating step, the sample was loaded in a laser chamber and melted using a 30 W, 10.6-µm-wavelength (CO$_2$) laser to extract the remaining Ar and a re-extraction was performed to ensure that all Ar was extracted from the sample. This last melting step allows calculation of the total amount of Ar in the sample, and thus the fractional gas loss at each temperature step necessary to obtain the diffusion coefficient as a function of $a^2$. Details of individual step heating analyses are reported in Table 1.

3. Results

3.1. Microstructures

A SEM image of RDPC1 is available in Fig. 2a, showing clean polycrystalline olivine with an equilibrated texture, and melt-free grain boundaries. Low residual porosity is the result of imperfect compaction at 0.3 and 1 GPa. As Ar is a volatile element, these defects could potentially store a significant amount of Ar, but the amount stored in porosity is small (less than 10% of the total Ar) as previously discussed in section 2.3. EBSD maps show that grain sizes range from 1 to 50 µm (averaging 16.3 µm) for RDPC1, and from 1 to 30 µm (averaging 8.8 µm) for RDPP1. These grain size ranges and average values are slightly different from those obtained by laser diffraction. In the case of RDPC1, the increased grain size probably resulted from olivine grain growth during piston-cylinder sintering experiments.
since they were long duration experiments (ca. three days). For RDPP1, the decreased grain size might be due to brittle/cataclastic deformation during cold pressing, as the sintering experiments were too short to permit significant grain growth.

TEM images are shown in Fig. 2b and 2c. TEM analyses revealed the presence of dislocations, rare pores at junctions, and a few nanometric bubbles that were not systematically linked with dislocations or grain boundaries (e.g., Burnard et al., 2015; Delon et al., 2018). Grain boundaries are linear or quasi linear, indicating a near-equilibrium texture. RDPC1 shows a lower dislocation density than RDPP1, which might be due to microstructure recovery during the longer annealing period at higher temperature and pressure (Farla et al., 2011). HR-TEM analyses (Fig. 2d), confirmed that grain boundaries are highly crystalline and melt-free. Additional SEM and TEM images are available in Delon et al. (2018).

3.2. Ar diffusivity

Diffusion coefficients are reported in Fig. 3. The detailed data treatment is provided in supplementary material as well as the plots $T = f(t)$, $F = f(t)$, and the isotopic ratios as a function of $F$. To constrain the fit of our data by one or two linear regressions (as it the case for He data, see Delon et al., 2018), we used a $F$-test (see appendix for further details). Despite some scatter in the data, the fit of diffusivities by one single linear regression cannot be rejected and represents the simplest model. Thus, we performed only one linear regression and obtained activation energies for $^{40}$Ar diffusion of 37 ± 10, 39 ± 14, and 22 ± 10 kJ·mol$^{-1}$, for RDPC1, RDPP1 and RDPP1-2, respectively. The extracted diffusion parameters are reported in Table 2. Linear regression on $^{38}$Ar and $^{36}$Ar diffusivities shows approximatively the same $E_a$ values for $^{38}$Ar diffusion (35 ± 12 kJ·mol$^{-1}$ and 20 ± 16 kJ·mol$^{-1}$ for RDPC1 and RDPP1-2, respectively) and $^{36}$Ar diffusion (33 ± 12 kJ·mol$^{-1}$ and 27 ± 12 kJ·mol$^{-1}$ for RDPC1 and RDPP1-2, respectively; Table 2). Errors are reported at 2$\sigma$. 

11
These results could be influenced by the release of Ar trapped in pores during the last laser extraction, which can modify the total amount of Ar in the sample and thus, the resulting diffusivities because of Eqs. (1-3). Indeed, reducing the total amount of Ar by 10% enhances the resulting pre-exponential factor although the activation energy is not modified in the error bar. However, this process did not influence He data since the resulting pre-exponential factors agreed with literature data, meaning that He extracted during the fusing stage mainly comes from the crystal lattice and grain boundaries (and not from pores). Thus, the same conclusion can be done for Ar as the same storage behavior is expected.

3.3. Segregation factor

To investigate Ar storage in grain boundaries, the segregation factor \( s \) between grain boundaries and the crystal lattice is defined as the ratio between the concentrations in grain boundaries \( C^{GB} \) and in the crystal lattice \( C^{LAT} \):

\[
s = \frac{C^{GB}}{C^{LAT}}.
\]

Similarly, the molar segregation factor \( \chi \) is defined as the ratio between the molar quantities in grain boundaries \( X^{GB} \) and in the lattice \( X^{LAT} \):

\[
\chi = \frac{X^{GB}}{X^{LAT}}.
\]

\( \chi \) was calculated by considering \( X^{GB} \) as being the total amount of the element extracted in the temperature range where both grain boundary and lattice diffusions occur, and \( X^{LAT} \) is the total amount of the element subtracted to \( X^{GB} \). However, only a single diffusion process with a low \( Ea \) is observed in this study, suggesting that grain boundaries retained Ar through the entire step heating experiments (up to 1100 °C). In this case, only a minimum \( X^{GB} \) value can be determined and, thus, minimum values of the segregation factor \( s_{min} \) and the molar segregation factor \( \chi_{min} \). Here, we obtained \( \chi_{min} \) by defining \( X^{GB} \) as the total amount of Ar
extracted during the step heating experiments, and $X_{\text{LAT}}$ as the amount of Ar extracted during
the last laser melting. Then, $s_{\text{min}}$ was determined from $X_{\text{min}}$ since:

$$s = \frac{C_{\text{GB}}}{C_{\text{LAT}}} = \frac{X_{\text{GB}}V_{\text{LAT}}}{X_{\text{LAT}}V_{\text{GB}}} = \frac{X}{v}, \quad (6)$$

where $V_{\text{LAT}}$ and $V_{\text{GB}}$ are the respective lattice and grain boundary volumes, and $v = 2.84 \cdot \delta/d$ is
the volume fraction of grain boundaries in the sample (Hiraga & Kohlstedt, 2009) based on
the grain boundary width $\delta$ (1 nm, Hayden & Watson, 2007) and grain size $d$ (16.3 µm for
RDPC1 and 8.8 µm for RDPP1 and RDPP1-2). The minimum molar segregation factors and
segregation factors are reported in Table 2.

### 3.4. Isotopic diffusion

Since Ar isotopes could be analyzed, isotopic diffusion has been determined by
comparing the diffusion coefficients of the different Ar isotopes. Graham’s law predicts that,
in gases, the mobility ratio of different isotopes is equal to the square root of the inverse of
their mass ($m$) ratio. This law can be applied to the diffusion coefficient ratio as:

$$\frac{D_x}{D_y} = \left(\frac{m_y}{m_x}\right)^\beta,$$  \quad (7)

where $x$ and $y$ are two different isotopes of the same element and $\beta=0.5$ in gases. A similar
law is generally assumed for noble gas isotopes in solids (Burnard & Harrison, 2005; Craig &
Lupton, 1976; Kaneoka, 1980; Pinti et al., 1999; Ruzié & Moreira, 2010; Yamamoto et al.,
2009), except in glasses below their glass transition temperature (see Amalberti et al., 2016).
We calculated $D_{40}/D_{36}$, $D_{40}/D_{38}$, and $D_{36}/D_{38}$ (subscripts denote the Ar isotopic mass number)
for each temperature step for samples RDPC1 and RDPP1-2 and compared them to Graham’s
law. Results are reported in Fig. 4 and the ratios are relatively constant at low temperatures (T
$\leq 800$ °C) but vary widely at higher temperatures (900-1200 °C). The low-temperature
averages of these ratios ($D_{40}/D_{36} = 0.89 \pm 0.06$, $D_{40}/D_{38} = 0.83 \pm 0.12$, and $D_{36}/D_{38} = 0.90 \pm
0.10, calculated excluding data beyond the 2σ range, i.e., one point for each ratio) are close to the values predicted by Graham’s law (0.95, 0.97 and 1.08 respectively). These isotopic diffusion coefficient ratios are slightly inferior to 1 and could be below the values predicted by Graham’s law (except for the $D_{36}/D_{38}$ ratio), suggesting that diffusive isotopic fractionation could be slightly more important than estimated by Graham’s law. Whereas at higher temperatures, the ratios are more variable and farther from those predicted by Graham’s law, indicating a more important isotopic fractionation.

4. Discussion

4.1. Ar source during the doping experiments

Although the Ar source used in the doping experiments was orthoclase containing quasi-exclusively the $^{40}$Ar isotope, $^{38}$Ar and $^{36}$Ar signals were above blank intensities for RDPC1 and RDPP1-2, suggesting that Ar was also incorporated from the pressure medium (Ar gas) in the HP-HT apparatus. Moreover, the $^{40}$Ar/$^{36}$Ar isotopic ratios of the samples were 352 ± 28 and 292 ± 23 for RDPC1 and RDPP1-2, respectively, very close to the atmospheric ratio (298.56 ± 0.31, Lee et al., 2006) and that of the pressure medium in the Paterson press. These results indicate that most of the Ar in the samples was incorporated from the pressure medium during the long-duration doping experiments. Thus, Ar was incorporated at high fugacity, and the doping conditions did not directly mimic mantle conditions. Nevertheless, as diffusion occurs during the step heating analyses, Ar incorporation at high pressure does not affect the accuracy of the resulting diffusivities, except maybe in modifying the initial concentration profile in the polycrystalline sample (whereas Eqs. 1-3 were developed for a homogeneous concentration; Crank, 1975; Fechtig & Kalbitzer, 1966; McDougall & Harrison, 1999). However, as demonstrated in the recent study by Delon et al. (2018), the calculated diffusion parameters were not affected by the initial concentration profile, implying that the
diffusivities obtained here are accurate and representative of Ar diffusivities in fine-grained polycrystalline olivine. Only the segregation of Ar between grain boundaries and the crystal lattice cannot be considered as representative of mantle rocks.

4.2. Interpretation of the diffusion parameters

In previous studies, a change of slope was observed at the transition temperature for He and Ar diffusivities, which was interpreted as two different diffusion processes occurring as a function of temperature (see Burnard et al., 2015; Delon et al., 2018): (i) lattice diffusion occurs above the transition temperature, and (ii) combined lattice and grain boundary diffusion occur below the transition temperature. Delon et al. (2018) referred to lattice diffusion as LAT, grain boundary diffusion as GB, and diffusion controlled by both lattice and grain boundary diffusion as LAT+GB, and we follow that usage here. However, in our current study, the F-test do not reject the model with only one linear regression to fit our data, thus only a single linear regression was performed for each sample. The calculated diffusion parameters show that the three analyzed samples were governed by the same diffusion process with a low $E_a$. These low $E_a$ values indicate that most of the Ar extracted during step heating experiments was released from a poorly retentive storage site. It is therefore important to refer to previous studies to identify the diffusion mechanisms controlling Ar mobility in our polycrystalline samples.

The $E_a$ values obtained in this study are in agreement with those calculated for the LAT+GB temperature range in Burnard et al. (2015), at least for one of their samples, suggesting that only LAT+GB temperature range is observed here. The other sample from Burnard et al. (2015) shows an $E_a$ value of 114 kJ·mol$^{-1}$, but this value was mostly controlled by one diffusion coefficient obtained at 450 °C. Indeed, an $r^2$ value of 0.10 instead of 0.68 is obtained if this point is excluded from the regression. For this reason, the diffusion parameters
of the LAT+GB temperature range for this sample will not be compared to our data. Moreover, the $E_a$ values from this study are also consistent with reported values for He diffusivities in the LAT+GB temperature range (Burnard et al., 2015; Delon et al., 2018).

We interpret the absence of the transition between the LAT and the LAT+GB processes to indicate that the step heating experiments were not long enough or did not reach sufficiently high temperatures. Indeed, the transition temperature is reached only when grain boundaries are fully emptied (Delon et al., 2018), meaning that Ar was not fully extracted from grain boundaries during the step heating experiments in this study. Thus, only the LAT+GB temperature range is identified here.

4.3. Lattice diffusion

Because we were only able to observe LAT+GB, Ar diffusion parameters in the olivine crystal lattice alone cannot be directly determined. However, literature data can be used to estimate these parameters. Only a few studies have focused on Ar diffusion in the olivine lattice: Futagami et al. (1993) reported $E_a = 135 \pm 12$ kJ·mol$^{-1}$ and $\log(D_0) = -7.84 \pm 0.62$ for Ar diffusion in synthetic ion-implanted forsterite, and Thomas et al. (2008) reported $E_a = 42 \pm 2$ kJ·mol$^{-1}$ and $\log(D_0) = -19.14 \pm 0.1$ (D$_0$ in m$^2$·s$^{-1}$) for Ar diffusion in previously polished iron-free forsterite experimentally doped at high Ar pressure. The low diffusivities reported by Thomas et al. (2008) would indicate that Ar behaves compatibly in mantle rocks (Watson et al., 2007), but their values can also be explained by a high population of nanometric defects at the sample surface (possibly due to polishing before the doping experiments or to analytical limitations) and by Ar incorporation at high fugacity. For these reasons, we avoid further discussion of their diffusion parameters. Ar diffusion has also been investigated in experimentally doped polycrystalline olivine (Burnard et al., 2015). They obtained diffusion parameters for HT lattice diffusion in two samples: $E_a = 338 \pm 98$ kJ·mol$^{-1}$, $\log(D_0) = 0.32 \pm$
4.49 above 950 °C and $E_a = 445 \pm 90 \text{kJ mol}^{-1}$, $\log(D_0) = 2.47 \pm 2.11$ with $D_0$ in $\text{m}^2\text{s}^{-1}$ above 1100 °C. The values of the pre-exponential factors were calculated by taking $a = 150 \mu\text{m}$ (half the sample size) as was suggested in Burnard et al. (2015) and confirmed by Delon et al. (2018). All these diffusion parameters are presented in Fig. 5, showing that the diffusion parameters reported by Burnard et al. (2015) are exceptionally high. The corresponding linear regressions were highly controlled by the two highest temperature points with very fast diffusivities. These high diffusivities are distinct from the trend described by the lower temperature diffusivities, and by excluding them, lower diffusion parameters are obtained: $E_a = 198 \pm 44 \text{kJ mol}^{-1}$ and $\log(D_0) = -3.53 \pm 1.76$ above 950 °C and $E_a = 197 \pm 82 \text{kJ mol}^{-1}$ and $\log(D_0) = -6.24 \pm 2.86$ above 1100 °C. These recalculated diffusion parameters are in agreement with those of Futagami et al. (1993), providing the mean values: $E_a = 166 \pm 44 \text{kJ mol}^{-1}$ and $D_0 = 10^{-7.04} \pm 1.13 \text{m}^2\text{s}^{-1}$. These new diffusion parameters were obtained by excluding the sample from Burnard et al. (2015) that induced an abnormally high pre-exponential factor ($\log(D_0) = -3.53 \pm 1.76$).

The increased HT diffusivities for samples from Burnard et al. (2015) are significantly faster than diffusivities extrapolated from lower temperatures and might be explained by two hypotheses: (i) a change of slope related to a change in diffusion mechanism in the olivine crystal lattice, or (ii) early partial melting (EPM) inducing an important partition of Ar leading to its faster release. Hypothesis (i) would indicate two transition temperatures ($1075 \pm 25$ and $1300 \pm 100$ °C), suggesting a change in diffusion mechanism related to two different Ar storage sites in the olivine lattice (e.g., different point defects), as is the case for He (Delon et al., 2018). Thus, the higher transition temperature would represent the emptying of Ar from a less-retentive storage site in the olivine lattice (with the lowest diffusion parameters); at higher temperatures, Ar diffusion would occur only from the more-retentive storage site (with higher values of the diffusion parameters). However, diffusion parameters cannot be
determined for this potential more-retentive storage site using the values from Burnard et al. (2015) since only two temperature steps for each sample can be used to extract the diffusivities of this diffusion mechanism. Hypothesis (ii) would suggest that inter- and/or intra-granular EPM of olivine occurred, inducing a fast Ar release and increasing the observed diffusivities at high temperature during the last heating steps. Such a phenomenon has been observed in step heating experiments for Ar in pyroxenes (Cassata et al., 2011). EPM of olivine has been observed between 1100 and 1500 °C (Jaoul et al., 1987), which includes the transition temperature determined in Burnard et al. (2015). However, if EPM had occurred, increased He diffusivities related to a He release should also be observed in the same temperature range, which is not the case (Burnard et al., 2015). Therefore, we argue in favor of hypothesis (i) that the observed change of $E_a$ seems to be related to a change in the diffusion mechanism induced by the emptying of a less-retentive storage site in the olivine lattice.

4.4. Grain boundary diffusion

To determine the diffusion parameters for Ar in olivine grain boundaries, it is important to determine the diffusion regime occurring at each temperature step. Indeed, bulk (or effective) diffusion results from the combined contributions of GB and LAT depending on the diffusion regime. Three diffusion regimes (A-, B- and C-) have been defined based on the lattice diffusion length value (e.g., Mortlock, 1960; Dohmen & Milke, 2010; Harrison, 1961; Mishin & Herzig, 1995, 1999). The A-regime occurs when the lattice diffusion length $\sqrt{D_{LAT}t}$ is longer than the grain size $d$ of the polycrystalline material. In this case, bulk diffusion appears to obey Fick’s law and bulk diffusivities ($D_{bulk}$) can be expressed as a function of lattice and grain boundary diffusivities as:
However, this equation might not be relevant for species which highly segregate into grain boundaries and then $\chi$ can be greater than 1. More recently, Eq. (8) has been generalized by considering the concept of tortuosity leading to the following equation (Zhang & Liu, 2012):

$$D_{\text{bulk}} = (1 - \chi)D^{\text{LAT}} + \chi D^{\text{GB}}$$  \hspace{1cm} (8)

$$D_{\text{bulk}} = \frac{(1 - \nu)D^{\text{LAT}} + \frac{svD^{\text{GB}}}{\theta^2}}{sv + (1 - \nu)}$$  \hspace{1cm} (9)

with $\theta$, the tortuosity factor for grain boundaries and $\nu$ the volume fraction of grain boundaries.

The B-regime occurs when $d > \sqrt{D^{\text{LAT}}t} > s\delta/2$; bulk diffusivities do not follow Fick’s law and $D^{\text{bulk}}$ cannot be easily expressed as a function of $D^{\text{LAT}}$ and $D^{\text{GB}}$. The C-regime occurs when $\sqrt{D^{\text{LAT}}t} < s\delta/2$ and bulk diffusion obeys Fick’s law since $D^{\text{bulk}} = D^{\text{GB}}$. If the concept of tortuosity is implemented, $D^{\text{bulk}} = D^{\text{GB}}/\theta^2$ with $\theta$ the tortuosity factor (Zhang & Liu, 2012), which is typically in the range of 1.5-2.0 (Farver & Yund, 2000a) in dense polycrystals. Thus, the concept of tortuosity modifies the diffusion coefficient by a very limited factor (of 4 at the maximum value of $\theta$), which is in the diffusivity error bar of our study and this concept will not be considered further in this study. Although these kinetic regimes have been defined for the incorporation of the diffusive species into a polycrystalline material, they can also be used for degassing experiments. Thus, during an extraction step with duration $t$ and at constant temperature, the boundary times $t'$ and $t''$ between the C- and B-regimes and between the B- and A-regimes, respectively, can be defined as:

$$t' = \frac{(s\delta)^2}{4D^{\text{LAT}}}$$  \hspace{1cm} (10)

$$t'' = 150 \cdot \frac{d^2}{D^{\text{LAT}}}$$  \hspace{1cm} (11)

However, the segregation factor $s$ cannot be estimated in our experiments since the transition temperature between LAT and LAT+GB temperature ranges was not reached. Thus, only the
minimal segregation factor $s_{min}$ can be calculated, and the minimal duration $t'_{min}$ is defined as the minimal time to reach the B-regime. This implies that $t' > t'_{min}$ thus, the C-regime occur if $t' > t > t'_{min}$ and when $t < t'_{min}$.

The durations $t'_{min}$ and $t''$ were calculated at each temperature step and for each sample by determining $D^{LAT}$ from the diffusion parameters obtained in section 4.2, and $s_{min}$ was calculated from $s_{min}$, the ratio between the amount of Ar extracted in later heating steps to that extracted during the laser extraction, with $\delta' = 1$ nm (e.g., Hayden & Watson, 2007; Hiraga et al., 2007). The obtained values of $t'_{min}$ and $t''$ are compiled in supplementary materials, and they are compared to the extraction duration $t$ to define the kinetic regime. These results show that only the C- and B-regimes occurred during the step heating experiments ($d$ has to be less than 1.19 µm to observe the $t''$ transition at 1200 °C in our experiments). As shown above, grain boundary diffusivities cannot be easily extracted from bulk diffusivities in the B-regime, whereas in the C-regime, $D^{bulk} = D^{GB}$. Thus, we performed a linear regression on the diffusivities obtained in the C-regime to extract the grain boundary diffusion parameters. These diffusion parameters are reported in Table 3 and the grain boundary diffusivities are reported in Fig. 6 for $a = 0.48$ µm, corresponding to the grain boundary network, and $a = 150$ µm, corresponding to half the sample size (i.e., half the grain size of the resulting powder after crushing experiment), as proposed by Burnard et al. (2015). Comparison of grain boundary and lattice diffusivities shows that for $T > 800$ °C and $a = 0.48$ µm, grain boundary diffusivities are slower than lattice diffusivities, which is not the case for $a = 150$ µm. Nevertheless, as the crystalline structure is expected to be more disordered in grain boundaries than in the olivine lattice, statistically, grain boundary diffusion should be faster than lattice diffusion in the olivine stability field (i.e., up to at least 1400 °C, Akaogi et al., 1989). Indeed, diffusivities depend on defect concentrations (Nakamura & Schmalzried, 1984), which are expected to be higher in grain boundaries, except for very specific grain
boundary geometries (e.g., kinks; see also Dillon & Harmer, 2008a, for grain boundary
complexion). Thus, only the diffusivities obtained using an a value of half the sample size
yield grain boundary diffusivities higher than lattice diffusivities in the error range. We
conclude that a is equal to half the sample size for Ar diffusion in grain boundaries as is the
case for He (Delon et al., 2018), resulting in mean values for the grain boundary diffusion
parameters of $E_a = 22 \pm 5 \text{kJ.mol}^{-1}$ and $\log(D_0) = -12.87 \pm 0.3$ with $D_0$ in $\text{m}^2\cdot\text{s}^{-1}$.

Moreover, the scattering of our data remains to be explained, especially at high
temperature. One possibility is the remobilization of Ar trapped in residual pores since
crushing under vacuum might not be sufficiently effective (e.g., the resulting grain size was
still larger than pore size after crushing). However, the energy of remobilization is very high
(for He, $\sim 420 \text{kJ.mol}^{-1}$, Trull & Kurz, 1993), which implies an important (high) temperature
dependency. Thus, the release of Ar trapped in pores should increase with increasing
temperature, in enhancing diffusivities which is not observed in our data set. Instead, data
scattering at high temperature of our data seems to coincide with the hypothetical boundary
between the C- and the B-regime. It suggests that the data scattering can be explained by the
breakdown of Arrhenius law in the B-regime rather than a significant contribution of Ar
trapped in pores.

4.5. Diffusive Ar isotopic fractionation in polycrystalline olivine

As bulk diffusivities depend on the diffusive kinetic regime occurring in polycrystalline
rocks, diffusive isotopic fractionation should also be related to the diffusion regime. Because
only the C- and B-regimes occurred in our experiments, only the diffusive fractionation of Ar
isotopes in the C- and B-regimes can be directly studied using our data. The transition
between the C- and B-regimes is reported in Fig. 4 and in supplementary materials. In the C-
regime, the ratio between the different isotopic diffusivities seems to be constant for $D_{40}/D_{36}$,
$D_{40}/D_{38}$, and $D_{36}/D_{38}$, suggesting that Eq. (7) can be applied. However, the value of $\beta$ seems to be slightly different than 0.5, at least for $D_{40}/D_{38}$ and $D_{36}/D_{38}$, since the value predicted by Graham’s law is not within error (standard deviation) for these ratios. Because bulk diffusion in the C-regime corresponds to grain boundary diffusion, we conclude that the law described by Eq. (7) can be applied to grain boundaries, as is the case for noble gases in solids (Burnard & Harrison, 2005; Craig & Lupton, 1976; Kaneoka, 1980; Pinti et al., 1999; Ruzié & Moreira, 2010; Yamamoto et al., 2009), except perhaps in glasses at low temperature (Amalberti et al., 2016).

The diffusive fractionations in the B-regime do not seem to follow a similar law, as shown by the large variations of $D_{40}/D_{36}$, $D_{40}/D_{38}$, and $D_{36}/D_{38}$ above the transition between the C- and B-regimes (Fig. 4). These large variations do not start at the exact reported transition to the B-regime, though the estimated boundary duration between the C- and B-regimes is a minimum and not an absolute value (see section 3.2). Thus, several heating steps that were identified as belonging to the B-regime may actually belong to the C-regime, which could explain the relatively constant value of the different ratios in the first few extraction steps identified in the B-regime. In later steps, the ratios vary irregularly from 1.5 to 0.5, suggesting an important Ar isotopic fractionation in polycrystalline olivine. These large isotopic fractionations highlight that diffusive fractionation can occur in the B-regime and should not be neglected.

In the A-regime, the bulk diffusion coefficient is defined by Eq. (8), and the ratio between the bulk diffusion coefficients of isotopes $x$ and $y$ ($f^{bulk}$) can be expressed based on the lattice and grain boundary isotopic diffusivity ratios ($f^{LAT} = D^{LAT}_x / D^{LAT}_y$ and $f^{GB} = D^{GB}_x / D^{GB}_y$, respectively) as:

$$f^{bulk} = \frac{D^{bulk}_x}{D^{bulk}_y} = \frac{(1 - \chi)D^{LAT}_x + \chi D^{GB}_x}{(1 - \chi)D^{LAT}_y + \chi D^{GB}_y} = \frac{(1 - \chi)D^{LAT}_x + \chi D^{GB}_x}{(1 - \chi)D^{LAT}_y + \chi D^{GB}_y}. \quad (12)$$
Thus, if $f_{LAT} \approx f_{GR}$, which is highly probable since these two ratios follow a similar law and are close to the value given by Graham’s law, then $f_{\text{bulk}} = f_{LAT} = f_{GB}$ in the A-regime. A similar result is obtained by using Eq. (9) instead of Eq. (8). Thus, Eq. (12) predicts that isotopic fractionations follow a law similar to Eq. (7) in the A-regime, as is the case in the C-regime.

4.6. Mantle implications

4.6.1. Storage of Ar in the Earth’s upper mantle

Since our experiments were performed on olivine, our results can only be extrapolated to the Earth’s upper mantle (i.e., within the olivine stability field), and differences in mineralogy (i.e., monomineralic versus polymineralic) must be considered. To study the storage of Ar in the upper mantle, it is important to determine the segregation factor $s$ between the grain boundaries and the olivine lattice. However, $s$ was highly variable between our different samples, and it as shown that these samples were not at the equilibrium for He (Delon et al., 2018): as Ar diffusion is slower than He diffusion, Ar cannot have been at equilibrium in these samples, and our segregation factors cannot be directly extrapolated to the upper mantle. Nevertheless, $s$ was always greater than 1 in our samples, highlighting that grain boundaries are a potentially important Ar storage site in polycrystalline minerals.

Only one study has attempted to determine the $s$ for Ar in mantle minerals (Baxter et al., 2007). They found that $s$ was bracketed between $1.47 \times 10^5$ and $4.17 \times 10^4$ in polycrystalline diopside. Another method to estimate $s$ is to determine the Ar partition coefficient between olivine and silicate melt ($K_{\text{ol-melt}}$). Indeed, to the first order, the segregation between olivine lattice and intergranular silicate melt is expected to be comparable to the segregation between olivine lattice and grain boundaries, and thus the $K_{\text{ol-melt}}$ values are similar to the inverse of $s$ (e.g., Hiraga & Kohlstedt, 2007). Nevertheless, $K_{\text{ol-melt}}$ values for nobles gases are poorly constrained and vary over several orders of magnitude (e.g., Broadhurst et al., 1990, 1992;
Brooker et al., 1998, 2003; Chamorro et al., 2002; Heber et al., 2007; Hiyagon & Ozima, 1986; Jackson et al., 2013; Watson et al., 2007). Since literature data were obtained from samples whose surfaces were polished before analyses, atmospheric contamination might have artificially increased the reported $K^{\text{ol-melt}}$ values (as Ar is the most abundant noble gas in the atmosphere, and thus the most affected by atmospheric contamination; for further details, see Burnard et al., 2015; Delon et al., 2018). Thus, the true $K^{\text{ol-melt}}$ values must be lower than the lowest reported values (for Ar in the upper mantle, $K^{\text{ol-melt}} < 10^{-3}$; Heber et al., 2007). However, values in the $10^{-5}$ range have been reported for all other noble gases (e.g., Heber et al., 2007; Jackson et al., 2013), suggesting that $K^{\text{ol-melt}}$ values are overestimated in the literature and must also be in the $10^{-5}$ range, in agreement with the $1/s$ value found by Baxter et al. (2007). The same estimation can be made for pyroxenes (Baxter et al., 2007; Heber et al., 2007; Jackson et al., 2013).

We calculated the proportion of Ar in grain boundaries ($X^{GB}$) and in the mineral lattice ($X^{LAT}$) as a function of grain size by using Eq. (6) and the results are presented in Fig. 7 for two extreme values of $s$: $10^4$ and $10^5$. Most Ar is stored in the lattice at typical mantle grain sizes: for $s = 10^5$ (close to the value reported by Baxter et al., 2007), $X^{GB} \sim 4\%$ for $d = 7$ mm, and $\sim 22\%$ for $d = 1$ mm. Thus, even at large mantle grain sizes, the amount of Ar stored in grain boundaries cannot be neglected and should be considered in geochemical models. This amount drastically increases for smaller grain sizes and most Ar is stored in grain boundaries at $d < 285$ $\mu$m for $s = 10^5$ and $d < 28$ $\mu$m for $s = 10^4$. Thus, processes that result in decreased grain size (i.e., upper mantle deformation) should redistribute Ar from crystal lattices to grain boundaries increasing the amount of Ar that can be mobilized during fluid percolation. In geological contexts where mantle deformation and fluid percolation occur together, such as below mid-ocean ridges or in subduction zones, the redistribution of Ar to grain boundaries can significantly change the equilibrium kinetics during partial melting and enrich the melt.
during percolation. Though several studies have used the degassing of noble gases at oceanic ridges to estimate the concentration of noble gases in the MORB source (e.g., Honda & Patterson, 1999; Marty & Tolstikhin, 1998), they did not account for increased equilibrium kinetics and melt enrichment during percolation, and likely overestimated the deep-Earth argon concentration.

4.6.2. Transport of Ar in the Earth’s mantle

To determine the diffusivity of Ar in the upper mantle, it is important to know which kinetic regime occurs in mantle rocks. Thus, we calculated the boundary times $t'$ and $t''$ defined by Eqs. (9) and (10) at mantle conditions as a function of grain size and temperature. These times were determined for $\delta = 1$ nm (Hayden & Watson, 2007), and for $s = 10^5$ or $10^4$ (the two extreme values used in section 4.6.1). The results are presented in Fig. 8 for $T = 600, 800, 1000,$ and $1400$ °C. The grain size range corresponding to special ultrafine-grained material ($d < s \delta / 2$) is reported following the description given by Mishin & Herzig (1995): in this case, the segregation between the lattice and grain boundaries is very high, implying that bulk diffusion is controlled by grain boundary diffusion ($D_{bulk} = D_{GB}$).

For larger grain sizes, the boundary time between the C- and B-regimes ($t'$) does not depend on grain size and occurs very rapidly for the two values of $s$, even at low temperature (after only 7 and 0.74 years for $s = 10^5$ and $10^4$, respectively, at 600 °C). Thus, we conclude that the C-regime is negligible over geological time scales in the upper mantle. The boundary time between the B- and A- regimes ($t''$) decreases as grain size decreases and temperature increases. For typical mantle grain sizes of 1 to 7 mm (Hiraga et al., 2010), the B-regime ends after 21.8 Myr at 600 °C, for $d = 7$ mm, regardless of the $s$ value, indicating that the B-regime dominates for kinetic diffusion in coarse-grained mantle rocks at low temperature. However, at 800 °C (a more realistic temperature value for the uppermost mantle) and for a
large grain size of 7 mm, the A-regime occurs after only 307 kyr, which may be neglected over geological time scales. This shows that the A-regime is the main kinetic regime controlling Ar diffusion in upper mantle rocks, except maybe at very low temperatures (<800 °C) and for large grain sizes (7 mm), which should represent only a very small portion of the upper mantle (e.g., lithospheric mantle section only).

As the A-regime should control bulk diffusion in the upper mantle, we predict that diffusive isotopic fractionation is low and follows a law similar to Eq. (7) as it is suggested by Eq. (12). Bulk diffusivities are described by Eq. (8) and are controlled by both lattice and grain boundary diffusivities. Thus, bulk diffusivities are highly dependent on grain size and will increase for finer grain sizes (Delon et al., 2018). Since the Ar storage capacity also increases with the volume fraction of grain boundaries (and thus with finer grain sizes), we can identify preferential zones of Ar storage in the upper mantle where Ar transport is more efficient than in the majority of the upper mantle. These zones correspond to mantle rocks with a relatively small grain size induced by deformation (e.g., dynamic recrystallization), such as mylonites and ultramylonites. Previous studies have reported that He concentrations in bulk mylonites depend on grain size (Kurz et al., 2009; Recanati et al., 2012), and the same process should be expected for Ar. To confirm this hypothesis, we must consider the presence of other minerals, as pyroxenes are more Ar-retentive than olivines (higher $E_a$, e.g., Cassata et al., 2011). Nevertheless, Ar is expected to partition between grain boundaries and the pyroxene lattice, which confirms fine-grained rocks as preferential Ar storage zones in the upper mantle.

Another important parameter to consider is pressure, as it can affect both diffusion and grain boundary complexion (Hirel et al., 2017). Only one experimental study has investigated the pressure effect on noble gas diffusivities in olivine between 1 atm and 2.7 GPa (Cherniak & Watson, 2012). These results are in agreement with hydrogen diffusion in olivine.
(Demouchy et al., 2016). They did not observe a pressure effect in this pressure range, though models predict decreasing diffusivities with increasing pressure (e.g., Wang et al., 2015), which could affect the boundary times between the different kinetic regimes by increasing \( t' \) and \( t'' \). However, as \( t' \) and \( t'' \) are mostly controlled by temperature, the pressure effect should be very limited in the lithospheric mantle and the A-regime should always occur with depth increase. Regarding grain boundary complexion (e.g., Dillon & Harmer, 2008b), segregation between grain boundaries and the mineral lattice is pressure dependent (e.g., Hirel et al., 2018; Marquardt & Faul, 2018) since the grain boundary structure becomes less disordered, and denser with increasing confining pressure. Thus, grain boundary segregation should decrease with increasing pressure.

5. Conclusions

Argon diffusivities were obtained by analyzing fractional Ar gas losses by mass spectrometry on three samples, which allows constraint of Ar storage sites and mobility in polycrystalline olivine.

- The activation energies of Ar diffusion do not vary, indicating that diffusion is controlled combined lattice and grain boundary diffusions. Thus, transition temperature was not reached in this study and the grain boundaries were not fully emptied at the end of the step heating experiments.

- Since the transition temperature was not reached in our experiments, only a minimal value for the segregation factor can be determined for our samples. This minimal value permits calculation of the minimal time \( t'_{\text{min}} \), necessary to reach the B-regime, and the extraction steps, which were in the C-regime, can be estimated. We conclude that the C-regime occurred during extraction steps below 750, 775 and 700 °C, for RDPC1, RDPP1, and RDPP1-2, respectively.
By reprocessing literature data, we determined the mean values of the diffusion parameters for Ar diffusion in the olivine lattice to be $E_a = 166 \pm 44 \text{kJ} \cdot \text{mol}^{-1}$ and for $D_0 = 10^{7.04 \pm 1.13} \text{m}^2 \cdot \text{s}^{-1}$. The extraction steps, which express the C-regime, were identified and a linear regression on the corresponding diffusivities was performed revealing the mean grain boundary Ar diffusion parameters to be $E_a = 22 \pm 5 \text{kJ} \cdot \text{mol}^{-1}$ and $D_0 = 10^{12.87 \pm 0.3} \text{m}^2 \cdot \text{s}^{-1}$.

Ar isotopic fractionation is constant at low temperature but increases with increasing temperature above 750 °C. This is interpreted as a result of the diffusion regime occurring during the extraction steps. In the C-regime, the isotopic diffusion coefficient ratios seem to be constant with a single value close to that predicted by Graham’s law, whereas in the B-regime, those ratios are variable and clearly different from 1 and the value predicted by Graham’s law. We obtained the same results for the A-regime by extrapolation from the C-regime. Thus, isotopic fractionations are small in the A- and C-regimes, but significantly larger in the B-regime.

In the Earth’s upper mantle, the Ar segregation factor between grain boundaries and the olivine lattice can be estimated as the inverse of the Ar partition coefficient between olivine and silicate melt. This value should be bracketed between $10^5$ and $10^4$, in agreement with previous studies. For a segregation factor of $10^5$ and a grain size of 1 mm, around 22 % of Ar is stored at grain boundaries. Ar storage increases with decreasing grain size, and for grain sizes lower than 285 µm, the majority of Ar is stored at grain boundaries.

We calculated the boundary time between the B- and A-regimes as a function of grain size for the upper mantle, and showed that Ar diffusion is mostly controlled by the A-regime, regardless of the segregation factor. This implies low diffusive isotopic fractionations that follow a law similar to Graham’s law. Moreover, bulk diffusivities in the upper mantle are described by Eq. (8) and are controlled by both lattice and grain boundary diffusivities. Bulk diffusivities increase with decreasing grain size as determined by previous studies.
• Since the storage and mobility of Ar are highly dependent on grain size, we determined that preferential Ar storage zones in the upper mantle would be linked to grain size reduction (e.g., by dynamic recrystallization), such as in shearing zones and associated ultramylonites. Moreover, as a significant Ar storage site, grain boundaries modify the equilibrium kinetics during partial melting, and increase the noble gas enrichment of the melt during partial melting and fluid percolation. Thus, grain boundaries are important storage sites in mantle zones where deformation is coupled with melting and fluid percolation, such as below oceanic ridges or in subduction zones.

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Appendix A: The F-test

To constrain the modelling of our data by one or two linear regressions, we used a $F$-test
(e.g., Box, 1953; Chow, 1960; Hahs-Vaughn & Lomax, 2013), which consists in comparing two models: a model 1 with $p_1$ parameters and a model 2 with $p_2$ parameters with $p_2 > p_1$. Here, the model 1 has one linear regression ($p_1 = 2$, the slope and the intercept of the linear regression) and the model 2 has two linear regressions ($p_2 = 4$, the slopes and the intercepts of the two linear regressions). The $F$-test can be used to establish if the model 1 have to be rejected or not. It consists in calculating the $F$ value of our comparison, which is defined by the following equation:

$$F = \frac{(RSS_1 - RSS_2)}{(p_2 - p_1)} \times \frac{(n - p_2)}{RSS_2},$$

where $RSS_i$ is the residual sum of squares of model $i$, and $n$ is the number of data points. Then this $F$-value is compared with a critical value ($F_{crit}$) of the $F$-distribution with $(p_2 - p_1, n - p_2)$ degrees of freedom (here $(2, n - 4)$ degrees of freedom) for some desired false-rejection probability (here 0.05). The $F_{crit}$ values are available in $F$ tables. If the $F$ value calculated from our data is greater than $F_{crit}$, then the model 1 is rejected, otherwise, there is no reason to reject the model 1. It does not mean that if $F < F_{crit}$, the model 2 is rejected, in this case, we chose the simpler model, which is the model 1 (with fewest parameters).

We verified this method on the He data (see Delon et al., 2018), and especially, on the sample RDPP1 where the transition between the LAT and LAT+GB domains is the most blurred. In this case, $n = 21$ and $F_{crit} = 3.59$ with $(2, 17)$ degrees of freedom and with a confidence level of 5%. The resulting $F$ value is 5.40, thus $F > F_{crit}$, which means that the model with one linear regression is rejected and only the model with two linear regressions is possible (i.e., one regression for the LAT + GB domain and another one for the LAT domain).

The $F$-test was performed on our Ar diffusivity data (Fig. 3), between a model 1 with one linear regression and all other models with two linear regressions (only regressions with less
than 5 points are not tested since they are considered as not relevant). The $F$ values for the different tests are compiled in the following table:

<table>
<thead>
<tr>
<th>Sample</th>
<th>$F_{\text{crit}}$ with a level confidence of 5 %</th>
<th>Number of points in the low-temperature domain</th>
<th>Number of points in the low-temperature domain</th>
<th>$F$ value</th>
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Table A.1: Calculated $F$-values for each comparison between the model 1 (with a single linear regression) and models 2 (with two linear regressions, one at low temperature and another at high temperature).
Here for Ar diffusivity data, we can conclude that $F$ is always inferior to $F_{\text{crit}}$ and thus, the model with only one linear regression is essentially never rejected and since it is the simplest model with the fewest parameters, we chose this model to fit our data.

Appendix B: Supplementary materials

Supplementary data associated with this article can be found, in the online version, at … (insert DOI).

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**Figure captions**

Fig. 1: Sample assembly for doping experiments. The assembly was annealed at 0.30 ± 0.01 GPa and 1060 ± 25 °C during 24 h, using a Paterson press.

Fig. 2: (a) SEM image of the sample RDPC1, TEM images of microstructures in polycrystalline samples (b) RDPC1 and (c) RDPP1, and HR-TEM image of a characteristic grain boundary in (d) RDPC1.

Fig. 3: Arrhenius diagrams for $^{40}$Ar, $^{38}$Ar, and $^{36}$Ar diffusion coefficients obtained from step heating analyses of polycrystalline olivine samples (a) RDPC1, (b) RDPP1, and (c) RDPP1-2.
Fig. 4: Isotopic diffusivity ratios (a) $D_{40}/D_{36}$, (b) $D_{40}/D_{38}$, and (c) $D_{36}/D_{38}$ as a function of temperature. The dotted vertical line expresses the estimated boundary between the C- and supposed B-regimes of diffusion (as determined in supplementary materials). Gray lines represent the mean values of the diffusivity ratios in the C-regime, and gray areas the standard deviation about the mean. Black lines represent the values of the diffusion coefficient ratios predicted by Graham’s law.

Fig. 5: Olivine lattice diffusion parameters for Ar from literature and retreated from Burnard et al. (2015). (a) Logarithm of the pre-exponential factors calculated for $a =$ half the grain size, and (b) activation energies. Black dashed lines represent the mean values of the corresponding diffusion parameter calculated from Futagami et al. (1993) and retreated data from Burnard et al. (2015), and gray areas give associated errors (standard deviation).

Fig. 6: Arrhenius diagram of grain boundary diffusion for each sample from this study calculated considering (a) $a =$ half the sample size and (b) $a =$ the grain boundary network. The corresponding diffusion parameters are reported in Table 3. The resulting mean values of grain boundary diffusivities (gray lines) are compared with lattice diffusivities (black dashed lines). Gray areas show errors on the means.

Fig. 7: The proportion of Ar stored at grain boundaries (black lines) and in the mineral lattice (gray lines) as a function of grain size for $s = 10^5$ (solid lines) and for $s = 10^4$ (dashed lines). The dark gray shaded areas represents the typical mantle grain size range (see Hiraga et al., 2010) and the light gray area represents the recorded grain size range of mantle peridotites (e.g., Karato, 1989; Hiraga et al., 2010).
Fig. 8: Durations of the boundary times $t'$ between the B- and C-regimes and $t''$ between the A- and B-regimes expressed as a function of grain size for (a) $s = 10^5$ and (b) $s = 10^4$ at 600, 800, 1000, and 1400 °C. The gray shaded area represents the typical mantle grain size range (Karato, 1989; Hiraga et al., 2010).

Table captions

Table 1: Experimental conditions, sample descriptions, average grain sizes obtained from SEM-EBSD maps, and analytical protocols for step heating noble gas analyses, as described in Delon et al. (2018).

Table 2: Ar diffusion parameters ($E_a$ and $\log(D_0/a^2)$), minimum molar segregation factors ($\chi_{min}$), and minimum segregation factors ($s_{min}$) in polycrystalline olivine obtained for each sample and each isotope.

Table 3: Activation energies ($E_a$) and pre-exponential factors ($D_0$) obtained for each sample by considering $a$ as half the sample size ($a = 150$ µm) or equivalent to the grain boundary network ($a = 0.48$ µm).
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8
Table 1

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<th>Temperature °C</th>
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<td>around 10⁻¹²</td>
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N.B. Data treatment is detailed in the main text and is identical to the procedure detailed in Delon et al. (2018).
Table 2

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N.B. For dimension consistency, activation energies are calculated with $a = 1$ m, since activation energies do not depend on the value of $a$ (see Burnard et al., 2015 for discussion)
Table 3

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*grain boundary network

**half the sample size