The objective of this study is to use molecular dynamics simulation (MD) to evaluate the vesicularity and noble gas fractionation, and to shed light on bubble formation during MORB degassing. A previous simulation study (Guillot and Sator (2011) GCA 75, 1829-1857) has shown that the solubility of CO$_2$ in basaltic melts increases steadily with the pressure and deviates significantly from Henry’s law at high pressures (e.g. ~9.5 wt% CO$_2$ at 50 kbar as compared with ~2.5 wt% from Henry’s law).

From the CO$_2$ solubility curve and the equations of state of the two coexisting phases (silicate melt and supercritical CO$_2$), deduced from the MD simulation, we have evaluated the evolution of the vesicularity of a MORB melt at depth as function of its initial CO$_2$ contents. An excellent agreement is obtained between calculations and data on MORB samples collected at oceanic ridges. Moreover, by implementing the test particle method (Guillot and Sator (2012) GCA 80, 51-69), the solubility of noble gases in the two coexisting phases (supercritical CO$_2$ and CO$_2$-saturated melt), the partitioning and the fractionation of noble gases between melt and vesicles have been evaluated as function of the pressure. We show that the melt/CO$_2$ partition coefficients of noble gases increase significantly with the pressure whereas the large distribution of the $^{4}$He/$^{40}$Ar* ratio reported in the literature is explained if the magma experiences a suite of vesiculation and vesicle loss during ascent. By applying a pressure drop to a volatile bearing melt, the MD simulation reveals the main steps of bubble formation and noble gas transfer at the nanometric scale. A key result is that the transfer of noble gases is found to be driven by CO$_2$ bubble nucleation, a finding which suggests that the diffusivity difference between He and Ar in the degassing melt has virtually no effect on the $^{4}$He/$^{40}$Ar* ratio measured in the vesicles.

**Keywords**: computer simulations, MORB, supercritical CO$_2$, noble gases, vesicularity, bubble formation, partition coefficient
1. Introduction

Noble gases are important tracers to understand the evolution and the degassing of the Earth's mantle through time (Allègre et al., 1983; Harper and Jacobsen, 1996; Pepin, 2006). The elemental fractionation of noble gases and their isotopes recorded in oceanic basalts (MORBs and OIBs), if properly deciphered, may give information on the source region and on the details of noble gas transport up to the surface. For instance the difference in $^{3}\text{He}/^{4}\text{He}$ ratios between MORBs and OIBs is at the basis of the canonical model in isotope geochemistry (Porcelli and Wasserburg, 1995; Graham, 2002) describing the lower mantle as undegassed (high $^{3}\text{He}/^{4}\text{He}$ ratio) and the upper mantle as degassed (low $^{3}\text{He}/^{4}\text{He}$ ratio). But this model is in conflict with other data (e.g. the He paradox, Anderson, 1998) and is periodically revisited (Meibom et al., 2003; Parman et al., 2005; Albarède, 2008; Gonnermann and Mukhopadhyay, 2009). On the other hand, MORB and OIB glasses show a large distribution of the $^{4}\text{He}/^{40}\text{Ar}^*$ ratio (~1-1000, where $\text{Ar}^*$ is corrected for air contamination) which is interpreted as the signature of different degassing scenarios. Thus a low $^{4}\text{He}/^{40}\text{Ar}^*$ ratio (~1) is explained by a closed system degassing where a $\text{CO}_2$-saturated basaltic melt ($\text{CO}_2$ is the main volatile component in oceanic basalts before $\text{H}_2\text{O}$, noble gases being present as traces) vesiculates by $\text{CO}_2$ exsolution and ascends with very little vesicle loss, up to the seafloor where volatiles are released (e.g. Sarda and Graham, 1990). In contrast, a high $^{4}\text{He}/^{40}\text{Ar}^*$ ratio can be accounted for either by a Rayleigh distillation process (Burnard, 1999; Moreira and Sarda, 2000; Colin et al., 2011), by a suite of vesiculation and vesicle loss during magma ascent (Sarda and Graham, 1990; Sarda and Moreira, 2002) or by a kinetic disequilibrium occurring just before eruption (Aubaud et al., 2004). However $\text{CO}_2$ has a very low solubility in basaltic melts at pressure corresponding to the seafloor (~0.5 ppmw at one bar, Dixon (1997)) and therefore an overwhelming majority of erupting lavas are strongly degassed and have lost their pristine volatile contents.

Remarkable exceptions are popping rocks (Hekinian et al., 1973) characterized by high $\text{CO}_2$ contents (~1. wt% $\text{CO}_2$ in the sample 2πD43, Sarda and Graham (1990), Javoy and Pineau (1991)) a large vesicularity (>10 % in volume), and a $^{4}\text{He}/^{40}\text{Ar}^*$ ratio (~1.5 in 2πD43) compatible with the
expected $K/U$ ratio of the mantle (Allègre et al., 1987). These tholeiitic basalts likely have experienced a $CO_2$ exsolution in the oceanic mantle and for this reason are considered as probing the source region (Sarda and Graham, 1990; Javoy and Pineau, 1991). Nonetheless, a pending question is to know if magmas even richer in $CO_2$ do exist and may exsolve a $CO_2$-rich fluid at greater depth in the mantle. In this context, it is noteworthy that evidences of explosive eruptions at ocean spreading centers are well documented (Hekinian et al., 2000; Eissen et al., 2003; Pineau et al., 2004; Sohn et al., 2008; Clague et al., 2009; Shaw et al., 2010; Helo et al., 2011). The presence of extended volcaniclastic deposits at great water depth (~4,000 m) suggests that this explosive volcanism with magma disruption could be driven by $CO_2$-rich melts (Sohn et al., 2008; Helo et al., 2011). More generally, there are growing evidences of the existence of $CO_2$-rich magmas in the upper mantle. Thus, seismological and magnetotelluric data suggest that incipient melting may begin at depths of 150-300 km in the upper mantle (Evans et al., 2005; Bologna et al., 2011). Experimental petrology data shows that deep melting can occur with carbonate-silicate assemblages leading to carbonatitic liquids at very low melt fraction (Eggler, 1976; Dalton and Pressnall, 1998; Dasgupta and Hirschmann, 2006; Zeng et al., 2010; Rooney et al., 2012). So, the electrical anomalies of the oceanic astenosphere could be explained by ~0.1 % volume fraction of carbonatite melts circulating in the silicate mantle (Gaillard et al., 2008). This melt fraction corresponds on average to ~300 ppmw $CO_2$ stored in the astenosphere, a value compatible with various estimates of the $CO_2$ contents in the source region of MORB (Marty and Tolstikhin, 1998; Saal et al., 2002; Cartigny et al., 2008). Furthermore these carbonatites can metasomatize the surrounding silicate matrix and lead to melt mixing during their ascent (Dixon et al., 2008).

When an upwelling volatile-bearing melt reaches the $CO_2$ saturation limit, the excess of $CO_2$ is exsolved by forming bubbles or vesicles. The noble gases initially present in the melt as traces (less than a ppmw, Moreira et al., 1998) fractionate between melt and $CO_2$ bubbles in a proportion which depends both on the vesicularity and on their respective solubility (or partition coefficient) in the two coexisting phases (Jambon et al., 1986). When a tholeiitic basalt vesiculates at shallow depth under the seafloor (e.g. a few kilometers), a simple way to estimate the noble gas partitioning is to assume that
the fluid filling the vesicles is an ideal gas and that the solubility of noble gases in the basaltic melt is that measured at laboratory at low pressures (Henry's law). Because noble gas solubilities in basaltic melts are very low ($S_{He-Xe} \sim 10^{-5} - 10^{-8}$ bar$^{-1}$, where $S$ is the inverse of Henry's constant, Jambon et al. (1986)), noble gases partition preferentially into the $CO_2$ bubbles, the heavier the noble gas the higher the fraction. This is the common view of closed-system noble gas degassing.

A different situation is encountered if the $CO_2$ saturation limit is reached at great depth in the mantle (e.g. in the oceanic astenosphere). The vesicles are filled with a very dense supercritical $CO_2$ fluid which limits the transfer of noble gases from the melt. A theoretical approach of this mechanism has been proposed by Sarda and Guillot (2005) and Guillot and Sarda (2006) by using a hard sphere model to describe the silicate melt, the fluid $CO_2$, and the incorporation of noble gases in the two coexisting phases. An important conclusion of this study is that the noble gas fractionation between melt and vesicles at high pressures deviates significantly from a simple evaluation based on noble gas solubility data at low pressures (Henry's law) and for which the deviation from ideality of the $CO_2$ fluid is neglected. Although this model is useful for theoretical guidance, there is a need for improvement. For instance, the solubility of $CO_2$ in silicate melts and especially in basalts is well documented at low pressures where Henry's law holds (Stolper and Holloway, 1988; Dixon et al., 1995; Jendrzejewsky et al., 1997; Botcharnikov et al., 2005) but is poorly known at high pressures above $\sim 20$ kbar (Pan et al., 1991; Brooker et al., 2001). Recently Guillot and Sator (2011) have evaluated by molecular dynamics simulation (MD) the pressure evolution of the $CO_2$ solubility in silicate liquids of various composition. In basaltic melts the calculated $CO_2$ solubility increases steadily above 20 kbar (where $X_{CO_2}^H \sim 1.6$ wt%) and reaches $\sim 20$ wt% at 80 kbar, a value much higher than the one estimated from Henry's law ($X_{CO_2}^H \sim 0.5$ ppmw per bar, see Dixon et al. (1995) ). These simulation results are in agreement with a few solubility data in melts of basaltic composition obtained from high-pressure partial melting experiments of silicate-carbonate assemblages (Hammouda, 2003; Thomsen and Schmidt, 2008).

Our objective is to evaluate by atomistic simulation, the pressure dependence of noble gas partitioning between a $CO_2$-saturated MORB melt and a coexisting $CO_2$ phase (closed system...
degassing), as also as the noble gas fractionation in melt and in vesicles during MORB degassing. For
that we have implemented the test particle method (TPM) to calculate the chemical potential of a trace
element (e.g. a noble gas) into a melt or a high density fluid (CO$_2$) modeled by MD simulation. This
method has been recently used to evaluate the solubility of noble gases in high-pressure silicate liquids
(Guillot and Sator, 2012). The theoretical framework and the simulation details are explained in
section 2, and the results are presented and discussed in section 3. In section 4, the kinetics of bubble
formation and noble gas transfer is investigated by devising a numerical experiment where a pressure
drop is applied to a volatile bearing MORB melt. The implications of such a decompression
experiment are discussed.

2. Method of calculation

2.1 Noble gas partitioning in a vesiculated MORB melt.

When a volatile bearing MORB melt is ascending under an oceanic ridge, it starts to degas when the
ambient pressure becomes lower than the saturation pressure of the major volatile component present
in the melt (Sparks, 1978; Bottinga and Javoy, 1990). In a MORB melt where CO$_2$ is the major
volatile component and noble gases are traces, the latter ones redistribute between CO$_2$ bubbles and
bulk melt. At given temperature (T) and pressure (P) conditions, the equality of the chemical
potentials of a noble gas $i$ in the vesiculated melt and in the CO$_2$ bubbles leads to the following
relationship,

$$\rho_i^{m}/\rho_i^{v} = e^{-(\mu_i^{m,ex} - \mu_i^{v,ex})/k_BT} = \gamma_i^{m}/\gamma_i^{v}$$  \hspace{1cm} (1)

where $k_B$ is the Boltzmann constant, $T$ the temperature, $\rho_i^{m}$ and $\rho_i^{v}$ are the number densities (number
of atoms per unit volume) of the noble gas $i$ in the melt and in the vesicles (CO$_2$ bubbles), respectively,
and where $\mu_i^{m,ex}$ and $\mu_i^{v,ex}$ are the excess chemical potentials of the noble gas in the corresponding
phases (notice that the ideal parts of the chemical potentials cancel out because they are identical in the
two phases). The quantity $\gamma_i^{m,v} = e^{-\mu_i^{m,ex}/k_BT}$ is named the solubility parameter in the corresponding
phase \((m\ or\ v)\). By introducing \(V_m\) the volume of melt and \(V_v\) the total volume of vesicles the Eq.(1) leads to the following equality,

\[
\frac{N_m^i}{N_v^i} = \left(\frac{V_m}{V_v}\right) \cdot \frac{\gamma_m^i}{\gamma_v^i}
\] (2)

where \(N_m^i\) is the number of noble gas atom in the melt and \(N_v^i\) the one in the vesicles.

For a closed system degassing, \(N_m^i\) and \(N_v^i\) are related by the following mass conservation law,

\[
N_0^i = N_m^i + N_v^i
\] (3)

where \(N_0^i\) is the number of noble gas atom \(i\) in the \(CO_2\)-bearing MORB melt before vesiculation.

Following the derivation of Guillot and Sarda (2006), the final step consists to introduce Eq.(3) into Eq.(2) and to make use of the definition of the vesicularity, \(V^* = V_v/(V_v + V_m)\). After some elementary algebra the numbers of noble gas atom \(i\) in the melt and in the vesicles are equal to,

\[
N_m^i = N_0^i \cdot \left(\frac{\gamma_m^i}{\gamma_v^i}\right) \cdot \frac{1 - V^*}{[V^* + \left(\frac{\gamma_m^i}{\gamma_v^i}\right) \cdot (1 - V^*)]} \] (4)

\[
N_v^i = N_0^i \cdot V^*/\left[\gamma^* + \left(\frac{\gamma_m^i}{\gamma_v^i}\right) \cdot (1 - V^*)\right]. \] (5)

The above expressions are exact at equilibrium (for any thermodynamic condition) and they replace the ones obtained by Jambon et al. (1986) which are valid only at very low pressure when the \(CO_2\) fluid filling the vesicles can be considered as ideal (in this case \(\gamma_v^i = 1\) and \(\gamma_m^i\) can be approximated by the solubility constant \(S^i\) in using Henry's law,

\[
\gamma_m^i = \rho_m k_B TS^i
\] (6)

where \(\rho_m\) is the numerical density of the melt. However, the simplicity of expressions (4) and (5) is somewhat misleading because to evaluate \(N_m^i\) and \(N_v^i\) at given \((T,P)\) conditions, the vesicularity of the degassing melt must be known and the solubility parameters \(\gamma_m^i\) and \(\gamma_v^i\) evaluated in the coexisting phases at these very thermodynamic conditions.
To estimate the evolution of the vesicularity with the thermodynamic conditions one needs to know
the pressure (and temperature) behaviour of the CO$_2$ solubility in the MORB melt. As a matter of fact,
in using the equality of the chemical potentials of CO$_2$ in the melt and in the vesicles as also as the
mass conservation law for the CO$_2$ molecules, it can be shown that the vesicularity, $V^*$, fulfils the
following relationship,

$$\frac{V^*}{1-V^*} = \left(\frac{n_m}{n_v}\right) \left[\frac{(1-W)}{W_0} - 1\right]$$  (7)

where $n_m$ and $n_v$ are the densities of the CO$_2$-saturated silicate melt and of the CO$_2$ fluid filling the
vesicles at (T,P) of interest, $W$ is the solubility of CO$_2$ (in $g_{CO_2}/g_{melt}$) in the silicate at (T,P)
conditions during magma ascent, and $W_0$ is the CO$_2$ content in the melt before degassing ($W < W_0$). If
exsolution only occurs when a degree of super saturation in CO$_2$ is reached (i.e. when magma ascent is
so rapid that chemical equilibrium cannot be achieved) then the term ",-1" on the right hand side of
Eq.(7) may be replaced by ",-\alpha " where the super saturation ratio, $\alpha = \frac{X_w^{CO_2}(P,T)/W(P,T)}{X_w^{CO_2}(P,T)}$, expresses
the ratio of the weight fraction of CO$_2$ molecules actually in the melt to the one expected at saturation.

In the following $\alpha (\geq 1)$ will be used as an adjustable parameter.

### 2.2 Calculation of noble gas solubility parameters.

As expressed by Eqs.(4) and (5), in a closed system degassing, the partitioning of a noble gas $i$
between melt and vesicles depends on the vesicularity, $V^*$, and on the ratio of the solubility
parameters, $\gamma_m^i/\gamma_v^i$. In a seminal work, Widom (1963) has shown that the solubility parameter, $\gamma_s^i$, of a
solute $i$ at infinite dilution in a solvent $s$ can be written under the following form,

$$\gamma_s^i = e^{-\mu_s^i/k_BT} = e^{-\psi/k_BT} > N_s$$  (8)

where $\psi = (U_{N_s+1} - U_{N_s})$ is the potential energy difference between a mixture composed of $N_s$
solvent molecules plus the solute particle (e.g. a noble gas atom) and the pure solvent. In the case
where the potential energy is pairwise additive (i.e. $U_{N_s+1} = \sum_{i<j=N_s} u_{ij}$ where $i$ and $j$ are two
particles and \( u_{ij} \) the pair interaction energy), \( \psi \) is nothing but the solute-solvent interaction energy \( (\psi = \sum_{j=1}^{N_s} u_{ij}) \) where \( u_{ij} \) is the interaction energy between the solute particle 1 and the solvent particle \( j \). A key feature of Eq. (8) is that the canonical average \( \langle e^{-\psi/k_B T} \rangle_{N_s} \) is taken over the configurations of the pure solvent, the solute particle acting as a ghost (or test) particle. In practice, the solute (i.e. the noble gas atom) is inserted at random in the solvent configurations generated by MD simulation and the Boltzmann factor, \( \langle e^{-\psi/k_B T} \rangle_{N_s} \), is evaluated by averaging over all insertion events. However, when the solvent density is high, the noble gas atom randomly inserted has a high probability to overlap a solvent molecule. The consequence is a strongly repulsive solute-solvent interaction energy \( (\psi_{k_B T} \gg 1) \) leading to a vanishingly small contribution of this event to the average \( (e^{-\psi/k_B T} \ll 1) \). What is needed for practical use of this method is a numerical recipe for detecting quickly undesirable positions of the inserted noble gas atom and for locating cavities that can accommodate it, cavities that appear and disappear at the mercy of the solvent density fluctuations. We have implemented the sampling method of Deitrick et al. (1989) which makes the evaluation of the solubility parameter by the test particle method (TPM) very effective. For a detailed description of the method and a discussion of the statistical uncertainties, the reader is referred to the paper by Guillot and Sator (2012) where the solubility of noble gases in silicate melts was evaluated in this framework.

To evaluate the noble gas solubility parameters \( \gamma_m^I \) and \( \gamma_p^I \) by the TPM one needs to generate by MD simulation a suite of atomic configurations which are representative of the \( CO_2 \)-bearing basaltic melt and of the \( CO_2 \) fluid assumed to coexist with each other at a given state point \((T,P)\). The accuracy of the calculation relies on the force field used to describe the interactions between the atoms of the phases under consideration. Six different kinds of interaction are involved: \( CO_2-CO_2 \) interaction, silicate-silicate interaction, \( CO_2 \)-silicate interaction, noble gas-\( CO_2 \) interaction, noble gas-silicate interaction and noble gas-noble gas interaction. Notice that noble gases are trace elements in the mantle (on average much less than a ppmw in MORBs) and therefore can be considered at infinite dilution both in the MORB melt and in the \( CO_2 \) bubbles. For silicate-silicate, \( CO_2-CO_2 \) and \( CO_2 \)-silicate interactions we have used the pair potentials developed by Guillot and Sator (2007a,b; 2011) in
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their MD studies of dry and CO₂-bearing silicate melts of various composition (the corresponding potential parameters are listed in Table 1 of Guillot and Sator (2011) and are not reproduced here). When CO₂ is incorporated into the basaltic melt, a reactive force field accounts for the chemical reactivity between the oxygens of the silicate and CO₂ molecules,

\[
CO_2 + (O^{2-})_{\text{melt}} \leftrightarrow (CO_3^{2-})_{\text{melt}},
\]

the equilibrium concentrations in CO₂ and carbonate ions \((CO_3^{2-})\) depending at once on the melt composition, the investigated thermodynamic conditions \((T,P)\) and the total CO₂ content. In the case of a MORB composition, the CO₂ solubility curve has been investigated by Guillot and Sator (2011) at isothermal conditions (between 1673 and 2273K) up to 150 kbar. We have used these simulation data as benchmarks for preparing our CO₂+MORB compositions.

To evaluate the interaction energy between noble gases and the elements of the silicate melt, we have implemented the atom-atom Lennard-Jones potentials recently developed by Guillot and Sator (2012), a force field which successfully reproduces the solubility data of noble gases in liquid silicates. As for the interactions between CO₂ and the noble gases we have developed specifically for the present study a force field based on the Lennard-Jones pair potential. The derivation of the potential parameters is presented in Appendix and their values are listed in Table A1.

2.3 Simulation details

Two series of MD runs were performed, one corresponding to a CO₂-saturated basaltic melt at various thermodynamic conditions, and the other one corresponding to the CO₂ phase assumed to be in coexistence with the melt. The composition of the simulated MORB (in wt%: 50.59 SiO₂, 1.5 TiO₂, 15.11 Al₂O₃, 1.15 Fe₂O₃, 8.39 FeO, 7.77 MgO, 11.87 CaO, 2.94 Na₂O and 0.13 K₂O) is the one of a sample (TK21B) of the mid-atlantic ridge. This composition has been investigated by Guillot and Sator (2011) to determine the CO₂ solubility curve as function of T and P. So the CO₂ contents at saturation used in the present study are those determined by these authors at T=1873K and P=10, 20, 30, 50, 80, and 100 kbar. With regard to the CO₂-saturated MORB melt, the simulation cell is composed of 1,000
ions (or 5,000 ions, to estimate system size effects) plus the necessary number of \( CO_2 \) molecules to reach \( CO_2 \) saturation at the investigated state point (the simulation conditions are summarized in Table 1). The coexisting \( CO_2 \) phase is simulated independently from the \( CO_2 \)-saturated melt and is composed of 500 (or 2,500) molecules.

The MD calculations were performed with the DL_Poly 2.0 code (Smith and Forrester, 1996). The equations of motion for ions and \( CO_2 \) molecules were solved with a time step of \( 10^{-15} \)s. The simulation box is cubic with periodic boundary conditions and the long range coulombic interactions are accounted for by an Ewald sum. For the two systems (the \( CO_2 \)-bearing melt and the \( CO_2 \) phase) the calculations were first performed in the isothermal isobaric ensemble (N,P,T) for equilibration and next were carried on in the microcanonical ensemble (N,V,E) for generating production runs. The latter ones were \( 10^8 \)s long (i.e. \( 10^7 \) MD steps) for small system sizes (N=1,000 ions for MORB and 500 molecules for fluid \( CO_2 \)), and \( 10^9 \)s long for large system sizes (5,000 ions and 2500 molecules, respectively). The statistical uncertainties on each investigated state point are about 1% for density, pressure and temperature. At each state point under consideration, atomic configurations were stored every \( 2.10^{-12} \)s (i.e. 2,000 MD steps) to be sampled afterwards by the TPM (this time interval is chosen so as the displacement of atoms between two successive recording is of the order of an atomic diameter, i.e. \( \sim 3 \)A).

As mentioned in section 2.2, the TPM was optimized in implementing the sampling procedure of Deitrick et al. (1989). A description of this recipe is discussed in details in Guillot and Sator (2011) and is not reproduced here. In short, the simulation box containing the atomic configurations to be sampled is divided into small cubelets (e.g. \( 100 \times 100 \times 100 \)). A cubelet is marked as occupied if its center is located within the repulsive core of a solvent atom. Thus, only insertions where the test particle is addressed to an unoccupied cubelet contribute to the average \( \langle e^{-\Psi/k_BT} \rangle_{N_s} \). However, the free volume accessible to the test particle (the volume fraction corresponding to unoccupied cubelets) decreases drastically with the size of the test particle (the noble gas) to insert and with the density of the solvent (the higher the density the smaller the free volume). For instance, the free volume
accessible to He in a MORB melt at 10 kbar is 19%, whereas it is equal to 12% for Ne, 1.3% for Ar and only 0.04% for Xe. At 50 kbar the free volume amounts to 11% for He, 5.5% for Ne, 0.2% for Ar and 0.002% for Xe. Thus, the occurrence to find at the mercy of density fluctuations, a cavity large enough to accommodate an Ar atom in a basaltic melt at 50 kbar is a rare event. This is why it is necessary to perform long MD runs with a system size large enough. Moreover, it is important that the number of cubelets mapping the simulation box is large enough to be certain that all cavities susceptible to accommodate the noble gas atom have been sampled.

With regard to the MD simulations, the parameters to be fixed are the system size and the length of the MD run. When these two parameters are fixed, the numerical uncertainties associated with the evaluation of the solubility parameters ($\gamma^{m}_{m,p}$) by the TPM increase drastically with the size of the noble gas to insert and with the density (i.e. with the pressure) of the solvent (for a discussion see Appendix A in Guillot and Sator, 2012). To estimate these uncertainties we have performed two independent series of MD calculations which approximately lead to the same computational cost. One series was performed with small system sizes (see Table 1) over a long simulation time (10 ns) and another series with larger system sizes but over a shorter simulation time (1ns). The results of these calculations are presented in Table 2. A fair agreement is found between the two series of calculations for He and Ne in the two phases (the deviation is less than 3 percent) and for Ar in $CO_2$ (except at 100 kbar where $\Delta \gamma^{Ar}_{m}/\gamma^{Ar}_{m} \approx 14\%$). However the deviation becomes more significant for Ar in the MORB melt above 50 kbar (e.g. $\Delta \gamma^{Ar}_{m}/\gamma^{Ar}_{m} \approx 20\%$ at 50 kbar and $\approx 40\%$ at 100 kbar) and is quite large for Xe in MORB from 30 kbar ($\approx 300\%$ at 30 kbar). A drastic reduction of the uncertainties for Xe in MORB at high pressures would require to perform very long MD runs ($\approx 1000$ ns) with a large number of atoms ($10^5$-$10^6$), a task which is too demanding for our numerical resources. Consequently values of $\gamma^{Xe}_{m}$ for pressure above 30 kbar will be discarded in the following. In considering that the calculations performed with the two system sizes are independent from each other, the final values of $\gamma^{l}_{m}$ and $\gamma^{l}_{v}$ have been obtained simply by doing the arithmetic mean of the two series of calculations.
3. Results

3.1 Vesicularity of MORBs

Before discussing the fractionation of noble gases between melt and vesicles it is worthwhile to analyze the pressure evolution of the vesicularity of a degassing magma (closed system degassing). In Fig.1 is reported the pressure dependence of the vesicularity of an ascending magma, described by our simulated MORB melt, at isothermal condition (1873 K) and for different initial conditions of CO$_2$ saturation at depth (with $P_{CO_2}^{sat} = 100, 80, 50, 30, 10, 5,$ and 1 kbar). The vesicularity, $V^*$, is evaluated from Eq.(7) in using for the pressure evolution of the CO$_2$ solubility ($W$) the one calculated by Guillot and Sator (2011), whereas the density ($n_m$) of the CO$_2$ bearing MORB melt and the density ($n_v$) of the coexisting CO$_2$ fluid are deduced from the present simulation study. By inspecting Fig.1, it appears that the growth rate of the vesicularity of an ascending magma is correlated with the CO$_2$ content of the source region (see in Fig.1 the evolution of the curvature of the vesicularity curve with increasing $P_{CO_2}^{sat}$). For instance, a MORB melt CO$_2$-saturated at $P_{CO_2}^{sat} = 10$ kbar (d~30 km) will show a vesicularity of 10% in erupting at 5,500 m below sea level (m.b.s.l.) whereas the one of an ascending magma CO$_2$-saturated at $P_{CO_2}^{sat} = 100$ kbar (i.e. d~300 km) will reach 10% at $P = 90$ kbar (d~270 km) and 50% at 15 kbar (d~45 km). So, if it exists a source region very enriched in CO$_2$ in the oceanic mantle (from a carbonatitic origin, for instance), the magma issuing from this setting will become highly vesiculated at great depth. In that case the supercritical CO$_2$ fluid is characterized by a liquid-like density (e.g. $n_{CO_2} \approx 1.40$ g/cm$^3$ at 30 kbar) and a degassing process at this depth is more related to a liquid-liquid immiscibility than to a gas bubble formation.

Actually, an overwhelming majority of MORB samples collected at oceanic ridges exhibit a weak or moderate vesicularity. In Fig.1 are reported vesicularity data obtained by Chavrit (2010) from the analysis of 65 MORB samples collected at the atlantic, pacific and indian ocean ridges and those of Hekinian et al. (2000) and Pineau et al. (2004) for MORB samples dredged on seamounts of the mid-atlantic ridge. These MORB samples were collected between ~1,000 and 5,000 m.b.s.l. (i.e. ~0.1-0.5 kbar of hydrostatic pressure). If one assumes that the observed vesicularity is due to a closed system
degassing without loss of vesicles between the source region and the seafloor, then our calculations suggest that most of the MORB samples are issuing from a source region located at shallow depth ($P_{\text{CO}_2}^{\text{sat}} \leq 5$ kbar i.e. d<15km). Moreover, if exsolution only occurs when some degree of super saturation in $CO_2$ is reached (for illustration, the dotted curves shown in Fig.1 correspond to a degree of super saturation $\alpha$=2), our calculations indicate that the vesicularity observed at eruption will be significantly lowered if the source region of the $CO_2$-saturated magma is located at shallow depth (for instance, if $P_{\text{CO}_2}^{\text{sat}}$=1 kbar, the vesicularity at 4,000 m.b.s.l. is three times smaller for a melt exhibiting a super saturation $\alpha$=2 than for a melt erupting at equilibrium). Incidentally, a super saturation in $CO_2$ is frequently reported in the bulk melt of MORB samples (Dixon et al., 1988; Jendrzejewski et al., 1997; Aubaud et al., 2004; Cartigny et al., 2008) and it seems to be higher when the vesicularity is low (<1%, see Chavrit, 2010).

In contrast, for $CO_2$-rich magmas their high vesicularity at eruption is barely affected by a possible super saturation (see dotted curves in Fig.1 when $V^* \geq 10\%$). With regard to those rare MORB samples exhibiting a high vesicularity (>10% in Fig.1), their source region is likely located at a depth between ~15 km and ~90 km (i.e. $P_{\text{CO}_2}^{\text{sat}}$ ~ 5-30 kbar). For instance, the $2\pi D43$ popping rock, which is considered as an undegassed MORB sample, is likely issuing from a $CO_2$-saturated magma located at ~36 km depth ($P_{\text{CO}_2}^{\text{sat}}$ ~12 kbar, according to Fig.1). In the same way, the highly vesiculated samples ($V^* \geq 0.50$ in Fig.1) collected in the rift valley of the mid-atlantic ridge near 34°N (Hekinian et al., 2000; Pineau et al., 2004), and which are associated with volcaniclastic deposits, could be issued from $CO_2$-saturated magmas at $P_{\text{CO}_2}^{\text{sat}}$ ~20-28 kbar (see Fig.1), a source region located about 60-90 km in the oceanic mantle. Moreover, according to our results, a magma saturated in $CO_2$ at 30 kbar reaches the fragmentation limit, $V^*$=0.75 (Sparks, 1978; Namiki and Manga, 2008), if it erupts at about 1,600 m.b.s.l., precisely the depth at which volcaniclastic deposits are observed. Notice that to reach the fragmentation limit at a greater water depth (e.g. 4,000 m.b.s.l.) the magma must be saturated in $CO_2$ at a much higher pressure (e.g. ~50 kbar or at 150 km in the upper mantle, according to Fig.1).
A more quantitative way to compare the vesicularity of MORB samples with that deduced from simulation data is to represent the vesicularity measured (or evaluated) at a given hydrostatic pressure as function of the total CO₂ content in the undegassed sample. Experimentally, the CO₂ content is evaluated by summing the amount of CO₂ in the bulk melt, measured by step heating or by IR spectroscopy, and that in the vesicles, measured by crushing or estimated from the vesicularity in treating the CO₂ phase filling the vesicles as an ideal gas (Graham and Sarda, 1991; Javoy and Pineau, 1991; Hekinian et al., 2000; Pineau et al., 2004). However, the CO₂ content in the glass is generally much smaller than the one in the vesicles, except for samples exhibiting a very low vesicularity ($V^* \leq 10^{-3}$). In Fig. 2 is reported the vesicularity as function of the total CO₂ content (in $g_{CO_2} / g_{melt}$) of MORB samples collected at the Atlantic, Indian and Pacific ocean ridges at various water depth (minimum and maximum water depths are indicated in the figure). These experimental data (Chavrit (2010) and Pineau et al. (2004)) are compared with our calculations for a CO₂-saturated magma ascending under isothermal condition (T=1873 K) and erupting at 1,000 m.b.s.l. (upper dots) or at 5,000 m.b.s.l. (lower dots), these two depths enclosing approximately the range of depth encountered at oceanic ridges. The agreement with experimental data is remarkable, especially if one emphasizes that the vesicularity of MORBs is evaluated from glassy samples whereas the vesicularity of our model is for a liquid sample erupting at 1873 K. It is commonly admitted (even if this is questionable) that the vesicularity of a magma erupting on the seafloor is frozen in when the temperature of the melt passes through the glass transition temperature ($T_g \sim 1000$ K, Ryan and Sammis (1981)). But if one considers that the solubility of CO₂ at the pressure of eruption changes very little when the temperature drops (Pan et al., 1991), and that the CO₂ phase filling the vesicles behaves as an ideal gas, then the vesicularity at $T_g$ will be smaller than the vesicularity of the high temperature liquid just before eruption by a ratio equal to $T_g / T$ ($\approx 0.53$ for the simulated MORB at 1873 K). Nevertheless, this estimation has to be taken with some caution as it likely overestimates the decrease of the vesicularity during the quench. As a matter of fact, upon rapid cooling, the viscosity of a basalt can be sufficiently high even above $T_g$ to limit vesicle shrinkage (Gardner et al., 2000). However, the important point is that a small decrease of the vesicularity is expected in going from the liquid to the glass, a feature
which can explain why the calculated vesicularity is systematically (but slightly) larger than the observed one in Fig.2. For instance, the \(2\pi D^{43}\) \textit{popping rock} dredged at 3,770 m on the mid-atlantic ridge has a vesicularity of 17\% and a \(CO_2\) content evaluated around 0.85-1.24 wt\% (Graham and Sarda, 1991; Javoy and Pineau, 1991; Cartigny et al., 2008; Chavrit, 2010) as compared with 20-28\% for the vesicularity of our simulated melt at 1873 K bearing the same \(CO_2\) content. It is noteworthy that the calculations presented in Fig.2 do not take into account a possible super saturation in \(CO_2\). We have emphasized earlier that the vesicularity of a melt erupting on the seafloor is significantly affected by super saturation only when the source region is very shallow (a few km in the oceanic crust). In this case the vesicularity of the super saturated melt can be much smaller than the one of a sample at equilibrium (this is illustrated in Fig.1 for a super saturation equal to 2). The very low vesicularity exhibited by MORB samples of the Pacific ridge (see the crosses in Fig.1 and 2) can then be explained in noting that their degree of super saturation is in the range 1.5-2.5 (Chavrit, 2010).

In conclusion, the large distribution of vesicularity which characterizes MORB samples can be described by a \(CO_2\) degassing process initiated at various depths in the oceanic mantle. However, the vesicularity observed after eruption on the seafloor is only the evidence of the last vesiculation episode experienced by the ascending magma, an evidence which gives no information about the degassing history prior this episode (if any). But, as discussed in the following, complementary information about the degassing trajectory can be obtained from the inventory of noble gases.

### 3.2 Partitioning and fractionation of noble gases.

According to Eqs.(4) and (5), the partitioning of noble gases between melt and vesicles is controlled by \(\gamma^i_m\) and \(\gamma^i_v\), the noble gas solubility parameters in the two coexisting phases. Values of these parameters evaluated by the TPM at isothermal condition (T=1873 K) are listed in Table 2 as function of the pressure. For a given noble gas (He, Ne, Ar or Xe) both solubility parameters, \(\gamma^i_m\) and \(\gamma^i_v\), decrease strongly when the pressure is increased, whereas at a given pressure, the heavier the noble gas the smaller the solubility parameters in the two coexisting phases (\(\gamma^He > \gamma^Ne > \gamma^Ar > \gamma^Xe\)). These trends are similar to those obtained by Guillot and Sator (2012) in their study of the solubility of noble
gases in dry silicate melts. According to Eq.(2) the ratio, $\gamma_i^m/\gamma_i^v$, is equal to $\rho^{\text{m}}_i/\rho^{\text{v}}_i$, where $\rho^{\text{m}}_i$ is the number density of noble gas of species $i$ in the $\text{CO}_2$-saturated melt (i.e. the number of noble gas atoms in the melt per volume of melt) and $\rho^{\text{v}}_i$ is the one in the $\text{CO}_2$ phase. This ratio is nothing but the noble gas partition coefficient which expresses the distribution of the noble gas ($i$) between the two phases.

As shown in Fig.3, the noble gas partition coefficient increases with the pressure but tends to level off above 50 kbar. More precisely, between 0 and 50 kbar the partition coefficient for $\text{He}$ increases by ~400%, that for $\text{Ne}$ by ~500% and that for $\text{Ar}$ by ~600%. This pressure effect implies that the transfer of a noble gas from the melt to the vesicles is hindered at depth (high $P$) by the high density of the $\text{CO}_2$ phase filling the vesicles. So, to properly estimate the melt/$\text{CO}_2$ partitioning of noble gases in a magma at depth, it is inaccurate to use the low pressure solubility of noble gases in the basaltic melt and to consider the $\text{CO}_2$ phase as an ideal gas (for which $\gamma_i^{\text{v}}=1$).

The inventory of noble gases in MORB samples is well documented (Graham, 2002). In the following our analysis will focus on $^4\text{He}$ and $^{40}\text{Ar}$ for which a consistent set of data is available. Before to compare these data with the prediction of our model calculation, it is worthwhile to examine how $\text{He}$ and $\text{Ar}$ distribute between melt and vesicles for a closed system degassing. In Fig.4 is shown the evolution of $\text{He}$ and $\text{Ar}$ contents, as calculated from Eqs.(4) and (5), in melt and in vesicles as function of the vesicularity evaluated for an hydrostatic pressure equivalent to 3,000 m.b.s.l. (the average water depth at oceanic ridges). The $\text{He}$ and $\text{Ar}$ contents are normalized with their initial abundance in the undegassed melt. Various initial $\text{CO}_2$ contents are investigated (controlled by the parameter $W_0$ in Eq.(7)). They correspond to a $\text{CO}_2$-saturation pressure, $P_{\text{CO}_2}^{\text{sat}}$, varying from 100 to 0.4 kbar (the value of $P_{\text{CO}_2}^{\text{sat}}$ is indicated in Fig.4). An attentive examination of Fig.4 shows that when the vesicularity is large (i.e. $V^* \geq 10\%$ or $P_{\text{CO}_2}^{\text{sat}} > 5$ kbar), more than 99% of $\text{Ar}$ atoms and 90% of $\text{He}$ atoms are in the vesicles at eruption, whereas for a 1% vesicularity, about 90% of $\text{Ar}$ atoms are in the vesicles but only 40% of $\text{He}$ atoms. If outgassing starts at very shallow depth, for instance at 1,000 m below the seafloor (i.e. at $P_{\text{CO}_2}^{\text{sat}} = 0.4$ kbar), the vesicularity becomes as small as 0.2% and yet 60% of $\text{Ar}$ atoms are in the vesicles when 90% of $\text{He}$ atoms are staying in the melt. These results are easily understandable if one
recalls that the melt/CO$_2$ partition coefficient for He is much greater than for Ar (a factor of ~10, see Fig.3). So, according to the vesicularity of the sample at eruption, the fractionation of noble gases (i.e. the ratio He/Ar) in melt and in vesicles will be different.

In order to compare in absolute value the noble gas contents measured in MORB samples with those calculated from Eqs.(4) and (5), we make the assumption that the concentration in $^{40}$Ar and the $^{4}$He/$^{40}$Ar ratio extracted from the 2πD43 popping rock reflect best the noble gas composition of the source region for MORBs (~0.1 ppmw of $^{40}$Ar after correction for atmospheric contamination, and $^{4}$He/$^{40}$Ar ~1.5, see Moreira et al. (1998), Moreira and Sarda (2000) and Raquin et al. (2008)). In Fig.5 is presented the evolution of Ar content in vesicles (in 10$^{-6}$ g$_{Ar}$/g$_{melt}$) as function of the vesicularity of the simulated MORB evaluated at 3,000 m.b.s.l., and in Fig.6 is presented the evolution of the $^{4}$He/$^{40}$Ar ratio. Here again, several initial conditions in CO$_2$ content for the source region are considered (the corresponding CO$_2$-saturation pressure evolving from 50 to 0.4 kbar). In both figures are shown literature data (black squares) compiled by Chavrit (2010) and obtained by crushing MORB samples (for this reason only noble gas contents in vesicles are reported). It is clear that a simple closed system degassing (see the red dots defining the curve with index V$^1$ in Figs.5 and 6) is unable to reproduce the literature data except those of the 2πD43 popping rock which are well represented by a single stage of vesiculation starting at ~30 km depth ($P_{CO_2}^{Sat}$ ~10 kbar). For the other MORB samples, the Ar contents in vesicles are found to be much weaker (by one to three orders of magnitude) than those predicted by a one-stage vesiculation mechanism. Correlatively, the $^{4}$He/$^{40}$Ar ratios observed in MORB samples are generally much higher than predicted.

These findings imply that either the initial noble gas contents of the MORB source vary from one sample to another, or the degassing trajectory is more complex than the one described by a simple closed system degassing. Although it cannot be excluded that for some settings the noble gas contents may vary significantly or be affected by diffusive fractionation during mantle melting (Burnard, 2004; Burnard et al., 2004; Yamamoto et al., 2009), it is generally accepted that the upper mantle is compositionally homogeneous with regard to noble gases, and because the latter ones are incompatible
elements (Brooker et al., 1998; Chamorro et al., 2002; Brooker et al., 2003; Heber et al., 2007), the melt composition in noble gases reflects that of the solid mantle. In contrast, the C contents of the upper mantle likely is more heterogeneous (Saal et al., 2002; Cartigny et al., 2008). Furthermore it may happen that during ascent the magma loses its CO$_2$-rich bubbles (e.g. slow ascent in a tortuous conduit), with the noble gases dissolved into it. Next, after this resetting step, the ascending melt starts again to degas when the residual amount of CO$_2$ oversteps the saturation limit. If this stage of vesicle loss occurs when the vesicularity of the magma is significant (a few percent or more) then the residual melt is strongly depleted in noble gases as a large proportion of the latter ones have been taken away with the CO$_2$ bubbles (see Fig.4 for the respective proportion of noble gases in melt and in vesicles).

According to Sarda and Moreira (2002), Sarda and Guillot (2005) and Guillot and Sarda (2006), several stages of vesiculation followed by vesicle loss can explain the low $^{40}$Ar contents and the high $^4He/^{40}Ar$ ratio measured in many of MORB samples.

In Figs.5 and 6 are reported the Ar content and the $^4He/^{40}Ar$ ratio in vesicles of the simulated MORB after having experienced several stages of vesiculation with vesicle loss. In practice, after each stage of vesicle loss, the noble gas content, $N_i^m$ (with $i = He$ or $Ar$), figuring in Eq.(4), is substituted to $N_i^0$ in Eqs.(4) and (5) while $V^*$ is set to 0. For illustration, in Figs.5 and 6 are shown 2-stage (marked $V^2$), 3-stage (marked $V^3$) and 4-stage (marked $V^4$) vesiculations. In the case of $V^2$, three degassing paths are presented (see blue dots): ($P_1$=20; $P_2$=19, 18,.., 0.4), ($P_1$=5; $P_2$=4, 3,.., 0.4) and ($P_1$=1; $P_2$=0.9, 0.8,.., 0.4). The first number $P_1$ corresponds to the CO$_2$ saturation pressure (in kbar) at which the first vesiculation stage occurs, and the second number $P_2$ is the saturation pressure of the second vesiculation stage in assuming that in between the two stages, the ascending MORB melt has experienced a total loss of vesicles. In looking at Fig.5, one notices that the higher the pressure threshold $P_1$ of the first vesiculation (i.e. the deeper in the oceanic mantle the first degassing episode), the lower the Ar contents in vesicles of a MORB sample of a given vesicularity at eruption (e.g. for $V^*$$=$1% i.e. for $P_2$=0.8 kbar, the Ar content is equal to $\approx 0.04$ ppmw if $P_1$=1 kbar, $\approx 0.0035$ ppmw if $P_1$=5 kbar and $\approx 0.0006$ ppmw if $P_1$=20 kbar). As shown in Fig.5, it is clear that a 2-stage vesiculation process may account of a significant part of the literature data (compare the squares with the blue...
dots). However, 3-stage and 4-stage vesiculations (or higher order) may be necessary to describe highly Ar-depleted samples (<10⁻⁴ ppmw): two examples are given for illustration, \( V^3 \) (\( P_1 = 20; P_2 = 3; P_3 = 2, 1, \ldots, 0.4 \) see green dots) and \( V^4 \) (\( P_1 = 20; P_2 = 3; P_3 = 1; P_4 = 0.9, \ldots, 0.4 \) see cyan dots). Incidentally, one notices that most of the measured vesicularities are below ~5%, a value which suggests that most of MORB samples have experienced a last vesiculation episode not as deep as ~10 km in the mantle (or \( P_{\text{CO}_2}^{\text{sat}} < 3 \text{kbar} \)).

With regard to the \(^4\text{He}/^4\text{Ar}\) ratio presented in Fig. 6, similar conclusions are obtained (compare squares with dots in the figure). Thus in introducing a 2-stage vesiculation the \(^4\text{He}/^4\text{Ar}\) ratio lies between 1 and 10, whereas higher values (~10-100) are reached with 3- or 4-stage vesiculations. Nevertheless, the highest values of the \(^4\text{He}/^4\text{Ar}\) ratio (in the range 100-1000) and the lowest Ar contents (<10⁻⁴ ppmw) measured in MORB could originate from a Rayleigh distillation process (Moreira and Sarda, 2000; Burnard, 2001) where \( \text{CO}_2 \) bubbles are extracted from the melt as soon as they are formed (e.g. in a shallow magma chamber). But other mechanisms have been proposed to explain high values of the \(^4\text{He}/^4\text{Ar}\) ratio as, for instance, a fractional crystallization-assimilation-degassing in a shallow magma chamber (Marty and Zimmermann, 1999) or a kinetic fractionation controlled by diffusion during incomplete degassing (Aubaud et al., 2004; Paonita and Martelli, 2006, 2007). The cornerstone of this latter mechanism is that the larger diffusivity of He atoms into the MORB melt with respect to that of Ar and \( \text{CO}_2 \) may enrich in He atoms incipient \( \text{CO}_2 \) bubbles, a kinetic disequilibrium which can be frozen in at eruption if the ascent rate is sufficiently high. We show in the next section that this hypothesis can be tested by MD simulation.

4. Kinetics of noble gas transfer during bubble formation

In the course of a MD simulation it is possible to reproduce a degassing process in applying a pressure drop to a volatile-saturated melt. For instance, in starting from a well equilibrated \( \text{CO}_2 \) bearing melt at 1873K and 50 kbar (the \( \text{CO}_2 \) content is ~ 9.5 wt%) and in applying a sudden pressure drop from 50 to 5 kbar, a 3D visualization of the simulation box shows the growth of a \( \text{CO}_2 \) nanobubble fully developed after about a few ns of running time (see Fig.7). The vesicularity of the
MORB sample after the pressure drop is that expected from the thermodynamic relationship (see Eq.(7) and Fig.1), i.e. about 30% in the present case. Correspondingly the bulk melt around the \( CO_2 \) bubble has a \( CO_2 \) content of \( \sim 0.3 \) wt\%, a value in agreement with the solubility of \( CO_2 \) at these thermodynamic conditions (in Fig.7, the initial state is a melt made of 5,000 ions, \( \sim 176 \) carbonate ions and \( \sim 99 \) \( CO_2 \) molecules, whereas the final state is a melt composed of 5,000 ions, \( \sim 2 \) carbonate ions and \( \sim 6 \) \( CO_2 \) molecules and a bubble formed by \( \sim 267 \) \( CO_2 \) molecules). We have repeated the above degassing experiment for other thermodynamic conditions (e.g. \( 100 \rightarrow 50 \) kbar, \( 100 \rightarrow 10 \) kbar, and \( 30 \rightarrow 3 \) kbar) and the final state is characterized by a single \( CO_2 \) bubble whose the size agrees with the vesicularity estimated by thermodynamics. But, because of the small system size investigated (a few thousand particles), only a few nucleation loci are observed initially in the simulation box (see Fig.7), and hence it is not possible to investigate the nucleation rate quantitatively (very large system sizes are then required). In practice, to render more effective bubble nucleation it is important to deal with a high initial \( CO_2 \) content, i.e. to prepare the initial state at a high enough pressure (e.g. \( 100, 50 \) or \( 30 \) kbar), and to apply a large decompression rate (here the pressure drop is applied quasi instantaneously over one MD step, i.e. \( 10^{15} \) s, a more detailed analysis of bubble nucleation by changing the decompression rate is beyond the scope of this article). But this is immaterial with regard to our primary objective which is to quantify how fast is the transfer of noble gases from the melt to a growing \( CO_2 \) bubble.

A small number (~10) of \( Ar \) or \( He \) atoms is incorporated into a \( CO_2 \)-saturated MORB melt at given \( (T,P) \) conditions, and after a period of equilibration (~1 ns) the system is suddenly decompressed (e.g. from \( 100 \rightarrow 10 \) kbar). It may happen that the number of noble gas atoms incorporated into the melt is high enough for the melt to be supersaturated in noble gases (this is the case for \( Ar \) atoms but not for \( He \) atoms in the pressure range investigated, for a discussion on noble gas solubility in silicate melts see Guillot and Sator (2012)). However there is no evidence of noble gas atom clustering in the simulated melt before decompression, likely because the nucleation rate for such an event is so low that the time to spend for observing noble gas nucleation exceeds by far our simulation time. Thus during the \( CO_2 \) degassing process, each noble gas atom behaves independently from each other and for
this reason they are used as independent tracers. We have checked this point by performing simulation runs with a single noble gas atom and have found essentially the same results (except a poorer statistics).

In order to follow the kinetics of bubble formation, we have evaluated as function of running time the average elemental fraction (on an atomic basis), \( f_{CC} \), of \( CO_2 \) molecules which are in the immediate vicinity (first shell) of a carbon atom (this one belonging to a \( CO_2 \) molecule or to a \( CO_3^{2-} \) carbonate ion, without distinction). The radius (\( r_s=5\AA \)) of the first shell around each carbon atom was chosen empirically from an analysis of the atom-atom pair distribution functions, and we have checked that the results are robust when changing its value on a limited range. During a decompression experiment \( f_{CC} \) is expected to vary from a low or moderate value to a high value. Indeed, before decompression each carbon atom of the \( CO_2 \)-saturated melt is surrounded primarily by the elements of the silicate, whereas after the pressure drop a majority of \( CO_2 \) molecules are in the bubble.

To improve the statistics, our results were averaged over a series of 20 independent decompression experiments (each one long of 5ns). For illustration, the time evolution of \( f_{CC} \) is shown in Fig.8 for a 100→10 kbar pressure drop. Before the pressure drop the value of \( f_{CC} \) in the \( CO_2 \)-saturated melt at equilibrium is \( \approx0.40 \) (a rather high value because the \( CO_2 \) content is \( \approx29\text{wt}\% \) at 100 kbar), and after the pressure drop \( f_{CC} \) increases rapidly to reach a plateau value, \( \approx0.76 \), after about 2,000 ps. This evolution of \( f_{CC} \) is the signature of \( CO_2 \) bubble formation as shown by the correlated evolution of the vesicularity of the simulated sample (see \( V^* \) in Fig.8). Indeed, when a bubble nucleates and grows, the silicate atoms surrounding a carbon atom are progressively replaced by \( CO_2 \) molecules. Notice that in a bulk \( CO_2 \) fluid \( f_{CC} \) is equal to one, but in our simulations the high surface/volume ratio of the nanobubble modifies this value (hence \( f_{CC}<1 \)). As a matter of fact, the \( CO_2 \) molecules in contact with the melt at the surface of the bubble represent a significant proportion of the bubble forming molecules (\( \approx40\% \) for a bubble of 40A in diameter).

A quick glance at Fig.8 reveals that the time evolution of \( f_{CC} \) (and \( V^* \) as well) exhibits two different regimes: a rapid evolution of great amplitude at short times \( (0<t<100 \text{ ps}) \) followed by a slower
evolution of a much weaker amplitude at long times (100<t<2,000 ps). This time evolution is well
described by the following bi-exponential function,

\[ f_{cc} = (f_{cc}^{\text{min}} - f_{cc}^{\text{max}}) e^{-t/\tau_1} + f_{cc}^{\text{inter}} (e^{-t/\tau_2} - e^{-t/\tau_1}) + f_{cc}^{\text{max}} \]  

(10)

where \( f_{cc}^{\text{min}} \), \( f_{cc}^{\text{inter}} \) and \( f_{cc}^{\text{max}} \) are fitting parameters and \( \tau_1 \) and \( \tau_2 \) are time constants (the curve fitting
shown in Fig. 8 corresponds to the following parameters: \( f_{cc}^{\text{min}} = 0.40 \), \( f_{cc}^{\text{inter}} = 0.04 \), \( f_{cc}^{\text{max}} = 0.76 \),
\( \tau_1 = 60 \) ps and \( \tau_2 = 600 \) ps). The two time constants give an estimate of the bubble growth rate at
the nanometric scale. The time constant \( \tau_1 \), associated with the short time evolution, corresponds to
the time spent for the formation of a critical nucleus, i.e. a cluster in which a central \( \text{CO}_2 \) molecule has
essentially \( \text{CO}_2 \) molecules as first neighbors. On the other hand, the time constant \( \tau_2 \) gives an estimate
of bubble growth at long time. It expresses the coalescence time of critical nuclei and the expansion
duration of bubble growth. Notice that the bubble ceases to grow after about 2,000 ps, when the melt
super saturation in \( \text{CO}_2 \) molecules is exhausted, i.e. when the chemical equilibrium between the
silicate melt and the \( \text{CO}_2 \) phase is achieved. Consequently the size of the bubble depends on the size of
the simulated sample but the vesicularity does not.

Although our simulation gives information on bubble formation at the nanometric scale, for the sake
of completeness it is useful to compare this microscopic description with a macroscopic point of view
as given by classical nucleation theory. In this framework, for early-stage bubble growth when the
surface/volume ratio is large, growth is limited by the viscosity of the melt (Prousevitch et al., 1993;
Toramaru, 1995; Navon et al., 1998), and the bubble radius grows exponentially with time,

\[ R(t) \approx \exp \left[ \frac{\Delta P}{4\eta} t \right] \]  

(11)

where \( \Delta P \) is the difference between the volatile pressure inside the bubble and the ambient pressure
(equated to the pressure drop in a first approximation) and \( \eta \) the melt viscosity. In our simulation, the
volume of an initial nucleus being proportional to the number of incoming \( \text{CO}_2 \) molecules, the latter
one grows approximately as $R^3(t)$. From the analogy between the microscopic definition expressed by Eq.(10) and the macroscopic relationship given by Eq.(11) one can deduce the following relation,

\[ \tau_1 \sim \frac{4\eta}{3\Delta P} \tag{12} \]

where $\tau_1$ is the formation time of a critical nucleus. For the decompression experiment presented in Fig.8, the Eq.(12) leads to $\tau_1 = 6.7$ ps in using $\Delta P = 90$ kbar and $\eta = 0.045$ Pa.s for the viscosity of our $CO_2$-bearing MORB melt evaluated at 1873K and 10 kbar (notice that the viscosity of our simulated melt is much lower than that of a real basaltic melt, by roughly a factor of ten at 1873 K, for a discussion see Bauchy et al. (2012), but this is immaterial in the present context). But this value of $\tau_1$ is about 9 times shorter than the result of the simulation ($\tau_1^{\text{sim}} = 60$ ps), a finding which implies that the simulation and the nucleation theory do not probe the same process or that the strict application of Eq.(11) is doubtful over a time scale of a few ps (for instance the relaxation time for the viscosity is much larger than a ps). Moreover the Eq.(11) is valid so long as a well formed interface between the $CO_2$ bubble and the silicate melt can be identified, and this is not yet the case when the system is made of scattered clusters. Nevertheless, for nucleation theory, the scale of the critical nucleus radius (given by $2\gamma/P$, where $\gamma \sim 0.36$N/m is the surface tension for molten basalt as evaluated by Walker and Mullins, 1981), is about 3.8Å at P=10 kbar, a value which agrees well with the size of clusters observed in our simulation during the early stage of bubble formation. Moreover, the nucleation time $\tau_1$ increases strongly when the volatile initial concentration becomes lower or when the pressure drop is decreased (e.g. $\tau_1$ evolves from $\sim$60 ps to $\sim$230 ps when $\Delta P$ varies from 90 to 50 kbar). All these findings are in a qualitative agreement with classical nucleation theory (Proussevitch and Sahagian, 1998) which predicts a slowing down of bubble growth at once with lower volatile oversaturation and with lower initial volatile concentration.

For noble gases we have proceeded similarly by defining the average fractions in $CO_2$ molecules, $f_{HeC}$ and $f_{ArC}$, within a sphere of radius 5Å centered on a $He$ or an $Ar$ atom. As illustrated in Fig.8, an important result is that the time evolutions of $f_{HeC}$ and $f_{ArC}$ are not only very similar to
each other but they are virtually identical to that of $f_{CC}$. More precisely they can be described by Eq.(10) with $\tau_1^He \approx \tau_1^Ar (\approx \tau_1^C) = 60 \text{ ps}$, $\tau_2^He \approx \tau_2^Ar (\approx \tau_2^C) = 600 \text{ ps}$, $f_{\text{He}}^\text{min} = 0.42$, $f_{\text{He}}^\text{inter} = 0.04$, $f_{\text{He}}^\text{max} = 0.78$, $f_{\text{Ar}}^\text{min} = 0.50$, $f_{\text{Ar}}^\text{inter} = 0.04$, and $f_{\text{Ar}}^\text{max} = 0.83$. Moreover, there is no time lag between the rises of $f_{\text{He}}$ and $f_{\text{Ar}}$ and that of $f_{CC}$, they are concomitant with each other. In other words, as soon as nucleation takes place, the He and Ar atoms located nearby a nucleation locus attach to it and become observers of its evolution. At the scale of our simulation (the simulation cell is a few nm long) the transfer of He and Ar atoms from the melt to a CO$_2$ bubble is achieved before the latter one is fully developed. There is no quantitative difference between He and Ar even if He atoms are more mobile than Ar atoms in the melt (at 1873K and 10 kbar their respective diffusion coefficients differ by roughly one order of magnitude: $D_{\text{He}} \sim 10^{-8} \text{ m}^2/\text{s}$ and $D_{\text{Ar}} \sim 1.5 \times 10^{-9} \text{ m}^2/\text{s}$ after our own evaluation). In fact the limiting step is the nucleation process itself and the noble gases present in the halo surrounding a nucleation locus stick to it and works one's way into it. A 3D visualization of the atomic trajectories into the simulation box is fully illustrative on this point (see Fig.7).

After the formation of the nanobubble is completed (equilibrium), it is observed along the simulation run that the rapid diffusion of a He atom into the CO$_2$ bubble leads from time to time to brief excursions of the noble gas atom into the bulk melt. This behavior is expected because the melt/CO$_2$ partition coefficient of a He atom being equal to about 3% at 5 kbar (see Fig.3), in a highly vesiculated basaltic melt ($V^* \sim 0.3$ in the exemple of Fig.7) the noble gas will spent approximately ~3% of its time in the bulk melt and ~97% in the CO$_2$ bubble. For Ar atoms the partition coefficient is ten times smaller (~0.3% at 5 kbar, see Fig.3) and indeed we observe very scarcely an excursion of an Ar atom out of the bubble. In summary, during a degassing episode the noble gas atoms present in the halo surrounding an incipient CO$_2$ bubble are transferred in the latter one at the same rate than the CO$_2$ molecules themselves. So, when bubble growth is ended (or stopped) the concentration in noble gases becomes stationary and its value in the vesicles can be evaluated from Eq.(5) in introducing for $V^*$ the current vesicularity.
Although our calculations were performed at the nanometric scale we believe that the conclusions which can be inferred are meaningful at the macroscopic scale. Thus, our results don't support the hypothesis that a kinetic fractionation between $He$ and $Ar$ is at the origin of the high $He/Ar$ ratio observed in vesicles of some MORB samples (Aubaud et al., 2004). According to this hypothesis, the transfer of noble gases from the melt to the bubbles is considered as decoupled from the very process of bubble formation. When degassing is taking place, the $He$ atoms diffusing faster than $Ar$ atoms into the melt, the $CO_2$ bubbles (assumed to be depleted in noble gases) would be transiently enriched in $He$ atoms with respect to $Ar$ atoms, a disequilibrium leading to increase the $He/Ar$ ratio in the vesicles. Furthermore, if the magma erupts before degassing is completed (due to a rapid ascent rate for instance) the high $He/Ar$ ratio can be imprinted in the MORB glass (Paonita and Martelli, 2006). Our results show that the prerequisite of this scenario (the decoupling between bubble formation and noble gas transfer) is unrealistic. As a matter of fact, the noble gases are present from the formation of critical nuclei and consequently their abundances in the vesicles are controlled by the current vesicularity of the sample. For instance, a MORB melt $CO_2$-saturated at 0.8 kbar and erupting at 3,000 m.b.s.l. (i.e. $P_{eq}=0.3$ kbar) will exhibit at equilibrium a vesicularity about 1% (see Fig.1). In this case the $He/Ar$ ratio in the vesicles (see Fig.4) is equal to $\sim 0.4(C^H_0/C^A_0)$ where $C^H_0$ and $C^A_0$ are the noble gas contents before vesiculation (notice that $C^H_0/C^A_0$ may vary with the source region, see the discussion in section 3.2). But if during magma ascent, the $CO_2$ exsolution is delayed up to a super saturation ratio $\alpha=2.6$ is reached (for example), then the vesicularity at eruption is as low as $\sim 1.5 \times 10^{-4}$ and the corresponding $He/Ar$ ratio is equal to $\sim 0.1(C^H_0/C^A_0)$. Thus, for a closed system degassing, the higher the $CO_2$ super saturation ratio the lower the $He/Ar$ ratio in the vesicles at a given pressure (because $He$ is more soluble than $Ar$ in the silicate melt). Even if some $He$ and $Ar$ atoms of the melt are sufficiently distant from vesicles for migrating with delay in the latter ones, the incoming fluxes in noble gases are compensated by outgoing fluxes to fulfill equilibrium (Fick's law). In summary, an incomplete degassing lowers the vesicularity (with respect to a complete degassing) and diminishes the $He/Ar$ ratio in the vesicles. So, to reconcile theory and observation (MORB samples exhibiting a low vesicularity and a strong $CO_2$ super saturation are generally displaying a high $He/Ar$ ratio in the...
vesicles) one must put forward other mechanisms capable of producing high $c_0^{He}/c_0^{Ar}$ ratio in the melt before the last vesiculation episode. We think that the sequential degassing mechanism with vesicle loss, presented in section 3.2, can solve this outstanding question.

5. Conclusions

In this paper it has been shown that several aspects of MORB degassing can be described realistically by atomistic simulations. The main results of this study are the following.

1- In using a force field developed by Guillot and Sator (2011) to model by MD simulation the incorporation of $CO_2$ into silicate melts, the vesicularity of a MORB melt has been evaluated as function of initial $CO_2$ contents and pressure at eruption. An excellent agreement is obtained between calculated values and vesicularity data of MORB samples collected at mid-ocean ridges. This comparison also indicates that most of MORB samples have experienced a last vesiculation episode at shallow depth (d<15 km) in the oceanic mantle. In contrast, a few highly vesicular samples (e.g. popping rocks) could be issued from deep-seated $CO_2$-rich magmas. A possible origin of the latter ones are $CO_2$-rich silica-undersaturated melts (e.g. carbonatite-like) in transit through the oceanic mantle which, in assimilating the silicate matrix, could drive the melt to a basaltic composition. If their $CO_2$ content is sufficiently high, the MORB melt may exsolve a great amount of $CO_2$ leading in special cases to a submarine explosive volcanism. For instance, according to our results, the vesicularity of a MORB composition with 9.5 wt% $CO_2$ reaches the fragmentation threshold ($V^* \sim 0.75$) at a water depth of 4,000 m whereas a MORB melt with 4.6 wt% $CO_2$ will experience an explosive fragmentation in erupting at 1,500 m.b.s.l.. In short, the possibility that $CO_2$-rich magmas may drive explosive volcanism at some mid-ocean ridges has been underestimated up to now.

2- The evaluation of the pressure dependence of the noble gas partition coefficients between a MORB melt and a supercritical $CO_2$ phase shows that noble gas transfer from the silicate melt to the $CO_2$ phase is hindered at high pressure by the density of the fluid. Thus, the partition coefficients of $He$ and $Ar$ increase by a factor of about 4-5 between 0 and 50 kbar. So MORB degassing at great depth would
be less efficient than expected to deplete the upper mantle in noble gases. Furthermore it is shown that
the large distribution in Ar contents and of the He/Ar ratio measured in MORB samples can be
explained if the ascending magma experiences a series of vesiculation at depth followed by vesicle
loss.

3- By performing a decompression numerical experiment where a pressure drop is applied to a volatile
(CO$_2$+noble gas) bearing MORB melt, it is possible to investigate (and to visualize) the formation of
critical nuclei leading to CO$_2$ bubble formation. Interestingly, noble gases present in the neighborhood
of nucleation loci exhibit a great affinity for CO$_2$ clusters. In fact, the transfer of noble gases from the
melt to these embryos is so effective that the transfer rate in a growing CO$_2$ bubble is identical to that
of the CO$_2$ molecules themselves. Thus, when bubble growth is stopping the concentration of vesicles
in noble gases becomes stationary and is a function of the current vesicularity (see Eq.(4)). This
finding doesn't support the hypothesis that a kinetic fractionation between He and Ar (induced by their
diffusivity difference in the melt) is at the origin of the high He/Ar ratio observed in vesicles of some
MORB samples.

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Simulation conditions. All simulations were performed at 1873K. In the table below, the simulated MORB melt is composed of 5,000 ions plus the number of $CO_2$ molecules, $(N_{CO_2})_{melt}$, necessary to reach $CO_2$-saturation (indicated by $W$) at the investigated pressure. The density of the $CO_2$-saturated MORB is given by $n_{melt}$ and that of the coexisting supercritical $CO_2$ phase by $n_{CO_2}$. To evaluate the system size dependence, the calculations were also performed with a smaller system where the MORB was composed of only 1,000 ions plus the corresponding number of $CO_2$ molecules (in that case $(N_{CO_2})_{melt}$ reported below has to be divided by 5). As for the pure $CO_2$ phase, it was also simulated with two system sizes, a large system with 2,500 $CO_2$ molecules and a smaller one with 500 molecules.

| P(kbar) | $W(g_{CO_2}/g_{melt})$ | $(N_{CO_2})_{melt}$ | $n_{melt}(g/cm^3)$ | $n_{CO_2}(g/cm^3)$ |
|---------|-----------------|-----------------|-----------------|-----------------|
| 0.001   | 5.10^{-7}       | 0               | 2.63            | 3.10^{-4}       |
| 10      | 0.006           | 15              | 2.74            | 0.94            |
| 20      | 0.016           | 40              | 2.83            | 1.21            |
| 30      | 0.046           | 120             | 2.88            | 1.38            |
| 50      | 0.095           | 275             | 2.99            | 1.60            |
| 80      | 0.21            | 660             | 3.07            | 1.81            |
| 100     | 0.29            | 1065            | 3.09            | 1.91            |
Pressure dependence of noble gas solubility parameters in the $CO_2$-saturated MORB melt ($\gamma^i_m$) and in the coexisting supercritical $CO_2$ phase ($\gamma^i_{CO_2}$) at 1873K. Values calculated with the two system sizes are indicated: S is for small system sizes and L is for large system sizes (see Table 1 for the number of atoms in each system). For each investigated pressure, the reference value of the solubility parameter (noted mean) is given by the arithmetic mean of the S and L values. Notice that the evaluation of $\gamma^Xe_m$ becomes inaccurate from 30 kbar whereas that of $\gamma^Xe_{CO_2}$ is accurate up to 80 kbar.

| P(kbar) | $\gamma^He_m$ | $\gamma^He_{CO_2}$ | $\gamma^Ne_m$ | $\gamma^Ne_{CO_2}$ | $\gamma^Ar_m$ | $\gamma^Ar_{CO_2}$ | $\gamma^Xe_m$ | $\gamma^Xe_{CO_2}$ |
|---------|---------------|---------------------|---------------|---------------------|---------------|---------------------|---------------|---------------------|
| 0.001   | 1.83(-2)      | 1.00                | 9.81(-3)      | 1.00                | 1.47(-3)      | 1.00                | 2.88(-4)      | 1.00                |
|         | mean          | 1.83(-2)            | 1.00          | 9.81(-3)            | 1.00          | 1.47(-3)            | 1.00          | 2.88(-4)            |
| 10      | S 5.49(-3)    | 1.71(-1)            | 2.87(-3)      | 1.39(-1)            | 1.96(-4)      | 6.60(-2)            | 1.39(-5)      | 3.21(-2)            |
|         | L 5.56(-3)    | 1.72(-1)            | 2.97(-3)      | 1.39(-1)            | 2.18(-4)      | 6.67(-2)            | 1.40(-5)      | 3.26(-2)            |
|         | mean          | 5.53(-3)            | 1.72(-1)      | 2.92(-3)            | 1.39(-1)      | 2.07(-4)            | 6.64(-2)      | 1.40(-5)            |
| 20      | S 2.81(-3)    | 6.17(-2)            | 1.25(-3)      | 4.23(-2)            | 4.50(-5)      | 1.03(-2)            | 1.20(-6)      | 2.59(-3)            |
|         | L 2.87(-3)    | 6.18(-2)            | 1.28(-3)      | 4.24(-2)            | 4.92(-5)      | 1.04(-2)            | 1.26(-6)      | 2.62(-3)            |
|         | mean          | 2.84(-3)            | 6.18(-2)      | 1.27(-3)            | 4.24(-2)      | 4.71(-5)            | 1.04(-2)      | 1.23(-6)            |
| 30      | S 1.54(-3)    | 2.72(-2)            | 5.91(-4)      | 1.60(-2)            | 1.14(-5)      | 2.11(-3)            | 9.31(-8)      | 2.91(-4)            |
|         | L 1.59(-3)    | 2.70(-2)            | 6.12(-4)      | 1.59(-2)            | 1.35(-5)      | 2.11(-3)            | 3.24(-7)      | 2.92(-4)            |
|         | mean          | 1.57(-3)            | 2.71(-2)      | 6.02(-4)            | 1.60(-2)      | 1.25(-5)            | 2.11(-3)      | 2.09(-7)            |
| 50      | S 5.21(-4)    | 6.66(-3)            | 1.49(-4)      | 2.97(-3)            | 9.94(-7)      | 1.27(-4)            | 1.05(-8)      | 5.92(-6)            |
|         | L 5.31(-4)    | 6.78(-3)            | 1.54(-4)      | 3.04(-3)            | 1.18(-6)      | 1.33(-4)            | 6.26(-8)      | 6.13(-6)            |
|         | mean          | 5.26(-4)            | 6.72(-3)      | 1.52(-4)            | 3.01(-3)      | 1.09(-6)            | 1.30(-4)      | 3.66(-8)            |
| 80      | S 1.19(-4)    | 1.18(-3)            | 2.33(-5)      | 3.65(-4)            | 2.84(-8)      | 3.59(-6)            | n.e.          | 4.08(-8)            |
|         | L 1.19(-4)    | 1.19(-3)            | 2.34(-5)      | 3.67(-4)            | 4.61(-8)      | 3.67(-6)            | n.e.          | 3.43(-8)            |
|         | mean          | 1.19(-4)            | 1.19(-3)      | 2.34(-5)            | 3.66(-4)      | 3.73(-8)            | 3.63(-6)      | 3.76(-8)            |
| 100     | S 4.63(-5)    | 4.19(-4)            | 7.70(-6)      | 1.03(-4)            | 3.94(-9)      | 3.50(-7)            | n.e.          | 1.73(-9)            |
|         | L 4.78(-5)    | 4.19(-4)            | 7.89(-6)      | 1.02(-4)            | 6.00(-9)      | 3.02(-7)            | n.e.          | 4.37(-10)           |
|         | mean          | 4.71(-5)            | 4.19(-4)      | 7.80(-6)            | 1.03(-4)      | 4.97(-9)            | 3.26(-7)      | 1.08(-9)            |
| n.e.    | not evaluated |                     |               |                     |               |                     |               |                     |
**Figure captions**

**Fig.1** Pressure dependence of the vesicularity of an ascending magma as described by our simulated MORB melt at 1873K and for different initial CO$_2$ contents at depth (namely 0.06, 0.3, 0.6, 1.6, 4.6, 9.5, 21 and 29 wt% corresponding to $P_{CO_2}^{sat}$ = 1, 5, 10, 20, 30, 50, 80 and 100 kbar). The full curves correspond to a super saturation ratio $\alpha$=1, and the dotted curves to $\alpha$=2 (see text). Symbols represent the vesicularity of MORB samples collected on the Atlantic (squares), Indian (triangles) and Pacific (crosses) ridges (data are from Chavrit (2010), Hekinian et al. (2000) and Pineau et al. (2004)). Values of the initial CO$_2$ contents (in wt% CO$_2$) are indicated along the curves.

**Fig.2** Vesicularity of our simulated MORB evaluated at 1,000 m.b.s.l. (upper set of red dots, color online) and at 5,000 m.b.s.l. (lower set of red dots, color online) as function of the initial CO$_2$ content before degassing (the corresponding CO$_2$-saturation pressure is indicated on the upper axis). Data for MORB samples dredged between ~1,000 m.b.s.l. and 5,400 m.b.s.l. on the Atlantic (squares), Indian (triangles), and Pacific (crosses) ridges are shown for comparison (data source: Chavrit (2010) and Pineau et al. (2004)). Notice that the CO$_2$ content in the (bulk) saturated melt at 1,000 m.b.s.l. is about 50 ppmw, and is about 250 ppmw at 5,000 m.b.s.l., values which become non negligible with respect to the CO$_2$ content in vesicles only when the vesicularity is very low ($V^* \leq 10^{-3}$).

**Fig.3** MORB-CO$_2$ noble gas partition coefficients as function of pressure. The dotted curves represent the raw results obtained with small system sizes (lower curve) and with large system sizes (upper curve), respectively, whereas the full curves are obtained from their arithmetic mean. The separation between the two dotted curves gives an estimation of the error bar (see text and Table 2). Notice that the distinction between dotted curves and full curves is barely visible for He and Ne over the entire pressure range. For Xe the results become unreliable above 30 kbar and are not shown (see Table 2).

**Fig.4** $^4$He and $^{40}$Ar contents in melt ($m$) and in vesicles ($v$) as function of the vesicularity evaluated at an hydrostatic pressure equivalent to 3,000 m.b.s.l.. The abundances in noble gases are normalized
with their initial values in the undegassed sample. The total CO$_2$ content of the MORB melt is indicated by a number which corresponds to the CO$_2$-saturation pressure, $P_{\text{sat}}^{\text{CO}_2}$, given in kbar.

**Fig. 5** Ar content in vesicles (in 10$^{-6}$ g$_{\text{Ar}}$/g$_{\text{melt}}$ or ppmw) as function of the vesicularity evaluated at 3,000 m.b.s.l.. The initial abundance in $^{40}$Ar of the source region is assumed to be equal to that measured in the 2πD43 popping rock (~0.1 ppmw, Moreira et al. (1998)) whereas different initial conditions of CO$_2$-saturation are investigated (namely $P_{\text{sat}}^{\text{CO}_2} = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 2, 3, 4, 5, 10, 20, 30, 40$ and 50 kbar). The numbers associated with arrows indicate the value of $P_{\text{sat}}^{\text{CO}_2}$. The curve labeled $V^1$, and corresponding to the red dots (color on line), describes a closed system degassing without vesicle loss. The curves labeled $V^2$ (blue dots) describe a 2-stage vesiculation process with vesicle loss. For illustration, three degassing paths are shown: ($P_1=20$; $P_2=19, 18, ..., 0.4$ kbar), ($P_1=5$; $P_2=4, 3, ..., 0.4$ kbar) and ($P_1=1$; $P_2=0.9, 0.8, ..., 0.4$ bar) where $P_1$ is the pressure at which the first vesiculation stage occurs and $P_2$ the pressure of the second vesiculation stage, knowing that in between the ascending magma has experienced a total loss of vesicles. For 3-stage vesiculation (labeled $V^3$ and green dots), and 4-stage vesiculation (labeled $V^4$ and cyan dots), for the sake of clarity only one degassing path is shown: ($P_1=20$; $P_2=3$; $P_3=2, 1, ..., 0.4$ kbar) and ($P_1=20$; $P_2=3$; $P_3=1$; $P_4=0.9, 0.8, ..., 0.4$ kbar). Notice that most of the experimental data (black squares, data taken from Chavrit (2010)) can be explained by a 2-, 3- or 4- stage vesiculation process, whereas the 2πD43 popping rock is well described by a closed system degassing starting at 10 kbar (i.e. ~30 km in the oceanic mantle).

**Fig. 6** As in Fig. 5 but for the $^4\text{He}/^{40}\text{Ar}$ ratio. The $^4\text{He}/^{40}\text{Ar}$ ratio of the source region is assumed to be identical to that of the 2πD43 popping rock (~1.5, see Moreira et al. (1998)).

**Fig. 7** Snapshots of the simulation cell during a decompression experiment. Picture (a) shows a snapshot of the simulation cell containing a MORB melt CO$_2$-saturated at 1873K and 50 kbar. The system is composed of 5,000 silicate atoms, 275 CO$_2$ molecules (in fact ~99 CO$_2$ molecules and ~176 carbonate ions, CO$_3^{2-}$, on average) and one He atom. For clarity, the size of the silicate atoms are arbitrarily reduced with respect to that of the CO$_2$ molecules (carbon atoms are in blue, oxygen atoms
are in red and carbonate ions appear as bent $CO_2$ molecules) whereas the size of the $He$ atom (in yellow) is magnified. Notice that the distribution of $CO_2$ molecules within the melt is homogeneous and that the $He$ atom is not preferentially solvated by $CO_2$ molecules. The system is suddenly decompressed from 50 to 5 kbar and it is observed, in picture (b), at a time $t=250$ ps after the pressure drop. On this snapshot most of the $CO_2$ molecules are forming clusters: one is visible near the center of the box and another one, solvating the $He$ atom, is located on the right side of the box. After 5,450 ps (picture (c)) all the nuclei have clustered together in a unique bubble in which the $He$ atom is enclosed. The final vesicularity of the system is about $\sim 30\%$ as expected from thermodynamics (see Fig.1 for a $50 \rightarrow 5$ kbar decompression path).

**Fig.8** Kinetics of bubble formation and noble gas transfer during a decompression experiment. The initial state is a well equilibrated MORB melt $CO_2$-saturated at 100 kbar and 1873K, and the final state is a vesiculated melt at 10 kbar and 1873K. The decompression step (100 $\rightarrow$ 10 kbar) takes place at $t=0$ and is quasi instantaneous (the pressure drop is applied over one MD step, i.e. 0.001 ps). The figure shows as function of running time the evolution of the atomic fraction in $CO_2$ molecules which are in the immediate neighborhood of a $CO_2$ molecule, $f_{CC}$, of a $He$ atom, $f_{HeC}$, and of an $Ar$ atom, $f_{ArC}$. The raw data are the wiggling curves (blue for $CO_2$, red for $He$ and green for $Ar$, color online) whereas the black dotted curves are least squared fits based upon a bi-exponential function (see text and Eq.(10)). The statistical noise of the raw data is much larger with $He$ and $Ar$ than with $CO_2$ because the number of $CO_2$ molecules in the simulated sample is much larger than that of the noble gases (213 instead of 10). Notice that for $t>0$ the three functions $f_{CC}, f_{HeC}$, and $f_{ArC}$ exhibit a quasi identical steep rise at short times without time lag, suggesting that bubble formation and noble gas catchment are simultaneous. The time evolution of the vesicularity $V^*$ is also shown for comparison (thick black curve). Notice that the vesicularity of the sample reaches a plateau value equal to 0.534 which is precisely the value expected from thermodynamics at equilibrium (Eq.(7)). For a rapid check, read in Fig.1 the value of the vesicularity at 10 kbar for an ascending melt saturated at 100 kbar (the curve marked 29 wt% in Fig.1).
To describe the noble gas-CO$_2$ interactions, we have used the molecular models for binary mixtures developed by Vrabec et al. (2001, 2009) where the pair potential between a noble gas atom $X$ and a $CO_2$ molecule is given by a sum of two Lennard-Jones (L-J) potentials,

$$u_{X,CO_2} = \sum_{n=1,2} \sum_{XO_n} 4\varepsilon_{XO} \left[ \left( \frac{\sigma_{XO}}{r_{XO_n}} \right)^{12} - \left( \frac{\sigma_{XO}}{r_{XO_n}} \right)^6 \right]$$  \hspace{1cm} (A1)

where $\varepsilon_{XO}$ and $\sigma_{XO}$ are L-J parameters and $r_{XO_n}$ is the distance between the noble gas atom $X$ and one of the two oxygen atoms ($n=1,2$) belonging to the $CO_2$ molecule. The interaction between the noble gas and the carbon atom is not considered because the latter one is deeply embedded into the electronic clouds of the oxygen atoms. Trial values for $\varepsilon_{XO}$ and $\sigma_{XO}$ are deduced from the Lorentz-Berthelot combining rules,

$$\sigma_{XO} = \frac{\sigma_X + \sigma_O}{2} \hspace{1cm} (A2)$$

$$\varepsilon_{XO} = \sqrt{\varepsilon_X \varepsilon_O} \hspace{1cm} (A3)$$

where $\sigma_X, \sigma_O, \varepsilon_X$ and $\varepsilon_O$ are L-J parameters describing the pure fluids (for He, see Dykstra (1989), and for Ne, Ar and Xe, see Vrabec et al. (2001). Although the Lorentz-Berthelot combining rules are widely used to model binary mixtures, there is room for improvement. So, we have followed the procedure of Huang et al. (2009) which consists in introducing an adjustable parameter, $\xi_X$, in the Lorentz-Berthelot rule for the pair energy parameter,

$$\varepsilon_{XO} = \xi_X \sqrt{\varepsilon_X \varepsilon_O} \hspace{1cm} (A4)$$

to reproduce at best Henry's constant of noble gases in liquid $CO_2$.

From a computational standpoint, Henry's constant, $H_X$, of a noble gas $X$ in a liquid solvent $S$ writes

(Shing et al., 1988)
where \( \rho \) is the numerical density of the solvent (e.g. \( CO_2 \)), \( T \) the temperature, \( k_B \) the Boltzmann constant, and \( \gamma_S^X \) the solubility parameter of the noble gas \( X \) in the solvent. We have evaluated the Henry constant of He, Ne, Ar and Xe in liquid \( CO_2 \) at 273K by implementing the TPM (see Eq.(8)). Computational details are the same as those given in section 2.3. Thus, the simulated liquid sample is composed of 500 \( CO_2 \) molecules interacting through the Zhang and Duan potential (2005) modified by Guillot and Sator (2011) for bending, and the insertion energy of the noble gas atom in liquid \( CO_2 \) is calculated with the pair potential described above. For each noble gas, the Henry constant is evaluated via Eq.(A5) in adjusting by trial and error the parameter, \( \xi_X \), to reproduce at best the noble gas solubility data of the literature. Final values of the L-J potential parameters for noble gas-\( CO_2 \) interactions are given in Table A1 as also as the comparison between calculated and measured Henry’s constants.

### Table A1

L-J potential parameters for noble gas-\( CO_2 \) interactions and comparison between calculated and experimental values for the Henry constant at 273K.

| \( X \) | \( \sigma_{XO} \)(Å) | \( \varepsilon_{XO} \)(kJ/mol) | \( H_X^{calc} \)(bar) | \( H_X^{exp} \)(bar) |
|---|---|---|---|---|
| He | 2.81 | 0.525 | \( 2.0 \pm 0.2 \times 10^3 \) | \( a_{2.05 \pm 0.35 \times 10^3} \) |
| Ne | 2.89 | 0.671 | \( 1.5 \pm 0.2 \times 10^3 \) | \( b_{1.2 \pm 0.2 \times 10^3} \) |
| Ar | 3.19 | 1.131 | \( 3.0 \pm 0.3 \times 10^2 \) | \( c_{3.4 \pm 0.6 \times 10^2} \) |
| Xe | 3.44 | 1.317 | 90±10 | \( d_87 \) |

a Mackendrick et al., 1968
b Sasinovskii, 1979
c Kaminishi et al., 1968
d Ackley and Notz, 1976
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Fig. 1
Fig. 2

- This study
- Atlantic
- Indian
- Pacific

Vesicularity vs. CO$_2$ (g/g)
Fig. 3
Fig. 4
Fig. 5
Fig. 6
Fig. 7

(a)
Fig. 8