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Noble gases in carbonate melts: constraints on the solubility and the surface tension by molecular dynamics simulation

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Although they are rare elements in the Earth’s mantle, noble gases (NG) are important geochemical tracers because of their chemical inertness, the specificity of their isotopes and their strongly varying sizes (a factor > 50 in mass from He to Rn). When partial melting occurs at depth, the partitioning of NGs between phases is controlled by a distribution coefficient that can be determined from the solubility of the NGs in each phase. Here we report quantitative calculations of the solubility of He, Ne, Ar and Xe in carbonate melts based on molecular dynamics simulations. The NG solubilities are first calculated in K2CO3-CaCO3 mixtures at 1 bar and favorably compared to the only experimental data available to date. Then we investigate the effect of pressure (up to 6 GPa), focusing on two melt compositions: a dolomitic one and a natrocarbonatitic one (modeling the lava emitted at Ol Doinyo Lengai, Tanzania). The solubility decreases with the amount of alkaline-earth cation in the melt and with the size of the noble gas. In the natrocarbonatitic melt, Henry’s law is fulfilled at low pressures (up to ~ 0.1 GPa). At higher pressures (a few GPa) the solubility levels off or even starts to diminish smoothly (for He at \( P > 2 \) GPa and Ar at \( P > 4 \) GPa). In contrast, in molten dolomite the effect of pressure is negligible on the studied \( P \) range (3 – 6 GPa). At the pressures of the upper part of the upper mantle, the solubilities of noble gases in carbonate melts are still of the same order of magnitude as the ones in molten silicates (100 – 101 mol%). This suggests that carbonatitic melts at depth are not preferential carriers of noble gases, even if the dependence with the melt composition is not negligible and has to be evaluated on a case-by-case basis.

Finally we evaluate the surface tension at the interface between carbonate melts and noble gases and its evolution with pressure. Whatever the composition of the melt and of the NG phase, the surface tension increases (by a factor ~ 2) when \( P \) increases from 0 to 6 GPa. This behavior contrasts with the situation occurring when \( \text{H}_2\text{O} \) is in contact with silicate melts (then surface tension drops when pressure increases to a few GPa).

Keywords: molten carbonates, noble gases, solubility, surface tension

I. INTRODUCTION

By the time of accretion, noble gases were already present in proto-Earth material.1,2 Their concentration in the mantle has since evolved through the competing effect of volcanic degassing and radioactive decay. Although they are inert species their strongly varying masses in the series from He to Rn confer them contrasting physical behaviors in the Earth’s mantle. Hence these elements (and their isotopes even more so) constitute important geochemical tracers.3 More specifically, noble gases are incompatible in mantle rocks and tend to partition into the liquid phase when partial melting occurs at depth. In a more general perspective, the noble gas systematics provides an insight into the past and present dynamics of the carbon-bearing phases (silicates and/or carbonates) in the Earth’s mantle (e.g. the carbon cycle).4 Hence solubility data under high pressure and in different magmatic liquids, are required in order to study these phenomena. Whereas many studies have been devoted to the solubility of noble gases in molten silicates (mainly at low pressures),5–10 very little is known concerning their behavior in carbonate melts which are yet of particular interest.11–14

To date, the only experimental constraints are given by Burnard et al.,13 who measured the solubility of noble gases in quenched carbonate melts. In this approach the concentration in the liquid is assumed to be the same as in the glass resulting from the quenching. Moreover the quenching is considered to be fast enough to avoid crystal quenching. The study reported the solubility of He and Ar in some \( \text{K}_2\text{CO}_3\)-\( \text{CaCO}_3 \) mixtures at 1 bar between 1123 and 1223 K. The authors also attempted to study Mg-bearing carbonate melts, but could not succeed in quenching them into a glass.

By contrast, in a molecular dynamics (MD) simulation the liquid phase can always be studied, regardless of its composition (and of the pressure/temperature condition). The relevance of the liquid properties calculated from a MD simulation relies on the quality of the implemented interaction potential or force field (FF). The adjustment of the FF generally is system-specific. In a previous study we have presented a FF to model carbonate melts in the \( \text{CaCO}_3\)-\( \text{MgCO}_3\)-\( \text{K}_2\text{CO}_3\)-\( \text{Na}_2\text{CO}_3\)-\( \text{Li}_2\text{CO}_3 \) system, and demonstrated that it leads to an accurate reproduction of their thermodynamics, structure and transport properties.15,16 Here we perform molecular dynamics simulations based on this FF to study the solu-
bility of noble gases (from He to Xe) into K$_2$CO$_3$-CaCO$_3$ mixtures (for comparison with the data of Burnard et al.\textsuperscript{13}) and into dolomitic and natrocarbonatitic melts to investigate the evolution with pressure (up to 6 GPa). First we present in the Method section II how to evaluate the noble gas solubility. The results are discussed in the section Solubility. Finally, the surface tension of carbonate melts in contact with a noble gas fluid is evaluated and discussed (section Surface Tension).

II. METHOD

A. Force Field

To describe the interactions within the carbonate melt we used the interatomic FF proposed by Desmaele \textit{et al.}\textsuperscript{15,16} The interactions between noble gas (NG) atoms were modeled by the FF used by Guillot and Sator.\textsuperscript{17} These Buckingham potentials (see Eq. (A.1) in Appendix A) were adjusted on the accurate potential energy surface derived by Tang and Toennies.\textsuperscript{18} As for the interactions between the NG and the carbonate melt elements, they are described by two contributions, a NG-cation and a NG-carbonate one, both of them being modeled by Lennard-Jones (LJ) potentials (Eq. (A.2)). For the NG-cation interactions we used the LJ parameters established by Aubry \textit{et al.}\textsuperscript{19} for the system {silicate + CO$_2$ + NG} and the interactions between the NG and the oxygen atoms of the carbonate ions, we retained the parameters established by Aubry \textit{et al.}\textsuperscript{19} for the system {silicate + CO$_2$ + NG} and set the interactions between the NG and the carbon atom of the carbonate anion to zero, as the carbon is considered to be screened by the surrounding oxygen atoms\textsuperscript{15,16} (in fact, the carbon atom is deeply embedded into the oxygen electronic clouds). The choice of such a force field is based on the assumption that the interaction potentials between NGs and melts cited above are transferable from a melt to another (e.g. CO$_2$-bearing silicate to carbonate). It is justified a posteriori by the agreement between the calculated solubilities and the solubility data of Burnard \textit{et al.}\textsuperscript{13} (see the section IIIISolubility).

B. Solubility calculations

1. Test Particle Method (TPM)

At low pressure $P$, the solubility $X$ of a noble gas in a melt is given by Henry’s law

$$X = P/k_B T.$$  \hspace{1cm} (1)

In this relation the Henry constant is written as

$$k_H = \rho_m k_B T/\Gamma_m,$$  \hspace{1cm} (2)

where $\rho_m$ is the number density of the pure melt, $k_B$ the Boltzmann constant, $T$ the temperature, and $\Gamma_m = e^{-\mu_{i,x}^T/k_B T}$ an activity coefficient with $\mu_{i,x}^T$ the excess chemical potential of the solute $i$ (e.g. a noble gas) in the melt for a given set of $T, P$ conditions (for a detailed thermodynamic derivation see Appendix B 1).

The solubility of noble gases in the melt was calculated by the Test Particle Method (TPM) introduced by Widom.\textsuperscript{20} This method allows to determine the excess chemical potential of a solute in a solvent, as a function of the potential energy distribution seen by the solute inserted in the solvent (at infinite dilution), namely

$$\mu_{i,x} = -k_B T \ln(e^{-\Psi_i/k_B T})_0,$$  \hspace{1cm} (3)

where $\Psi_i$ is the interaction energy between the solute $i$ and the solvent (e.g. a carbonate melt) in which it is solvated, and $\langle \cdots \rangle_0$ means that a statistical averaging is done on the solvent molecules only, at a given $(T,P)$ condition. Notice that the solute particle acts as a ghost particle, and that many insertions of the latter particle in the solvent configurations are needed to accurately evaluate $\mu_{i,x}$ (for further details see Guillot and Sator\textsuperscript{17} and Appendix B 2).

In practice a set of microscopic configurations of the melt is first generated by MD. Then the insertion of the solute particle (the noble gas atom) is attempted many times into the MD-generated configuration. For each insertion of the solute particle the interaction energy $\Psi$ is calculated.

The solubility parameter $\Gamma_i$ is then evaluated by the averaging over all the attempted insertions

$$\Gamma_i = e^{-\mu_{i,x}^T/k_B T} = \langle e^{-\Psi_i/k_B T} \rangle,$$  \hspace{1cm} (4)

where $N_{\text{test}}$ is the number of attempted insertions. According to this method, the solubility parameter $\Gamma_i$ can be evaluated in the two coexisting phases: the carbonate melt and the noble gas phase (providing $\Gamma_m$ and $\Gamma_v$), and the solubility of the NG can be easily obtained from Eqs. (1) or (B.4).

C. Explicit Interface Method (EIM)

As an alternative to the TPM, the solubility of a gas in a melt can be calculated from a numerical experiment which consists in simulating explicitly the equilibrium between the two phases (for further details see Guillot and Sator\textsuperscript{17,21}). The solubility is then simply obtained by counting the average number of noble gas atoms in the melt, once equilibrium is reached between the two phases, i.e. when the liquid is saturated in gas (Figure 1).

D. Complementarity between the two methods

Depending on the thermodynamic conditions of interest, one of the two methods presented above is the most...
appropriate one to calculate the solubility. Thus in the framework of the TPM, the solubility parameter $\Gamma_m$ is theoretically defined at infinite dilution, which means that it is only meaningful for low concentrations of NG in the melt. On the contrary the explicit interface method (EIM) becomes useful when the pressure of the gas phase is sufficiently high for the simulated melt to accommodate a significant number of NG atoms. In brief, the TPM will be used at low pressures and the EIM at high pressures.

In this context we have checked that the two methods give results that are consistent with one another. For example in natrocarbonatite ($\text{Na}_{1.13}\text{K}_{0.18}\text{Ca}_{0.6}\text{CaCO}_3$) at 1600 K and 0.1 GPa: $X_{\text{Ne}}^{\text{TPM}} = 0.78 \pm 0.01 \text{ mol\%}$ (using Eq. (B.4) with $\Gamma_m = 16.66 \pm 0.04 \times 10^{-3}$, $\Gamma_v = 820.5 \pm 0.1 \times 10^{-3}$, $\rho_m = 17.98 \text{ mol/L}$ and $\rho_v = 6.947 \text{ mol/L}$) and $X_{\text{Ne}}^{\text{EIM}} = 0.84 \pm 0.10 \text{ mol\%}$. Note that the rather large uncertainty on $X_{\text{Ne}}^{\text{EIM}}$ (see Figure 1) is due to the relatively low pressure (0.1 GPa) considered here.

III. SOLUBILITY

A. Low pressure

First we focus on the mixtures studied by Burnard et al.\textsuperscript{13} namely $K_2\text{CO}_3-\text{CaCO}_3$ mixtures at 1173 K ($\pm 50$ K in the experimental study) and 1 bar. The solubilities calculated by MD by the means of the TPM, and the ones measured by Burnard et al.\textsuperscript{13} are reported on Figure 2. For some mixtures Burnard et al.\textsuperscript{13} have made several measurements of the solubility of helium. However their measurements show considerable scatter and vary by a factor $> 2$ and sometimes by as much as 10 for a given composition (the effect of temperature cannot be discerned given the large scattering of the measured values and is likely small in the range 1123 – 1223 K). According to the authors, this could be due to the fast diffusion of the He gas out of the glass upon quenching. This He loss is likely systematic although its magnitude is variable. Moreover they stress that some samples are partially crystallized which proportionally diminishes the value of the solubility. So the solubility data given by Burnard et al.\textsuperscript{13} for He should be considered as a lower limit. Hence the results of our simulations for He are compatible with the measurements of Burnard et al.\textsuperscript{13} For Ar, Burnard et al.\textsuperscript{13} only provide the result of one batch of experiments which strongly suggest that the experimental results are only preliminary and very likely prone to large errors. For example, as it may be seen on Figure 2, the value at $x_{K_2\text{CO}_3} = 1/3$ seems off-trend (unexpectedly low).

Beside He and Ar, we report the solubility for Ne and Xe. For a given composition of the liquid, the solubility increases as the atomic radius of the NG decreases. This behavior is similar to the one observed in silicates. In using the TPM, two of us have shown that the NG solubility is the result of an entropy-enthalpy balancing (see Guillot and Sator\textsuperscript{17} for a detailed discussion). As a matter of fact, the excess chemical potential of a NG in a liquid solvent (Eq. (3)) can be expressed as a sum of an energetic contribution ($E_i^\mu$) and an entropic one ($\Delta S_i^\mu$), namely

$$\mu^{ex,i} = E_i^\mu - T\Delta S_i^\mu.$$  \hspace{1cm} (5)

In molten carbonates as in molten silicates, the entropic cost for inserting the NG in the melt (i.e. the entropy cost for cavity formation and reorganization of the solvent particles around the solute) is the dominant contribution to the excess chemical potential ($\Delta S_i^\mu < 0$ for all NGs), whereas the solute-solvent energy ($E_i^\mu$) leads to a much weaker contribution. Thus it is the entropic contribution which makes the solubility decrease when the size of the NG increases (not shown).\textsuperscript{17}

In their study, Burnard et al.\textsuperscript{13} reported that the solubility is hardly sensitive to the composition of the melt. We believe that the high uncertainties on their data are accountable for this observation. On the contrary...
FIG. 2. Molar fraction of He, Ne, Ar and Xe dissolved in various K$_2$CO$_3$–CaCO$_3$ mixtures at 1173(±50) K and 1 bar. The TPM results from this study (T = 1173 K) are represented by plain black symbols, the measurements of Burnard et al.$^{13}$ (T = 1123 – 1223 K) by red empty symbols. The error bars for the MD results are of the order of the size of the symbols (see text).

MD simulations reveal that the composition of the melt has a strong effect (especially for $x_{K_2CO_3} < 0.25$ and $x_{K_2CO_3} > 0.4$), regardless of the noble gas species that is considered. In fact the solubility decreases continuously when the content of calcite increases. For instance the solubility of He contrasts by an order of magnitude between the two end-members K$_2$CO$_3$ end CaCO$_3$ (see Figure 2).

B. Evolution with pressure

Simulating a biphasic system (EI method) enables to calculate the NG solubility under high pressures. We focus on two carbonate melts: molten dolomite (Ca$_{0.5}$Mg$_{0.5}$CO$_3$) at 1673 K and a Na$_2$CO$_3$–K$_2$CO$_3$–CaCO$_3$ mixture (in proportions 55, 9 and 36 mol%, respectively) at 1600 K, modeling the natrocarbonatite emitted at Ol Doinyo Lengai.$^{16,22}$ Figure 3 reports the solubility of He, Ne, Ar and Xe calculated at pressures ranging from 3 to 6 GPa for dolomite, and from 0.1 to 6 GPa for the natrocarbonatite. The solubilities in the natrocarbonatite were also calculated at 1 bar using the TPM.

Over the whole studied pressure range, the solubility of a given NG is greater in the natrocarbonatite than in molten dolomite. This is consistent with the decrease of the solubility when increasing the molar fraction of alkaline-earth cation as observed at low pressure in K$_2$CO$_3$–CaCO$_3$ mixtures (Figure 2). The observation that the solubility is negatively correlated with the size of the NG still stands at high pressure (at least up to 3 GPa). However beyond 3 GPa, the solubilities of Ne and He come close to each other in natrocarbonatite and even tend to cross at about 6 GPa (He shows a solubility maximum at about 2 GPa), features which are also observed in dolomite. In the same way, the solubility of Xe in natrocarbonatite increases steadily and becomes as high as the one of Ar at 6 GPa, the latter leveling off at about 1 GPa.

In the natrocarbonatite melt, the solubility of NGs first increases quasi linearly with pressure, so Henry’s law is fulfilled up to a few kbar (Figure 3). Above ~ 1 GPa the solubility generally levels off and it even goes through a maximum for He at $P \sim 2$ GPa and for Ar at $P \sim 4$ GPa. As for Xe, its solubility is quasi linear with $P$ (up to ~ 2 GPa). In molten dolomite, the solubility of noble gases barely depends on pressure between 3 and 6 GPa. In comparison the solubility of noble gases in silicate
melts increases up to ~ 5 GPa. At higher pressures, some experimental studies report a drop of the solubility\cite{10} and other do not.\cite{9,23} In their simulation study Guillot and Sator\cite{17} show a good agreement with the experimental results up to ~ 5 GPa and predict a plateau value for the solubility with a slowly decreasing behavior at higher pressures. This trend is similar to what we observe in molten carbonates (Figure 3), although the solubility plateau occurs at a lower pressure for carbonates. Notice that the solubility plateau is reached when the density of the NG phase becomes liquid-like (i.e. is greater than the density of the corresponding low temperature liquid at the triple point) and competes with that of the carbonate phase. In any case at the pressures of the upper part of the upper mantle, our results point out that the solubility of the noble gases has the same order of magnitude in molten carbonates and in molten silicates.\cite{17} This suggests that noble gases would not partition massively in a carbonated phase. However, seeing the significant dependence of the NG solubilities with the composition of the melt (a factor of ~ 3 for Ar in dolomitic versus natrocarbonatitic melts, see the inset of Figure 3) the investigation of the partition coefficients between carbonate and silicate deserves further studies. Still, considering that carbonate melts only represent a minor fraction of magmatic liquids, they can unlikely be the main carrier of noble gases.

IV. SURFACE TENSION

To our knowledge, there are no data of the pressure evolution of the surface tension at the interface between a noble gas phase and molten carbonates, despite the interest from a geochemical perspective. For example if we consider a gas-saturated magmatic melt, it is the liquid/gas surface tension that controls the formation, the growth and the coalescence of gas bubbles below a certain supersaturation pressure.\cite{24} By simulating a biphasic system in MD as shown in Figure 1 for the calculation of the solubility by the EIM, the surface tension $\gamma$ can be calculated simultaneously for the same computational cost. It is given by the long time limit of the average of the diagonal components of the stress tensor:\cite{25}

$$\gamma = \lim_{t \to \infty} \gamma(t),$$

with

$$\gamma(t) = \frac{L_z}{2} \langle \Pi_{zz} - \frac{1}{2}(\Pi_{xx} + \Pi_{yy}) \rangle,$$

where

$L_z$ is the length of the simulation box perpendicular to the interface and $\Pi_{xx}$, $\Pi_{yy}$ and $\Pi_{zz}$ are the diagonal components of the stress tensor evaluated in the entire simulation box (see Desmaele et al.\cite{15} for more details).

Figure 4 plots the surface tension between the natrocarbonatitic (or dolomitic) melt and the noble gas phase (He, Ne, Ar and Xe), calculated at different pressures. For natrocarbonatite at 1600 K the surface tension was also calculated at the interface with a vacuum (190 ± 3 mN/m). This value compares well with the ones obtained at the interface with noble gases at 0.1 GPa (171 – 206 mN/m).

Irrespective of the nature of the melt and of the noble gas considered, the surface tension increases with increasing pressure. In contrast, it is known that the surface tension of silicate melts in contact with H$_2$O decreases with pressure,\cite{26} because the solubility of water is high (about 30 mol% at 0.5 GPa) and tends to depolymerize the silicate melt. In the case of water, the vapor phase contains a significant concentration of silicate elements, whereas in the present case the coexisting noble gas phase is pure and is not contaminated by the carbonate phase. However the dissolved gas does not seem to play an important role as the rather large differences of solubility observed between the four gases (almost a factor of ten between He and Xe, see Figure 3) are not retrieved for the surface tension (see Figure 4). In fact it is found that the increase of the surface tension with pressure is correlated with the decrease of the compressibility of the carbonate melt with pressure (not shown).\cite{15,16,27,28}

There is also a distinct effect of the melt composition on the surface tension: For a given noble gas species and at a given pressure, the surface tension of dolomite is greater than the one of the natrocarbonatite by ~ 50%. This increase of the surface tension with the amount of alkaline-earth cations in the melt is also observed at the
interface with a vacuum (compare the values of $\gamma$ for the natrocarbonatite and for the CaCO$_3$ melt on Figure 4).

As for the effect of the gas composition, it is trickier to decipher. At a given pressure and for a given melt composition, there is no systematic trend of the surface tension as a function of the size of the noble gas atom (except for He in dolomite, see Figure 4). Moreover, when pressure is increased the hierarchy between noble gases seems to modify somewhat. It is possible that the uncertainties on the calculated values are greater than the ones we estimate from the fluctuations ($\sim 5\%$, see Figure C.1 in the appendix) of the running average of Eq. (6).

V. CONCLUSION

To complete and go beyond the precursory study of Burnard et al., the solubility of noble gases (He, Ne, Ar and Xe) in carbonate melts was calculated by molecular dynamics simulations. These simulations used empirical interaction potentials whose accuracy was previously demonstrated in studying the thermodynamic and transport properties of carbonate melts and the solubility of noble gases in silicate melt.\textsuperscript{15–17,29}

The NG solubilities were first calculated in K$_2$CO$_3$–CaCO$_3$ mixtures at 1 bar and the results are in a fair agreement with the data of Burnard et al.\textsuperscript{13} once the uncertainties on the experimental values are considered. Then we investigated the effect of pressure (up to 6 GPa), focusing on two melt compositions: a dolomitic one and a mixture modeling the carbonatitic lava emitted at Ol Doinyo Lengai. We observed that the solubility decreases with the amount of alkaline-earth cation in the melt and with the size of the noble gas (entropy-driven solubility). Concerning the solubility in the natrocarbonatitic melt, Henry’s law is fulfilled at low pressures ($\sim 0.1$ GPa). At higher pressures (a few GPa) the solubility levels off or even starts to diminish smoothly (for He at $P > 2$ GPa and Ar at $P > 4$ GPa). In contrast, in molten dolomite the effect of pressure is negligible on the studied $P$ range ($3 – 6$ GPa). At the pressures of the upper part of the upper mantle, the solubilities of noble gases in carbonate melts are still of the same order of magnitude as the ones in molten silicates, a finding in agreement with the ratio $^{4}\text{He}/^{10}\text{Ar}$ measured in the gas emitted from Ol Doinyo Lengai crater in 2005, which is close to the mantle value (see Fischer et al.\textsuperscript{30}). Furthermore this finding also suggests that carbonatitic melts at depth cannot be preferential carriers of noble gases. Finally we provided some insight into the surface tension at the interface between carbonate melts and noble gases. With increasing pressure ($P$ from 0 to 6 GPa), the surface tension increases (by a factor $\sim 2$), irrespective of the composition of the melt and of the NG phase. This is in strong contrast to the effect of H$_2$O on the surface tension of silicate melts which drops when pressure increases to a few kbar.

ACKNOWLEDGMENTS

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Appendix A: Force Field

The interactions between two noble gas (NG) atoms $i$ and $j$ were modeled by the FF used by Guillot and Sator\textsuperscript{17} and consisting of Buckingham potentials:

$$V_{ij}(r_{ij}) = A_{ij} \exp\left(-r_{ij}/\rho_{ij}\right) - C_{ij}/r_{ij}^6. \quad (A.1)$$

Values of the parameters for these interactions are summarized in Table A.1.

For the interactions within the carbonate melts we used the FF developed in Desmaele et al.\textsuperscript{15,16}. The intramolecular potential energy associated with a carbonate molecule anion consists of an oxygen-oxygen repulsive potential as in Eq. (A.1) and of a carbon-oxygen potential (harmonic stretching + coulombic interaction):

$$V_{\text{intra}}^{CO}(r_{CO}) = \frac{1}{2}k_{CO}(r_{CO} - r_{0,CO})^2 + q_CO/q_C/4\pi\epsilon_0r_{CO}. \quad (A.2)$$

Moreover, two elements $i$ and $j$, with $i, j = \text{Na, K, Ca, Mg, O and C}$ (with O and C not belonging to a same carbonate group) interact through a pair potential:

$$V_{ij}(r_{ij}) = A_{ij} \exp\left(-r_{ij}/\rho_{ij}\right) - C_{ij}/r_{ij}^6 + q_iq_j/4\pi\epsilon_0r_{ij},$$

that is a sum of a van der Waals (Buckingham-like) and of a coulombic term. All the parameters for the melt-melt interactions are summarized in Table A.2.

For the NG-melt interactions we used Lennard-Jones potentials:

$$V_{ij}(r_{ij}) = 4\epsilon_{ij}\left((\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6\right), \quad (A.2)$$

as adjusted by Guillot and Sator\textsuperscript{17} and by Aubry et al.\textsuperscript{19} (Table A.3).

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<td>2.142</td>
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<td>0.663</td>
<td>3.056</td>
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<td>3.386</td>
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<tr>
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<td>1.317</td>
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<th>$\sigma_{He}$</th>
<th>$\epsilon_{Ne}$</th>
<th>$\sigma_{Ne}$</th>
<th>$\epsilon_{Ar}$</th>
<th>$\sigma_{Ar}$</th>
<th>$\epsilon_{Xe}$</th>
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Appendix B: The Test Particle Method

1. Thermodynamics

Calculating the solubility of a noble gas within a melt involves considering a thermodynamic equilibrium between the gas and the melt (in contact with each other), expressed by the equality of the chemical potentials of the gas in both phases:

\[ \mu_v = \mu_m \quad \text{(B.1)} \]

The chemical potentials can be decomposed as the sum

\[ \mu_{v,m} = \mu_{v,m}^{IG} + \mu_{v,m}^{ex} \]

of an ideal gas part

\[ \mu_{v,m}^{IG} = C + k_B T \ln \rho_v^{\theta} \quad \text{(B.2)} \]

where \( \rho^\theta \) is the number density of the noble gas phase in its pure phase (\( \rho_v^\theta \)) or in the melt (\( \rho_m^\theta \)) and \( C \) is a constant that is equal in both phases (gas and melt), and an excess part \( \mu_{v,m}^{ex} \) (\( \mu_v^{ex} \) in the gas phase, \( \mu_m^{ex} \) in the melt). Introducing Eq. (B.2) into Eq. (B.1) leads to:

\[ \frac{\rho_v^\theta}{\rho_v^M} = e^{-(\mu_m^{ex} - \mu_v^{ex})/k_BT} = \frac{\Gamma_v^m}{\Gamma_v} \quad \text{(B.3)} \]

where \( \rho_v^\theta \) and \( \rho_v^M \) are the number densities of the gas in the melt and in the vapor phase, respectively, and \( \Gamma_v^m \) and \( \Gamma_v \) are the inverse of an activity coefficient and of a fugacity coefficient, respectively.

The solubility of the gas in the melt, expressed as the number of moles of gas in the melt divided by the number of moles of melt and of noble gas (throughout the present manuscript the number of moles of melt is taken as the number of moles of \( \text{CO}_3^{2-} \) units), is given by

\[ X = \frac{\rho_v^\theta \cdot \Gamma_v^m}{1 + \rho_v^\theta \cdot \frac{\Gamma_v}{\Gamma_v^m}} \quad \text{(B.4)} \]

where \( \rho_v \) is the number density of the gas phase and \( \rho_m \) is the number density of the melt.

At low pressure, the gas phase can be considered as ideal: \( \mu_v^{ex} = 0 \) (i.e. \( \Gamma_v = 1 \) and \( P = \rho_v k_B T \)) thus

\[ \rho_v^\theta = \Gamma_v^m \rho_v^M = \Gamma_v P/k_BT \]

Then equation (B.4) leads to Henry’s law:

\[ X = P/k_H \quad \text{(B.5)} \]

where \( k_H = \rho_m k_B T/\Gamma_m \). In this case, only the solubility parameter of the noble gas in the melt, \( \Gamma_m \), has to be calculated.

2. Simulation details

Classical MD simulations of the carbonate melt (\( N \approx 1000 \) atoms) were carried out using the DL_POLY 2 software,\(^{31}\) with a timestep of 1 fs. The simulations were performed in the NVE ensemble with an equilibration run of 0.5 ns, followed by a production run of at least 10 ns. Insertion of the test particle in the simulation box was attempted every 1000 timesteps (1 ps) on a grid of width \( dL \), with \( L/dL = 10 \) to 50 (i.e. the grid has \( 10^3 = 1000 \) to \( 50^3 = 125000 \) nodes, Figure B.2 evidences that convergence is reached for \( L/dL \geq 30 \)). In practice, if the distance between the node and a solvent atom is too small (within a defined cutoff radius \( r_{min} \)), the test-particle is rejected and its contribution to \( e^{-\Psi_i/k_BT} \) is null. Only the events where the test-particle is inserted within a solvent cage are significant for the solubility (green circle).

3. Data

For more detailed applications with MD, see Guillot and Aubry\(^{17}\) and Aubry et al.\(^{19}\)
FIG. B.2. Solubility parameter $\Gamma = \langle e^{-\Phi/k_BT} \rangle$ of He, Ne, Ar and Xe in a carbonate melt (e.g. natrocarbonatite at 1600 K and 0.1 GPa) calculated as a cumulative average over simulation length. The distance between two attempted insertions of the particle is given by $dL$, $L$ is the length of the simulation box (see text).

<table>
<thead>
<tr>
<th>$x_{\text{K}_2\text{CO}_3}$</th>
<th>$\rho_m$ (mol/L)</th>
<th>$\Gamma_{\text{He}}$ ($\times 10^3$)</th>
<th>$\Gamma_{\text{Ne}}$ ($\times 10^3$)</th>
<th>$\Gamma_{\text{Ar}}$ ($\times 10^3$)</th>
<th>$\Gamma_{\text{Xe}}$ ($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>24.08</td>
<td>2.69 ± 0.03</td>
<td>1.74 ± 0.04</td>
<td>0.27 ± 0.01</td>
<td>0.059 ± 0.05</td>
</tr>
<tr>
<td>0.25</td>
<td>20.12</td>
<td>6.70 ± 0.02</td>
<td>4.43 ± 0.02</td>
<td>0.96 ± 0.02</td>
<td>0.26 ± 0.02</td>
</tr>
<tr>
<td>0.33</td>
<td>19.39</td>
<td>6.65 ± 0.03</td>
<td>4.24 ± 0.03</td>
<td>0.80 ± 0.02</td>
<td>0.17 ± 0.03</td>
</tr>
<tr>
<td>0.4</td>
<td>19.67</td>
<td>7.29 ± 0.05</td>
<td>4.60 ± 0.04</td>
<td>0.83 ± 0.02</td>
<td>0.17 ± 0.02</td>
</tr>
<tr>
<td>0.5</td>
<td>17.66</td>
<td>8.63 ± 0.03</td>
<td>5.47 ± 0.03</td>
<td>1.08 ± 0.03</td>
<td>0.26 ± 0.03</td>
</tr>
<tr>
<td>1</td>
<td>13.77</td>
<td>16.00 ± 0.07</td>
<td>10.62 ± 0.06</td>
<td>2.66 ± 0.07</td>
<td>0.79 ± 0.03</td>
</tr>
</tbody>
</table>

| $P = 1$ bar | 17.64 | 27.97 ± 0.05 | 20.90 ± 0.05 | 6.95 ± 0.06 | 3.22 ± 0.06 |
| $P = 0.1$ GPa | 17.98 | 22.91 ± 0.04 | 16.66 ± 0.04 | 4.94 ± 0.03 | 2.09 ± 0.03 |

TABLE B.1. Solubility parameters of NGs in melts: $\text{K}_2\text{CO}_3$–$\text{CaCO}_3$ (KC) mixtures of different ratios at 1173 K and 1 bar and natrocarbonatite ($\text{Na}_{1.18}\text{K}_{0.18}\text{Ca}_{0.36}\text{CO}_3$, NKC) at 1600 K, calculated by MD using the TPM.
Appendix C: The Explicit Interface Method

1. Simulation details

The EIM simulations consisted in modeling the solvent ($N \approx 2000$ atoms of melt) in contact with a NG phase in a parallelepipedic simulation box. The number of NG atoms in the box ($N \approx 300 - 900$ atoms) was chosen so that the vapor phase was large enough for the consecutive periodic images of the melt to not interact with one another.

An equilibration run was first performed in the $NPT$ ensemble (using a Nosé-Hoover thermostat) for 0.9 ns (including 0.5 ns to equilibrate the temperature) allowing to reach an accuracy on the density value of $\Delta n/n \sim \pm 1\%$ for the two coexisting phases. To evaluate the solubility $X$, simulations were performed in the $NVE$ ensemble with an equilibration run of 0.5 ns, followed by a production run of 10 ns. Configurations were extracted every 1 ps to determine the density profiles and calculate the surface tension between the NG fluids and the carbonate melts (Figure C.1).

![Figure C.1](image_url)

2. Data

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$X_{He}$ (mol%)</th>
<th>$X_{Ne}$ (mol%)</th>
<th>$X_{Ar}$ (mol%)</th>
<th>$X_{Xe}$ (mol%)</th>
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</thead>
<tbody>
<tr>
<td>NKC 0.1</td>
<td>$1.5 \pm 0.05$</td>
<td>$0.84 \pm 0.1$</td>
<td>$0.28 \pm 0.1$</td>
<td>$0.16 \pm 0.1$</td>
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<tr>
<td>1.0</td>
<td>$7.5 \pm 0.5$</td>
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<td>$1.7 \pm 0.1$</td>
<td>$0.5 \pm 0.15$</td>
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<td>2.0</td>
<td>$9.0 \pm 0.2$</td>
<td>$6.6 \pm 0.4$</td>
<td>$1.8 \pm 0.10$</td>
<td>$1.0 \pm 0.15$</td>
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<tr>
<td>4.5</td>
<td>$8.3 \pm 0.2$</td>
<td>$7.3 \pm 0.3$</td>
<td>$1.95 \pm 0.15$</td>
<td>$1.4 \pm 0.15$</td>
</tr>
<tr>
<td>6.0</td>
<td>$7.5 \pm 0.5$</td>
<td>$7.4 \pm 0.3$</td>
<td>$1.35 \pm 0.1$</td>
<td>$1.6 \pm 0.15$</td>
</tr>
</tbody>
</table>

| CM 3.0    | $3.1 \pm 0.4$  | $2.7 \pm 0.4$  | $0.45 \pm 0.05$| $0.12 \pm 0.03$ |
| 4.5       | $3.1 \pm 0.4$  | $3.0 \pm 0.3$  | $0.55 \pm 0.05$| $0.17 \pm 0.06$ |
| 6.0       | $2.7 \pm 0.2$  | $2.9 \pm 0.4$  | $0.55 \pm 0.1$ | $0.15 \pm 0.05$ |

TABLE C.1. Solubility of NGs in melts: natrocarbonatite (Na$_{1.1}$K$_{0.18}$Ca$_{0.36}$CO$_3$, NKC) at 1600 K and dolomite (Ca$_{0.5}$Mg$_{0.5}$CO$_3$, CM) at 1623 K, calculated using the EIM.

<table>
<thead>
<tr>
<th>$P$ (GPa)</th>
<th>$\gamma_{He}$ (mN/m)</th>
<th>$\gamma_{Ne}$ (mN/m)</th>
<th>$\gamma_{Ar}$ (mN/m)</th>
<th>$\gamma_{Xe}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NKC 0.1</td>
<td>$206 \pm 2$</td>
<td>$182 \pm 3$</td>
<td>$171 \pm 3$</td>
<td>$195 \pm 5$</td>
</tr>
<tr>
<td>1.0</td>
<td>$229 \pm 7$</td>
<td>$202 \pm 7$</td>
<td>$225 \pm 6$</td>
<td>$222 \pm 6$</td>
</tr>
<tr>
<td>2.0</td>
<td>$242 \pm 4$</td>
<td>$250 \pm 8$</td>
<td>$259 \pm 4$</td>
<td>$252 \pm 5$</td>
</tr>
<tr>
<td>4.5</td>
<td>$304 \pm 4$</td>
<td>$277 \pm 4$</td>
<td>$314 \pm 10$</td>
<td>$266 \pm 5$</td>
</tr>
<tr>
<td>6.0</td>
<td>$363 \pm 10$</td>
<td>$309 \pm 15$</td>
<td>$326 \pm 6$</td>
<td>$293 \pm 8$</td>
</tr>
</tbody>
</table>

| CM 3.0    | $398 \pm 7$           | $381 \pm 9$           | $357 \pm 6$           | $364 \pm 8$           |
| 4.5       | $444 \pm 9$           | $388 \pm 7$           | $406 \pm 12$          | $382 \pm 11$          |
| 6.0       | $468 \pm 10$          | $435 \pm 9$           | $413 \pm 11$          | $407 \pm 10$          |

TABLE C.2. Surface tension between NG fluids and melts: natrocarbonatite (Na$_{1.1}$K$_{0.18}$Ca$_{0.36}$CO$_3$, NKC) at 1600 K and dolomite (Ca$_{0.5}$Mg$_{0.5}$CO$_3$, CM) at 1623 K.


