The MgCO$_3$–CaCO$_3$–Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$ Carbonate Melts:
Thermodynamics and Transport Properties by Atomistic Simulations

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Atomistic simulations provide a meaningful way to determine the physico-chemical properties of liquids in a consistent theoretical framework. This approach takes on a particular usefulness for the study of molten carbonates, in a context where thermodynamic and transport data are crucially needed over a large domain of temperatures and pressures (to ascertain the role of these melts in geochemical processes) but are very scarce in the literature, especially for the calco-magnesian compositions prevailing in the Earth’s mantle.

Following our work on Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$ melts,$^{1, 2}$ we extend our force field to incorporate Ca and Mg components. The empirical interaction potentials are benchmarked on the density data available in the experimental literature (for the crystals and the K$_2$Ca(CO$_3$)$_2$ melt) and on the liquid structure issued from an ab initio molecular dynamics simulations. Molecular dynamics simulations are then performed to study the thermodynamics, the microscopic structure, the diffusion coefficients, the electrical conductivity and the viscosity of molten Ca, Mg-bearing carbonates up to 2073 K and 15 GPa. Additionally, the equation of state of a Na–Ca–K mixture representative of the lavas emitted at Ol Doinyo Lengai (Tanzania) is evaluated.

The overall agreement between the MD results and the existing experimental data is very satisfying and provides evidence for the ability of the force field to accurately model any MgCO$_3$–CaCO$_3$–Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$ melt over a large T–P range. Moreover it is the first report of a force field allowing to study the transport properties of molten magnesite (MgCO$_3$) and molten dolomite (CaMg(CO$_3$)$_2$).

Keywords: molten carbonates, molecular dynamics, equation of state, microscopic structure, transport properties, diffusion coefficients, electrical conductivity, viscosity, carbonatite

I. INTRODUCTION

Whether it is for the applied or the fundamental fields in which carbonate melts are implied (electrochemistry, geochemistry), having a reliable model for their alkali, alkaline-earth mixtures (and their end-members) is essential. For instance the longevity of molten carbonate fuel cells, usually based on alkali eutectic mixtures, is known to be improved by the addition of alkaline-earth cations,$^3$ in a small enough amount that doesn’t compromise the efficiency of the cell.$^3–7$ From the viewpoint of geosciences, carbonate melts, although they constitute a very minor phase of the Earth’s mantle (the most part is silicate), are thought to have important implications in the lowering of the melting temperature of silicate rocks, the deep carbon cycle or the high conductivity anomalies observed in the 70–200 km depth region.$^8–12$ On Earth, evidence of a past volcanic activity induced by carbonatitic lava (SiO$_2$ < 20 wt%) is given by petrology.$^{13, 14}$ Nowadays, Ol Doinyo Lengai in Tanzania is the only active volcano to produce these remarkable (low temperature, low viscosity) carbonatitic lavas. The carbonatitic melt is mainly composed of a Na$_2$CO$_3$–K$_2$CO$_3$–CaCO$_3$ mixture (in proportions 55:9:36 mol% according to Keller and Zaitsev$^{15}$), called natrocarbonatite, whereas the majority of other inventoried carbonatites are of calco-magnesian composition.$^{16}$ In addition, in the Earth’s mantle the most abundant carbonate compositions are calcite, CaCO$_3$, predominating at shallow depth and magnesite, MgCO$_3$, progressively taking over as depth increases. As a consequence their mixture and particularly dolomite, CaMg(CO$_3$)$_2$, are of major interest. For pressure of a few kbars and beyond, these Ca,Mg-carbonates form stable liquid phases over a wide temperature domain.$^{17–19}$ But at atmospheric pressure they break down into CO$_2$ + oxide (CaO, MgO) at temperatures below their melting point (decarbonation occurs for P below ~1 GPa for calcite and ~3 GPa for magnesite and dolomite)$^{20, 21}$ Consequently only a few data are available in the literature for calco-magnesian compositions (most of which are alkali-bearing mixtures stable at low pressure)$^{3, 9, 22}$ and very few at high pressures.$^{23–25}$ Thus for molten MgCO$_3$ there is simply no data to our knowledge.$^{20}$ In this context where experimental data are sparse in terms of thermodynamic conditions, chemical composition and physical properties, a noticeable advantage of molecular dynamics simulations (classical and ab initio) is that a variety of properties (structure, equation of state and transport coefficients) can be computed in the same theoretical framework. However, one has to be aware that collective quantities such as the ionic conductivity and the viscosity are calculated from slowly converging time correlation functions, that necessarily require (to be accurate) a rather large number of atoms and long time
runs. For this reason, ab initio molecular dynamics simulations (AIMD), deriving from electronic density calculations, are either restricted to the study of thermodynamic and structure properties or only provide crude estimates of transport coefficients, especially when it is question to establish their evolution with pressure and temperature. As for classical molecular dynamics simulations (MD), based on a more empirical approach, very few studies have provided estimates of the viscosity and electrical conductivity of carbonate melts, namely CaCO$_3$, the Li$_2$CO$_3$–K$_2$CO$_3$ eutectic mixture (62.38 mol%) and more recently the Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$ mixtures and end-members. Obviously, the scarcity of thermodynamic data does not help for developing empirical potentials. As a consequence, very few force fields (FF) are available for Ca-Mg and most of them were developed for crystals based on the Born model of solids. A first step towards an accurate description of the CaCO$_3$ melt was made by Genze et al. by adapting the FF of Dove et al. (for the crystal). The resulting FF reproduces quite well the liquid structure issued from a AIMD calculation published long after, but the calculated pressure is overestimated by $\sim +15$ kbar, compared to the recently published equation of state of Zhang and Liu based on AIMD calculations. Moreover the melting temperature is underestimated. Both these features point toward a too weakly cohesive melt, that may result from the absence of dispersion interaction in the FF. In another attempt Hurt and Wolf adapted the model of Archer et al. and proposed a FF fitted on crystalline properties for carbonates in the CaCO$_3$–SrCO$_3$–BaCO$_3$ system.

For MgCO$_3$, in absence of experimental data, Hurt and Wolf only list in their study some FF parameters, but no explanation on the way they were derived and no result is given for this composition. In the present study, we have developed an empirical force field to describe the thermodynamics and transport properties of MgCO$_3$–CaCO$_3$ melts.

In a previous study devoted to the Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$ system, we have demonstrated the ability of molecular dynamics (MD) simulations to reproduce experimental data for alkali carbonate melts. Here we extend the latter study to incorporate alkaline-earth components (Mg, Ca). In our study of alkali carbonates we evidenced the need to take into account in the FF the dispersion interactions, which were not included in the FF previously developed by our team for CaCO$_3$. Thus for the sake of consistency the interactions between the carbonate anions and the alkali or alkaline-earth cations are treated on the same footing in the present FF. In section II the details of the simulations are presented. In section III the thermodynamic properties (equation of state) and the liquid structure are reported, whereas in section IV we evaluate the transport coefficients (diffusion coefficients, electrical conductivity and viscosity). Furthermore, the heuristicity of the Nernst-Einstein equation (relating the electrical conductivity and diffusion coefficients) and of the Stokes-Einstein equation (relating the viscosity and diffusion coefficients) is evaluated and commented.

II. METHOD

A. Computational details

1. Ab initio molecular dynamics (AIMD)

Two AIMD simulations were run for this study, one for molten magnesite (MgCO$_3$) and one for molten dolomite (CaMg(CO$_3$)$_2$). They were based on the density functional theory (DFT) within the Born-Oppenheimer approximation using the freely available QUICKSTEP/CP2K software that applies a hybrid Gaussian/plane-wave method. For the study of CaMg(CO$_3$)$_2$ we used for the valence electrons of carbon and oxygen a triple-zeta valence plus polarization basis set optimized for molecules (TZV2P). Otherwise we used a double-zeta plus polarization basis set (DZVP). The cutoff for the electronic density was set to 700 Ry. Exchange and correlation interactions were accounted for by the gradient corrected BLYP functional using a semi-empirical D3 dispersion correction scheme with a cutoff $\geq \sqrt{3}L$, where $L$ is the length of the simulation box. All DFT calculations were run in the NVT ensemble with the temperature set constant by a Nosé-Hoover thermostat.

For MgCO$_3$ and for CaMg(CO$_3$)$_2$ the simulations were run with 200 atoms for 20 ps and with 640 atoms for 12 ps at state points (1873 K, 2.49 g/cm$^3$) and (1773 K, 2.25 g/cm$^3$), leading to an average pressure of 4.5 $\pm$ 1.5 and 1.8 $\pm$ 1.0 GPa, respectively. For information, congruent melting is known to occur at 2.7 GPa and 1850 K for magnesite and at 2.7 GPa and 1653 K for dolomite. As for molten calcite (CaCO$_3$), the AIMD simulations of Vuilleumier et al. based on the same DFT approach, were used as benchmark.

B. Classical molecular dynamics (MD)

Classical MD simulations were carried out using the DL_POLY 2 software, with a timestep of 1 fs. Density calculations were performed in the NPT ensemble with a Nosé-Hoover thermostat for a simulation time of $t \approx 0.9$ ns (including a 0.5 ns equilibration run) allowing to reach an accuracy on the density value of $\Delta n/n \sim \pm 1\%$. To evaluate the transport coefficients, simulations were performed in the NVE ensemble with an equilibration run of 0.5 ns, followed by a production run of 10 to 30 ns. Structural data were extracted from the same simulations. All simulations had a system size $N \approx 2000$
TABLE I: Intermolecular Buckingham parameters and partial charges. Note that for electroneutrality considerations $q_C = +1.04085$ e. Intramolecular Born repulsion parameters between oxygen atoms of a same carbonate ion are $A_{OO}^{\text{intra}} = 2611707.2$ kJ/mol and $\rho_{OO}^{\text{intra}} = 0.22$ Å.

| $i$ | $j$ | $A_{ij}$ (kJ/mol) | $\rho_{ij}$ (Å) | $C_{ij}$ (Å$^6$/mol) | $q_i$ (e) |
|-----|-----|-------------------|-----------------|----------------------|-----------|
| Mg  | O   | 243 000           | 0.24335         | 1 439                | +1.64202  |
| Ca  | O   | 200 000           | 0.2935          | 5 000                | +1.64202  |
| Li  | O   | 300 000           | 0.2228          | 1 210                | +0.82101  |
| Na  | O   | 1 100 000         | 0.2228          | 3 000                | +0.82101  |
| K   | O   | 900 000           | 0.2570          | 7 000                | +0.82101  |
| O   | O   | 500 000           | 0.252525        | 2 300                | -0.89429  |

atoms, except for specific calculations that used the number of atoms as the AIMD simulations in order to compare at best the pair distribution functions obtained by both approaches.

C. Force Field

The force field is composed of interionic pair potentials as presented in a previous paper. The intramolecular part (interactions within a carbonate molecule) contains an oxygen-oxygen term: $V_{OO}^{\text{intra}}(r_{OO}) = A_{OO}^{\text{intra}} - CO_3 \exp(-r_{OO}/\rho_{OO}^{\text{intra}})$, and a carbon-oxygen term: $V_{CO}^{\text{intra}}(r_{CO}) = k_{CO}(r_{CO} - r_{0,CO})^2/2 + q_i q_j/4\pi\epsilon_0 r_{CO}$, with a force constant $k_{CO} = 6118.17$ kJ/mol and an harmonic equilibrium distance $r_{0,CO} = 1.30$ Å adjusted so as to obtain a mean C–O distance of 1.29 Å, as found by X-ray diffraction measurements and AIMD simulations.

Two ions $i$ and $j$, with $i, j = Li$, Na, K, Ca, Mg, O and C (with O and C not belonging to a same carbonate group) interact through the following intermolecular potential: $V_{ij}^{\text{inter}}(r_{ij}) = A_{ij} \exp(-r_{ij}/\rho_{ij}) - C_{ij}/r_{ij}^6 + q_i q_j/4\pi\epsilon_0 r_{ij}$.

Table I recaps the previously published parameters for the Li–Na–K melts and provides the parameters for Mg and Ca. The latter parameters were adjusted so as to reproduce at best (i) the density measurements of crystalline MgCO$_3$, CaCO$_3$ and CaMg(CO$_3$)$_2$ at 300 K and 1 bar, the density and the compressibility of the K$_2$CO$_3$–CaCO$_3$ melt at 1 bar and 1100–1200 K, and (ii) the microscopic structure, in the form of atomic pair distribution functions (PDFs), issued from AIMD simulations of the CaCO$_3$, MgCO$_3$ and CaMg(CO$_3$)$_2$ melts.

At variance with alkali carbonates, alkaline-earth carbonates do not form stable melts under atmospheric pressure and no reliable measurement of their density under high pressure has been published yet. However molten calcium carbonate is stable at 1 bar in mixtures with alkalis. In particular, the density of the equimolar K$_2$CO$_3$–CaCO$_3$ mixture has been measured by Liu and Lange using an advanced double-bob Archimedean method overcoming artifacts...
TABLE II: Density and bulk modulus of MgCO$_3$, CaCO$_3$ and CaCO$_3$-bearing mixtures at $T = 1100$ K calculated either by MD simulations ($n_{MD}^0$, $K_{MD}^0$) or by using ideal mixing rules ($n_{MD,mix}^0$, $K_{MD,mix}^0$). Extrapolation from experiments ($n_{Exp,mix}^0$, $K_{Exp,mix}^0$) are given for comparison.$^{29,54}$ Note that for MgCO$_3$ an additional assumption relative to the cationic mass is needed to estimate $n_{Exp,mix}^0$ (see Hurt and Lange.$^{26}$). In parenthesis are given the MD results from the models of Vuilleumier et al.$^{29}$ ($^{1}$) and Hurt and Wolf.$^{43}$ ($^{1}$).

|                  | MgCO$_3$ | CaCO$_3$ | CaMg(CO$_3$)$_2$ | K$_2$Ca(CO$_3$)$_2$ | Natro |
|------------------|----------|-----------|------------------|---------------------|-------|
| $n_{MD}^0$ (g/cm$^3$) | 2.49     | 2.44      | 2.49             | 2.14                | 2.11  |
| $n_{MD,mix}^0$ (g/cm$^3$) | –        | –         | 2.46             | 2.12                | 2.11  |
| $n_{Exp,mix}^0$ (g/cm$^3$) | 2.45     | 2.49      | 2.47             | 2.13                | 2.13  |
| $K_{MD}^0$ (GPa) | 15.0     | 17.6      | 12.8             | 9.1                 | 11.4  |
| $K_{MD,mix}^0$ (GPa) | –        | –         | –               | 8.6                 | 10.4  |
| $K_{Exp,mix}^0$ (GPa) | –        | 18.7      | –               | 8.9                 | 10.4  |

...due to surface tension and to the mass of the bob, and which reproduced with a great accuracy the density of many liquid standards.$^{65}$ As shown on Fig. 1 the agreement between the density measurements of Liu and Lange$^{32}$ on the K–Ca melt and our MD calculation is excellent. Note that Dobson et al.$^{23}$ also measured the density of this mixture but the values they report are by $\sim 5\%$ lower than the ones from Liu and Lange.$^{32}$ Additionally, Liu and Lange$^{32}$ have suggested that the density of molten carbonates virtually has an ideal behavior regarding composition.$^{1,32}$

$$n_{mix} = \frac{\sum_i n_i M_i}{\sum_i n_i \bar{V}_i},$$

where $n_i$ is the molar fraction of species $i$ of molar mass $M_i$ and molar volume $\bar{V}_i$. Although this approximation is fairly good for purely alkali mixtures, it seems less accurate for mixtures containing both alkali and alkaline-earth cations (see Fig. 1 and next section). Still this mixing rule allows to extrapolate the density of an hypothetical CaCO$_3$ liquid at 1 bar.$^{32}$ In a MD simulation such a liquid is metastable, meaning that it is possible to evaluate its density straightforwardly, at variance with the experiments. Satisfactorily the density calculated by MD (e.g. 2.44 g/cm$^3$ at 1100 K) is fairly compatible with the extrapolation proposed by Liu and Lange$^{32}$ (2.49 g/cm$^3$ at 1100 K).

For MgCO$_3$ no measurement of density, not even in a mixture, has been published yet. But based on the density of various carbonates (in the Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$–Rb$_2$CO$_3$–Cs$_2$CO$_3$–CaCO$_3$–SrCO$_3$–BaCO$_3$ system) and considering how this property evolves as a function of the cationic radius, Hurt and Lange$^{26}$ suggested that an hypothetical MgCO$_3$ melt at 1 bar and 1100 K would have a density of 2.45 g/cm$^3$. This guess is within 2% of the density we obtained by simulating the metastable liquid (2.49 g/cm$^3$). So by introducing in Eq. (1) the density of molten calcite (from Liu and Lange$^{32}$) and that of magnesite (from Hurt and Lange$^{26}$) at the chosen reference state of 1 bar and 1100 K gives a density of 2.47 g/cm$^3$ for the CaMg(CO$_3$)$_2$ melt, in close match with the value of 2.49 g/cm$^3$ as obtained by MD (Table II).

As the densities of molten magnesite and calcite proposed by Hurt and Lange$^{26}$ are merely an approximate estimation, we chose to test the accuracy of our FF by calculating the density of the crystalline phases that are well constrained even under high $T \sim P$.$^{57,60,66}$ We chose to focus on the calcite structure (rhombohedral) as it is a common polymorph to MgCO$_3$, CaCO$_3$ and CaMg(CO$_3$)$_2$.$^{67}$ For magnesite at 300 K up to 4 GPa (Fig. 2), the calculated density is in excellent agreement with the experimental values, well within the scattered data of the experimental literature. Moreover MD simulations reproduce very well the compressibility: $K_T = 125$ GPa as compared to 117 GPa according to Ross.$^{60}$ We believe this should lead to a reliable evaluation of densities for the liquid phase. We also calculated the density of calcite (CaCO$_3$) at room conditions and obtained 2.63 g/cm$^3$, against 2.71 and 2.72 g/cm$^3$ according to Redfern et al.$^{57}$ and Fiquet et al.$^{58}$ respectively, that is within $\sim 3\%$. For comparison, at the same conditions AIMD yielded 2.67 g/cm$^3$.$^{29}$ For dolomite, the agreement between MD ($n = 2.81$ g/cm$^3$) and the X-ray diffraction data ($n = 2.84$ g/cm$^3$)$^{58}$ is even better with a deviation of $\sim 1\%$. The densities were also calculated by anisotropic relaxation of the crystal structure (MD simulations in the N$^{3}$$S$$T$ ensemble). The accuracy of the MD-calculated values deteriorates slightly for magnesite ($n = 3.04$ g/cm$^3$ instead of 3.01, see Fig. 2) but improves for dolomite ($n = 2.84$ g/cm$^3$) and remains unchanged for calcite. Tables S1 and S2 in the supplementary material detail the lattice parameters and the calculated density values up to 4 GPa.

III. THERMODYNAMICS

A. Equation of State

Although there exist no measured data of the density of calco-magnesian carbonate melts, an estimation can be made by assuming that carbonate liquids mix linearly with respect to carbonate components (ideal mix-
FIG. 3: MD (black) and AIMD (red) calculated density-pressure points. Compression isotherms (black or red curves) are interpolated from the MD points by the Birch-Murnaghan equation of state (BMEoS). The temperature of the MD isotherms are: \{1873 K, 1973 K, 2073 K, 2173 K, 2273 K\} for MgCO$_3$ (a), \{1500 K, 1623 K, 1773 K, 1923 K, 2073 K\} for CaCO$_3$ (b), \{1653 K, 1773 K, 1873 K, 2073 K\} for CaMg(CO$_3$)$_2$ (c) and \{823 K, 1073 K, 1423 K, 1600 K\} for the natrocarbonatite (Natro) Na$_{0.18}$K$_{0.18}Ca_{0.36}CO_3$ (d). Red squares are AIMD points: 1873 K for MgCO$_3$, 1623 K, 1773 K and 2073 K for CaCO$_3$ and 1773 K for CaMg(CO$_3$)$_2$. The compression curved at the corresponding temperatures are plotted in red to facilitate the comparison between MD and AIMD results.

For CaCO$_3$ a BMEoS isotherm issued from the experimental thermodynamics data and fusion curve analysis at 1500 K is also plotted in the inset (dashed dotted blue curve)\textsuperscript{32,61,68} along with the isotherms calculated from AIMD by Zhang and Liu\textsuperscript{27} (dashed red curve) and from MD by Vuilleumier \textit{et al.}\textsuperscript{29} (green) at the same temperature (the present study is the black curve).
ing assumption). As discussed above, this allowed Liu and Lange \(^{32}\) to estimate the density of molten CaCO\(_3\) at 1-bar. Now, to infer the high pressure properties of these liquids, constraining the 1-bar compressibility is also needed. Then the density of molten carbonates can be accurately modeled by the third-order Birch Murnaghan equation of state (BMEoS): \(^{69}\)

\[
P = \frac{3}{2} K^0(T) \left( \left( \frac{n}{n_T^0} \right)^{7/3} - \left( \frac{n}{n_T^0} \right)^{5/3} \right) \times \left(1 - \frac{3}{4} (4 - K^0) \left( \left( \frac{n}{n_T^0} \right)^{2/3} - 1 \right) \right), \tag{2}
\]

where \(n_T^0\) is the atmospheric density at temperature \(T\), \(K^0\) the bulk modulus (inverse of the compressibility) and \(K^0\) its pressure derivative at 1 bar (note that it is a constant under the thermodynamic conditions of this study). After fitting our MD data, we propose an equation of state for MgCO\(_3\), CaMg(CO\(_3\))\(_2\) and for a natrocarbonatite (Na\(_{3}\)Al\(_{10}\)K\(_{4}\)Ca\(_{2}\)Na\(_{3}\)CO\(_{3}\))\(_{3}\) modeling the carbonatic lavas from Ol Doinyo Lengai (see Table III). O’Leary \textit{et al.}\(^{61}\) measured the compressibility of the alkali end-members and several mixtures of the system CaCO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\)–Li\(_2\)CO\(_3\), including mixtures containing various ratios of CaCO\(_3\). Then they extrapolated the 1 bar compressibility of molten CaCO\(_3\), that is a metastable liquid at this pressure, by using an ideal mixing rule:

\[
K_{\text{mix}} = \frac{\sum_i x_i \bar{V}_i}{\sum_i x_i \bar{V}_i / K_i}. \tag{3}
\]

The comparison of our MD results with their study is good as shown in Table II. In particular our results are in a better agreement than when using the FFs developed by Vuilleumier \textit{et al.}\(^{29}\) and by Hurt and Wolf\(^{43}\). Then O’Leary \textit{et al.}\(^{68}\) used fusion curve analysis to constrain \(K^0 = 7 \pm 1\), still for CaCO\(_3\). Note that this value is closer to the one produced using our FF (\(K^0 = 8.2\), as in\(^{29}\)) than using the one of Hurt and Wolf\(^{43}\) (\(K^0 = 10.3\)). Inserting this value, as well as the 1-bar density from Liu and Lange\(^{32}\) and the 1-bar compressibility from O’Leary \textit{et al.}\(^{68}\) in Eq. (2) we built an experimental compression curve for CaCO\(_3\) at 1500 K (see the inset in Fig. 3b). This estimation is very close to the one issued from our MD simulations.

Based on AIMD simulations, Zhang and Liu\(^{27}\) proposed an equation of state for CaCO\(_3\). However, because of the LDA approximation they used to compute exchange-correlation energies, an approximation which tends to overestimate the density (at a given \(P\)), the authors have applied a rescaling method. The compression curve given by their equation of state at 1500 K is plotted in the inset of Fig. 3b for CaCO\(_3\). It fits our MD compression curve quite well although there remains a slight deviation at low pressure. Moreover, the compressibility provided by our model is slightly lower than the one from Zhang and Liu\(^{27}\). However that may be, at 1500 K, we get \(K^0_{\text{AIMD}} = 13.7\) GPa, just like O’Leary \textit{et al.}\(^{61}\) whereas Zhang and Liu\(^{27}\) give a value of 11.9 GPa. As for the AIMD calculations we performed (this study and Vuilleumier \textit{et al.}\(^{29}\)), they are based on the GGA approximation and include a (semi-empirical) correction for dispersion forces. The introduction of dispersion interactions enhances interionic cohesion in the liquid, but maybe not sufficiently, a feature which could account for the slight remaining difference between MD and AIMD (\(P_{\text{MD}} < P_{\text{AIMD}}\) in general, see Fig. 3).

If the number density, \(\rho\), is considered (rather than mass density \(n\)), it goes as follow at 3 GPa and 1873 K: \(\rho_{\text{MgCO}_3} = 40.1\) mol/L > \(\rho_{\text{CaCO}_3} = 25.2\) mol/L, which is consistent with the observation made for alkali melts,\(^1\) that the number density is negatively correlated to the cation size. However, the bulk modulus is the same in magnesite and calcite (\(K^0_{\text{MgCO}_3} = K^0_{\text{CaCO}_3} = 11.0\) GPa), at variance with alkali melts where \(K^0\) increases with increasing cation radius. This suggests that the compressibility of calcio-magnesian carbonate melts is not similar to that of a hard sphere system and instead is dominated by the coulombic repulsion between divalent cations. If we consider the compressibility at 1 bar and 1100 K of the metastable MgCO\(_3\) and CaCO\(_3\) melts (\(K^0_{\text{MgCO}_3} = 14.0\) GPa and \(K^0_{\text{CaCO}_3} = 17.6\) GPa), it is greater by a factor \(\approx 2\) than that of alkali carbonates at the same \(T \sim P\) conditions. However, the compressibilities calculated in corresponding states (i.e. near the melting point, 1823 K and 3 GPa for MgCO\(_3\), and 1623 K and 1 GPa for CaCO\(_3\)) are very similar (\(K^0_{\text{MgCO}_3} = 7.5\) GPa for MgCO\(_3\) and \(K^0_{\text{CaCO}_3} = 6.4\) GPa for CaCO\(_3\)) for both alkali and alkaline-earth carbonates.

Knowing the equations of state for MgCO\(_3\), CaCO\(_3\), Na\(_2\)CO\(_3\), K\(_2\)CO\(_3\) and Li\(_2\)CO\(_3\) and some mixtures (dolomite and natrocarbonatite) it is worth checking how these latter melts behave regarding ideality (Table II). For that we consider, for instance, the density of molten dolomite at 1 bar and at 3 GPa, let’s say at 1873 K. The comparison between the raw MD data and the ideal mixing rules (Eqs. (1) and (3)) using the data of Table III gives: \(n_0^0 = n_{T, \text{mix}}^0 = 2.19\) g/cm\(^3\) and \(K^0 = K_{T, \text{mix}}^0 = 11.0\) GPa, and \(n_{T, \text{mix}}^{GPa} = n_T^{GPa} = 2.55\) g/cm\(^3\). Proceeding the same way for the natrocarbonatite at 1 bar and 1073 K we get \(n_0^0 = 2.11\) g/cm\(^3\) and \(n_{T, \text{mix}}^{GPa} = 2.13\) g/cm\(^3\), and \(K^0 = 11.4\) GPa and \(K_{T, \text{mix}}^{GPa} = 10.4\) GPa. Hence it comes out that dolomite is an ideal mixture on a certain \(P\)-domain, whereas natrocarbonatite slightly deviates from ideality. Most likely the latter finding can be explained by the fact that the natrocarbonatite includes both uni- and divalent cations. In practice, as the deviation from ideality seems to be fairly small, the EoS of the end-members of the Mg–Ca–Li–Na–K system can be used to estimate with confidence the density of any mixture.
|             | MgCO$_3$   | CaCO$_3$   | CaMg(CO$_3$)$_2$ | Natro       |
|-------------|------------|------------|------------------|-------------|
| $T$ (K)     | 1873−2073  | 1100−2073  | 1653−2073        | 823−1600    |
| $P$ (GPa)   | 0−15       | 0−15       | 0−15             | 0−6         |
| $T_{ref}$ (K) | 1873      | 1623       | 1653             | 1073        |
| $n_{ref}$ (g/cm$^3$) | 2.23    | 2.25       | 2.26             | 2.14        |
| $\alpha_0$ (K$^{-1}$) | $-1.50 \times 10^{-4}$ | $-1.54 \times 10^{-4}$ | $-1.23 \times 10^{-4}$ | $-2.36 \times 10^{-4}$ |
| $\alpha_1$ (K$^{-2}$) | 8.22 $\times 10^{-8}$ | 0.49 $\times 10^{-8}$ | $-7.65 \times 10^{-8}$ | $-0.20 \times 10^{-8}$ |
| $K_{ref}$ (GPa) | 10.98    | 12.74      | 12.13            | 11.72       |
| $b_1$ (K$^{-1}$) | 5.0 $\times 10^{-4}$ | 6.1 $\times 10^{-4}$ | 3.7 $\times 10^{-4}$ | 10.2 $\times 10^{-4}$ |
| $b_2$ (K$^{-2}$) | 2.0 $\times 10^{-7}$ | 1.5 $\times 10^{-7}$ | 5.0 $\times 10^{-7}$ | 7.7 $\times 10^{-7}$ |
| $K_0$       | 8.5        | 8.2        | 8.5              | 8.0         |

TABLE III: Parameters of the third-order Birch-Murnaghan equation of state and $T-P$ domain of validity. Natro refers to the natrocarbonatite melt of composition Na$_{4.1}$K$_{0.18}$Ca$_{0.36}$CO$_3$ (see text).

The reference temperature $T_{ref}$ is defined for numerical purposes and set to the melting temperature for each composition, $n_{ref}$ and $K_{ref}$ are the density and bulk modulus at 1-bar and $T_{ref}$. Other empirical parameters ($\alpha_0$, $\alpha_1$, $b_1$ and $b_2$) are defined by $n_{ref}^0 = n_{ref}^0 e^{\int_{T_{ref}}^T (\alpha_0 + \alpha_1 T) dT}$ and $K_{T}^0 = K_{ref}^0 / (1 + b_1 (T - T_{ref}) + b_2 (T - T_{ref})^2)$. See Desmaele et al.\textsuperscript{1} for details on the fitting method.

**B. Structure**

In the $T-P$ range of this study ($T \leq 2013$ K and $P \leq 15$ GPa), the stability of the internal structure of the carbonate ion has been pointed out by neutron diffraction measurements,\textsuperscript{70} in situ X-ray diffraction measurements\textsuperscript{33} and by AIMD simulations (Ref. 1 and 29 and this study). Moreover the carbonate anion, unlike the SiO$_4$ units in silicates, cannot share a covalent bond with other atoms. Therefore carbonate melts display a structure contrasting with that of most geological melts (silicate) that are always polymerized to a certain degree. This is why carbonate melts share with molten salts (e.g. NaCl) a high ionic diffusivity and a low viscosity.

Until now, among the alkaline-earth carbonates, only the structure of calcite melt has been investigated by classical molecular dynamics simulations\textsuperscript{29,42,43} and by AIMD simulations.\textsuperscript{29,30} Fig. 4 shows the PDFs for MgCO$_3$ and CaCO$_3$ at corresponding states (i.e. near melting point: $T = 1873$ K, $P \sim 2$ GPa and $n = 2.49$ g/cm$^3$ for MgCO$_3$; $T = 1623$ K, $P \sim 0.5$ GPa and $n = 2.30$ g/cm$^3$ for CaCO$_3$). Note that, as expected, they are in very good agreement with the PDFs issued from AIMD (compare the plain lines with the dotted lines). The first peak of $g_{CO}(r)$ at $r_{CO} = 1.29$ Å corresponds to the three oxygen atoms bonded to a same carbon atom in a carbonate unit. Between 1.7 Å and 2.1 Å $g_{CO}(r) = 0$ because no C–O bond dissociation occurs during the simulation. On the other hand, the first peak of $g_{OO}$ represents the O–O intramolecular distance ($r_{OO} = 2.22$ Å) in a carbonate ion. The first minimum of $g_{OO}$ is non-zero, meaning that the distance between two oxygen atoms of two different CO$_3^{2-}$ units may be as short as the O–O intramolecular distance. Concerning the anion-anion correlations, each CO$_3^{2-}$ unit is surrounded by 12−15 other carbonate ions at $r_{CC} \simeq 4−6$ Å on average. The first C–C peak on Fig. 4a is broad with a shouldering on its low-r flank (3.5−4 Å), that is especially noticeable for MgCO$_3$, and a small bump at $\sim 5−7$ Å in the region of the first minimum, this time more pronounced in CaCO$_3$. Each cation (Mg$^{2+}$ or Ca$^{2+}$) ion is surrounded by 6 carbonate groups (against 4.5−4.8 for alkali), at a mean cation-carbon distance of 3−4 Å in MgCO$_3$ and 3.15−4.5 Å in CaCO$_3$ (note that these distances are the same in CaMg(CO$_3$)$_2$ at 1773 K and 2.25 g/cm$^3$). As for the ratio of the coordination numbers $N_{X-O} / N_{X-C}$ (where $X = $ Mg or Ca), indicative of the orientation of the carbonate ions around the cations, it is 1.1 for Mg and 1.3 for Ca (as compared to 1.3−1.6 for alkali cations). In comparison to pair distribution functions for alkali carbonate melts, the cation-anion PDF $g_{XC}(r)$ for alkaline-earth carbonates are more simple as they show no shoulder on the first peak (see Fig.4b and compare with Fig. 2 in Desmaele et al.\textsuperscript{1}). Moreover, the second peak of $g_{XC}(r)$ is broader, especially for Mg. It can also be noted that the shape of the PDFs is less sensitive to the size of the cation. Looking at the cation-cation PDFs, the only difference between Mg and Ca is the amplitude, greater for the Ca–Ca pair with a coordination number around $\sim 10$ instead of $\sim 7$ for Mg–Mg. It is noteworthy that the PDFs of CaMg(CO$_3$)$_2$ are intermediate between those of CaCO$_3$ and MgCO$_3$. In fact, most structural features observed in molten calcite and magnesite are similar and can be interpreted as a simple homothetic transformation upon volumetric change from CaCO$_3$ to MgCO$_3$. Thus the pair distribution functions X–C, X–O and X–X in CaMg(CO$_3$)$_2$ are almost identical to the corresponding ones observed in CaCO$_3$ and MgCO$_3$ (Fig. 4b) and this remains true even at high pressures (Figs. S1, S2 and S3 in the supplementary material). Under pressure (and up to 12 GPa), the PDFs shift progressively towards lower distances, reflecting the melt compaction (see Figs. S1, S2 and S3). Moreover the average number of CO$_3^{2-}$ anions around cations increases slightly under pressure,
from 6 to 7. In contrast, the coordination number of $\text{CO}_3^{2-}$ around $\text{CO}_3^{2-}$ ($\sim 12 - 15$) does not evolve with pressure, neither does the $N_e^{X-O}/N_e^{X-C}$ ratio.

IV. TRANSPORT PROPERTIES

For $\text{MgCO}_3$, $\text{CaCO}_3$ and $\text{CaMg(CO}_3)_{2}$, a series of simulations ($\sim 15$) was performed at different thermodynamic conditions, with a duration long enough to reach the diffusive regime (10 - 20 ns). From each run we calculated accurately (see below) the self-diffusion coefficients $D_s$ of each chemical species $s = \text{Ca, Mg and CO}_3^{2-}$, the electrical conductivity $\sigma$ and the viscosity $\eta$.
given by:71,72

\[
D_s = \lim_{t \to \infty} \frac{1}{6t N_s} \sum_{i=1}^{N_s} \langle |r_i(t) - r_i(0)|^2 \rangle , \tag{4}
\]

\[
\sigma = \lim_{t \to \infty} \frac{1}{6t k_B T} \langle \sum_{i=1}^{N_s} z_i(t) \cdot (r_i(t) - r_i(0)) \rangle^2 , \tag{5}
\]

\[
\eta = \lim_{t \to \infty} \frac{V}{k_B T} \int_0^t d\tau \langle \Pi_{\alpha\beta}(\tau) \cdot \Pi_{\alpha\beta}(0) \rangle , \tag{6}
\]

where \(\Pi_{\alpha\beta}(t)\) refers to the off-diagonal pressure tensor components (\(\alpha, \beta = x, y, z\), see references71,72 for more details), \(N\) is the total number of ions in the simulation box of volume \(V\), \(N_s\) the number of ions of species \(s\), \(k_B\) the Boltzmann constant and \(e\) the elementary charge, \(m_i\) is the mass of ion \(i\), \(r_i(t)\) its position, \(v_i\alpha(t)\) the component \(\alpha\) of its velocity, \(F_{ij\beta}(t)\) is the component \(\beta\) of the force exerted by ion \(j\) on ion \(i\), separated by a distance \(r_{ij}(t)\) at time \(t\). The conduction charge \(z_i\) is taken as the formal charge, which is usual for simple ionic liquids.73

Note from the equations above that the self-diffusion coefficient \(D_s\), resulting from an average over the \(N_s\) ions of a specific species \(s\) (sum \(\sum_{i=1}^{N_s}\) in Eq. (4)), are calculated with a great accuracy (calculation uncertainty of 1\% in this study). On the other hand, the electrical conductivity and the viscosity, as collective observables, are trickier to estimate due to the slow convergence of the corresponding time correlation functions. In the following the values we present for these quantities have an error bar within 5 – 10\%.

The temperature and pressure dependence of the transport coefficients can be modeled by an Arrhenius activation law

\[
D_s(P, T) = D_0^s e^{-\left(\frac{E_a^s + PV^a}{RT}\right)} , \tag{7}
\]

\[
\sigma(P, T) = \alpha^0 e^{-\left(\frac{E_x^s + PV}{RT}\right)} , \tag{8}
\]

\[
\eta(P, T) = \eta^0 e^{\left(\frac{E_v^s + PV_v}{RT}\right)} , \tag{9}
\]

where \(E^X_s\) is the activation energy associated to the physical quantity \(X\) and \(V^a_s\) is an activation volume accounting for its pressure dependence.1,29,31 The values of \(X^0\), \(E^X_s\) and \(V^a_s\) were determined by fitting the molecular dynamics data for the three melts MgCO\(_3\), CaCO\(_3\) and CaMg(CO\(_3\))\(_2\) (see Figs. 5, 6, 7, 10, 11). They are given in Table IV for \(D_s\) and in Table V for \(\sigma\) and \(\eta\), for the temperature and pressure range mentioned in Table III.

A. Diffusion coefficient

The diffusivity of calco-magnesian carbonate melts has never been measured and it is only recently that estimations have been provided by the AIMD simulations of Vuilleumier et al.29 According to their calculations the diffusion coefficients of Ca and CO\(_3^{2-}\) in CaCO\(_3\) along its melting curve (up to 12 GPa) are of comparable magnitude with the ones in purely alkali melts.1 The agreement between the data of the present MD study and the AIMD simulations of Vuilleumier et al.29 is very good at 0.5 and 4.5 GPa, a bit less at 12 GPa where the values of MD are below those of AIMD (Fig. 5). We have also evaluated the diffusion coefficients from our AIMD simulations of MgCO\(_3\) at 4.5 GPa and CaMg(CO\(_3\))\(_2\) at 2 GPa. In the two cases they are greater than the values issued from MD (Figs. 6 and 7). This is consistent with the slight discrepancy between the two models for the equation of state. Indeed at a given \(T, P\) point, the densities yielded by MD simulations are systematically greater than the ones yielded by AIMD (Fig. 3). This means that the free volume of diffusion is smaller in the MD model. By performing a MD simulation of MgCO\(_3\) at the same density as AIMD (1873 K and 2.49 g/cm\(^3\)), and recalculating the coefficients from this run, we get larger values (namely
TABLE IV: Parameters of the Arrhenius activation law (7) obtained by the interpolation of all MD simulation points. \( P \) is in GPa.

|                  | MgCO\(_3\) | CaCO\(_3\) | CaMg(CO\(_3\))\(_2\) (left: X=Mg, right: X=Ca) |
|------------------|-------------|-------------|--------------------------------------------------|
| \( D_0 \times 10^9 \) (m\(^2\)/s) | 117         | 122         | 164                                               |
| \( E_{A}^0 \)  (kJ/mol)         | 54          | 54          | 58                                                |
| \( V_{0}^{2/3} \) (cm\(^3\)/mol) | 2.5 × 0.07 \( P \) + 0.0016\( P^2 \) | 4.6 × 0.28 \( P \) + 0.0100\( P^2 \) | 3.5 × 0.13 \( P \) + 0.0029\( P^2 \) |
| \( D_0 \times 10^{-9} \) (m\(^2\)/s) | 83          | 86          | 100                                               |
| \( E_{A}^0 \)  (kJ/mol)         | 54          | 51          | 54                                                |
| \( V_{0}^{2/3} \) (cm\(^3\)/mol) | 2.6 × 0.11 \( P \) + 0.0036\( P^2 \) | 3.3 × 0.08 \( P \) + 0.0007\( P^2 \) | 2.1 × 0.08 \( P \) + 0.0085\( P^2 \) |

\( D_{\text{Mg}} = 3.11 \) and \( D_{\text{CO}_3} = 2.13 \times 10^{-9} \) m\(^2\)/s, instead of 1.85 and 1.30, but still below the values from AIMD: 4.4±0.5 and 3.5 ± 0.5 \( 10^{-9} \) m\(^2\)/s, respectively. This could indicate that our empirical force field fails to some extent to describe cohesive forces in every detail. However there is no evidence that AIMD sketches them much more accurately.

The activation energy (51 – 58 kJ/mol) depends little on the ion species (Ca, Mg or CO\(_3\)). But it is perceptibly higher than that for alkali melts at 1 bar in which the coulombic forces are weaker.\(^1\) The magnitude of the diffusion coefficients are also slightly smaller in Ca-Mg carbonate melts than in their alkali counterparts. Interestingly if we consider the K\(_2\)CO\(_3\)-CaCO\(_3\) mixture (at 1 bar and 1100 – 1200 K) \( D_{\text{Ca}} \) is lower than \( D_{\text{K}} \) (by a factor \( \sim 2 \)) and very close to \( D_{\text{CO}_3} \). Moreover, compared to pure K\(_2\)CO\(_3\), the presence of the divalent cation decreases \( D_{\text{CO}_3} \) and \( D_{\text{K}} \) by a factor 2 and increases their activation energies by \( \sim +50\% \).

B. Electrical Conductivity

As molten salts, carbonate melts are characterized by a high electrical conductivity in the range of \( 10^4 – 10^6 \) S/m, depending on composition, temperature and pressure, which is up to two orders of magnitude more conductive than silicate melts at the same thermodynamic conditions.\(^9\) The knowledge of the electrical conductivity of alkali carbonates is crucial for their industrial applications as electrolytes in fuel cell devices. Many experimental and numerical studies have been devoted to this issue. Hence, the electrical conductivity of the end-members and of binary and ternary mixtures of the system Li\(_2\)CO\(_3\)-Na\(_2\)CO\(_3\)-K\(_2\)CO\(_3\) have been abundantly documented.\(^1\),\(^2\),\(^3\),\(^5\),\(^6\),\(^7\)\(^8\) Because the addition of small amounts of alkaline-earth carbonates improves the performance of fuel cell devices, in particular in terms of durability,\(^7\) the electrical conductivity of the Li–K (62–38 mol\%) molten carbonate was measured by impedance spectroscopy and found to decrease linearly with small amounts of CaCO\(_3\).\(^3\) The electrical conductivity of carbonate melts is not only important for industrial applications, it is also of fundamental interest to understand the conductivity anomalies in the asthenosphere of the Earth’s mantle. To address this question, Gaillard \textit{et al.}\(^9\) measured the electrical conductivity of binary and ternary mixtures in the Na–K–Ca system at atmospheric pressure. With regard to Ca-bearing mixtures, MD is in quantitative agreement with their values (deviation of 30% at most), but with a slightly higher activation energy (Fig. 8). Following the work of Gaillard \textit{et al.}\(^9\), Sifré \textit{et al.}\(^25\) studied (up to 3 GPa) Ca and Mg-bearing carbonate compositions: CaCO\(_3\), a natural dolomite (\( \sim \) CaMg(CO\(_3\))\(_2\)), K\(_2\)Mg(CO\(_3\))\(_2\), K\(_2\)Ca(CO\(_3\))\(_2\) and Na\(_2\)Mg(CO\(_3\))\(_2\). These studies\(^9\),\(^25\) show that the electrical conductivity depends slightly on the chemical composition (see Figs. 8 and 9). The smaller the cation and the lower its charge, the higher is the electrical conductivity.\(^25\),\(^26\) As a consequence, the addition of CaCO\(_3\) or MgCO\(_3\) in a pure alkali carbonate reduces somewhat the conductivity.

Fig. 9 reports the calculated and measured conductivities for CaCO\(_3\) and for the above-mentioned Ca or Mg-bearing mixtures at 3 GPa. The agreement is very good for dolomite and for the Na\(_2\)Mg(CO\(_3\))\(_2\) mixture. Note that for dolomite at 3 GPa and 1800 K, Yoshino \textit{et al.}\(^78\) reported an electrical conductivity of 105 S/m, which is almost twice lower than the values of this study and from Sifré \textit{et al.}\(^74\) Concerning CaCO\(_3\), the calculated and the measured electrical conductivities overlap within uncertainty (e.g. at 3 GPa and 1923 K MD yields 210 ± 10 S/m and Sifré \textit{et al.}\(^25\) 230 ± 25 S/m). The agreement between MD and experiments is also good for K\(_2\)Ca(CO\(_3\))\(_2\), although it slightly degrades towards low temperatures. Most striking is our disagreement on the K\(_2\)Mg(CO\(_3\))\(_2\) mixtures (by a factor \( \sim 2 – 3 \), Fig. 9), although our force field satisfactorily reproduced the behavior of other Mg-containing mixtures. An explanation could be that this composition is the most dissymmetric one of our study (a small divalent cation coexists with a large monovalent cation in equal proportions). On the other hand, an experimental bias cannot be excluded because this mixture is known for being glass-forming and for easily decomposing.\(^23\) As already emphasized in previous studies, the increase of conductivity with temperature is well fitted by an Arrhenius law with activation energies ranging from 34 to 42 kJ/mol at \( P = 1 \) atm (Table V). Note that Gaillard \textit{et al.}\(^9\) found \( E_A^0 \) in the range 30 to 35 kJ/mol in alkali-bearing melts and Desmaele \textit{et al.}\(^1\) \( \sim 20 \) kJ/mol for purely alkali melts by MD. The conductivity decreases weakly with pressure, which can be accounted for by an
increase of the activation energy with $P$. Hence, we calculated that this energy is between 42 and 51 kJ/mol at 3 GPa depending on the melt composition, whereas Sifré et al.\textsuperscript{25} reported values from 37 to 48 kJ/mol. For dolomite, these authors found an activation energy of 48 kJ/mol, while our calculated value is 41 kJ/mol. That is a fairly good agreement considering that the experimental error on each measurement is about 10%. As for Yoshino et al.\textsuperscript{78} they reported a value of 38 kJ/mol at 3 GPa. With regard to the calcite melt (CaCO$_3$), the activation energy calculated by MD (41 kJ/mol at 3 GPa) is much lower than the value reported by Sifré et al.\textsuperscript{25} (76 kJ/mol at the same pressure), but consistent with the ones they reported for other carbonate compositions (in the range 37 – 48 kJ/mol).

The electrical conductivity estimated from AIMD simulations (this study for CaMg(CO$_3$)$_2$ and Vuilleumier et al.\textsuperscript{29} for CaCO$_3$) are reported on Figs. 10. For CaCO$_3$ the agreement between MD and AIMD is good at 0.5 GPa but diminishes at higher pressures. As evolved in the case of diffusion coefficients, most of these discrepancies may be related to the small difference between the equation of state provided by the two models. At a given $T$ – $P,$ the density is smaller in the AIMD simulations, hence the ionic mobility and the electrical conductivity are higher. For dolomite, given the large uncertainty on the AIMD value ($\sim$ 50%), it can only be stated that the results of the two simulations models (MD and AIMD) are compatible.

Another advantage of the MD approach is that phenomenological relations for transport properties can be tested. It can be shown that the electrical conductivity $\sigma$ and the diffusion coefficients are linked by a generalized Nernst-Einstein relation, which takes into account the cross correlations between ionic motions, $\sigma = H \sigma^{NE}$ where

$$ \sigma^{NE} = \frac{e^2}{k_B T V} \sum_s N_s z_s^2 D_s , \quad (10) $$

with $N_s$, $z_s$ and $D_s$ are the number, the formal charge and the self diffusion coefficient of ions of atomic species $s$. The Nernst-Einstein relation assumes that ions move independently from each others. The Haven ratio:

$$ H = \frac{\sigma}{\sigma^{NE}} = 1 + \sum_s H_s + \sum_s \sum_{s' \neq s} H_{ss'}, \quad (11) $$

accounts for the average cross correlations (through a scalar product) between the displacements of ions of species $s$

$$ H_s = \lim_{t \to \infty} \frac{1}{6 t} \sum_{i=1}^{N_s} \sum_{j=1}^{N_s} \left( \langle \Delta_i^s(t) \cdot \Delta_j^s(t) \rangle - \langle \Delta_i^s(t) \rangle \langle \Delta_j^s(t) \rangle \right), \quad (12) $$

where $\Delta_i^s(t) = \vec{r}_i^s(t) - \vec{r}_i^s(0)$ and the average cross correlations between the displacement of an ion $i$ of species $s$ ($\Delta_i^s(t)$) and that of an ion $j$ of another species $s'$ ($\Delta_j^{s'}(t)$), and $H_{ss'}$ is close to 1 ($H = 1.10$) although its decrease is not fully overbalanced by the correlation of the displacements of the cations and of the anions, that is to say, they are, on average, moving towards opposite directions, which increases the conductivity. For CaCO$_3$, an anti-correlation of all the ionic displacements is also observed: a positive contribution of the anion-cation correlation $H_{Ca-CO_3}$ is not fully overbalanced by the correlations between ions of a same species leading to a Haven ratio less than 1 ($H = 1 + H_{Ca} + H_{CO_3} + H_{Ca-CO_3} = 0.81$).

We carried on this approach with some binary mixtures.
TABLE VI: Haven ratio and its ionic contributions, where X denotes all cations. Note that the error bar on these quantities is of the order of the error bar on the electrical conductivity: \( \sim 5 - 10\% \). For mixtures, the notation \( X_1 \) (= Mg, Na or K) and \( X_2 \) (= Ca or Mg) is the same as the one appearing in the composition name (first column, with \( M = \text{Mg}, C = \text{Ca}, N = \text{Na} \) and \( K = \text{K} \)).

(see Table VI), including dolomite. It is worth noticing that the displacements of cations of the same species are mostly not correlated to one another \( (H_{X_1} \text{ and } H_{X_2} \text{ both } \sim 0, \text{ where } X_1, X_2 = \text{Mg}, \text{Ca}, \text{Na} \text{ or K}) \). However the cross correlations between cationic displacements (as expressed by the term \( H_{X_1} - X_2 \)) seem to depend on the charge of the cations. Indeed, in dolomite \( H_{X_1} - X_2 \) is close to 0 \( (H_{\text{Mg-Ca}} = -0.03) \), while in the investigated alkaline earth mixtures it ranges between -0.16 and -0.22. As for the other terms \( (H_{\text{CO}_3} \text{ and } H_{\text{X}_1\text{CO}_3}) \), they give opposite contributions to \( H \) (see Table VI). So, although the Nernst-Einstein equation yields, for the melts studied here, a reasonable estimation of the electrical conductivity \( (+10 - 30\% \text{ from the exactly calculated one, } \sigma) \), it provides no information on the relevance of its underlying assumption (the ions move independently from each other). In fact, as we show it here, its usefulness relies on a cancellation effect between the different ion-ion correlations. As the dependence of this cancellation effect with composition, \( T \) or \( P \) is non-trivial, we recommend a circumspect use of the Nernst-Einstein approximation.

C. Viscosity

Very little is known on the pressure dependence of the viscosity of molten carbonates. Based on molten salt data reviewed by Janz,\textsuperscript{65} Wolff\textsuperscript{80} roughly estimated an order of magnitude \( (\sim 100 \text{ mPa-s}) \) for the viscosity of calcium-rich carbonatites at 973 K and ambient pressure. The ex-situ measurements at mantle pressures \( (P = 3 \text{ GPa}) \) made by Sykes \textit{et al.}\textsuperscript{81} seem to greatly overestimate the viscosity of dolomitic melts \( (e.g. \text{ for } 70:30 \text{ mol\% CaCO}_3-\text{MgCO}_3, \eta = 600 \text{ mPa.s at } 1473 \text{ K and } 1 \text{ GPa}) \) in light of the very high activation energy they obtained,\textsuperscript{24} probably because of an incomplete melting of the sample.\textsuperscript{79} On the other hand, Dobson \textit{et al.}\textsuperscript{23} performed the first in-situ measurements of the viscosity of \( \text{K}_2\text{Ca(CO}_3)_2 \) and \( \text{K}_2\text{Mg(CO}_3)_2 \) melts, up to 5.5 GPa, by using the falling sphere method with X-ray radiography. In this pioneering experiment, the temperature was difficult to control and the relative error on viscosity was typically 50\%, due to incomplete melting of the

| T(K) | P (GPa) | \( \sigma \) (S/m) | \( H \) | \( H_{X_1} \) | \( H_{X_2} \) | \( H_{\text{CO}_3} \) | \( H_{X_1-X_2} \) | \( H_{X-\text{CO}_3} \) |
|------|--------|----------------|------|--------|--------|--------|--------|--------|
| MgCO\(_3\) | 1823 | 3.0 | 245 | 0.92 | -0.14 | -0.32 | -0.38 |
| CaCO\(_3\) | 1773 | 1.0 | 220 | 0.81 | -0.22 | -0.35 | -0.38 |
| MC | 1573 | 3.0 | 112 | 0.85 | -0.08 | 0 | -0.36 | -0.03 | 0.34 |
| NM | 1573 | 3.0 | 186 | 0.87 | -0.04 | -0.04 | -0.29 | -0.16 | 0.40 |
| KM | 1573 | 3.0 | 75 | 0.72 | -0.10 | -0.03 | -0.23 | -0.22 | 0.29 |
| KC | 1573 | 3.0 | 95 | 0.75 | -0.10 | -0.05 | -0.25 | -0.20 | 0.35 |

FIG. 6: Diffusion coefficients in MgCO\(_3\) calculated by MD (crosses) and isobaric activation laws obtained by fitting all the simulation points. The AIMD calculations (this study) are represented by plain squares. The pressures of the isobars are \{2, 3, 3.5, 4.5, 6, 8, 10, 12, 15\} in GPa and are referred to with a color code (vertical scale).
FIG. 7: Diffusion coefficients in CaMg(CO$_3$)$_2$ calculated by MD (crosses) and isobaric activation laws obtained by fitting all the simulation points. The AIMD calculations (this study) are represented by plain squares. The pressures of the isobars are {0.1, 2, 3, 3.5, 4, 4.5, 5, 6, 8, 10, 12} in GPa and are referred to with a color code (vertical scale).

FIG. 8: Electrical conductivity at 1 bar from MD (square and plain lines as a guide to the eye) and from the experiments of Kojima$^{22}$ (dashed line) and of Gaillard et al.$^9$ (long dashed and double dotted lines) for K$_2$Ca(CO$_3$)$_2$ (KC), Li$_2$Na$_2$Ca(CO$_3$)$_3$ (LNC) and Na$_2$K$_2$Ca(CO$_3$)$_3$ (NKC).

FIG. 9: Electrical conductivity at 3 GPa calculated in MD (square) and measured by Sifr´e et al.$^{25}$ (dashed line) for CaCO$_3$ (C) and several equimolar mixtures: Na$_2$Mg(CO$_3$)$_2$ (NM), K$_2$Mg(CO$_3$)$_2$ (KM), CaMg(CO$_3$)$_2$ (MC) and K$_2$Ca(CO$_3$)$_2$ (KC). Plain lines are the Arrhenius activation slopes for C and CM (see Table V) and guides to the eye for NM, KM, NK and KC.
FIG. 10: Electrical conductivity from MD (crosses) and isobaric activation laws (plain lines). The pressures (in GPa) of the isobars are \{2, 3, 3.5, 4.5, 6, 8, 10, 12, 15 GPa\} for MgCO$_3$ (top left), \{0.5, 1, 2, 3, 4.5, 5, 6, 8, 10, 12 GPa\} for CaCO$_3$ (top right) and \{0.1, 2, 3, 3.5, 4, 4.5, 5, 6, 8, 10, 12\} for CaMg(CO$_3$)$_2$ (bottom) and are referred to with a color code (vertical scale). Estimates from AIMD calculations (this study for CaMg(CO$_3$)$_2$ and Vuilleumier et al.\textsuperscript{29} for CaCO$_3$) are represented by plain squares.

FIG. 11: Viscosity from MD (crosses) and isobaric activation laws (plain lines). The pressures (in GPa) of the isobars are \{2, 3, 3.5, 4.5, 6, 8, 10, 12, 15 GPa\} for MgCO$_3$ (top left), \{0.5, 1, 2, 3, 4.5, 5, 6, 8, 10, 12 GPa\} for CaCO$_3$ (top right) and \{0.1, 2, 3, 3.5, 4, 4.5, 5, 6, 8, 10, 12\} for CaMg(CO$_3$)$_2$ (bottom) and are referred to with a color code (vertical scale). The data recently reported by Kono et al.\textsuperscript{24} are plotted as circles, the corresponding isobars (0.9, 1.5, 2.8, 4.8 and 6.2 GPa for CaCO$_3$ and 3.0, 3.9 and 5.3 GPa for CaMg(CO$_3$)$_2$) obtained from the present MD study are reported for comparison (bold blue lines).
sample and to convection effects at the highest temperatures. Besides the limited frame rate used to capture the images of the falling sphere greatly reduces the accuracy of the final velocity measurement, which is crucial for determining the viscosity. Nevertheless it was found that Ca, Mg-bearing carbonates under high $T - P$ have a viscosity similar to that of alkali carbonates at 1 bar ($6 - 36$ mPa·s in the range $2.5 - 5.5$ GPa). This qualitative observation is consistent with the results of our MD calculations (see Fig. 11). However we do not agree with the assertion of the authors that the effect of pressure on viscosity is negligible in the pressure range investigated (up to 5.5 GPa) and we think that this observation results from the large error bars of the study ($\sim 50\%$ on $\eta$ and $\pm 0.5$ GPa on $P$; see also the discrepancy with the first results of Jones et al.\textsuperscript{79}). We calculated the viscosity of K$_2$Ca(CO$_3$)$_2$ at 0, 2.5 and 3 GPa and the viscosity of K$_2$Mg(CO$_3$)$_2$ at 3 GPa. The viscosity depends strongly on the temperature by following an Arrhenius law with an activation energy a little higher for K$_2$Mg(CO$_3$)$_2$ than for K$_2$Ca(CO$_3$)$_2$. Even at these moderate pressures it is obvious that the activation energy depends on pressure (Fig. 12), in contrast with the observation of Dobson et al.\textsuperscript{23}. At a given pressure, we obtained similar activation energies for the two compositions K$_2$Mg(CO$_3$)$_2$ and K$_2$Ca(CO$_3$)$_2$ ($\sim 80$ kJ/mol at 3 GPa). However these activation energies differ from the ones calculated for the end-members CaCO$_3$ and MgCO$_3$ (43 – 49 kJ/mol), for dolomite (60 kJ/mol) and for alkali melts (31 – 39 kJ/mol)\textsuperscript{1} at the same pressure. This illustrates that the viscosity not only depends on the temperature, but also on the chemical composition. Recently, Kono et al.\textsuperscript{24} have reported viscosities of calcite and dolomitic (Mg$_{0.40}$Fe$_{0.09}$Ca$_{0.51}$CO$_3$) melts at temperatures just above the melting point up to 6.2 GPa, by using the falling sphere method with a powerful technique of ultra-fast synchrotron X-ray imaging. The measured viscosities ($6 - 10$ mPa·s, with an error of 9\%) are of the same order of magnitude as those of Dobson et al.\textsuperscript{23}, although the composition and the temperature differ in the two studies. The values of Kono et al.\textsuperscript{24} (at 0.9 – 6.2 GPa and 1653 – 2063 K for calcite, 3.0 – 5.3 GPa and 1683 – 1783 K for dolomite) are reported on Fig. 11. For calcite a satisfying agreement (within 10 – 15\%, i.e. within the overlap of error bars) is found with our calculations, better than with the values of Vuilleumier et al.\textsuperscript{29} For dolomite the agreement, although comprised between 3 and 30\%, is reasonable once considered some anomalous trend in the experimental data. Indeed the viscosities measured by Kono et al.\textsuperscript{24} at 3.9 GPa and 1000/T $\sim 0.6$ is lower than the one measured at 3.0 GPa at the same temperature, whereas the viscosity is expected to increase upon increasing pressure. Incidentally, we do not think that the small content (9 mol\%) of FeCO$_3$ in the experimental composition has a significant contribution to the viscosity and could account for the MD-experiment discrepancy.

For natrocarbonatite (Natrol, Na$_{1.1}$K$_{0.18}$Ca$_{0.36}$CO$_3$) at 1 bar and 823 K (near eruption conditions at the Ol
FIG. 14: Electrical conductivity as a function of viscosity. The squares are the MD data and the lines are empirical fits of the MD data by equation

\[ \sigma = A/\eta^{0.8} \]

(15)

where \( A = 4.80, 3.25 \) and 3.58 for MgCO\(_3\), CaCO\(_3\) and CaMg(CO\(_3\))\(_2\) respectively. These values are almost identical (±0.1 Å) to the ones obtained by fitting the values of \( d \) to Eq. (14).

Finally, the electrical conductivity \( \sigma \) (in S/m) and the viscosity \( \eta \) (in Pa s) can be related by the following empirical formula:

\[ \eta_{SE} = k_B T / 2\pi D d \]

(14)

where \( d \) is the diameter of the diffusing particle and \( D \) its diffusion coefficient. In the present case, the latter is assumed to be given by the arithmetic mean of the diffusion coefficients,

\[ D = \sum x_s D_s / \sum x_s \]

where \( x_s \) is the molar fraction of ion of species \( s \) in the melt. We chose \( d = 3.2, 3.5 \) and 3.4 Å for MgCO\(_3\), CaCO\(_3\) and CaMg(CO\(_3\))\(_2\) respectively. The behavior of the MD-calculated viscosity with pressure and temperature was very well reproduced by Eq. (14) using these parameters (Fig. 13). To calculate the hydrodynamic diameter in a more grounded framework we used the following expression:

\[ d = x_X d_X + x_C d_C + 2 x_X x_C d_{XC} \]

where \( d_X \) and \( d_C \) are the molar fractions ofcation X and of anion CO\(_3\), respectively, and \( d_{XC} \), \( d_{COSO_3} \) and \( d_{XCO_3} \) the cation-cation, carbonate-carbonate and cation-carbonate distances issued from the closest approach distances indicated by the corresponding PDFs (in fact, the \( d \) parameters correspond to the distances at which the integral of the PDFs is equal to 1). This ansatz leads to \( d = 3.1, 3.4 \) and 3.3 Å for MgCO\(_3\), CaCO\(_3\) and CaMg(CO\(_3\))\(_2\) respectively. These values are almost identical (±0.1 Å) to the ones obtained by fitting the values of \( d \) to Eq. (14).

V. CONCLUSION

Following our previous work on the Li\(_2\)CO\(_3\)—Na\(_2\)CO\(_3\)—K\(_2\)CO\(_3\) melts, we have studied the thermodynamics, the microscopic structure and the transport properties (diffusion coefficients, electrical conductivity and viscosity) of Ca and Mg-bearing carbonate melts up to 2073 K and 15 GPa. For that we have developed an empirical force field benchmarked on data from experiments (density of the rhombohedral crystal phases at 300 K and up to 4 GPa, and the density and the compressibility of the K\(_2\)Ca(CO\(_3\))\(_2\) melt) and from AIMD simulations (microscopic structure of five liquids). The density and compressibility, evaluated for the metastable melts of MgCO\(_3\) and CaCO\(_3\) at 1100 K and 1 bar, are in very good agreement with the estimates of the experimental literature. Moreover we have shown that alkaline-earth carbonate
mixtures behave ideally regarding the density and the compressibility. Based on the example of a Na–Ca–K melt (natrocarbonatite), the assumption of an ideal behavior for alkali-alkaline-earth mixtures seems a little less accurate but still reasonable.

The equations of state of carbonate melts with a composition of prior interest in the study of the Earth’s mantle (MgCO$_3$, CaCO$_3$ and CaMg(CO$_3$)$_2$), as well as that modeling the natrocarbonatite emitted at the Ol Doinyo Lengai volcano (Na$_{1.10}$K$_{0.18}$Ca$_{0.36}$CO$_3$), were evaluated and modeled by a third-order Birch-Murnaghan formula. Covering a large $T$, $P$ range, these data may help in the debate on the geodynamics of carbonatitic melts relative to silicate melts.$^{86}$

The analysis of the PDFs associated to the dolomitic melt showed an ideal behavior of the microscopic structure, as the PDFs in CaMg(CO$_3$)$_2$ are similar to the corresponding ones in CaCO$_3$ and in MgCO$_3$. Moreover, no major modification of the structure was observed with increasing pressure.

As for the transport properties (diffusion coefficients, electrical conductivity and viscosity), they evolve smoothly (Arrhenius-like) over the studied $T$ – $P$ domain. Thus at the high $T$ – $P$ conditions of the Earth’s mantle, Mg and Ca-bearing molten carbonates keep the main features of molten salts, namely the ions are highly mobile. For example the viscosity is comprised in the range 1 – 100 mPa·s, that is between the one of water and the one of olive oil at room conditions. However, the composition has a non negligible effect on transport coefficients: calco-magnesian melts are systematically more viscous than their alkali counterparts. These results may provide new insights into magmatic processes implying carbonatitic melts.$^{80,82,87}$

Finally we discussed the reliability of the phenomenological Nernst-Einstein and the Stokes-Einstein equations, that relate the diffusion coefficients to the electrical conductivity and to the viscosity, respectively. These relations are often used to infer one of the transport coefficient from another one that has been measured. According to the present study, both formulas lead to reasonable values. However the underlying assumptions of the relations are not always representative of the transport mechanism itself. We have shown that the fairly good predictions provided by the Nernst-Einstein equation (which assumes that the ions move independently from one another) result from a partial cancellation of interionic dynamic correlations whose dependence with composition, $T$ or $P$ is non-trivial. As a consequence we recommend a circumspect use of the Nernst-Einstein approximation.

In summary, the overall agreement between the results of the MD simulations using this force field and the full set of available experimental data (thermodynamics and transport coefficients) provides evidence of the ability of our FF to describe with accuracy the properties of any melt in the MgCO$_3$–CaCO$_3$–$\text{Li}_2\text{CO}_3$–$\text{Na}_2\text{CO}_3$–$\text{K}_2\text{CO}_3$ system.

**SUPPLEMENTARY MATERIAL**

See supplementary material for the density of crystal phases calculated by anisotropic relaxation of the rhombohedral structures up to 4 GPa, the evolution of the PDFs issued by MD with increasing pressure (up to 15 GPa), a summary of all calculated properties with their uncertainties.

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1. E. Desmaele, N. Vuilleumier, and B. Guillot, J. Chem. Phys. 150, 094504 (2019).
2. E. Desmaele, Physicochemical Properties of Molten Carbonates from Atomistic Simulations, Ph.D. thesis, Sorbonne Université (2017).
3. V. Lair, V. Albin, A. Ringued, and M. Cassir, Int. J. Hydrogen Energy 37, 19357 (2012).
4. D. Chery, V. Lair, and M. Cassir, Electrochim. Acta 160, 74 (2015).
5. D. Chery, V. Lair, and M. Cassir, Front. Energy Res. 3, 43 (2015).
6. M. Cassir, S. McPhail, and A. Moreno, Int. J. Hydrogen Energy 37, 19345 (2012).
7. M. Cassir, A. Ringued, and V. Lair, in Molten Salts Chemistry, edited by F. Lantelme and H. Grout (Elsevier, Oxford, 2013).
8. R. Dasgupta and M. M. Hirschmann, Nature 440, 659 (2006).
9. F. Gaillard, M. Malki, G. Iacono-Marziano, M. Pichavant, and B. Scaillet, Science 322, 1363 (2008).
10. R. Dasgupta and M. M. Hirschmann, Earth Planet. Sci. Lett. 298, 1 (2010).
11. R. Dasgupta, Rev. Mineral. Geochem. 75, 183 (2013).
12. F. Hammond and S. Keshav, Chem. Geol. 418, 171 (2015).
13. R. H. Mitchell, Can. Mineral. 43, 2049 (2005).
14. A. Woolley and B. Kjarsgaard, “Carbonatite Occurrences of the World: Map and Database. Geological Survey of Canada. Open File 5796,” (2008).
15. I. Keller and A. N. Zaitsev, Lithos 148, 45 (2012).
16. A. R. Woolley and A. A. Church, Lithos 85, 1 (2005).
17. A. V. Spivak, Y. A. Litvin, S. V. Ovsyannikov, N. A. Dubrovinskaya, and L. S. Dubrovinsky, J. Solid State Chem. 191, 102 (2012).
18. N. A. Solopova, Y. A. Litvin, A. V. Spivak, N. A. Dubrovinskaya, L. S. Dubrovinsky, and V. S. Urusov, Dokl. Earth Sci. 453, 1106 (2013).
19. N. A. Solopova, L. Dubrovinsky, A. V. Spivak, Y. A. Litvin, and N. Dubrovinskaya, Phys. Chem. Miner. 42, 73 (2015).
20. A. J. Irving and P. J. Wylie, Geochim. Cosmochim. Acta 39, 35 (1975).
21. K. Suito, J. Namba, T. Horikawa, Y. Taniguchi, N. Sakurai, M. Kobayashi, A. Onodera, O. Shimomura, and T. Kikogawa, Am. Mineral. 86, 997 (2001).
22. T. Kojima, Physical and Chemical Properties of Molten Carbonates, Ph.D. thesis, Kobe University (2009).
23. D. P. Dobson, A. P. Jones, R. Rabe, T. Sekine, K. Kuriita, T. Taniguchi, T. Kondo, T. Kato, O. Shimomura, and S. Urakawa, Earth Planet. Sci. Lett. 143, 207 (1996).
Supplementary Material for "The MgCO$_3$–CaCO$_3$–Li$_2$CO$_3$–Na$_2$CO$_3$–K$_2$CO$_3$
Carbonate Melts: Thermodynamics and Transport Properties by Atomistic Simulations"

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| $P$(GPa) | $n$ (g/cm$^3$) | a (Å) | b (Å) | c (Å) | $\gamma$ (°) |
|----------|----------------|-------|-------|-------|--------------|
| MgCO$_3$ |                |       |       |       |              |
| MD 0     | 3.04           | 4.60  | 4.60  | 15.07 | 120.0        |
| Exp.$^{S1}$ 0 | 3.01        | 4.64  | 15.02 | 120   |
| Exp.$^{S2}$ 0 | 3.02        | 4.64  | 14.96 | 120   |
| Exp.$^{S3}$ 0 | 3.00        | 4.64  | 15.03 | 120   |
| Exp.$^{S4}$ 0 | 3.01        | 4.64  | 15.01 | 120   |
| Exp.$^{S5}$ 0 | 3.01        | 4.63  | 15.02 | 120   |
| MD 2     | 3.07           | 4.58  | 4.58  | 14.91 | 120.0        |
| Exp.$^{S4}$ 2 | 3.06        | 4.62  | 14.91 | 120   |
| Exp.$^{S2}$ 2 | 3.03        | 4.63  | 14.95 | 120   |
| Exp.$^{S3}$ 2 | 3.06        | 4.62  | 14.91 | 120   |
| Exp.$^{S5}$ 2 | 3.06        | 4.62  | 14.88 | 120   |
| MD 4     | 3.15           | 4.57  | 4.57  | 14.77 | 119.8        |
| Exp.$^{S4}$ 4 | 3.12        | 4.59  | 14.75 | 120   |
| Exp.$^{S2}$ 4 | 3.06        | 4.62  | 14.80 | 120   |
| Exp.$^{S3}$ 4 | 3.09        | 4.60  | 14.82 | 120   |
| Exp.$^{S5}$ 4 | 3.11        | 4.60  | 14.75 | 120   |

**TABLE S1.** Crystal structure parameters for rhombohedral MgCO$_3$ at 300 K from the experimental literature (Exp.) and calculated by anisotropic MD simulations (NST ensemble).
|                | P(GPa) | n (g/cm³) | a (Å) | b (Å) | c (Å) | γ (°) |
|----------------|--------|-----------|-------|-------|-------|-------|
| CaCO₃          |        |           |       |       |       |       |
| MD             | 0      | 2.63      | 5.04  | 5.04  | 17.23 | 120.0 |
| Exp. S¹        | 0      | 2.71      | 4.99  |       |       | 17.06 |
|                |        |           |       |       |       | 120   |
| CaMg(CO₃)₂     |        |           |       |       |       |       |
| MD             | 0      | 2.84      | 4.84  | 4.84  | 16.00 | 120.0 |
| Exp. S³        | 0      | 2.84      | 4.83  |       |       | 16.01 |
|                |        |           |       |       |       | 120   |
|                | 2      | 2.91      | 4.81  | 4.81  | 15.74 | 120.0 |
| Exp. S³        | 2      | 2.89      | 4.81  |       |       | 15.87 |
|                |        |           |       |       |       | 120   |
|                | 4      | 2.97      | 4.80  | 4.80  | 15.51 | 120.2 |
| Exp. S³        | 4      | 2.94      | 4.79  |       |       | 15.74 |
|                |        |           |       |       |       | 120   |

TABLE S2. Crystal structure parameters for rhombohedral CaCO₃ and CaMg(CO₃)₂ at 300 K from the experimental literature (Exp.) and calculated by anisotropic MD simulations (NST ensemble).
FIG. S1. Pressure evolution of MD pair distribution functions in MgCO$_3$ at 2073 K (3 GPa) and at 2273 K (4.5, 6, 8, 10, 12 and 15 GPa). The color scale refers to the pressure (in GPa). To facilitate visualization, the different PDFs were shifted vertically.
FIG. S2. Pressure evolution of MD pair distribution functions in CaCO$_3$ at 1773 K (0.5 and 1 GPa), 1923 K (2 and 3 GPa) and 2073 K (5, 8, 10 and 12 GPa). The color scale refers to the pressure (in GPa). To facilitate visualization, the different PDFs were shifted vertically.
FIG. S3. Pressure evolution of MD pair distribution functions in CaMg(CO$_3$)$_2$ at 1873 K (3, 4 and 6 GPa) and 2073 K (8, 10 and 12 GPa). The color scale refers to the pressure (in GPa). To facilitate visualization, the different PDFs were shifted vertically.
| $T$ | $\langle T \rangle$ | $n$ | $\langle P \rangle$ | $\sigma$ | $\eta$ | $D_{\text{Mg}}$ | $D_{\text{CO}_3}$ |
|-----|----------------|-----|----------------|------|------|-------------|-------------|
| (K) | (K) (g/cm$^3$) | (kbar) | (S/m) | (mPa·s) | (10$^{-9}$m$^2$/s) | (10$^{-9}$m$^2$/s) |
| MgCO$_3$ | | | | | | | |
| 1940 | 1897 | 2.49 | 20 | 298 ± 5 | 5.3 ± 0.2 | 2.89 | 1.98 |
| 1940 | 1943 | 2.49 | 22 | 323 ± 5 | 5.1 ± 0.2 | 3.11 | 2.13 |
| AIMD | 1873 | 1936 | 2.49 | 45 ± 15 | / | / | 4.4 ± 0.5 | 3.2 ± 0.5 |
| 1873 | 1868 | 2.61 | 35 | 258 ± 10 | 6.9 ± 0.3 | 2.24 | 1.53 |
| 1873 | 1880 | 2.68 | 44 | 225 ± 10 | 8.1 ± 0.3 | 1.85 | 1.30 |
| 2073 | 2039 | 2.64 | 44 | 285 ± 15 | 5.7 ± 0.5 | 2.70 | 1.83 |
| 2273 | 2265 | 2.60 | 45 | 373 ± 10 | 4.6 ± 0.2 | 4.02 | 2.75 |
| 2073 | 2098 | 2.73 | 61 | 275 ± 5 | 6.7 ± 0.5 | 2.55 | 1.80 |
| 2173 | 2183 | 2.71 | 60 | 315 ± 10 | 5.7 ± 0.6 | 3.05 | 2.12 |
| 2273 | 2250 | 2.69 | 59 | 335 ± 20 | 5.3 ± 0.4 | 3.30 | 2.37 |
| 2073 | 2046 | 2.83 | 79 | 210 ± 5 | 8.2 ± 0.2 | 1.90 | 1.35 |
| 2273 | 2276 | 2.79 | 80 | 290 ± 10 | 6.2 ± 0.3 | 2.95 | 2.20 |
| 2273 | 2280 | 2.88 | 100 | 235 ± 10 | 8.0 ± 0.3 | 2.40 | 1.75 |
| 2273 | 2264 | 2.96 | 120 | 215 ± 15 | 8.8 ± 0.5 | 2.00 | 1.45 |
| 2273 | 2261 | 3.06 | 149 | 174 ± 5 | 11.5 ± 0.5 | 1.55 | 1.18 |

**TABLE S3.** Thermodynamic averages and transport coefficients issued from all MD simulations of MgCO$_3$. Diffusion coefficients estimated from the AIMD simulations are also mentioned (AIMD).
| $T$ (K) | $\langle T \rangle$ (K) | $n$ (g/cm$^3$) | $\langle P \rangle$ (kbar) | $\sigma$ (S/m) | $\eta$ (mPa·s) | $D_{\text{Ca}}$ ($10^{-9}$m$^2$/s) | $D_{\text{CO}_3}$ ($10^{-9}$m$^2$/s) |
|--------|------------------|--------------|------------------|---------|---------|----------------|----------------|
| CaCO$_3$ |
| 1623 | 1622 | 2.33 | 4.9 | 210 ± 15 | 5.3 ± 0.3 | 1.95 | 1.82 |
| AIMD (Ref. S6)  1623 |
| 1773 | 1772 | 2.28 | 5.0 | 235 ± 20 | 4.1 ± 0.3 | 2.75 | 2.45 |
| 2073 | 2057 | 2.20 | 4.9 | 335 ± 10 | 2.9 ± 0.3 | 4.75 | 4.05 |
| 1653 | 1640 | 2.37 | 8.7 | / | 6.0 ± 0.3 | / | / |
| 1653 | 1648 | 2.37 | 8.8 | 195 ± 10 | 5.8 ± 0.2 | 1.84 | 1.74 |
| 1773 | 1773 | 2.35 | 10 | 220 ± 20 | 4.9 ± 0.3 | 2.38 | 2.18 |
| 2073 | 2046 | 2.27 | 9.5 | 330 ± 10 | 3.4 ± 0.3 | 4.00 | 3.65 |
| 1923 | 1906 | 2.42 | 20 | 236 ± 10 | 5.9 ± 0.4 | 2.50 | 2.37 |
| 1813 | 1796 | 2.52 | 28 | 170 ± 10 | 7.2 ± 0.5 | 1.63 | 1.60 |
| 1923 | 1919 | 2.51 | 30 | 210 ± 10 | 5.6 ± 0.5 | 2.03 | 2.02 |
| 2073 | 2058 | 2.48 | 30 | 230 ± 10 | 5.0 ± 0.5 | 2.70 | 2.56 |
| 1773 | 1771 | 2.66 | 45 | 120 ± 10 | 10.5 ± 0.5 | 1.05 | 1.11 |
| AIMD (Ref. S6)  1773 |
| 1923 | 1913 | 2.64 | 45 ± 5 | 147 ± 15 | 10.5 ± 2.0 | 1.2 ± 0.2 | 1.0 ± 0.2 |
| 2073 | 2063 | 2.63 | 45 | 156 ± 10 | 8.2 ± 0.3 | 1.57 | 1.57 |
| 2063 | 2041 | 2.70 | 61 | 155 ± 5 | 8.1 ± 0.2 | 1.57 | 1.59 |
| 2063 | 2060 | 2.70 | 62 | / | 7.9 ± 0.3 | / | / |
| 2073 | 2056 | 2.80 | 79 | 117 ± 5 | 9.7 ± 0.9 | 1.29 | 1.24 |
| 2073 | 2040 | 2.90 | 99 | 90 ± 5 | 13.8 ± 0.4 | 0.93 | 0.96 |
| 2073 | 2064 | 2.98 | 122 | 71 ± 5 | 16.3 ± 0.9 | 0.79 | 0.85 |
| AIMD (Ref. S6)  2073 |
| 2073 | 2073 | 2.94 | 122 ± 10 | 102 ± 20 | 12.4 ± 2.5 | 1.2 ± 0.2 | 1.1 ± 0.2 |

**TABLE S4.** Thermodynamic averages and transport coefficients issued from all MD simulations of CaCO$_3$. Diffusion coefficients estimated from the AIMD simulations are also mentioned (AIMD Ref. S6).
### Table S5.

| T (K) | 〈T〉 (K) | n (g/cm³) | 〈P〉 (kbar) | σ (S/m) | η (mPa·s) | $D_{\text{Mg}}$ (10⁻⁹ m²/s) | $D_{\text{Ca}}$ (10⁻⁹ m²/s) | $D_{\text{CO}_3}$ (10⁻⁹ m²/s) |
|-------|---------|---------|------------|------|-------|-----------------|-----------------|-----------------|
| CaMg(CO₃)₂ |
| 1773 | 1755 | 2.25 | 1 | 272 ± 5 | 4.1 ± 0.3 | 2.93 | 3.0 | 2.39 |
| **AIMD** | | | | | | | | |
| 1773 | 1775 | 2.49 | 20 | 201 ± 10 | 6.3 ± 0.3 | 2.08 | 1.90 | 1.66 |
| 1573 | 1571 | 2.62 | 30 | 112 ± 10 | 12 ± 0.5 | 0.91 | 0.80 | 0.77 |
| 1683 | 1700 | 2.59 | 30 | 158 ± 10 | 1.37 | 1.20 | 1.12 |
| 1683 | 1679 | 2.59 | 30 | / | 9.6 ± 1 | / | / | / |
| 1873 | 1859 | 2.55 | 31 | 195 ± 15 | 6.9 ± 1 | 2.05 | 1.80 | 1.63 |
| 2073 | 2065 | 2.51 | 30 | 275 ± 10 | 4.8 ± 0.5 | 3.15 | 2.80 | 2.47 |
| 1653 | 1650 | 2.64 | 35 | 123 ± 10 | 11.7 ± 0.6 | 1.08 | 0.92 | 0.89 |
| 1653 | 1685 | 2.67 | 41 | 118 ± 5 | 11.4 ± 0.2 | 1.06 | 0.92 | 0.91 |
| 1873 | 1850 | 2.63 | 39 | 173 ± 10 | 7.9 ± 0.2 | 1.65 | 1.47 | 1.40 |
| 1653 | 1659 | 2.71 | 45 | 103 ± 5 | 13.2 ± 0.3 | 0.90 | 0.78 | 0.76 |
| 1653 | 1627 | 2.74 | 49 | 92 ± 3 | 16.5 ± 0.5 | 0.73 | 0.62 | 0.62 |
| 1783 | 1782 | 2.73 | 53 | 125 ± 5 | 11.1 ± 0.5 | 1.13 | 0.98 | 0.96 |
| 1623 | 1604 | 2.80 | 59 | 72 ± 7 | 22.5 ± 1.5 | 0.55 | 0.47 | 0.48 |
| 1873 | 1878 | 2.75 | 60 | 130 ± 5 | 10.7 ± 0.5 | 1.33 | 1.15 | 1.11 |
| 2073 | 2078 | 2.71 | 60 | 188 ± 10 | 7.5 ± 0.5 | 2.10 | 1.85 | 1.73 |
| 2073 | 2060 | 2.85 | 79 | 150 ± 10 | 9.3 ± 0.2 | 1.60 | 1.34 | 1.30 |
| 2073 | 2054 | 2.91 | 99 | 118 ± 5 | 12.1 ± 0.5 | 1.25 | 1.05 | 1.05 |
| 2073 | 2067 | 2.99 | 120 | 83 ± 10 | 16.9 ± 0.5 | 1.02 | 0.85 | 0.85 |

**TABLE S5.** Thermodynamic averages and transport coefficients issued from all MD simulations of CaMg(CO₃)₂. Diffusion coefficients estimated from the AIMD simulations are also mentioned (AIMD).
| $T$ (K) | $\langle T \rangle$ (K) | $n$ (g/cm$^3$) | $\langle P \rangle$ (kbar) | $\sigma$ (S/m) | $\eta$ (mPa·s) | $D_{X_1}$ (10$^{-9}$m$^2$/s) | $D_{X_2}$ (10$^{-9}$m$^2$/s) | $D_{CO_3}$ (10$^{-9}$m$^2$/s) |
|---------|-----------------|--------------|-----------------|--------------|--------------|------------------|------------------|------------------|
| Na$_2$CO$_3$–MgCO$_3$ | | | | | | | | |
| 0.50:0.50 (mol) | 1323 1321 | 2.45 | 0.3-0.7 | 30 | 98 ± 5 | 15.3 ± 1 | 1.52 | 0.56 | 0.48 |
| | 1573 1576 | 2.40 | 29 | 186 ±10 | 6.9 ± 0.2 | 3.80 | 1.48 | 1.30 |
| K$_2$CO$_3$–MgCO$_3$ | | | | | | | | |
| 0.50:0.50 (mol) | 1273 1247 | 2.48 | 30 | 20 ± 3 | 60 ± 7 | 0.42 | 0.13 | 0.125 |
| | 1373 1367 | 2.45 | 30 | 38 ± 5 | 26.3 ± 1 | 0.87 | 0.32 | 0.30 |
| | 1473 1468 | 2.42 | 30 | 58 ± 5 | 16.5 ± 1 | 1.39 | 0.53 | 0.53 |
| | 1573 1561 | 2.40 | 30 | 75 ± 10 | 11.7 ± 0.5 | 1.98 | 0.81 | 0.79 |
| | 1673 1687 | 2.37 | 30 | 102 ± 5 | 7.7 ± 0.6 | 2.80 | 1.24 | 1.20 |
| 0.56:0.44 (mol) | 1673 1645 | 2.39 | 29 | 94 ± 5 | 9.6 ± 0.3 | 2.28 | 1.06 | 0.9 |
| 0.25: 0.75 (mol) | 1673 1654 | 2.47 | 29 | 102 ± 5 | 11.2 ± 0.2 | 1.70 | 1.06 | 0.88 |
| K$_2$CO$_3$–CaCO$_3$ | | | | | | | | |
| 0.50:0.50 (mol) | 1100 1094 | 2.14 | 0 | 70 ± 5 | 15.1 ± 1.5 | 1.38 | 0.45 | 0.43 |
| | 1200 1189 | 2.09 | 0 | 100 ± 10 | 9.0 ± 0.5 | 2.15 | 0.74 | 0.72 |
| | 1223 1211 | 2.44 | 25 | 30 ± 1 | 35 ±5 | 0.61 | 0.24 | 0.21 |
| | 1423 1403 | 2.38 | 24 | 75 ± 10 | 12 | 1.64 | 0.68 | 0.65 |
| | 1300 1288 | 2.46 | 30 | 37 ± 5 | 28 ± 5 | 0.77 | 0.31 | 0.29 |
| | 1573 1584 | 2.39 | 30 | 95 ± 10 | 9 ± 0.5 | 2.45 | 1.12 | 1.05 |

TABLE S6. Thermodynamic averages and transport coefficients issued from all MD simulations of binary mixtures Na$_2$CO$_3$–MgCO$_3$, K$_2$CO$_3$–MgCO$_3$ and K$_2$CO$_3$–CaCO$_3$. The notation $X_1$ (= Na or K) and $X_2$ (= Mg or Ca) are assigned in the same order as appearing in the composition name (first column).
TABLE S7. Thermodynamic averages and transport coefficients issued from all MD simulations of ternary mixtures Li$_2$CO$_3$–Na$_2$CO$_3$–CaCO$_3$ and Na$_2$CO$_3$–K$_2$CO$_3$–CaCO$_3$. The notation $X_1$ (= Li or Na) and $X_2$ (= Na or K) are assigned in the same order as appearing in the composition name (first column).
REFERENCES

[S1] S. A. Markgraf and R. J. Reeder, *Am. Mineral.* **70**, 590 (1985).
[S2] S. A. T. Redfern, B. J. Wood, and C. M. B. Henderson, *Geophys. Res. Lett.* **20**, 2099 (1993).
[S3] G. Fiquet, F. Guyot, and J.-P. Itie, *Am. Mineral.* **79**, 15 (1994).
[S4] J. Zhang, I. Martinez, F. Guyot, P. Gillet, and S. K. Saxena, *Phys. Chem. Miner.* **24**, 122 (1997).
[S5] N. L. Ross, *Am. Mineral.* **82**, 682 (1997).
[S6] R. Vuilleumier, A. Seitsonen, N. Sator, and B. Guillot, *GCA* **141**, 547 (2014).