

The effect of volatiles on properties of kimberlite melts

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Introduction

Kimberlite magmas derive from a carbon-rich parental melt [Wyllie 1980; Dalton and Presnall 1998] and ascent through narrow dykes at high speeds. Differences in emplacement styles are highly dependent on the primary melt compositions [Tovey et al. 2022]. CO₂ and H₂O are the main volatile component of kimberlite melts; they play a critical role in lowering the viscosity of the melt, promoting magma mixing, and enhancing bubble growth [Zhang and Gan 2022]. Kimberlites degas large quantities of CO₂ as they erupt, forming diatremes and other more irregularly shaped bodies.

While there has been significant research on kimberlite volcanism [Sparks et al. 2006; Sparks 2013; Giuliani 2023; Tovey et al. 2022], the lack of knowledge about the composition of the parental melt hampers our understanding of it. Kimberlite melts are generated with a low degree of partial melting of a carbonated peridotite when its solidus meets the cratonic geotherm [Wyllie 1980, Bailey 1980]. Melts formed this way would likely inherit high concentrations of carbon.

Here, we use ab initio molecular dynamics simulations (AIMD) to determine the effect of the composition, and in particular, the role of carbon, on the dynamic behavior of kimberlite melts. We study the kimberlite melts across a pressure-temperature range characteristic to the upper mantle and the crust. We analyze the behavior of carbon in the kimberlite magmas in terms of diffusion, speciation, and melt structure.

Methods

The AIMD simulations were performed using the Vienna Ab initio Simulation Package [Kresse et al. 1996]. The electronic structure is calculated using the projector augmented wave method [Bloch 1994] within the Density Functional Theory [Kohn and Sham 1965]. We employ the general gradient approximation in Perdew–Burke–Ernzerhof [Perdew et al. 1996] formulation for the exchange–correlation function. The kinetic cutoff energy for the plane-wave expansion of the wave functions was set to 600 eV, the augmentation charge at 800 eV. The electronic wavefunctions were sampled at the Gamma point in the reciprocal space. With these parameters, the internal energy converged to better than 15 meV/atom. The simulations were performed within the canonical ensemble with constant volume, V and number of atoms, N; the temperature, T, was controlled using a Nose-Hoover thermostat [Hoover 1985, Nose 1984]. The timestep was 1 fs, after a thermalization period of 1 ps, the runs lasted between 2 and 8 picoseconds. The simulations were performed at temperatures of 1500, 2000, 2500, and 3000 K.

We start our simulations using the Jericho kimberlite composition [Kopylova et al. 2007]. Starting with measurements of the whole-rock composition, we first build a ‘dry’ kimberlite melt, i.e., devoid of volatiles, with stoichiometry Mg₅₂Si₃₃Ca₁₇Fe₈Ti₂Al₁K₁O₁₅₁. For this dry kimberlite melt composition, we use a cubic cell containing 265 atoms. In a second set of simulations, we add 17 molecules of CO₂ to the thermalized dry kimberlite melt to simulate the carbonated kimberlite composition.

We use the UMD package [Caracas et al. 2021] to perform the post-processing of the AIMD results. First, we extract the thermodynamic parameters, like pressure, temperature, and energy. Then, we compute the mean squared displacements (MSD) of the atoms. The linear regression fit of the diffusive regime of the MSD curves yields the self-diffusion coefficients of each element. Then, we calculate the pair distribution function (PDF). The PDFs describe the relative geometric relations between the atoms. The first maximum of the PDF marks the most common interatomic distance, oftentimes considered as the average bond length. The first minimum of the PDF determines the radius of the first coordination sphere. We use the value of this radius to define whether or not two atoms are bonded. This also allows us to construct a connectivity matrix, to identify the different chemical species in the melt, and to separate the melt from the vapor phase.

Results and discussion

The average bond lengths between the atoms at 3000 K and 0.97 GPa, obtained from the analysis of the PDFs, are 1.83 Å for Fe-O, 1.63 Å for Si-O, 1.82 Å for Al-O, 1.97 Å for Mg-O, 1.83 Å for Ti-O, 2.28 Å for Ca-O, 2.7 Å for K-O and 1.27 Å for C-O. Over the 0 – 45 GPa pressure range, the bond distances between cations and oxygen decrease by less than 10%. In addition to oxygen, at certain temperatures and pressures, carbon also shows clear maxima and minima in the PDFs with Fe, C, and Si, with maxima at 1.9 Å, 1.5 Å, and 1.9 Å, respectively.

The speciation of carbon in the melt is dominated by the carbonate ion CO_3^{2-} . This is in full agreement with other observations, both theoretical and experimental, on carbonated silicate melts. CO and CO_2 are the second most common species at lower pressures but CO_4 steadily becomes more prominent as pressure increases. We observe that at higher temperatures, the pressure at which CO_4 starts to be more abundant than CO and CO_2 decreases.

At low pressures, the formation of vapor starts with the nucleation of nanobubbles. We identify the nanobubbles from the bimodal distribution of the polymerization clusters in the melt. At high densities, all the atoms are bonded, resulting in a large infinite polymer. Upon decompression, as the bonds are continuously stretched, there is a density below which the metastability limit is breached. At densities lower than this value, a nanocavity separates spontaneously in the simulation cell, where small atomic clusters can freely fly. The cavity represents a nanobubble, and the clusters represent the gas phase.

We obtain that the liquid and gas phases start to separate at 2.3 GPa and 3000 K, corresponding to a depth of about 60 kms. Considering that the depth of CO_2 exsolution is a function of melt composition, primarily the SiO_2 and H_2O content of the melt, and the anhydrous nature of our system, water enabling a deeper exsolution of the CO_2 phase, these results indicate a possibility of a deeper starting point of CO_2 exsolution. This supports the ability of kimberlite magmas to transport xenoliths and xenocrysts from mantle depths.

The self-diffusivity coefficients values are between 10^{-9} and 10^{-8} , which are typical values for a liquid. The CO_2 does not influence largely the diffusivity values of the atoms present in the anhydrous silicate melt. This consists of previous experiments [Watson 1991, Blank 1993, Sierralta et al. 2002] and theoretical [Zhang and Ni 2010, Davis et al. 2022, Solomatova and Caracas 2021] determinations.

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