



Ni partitioning between metal and silicate melts: An exploratory *ab initio* molecular dynamics simulation study



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ABSTRACT

Element partitioning is a key geochemical process. While partition coefficients between phases including melts have been measured in many experimental studies, new insight into the mechanisms of partitioning may be obtained by relating partitioning to melt structure. Here, we address this problem by exploring an *ab initio* molecular dynamics simulation approach. Combined with the thermodynamic integration method, these simulations provide a unique way to predict simultaneously thermodynamic properties related to element partitioning and information about the molecular structure of the melt. Thus, it should be possible not only to predict the partitioning of elements, but also to provide an explanation for this behavior based on atomic structures of the coexisting phases. Using this approach, we derive from first-principles the Ni partition coefficient between a metal and a silicate melt at 2500 K and ambient pressure, which is at least in qualitative agreement with experiment. Structural analysis of various (Mg,Fe,Ni)₂SiO₄ silicate and (Fe,Ni) metal melts reveals that the Ni partitioning is mainly determined by its structural environment in the silicate melt, whereas the coordination environments of Ni and Fe are almost indistinguishable in the metal melt. Possible strategies to improve the predictive power of the proposed approach are discussed.

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1. Introduction

Element partitioning is a fundamental geochemical process that has occurred throughout the whole history and in all parts of the Earth. Scientific interest to understand element partitioning, e.g., for constraining the conditions during Earth accretion and its further evolution has been prevalent for decades (Goldschmidt, 1937; Ringwood, 1966). Besides measuring element concentrations in natural samples, experimental approaches have been used widely to determine element partition coefficients. In particular, many of these experimental studies were focussed on systems related to partitioning processes during Earth and planetary formation, e.g. Boujibar et al. (2014), Chi et al. (2014), Mann et al. (2012), O'Neill et al. (1995), Righter and Ghorso (2011), Rubie et al. (2003), Siebert et al. (2012, 2011), Thibault and Walter (1995), Wade and Wood (2005), Wade et al. (2012), and Rai and van Westrenen (2014). One of the biggest challenges in recent years has been to access the extreme conditions of pressure and temperature during accretion and deep inside planetary bodies

and exciting progress has been made in this respect. For instance, metal–silicate melt partition coefficients have been determined up to conditions of the base of a presumed terrestrial magma ocean, from which unique information about Earth's core formation could be obtained (e.g. Bouhifd and Jephcoat, 2011, Siebert et al., 2012).

Knowledge of the structural properties of the phases between which elements are distributed can be instrumental in obtaining a deeper understanding of the processes involved. While most of the relevant crystal structures are relatively well known, the structure of melts (or fluids) and especially the local atomic coordination environment of the fractionating elements are not well constrained in many cases. Yet, structural information about melts and fluids on the atomic scale is even more challenging to derive from experiments, especially for minor and trace elements. Recently, silicate melt structures have been studied up to extreme conditions, including those of Fe₂SiO₄ (Sanloup et al., 2013) or aluminosilicate melts (Drewitt et al., 2015).

In recent years, computational performance and methods have expanded greatly, so that it is now possible to use *ab initio* methods to model element exchange reactions and to receive structural information at the same time. These methods are based on quantum-mechanics, often in the framework of density functional theory (DFT). In combination with the molecular dynamics method

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(Marx and Hutter, 2012), melt structures as well as their physical and thermodynamic properties have been predicted in a wide range of pressures and temperatures (e.g. Alfè et al., 2002; de Koker et al., 2008; Muñoz Ramo et al., 2014; de Koker et al., 2013). Many thermodynamic properties require the evaluation of the Helmholtz or the Gibbs free energy, which is not directly accessible by standard molecular dynamics methods. One way of calculating free energy differences is to combine molecular dynamics simulations with the thermodynamic integration method (Frenkel and Smit, 2002). For instance, the free energy difference of element exchange between silicate melts with different degrees of polymerization was examined recently using the thermodynamic integration method of alchemical transmutation in conjunction with classical molecular dynamics simulations (Haigis et al., 2013).

The goal of this study is to explore the possibility to predict element partition coefficients between metal and silicate melts using an *ab initio* approach. We will combine *ab initio* molecular dynamics simulations with the thermodynamic integration method to model the metal–silicate partitioning of Ni at ambient pressure, where both structural and partitioning data is available from experiments (e.g. Thibault and Walter, 1995; Farges and Brown Jr., 1996; Schenk et al., 2002; Drewitt et al., 2013; Sanloup et al., 2013). Ni is assumed to be the second most abundant element in the Earth's core and Ni partitioning between metal and silicate melts has been studied extensively (Thibault and Walter, 1995; Bouhifd and Jephcoat, 2011; Siebert et al., 2012), e.g., to constrain the depth of the magma ocean. Thus, if eventually accurate enough, this computational approach has the potential to provide unprecedented insight into partitioning behavior also at extreme conditions and for other important elements such as Co and Cr.

2. Computational details

2.1. *Ab initio* molecular dynamics simulations

A computationally rather costly *ab initio* approach becomes necessary for this study, because classical potentials are not suitable for an accurate description of atomic interactions in both a metal phase and a silicate phase. DFT provides an efficient way of treating larger systems of interacting particles in the framework of quantum theory. Here, we used the QUICKSTEP module (VandeVondele et al., 2005) as implemented in the CP2K program package (Hutter et al., 2014). A hybrid Gaussian plane-wave (GPW) method (Lippert et al., 1997) was employed that combines double-zeta valence plus polarization basis sets (DZVP) (VandeVondele and Hutter, 2007) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional (Perdew et al., 1996) and Goedecker–Teter–Hutter norm-conserving pseudopotentials (Goedecker et al., 1996; Hartwigsen et al., 1998; Krack, 2005). A plane wave cutoff of 400 Ry for the Kohn–Sham orbitals was chosen as a compromise between accuracy and computational speed.

Periodic boundary conditions were applied to the individual melt systems. Volumes of the cubic simulation cells were adjusted to represent melt densities at ambient pressure from the literature. For the silicate melts, the simulation cells contained 112 atoms of M_2SiO_4 with different amounts of M = Mg, Fe and Ni (see Table 1). The molar volume of the silicate melts was fixed to 56.5 cm³/mol, which corresponds closely to experimental and simulation data of Mg_2SiO_4 melts (see e.g. Table 1 of Adjaoud et al., 2008). The simulation boxes of the metal melts contained 64 atoms with varying amount of Fe and Ni (see Table 1). Here, the simulation box size was chosen according to the experimental density of pure Fe melt at 2500 K, $\rho = 6.4$ g/cm³ (Assael et al., 2006). The Mg–Fe–Ni ratios of runs #SLN (silicate melt with low Ni content) and #MHN (metal melt with high Ni content) were chosen to sample approximately the compositions of the silicate and metal melts from experimental studies

Table 1

Composition and simulation cell length (Å) of the different silicate (S) and metal (M) melts with low Ni (LN) and high Ni (HN) concentrations.

Run #	Composition	Cell length (Å)
#SLN	Mg ₂₇ Fe _{5–4} Ni _{0–1} Si ₁₆ O ₆₄	11.45
#SHN	Mg ₂₀ Fe _{5–4} Ni _{7–8} Si ₁₆ O ₆₄	11.45
#MLN	Fe _{63–62} Ni _{1–2}	9.75
#MHN	Fe _{49–48} Ni _{15–16}	9.75

(Thibault and Walter, 1995; Bouhifd and Jephcoat, 2011). In addition, a Ni-poor metal phase (#MLN) and a Ni-enriched silicate (#SHN) are simulated to investigate the effect of different Ni concentrations on the molecular structure and the thermodynamic properties of element exchange. Please note that the molecular formulae in Table 1 contain the total number of atoms in the simulation cell. The temperature in the simulation (2500 K) was chosen to be relatively close to the experimental one from Thibault and Walter (1995) (2123 K). At temperatures lower than 2500 K, Si–O bonds are not sufficiently often broken or formed to reach equilibrium on the MD time scale (Spiekermann et al., 2016). Melt densities above ambient pressure are not well known for the melt pair. Thus, we chose to run the simulations at ambient pressure compared to 1.2 GPa in the experimental study by Thibault and Walter (1995).

Time-averaged structure models of all melts were obtained from Born–Oppenheimer-type *ab initio* molecular dynamics (AIMD) simulations using an NVT ensemble (constant number of particles, volume and temperature). A temperature of 2500 K is maintained using a Nosé–Hoover (Nosé, 1984a, b) thermostat. A time step of 0.95 fs was used for the numerical integration of the equations of motion. Initial configurations for the AIMD simulations of the silicate melts were obtained from classical molecular dynamics simulations of Mg_2SiO_4 melts using an advanced polarizable ion potential (Jahn and Madden, 2007). Initial metal melt configurations were obtained from the silicate melt by transforming the 64 oxygen atoms into Fe/Ni and squeezing the simulation cell to the desired density. Subsequently, the metal melt was equilibrated using AIMD for 7 ps. Trajectories of production runs were collected for approximately 7 ps, of which the last 5 ps were used for structural and energetic analysis.

2.2. Structural analysis

The atomic structure of melts is commonly described in terms of radial distribution functions, which represent the probabilities for finding pairs of atoms at a certain distance r normalized to the mean atomic number density. For a multicomponent system, partial radial distribution functions are defined for each pair of elements i and j

$$g_{ij}(r) = \frac{1}{c_i c_j \rho_0 N} \sum_{\alpha=1}^{N_i} \sum_{\beta=1}^{N_j} \delta(\mathbf{r} - (\mathbf{r}_\alpha - \mathbf{r}_\beta)) \quad (1)$$

where N and ρ_0 are the total number of atoms in the system and the number density of the melt. c_i and N_i are the concentration and the number of atoms of element i . $\delta(\mathbf{x})$ is equal to one if $\mathbf{x} = \mathbf{0}$ and zero otherwise. \mathbf{r}_α and \mathbf{r}_β are position vectors of atoms α and β and \mathbf{r} is a distance vector with length r . Average coordination numbers n_i^j of atom i by atoms j are obtained from the integration over the first peak of $g_{ij}(r)$ up to the first minimum at r_{min}

$$n_i^j = 4\pi\rho_0 c_j \int_0^{r_{min}} g_{ij}(r) r^2 dr. \quad (2)$$

The peak positions of $g_{ij}(r)$ represent the most probable interatomic distances of the different coordination shells.

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