Metal transport in vapor fluids: Insights from *ab initio* molecular dynamics simulation

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In recent years there has been considerable speculation that low-density vapors play an important role in metal transport in magmatic-hydrothermal systems. A number of experiments have been carried out to investigate metal solubilities in the vapor phase and the partitioning of metal species between liquid/vapor/melt (reviewed in Seward et al, 2014). Metal solubility in vapors is a consequence of the complexation by ligands such as H_2O, H_2S, HCl; knowledge of the identity, stoichiometry and thermodynamic properties of metal complexes is thus essential for modeling the dissolution, transport of metals in the vapor phase and deposition. Solubility experiments (Migdisov et al, 2013a,b) show an exponential increase of species hydration as a function of water fugacity.

In this study, we used *ab initio* Molecular Dynamics (MD) simulations to investigate the complexation, geometries, thermodynamic properties, and the nature of hydration of metal complexes in the vapor phase. The Density Functional Theory (DFT) based Car-Parrinello MD (CPMD) method enables us to model transition metals as well as hydrogen bonding around the complexes accurately. Au-Cl and Cu-Cl complexes over a wide range of fluid density (0.02 to 1.18 g/cm^3) were investigated, covering the full range from dense fluids to vapors. The simulation results confirm that changes in hydration contributes to the change of metal solubility in low-density fluids, as suggested by the solubility experiments of Migdisov et al (2013a,b).

[1] Seward, *et al* in *Treatise on Geochemistry (Second Edition)*. (Elsevier, Oxford, 2014), pp. 29-57 [2] Migdisov and Williams-Jones, *Geochimica et Cosmochimica Acta* **104**, 123 (2013a) [3] Migdisov, *et al Geochimica et Cosmochimica Acta*, (2013b), doi: 10.1016/j.gca.2013.12.024