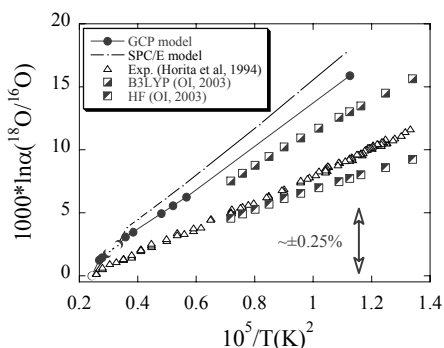


## Molecular-based Simulation of Liquid-vapor equilibrium isotopic fractionation of water

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Liquid-vapor equilibrium isotopic fractionation of water is determined via Gibbs Ensemble Monte Carlo and isothermal-isochoric molecular dynamics simulations of two radically different but realistic models, the extended simple point charge (SPC/E) and the Gaussian charge polarizable (GCP) models. The predicted temperature dependence of the liquid-vapor equilibrium isotopic fractionation factors for  $\text{H}_2^{18}\text{O} / \text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O} / \text{H}_2^{16}\text{O}$ , and  $^2\text{H}^1\text{H}^{16}\text{O} / ^1\text{H}_2^{16}\text{O}$  are compared against the most accurate experimental datasets [1, 2] to assess the ability of these intermolecular potential models to describe quantum effects according to the Kirkwood-Wigner free energy perturbation  $\hbar^2$ -expansion [3].



**Figure 1:** Liquid-vapor  $\text{H}_2^{18}\text{O} / \text{H}_2^{16}\text{O}$  fractionation.

Representative results in Figure 1 illustrate the agreement between the model predictions and the experimental data; they are within  $\pm 3\%$  even though the GCP model appears more accurate. In contrast, the experimental data are sandwiched between the two sets of *ab initio* predictions [4] whose deviations from each other are similar in magnitude to that between our simulation and experiment. Predictions of the corresponding vapor-pressure isotopic effect are also given in comparison with experimental data and two recently proposed thermodynamic modeling approaches. Extensive discussion on the other fractionation pairs, including the mechanism underlying the rule of the geometric mean for the H/D substitution and its relation to roto-translational coupling, are given in [5].

## Copper behaviour in andesitic magmas evolving at high $p\text{H}_2\text{O}$ (Pilavo volcano, Ecuador)

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Formation of porphyry-type deposits results from the positive coincidence of several geodynamic, tectonic and magmatic factors. Magmatic evolution may play an important role in sequestering chalcophile metals (e.g., Cu, Au) into early crystallizing mineral phases or leaving them available until later stages when a fluid phase exsolves from the magma. In this study we investigate the behaviour of Cu in andesitic lavas of the Pleistocene Pilavo volcano, Western Cordillera of Ecuador, through LA-ICP-MS analyses of amphibole, the most abundant phenocrystic phase in these lavas. Pilavo lavas result from magma mixing between two end-members: (i) a low Ni (<10 ppm) mafic magma that has undergone abundant fractional crystallization of olivine, clinopyroxene  $\pm$  amphibole at subcrustal or lower crustal depths and (ii) a felsic magma that has evolved through extensive amphibole fractionation under high  $p\text{H}_2\text{O}$ , probably at mid-crustal levels. Mixing resulted in a wide range of incompatible element contents for a limited range of major elements, correlations between elements and radiogenic isotopes, and inverse zoning in amphibole phenocrysts.

Copper (and to less extent also Zn and Co) contents decrease steadily from a maximum of 220 ppm in amphiboles of the least evolved lava to a maximum of 40 ppm in amphiboles of the most evolved lava. The Cu decrease in amphibole does not correspond to a Cu decrease in the host rocks (which remains the same  $\sim 45$  ppm). This is because in the most evolved lavas Cu occurs in abundant droplets (few micrometers in size) of Cu-Fe sulfides hosted by magnetite micro-phenocrysts in the matrix of the lava, whereas in the least evolved lavas Cu-Fe sulfides are absent. These data suggest Cu sequestration by amphibole in the mafic end-member at high pressure and Cu partitioning into a non-silicate melt/fluid during fractionation of the felsic end-member under high  $p\text{H}_2\text{O}$  conditions at lower pressures. This is supported by positive correlations between Cu and Li in amphiboles. The association of Cu-Fe sulfides with magnetite might suggest sulfide saturation due to Fe subtraction by magnetite crystallization or direct partitioning of Cu into a Fe-O-S melt at some stage of the magmatic evolution.

[1] Horita & Wesolowski (1994) *GCA* **58**, 3425. [2] Barkan & Luz (2005) *Rap. Comm. Mass Spect.* **19**, 3737. [3] Chialvo & Horita (2003) *J. Chem. Phys.* **119**, 4458, *ibid* (2006) *J. Chem. Phys.* **125**, Art. 34510. [4] Oi (2003) *J. Nucl. Sci. Tech.* **40**, 517. [5] Chialvo & Horita (2009) *J. Chem. Phys.* **130**, Art. 094509.