Equilibrium isotope fractionation factors in liquids from path integral molecular dynamics simulations

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The equilibrium fractionation factor between two phases is of importance for the understanding of many planetary and environmental processes. Although thermodynamic equilibrium can be achieved between minerals at high-temperature, many processes in Earth and environmental sciences involve reactions between liquids or aqueous solutions and solids [1]. In crystals, the fractionation factor α is theoretically modelled using a statistical thermodynamic approach to calculate the equilibrium constants of isotope exchange reactions from the vibrational energy levels of the phases [2]. These calculations are mostly based on empirical or ab-initio description of the systems to extract the harmonic vibrational information. In the case of a periodic systems such as liquid phases and solutions, further approximations are however required and could include the use of finite-size molecular clusters or the use of relaxed configurations taken from molecular dynamics (MD) runs.

In this work we present a systematic study of the calculation of the D/H and $^{18}O/^{16}O$ equilibrium fractionation factor in water for the liquid/vapour and ice/vapour phases using several levels of accuracy within the simulations. Namely, we use MD in combination with an empirical potential model for water. The exact fractionation factor for this potential is obtained from thermodynamic integration using Path Integral MD calculations. Compared with standard MD, this method makes it possible to take into account quantum effects in the thermodynamic modelling of liquids. We compare these results with those of the modelling strategies usually used, which involve the mapping of the quantum system on its harmonic counterpart. Accordingly, we discuss the implications of these approaches for the calculation of fractionation factors in liquid systems.

[1]Hoefs (1997) Stable Isotope Geochemistry (Springer, Berlin). [2] M. Blanchard *et al* (2009) Geochim. Cosmochim. Acta **73**, 6565-6578

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Insights into a volatile rich subcontinental lithospheric mantle: lherzolithe xenoliths from the Cameroon Volcanic Line, Africa

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We have carried out detailed petrographic, petrophysical (EBSD), geochemical and fluid inclusion study (e.g. Raman, FTIR coupled synchrotron radiation, FIB) on spinel lherzolite xenoliths from Barombi Mbo (BM) and Nyos Lake coupled with study of the H2O content of their nominally anhydrous minerals (NAMs). Results indicate that the BM protogranular xenoliths provide a characteristics of a juvenile subcontinental lithospheric mantle suffered low degree partial melting and record deformation regime governed by combination of simple and pure shear. The NAMs in BM xenoliths show moderate bulk water content (100-130 ppm). Their fluid inclusions consist of high-density CO2-H2O(-H2S) system, which also contain phlogopite as a step-daughter mineral. The porphyroclastic Nyos xenoliths preserve a transpressional deformation regime and metasomatism indicated by the presence of pargasite. Nyos xenoliths have low bulk NAMs H2O content (10-60 ppm) and their fluid inclusions also contain high-density CO_2-H_2O(-H_2S) fluids with phlogopite and pargasite step-daughter minerals.

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