From quantum mechanics to molecular diffusion and climate reconstruction

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(Atmospheric) noble gases (NG) are routinely used to reconstruct past climate conditions and to analyse water transport and phase partitioning. Molecular diffusive transport is one of the controls of such exchange mechanisms. To retrieve information on age and on past climate conditions lump parameter models (LPM) are applied to convert NG concentrations into environmental conditions prevailing air-water exchange. Some of these LPMs account for molecular diffusion. Thus, the possible isotopic fractionations of Ne and Ar are used often used discard certain conversion schemes. However, classical molecular dynamics simulations (MD) challenged the common, but principally unmotivated assumption that molecular transport through water forces isotopic fractionation of NGs. Consequently climate reconstruction from dissolved NG concentrations remained in a limbo as there was no decisive criteria to choose the adequate LPM. To close that conceptual limit we experimentally determined the isotopic fraction of Ne, Ar, Kr and Xe upon molecular diffusion though water and applied ab-initio MD accounting for quantum-mechanics (AIMD) to elucidate the molecular mechanisms ruling noble gas diffusion.

Remarkably, the experiments showed only Ar to undergo isotopic fraction. AIMD identified the atomic size and the polarizability to constrain molecular motion through water. Such small-scale transport is subject to different 'diffusive regimes' forcing He and Ar to isotopically fractionate, but much less so for Ne, Kr and Xe. These results allow using the possible fractionation of Ar isotopes to choose the 'correct' LPM and put climate reconstruction based on dissolved NGs back on solid conceptual grounds.