



Solute isotopic fractionation by diffusion in liquid water at the molecular and field scales, illustrated with argon: **(a)** MD simulations of real and hypothetical argon isotopes in liquid water (the snapshot shows ^{40}Ar and its first solvation shell) yield **(b)** data on the mass-dependence of the diffusion coefficient of argon (shown on a log-log plot). An inverse power-law mass-dependence of D is found for all solutes, with **(c)** inverse power-law exponents β consistent with experimental data (Richter et al., 2006; Bourg et al., 2008) (shown as a function of solute radius). The mass dependence of D can be used to model geochemical data such as **(d)** field data on $^{36}\text{Ar}/^{40}\text{Ar}$ isotopic ratios as a function of depth in low-permeability anoxic lake sediments [yellow symbols: experimental data (Brennwald et al., 2005); dotted curve: model prediction based on the “square root” relation $D \propto m^{-0.5}$ (Brennwald et al., 2005); thick curve, with confidence intervals shown as thin curves: model prediction based on our MD simulation results (Bourg and Sposito, 2008)].

