



(a) We used MD simulation and experimental methods to determine the mass (m) dependence of alkali metals diffusion coefficients (D) in liquid water at 348 K (Bourg and Spósito, 2007; Bourg et al., 2009), finding that $D \propto m^\beta$ for all alkali metals in the isotopic mass range $m \approx 2$ -100 Da. (b) Identical power-law exponents β were obtained experimentally and by MD simulation. The small β -value of the weakly-solvated Cs^+ ion contradicts a common assumption in isotopic geochemistry: that a mass dependence of D smaller than that predicted by kinetic theory models must imply that the solute diffuses as a “solventberg” of large effective mass. (c) To gain insight into the mass-dependence of D , we calculated the memory function $K(t)$, a measure of the relaxation of solvation interactions, for all solute isotopes. Our results, shown here for five isotopes of Cs^+ , are consistent with a decomposition of $K(t)$ into a short-time, Gaussian-like binary-collision component (at $t < 0.5$ ps) and a long-time hydrodynamic component. They show, apparently for the first time, that the binary-collision component of $K(t)$ relaxes more rapidly for light isotopes (i.e., the “rattling motions” of light ions in their solvation cages hasten the relaxation of solvation interactions). This mass-dependence of the short-time component of $K(t)$ is strongly dampened by the long-time hydrodynamic component. Thus, β is small if hydrodynamics contribute importantly to the overall friction [the integral of $K(t)$ from 0 to ∞], which is the case for large solutes (such as Cs^+) and for small, strongly solvated solutes (such as Li^+) (Bourg et al., 2009).

