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Kinetic isotopic fractionation during diffusion of ionic species in water

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Abstract

Experiments specifically designed to measure the ratio of the diffusivities of ions dissolved in water were used to determine $D_{\mathrm{Li}}/D_{\mathrm{K}}$, $D_{^{7}\mathrm{Li}}/D_{^{6}\mathrm{Li}}$, $D_{^{25}\mathrm{Mg}}/D_{^{24}\mathrm{Mg}}$, $D_{^{26}\mathrm{Mg}}/D_{^{25}\mathrm{Mg}}$, and $D_{^{37}\mathrm{Cl}}/D_{^{35}\mathrm{Cl}}$. The measured ratio of the diffusion coefficients for Li and K in water ($\mathrm{D_{Li}/D_K} = 0.6$) is in good agreement with published data, providing evidence that the experimental design being used resolves the relative mobility of ions with adequate precision to also be used for determining the fractionation of isotopes by diffusion in water. In the case of Li, we found measurable isotopic fractionation associated with the diffusion of dissolved LiCl ($D_{^{7}\mathrm{Li}}/D_{^{6}\mathrm{Li}} = 0.99772 \pm 0.00026$). This difference in the diffusion coefficient of ^{7}Li compared to ^{6}Li is significantly less than that reported in an earlier study, a difference we attribute to the fact that in the earlier study Li diffused through a membrane separating the water reservoirs. Our experiments involving Mg diffusing in water found no measurable isotopic fractionation ($D_{^{25}\mathrm{Mg}}/D_{^{24}\mathrm{Mg}} = 1.00003 \pm 0.00006$). Cl isotopes were fractionated during diffusion in water ($D_{^{37}\mathrm{Cl}}/D_{^{35}\mathrm{Cl}} = 0.99857 \pm 0.00080$) whether or not the co-diffuser (Li or Mg) was isotopically fractionated. The isotopic fractionation associated with the diffusion of ions in water is much smaller than values we found previously for the isotopic fractionation of Li and Ca isotopes by diffusion in molten silicate liquids. A major distinction between water and silicate liquids is that water surrounds dissolved ions with hydration shells, which very likely play an important but still poorly understood role in limiting the isotopic fractionation associated with diffusion.

1. Introduction

Mass-dependent kinetic isotope fractionation during chemical diffusion is a well-known phenomenon in gases and certain liquids. In the case of an ideal gas at sufficiently low pressure such that collisions are infrequent, kinetic theory predicts that the ratio of the diffusion coefficients of two gaseous species will be proportional to the inverse square root of their molecular mass, which we can write as

$$\frac{D_1}{D_2} = \left(\frac{m_2}{m_1}\right)^{\beta}, \tag{1}$$

where D_1 and D_2 are the diffusion coefficients of gas species of molecular weight m_1 and m_2, and $\beta = 0.5$. The more common situation of geochemical interest is that of isotope fractionation of a dilute gas diffusing through a different gas of finite pressure. A classic version of this can be found in Craig and Gordon's (1965) discussion of the relative rates of diffusion of $H_2{}^{16}O$, $HD^{16}O$, and $H_2{}^{18}O$ vapor in air. Taking collisions into account while still assuming that intermolecular forces are negligible, the ratio of the diffusion coefficients of the isotopically distinct species becomes proportional to the inverse square root of their reduced mass. The reduced mass μ_i of a species of molecular weight m_i colliding with a gas of molecular weight M is given by the expression

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$$\mu_i = \frac{m_i M}{m_i + M}. \tag{2}$$

The ratio of the diffusion coefficients of the dilute isotopically distinct molecules is then given by

$$\frac{D_1}{D_2} = \sqrt{\frac{\mu_2}{\mu_1}} = \sqrt{\frac{m_2(m_1 + M)}{m_1(m_2 + M)}}. \tag{3}$$

An interesting point is that when the molecular weight M of the medium is very large compared to that of the diffusing species, $\mu_i \to m_i$ as $m_i/M \to 0$, and the ratio of the diffusion coefficients reverts to that given by Eq. (1). Eqs. (1) and (3) provide an upper bound on mass-dependent kinetic isotope fractionation by diffusion in gases and serve as a point of comparison for the magnitude of fractionations observed in condensed systems. It should be kept in mind that even in the case of gases these relationships make a number of simplifying assumptions such as that the gas medium can be represented by its mean molecular weight, that intermolecular forces are negligible, and that differences in the molecular diameters of the diffusing species are not significant. Despite these simplifications, Eq. (3) was shown by Craig and Gordon (1965) to be in reasonably good agreement with experimental data on the isotopic fractionation of water vapor diffusing in air. While there is no theoretical expectation as to the value of β in Eq. (1) for anything other than dilute gases, we will nevertheless use β as a convenient way of specifying and comparing the mass-dependence of isotopic fractionations during diffusion in a variety of condensed systems.

The understanding of mass-dependent fractionation by diffusion in condensed systems is far less developed than for gases. Even such apparently simple situations as those involving the isotopic fractionation of dissolved trace gases (e.g., He, methane, and CO_2) in water have not yielded unambiguous results (see for example, Jähne et al., 1987; Prinzhofer and Pernaton, 1997; Zhang and Krooss, 2001). Jähne et al. (1987) carried out experiments to determine the relative diffusivities of noble gases dissolved in water at various temperatures and found that the ratios of the diffusion coefficients of the noble gases are very close to the inverse square root of the mass of the noble gases (i.e., $\beta = 0.5$ in Eq. (1)). In some cases, the experimental results for the relative diffusion coefficients of the noble gases in water imply β slightly greater than 0.5, a surprising result suggesting that interpreting the diffusion coefficients in terms of mass alone is not entirely correct. An alternative interpretation of the noble gas data is that the diffusion coefficients of neutral species are dominated by hydrodynamic drag (as indicated by the molecular calculations of Koneshan et al., 1998), in which case the diffusivity will be inversely proportional to the size. If we use the van der Waals radius as a measure of the relative sizes of the diffusing noble gases, then diffusion coefficients that are inversely proportional to size will appear to depend on the inverse square root of mass because of the close to linear correlation between the square root of the mass and the Van der Waals radius of noble gases other than helium. The most direct way of isolating the effect of mass on diffusion is to compare the behavior of isotopically substituted species. Jähne et al. (1987) also report on two experiments that were used to determine isotopic fractionation of dissolved $^{12}CO_2$ from $^{13}CO_2$ and ^{3}He from ^{4}He. The results for CO_2 showed an isotopic fractionation more than an order of magnitude less than what one calculates assuming that diffusivities are proportional to the inverse square root of the mass ratio of $^{12}CO_2/^{13}CO_2$ (i.e., $\sqrt{\frac{44}{45}}$). Jähne et al. (1987) discuss their measured isotopic fractionation in terms of an expectation based on the inverse square root of the reduced masses using the molecular weight of water for M in Eq. (2) (i.e., $\mu_{^{13}CO_2} = 12.86$ and $\mu_{^{12}CO_2} = 12.77$). The measured fractionation of carbon isotopes is then about one-third the value calculated from the inverse square root of the ratio of the reduced mass. Why a reduced mass derived from the kinetic theory of gases should be applicable to the behavior of dissolved trace gases in water is not explained. The fractionation of He isotopes reported by Jähne et al. (1987) corresponds to $D_{^3He}/D_{^4He} = 1.15 \pm .03$, which, given the uncertainty, is indistinguishable from the ratio calculated using the actual mass of the He isotopes (1.16) or that calculated using the reduced mass based on the molecular weight of water (1.13). The upshot of all this is that the effect of mass on the diffusion of neutral species in water is not at all simple, and it is not yet well documented or understood.

The work we report here focuses on the isotopic fractionation of dissolved ionic species in water. Because one of the principal applications we hoped to explore was the development of an isotopic monitor for the diffusive transport of mineral-forming solutes in water saturated sedimentary or metamorphic systems, we focused on dissolved ionic species rather than trace gases. Another context where isotopic fractionation during diffusive transport of ionic species in water could be very important involves biological systems, where isotopic fractionation has been measured, but remains poorly understood. For example, a recent interpretation of calcium isotopic fractionation during inorganic aragonite precipitation and in cultured foraminifera (Gussone et al., 2003) includes kinetic effects due to diffusion in water, but for the moment this is still in the realm of speculation due to the lack of relevant experimental data on the degree of isotopic fractionation produced during the diffusion of ions in water.

Previous work led us to expect that we might find large mass-dependent isotopic fractionation of dissolved ions as they diffuse in water. We recently demonstrated significant mass dependent isotopic fractionation by diffusion in molten silicate liquids (Richter et al., 1999, 2003), which when phrased in terms of the exponent β in Eq. (1), resulted in $\beta \approx 0.2$ for lithium isotopes and $\beta \approx 0.1$ for calcium isotopes. If diffusion in complex molten silicate liquids can produce such large isotopic fractionation, why would not