Negligible fractionation of Kr and Xe isotopes by molecular diffusion in water

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Abstract

Molecular diffusion is a key transport process for noble gases in water. Such diffusive transport is often thought to cause a mass-dependent fractionation of noble gas isotopes that is inversely proportional to the square root of the ratio of their atomic mass, referred to as the square root relation. Previous studies, challenged the commonly held assumption that the square root relation adequately describes the behaviour of noble gas isotopes diffusing through water. However, the effect of diffusion on noble gas isotopes has only been determined experimentally for He, Ne and Ar to date, whereas the extent of fractionation of Kr and Xe has not been measured. In the present study the fractionation of Kr and Xe isotopes diffusing through water immobilised by adding agar was quantified through measuring the respective isotope ratio after diffusing through the immobilised water. No fractionation of Kr and Xe isotopes was observed, even using high-precision noble

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gas analytics. These results complement our current understanding on isotopic fractionation of noble gases diffusing through water. Therefore this complete data set builds a robust basis to describe molecular diffusion of noble gases in water in a physical sound manner which is fundamental to assess the physical aspects of gas dynamics in aquatic systems.
Keywords: Graham's Law, noble gases, kinetic fractionation, isotope ratio, diffusion coefficient

1. Introduction

The inert noble gases and their isotopes have been established to trace physical processes in aquatic systems, e.g. the transport and exchange of solutes and fluids (Brennwald et al., 2013). Molecular diffusion in water is a key transport mechanism that plays an important role in aquatic systems and in particular in the sediments of lakes, rivers and oceans. Despite the great potential of noble gases and their isotopes to analyse diffusive transport in lacustrine sediments, the isotopic fractionation of noble gas diffusing through water has only be studied for He, Ne and Ar (Jähne et al., 1987; Tyroller et al., 2014). As a follow-up to our recent work on the diffusion of Ne and Ar isotopes in water (Tyroller et al., 2014), this paper assesses the possible fractionation of Kr and Xe isotopes by molecular diffusion in water. In general, the study used the same experimental set-up, analytical techniques, principles and equations as presented by Tyroller et al. (2014). The present study is motivated by the unexpected results of a computational simulation (Bourg and Sposito, 2008) and the aforementioned experimental study (Tyroller et al., 2014), both of which challenged the commonly held assumption that molecular diffusion in water results in a fractionation of noble gas isotope ra-

tios according to the square root relation, that is also refereed to as Graham's Law (Graham, 1833). This relation is derived from the kinetic theory of gases (Moore, 1999) and can be written as (e.g. Richter et al., 2006):

$$\frac{D_i}{D_j} = \left(\frac{M_j}{M_i}\right)^{\beta} \tag{1}$$

where D_i and D_j are the diffusion coefficients of the diffusing gases i and j, with their molecular mass M_i and M_j, respectively, and $\beta = 0.5$.

However, our previous study (Tyroller et al., 2014) found a different fractionation behaviour of Ne isotopes during molecular diffusion in water. Ar isotopes do fractionate as predicted by the square root relation, in contrast to Ne isotope fractionation, which was found to be much lower and which agreed to a reasonable extent with the results from molecular dynamics calculations (Bourg and Sposito, 2008). These molecular dynamics calculations simulate the diffusion of different noble gases and their isotopes in water on an atomic scale by applying a combination of chemical theories and classical, non-quantum-mechanical theories.

In order to explain the different behaviour of Ne and Ar isotope fractionation and to understand the fractionation behaviour of other noble gas isotopes as a results of molecular diffusion in water, this study aims to complete the experimental dataset on noble gases by assessing the fractionation behaviour of Kr and Xe. The fractionation of Kr (^{82}Kr, ^{83}Kr, ^{84}Kr, ^{86}Kr) and Xe (^{129}Xe, ^{132}Xe, ^{134}Xe, ^{136}Xe) isotopes was determined by directly measuring the relative differences of fluxes of isotopes through a diffusion column containing immobilised water. In addition, the elemental diffusion coefficients of Kr and Xe were determined with the same set-up in order to confirm the correct operation of the experiment.

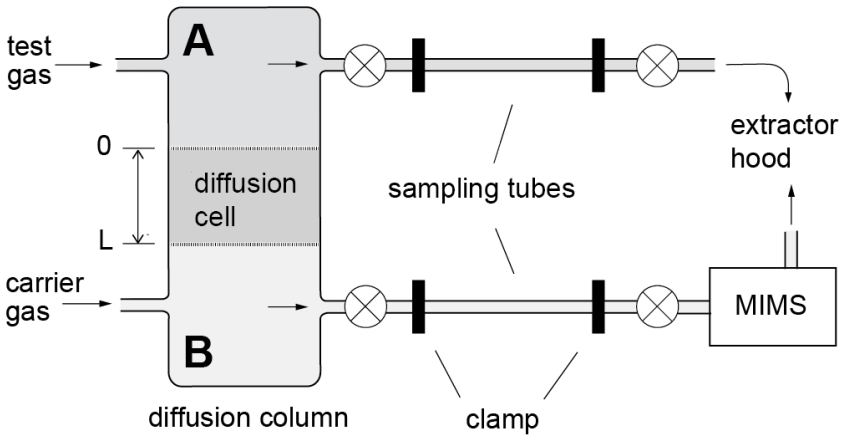

Figure 1: Drawing of the experimental set-up (adopted from Tyroller et al., 2014). Experimental conditions are presented in Table 1. The test gas, made up of Kr and Xe, was flushed through chamber A, while the carrier gas, pure N_2 was flushed through chamber B. After the system attained steady state, samples of both test gas and carrier gas were taken by closing the sampling copper tubes connected downstream with gas-tight clamps. As shown for Ne and Ar (Tyroller et al., 2014), the dissolved gas concentration at the gas/water interfaces can be assumed to be in solubility equilibrium.

2. Material and methods

2.1. Experimental setup

The method used to determine the fractionation of Kr and Xe isotopes closely follows the method described in our earlier work measuring the fractionation of Ne and Ar isotopes undergoing molecular diffusion in water (Jähne et al., 1987; Tyroller et al., 2014). In general, the same experimental set-up, analytical techniques, principles and equations were used, with the exception of a modification in sample processing which is discussed below in some detail.

The key constituent of the experimental set-up, the diffusion column, was composed of two continuously flushed gas chambers, A and B, which were separated by a diffusion cell (Figure 1). This diffusion cell consisted of an approxi-

mately 1.4 cm thick water layer which was immobilised by adding agar (1%) to suppress turbulent transport within the liquid thus guaranteeing that the gas was transported purely by molecular diffusion as in free water (Jähne et al., 1987; Cussler, 2009). The agar-water-gel lay on a glass frit (porosity 42%).

In an initial phase, the two gas-filled chambers, A and B were both flushed with carrier gas (N_2 of 99.999% purity, Carbagas, Switzerland). Samples were taken from chambers A and B during this initial phase, and no noble gases were detected in them, even when analysing on a low-blank system (Busemann et al., 2000; Heber, 2002). The experiment was initiated by flushing chamber A with noble gas bearing test gas (consisting of 30% Kr and 30% Xe and 40% pure N_2 gas), while chamber B was still flushed with the pure, i.e. noble gas free, carrier gas. Both the test and the carrier gas were saturated with water vapour before being flushed through chambers A and B, respectively, to prevent drying of the diffusion layer. Diffusion of the test gas through the diffusion cell from chamber A to chamber B was forced by the difference in the noble gas partial pressure between A ($\sim$ 0.3 bar) and B ($\sim$ 0 bar).

The experiment consisted of two sequences with different flow regimes:

1. Non-steady state: Initially the flow regime was in non-steady state. The test-gas flux diffusing from chamber A through the water cell was carried by the nitrogen gas flushed through chamber B to a quadrupole mass spectrometer operated in dynamic mode (miniRUEDI, Gasometrix GmbH, Mächler et al., 2012; Brennwald et al., 2016). The miniRUEDI measurements allowed the gas flow to be continuously monitored (measuring He, Ar, Kr, Xe, N_2 and O_2 concentrations; with mass/charge ratio 84 *m/z* for Kr and 130 for Xe) to assess the performance of the experimental apparatus. The measurements also determined the time when the

Table 1: Experimental parameters and their estimated uncertainties defining the set-up of the diffusion cell. Note that the uncertainties of these parameters did not affect the measurement of isotope fractionation because the isotope ratios were determined at steady state conditions, which were independent of the experimental conditions (Tyroller et al., 2014). However, the determination of the elemental diffusion coefficients was affected by the experimental design of our diffusion experiment. Thus, the uncertainty of the elemental diffusion coefficients was constrained mainly by the errors of the design of the diffusion cell.

Experimental parameter	Range	Absolute uncertainty
Thickness of the diffusion cell with agar-water-gel [cm]	1.4	0.1
Agar-water-gel/gas interface area [cm^2]	28.3	0.1
Temperature [K]	296.0	0.5
Flow rate, carrier gas [ml/min]	2.5	0.1
Kr concentration in the agar-water-gel [$\times 10^{-2} \frac{cc}{g}$]	1.62	
Xe concentration in the agar-water-gel [$\times 10^{-2} \frac{cc}{g}$]	2.83	

gas flux through the diffusion cell attained steady state. This gas specific breakthrough curves were also used to determine the elemental diffusion coefficients of Kr and Xe.

2. Steady state: When the gas composition of the outflow from chamber B became constant, the flow regime was in a steady state. This steady state flow was reached after waiting for at least three times the typical breakthrough time, T, of the respective gas (see Section 3). In steady state the isotopic fractionation factor for two isotopes i and j can be expressed as the ratio of their diffusion rates or as the ratio of their diffusion coefficients (i.e. D_i and D_j) and can be determined by applying the following formula:

$$\frac{R^L_{i,j}}{R^0_{i,j}} = \frac{F_i/F_j}{C_i(0)/C_j(0)} = \frac{D_i}{D_j} \tag{2}$$

Where $R^0_{i,j} = C_i(0)/C_j(0)$ is the concentration ratio at the upper interface of the

diffusion cell (x = 0) with $C_i(0)$ and $C_j(0)$ being the concentrations of the isotopes i and j respectively, measured in the outflow of chamber A. And $R^L_{i,j} = C_i(L)/C_j(L) = F_i/F_j$ is the flux ratio at the lower interface of the diffusion cell (x = L) with $C_i(L)$ and $C_j(L)$ being the isotope concentrations measured in the outflow of chamber B. Once the experiment was operating in steady state gas, samples were taken from the outflow of chamber A and B respectively and stored in copper tubes for later analysis of noble gas isotopes with noble gas mass spectrometry. For further details on the set-up, the experimental principles and the applied mathematics used to calculate isotopic fractionation refer to the previous work on Ne and Ar fractionation (Tyroller et al., 2014).

For the analysis of Kr and Xe isotopes, unlike the study on Ne and Ar isotope fractionation, the final sample of gas taken and stored in copper tubes had to be diluted by several orders of magnitude, e.g., from the 0.3 bar to the 10^{-6} bar range, because the final isotope analysis was carried out with a mass spectrometer designed for high accuracy and high-sensitivity analysis of Kr and Xe isotopes. This was operated in static mode at very low pressures ($< 10^{-9}$ mbar; Busemann et al., 2000; Heber, 2002). Dilution was carried out with a gas calibration apparatus designed to reach exact concentrations even when diluting noble gases over several orders of magnitude down to a pressure range that allowed analysis with the highly-sensitive, static noble gas mass spectrometer. The dilution procedure and dilution apparatus are described in Section 2.3.

2.2. Determination of diffusion coefficients

In principle, the set-up of the diffusion column can be used to determine diffusion coefficients in a quantitative manner (Saltzman et al., 1993). Here, the target of the experiments was to make specific determinations of the fractiona-

tion behaviour of Kr and Xe isotopes. Thus, the experiment was not designed to obtain elemental diffusion coefficients, but to identify possible isotopic fractionation within a single experiment (see Table 1). As a result, it was decided to use normalised noble gas breakthrough curves (see Figure 3), obtained in order to evaluate when the flow regime in the diffusion cell was in the steady state. As a by-product of this procedure the elemental diffusion coefficients were determined, but not in a rigorously quantitative manner. A theoretical breakthrough curve for this experimental set-up was calculated (Tyroller et al., 2014) and was fitted to the observed breakthrough curve by using the respective diffusion coefficient as fit parameter.

2.3. Gas dilution

For gas dilution, a gas-calibration apparatus built in-house at the noble gas laboratory at ETH Zürich was used. This special gas line was designed to prepare precisely known noble gas mixtures as standards in order to normalise noble gas mass spectrometry. It is also possible to determine the exact volumes of reservoirs and pipettes on it. The partial pressure of the test gas in the copper tube samples taken during the diffusion experiment were reasonably well known (chamber A: 0.3 bar Kr and Xe according manufacturer's instructions; chamber B: in the range of 10^{-6} bar according to miniRUEDI analysis). For the high-precision Kr and Xe analysis using static noble gas mass spectrometry, the gas partial pressures had to be reduced to minimum 10^{-12} bar. Samples were diluted according to a systematic dilution plan to reach the predefined gas pressure needed for the final analysis. The dilution plan defines the sequence of steps needed to expand the initial quantity of gas into the dilution volumes based on the initial partial pressure of gas in the precisely calibrated volume P_g (see Figure 2). In the final step, the sample

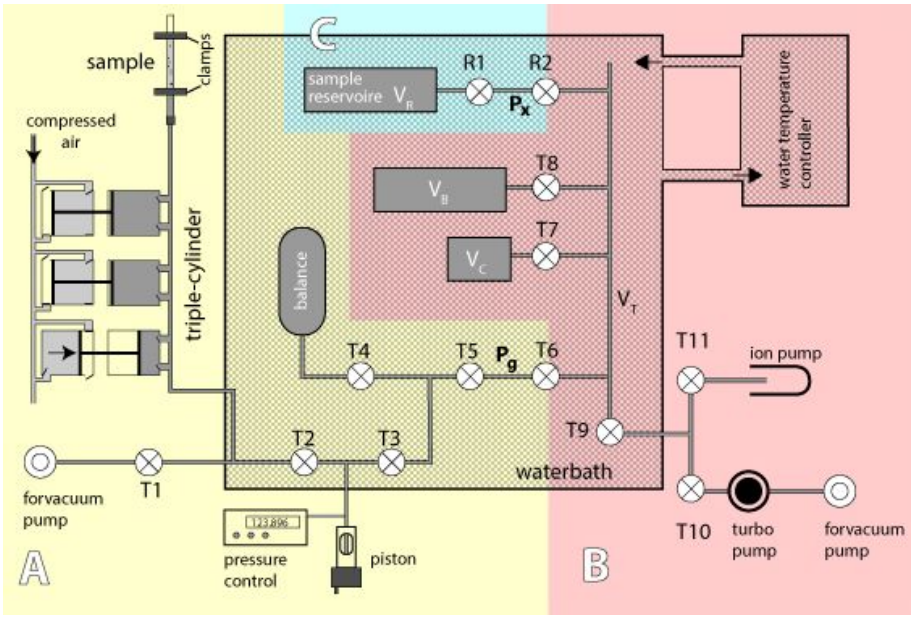

Figure 2: An apparatus designed to prepare noble gas standards at the ETH noble gas laboratory was used to dilute the gas. It consisted of three parts: A, B and C. **A. The gas line (yellow) was used to fill a defined gas amount into pipette P_g with an exactly known volume.** This part consisted of an adaptor for copper tube samples (swagelok fitting), a roughing pump, to evacuate the gas line to $\sim 5{\times}10^{-3}$ mbar before the gas inlet, a piston for fine adjustment of the pressure, a balance volume and a triple cylinder. This triple cylinder system was made of three segments each consisting of a double-actuation compressed air piston connected at the left to the end of flexi-bellows. By opening or closing the respective valves of the piston, the volume within the flexi-bellow could be changed. By moving the pistons of the triple cylinder in combination, gas could be compressed and expanded, thus enabling the pressure in the line to be adjusted. The triple cylinder was used to reach a defined pressure (measured by a calibrated, high precision manometer) in the gas line and volume P_g. Volume P_g (0.957845 ± 0.000811 cm^3) was the inlet to the dilution line. **B. The dilution line (red) was used to dilute the defined gas amount in P_g by several orders of magnitude.** The dilution line consisted of a roughing pump, a turbo pump and an ion getter pump. These pumps evacuated the dilution compartments, the tubing V_T (59.331 cm^3), the dilution volumes V_C (384.11 cm^3), V_B (2006.776 cm^3) and the reservoir, V_R, to a pressure of $\sim 10^{-7}$ mbar before noble gas dilution. Dilution factors were calculated from the known volumes of the dilution compartments. **C. The reservoir (blue) was filled with the diluted gas from the gas line.** For each sample to be diluted, a new reservoir with pipette was attached and pumped prior to being filled with gas. After being filled with the gas at low pressure the reservoir and its pipette, P_x, were disconnected from the dilution apparatus and connected to a mass spectrometer for the isotope ratio analysis. The volume of the pipette, P_x, was very small relative to the sample reservoir. As a result, the pipette could be filled repeatedly with the gas from the reservoir, i.e., gas aliquots could be taken from the reservoir, with virtually no effect on the amount of gas contained in the reservoir. All fittings, valves and tubing were ultra high vacuum-tight and made of stainless steel. Parts of the gas line, the dilution line and the reservoir are submerged in a water bath to keep the temperature and pressure constant and uniformly distributed during dilution.

reservoir, V_R, was filled. Later an adequate gas aliquot could be taken from this reservoir using the pipette P_x. Each sample was treated according its specific dilution plan. The gas-filled copper tube from the diffusion experiment was connected to the dilution gas line (initial valve setting: T1-T5, T7-T9, T11, R1, R2 open, T6, T10 closed) and the gas filling apparatus was pumped in order to reach a pressure in the range of 10^{-3} to 10^{-4} mbar in the gas line and a pressure of approximately 10^{-7} mbar within the dilution line. After evacuation, the gas dilution line was set for the sample gas inlet (T1-T11 closed) and the copper tube sample containing the gas from the diffusion experiment was opened. The sample gas was then expanded to the inlet of the gas dilution line by means of the triple cylinders. These triple cylinders were manipulated until the pre-set pressure in the inlet pipette, P_g, was reached. The gas was left for 30 minutes to equilibrate within the line. P_g was then disconnected from the inlet line by closing valve T5 and the amount of gas in P_g was subsequently expanded into the dilution line (valve T6 open) and diluted according the dilution plan. Each dilution step consisted of opening the valve of the respective dilution volumes (V_B, V_C) and waiting for approximately 30 minutes to allow the pressure in the respective volumes to equilibrate. The respective dilution reservoir was then closed and the residual gas was pumped out from the dilution line. In the last dilution step, the remaining gas was allowed to expand into the gas reservoir, V_R, and was separated by closing the valves of its pipette, P_x (R1, R2 closed).

The closed reservoir, V_R, and its pipette, P_x, were detached from the gas dilution line and connected to the noble gas spectrometer for final isotope analysis. In this way, V_R was used as a gas reservoir from which precise gas aliquots could be taken through the gas pipette, P_x, allowing multiple measurements of the isotopic

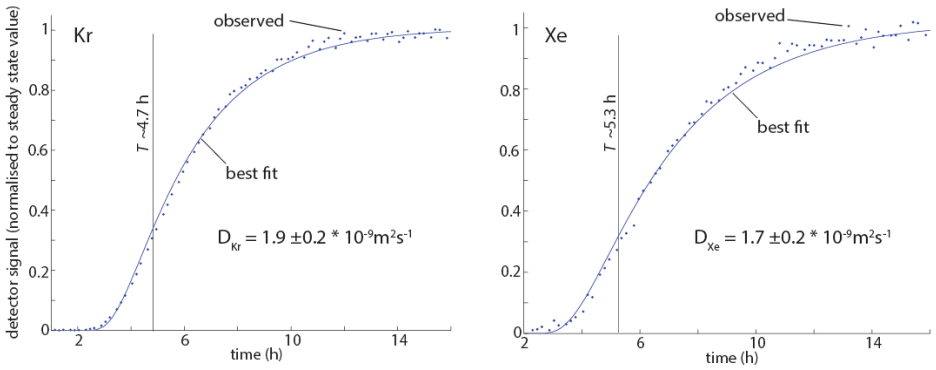

Figure 3: Breakthrough curves of Kr and Xe measured with miniRUEDI, uncalibrated raw data normalised to the steady state value obtained towards the end of the experiment. Dots indicate "observed" data, measured in the outlet of chamber B with a quadrupole mass spectrometer. The blue curve shown is the theoretical breakthrough curve fitted by adjusting the diffusion coefficient. The breakthrough time T was defined as $T = \frac{L^2}{6D_i}$ (Crank, 1975) where L indicates the thickness of the diffusion cell and D_i the diffusion coefficient of the respective gas species i.

composition of Kr and Xe from the sample gas.

2.4. Analysis of noble gas isotopes

The measurements of Kr and Xe isotopes from the gas sample in the reservoir were carried out on a magnet sector field noble gas mass spectrometer built in-house at the noble gas laboratory at ETH Zürich (e.g. Busemann et al., 2000; Heber, 2002). The mass spectrometer was equipped with a Baur-Signer ion source, a Faraday cup and a secondary electron multiplier (operated in counting mode). Kr and Xe were ionised with 100 eV electrons, whereby isotopes were easily separated by the achievable mass resolution of about 550 (M/ΔM) (Riebe et al., 2017).

3. Results

Figure 3 shows the observed and the theoretical breakthrough curves of the test gas diffusing through the water cell (see Section 2.2) normalised to the steady state concentration of Kr and Xe. The observed and the fitted breakthrough curves agree with each other. As a by-product of the measurements, the elemental diffusion coefficients of Kr and Xe were estimated.

Table 2 summarises the results of the different replicate gas dilution experiments and analyses to determine the relative isotopic fractionation of Kr and Xe due to diffusion in water. Note that the replicated experiments comprise four independent diffusion experiments that were carried out under the same conditions and using the same experimental set-up and experimental parameters. Each independent experiment included a renewal of the dilution cell, the flushing of the system with carrier gas before starting the experiment and observation of the breakthrough curve until steady state was achieved. Thus, the diffusion experiments were repeated four times. The isotopic compositions of Kr and Xe (i.e. the respective isotope ratios in chambers A and B) were measured in gas samples taken after the steady state was attained in chambers A and B. Note also that under such steady state conditions the relative isotopic fraction due to molecular diffusion can simply be calculated from the ratio of the respective isotope ratios in chamber A ("unfractionated") and chamber B ("fractionated"; see also the experimental set-up Figure 1).

4. Discussion

The good agreement of the observed and the fitted breakthrough curves of Kr and Xe (see Figure 3) suggests that our diffusion experiment performed well.

Table 2: Four independent experiments were carried out to determine the possible fractionation of Kr and Xe isotopes due to molecular diffusion in water. The ratios of Kr and Xe isotopes were determined 5 to 7 times for each sample from a corresponding experiment (typical errors of the measured ratios were in a range of 0.3 - 0.5 %). The fractionation factors were determined by dividing the isotope ratio of the "fractionated" sample through the ratio of the "unfractionated" sample, see text.

	$\frac{D_{86_{Kr}}}{D_{\ 84_{\mathrm{Kr}}}}$	$\frac{D_{83_{Kr}}}{D_{\ 84_{\mathrm{Kr}}}}$	$\frac{D_{82_{Kr}}}{D_{\ 84_{\mathrm{Kr}}}}$	
exp. 1	0.9950	0.9997	1.0000	
exp. 2	0.9949	1.0028	0.9979	
exp. 3	1.0040	1.0159	1.0035	
exp. 4	0.9920	0.9913	1.0006	
Mean, error of the mean:	0.9965 ± 0.0026	1.0024 ± 0.0051	1.0005 ± 0.0012	
	$\frac{D_{136_{Xe}}}{D_{\ 132_{\mathrm{Xe}}}}$	$\frac{D_{134_{Xe}}}{D_{\ 132_{\mathrm{Xe}}}}$	$\frac{D_{131_{Xe}}}{D_{\ 132_{\mathrm{Xe}}}}$	$\frac{D_{129_{Xe}}}{D_{\ 132_{\mathrm{Xe}}}}$
exp. 1	1.0008	1.0031	1.0018	0.9953
exp. 2	1.0001	1.0002	0.9997	0.9982
exp. 3	0.9999	1.0028	0.9989	1.0015
exp. 4	0.9964	0.9995	1.0006	0.9990
Mean, error of the mean:	0.9993 ± 0.0010	1.0014 ± 0.0009	1.0003 ± 0.0006	0.9985 ± 0.0013

Table 3: Comparison of literature values for the diffusion coefficients of Kr and Xe in water and results of this study. The diffusion coefficients of Kr and Xe determined in this study are the mean value of the diffusion coefficients determined with the best fit to the observed breakthrough curve of two experiments (see Figure 3), the errors are given at the 1 sigma level. The breakthrough curves of the other experiments were not suitable for such fitting because recording of the data started later approximately at half time of the breakthrough of the gas. We note that in the light of our results the higher diffusion coefficients of Kr and Xe reported in literature seem to be more robust.

	Experimental determination			MD simulation	**This study**
	Wise and Houghton (1968)	Boerboom and Kleyn (1969)	Jähne et al. (1987) (0.5% agar)	Bourg and Sposito (2008)	**(1% agar)**
	D_i [$10^{-9} m^2 s^{-1}$], (T = 298 K)				
D_{Kr}	1.93 *	0.803	1.84	1.97±0.13	**1.9 ± 0.2**
D_{Xe}	0.6 *	0.827	1.47	1.57±0.11	**1.7 ± 0.2**

*scaled to 25°C temperature

Furthermore, the calculated elemental diffusion coefficients for Kr and Xe agree with some of the previous results to a reasonable extent (see Table 3).

Our experimental data (Table 2) make the case that Kr and Xe isotopes do not significantly fractionate during molecular diffusion through liquid water. In addition our results reject the hypothesis that Kr and Xe isotopes fractionate according to the square root relation (continuous line in Figure 4). The results show that the isotope fractionation for Kr and Xe was much smaller then predicted by the square root relation. In contrast, these results are consistent with the assumption of negligible fractionation, i.e., molecular diffusion in water virtually does not fractionate either the Kr or Xe isotopes. To determine conclusively whether Kr and Xe isotopes do slightly fractionate when diffusing through water, additional experiments are needed achieving a much better experimental precision than our experiment.

As with earlier studies (Bourg and Sposito, 2008; Tyroller et al., 2014) this

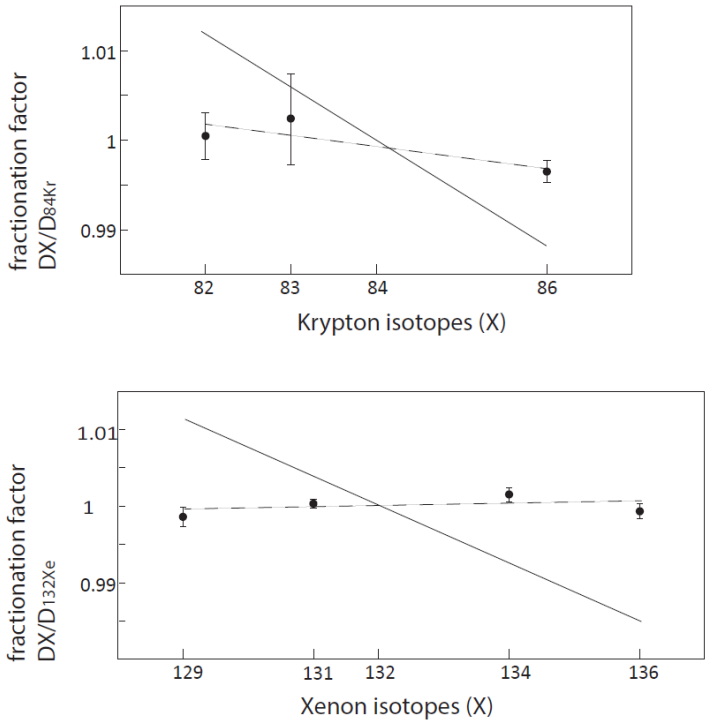

Figure 4: Experimentally determined fractionation of Kr and Xe isotopes (normalised to ^{84}Kr and ^{132}Xe, respectively) due to molecular diffusion in water. The continuous line reflects the expected fractionation according to the square root relation. The dashed line reflects the linear least squares regression through the experimental data.

work also challenges the applicability of the square root relation to scale the fractionation of noble gas isotopes undergoing molecular diffusion in water. For Ne, Kr and Xe, the fractionation of their isotopes as a result of molecular diffusion was found to be much smaller than predicted by the square root relation, whereas Ar was shown to fractionate according to the square root relation.

Currently, we do not have a clear explanation for the different isotopic fractionation patterns of atmospheric noble gases (Ne-Xe) diffusing in water. We hypothesise that factors other than molecular mass, such as the interaction of noble gas isotopes with the microstructure of liquid water, may constrain the different fractionation patterns of noble gas isotopes undergoing molecular diffusion in water.

A recent study on isotopic fractionation, using ab initio molecular dynamics (AIMD) to simulate dissolved gas species and the surrounding liquid, supports this hypothesis by showing the importance of configurational effects on isotopic fractionation (de Magalhães et al., 2017). This study shows that noble gases interact with the water molecules during diffusion, which results in different diffusion regimes. For small particles (Ne) inter-cavity hopping is the dominant transport mechanism, whereas for large particles (Kr, Xe) the transport is dominated by mass-independent viscous friction (see de Magalhães et al., 2017). Over long enough time scales neither transport mechanisms lead to a fractionation of the isotope ratio. However, Ar falls in between these two diffusion regimes, where the molecular collision with the surrounding water molecules prevails. This may explain the different isotope fractionation of Ar due to molecular diffusion in water.

5. Conclusions

We empirically quantified the elemental diffusion coefficients of Kr and Xe isotopes in water as well as the respective isotope fractionation in response to molecular diffusion in water. The estimated elemental diffusion coefficients of Kr (D_{Kr} =1.9 ±0.2 × $10^{-9} m^2 s^{-1}$) and Xe (D_{Xe} =1.7 ±0.2 × $10^{-9} m^2 s^{-1}$) in water agree reasonably well with preceding studies. This suggests that our diffusion experiment using a diffusive layer of immobilised water performed well.

Kr and Xe isotopes were found to only negligibly fractionate within the precision of our measurements. The determined fractionation was much smaller than the fractionation predicted by the square root relation for Kr and Xe isotopes diffusing through water. Thus, our results clearly contradict the commonly held assumption that the fractionation of Kr and Xe isotopes due to molecular diffusion in water can be approximated by the square root relation. These findings were confirmed by recent AIMD simulations where the fractionation of Kr and Xe isotopes as a result of molecular diffusion in water was also found to be negligible. This was attributed to a hydrodynamically controlled diffusion regime (Brownian motion, see de Magalhães et al., 2017).

To gain a conceptual understanding of the mechanism behind diffusive transport through water we suggest using different experimental approaches to measure the isotopic fractionation of all noble gases undergoing molecular diffusion in water. We expect that AIMD calculations accounting for the quantum-mechanical interactions of the electronic structure of the noble gases and the water molecules may reveal the fundamental mechanisms behind the fractionation behaviour of noble gas isotopes due to molecular diffusion in water. In addition we suggest to measure the isotopic fractionation of oxygen isotopes in water, because oxygen

is of a similar size as Ar and therefore may also be fractionated due to molecular diffusion in water.

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References

Boerboom, A. H. J., Kleyn, G., 1969. Diffusion coefficients of noble gases in water. J. Chem. Phys. 50(3), 1086–1088.

Bourg, I. C., Sposito, G., 2008. Isotopic fractionation of noble gases by diffusion in liquid water: Molecular dynamics simulations and hydrologic applications. Geochim. Cosmochim. Acta 72, 2237–2247.

Busemann, H., Baur, H., Wieler, R., 2000. Primordial noble gases in phase Q in carbonaceous and ordinary chondrites studied by closed-system stepped etching Meteorit. Planet. Sci 35(5), 949–973.

Brennwald, M. S., Vogel, N., Scheidegger, Y., Tomonaga, Y., Livingstone, D., and Kipfer, R., 2013. The Noble Gases as Geochemical Tracers, chapter Noble gases as environmental tracers in sediment porewaters and in stalagmite fluid inclusions. Advances in Isotope Geochemistry. Advances in Isotope Geochemistry. Springer, Berlin, Heidelberg, 123–153.

Brennwald, M. S., Schmidt, M., Oser, J., Kipfer, R., 2016. A portable and autonomous mass spectrometric system for on-site environmental gas analysis. Environ. Sci. Technol. 50(24), 13455–13463.

Crank, J., 1975. The mathematics of diffusion, 2nd ed. Clarendon Press, Oxford.

Cussler, E. L. (2009). *Diffusion: Mass transfer in fluid systems, 3rd ed.* Cambridge Univ. Press, Cambridge.

de Magalhães, H. P., Brennwald, M. S., Kipfer, R., 2017. Diverging effects of isotopic fractionation upon molecular diffusion of noble gases in water: mechanistic insights through ab initio molecular dynamics simulations Env. Sci. Process. Impact. 19(3), 405–413.

Graham, T., 1833. On the law of the diffusion of gases. Philosophical Magazine. 2(9), 175–190. (10), 269–276. (11), 351–358.

Heber, V. S., 2002. Ancient solar wind noble gases in lunar and meteoritic archives and tests for modern solar wind collection with the GENESIS mission. Ph.D. thesis, ETH Zürich.

Jähne, B., Heinz, G., Dietrich, W., 1987. Measurement of the diffusion coefficients of sparingly soluble gases in water. J. Geophys. Res. 92(C10), 10767–10776.

Mächler, L., Brennwald, M. S., Kipfer, R., 2012. Membrane inlet mass spectrometer for the quasi-continuous on-site analysis of dissolved gases in groundwater. Environ. Sc. Technol. 46(15), 8288–8296.

Moore, J., 1999. Physical chemistry, 5th ed. Prentice Hall.

Richter, F., Mendybaev, R., Christensen, J., Hutcheon, I., Williams, R., Sturchio, N., Beloso Jr., A., 2006. Kinetic isotopic fractionation during diffusion of ionic species in water. Geochim. Cosmochim. Acta. 70(2), 277–289.

Riebe, M. E. I., Welten, K. C., Meier, M. M. M., Wieler, R., Barth, M. I. F., Ward, M., Laubenstein, D., Bischoff, A., Caffee, M. W., Nishiizumi, K., Busemann, H., 2017. Cosmic-ray exposure ages of six chondritic Almahata Sitta fragments. Meteorit. Planet. Sci. 11, 2353 – 2374.

Saltzman, E. S., King, D. B., Holmen, K., Leck, C., 1993. Experimental determination of the diffusion coefficient of dimethylsulfide in water. J. Geophys. Res. Oceans 98(C9), 16481 – 16486.

Tyroller, L., Brennwald, M. S., Mächler, L., Livingstone, D. M., Kipfer, R., 2014. Fractionation of Ne and Ar isotopes by molecular diffusion in water. Geochim. Cosmochim. Acta 136, 60 – 66.

Wise, D. L., Houghton, G., 1968. Diffusion coefficients of neon, krypton, xenon, carbon monoxide and nitric oxide in water at 10–60 ^{o}C. Chem. Eng. Sci 23(10), 1211 – 1216.