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# 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 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.

## 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 gases 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 ratios 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

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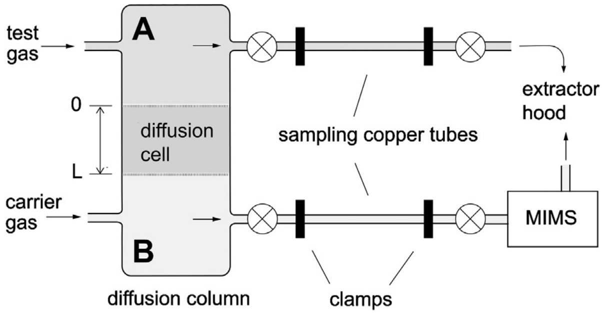

**Fig. 1.** Drawing of the experimental set-up (adopted from Tyroller et al., 2014). Experimental conditions are presented in Table 1. The test gas, made up of Kr and Xe, was flushed through chamber A, while the carrier gas, pure $N_2$ was flushed through chamber B. After the system attained steady state, 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.

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.

## 2. Material and methods

### 2.1. Experimental setup

The method used to determine the possible 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 (Fig. 1). This diffusion cell consisted of an approximately 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 the pure $N_2$-phase, 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 agar-water-gel 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 (∼0.3 bar) and B (∼0 bar).

**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 | Value | 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 | |

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 diffusion 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 $m/z = 84$ for Kr and $m/z = 130$ for Xe) to assess the performance of the experimental apparatus. The measurements also determined the time when the 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. $R^L_{i,j} = C_i(L)/C_j(L) = F_i/F_j$ 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).