**Determination of the fractionation of different isotopes under the influence of different soils**

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1. Introduction

Environmental tracers, which are natural and anthropogenic (manmade) chemical and isotopic substances can be measured in ground water and used to understand the properties of the hydrologic system. As a mature method, it can determine the amount of groundwater replenishment with a time scale of several days to several thousand years. Isotopes are relevant components of the environmental tracers and as a result, the research on the properties of the isotopes are consequential. Isotopes are the elements that have same number of protons in the atomic nucleus with different number of neutrons so they share the same chemical properties but diverse physical properties, such as weight, density and electric conductivity. The fractionation of an isotope is the isotope abundance ratio in the different substance or different phase. In the experiment, the isotope fractionation in different soils with various moisture are measured in order to discover the impact of them on isotope fractionation.

1. Theoretical principle
	1. Definition of isotopic abundance ratio

A substance containing the less abundant isotope species $N\_{i}$ and the more abundant isotope *N* has an isotopic abundance ratio R that is deﬁned by$:^{[1]}$

 $R=\frac{N\_{i}}{N}$ （2.1）

For oxygen and hydrogen, the standard mean ocean water (short SMOW) that has been deﬁned by the International Atomic Energy Agency (IAEA) in Vienna as a common standard for expressing isotope ratios (the so-called Vienna SMOW or V-SMOW) has isotopic abundance ratios of (Baertschi, 1976; Hageman et al., 1970):

$$ R\_{\frac{}{}}=(\frac{}{})\_{VSMOW}=\left(2005.2\pm 0.45\right)\*10^{-6} (2.2)$$

$$ R\_{\frac{D}{H}}=(\frac{}{})\_{VSMOW}=\left(155.76\pm 0.05\right)\*10^{-6} (2.2)$$

In general, the isotopic abundance ratio of a sample $R\_{sample}$ is given with respect to the internationally accepted standard V-SMOW with the isotopic abundance ratio $R\_{standard}$.

$$ δ=\frac{R\_{sample-}R\_{standard}}{R\_{standard}} (2.3)$$

2.2 Definition of isotope fractionation

Physical and chemical processes can cause the change of isotopic abundance ratio. Then the fractionation occurs, meaning the different isotopic composition. A fractionation factor α is used to describe the fractionation, that is deﬁned by$:^{[1]}$

$$ α=\frac{dR}{R} (2.4)$$

As suggested by Urey (1947), the isotope of different phases can come to an equilibrium and for the equilibrium, the degree of fractionation is then expressed by:

$$ α\_{A\leftrightarrow B}=\frac{R\_{A}}{R\_{B}} (2.5)$$

2.3 Brief introduction of analysis device

The analysis device used in this experiment is TDLAS (Tunable Diode Laser Absorption Spectroscopy). The producer is Los Gatos Research. The WVIA uses LGR’s patented O-axis ICOS technology, a fourth-generation cavity enhanced absorption technique. The system composed of the WVIA and WVISS provides automated, dual-inlet operation and accurate, traceable $H\_{2}$，$δ$，$δ$，$δD$and water vapor mole fraction measurements without drift. The total measurement uncertainty of the device is under 0.1% (with WVISS)$. ^{[2]}$ A basic TDLAS setup consists of tunable diode laser light source, transmitting optics, optically accessible absorbing medium, receiving optics and detectors$. ^{[3]}$ To determine the concentration, the wavelength of a diode laser is tuned over a particular absorption line of interest and the intensity of the transmitted radiation is measured. The transmitted intensity can be related to the concentration of the species present by the Beer-Lambert law.

1. Experimental procedure
	1. Production of aluminum bag

Firstly, several aluminum bags were sealed for one side. Then two pieces of silikons was added on each aluminum bags to make sure that the bags would not leak the air when the needles insert in them. Finally, one day was required to make sure the solidification of the silikons.

* 1. The adding of sample

Firstly, 100g sand was added to each aluminum bags. After that we extrude the air that enter the bags when we add the sand and make sure that there is no vapor in the bags. Then the dry air was sucked into the bags. To create different moisture of each bag, different volumes (1.2mL, 2.4mL, 4.8mL, 9.6mL, 14.4mL, 19.2mL, 24mL) of tap water was injected into the bags by pipettes. Repetition was processed of the same moisture. Finally, the sample bags were sealed and they were settled for one day in order to make isotopes in gas phase and liquid phase equilibrium. And the sample bags of clay were produced with the same method as sand.

* 1. Measurement of the isotopes

Each sample bags were placed before tunable diode Laser spectrometer. The two needles were inserted into the bags in order to create a circulation between the machine and the sample bag. The isotopic abundance ratios ($δ$*,* $δH$*,*$ δ$*,* $δ$) of each sample bag were recorded and analyzed.

1. Results
	1. Raw data

Table 4.1 isotopic abundance ratios of the sand sample bags

|  |  |
| --- | --- |
| Sand | 5% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 30430.0  | 30400.0  | 30560.0  |  |
| $δ$(‰) | -8.55  | -8.52  | -8.07  | -8.38  |
| $δD$(‰) | -41.53  | -40.62  | -40.90  | -41.02  |
| $δ$(‰) | -10.20  | -10.16  | -9.92  |  |
| Sand | 10% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 30818.0  | 30829.0  | 30100.0  |  |
| $δ$(‰) | -9.20  | -8.76  | -8.95  | -8.97  |
| $δD$(‰) | -43.30  | -42.25  | -42.50  | -42.68  |
| $δ$(‰) | -10.17  | -9.98  | -10.36  |  |
| Sand | 20% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 30821.0  | 30868.0  | 30029.0  |  |
| $δ$(‰) | -9.35  | -8.85  | -9.11  | -9.10  |
| $δD$(‰) | -44.17  | -41.89  | -44.30  | -43.45  |
| $δ$(‰) | -10.46  | -10.12  | -10.52  |  |
| Sand | 40% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 30543.0  | 30426.0  | 30072.0  |  |
| $δ$(‰) | -9.44  | -9.10  | -9.35  | -9.30  |
| $δD$(‰) | -45.45  | -43.90  | -45.54  | -44.96  |
| $δ$(‰) | -10.51  | -10.31  | -10.59  |  |
| Sand | 60% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 29994.0  | 29930.0  | 30006.0  |  |
| $δ$(‰) | -9.43  | -9.07  | -9.20  | -9.23  |
| $δD$(‰) | -46.36  | -45.75  | -44.45  | -45.52  |
| $δ$(‰) | -11.02  | -10.47  | -10.54  |  |
| Sand | 80% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 30400.0  | 30622.0  | 30853.0  |  |
| $δ$(‰) | -9.55  | -9.30  | -9.12  | -9.32  |
| $δD$(‰) | -44.95  | -46.29  | -43.20  | -44.81  |
| $δ$(‰) | -10.77  | -10.39  | -10.35  |  |
| Sand | 100% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 30771.0  | 30618.0  | 30102.0  |  |
| $δ$(‰) | -9.70  | -8.80  | -8.98  | -9.16  |
| $δD$(‰) | -44.80  | -41.12  | -43.77  | -43.23  |
| $δ$(‰) | -10.57  | -10.09  | -10.57  |  |

Table 4.2 isotopic abundance ratios of the clay sample bags

|  |  |
| --- | --- |
| Clay | 5% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 26819.4  | 28480.0  | 29110.8  |  |
| $δ$(‰) | -5.00  | -5.05  | -5.23  | -5.09  |
| $δD$(‰) | -38.65  | -36.07  | -35.97  | -36.90  |
| $δ$(‰) | -9.88  | -9.75  | -9.88  |  |
| Clay | 10% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 29022.0  | 29382.0  | 30096.0  |  |
| $δ$(‰) | -5.55  | -5.60  | -5.31  | -5.49  |
| $δD$(‰) | -38.05  | -38.46  | -36.64  | -37.72  |
| $δ$(‰) | -9.51  | -9.62  | -9.14  |  |
| Clay | 20% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 30733.5  | 30425.0  | 30723.9  |  |
| $δ$(‰) | -5.47  | -5.53  | -5.85  | -5.62  |
| $δD$(‰) | -36.35  | -35.96  | -38.72  | -37.01  |
| $δ$(‰) | -8.96  | -9.33  | -9.32  |  |
| Clay | 40% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 31071.4  | 31167.0  | 31068.0  |  |
| $δ$(‰) | -6.31  | -5.80  | -6.18  | -6.10  |
| $δD$(‰) | -40.11  | -36.88  | -36.36  | -37.78  |
| $δ$(‰) | -9.54  | -4.37  | -9.64  |  |
| Clay | 60% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 31080.0  | 31211.0  | 31358.0  |  |
| $δ$(‰) | -6.62  | -6.23  | -6.22  | -6.36  |
| $δD$(‰) | -39.91  | -39.67  | -34.81  | -38.13  |
| $δ$(‰) | -9.85  | -9.56  | -9.42  |  |
| Clay | 80% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 31400.2  | 31326.0  | 31388.0  |  |
| $δ$(‰) | -6.02  | -6.26  | -6.50  | -6.26  |
| $δD$(‰) | -38.44  | -39.24  | -40.50  | -39.39  |
| $δ$(‰) | -9.43  | -9.49  | -9.63  |  |
| Clay | 100% |
|  | 1 | 2 | 3 | mean |
| $H\_{2}$(ppm) | 31304.4  | 31050.0  | 31008.9  |  |
| $δ$(‰) | -6.83  | -6.12  | -6.67  | -6.54  |
| $δD$(‰) | -40.14  | -38.95  | -42.19  | -40.43  |
| $δ$(‰) | -9.92  | -9.66  | -9.87  |  |

The trend of the isotopic abundance ratios is shown in graph 4.1 and graph 4.2.

Graph 4.1 Tendency of isotopic abundance ratios of the sand sample bags

Graph 4.2 Tendency of isotopic abundance ratios of the clay sample bags

* 1. Calculation of isotopic fractionation

The common standard for expressing isotope ratios is shown:

$$ R\_{\frac{}{}(standard)}=(\frac{}{})\_{VSMOW}=\left(2005.2\pm 0.45\right)\*10^{-6} $$

$$R\_{\frac{D}{H}(standard)}=(\frac{}{})\_{VSMOW}=\left(155.76\pm 0.05\right)\*10^{-6}$$

So the isotopic abundance ratio of sample can be calculated:

$$R\_{sample}=δR\_{standard}+R\_{standard} $$

For the reason between gas phase and liquid phase at full equilibrium, the degree of fractionation is then expressed by:

$$α=\frac{R\_{sample}}{R\_{standard}}$$

As a result, the fractionation of the isotopes in sand and clay can be calculated and be shown in table 4.3 and table 4.4

Table 4.3 isotopic fractionation of the sand sample bags

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| moisture | 5% | 10% | 20% | 40% | 60% | 80% | 100% |
| $$α$$ | 1.008450818 | 1.009051189 | 1.009186965 | 1.00938 | 1.00932 | 1.00941 | 1.00924 |
| $$αD$$ | 1.04277099 | 1.044586431 | 1.045427301 | 1.04708 | 1.04769 | 1.04692 | 1.04518 |

Table 4.4 isotopic fractionation of the clay sample bags

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| moisture | 5% | 10% | 20% | 40% | 60% | 80% | 100% |
| $$α$$ | 1.005119408 | 1.005516936 | 1.005648392 | 1.00613 | 1.0064 | 1.0063 | 1.00658 |
| $$αD$$ | 1.038310185 | 1.03919497 | 1.038432382 | 1.03927 | 1.03964 | 1.04101 | 1.04213 |

1. Discussion

The water used in the experiment is tap water. The properties of the $H\_{2}$ and $δ$ are hard to analyze because their isotopic abundance ratios change irregularly. In this experiment the data of these isotopes were recorded but they won’t be discussed.

As the foregoing experiment has shown, the fractionation of $$ between dry air and tap water is about 1.007 and the fractionation of $$ is about 1.041. When the sand and clay are added in the system, they show a totally adverse result. The sand can help increase the fractionation of the two isotopes while clay lead the fractionation to decrease. Firstly, the gap between clay molecule and water molecule is smaller than the gap between sand molecule and water molecule so it is hard for clay to combine with water. Then the heavy isotopes will exist in the gas phase with higher concentration and as a result, the isotopic abundance ratios are higher and the fractionations are lower than that of sand sample. Secondly, different moisture means different water molecule combined in the soil. Both isotopic fractionation of sand and clay show an increasing trend depend on the increasing moisture, meaning that with more water molecules in the soil, the heavy isotopes prefer to leave the gas phase and combine with the soil.

1. Reference

[1] Christian Leibundgut, Piotr Maloszewski, and Christoph Kuells(2009). Tracers in Hydrology.

[2] <http://www.lgrinc.com/documents/LGR_WVIA_Datasheet_2016-06-30.pdf>

[3] P. Zorabedian, Tunable external cavity semiconductor lasers, in Tunable Lasers Handbook, F. J. Duarte (Ed.) (Academic, New York, 1995) Chapter 8.