2. Determination of the influence of salinity to the fractionation of isotopes

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1. **Introduction**

Isotopes are atoms of the same element that have the same numbers of protons and electrons but different numbers of neutrons. The difference in the number of neutrons between the various isotopes of an element means that the various isotopes have similar charges but different massesThe chemical properties of the isotopes are the same, while some of the physical properties are different, for instance, mass, density and conductivity. Isotope fractionation describes processes that affect the relative abundance of isotopes. Because of its difference in mass, the isotope abundance can be different in water phase and in gaseous phase in a close system. The represented experiment is aiming at determining the relationship between the isotope fractionation coefficient number and the salinity of different salt dissolved in water.

1. **Theoretical Principles**

**2.1 Isotopic abundance ratio**

A substance containing the less abundant isotope species and the more abundant isotope *N* has an isotopic abundance ratio R that is deﬁned by

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

In general, the isotopic abundance ratio of a sample is given with respect to the internationally accepted standard V-SMOW with the isotopic abundance ratio .

In δ notation, positive values indicate an enrichment of or compared to the standard being used whereas negative values signify a depletion of heavier isotopes in the sample.

**2.2 Isotope fractionation**

Physical and chemical processes can cause the change of isotopic abundance ratio. Then the fractionation occurs, meaning the different isotopic composition. 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:

1. **Experimental Procedure**

**3.1. Preparation of the aluminum bags and salt**

First, all the aluminum bags were prepared and sealed on one side for three times and paste the silicon on topside of the bag. Then, 24 hours were waited until the silicon is coagulated. After that, we weighed the salt (MgSO4, MgCl2, Na2SO4) and prepared the solution in volumetric flask. The concentration of the solution is designed to be 0.5 mol/L and the volume of the solution is 200 mL. That is to say 0.1 mol of each salt. After weighing the salt, the salt was dissolved in the beaker and later transferred into the volumetric flask. 10 minutes were waited for stabilizing before it is added to the bag.

**3.2 The adding of sample**

First, the aluminum bags were sealed on the open side with a small mouth. Then the dry gas, of which the composition is 21% of oxygen and 79% of nitrogen, was inflated in to the aluminum bag. After that, the solution which contains different concentration (0%, 5%, 10%, 20%, 35%, 50%, 65%, 80%, 90%, 100%) of the salt was added into the bag using pipette. Finally, the bags were sealed completely airtight by sealer.

**3.3 Measurement of the isotopes**

Each sample bags were placed in front of the tunable diode Laser spectrometer. The inlet needles were inserted into the bags to inhale the gas in the bags. After about 40 second the outlet needles were inserted in order to circulate between the machine and the sample bag. The vapor values and isotopic abundance ratios (*,,* ) of each bag were displayed and recorded.

1. **Results**

**4.1 raw data**

**Table 4.1** isotopic abundance ratios of different salt in various salinity

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| （‰） | | | | | | | | | | |
| concentration | 5% | 10% | 15% | 20% | 35% | 50% | 65% | 80% | 95% | 100% |
| MgSO4 | -6.98 | -7.05 | -7.55 | -7.59 | -7.65 | -7.40 | -7.90 | -7.80 | -8.05 | -8.12 |
| MgCl2 | -7.00 | -6.97 | -7.00 | -7.15 | -6.81 | -6.98 | -6.82 | -6.42 | -6.27 | -6.22 |
| Na2HPO4 | -7.04 | -6.83 | -6.07 | -6.98 | -6.58 | -6.26 | -6.30 | -5.95 | -5.75 | -5.70 |
| （‰） | | | | | | | | | | |
| concentration | 5% | 10% | 15% | 20% | 35% | 50% | 65% | 80% | 95% | 100% |
| MgSO4 | -42.00 | -41.42 | -40.20 | -41.00 | -40.00 | -42.45 | -41.62 | -41.77 | -42.90 | -42.10 |
| MgCl2 | -42.30 | -42.90 | -42.10 | -40.80 | -41.20 | -37.95 | -38.42 | -38.67 | -38.11 | -38.46 |
| Na2HPO4 | -40.67 | -41.50 | -40.21 | -39.56 | -40.15 | -38.91 | -37.01 | -37.38 | -36.44 | -35.10 |

**4.2 tendency of the isotopic abundance in salinity of different salt**

**Figure 4.1** Tendency of isotopic abundance ratios of the MgSO4 in salinity.

**Figure 4.2** Tendency of *D* isotopic abundance ratios of the MgSO4 in salinity.

**Figure 4.3** Tendency of isotopic abundance ratios of the MgSO4 in salinity.

**Figure 4.4** Tendency of *D*isotopic abundance ratios of the MgSO4 in salinity.

**Figure 4.5** Tendency of isotopic abundance ratios of the MgSO4 in salinity.

**Figure 4.6** Tendency of *D*isotopic abundance ratios of the MgSO4 in salinity.

**4.3 Calculation of isotopic fractionation**

The standard value of V-SMOW is addressed

The formula 2.4 can be deformed as following. Then the isotopic abundance ratio of sample can be calculated:

(2.6)

For the reason between gas phase and liquid phase at full equilibrium, the fractionation coefficient can be expressed by:

(2.7)

Taking the first value as an example, the MgSO4 value equals -6.98, then the

The fractionation coefficient number is shown in following table:

**Table 4.2** isotopic fractionation coefficient number of different salt in various salinity

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | | | | | | | | | |
| concentration | 5% | 10% | 15% | 20% | 35% | 50% | 65% | 80% | 95% | 100% |
| MgSO4 | 1.00703 | 1.00710 | 1.00761 | 1.00765 | 1.00771 | 1.00746 | 1.00796 | 1.00786 | 1.00812 | 1.00819 |
| MgCl2 | 1.00705 | 1.00702 | 1.00705 | 1.00720 | 1.00686 | 1.00703 | 1.00687 | 1.00646 | 1.00631 | 1.00626 |
| Na2HPO4 | 1.00709 | 1.00688 | 1.00611 | 1.00703 | 1.00662 | 1.00630 | 1.00634 | 1.00599 | 1.00578 | 1.00573 |
|  | | | | | | | | | | |
| concentration | 5% | 10% | 15% | 20% | 35% | 50% | 65% | 80% | 95% | 100% |
| MgSO4 | 1.04384 | 1.04321 | 1.04188 | 1.04275 | 1.04167 | 1.04433 | 1.04343 | 1.04359 | 1.04482 | 1.04395 |
| MgCl2 | 1.04417 | 1.04482 | 1.04395 | 1.04254 | 1.04297 | 1.03945 | 1.03996 | 1.04023 | 1.03962 | 1.04000 |
| Na2HPO4 | 1.04239 | 1.04330 | 1.04189 | 1.04119 | 1.04183 | 1.04049 | 1.03843 | 1.03883 | 1.03782 | 1.03638 |

1. **Discussion**

In this experiment tap water, dry magnesium sulfate, hydrated magnesium chloride and disodium hydrogen phosphate heptahydrate ware used. Tap water was used mainly because it can buffer the solution from too much pH changing, which may influence the result of the experiment greatly. And the value of was ignored because it changes tremendously so that it cannot be analyzed.

As can be seen in Figure 4.1 and Figure 4.2, the shows a tendency of decease with the increase of salinity. This is mainly because the salt provide an attraction force so that it is harder for the heavier isotopes to get through the phase interface. It means that with more salinity in the water, the heavy isotopes prefer to stay in the water.

Nevertheless, the other two salt shows a reverse tendency compare to the magnesium sulfate, which is shown from Figure 4.3 to Figure 4.6. It shows that with more salinity in the water, the heavy isotopes prefer to stay in the gaseous phase. The reason for this phenomenon is still unclear. Maybe it will be explained by the further experiment.

In addition, the value are correspondent. In respective salt it can be observed that if the value is higher, the value of will be relatively smaller. Maybe these two isotopes will influence each other in the fractionation.

1. **References**

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[2] Liebundgut, C; Kuells, C; Maloszewski, P. Tracers in hydrology. John Wiley & Sons, Ltd, Luebeck, 2009. Page 15,16,17.