Rayleigh Fractionation

Experiment F55

Short report for the Advanced Laboratory Course (FP)

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Contents

1. Introduction

The aim of this this experiment is to determine the isotope composition of different water samples and to gain insights into isotope effects occurring during fractionation processes.

The experiment was carried out with guidance from the provided lab report which is also used as the main reference for the information given in the introduction and used for the analysis (see under references in section 5).

Isotopes are atoms of the same element with different numbers of neutrons. For example, hydrogen exists as the isotope without any neutron (sometimes referred to as protium), deuterium (one neutron) and tritium (two neutrons). Molecules consisting of different isotopes are called isotopologues, but for clarity will be referred to as isotopes too. Different numbers of neutrons in the atomic nucleus cause the atoms to have slightly different physical properties. For example, while deuterium is nonradioactive like protium, tritium is radioactive. Different neutron numbers cause different binding energies which is why heavier isotopes are more reluctant to diffuse or react with other particles but they also have an effect on the binding energies which tend to be higher for heavier isotopes.

There are several quantities liked to describing isotope characteristics of molecules. First there is the isotope ratio R:

$$R = \frac{\text{abundance of heavy isotope}}{\text{abundance of light isotope}} \qquad 1$$

Since R is an absolute value, measurements from different instruments or even times cannot be compared to each other. For this reason, the δ-Notation is more commonly used as the δ-values are relative values in comparison to standards:

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \qquad 2$$

The slightly different properties of isotopes can cause the isotope ratio to change over time or during phase changes. This is called isotope fractionation. One example for this is the Rayleigh process during which a water from a reservoir evaporates. Because of their smaller mass the lighter water isotopes are going to evaporate first and will thereby change the isotope ratio in the remaining water. There are two different types of isotopic fractionation: there is the kinetic fractionation which is an irreversible process and the equilibrium fractionation which involves an equilibrium reaction. In nature isotopic fractionation is never just either one of them but a combination of the two types. In order to describe fractionation processes the isotope fractionation factor is used:

$$\alpha = \frac{R(A)}{R(B)} \qquad 3$$

Due to the fact that fractionation effects are rather small, another quantity called fractionation is usually used:

$$\varepsilon = \alpha - 1 \hspace{4cm} 4$$

Rayleigh fractionation has several effects on the isotopic composition of rain in different locations: The continental isotope effect includes that the longer water vapor travels inland over continents, the more precipitation will fall, so heavy isotopes are favored to rain out. Therefere, the further away a place is from the coast, the longer the water vapor in the rain clouds has traveled and the more depleted is the rain water in heavy isotopes. The latitude and temperature effect encompasses the decrease of the $\delta^{18}O$-value along latitudes. Again, the explanation can be found in the depletion in heavy isotopes in the water vapor as the rain clouds make their way from the warmer equator to the poles. The decreasing temperature along this route causes further vapor to turn into rain and intensities the fractionation. Another effect is the seasonal effect: As the sun changes the longitude of its peak, the intertropical convergence zone (ITC) shifts and thus the path the water vapor has traveled from the ITC to the place of rain fall. These varying pathlength of the rain clouds correspond to different amounts of rain already fallen and therefore to different seasonal isotope compositions of the rain water. Finally, the altitude effect connects the isotopic composition of the rain water to the altitude of the place of rain: Since higher altitudes are connected to lower temperatures, the rain water depletion in heavy isotopes will directly correspond to it.

2. Procedure

The instrument used for investigating the isotopic composition of the water samples is the Triple Isotope Water Analyzer TIWA-45EP which can handle liquid water samples as well as water vapour. The Water Vapour Isotope Analysis (WVIA) mode for is only used in the second part of the experiment where the complete evaporation of a water drop is observed. The water drop is inserted carefully into a glass cooling trap connected with the instrument and the change in water content and the δ-values can be directly observed from the data shown on the screen which is also saved as a .txt-document. The Liquid Water Isotope Analysis (LWIA) mode of the instrument is used for the rest of the experiment. In the first part, the evaporation of water at different temperatures is observed. Deionized water is heated to 40°C, 50°C, 60°C and 70°C and a sample is taken every half an hour. In part 3 local rainwater samples are investigated, in part 4 different unknown samples are compared and in the last part we investigate samples we brought from Heidelberg. A small volume sample is taken each and stored in a sealed vial until the measurement which takes place over night. The working of the instrument is ensured with test runs, afterwards a run configuration is set up according to the following rules: 4 standards are used to calibrate the measurements ("Alpen", "Colle", "VE" and "Sammelprobe"). Before any sample the standards are measured first. Since the isotopic ratios in the "Alpen" sample differ significantly from the other ratios, the "Alpen" sample needs to be measured twice to get accurate results and eliminate any memory effect. The same goes for any sample measured directly after "Alpen" and "Alpen" is never measured directly before an actual sample. After a measurement of the four standards, five samples are measured. Afterwards, the standards are measured again, but the sequence of the standards is changed by each standard measurement. Each sample is measured twice. Since each measurement includes 8 injections in total 16 injections are taken for each sample. The run is ended by a measurement of the standards. For the analysis of the result the LWIA Post Analysis software is used which automatically calibrates the δ-values using the given standards. It also applies a volume correction and identifies flawed measurements that are not suitable for further analysis. The software is then used to display the δ-values and manually sort through memory

effect affecting the measurements. Memory effects arise when measuring highly different isotopic ratios in a row and cause a distortion of the measured δ-values. The first measurement of a sample is always ignored due to memory effect from the previous sample. However, further memory effects might still affect the measurements and have to be discarded manually. Therefore, each measured sample is checked for memory effects and the data taken into account for the final evaluation is adjusted accordingly (Fig.1). This procedure is done for all three available different isotopic ratios. Afterwards, the post processor function of the software is used to calculate the average measured δ-values and standard deviations which are then used for further evaluation. This data processing procedure has the disadvantage of being highly depended on our evaluation of the memory effects, in especially on which measurements are taken into account for the final processing and which are not. Also, the number of measurements averaged to obtain the final δ-values differs greatly from sample to sample. Sometimes, samples with very different isotopic ratios were positioned next to each other and the memory effects were strongly affecting the measurements so that very few measurements could actually be taken which leads to a lower precision in the averaged value and the standard deviation. This is introducing uncertainties into our measurement which could be improved by performing more measurements and switching the order of the samples between measurements.
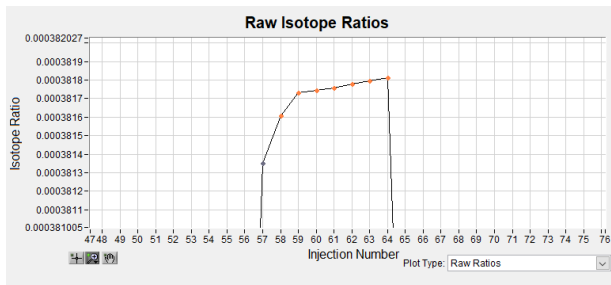

Fig.1: Raw isotope ratio $^{17}O/^{16}O$ in the LWIA Post Analysis software. While all data points belong to the same sample and should therefore yield the same isotopic ratio, the memory effect causes the measured isotope ratio to increase. The affected data points are discarded.

3. Results and Discussion

3.1. Evaporation at different water temperatures

The average temperature and humidity during the experiments is listed in Tab.1. Fig.2 shows the different obtained δ-values plotted against the fraction of remaining water. Since the deionized water used for the experiments was the same in all four measuring sequences, the δ-values δD, $δ^{17}O$ and $δ^{18}O$ are the same for the first sample which corresponds to a remaining fraction of water of 1. The differences in the different δ-values can be explained by different abundances of ^2H, ^{17}O and ^{18}O in the water. All four diagrams for the different water temperatures display dependencies of the δ-values on the amount of evaporated water: a lower fraction of remaining water (which is equivalent to more water being evaporated) corresponds to a rising δ-value. This can be explained by isotopic fractionation during the phase change from liquid water to water vapour where the evaporation of heavier isotopes like the observed ^2H, ^{17}O and ^{18}O is inhibited compared to the lighter and more abundant ^1H and ^{16}O. The reason is a lower kinetic energy for heavier isotopes as well as higher binding energies. The lighter isotopes will evaporate more easily while the heavier isotopes will enrich in the remaining liquid phase. The higher the water temperature the more water evaporates in the same amount of time. Therefore, for higher water temperatures lower fractions of remaining water can be reached and accordingly the final δ-values are the highest.

sample	temperature	humidity
40°C, 50°C	(24.9±0.5)°C	(44±4)%rH
60°C, 70°C	(23.9±0.3)°C	(34.6±0.6)%rH

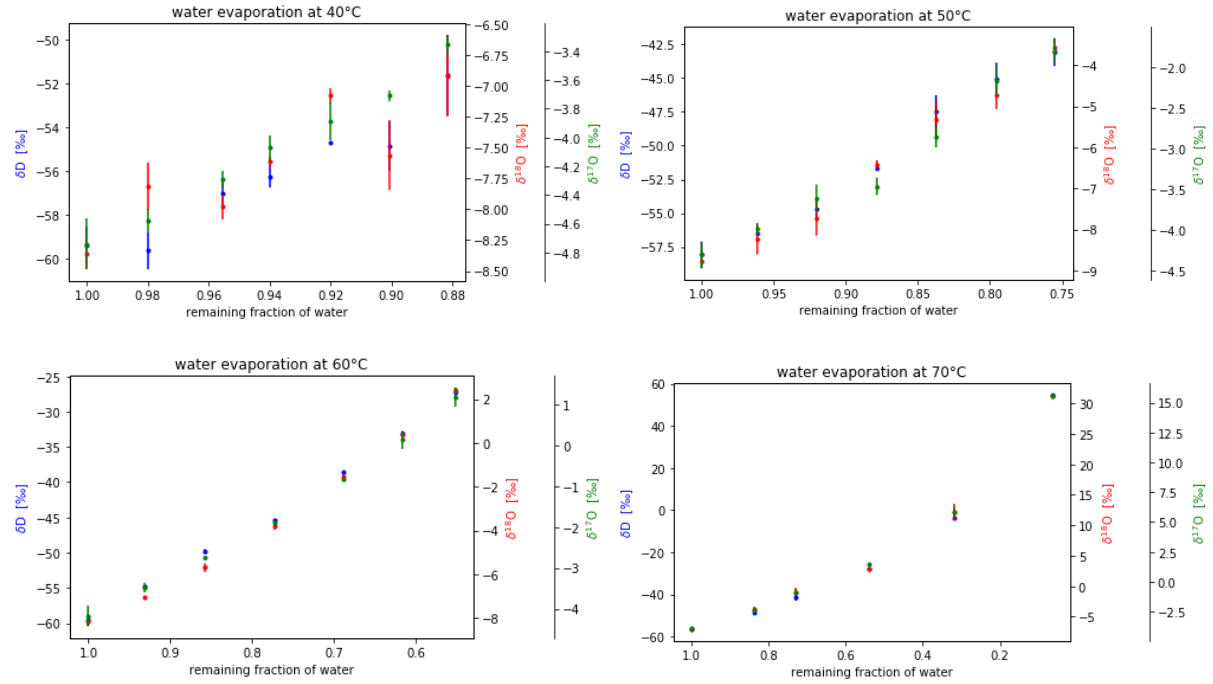Tab.1: Temperature and humidity of the room air during the experiments

Fig.2: δ-values plotted against the remaining fraction of water for different temperatures

Fig.3 shows the water lines for the different temperatures compared to the global meteoric water line (GMWL). The four individual water lines are generated by fitting the δ-values for each temperature with a linear fit. The calculated slopes and offsets for those fits are listed in Tab.2. They are in good agreement with each other, so all data points can be understood to form one common water line. As is clearly visible in Fig.3 this water line is significantly different from the GMWL described by

$$\delta D = 8 \cdot \delta^{18}O + 10‰$$ 5

The GMWL is an average relationship between the ^{2}H and ^{18}O ratios in meteoric water all over the world. The offset of the GMWL is a ^{2}H excess that is dependent on the region where the water evaporates, so the difference of the observed offset to the offset of the GMWL of 10‰ can be explained by the local conditions like humidity and temperature during the experiment and to a lesser degree by the isotopic composition of the used tap water. The slope on the other hand is dependent on the form of the evaporation process. Evaporation can happen as an equilibrium process or as an irreversible process (kinetic fractionation) with most evaporation processes being a mixture between both. A smaller slope than the GMWL slope of 8 indicates that kinetic fractionation is dominating the evaporation process. This is in accordance with the water in the experiment being heated to temperatures that normally would not exist in nature so the evaporation happens more quickly and less in a true equilibrium. In summary, the difference between the observed water line and the GMWL can be explained an interplay between by local differences in the water as well as the experiment settings that determine the evaporation process and the experiment environment (temperature and especially humidity).
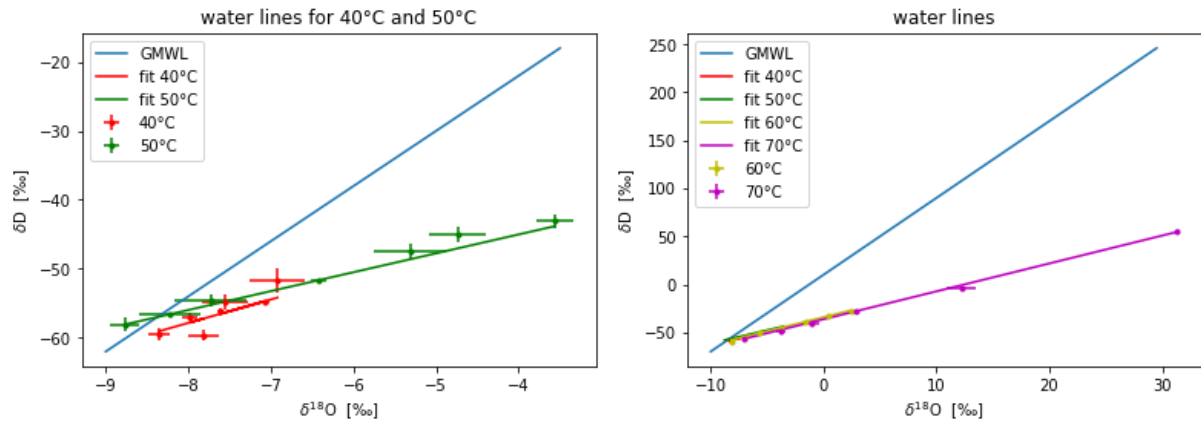
Fig.3: Water lines for different temperatures

sample	slope	offset
40°C	3.4±0.7	(-31±5)‰
50°C	2.74±0.09	(-34.1±0.6)‰
60°C	2.92±0.04	(-34.1±0.2)‰
70°C	2.90±0.01	(-36.3±0.3)‰

Tab.2: Fitting parameters of the water lines.

The Rayleigh process can be quantified by considering a liquid water reservoir where an infinitesimal number of molecules is evaporated which changes the isotopic ratios of the liquid and vapour phase. Solving the corresponding differential equation yields

$$\frac{\delta + 1}{\delta_0 + 1} = \left(\frac{N}{N_0}\right)^\epsilon$$

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where $\epsilon = \alpha - 1$. This equation can be used to calculate the fractionation factor α by correlating the δ-values to the fraction of remaining water (which is related to the number of molecules by the molecular mass M). Since seven measurements were taken for each temperature (except for 70°C where only six measurements could be taken since the water was completely evaporated afterwards), α was determined by fitting a linear function through the logarithmic ratios of the δ-values and masses. Fig.4 shows the determined fractionation factors plotted against the water temperature which are also listed in Tab.3. As expected, all fractionation factors are very close to 1 as fractionation processes are generally very small. There are small differences in the fractionation factors of the different isotopes due to different fractionations for the isotopes because of different weights. The fractionation factor increases with increasing temperature. Fractionation effects are therefore more significant for lower temperatures than in warmer conditions which can be explained by a decrease in the differences in the energy levels of the molecules due to different masses of isotopes with an increasing energy (a higher temperature).

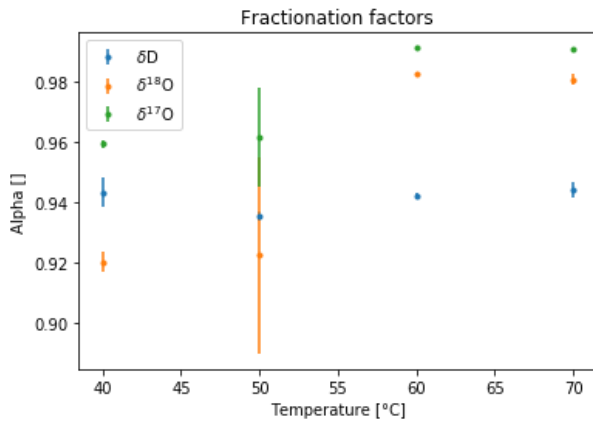| sample	α(δD)	α(δ¹⁷O)	α(δ¹⁸O)
40°C	0.943±0.005	0.920±0.003	0.959±0.001
50°C	0.935±0.002	0.923±0.003	0.962±0.002
60°C	0.942±0.001	0.9823±0.0002	0.99100±0.00005
70°C	0.944±0.003	0.981±0.002	0.9905±0.0003

Tab.3: Fractionation factors

Fig.4: Fractionation factors plotted against water temperature

3.2. Observing Rayleigh fractionation

During the second part of the experiment, the Rayleigh fractionation process was observed during the evaporation of a water drop. The changes in the water vapor concentration as well as the δD-, δ^{17}O- and δ^{18}O-values were determined over time in steps of 10s between measurements. The result can be seen in Fig.5, the x-axis has to be understood as a timeline in units of 10s.
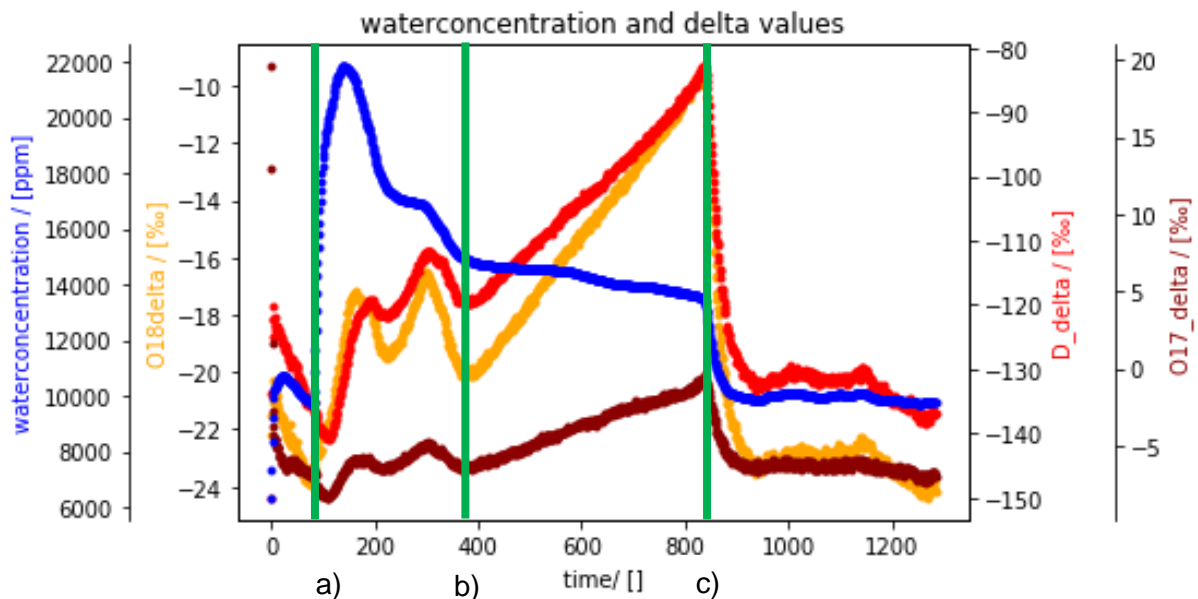

Fig.5: Rayleigh fractionation during the evaporation of a water drop, x-axis is in units of 10s

First, it can be noticed that all the δ-values follow approximately the same pattern. between a) and b) they show two peaks after which they drop a bit down to until b). The water concentration rises rapidly during the same time and then decreases quickly with a small constant period in between. From theory we expected one peak between a) and b) of the δ-values as when the water drop starts to evaporate the vapor must first mix with the surrounding air creating a 'false' high concentration at the sensor. As the small constant period in the water concentration appears around the same time as the second peaks in the δ-values, we assume that they may have been caused by minor amounts of water inside the glass tube that dropped into the glass container later because we did not manage to deliver the drop to the bottom of the container without the drop running down the tube leaving minor droplets behind. In between point b) and

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c) the water concentration decreases while the δ-values increase. This is due to the fact that while the drop evaporates initially lighter isotopes are favoured which causes the drop itself to be enriched with heavier isotopes. Thus, the rising vapor is enriched too causing the δ-values to rise at the same time as the water concentration decreases. At point c) the drop has fully evaporated and hence the water concentration and δ-values drop to their initial value (value of surrounding air) as there is no water vapor to measure anymore. For this experiment we must keep in mind, that the humidity and temperature that me measured in part one of the experiment changed over time and might have had an impact on the slope of the lines as the amount or speed of the evaporation process is dependent on the saturation of the air surrounding it. However, this did not have an impact on the pattern of the diagram itself.

3.3. Local rainwater samples

Two rainwater samples from Heidelberg were investigated: One was collected between the 11.09.2020 and the 28.09.2020 and describes those 17 days of precipitation, the other one is a mean for the month of September 2020. The measured δ-values were added to the list of previous rainwater measurements from Heidelberg. Fig.5 shows the δ-values for the samples collected in individual rain events while Fig.6 displays the monthly average values. There are small deviations between adjoining samples in Fig.5 but the overall trend follows the curves shown in Fig.6. This makes sense as the individual rain events in one month together form (by definition) the monthly average. Small fluctuations between precipitations in the same month cab be explained by slightly different weather conditions during the month.

Fig.6 shows seasonal effects in the isotopic composition of the rainwater in Heidelberg: Periodically the δ-values reach a local minimum during January while the local maxima are located in July. This can be explained by lower temperatures during the winter which are correlated via

$$p_{sat}(T) = p_0 e^{-\frac{L}{R_m}\left(\frac{1}{T}-\frac{1}{T_0}\right)} \hspace{2cm} 7$$

to the saturation water vapor pressure. Colder temperatures force more water vapor to turn into rain and accordingly the remaining water vapor is depleted in heavy isotopes as they predominantly enrich in the liquid phase of the liquid-vapor-equilibrium. An airmass travelling to Heidelberg in the winter is colder than in the summer, so more water vapor will precipitate before reaching its destination and the residual water vapor that is converted into rain over Heidelberg will have a lesser amount of heavy isotopes and therefore smaller δ-values. The maxima and minima in the δ-value curves correspond with the temperature extremes in Heidelberg. The measured sample for September 2020 fits, as expected, into the intermediate autumn.
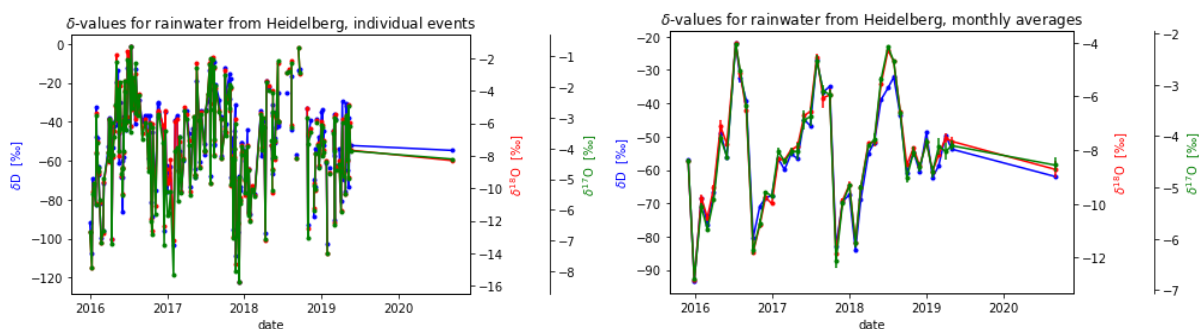

Fig.6: δ-values for rainwater in Heidelberg

Fig.7 shows the GMWL and the local meteoric water line (LMWL) for Heidelberg obtained by fitting the monthly average values for rainwater. The GMWL describes the average relationship between the ^{2}H and ^{18}O ratios in meteoric water acquired by evaluating samples from all over the world:

$$\delta D = 8 \cdot \delta^{18}O + 10\text{‰} \qquad\qquad 8$$

LMWLs can differ from the GMWL as the fractionation process during the evaporation is highly influenced by a number of local factors like latitude, continentality, temperature and humidity. For Heidelberg, the equation for the LMWL is

$$\delta D = (7.6 \pm 0.2) \cdot \delta^{18}O + (5 \pm 2)\text{‰} \qquad\qquad 9$$

Both slope and offset of the determined LMWL do not differ from the GMWL by more than three standard deviations, so there is no significant deviation. This might be explained by the environmental conditions in Heidelberg: The average temperature in Heidelberg is 10.2°C whereas the world average temperature (14°C) is quite similar, especially when taking into account the big uncertainties in the determination of the world average temperature. Heidelberg is only 144m high, so latitude effects won´t have a great effect on the isotopic composition of the water. It is also located in central Europe with medium distance to the oceans so that there are no great isotopic effects from either heavy rainwater coming from the sea nor extreme isotope depletion due to a great continentality.
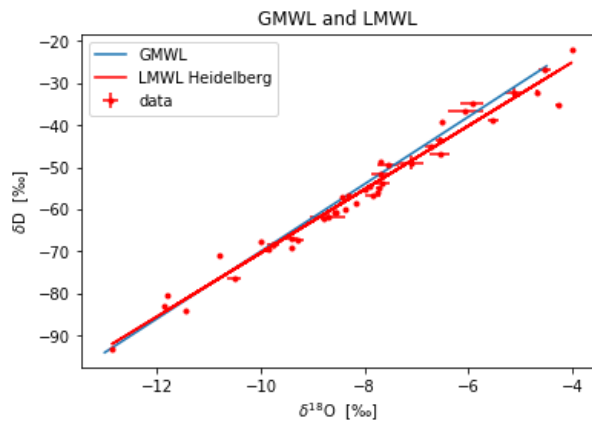

Fig.7: GWML and LMWL for Heidelberg

3.4. Finding the source of unknown samples

Although the considered mineral waters are not directly bottled from rain water, the isotope concentration in rain water is directly connected via local water cycles to the mineral water of a region, so the isotope effects on rain water will directly determine the mineral water concentration. Looking at the maps given in Fig.8 and Fig.9, it becomes clear that in countries located at a coast like France, Spain, Portugal, the UK and the north of Germany the δD- and δ^{18}O-values are significantly smaller than in continental countries and regions like Switzerland, the Czech Republic, Austria, Slovakia or the south of Germany. This is due to the continental effect which includes that the greater the distance from a place to the ocean, where the rain water ultimately comes from, the higher is the chance of precipitation favoring heavier isotopes for the cloud making its way towards the considered region. Therefore, the higher the continentality, the lower is the rain water concentration in heavy isotopes. The high δ-values in the alps can be explained with the altitude effect: A higher altitude corresponds to lower temperatures and therefore a lower concentration in heavy isotopes. This temperature-isotope relation might also explain the high δ-values of Norway or Sweden. Interestingly, the latitude

effect cannot be observed. This might be due to the fact that Europe does not cover a lot of degrees of latitude and the mentioned other effect probably dominate the isotopic composition of the water.

Following from those general trends, the lowest δ-values worldwide can be expected at places with a great continentality, high altitude, low temperatures and great latitude. Accordingly, an example for very low δ-values should be found in the Ural mountains in eastern Russia. On the other hand, the highest δ-values can probably be found close to the ocean, on low latitudes and altitudes at regions with high temperatures, like Sicily.

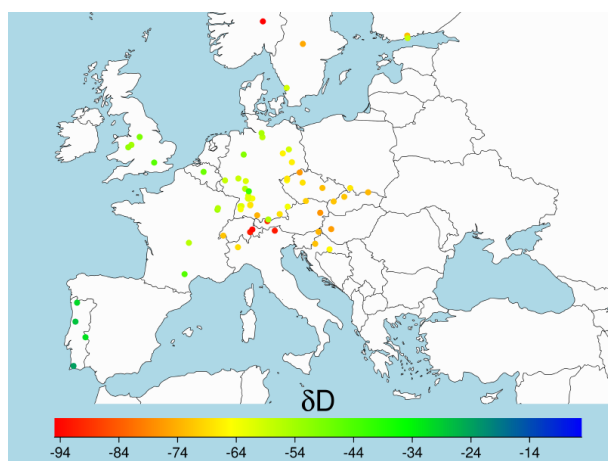Fig.8: δD-values in rainwater in Europe, picture taken from "Advanced Lab Course (F55): Rayleigh Fractionation", S. Therre at al., script for the experiment.
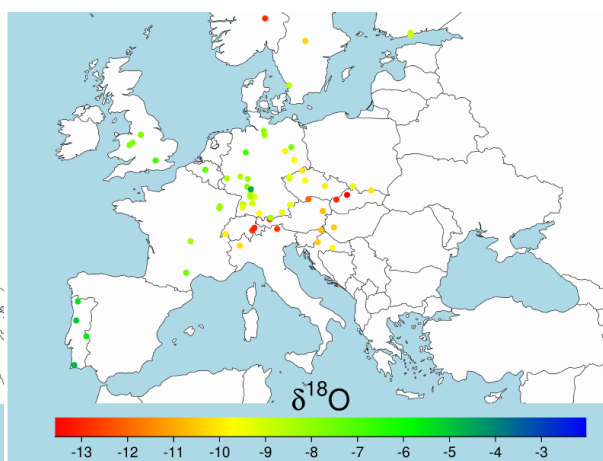
Fig.9: $\delta^{18}O$ -values in rainwater in Europe, picture taken from "Advanced Lab Course (F55): Rayleigh Fractionation", S. Therre at al., script for the experiment.

In this part of the experiment, we received water samples from unknown sources and determined their respective delta values. The results are shown in the Tab.4.

sample	δD	δ17O	δ18O
W089	(-74.3±2.3)‰	(-11.0±0.4)‰	(-5.89±0.08)‰
W006	(-52.3±1.2)‰	(-7.22±0.01)‰	(-4.36±0.08)‰
W048	(-58.7±0.9)‰	(-7.6±0.7)‰	(-4.4±0.1)‰
W062	(-64.8±0.6)‰	(-9.04±0.27)‰	(-5.13±0.12)‰
W099	(-124.70±0.02)‰	(-15.8±0.2)‰	(-8.70±0.15)‰

Tab.4: δ-values for the unknown water samples

The first four samples (W089, W006, W048, W062) are from European mineral water while the sample W099 is non-European. By comparing our results to the provided data, the W089 can be determined to be from either *Radenska Classic, Slovenia* (δD=-73.8, $\delta^{17}O$=-10.8, $\delta^{18}O$=-5.9), *Vöslauer, Austria* (δD=-77.7, $\delta^{17}O$=-10.7 $\delta^{18}O$=-5.8), *Vöslauer ohne, Austria* (δD=-77.5, $\delta^{17}O$=-10.7 $\delta^{18}O$=-5.77) or *Jana, Czech Republic* (δD=-72, $\delta^{17}O$=-10.4 $\delta^{18}O$=-5.87). While the two *Vöslauer* samples originate from the same spring and should therefore have the same isotopic composition, the Slovenian water is bottles in just about 170km distance. The water from the Czech Republic is actually bottled in the Prigorje region in Croatia, which in turn is just 70km from the Slovenian water source. So all samples are bottled very close to each other in regions with approximately the same continentality. Additionally, the regions are in the same clime zone, at the same altitude (about 400m) and the Austrian and Slovenian location have the same year-average temperature (14°C) while the Croatian region´s year-average is just a little bit cooler (12°C). There is a small difference in the latitude of these places which reflect directly in the small differences in the δ-values. Overall, the climate conditions of those three

places are very similar, which explains the similar δ-values and why they cannot be distinguished only using the isotopic concentration. Additional investigations of for example the ionic concentrations in those mineral water samples could reveal which source the sample came from.

The W006 sample could be from *Waitrose, UK* (δD=-54, $\delta^{17}O$=-7.7 $\delta^{18}O$=-4.35). The measured value for $\delta^{17}O$ shows a significant deviation, however this was the best match that could be found when taking into account all three δ-values.

W048 should be from *Classic natürliches Mineralwasser, Germany* (δD=-60, $\delta^{17}O$=-7.6, $\delta^{18}O$=-4.2).

The sample W062 is from *Griesbacher still, Germany* (δD=-63.7, $\delta^{17}O$=-9.4 $\delta^{18}O$=-5.01).

Finally, the non-European sample W099 is from *imivik, Greenland* (δD=-111, $\delta^{17}O$=-15.5, $\delta^{18}O$=-8.2). Although the measured values differ statistically significantly form the literature, the high δ-values only allow this match as no other literature location has δ-values in this range. Because of the extremely different composition of this sample in comparison to the other measured samples the measurement was highly affected by the memory effect. Out of the 16 measured injections only 5 could be used for determining the average, so the statistics for this sample are quite low. This could be improved upon by repeating the measurements more often.

3.5. Samples from Heidelberg

The determined δ-values for the samples from Heidelberg are listed in Tab.5. All three samples show no significant deviation from each other which can be explained by all three samples coming from the same local water cycle.

sample	δD	$\delta^{17}O$	$\delta^{18}O$
INF	(-61±2)‰	(-9.0±0.4)‰	(-4.8±0.1)‰
Neckar	(-62.1±0.1)‰	(-9.3±0.1)‰	(-4.7±0.1)‰
Keplerstraße	(-60.80±0.01)‰	(-8.8±0.2)‰	(-4.70±0.06)‰

Tab.5: δ-values for the samples from Heidelberg

4. Conclusion

In the first part of the experiment, Rayleigh fractionation was investigated by heating water to different temperatures and sampling it every 30 minutes. As the water evaporates, the molecules containing heavier isotopes will enrich in the remaining liquid water as the lighter isotopes are favored in the evaporation equilibrium. Accordingly, the δ-values δD, $\delta^{17}O$ and $\delta^{18}O$, which describe deviation of the isotopic ratio of a sample in relation to a standard, in the liquid water increase. The four different considered temperatures all yield results on the same water line (the relation δD and $\delta^{18}O$), which however significantly differs from the Global Meteoric Water Line (GMWL) which describes the average relationship between the ^2H and ^{18}O ratios in meteoric water acquired by evaluating samples from all over the world. The deviation of the water lines can be explained by the interplay between by local differences in the water as well as the experiment settings that determine the evaporation process and the experiment environment (temperature and especially humidity). To quantify the fractionation, fractionation factor was calculated which was, as expected, very close to 1 as fractionation processes are generally very small. It was observed that the fractionation factor increases with increasing temperature. It has to be taken into account that the temperature and humidity in

the room changed during the experiment which will have small effects on the evaporation equilibrium. Also uncertainties arise due to inaccurate time and weight measurements, but these effects can be considered to be quite small and not affect the outcome of the experiment.

Rayleigh fractionation during the evaporation of a single water drop was observed in more detail in the second part of the experiment. Although there were some irregularities in the results, probably due to a partly unsuccessful injection of the water drop into the glass bottle used for the measurement, the general expected trend could be observed: Light isotopes will evaporate first while the heavier isotopes enrich in the liquid phase and evaporate last.

The isotopic composition of rain water undergoes seasonal changes which can be seen in rain water from Heidelberg. In the winter, colder temperatures will force more water vapor to precipitate before a rain cloud reaches Heidelberg and the rain will be more depleted in heavy isotopes. The current sample from September 2020 fits perfectly into this periodic isotopic change. The Local Meteoric Water Line for Heidelberg is not statistically different from the GMWL which can probably be explained by the location and climate in Heidelberg which is a good representation of the world-average.

Determining the isotopic composition can be used for investigating the origin of unknown water samples. In the fourth part of this experiment, five mineral water samples could be matched to their region of origin. Finally, three different water samples from Heidelberg were investigated which show no significant deviation rom each other as is to be expected since they were taken from the same local water cycle.

For all samples investigated, the used instrument and data processing procedure has the drawback of being highly influenced by memory effects and the manual evaluation of this effect. The number of measurements averaged to obtain the final δ-values differs greatly from sample to sample as samples with very different isotopic ratios positioned next to each other are greatly affected by memory effects so that very few measurements could be used for the analysis. This is introducing uncertainties into the measurement which could be improved by performing more measurements and switching the order of the samples between measurements.

5. References

"Advanced Lab Course (F55): Rayleigh Fractionation", S. Therre at al., script for the experiment.

Weather data:

https://www.dwd.de/DE/service/lexikon/Functions/glossar.html?lv2=100932&lv3=101038

https://de.climate-data.org/europa/deutschland/baden-wuerttemberg/heidelberg-2122/

https://weather-and-climate.com/average-monthly-min-max-Temperature,bad-voslau-lower-austria-at,Austria

https://weather-and-climate.com/average-monthly-min-max-Temperature-fahrenheit,radenci-pomurje-si,Slovenia

https://weather-and-climate.com/average-monthly-Rainfall-Temperature-Sunshine,Zagreb,Croatia

Mineral water:

https://www.radenska.si/en/

https://www.voeslauer.com/de/

https://jamnica.company/en/brands