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Stable isotope composition of precipitation in Austria

Benedikt HAGER[1)2)*)] & Ulrich FOELSCHE[1)3)]

[1)] Institute for Geophysics, Astrophysics, and Meteorology, Institute of Physics (IGAM/IP), University of Graz, Graz A-8010, Austria;

[2)] now at: High Field MR Centre, Department of Biomedical Imaging and Image-Guided Therapy, Medical University of Vienna, Vienna A-1090, Austria;

[3)] Wegener Center for Climate and Global Change (WEGC), Graz A-8010, Austria;

[*)] Corresponding author, hager.benedikt@gmail.com

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Abstract

It is well established that climatic and geographic factors control the stable isotope composition of precipitation. These relationships are of major importance in climate studies, in particular for the interpretation of isotope data from paleoclimate archives.

Austria's topography is highly complex, mainly due to the large mountain ranges of the Alps. The Alps divide Austria into several distinct climate zones. The particular geographical condition and climate situation of Austria result in complex stable isotope patterns which are still not fully understood. In order to improve our understanding, we investigate the influence of meteorological and geographical conditions on isotope records for several Austrian sampling sites. The Austrian Network of Isotopes in Precipitation and Surface Waters (ANIP) has recorded monthly isotope and meteorological data since 1973. In the present study, we determined baseline data which can be used in future stable isotope studies. An Austrian Meteoric Water Line (AMWL), based on amount-weighted isotope values (weighted by the monthly precipitation amount) of 14 stations, was found to be $\delta D = 7.5\ \delta^{18}O + 3.2$. The slope and the intercept are close to, but lower than corresponding values of the Global Meteoric Water Line, most probably as a result of secondary evaporation during precipitation. Local Meteoric Water Lines (LMWLs) of single stations have been computed on a monthly and an amount-weighted annual basis. The correlation between altitude and amount-weighted annual mean $\delta^{18}O$ values yields an altitude effect of - 0.19 ‰ • 100 m^{-1} for Austria. Regression analyses reveal that, on a temporal basis, the $\delta^{18}O$ values are controlled by temperature and, in some cases, correlate inversely to the precipitation amount. Spatially, the predominant factor is altitude.

Es ist bestens bekannt, dass klimatische und geografische Faktoren die Isotopenzusammensetzung des Niederschlags steuern. Diese Zusammenhänge sind von großer Bedeutung für Klimastudien, insbesonders bei der Interpretation von Isotopendaten aus Klimaarchiven. Die österreichische Landschaft ist sehr gebirgig, was auf das große Gebirgsystem der Alpen zurückzuführen ist. Die Alpen teilen Österreich in verschiedene Klimazonen. Die besonderen geografischen Verhältnisse und klimatischen Bedingungen von Österreich führen zu komplexen Isotopenverteilungen, welche bis heute noch nicht vollständig verstanden werden. Um hier zur Klärung beizutragen, haben wir die Einflüsse von meteorologischen und geografischen Verhältnissen auf die Isotopendatensätze mehrerer österreichischer Probenahmestellen untersucht. Das Österreichische Messnetz für Isotope im Niederschlag und in Oberflächengewässern (ANIP) zeichnet seit 1973 monatliche Isotopen- und meteorologische Daten auf. In der vorliegenden Studie legen wir Basisdaten fest, welche in zukünftigen Studien mit stabilen Isotopen verwendet werden können. Eine österreichische meteorische Wasserlinie (AMWL) basierend auf mengengewichteten (gewichtet mit der monatlichen Niederschlagsmenge) Isotopenwerten von 14 Stationen wurde bestimmt als $\delta D = 7.5\ \delta^{18}O + 3.2$. Sowohl die Steigung als auch der Ordinatenabschnitt sind nahe an den Werten der globalen meteorischen Wasserlinie, aber jeweils kleiner, was höchstwahrscheinlich das Ergebnis sekundärer Verdunstung während des Niederschlags ist. Lokale meteorische Wasserlinien (LMWLs) von einzelnen Stationen wurden sowohl auf monatlicher als auch auf mengengewichteter jährlicher Basis (gewichtet nach der monatlichen Niederschlagsmenge) berechnet. Die Korrelation zwischen Höhe und gewichteten $\delta^{18}O$- Werten ergibt einen Höheneffekt von - 0.19 ‰ • 100 m^{-1} für Österreich. Die Regressionsanalyse zeigt, dass auf zeitlicher Basis die $\delta^{18}O$- Werte von der Temperatur gesteuert werden, während auf räumlicher Basis die Höhe der dominierende Faktor ist.

1. Introduction

Determining and interpreting the concentration of stable water isotopologues (especially HDO and $H_2{}^{18}O$) in precipitation and other water reservoirs has applications in several scientific fields including paleoclimatology, hydrology and hydrogeology. The reason for this applicability is explained by the close relationship of stable isotope compositions of meteoric waters (rain and snow), prevailing meteorological parameters, and geographical conditions. On a global scale,

several "isotope effects" are found to control the stable isotope composition of precipitation; namely the temperature-, amount-, altitude-, latitude- and continental effect (e.g. Gat et al., 2001). At high latitudes, stable isotope concentrations are strongly correlated with ambient surface temperatures ("temperature effect"), whereas at low latitudes the concentrations primarily depend on the precipitation amount ("amount effect"). At middle latitudes, the amount effect can be identified during summer (Dansgaard, 1964). Bowen (2008) showed that a significant correlation between $\delta^{18}O$ values and temperature can be found poleward of 30°N/S, with exceptions at some maritime stations and in south-east Asia. Moreover, it was indicated that there is a correlation between $\delta^{18}O$ values and precipitation amount across much of the land area at latitudes < 30°N/S.

Stable isotope analysis has numerous applications in earth sciences. In ice cores collected from high-latitude ice sheets and from mid-latitude and tropical mountain glaciers, stable isotope records are used to reconstruct past climate conditions (e.g. Johnsen et al., 1995; Thompson et al., 2000). Isotope values in lake and ocean sediments (e.g. Gat, 1996), cave speleothems (Spötl and Mangini, 2002), tree rings (McCarroll and Loader, 2004) etc. are analyzed and interpreted for similar reasons.

In groundwater studies, stable isotopes and the radioactive hydrogen isotope tritium are used to study infiltration processes and to determine the age and origin of the groundwater (e.g. Schlosser et al, 1988).

In general, isotope hydrology studies share the prerequisite that the stable isotope ratios of precipitation is known, since precipitation is the primary input to surface water (e.g. ocean, lake and river) and groundwater (Harvey and Welker, 2000).

Stable isotopes in precipitation and in related climate proxies are used to improve our understanding and to reconstruct periodicities of climate oscillations, such as the El Niño Southern Oscillation (ENSO), the Pacific Decadal Oscillation (PDO) and the North Atlantic Oscillation (NAO) (Brienen et al., 2012; Mantua and Hare, 2002; Barlow et al., 1993).

Sequential sampling and analysis of isotope values during individual rainfall events allows the investigation of precipitation formation conditions (Celle-Jeanton et al., 2004; Miyake et al., 1968).

Models of varying complexity, such as the Rayleigh and Atmospheric General Circulation Models (AGCM), have been developed and applied to improve our understanding of the isotope water cycle and isotope climate dynamics, both on a global and on a regional scale (Hoffmann et al., 2000; Sturm et al.,2005).

In isotope studies, the ratio of heavy isotopes (D and ^{18}O) in comparison with the light and most abundant isotopes (H and ^{16}O) is usually given in relation to a reference standard. This leads to the so-called delta values: δD and $\delta^{18}O$ (Coplen, 1994).

$$\delta^{18}O = \left[\frac{\left(\frac{^{18}O}{^{16}O}\right)_{sample}}{\left(\frac{^{18}O}{^{16}O}\right)_{VSMOW}} - 1\right] \times 10^3‰ \qquad \delta D = \left[\frac{\left(\frac{D}{H}\right)_{sample}}{\left(\frac{D}{H}\right)_{VSMOW}} - 1\right] \times 10^3‰$$

Currently, stable hydrogen and oxygen isotope abundances are expressed in relation to the Vienna Standard Mean Ocean Water (VSMOW), which is provided by the IAEA (International Atomic Energy Agency) (Coplen et al., 1994).

On a global scale, δD and $\delta^{18}O$ values in meteoric waters reveal a quasi-linear relationship that can be approximated by the Global Meteoric Water Line (GMWL) (Craig, 1961):

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

The slope relates to the ratio of the equilibrium fractionation factors for deuterium and oxygen-18. These fractionation factors, and thus the slope, are temperature dependent. For instance, at a temperature of 25°C the slope is roughly 8 (Clark and Fritz, 1997). The y-intercept value is termed deuterium excess (d). It is controlled by kinetic processes (Dansgaard, 1964).

$$d = \delta D - 8\ \delta^{18}O$$

Generally, evaporation into an unsaturated environment

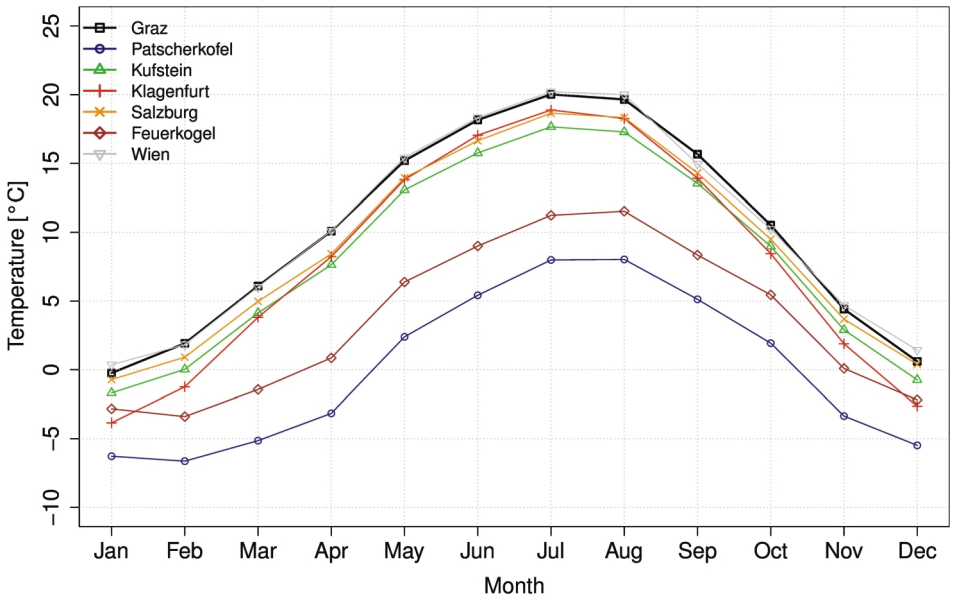

Figure 1: The seasonal variation of temperature recorded at selected stations of the ANIP in the period from 1973 to 2002.

leads to higher deuterium excess values in the vapor and lower values in the residual. Thus, there are two main stages controlling deuterium excess values: During evaporation from the ocean and during the fall of water-droplets from the cloud base to the ground.

Several different types of models have been developed to understand and simulate the global distribution of stable isotope concentrations in precipitation (Hoffmann et al., 2000). However, even Rayleigh models, which take kinetic fractionation processes during evaporation (Merlivat and Jouzel, 1979) and during ice formation (Jouzel and Merlivat, 1984) into account, cannot do justice to the complexity of the global hydrologic cycle; e.g. they do not include mixing of different air masses, the complex behavior of convective cloud processes or the influence of evapotranspiration over continental surfaces (Sturm et al, 2005; Hoffmann et al., 2000).

In Austria, the factors that specifically affect δ - values and deuterium excess values are: the ratio of re-evaporation (in summer), the evaporation of nearby water bodies such as lakes, Mediterranean versus Atlantic origin, seasonal shift of the vapor source region and altitude of the sampling station.

Several isotope studies have been conducted in Austria. A study of isotopes in precipitation by Humer et al. (1995) summarized several isotope effects and an Austrian Meteoric Water Line was defined as: $\delta D = 8.2\ \delta^{18}O + 10.6$. Moreover, an altitude effect was found to be 0.16 ‰ • 100 m-1. Kaiser et al. (2001) studied long-term isotope records and the connection between isotope values of precipitation and air moisture origin. It was found that long term records of isotope values are in accordance with surface air temperatures and that isotope values also largely correlate to the North Atlantic Oscillation (NAO) index. Local variations of deuterium excess were found in the Alpine region and attributed to secondary fractionation processes. Moreover, first attempts at using statistical analysis of back trajectories were made to trace the path and isotopic evolution of air masses.

Rank and Papesch (2005) studied deuterium excess patterns of precipitation. They found that there is no significant difference between northern and southern stations and that the reason for the differences in deuterium excess is evaporation and/or isotopic exchange with air moisture during the fall of raindrops. This study concludes that deuterium excess values do not seem to be a reliable tool to trace the origin of air masses in Austria.

Although stable isotope studies for Austria already exist, the present study is more comprehensive than former studies in many respects. For example, the observational period of our study (1973-2002) is longer compared to other isotope studies in Austria (e.g. the observational period of Humer et al., 1995, was from 1973-1992). As mentioned earlier, stable isotope values are temperature dependent. In Austria, the last decades were marked by a considerable surface temperature increase (Auer et al., 2001) which might have affected stable isotope patterns. Therefore, we believe that there is a great need for more up to date baseline stable isotope data. Moreover, we believe that this is the first study that defines Local Meteoric Water Lines and isotope/temperature gradients on a monthly and amount-weighted basis in the period from 1973 to 2002. To the best of our knowledge, an Austrian Meteoric Water Line and an altitude effect on an amount-weighted basis have not previously been defined for the period from 1973 to 2002.

The analysis of isotope data collected at stations across Austria will improve the understanding of isotope fractionation processes in mountainous mid-latitude continental regions. In addition, the results of our study can be used in future hy-

Figure 2: ANIP stations used in this study.

drological studies and for paleoclimate reconstruction. In summary, the aims of the present study are:

1. Determining the spatial and temporal patterns of stable isotopic composition in precipitation in Austria.
2. Investigating the influence of meteorological and geographical parameters on $\delta^{18}O$ values using simple and multiple regression analysis.
3. Determining baseline data for each ANIP station, including for instance Local Meteoric Water Lines and $\delta^{18}O/T$ coefficients.
4. Evaluating deuterium excess (d) patterns for Austria and discussing their utility for identifying vapor source regions.

2. Climate and topography of Austria

Austria is located in Central Europe. Due to the Alps, the territory is highly mountainous. The lowest point of Austria is Hedwighof in the state of Burgenland, at 114 m (above the Adriatic) and the highest point is the summit of Großglockner, which lies between the states of Tyrol and Carinthia, at 3798 m.

Austria is made up of major parts of the eastern Alps, the southern sector of the Variscan Bohemian Massif and the north-western Molasse basin, which is located north of the Alps (Neubauer and Höck, 1999; Véron, 2005). In the east, Austria covers the western part of the Pannonian Basin.

Austria can be assigned to the temperate climate zone. More precisely, the climate situation in Austria can be explained by the influence and interaction of four climates:

1. Alpine climate - a great extent of the Austrian territory is mountainous. The term "Alpine climate" refers to a cold mountain climate. The precipitation signal is characterized by strong spatial variability covering the scale of the whole Alps to the scale of single slopes. This concerns both, the occurrence of heavy precipitation events as well as the long term mean (Cebon, 1998).
2. Pannonian climate - the eastern part of Austria is part of the Pannonian Basin (Pannonian Plain). This lowland region covers the region from the northern Burgenland to the Vienna basin. A characteristic cyclone influencing this region is the "Genoa low". Genoa cyclones are low pressure systems which are generated over the Gulf of Genoa and northern Italy. The climate in eastern Austria is warm compared to other regions in Central Europe and is also characterized by low precipitation amounts in winter.
3. Illyric climate - this climate is dominant in southeastern Austria. It is a combination of Mediterranean, Pannonian and Alpine climate. The precipitation amounts in summer for this region are high compared to the regions controlled by the Pannonian climate.
4. Atlantic climate - Several regions of Austria are influenced by Atlantic climate from the north-east. This climate primarily influences the northern parts of the Alps.

In general, the main sources of precipitation are the Atlantic Ocean and the Adriatic Sea (Liebminger et al., 2007).

The Alps act as a meteorological divide for the movement of cold air masses passing to the south from the northwest Atlantic and northern Arctic regions. As a result, the regions south of the Alps are less affected by the Atlantic climate and are more strongly influenced by the Mediterranean climate. The extent to which the Alps act as a weather divide depends primarily on the respective time of the year. The shielding effect mainly appears in the winter season and is less prevalent to non-existent during summer and autumn. The effect itself can be explained by the cloud base height (i.e. the height at which the temperature equals the dew point). In winter, the cloud base is rather low. Thus, humid air masses cannot pass the Alpine mountain range during that season. Consequently, the precipitation signal in southern Austrian regions (e.g. at the station Graz) during winter can mainly be associated with a southern region as its source (e.g. Adriatic Sea) (Wakonigg, 1978).

All climate regions in Austria show strong seasonal air temperature (Fig. 1) and precipitation amount variability, with the highest values in summer and the lowest values in winter. The variability of precipitation amount is highest (relatively speaking) at stations south of the Alpine divide. The highest mean annual precipitation amounts are detected at Mt. Feuerkogel (1895 mm) and the lowest are detected at the station in Vienna (628 mm).

STATION	T_a [°C]	P_a [mm]	Longitude	Latitude	Altitude [m]	$\delta^{18}O_w$ [‰]	δD_w [‰]	d_w [‰]
GRAZ	10.2	810	15° 27′	47° 05′	366	-8.8	-62	9
VIENNA	10.3	628	16° 21′	48° 14′	203	-9.9	-71	8
PATSCHERKOFEL	0.1	887	11° 28′	47° 13′	2245	-13.5	-96	8
LÄNGENFELD	5.7	742	10° 58′	47° 05′	1180	-11.8	-88	7
SCHARNITZ	6.4	1358	11° 16′	47° 23′	960	-12.0	-87	9
KUFSTEIN	8.2	1324	12° 10′	47° 35′	495	-10.8	-79	7
SALZBURG	9.1	1288	13° 00′	47° 48′	430	-10.2	-73	8
BREGENZ	9.5	1516	09° 44′	47° 29′	430	-10.3	-74	8
FEUERKOGEL	3.6	1895	13° 43′	47° 49′	1618	-11.9	-82	13
LAHN	6.9	1284	13° 38′	47° 33′	518	-11.1	-81	8
KLAGENFURT	8.0	887	14° 19′	46° 37′	442	-9.8	-70	9
BÖCKSTEIN	-	1283	13° 07′	47° 05′	1112	-12.0	-88	8
GOLLING	-	1433	13° 10′	47° 36′	476	-10.6	-76	9
ACHENKIRCH	-	-	11° 42′	47° 31′	910	-	-	-
NASSWALD	-	1382	15° 42′	47° 45′	774	-10.5	-75	9

Table 1: Geographical and climatological conditions and stable isotope characteristics of selected ANIP-stations in the period from 1973 to 2002. $\delta^{18}O$, δD and deuterium excess (d) are weighted mean values. T_a is the mean annual temperature and P_a is the mean sum of annual precipitation. No temperature records are available for the stations in Böckstein, Golling, Nasswald and Achenkirch. The altitude is given as meters above the Adriatic. Geographical parameters are mainly obtained from Kralik et al. (2005).

3. Data and methods

The Austrian Network of Isotopes in Precipitation and Surface Waters (ANIP) documents $\delta^{18}O$, δD and tritium data from 72 monitoring stations (Kralik et al., 2004) in the whole country. This database collects isotope data and relevant meteorological data (temperature, precipitation amount) on a monthly basis.

Isotope values from many ANIP stations are available for limited time periods. Since 15 ANIP stations share an observational period from 1973 to 2002, we used those records for further analysis (Fig. 2). Details on how missing values were handled in this study can be found in Hager (2012). In short, we used the method of least squares on the temporal monthly (1973 – 2002) $\delta^{18}O$ trend to calculate the missing monthly $\delta^{18}O$ values. The δD values were calculated using the linear monthly relationship between $\delta^{18}O$ and δD.

Basic geographical, meteorological and stable isotope information of these stations is listed in table 1.

Monthly information can generally not be derived from paleoclimate archives. In an idealized case, the best isotope signal preserved in an annual layer of an archive is attributed to the annual sum of precipitation. To gain weighted annual isotope values similar to those preserved from climate proxies, we used monthly isotope data and precipitation amounts (e. g. Zuppi, 1981):

$$\delta_w = \frac{\sum_{i=1}^{n} P_i^m \delta_i^m}{\sum_{i=1}^{n} P_i^m}$$

P_i^m refers to the monthly precipitation amount and δ_i^m to the respective δ value, $\delta^{18}O$ or δD.

We assume that a better correlation of isotope values would be found with cloud base temperatures rather than surface temperatures (Rindsberger et al., 1983). However, such data were not available for Austria. Nevertheless, the differences between the mean surface temperature and the temperature during precipitation events must be emphasized. Temperatures during precipitation events ("precipitation temperature") were calculated using hourly data of temperature and precipitation amount.

$$T_p = \frac{\sum_{i=1}^{n} P_i^h T_i^h}{\sum_{i=1}^{n} P_i^h}$$

4. Multiple linear regression analyses

Similar to other studies in mid and low latitudes, e.g. in China (Johnson and Ingram, 2004), Guatemala, and Belize (Lachniet and Patterson, 2009), we run single and multiple regression analyses to emphasize the dependence of isotope values on the temperature and precipitation amount at the study sites. The results of the multiple linear regression analyses are summarized in table 2. Details on how the regression analyses were performed in this study can be found in the appendix section.

At the stations in Graz, Vienna, Längenfeld, Bregenz, Feuerkogel and Klagenfurt, a significant relationship between the two predicting variables (T, P) and the dependent variable ($\delta^{18}O$) in the linear regression model was found, indicating that the p-values of both predicting variables are less than 0.05. For instance, for the station in Graz, the model formula is: $\delta^{18}O_m = 0.47\ T_m$ [°C] – $0.01\ P_m$ [mm] -13.96 ($R^2 = 0.72$). By contrast, at the stations in Patscherkofel, Scharnitz, Kufstein, Salzburg and Lahn, the influence of the precipitation amount is not statistically significant. As can be seen in table 2, the precipitation amount contributes less to the $\delta^{18}O$ values than the temperature does. These results emphasize that the main driving factor in Austria is temperature, which confirms the findings of Bowen (2008).

On a global scale, stable isotope values in precipitation vary spatially depending on geographic parameters such as altitude, latitude and longitude.

For Austria, the effect of these parameters on $\delta^{18}O$ values is investigated with linear regression analysis. The influences of the variables latitude and longitude are not statistically significant on any significance level. As mentioned earlier, Austria is affected by different climates ranging from Atlantic and Mediterranean influences in the west and south to continental features in the east, and from low elevation valleys and basins to high elevation mountain climate (Böhm et al., 2001). We hypothesize that the dependence of isotope values on longitude and latitude cannot be shown because the different climates in Austria average out the global circulation patterns. Spatially, isotope values in precipitation therefore primarily depend on altitude. The altitude effect, using the weighted mean annual average $\delta^{18}O$ values of 14 ANIP stations is - 0.19 ‰ • 100 m^{-1} (R^2 = 0.81). Considering arithmetic

STATION	β'_0	SE-β'_0	β'_1	SE-β'_1	β'_2	SE-β'_2	R^2	R^2 adj.	p value-prec.
GRAZ	-13.7	0.178	0.453	0.0168	-0.0118	0.00252	0.73	0.73	<0.05
VIENNA	-12.4	0.248	0.377	0.0162	-0.0238	0.00360	0.60	0.60	<0.05
PATSCHERKOFEL	-14.5	0.232	0.525	0.0215	0.00119	0.00280	0.69	0.69	0.68
LÄNGENFELD	-16.5	0.231	0.661	0.0230	-0.0112	0.00401	0.78	0.78	<0.05
SCHARNITZ	-15.6	0.267	0.465	0.0190	0.000252	0.00221	0.69	0.69	0.91
KUFSTEIN	-14.3	0.228	0.403	0.0161	-0.00343	0.00198	0.67	0.66	0.08
SALZBURG	-13.5	0.227	0.312	0.0180	-0.00118	0.00212	0.53	0.53	0.57
BREGENZ	-13.4	0.232	0.354	0.0179	-0.00583	0.00171	0.55	0.55	<0.05
FEUERKOGEL	-13.9	0.221	0.302	0.0184	0.00374	0.00129	0.48	0.47	<0.05
LAHN	-14.6	0.267	0.400	0.0231	0.000866	0.00220	0.53	0.52	0.69
KLAGENFURT	-13.1	0.200	0.443	0.0154	-0.0142	0.00261	0.73	0.73	<0.05

Table 2: Summary of the multiple linear regression analysis. The p value of temperature is < 0.05 for every ANIP station and is not explicitly shown in the table. No temperature records are available for the stations in Böckstein, Golling, Nasswald and Achenkirch.

mean $\delta^{18}O$ values, the altitude effect is - 0.17 ‰ • 100 m^{-1} (R^2 = 0.77). This value is close to the altitude effect for Austria found by Humer et al. (1995) (- 0.16 ‰ • 100 m^{-1}) and is similar to the one observed in Switzerland (- 0.2 ‰ • 100 m^{-1} (Schotter et al., 2010)), Italy (- 0.2 ‰ • 100 m^{-1} (Longinelli and Selmo, 2003)) and to those in many other European countries (e.g. Siegenthaler and Oeschger, 1980).

5. Local Meteoric Water Lines

In general, local meteoric water lines (LMWL) can provide information regarding the vapor origin, the aggregate phase of the precipitation (snow or rain) and the secondary evaporation and moisture recycling history of falling rain droplets (Gat, 2000). Moreover, a local meteoric water line (LMWL) of precipitation provides information about the isotopic composition of precipitation at a specific location and it can be compared to the LMWL of other water sources to identify the origin of e.g. groundwater and surface-water (Liu et al., 2010). Consequently, the results of this study can be used in future groundwater, surface-water and catchment studies.

To define an overall Austrian Meteoric Water Line (AMWL), the average of the weighted annual mean isotope values of 14 ANIP stations is used. The line of best fit for this relationship is $\delta D = 7.5\ \delta^{18}O + 3.2$ (Fig. 3) with a high correlation (R^2 = 0.97). Both the slope and the intercept are lower than for the GMWL. This can be assigned to secondary evaporation processes into unsaturated air as kinetic fractionation leads to a lower slope and a lower intercept of meteoric water lines (Gat, 2000). The AMWL is similar to the local meteoric water lines of other Alpine regions. For example, the LMWL of Italy is $\delta D = 7.61\ \delta^{18}O + 9.21$ (Longinelli and Selmo, 2003) and the line of Germany is $\delta D = (7.09 \pm 0.60)\ \delta^{18}O + (0.31 \pm 0.07)$ (Stumpp et al., 2014). The Local Meteoric Water Line for Austria determined by Humer et al., (1995) ($\delta D = 8.2\ \delta^{18}O + 10.6$) is very different to the one found in our study. One reason for this could be the different observation periods, with the time period having been considerably shorter in the study of Humer et al., (1995), while another explanation could be the fact that different stations were used in their study.

The local meteoric water lines using weighted annual (weighted by the monthly amount of precipitation) and un-weighted monthly isotope values of single stations are presented in table 3. The respective correlations are strong for annual weighted ($R^2 > 0.9$) and very strong for monthly un-weighted values ($R^2 > 0.97$). As mentioned before, these lines are affected by a combination of several factors including air mass origin,

STATION	*LMWL(w) slope(a)*	*LMWL(w) int.(b)[‰]*	*R^2*	*LMWL(m) slope(a)*	*LMWL(m) int.(b) [‰]*	*R^2*
GRAZ	8.3	11.4	0.96	7.8	6.8	0.99
VIENNA	7.4	2.6	0.96	7.6	3.5	0.97
PATSCHERKOFEL	7.5	5.5	0.98	8.3	16.0	0.99
LÄNGENFELD	8.5	12.6	0.99	8.0	6.3	0.99
SCHARNITZ	8.3	12.3	0.98	7.9	7.7	0.99
KUFSTEIN	7.2	-1.0	0.97	7.8	5.7	0.99
SALZBURG	8.5	13.6	0.98	8.1	9.0	0.99
BREGENZ	8.0	8.3	0.98	8.0	7.8	0.99
FEUERKOGEL	8.2	15.0	0.99	8.3	15.5	0.99
LAHN	8.6	14.0	0.99	7.9	6.8	0.99
KLAGENFURT	7.8	7.1	0.97	7.9	7.6	0.99
BÖCKSTEIN	8.2	10.6	0.98	8.0	8.0	0.99
GOLLING	7.4	2.3	0.97	8.0	9.2	0.99
NASSWALD	8.0	7.8	0.98	7.8	6.2	0.99
ACHENKIRCH	-	-	-	8.0	5.6	0.98

Table 3: Local meteoric water lines of ANIP stations. The relationship was calculated using weighted annual (w) and un-weighted monthly (m) isotope values. No precipitation records are available from the station in Achenkirch and therefore an amount-weighted LMWL could not be calculated.

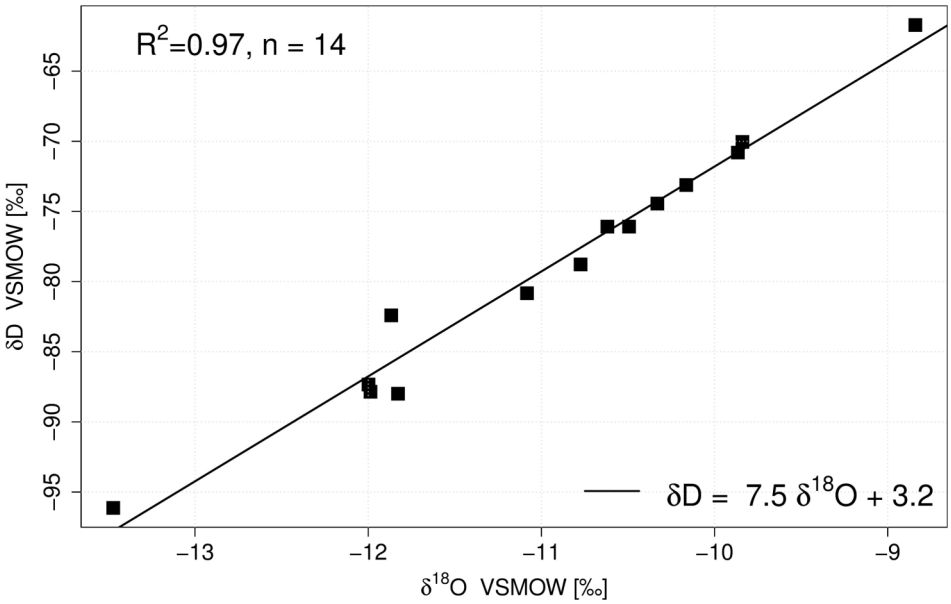

Figure 3: Austrian meteoric water line calculated by using average weighted annual mean isotope data of 14 Austrian stations in the period from 1973 to 2002. No precipitation amount records were available for the station in Achenkirch.

re-evaporation and mixing of air moisture (Gat, 2000). Therefore, interpreting these data is rather difficult. Several stations (i.e. Graz, Scharnitz, Bregenz, Böckstein) feature local meteoric water lines (weighted) close to the Global Meteoric Water Line of Craig (1961) ($\delta D = 8\ \delta^{18}O + 10$) and Rozanski et al. (1993) ($\delta D = 8.17\ \delta^{18}O + 10.35$). Local meteoric water lines using monthly isotope values are even less scattered and closer to the Global Meteoric Water Line (e.g. LMWL of Graz: $\delta D = 7.8\ \delta^{18}O + 6.8$, $R^2 = 0.99$) and correlations are very high with values between $R^2 = 0.97$ and $R^2 = 0.99$. The slopes and intercepts (in accordance to the deuterium excess values) are very high for mountain stations (e.g. LMWL of Patscherkofel: $\delta D = 8.3\ \delta^{18}O + 16.0$, $R^2 = 0.99$)

6. Isotope-temperature correlation

Correlations of isotope values in precipitation with temperature have been demonstrated by a number of different approaches. An initial study was carried out by Dansgaard in 1964. It showed a good correlation of surface temperature and isotope values on a global scale.

Generally, on a seasonal (monthly) basis, the $\delta^{18}O$/T relationship ranges from a slope of 0.5 ‰/°C at higher latitudes to 0 ‰/°C at lower latitudes (Gat et al., 2001). Austria is located at middle latitudes (~47°N). The calculated seasonal $\delta^{18}O$/T relationships of ANIP- stations are between $\delta^{18}O = 0.31\ T - 13.59$ ‰ (Salzburg) and $\delta^{18}O = 0.62\ T - 16.94$ ‰ (Längenfeld) with an average slope of 0.41 ‰/°C. The correlation is moderate to strong ($R^2 > 0.5$) (Tab.4).

Stable isotope values ($\delta^{18}O$ and δD) have repeatedly been used to reconstruct paleotemperatures from climate archives. At high latitudes, for instance, $\delta^{18}O$ values in ice cores are interpreted as a measure for temperatures at the core sampling site (Cuffey et al., 1995). For the global spatial $\delta^{18}O$/T relationship, the study of Dansgaard (1964) revealed a linear fit of $\delta^{18}O = 0.69\ T - 13.6$ ‰. The spatial $\delta^{18}O$/T relationship in Austria is calculated using the particular weighted mean annual average $\delta^{18}O$ values and the annual mean temperature values of the eleven ANIP stations. The resulting spatial isotope-temperature coefficient is 0.39 ‰/°C and the correlation is high ($R^2 = 0.85$) (Fig. 4).

It has previously been noted that the various Alpine regions are subjected to different vapor source regions. They therefore show substantial differences in the distribution of precipitation and differ in their precipitation generating mechanisms. Thus, defining an exact and universally valid isotope/temperature gradient for Alpine regions is generally not possible (Schotter et al., 2010).

Compared to the European $\delta^{18}O$/T gradient of 0.58 ‰/°C as defined by Rozanski et al. (1992) the gradient is rather low. Moreover, Rozanski et al. (1992) used un-weighted $\delta^{18}O$ values, which make the comparison of the gradients rather difficult.

We also calculated temporal $\delta^{18}O$/T gradients of single stations, demonstrating that the coefficient of determination between surface temperature means and weighted mean annual values is mainly low and that the isotope/temperature gradient ranges from 0.17 to 0.90 ‰/°C (Tab. 5).

In summary, there are strong

STATION	$\delta^{18}O_m$-T_m slope(a)[‰/°C]	$\delta^{18}O_m$-T_m int.(b)[‰]	R^2	σ_a [‰/°C]	σ_b [‰]	SEE [‰]
GRAZ	0.40	-14.05	0.71	0.01	0.17	1.91
VIENNA	0.35	-13.43	0.55	0.02	0.21	2.33
PATSCHERKOFEL	0.53	-14.44	0.69	0.02	0.11	2.03
LÄNGENFELD	0.62	-16.94	0.77	0.02	0.16	2.29
SCHARNITZ	0.47	-15.54	0.69	0.02	0.17	2.09
KUFSTEIN	0.39	-14.54	0.66	0.01	0.16	1.99
SALZBURG	0.31	-13.59	0.53	0.02	0.18	2.08
BREGENZ	0.33	-13.85	0.53	0.02	0.19	2.08
FEUERKOGEL	0.32	-13.39	0.46	0.02	0.12	1.97
LAHN	0.40	-14.57	0.53	0.02	0.21	2.74
KLAGENFURT	0.40	-13.85	0.71	0.01	0.16	2.12

Table 4: Relationship between temperature and $\delta^{18}O$ content in precipitation on a monthly basis. The selected stations share the same monitoring period from 1973 to 2002, except for the station in Lahn (1973 - 2000), Scharnitz (1973 - 1997) and Längenfeld (1973 – 1999). No temperature records are available from the stations in Böckstein, Golling and Nasswald. σ_a is the standard error of the slope, σ_b is the standard error of the intercept and SEE is the standard error of the estimate.

STATION	n	$\delta^{18}O_w$-T_w slope(a)[‰/°C]	$\delta^{18}O_w$-T_w int.(b)[‰]	R^2	σ_a [‰/°C]	σ_b [‰]	SEE [‰]
GRAZ	30	0.32	-12.1	0.14	0.15	1.5	0.70
VIENNA	30	0.74	-17.5	0.34	0.20	2.0	0.77
PATSCHERKOFEL	30	0.67	-13.5	0.36	0.17	0.13	0.69
LÄNGENFELD	27	0.90	-16.9	0.25	0.31	1.8	0.85
SCHARNITZ	25	0.19	-13.2	0.01	0.34	2.2	0.93
KUFSTEIN	30	0.37	-13.8	0.11	0.20	1.6	0.78
SALZBURG	30	0.19	-11.9	0.05	0.16	1.5	0.66
BREGENZ	30	0.17	-12.0	0.04	0.18	1.6	0.77
FEUERKOGEL	30	0.36	-13.2	0.18	0.15	0.53	0.53
LAHN	28	0.51	-14.6	0.35	0.14	0.96	0.79
KLAGENFURT	30	0.43	-13.3	0.18	0.18	1.4	0.76

Table 5: Temporal $\delta^{18}O_w$ - temperature relationship at different ANIP-stations in the period from 1973 to 2002. No temperature records are available from the stations in Böckstein, Golling and Nasswald.

differences between the temporal $\delta^{18}O$/T gradients and a strong deviation of the gradients (for most stations) to the spatial gradient. In addition, the correlation coefficients of these temporal $\delta^{18}O$/T relationships are mostly low.

If isotope records should in fact encode temperature, it must be precipitation temperature, not the average temperature (Kohn and Welker, 2005). There is a direct connection between the temperature and precipitation amount - meaning that events with higher precipitation amounts contribute more to an isotope record. If we want to interpret isotope values in terms of temperature change, the connection between mean temperature and precipitation temperature should be examined in more detail.

For Austria, the difference between the temperature during precipitation events and the average temperature values is emphasized by the example of the station in Graz.

As illustrated in table 4, the correlation between the mean monthly temperature and $\delta^{18}O$ values at the station in Graz is good. Subsequently, we investigated whether isotope values are better correlated with precipitation temperature values than with temperature means. For Graz, hourly temperature and precipitation amount values are available for the period from 1991 to 2002. We calculated the temperature during precipitation events (precipitation temperature) similarly to Kohn and Welker (2005) by using the formulas presented in chapter 3. The mean monthly precipitation temperatures are significantly lower than the mean monthly surface temperatures in summer and slightly higher in winter (Fig. 5). The difference in summer results from evaporative processes and negative advective heat transport. The difference in winter (December and January) might be due to cloud cover, which reduces cooling, and due to warmer air, which holds more moisture and thus leads to higher precipitation amounts (Kohn and Welker, 2005).

The temporal $\delta^{18}O$/T gradient using monthly data is higher for the precipitation temperature (0.52 ‰/°C) than for the mean temperature (0.42 ‰/°C).

As can be seen in table 5, there is evidently a lack of significance between amount-weighted $\delta^{18}O$ values and temperature values. There are several reasons for this. Firstly, the seasonality of precipitation, with the dominant season in terms of the precipitation amount being summer, plays a role. Thus, changes in winter temperature give much less weight to the amount-weighted $\delta^{18}O$ values than changes in summer temperature. A second reason is a change in vapor source regions (e.g. Boyle, 1997). This is of particular importance when studying periods in the range of glacial/interglacial time scales,

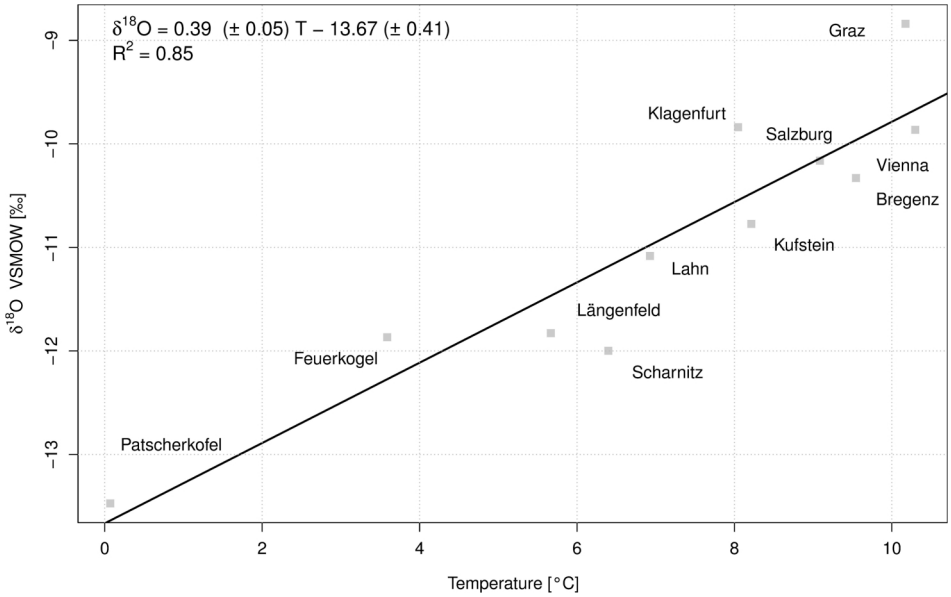

Figure 4: The spatial relationship between average weighted annual mean $\delta^{18}O$ values and the mean temperature at the site of precipitation in the period from 1973 to 2002. No temperature records were available for the stations in Böckstein, Golling, Nasswald and Achenkirch.

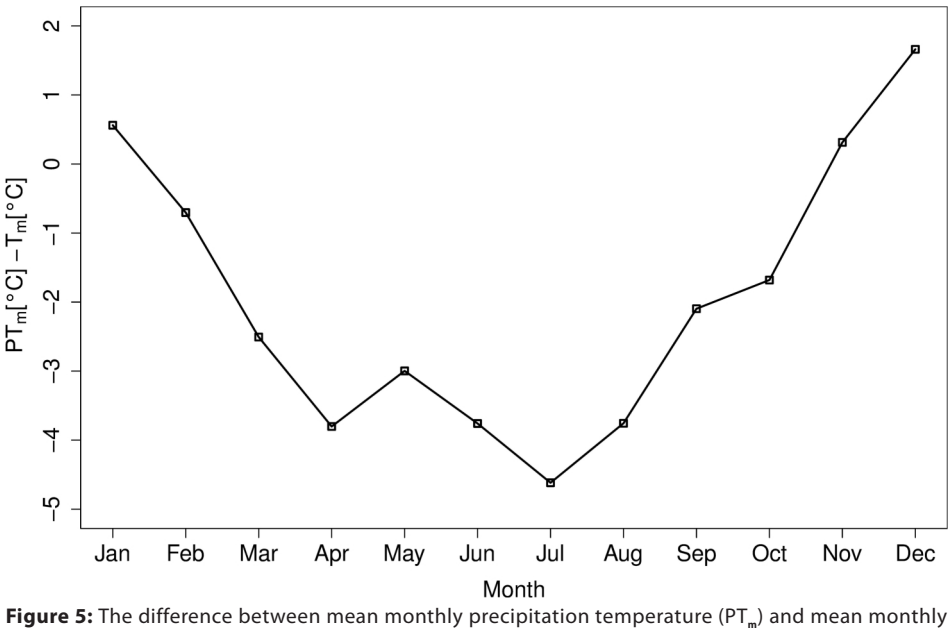

Figure 5: The difference between mean monthly precipitation temperature (PT_m) and mean monthly temperature (T_m) at the station in Graz in the period from 1991 to 2002.

but also relevant in modern times, especially due to the global climate change of the last decades. Thirdly, if isotope records actually encode temperature, it must be the precipitation temperature (i.e. temperature during precipitation events) rather than mean temperature (Kohn and Welker, 2005).

7. Seasonal isotopic variability

The seasonal variation of $\delta^{18}O$ values in precipitation from selected ANIP stations is presented in Figure 6.

The mean monthly $\delta^{18}O$ concentrations of ANIP stations indicate an almost parallel evolution with annual temperature cycles (Fig. 1).

For instance, stations such as those in Graz and Vienna are among the stations with the highest temperatures all year round and their $\delta^{18}O$ values are high in comparison to other $\delta^{18}O$ records. In contrast, the station in Patscherkofel features the lowest mean monthly temperature as well as $\delta^{18}O$ values all year round.

Seasonal variation is quite homogeneous at these stations. The seasonal range from the maximum to minimum level is around 5 – 8 ‰ in each case.

Figure 7 illustrates the seasonal variation of deuterium excess values of selected ANIP stations. The strong differences in deuterium excess values in Austria (meaning higher values at mountain stations and lower values at valley and foreland stations) cannot be attributed to different vapor source regions. Therefore, tracing the origin of the air masses by using deuterium excess values is not a reliable method for this region (Rank and Papesch, 2005). Higher deuterium excess values at mountain stations are also documented in other studies (e.g. Aouad Rizk et al., 2005; Argiriou and Lykoutis, 2005).

A possible explanation for these high deuterium excess values in precipitation at mountain stations is given by Clark and Fritz (1997) in general, and for Austria by Fröhlich et al. (2008) in particular. The issue can be summarized as follows:

Secondary evaporation and moisture recycling processes are controlled by regional conditions. Whereas secondary evaporation decreases deuterium excess values of precipitation (and on the other hand increases deuterium excess of the ambient vapor), moisture recycling increases deuterium excess of precipitation. Secondary evaporation is controlled by saturation deficit and by the distance from the cloud base to the ground. Thus, the effect on the deuterium excess value is higher at valley and lowland stations than at mountain stations. Moreover, the cloud base height is higher during summer and autumn, which means that the secondary evaporation effect is higher during these seasons.

In addition, Figure 7 indicates

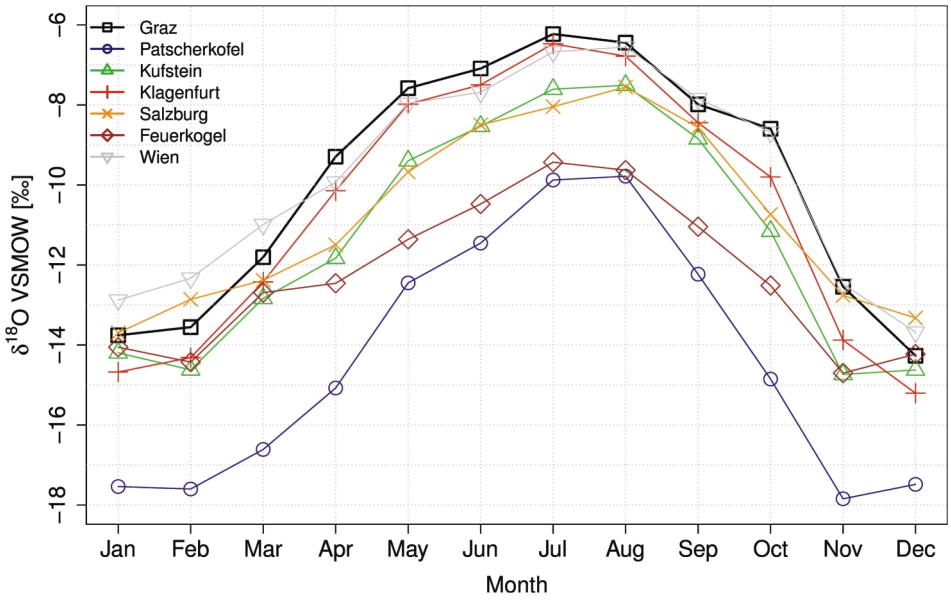

Figure 6: The seasonal variation of $\delta^{18}O$ content in precipitation recorded at selected stations of the ANIP in the period from 1973 to 2002.

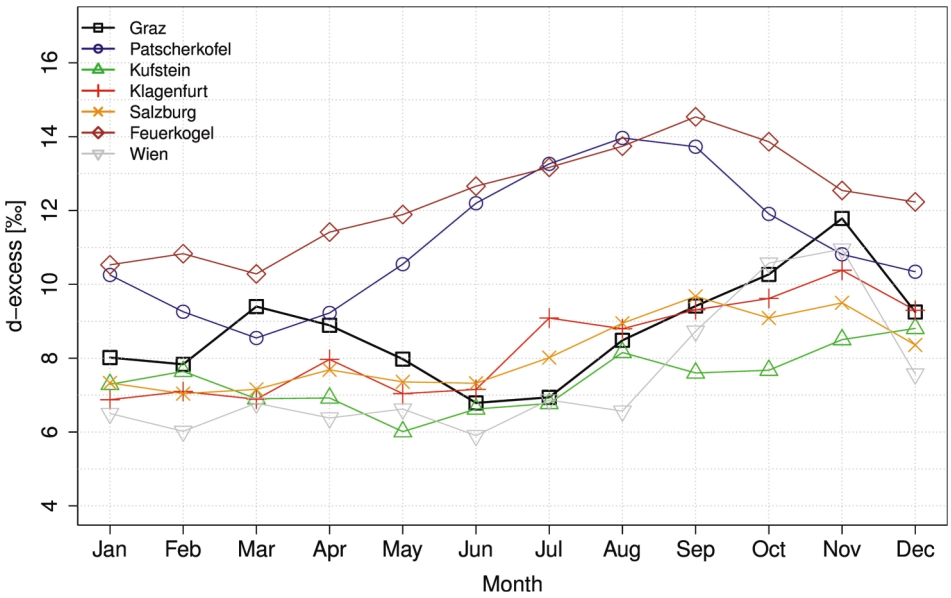

Figure 7: Mean monthly deuterium excess values of selected stations in Austria in the period from 1973 to 2002.

that the difference between mountain stations (e.g. Patscherkofel) and lowland stations (e.g. Graz) is less pronounced in winter, which can be explained by the dominant form of precipitation during that season, snow, which mainly stays unchanged during its fall to the ground (Clark and Fritz, 1997).

8. Conclusion

In this study, the isotope records of ANIP stations were analyzed and evaluated. The observational period was from 1973 to 2002. This study provides baseline data which can be used for future palaeoclimate, hydrological and hydrogeological studies in Austria.

There is a good correlation ($R^2 = 0.85$) between average annual temperatures and the average of weighted annual mean $\delta^{18}O$ values obtained at ANIP stations. The corresponding equation is $\delta^{18}O = 0.39\ T - 13.7$ ‰. Regression analyses emphasize that the temporal isotope variability is controlled by both temperature and precipitation amounts at the stations in Graz, Vienna, Längenfeld, Bregenz, and Feuerkogel. At the stations in Patscherkofel, Scharnitz, Kufstein, Salzburg and Lahn the dependence on the precipitation amount is statistically not significant.

On a spatial basis, altitude is the predominant factor, whereas the influence of latitude and longitude is statistically not significant. This is most likely due to the influence of different climates in Austria, which average out the global circulation patterns.

The seasonal $\delta^{18}O$ variability is in accordance with the seasonal temperature variability of each study site. Highest values are found at the stations in Graz and Vienna, the lowest values are observed at mountain stations in Patscherkofel and Feuerkogel.

An Austrian Meteoric Water Line can be determined using the averages of weighted annual mean values of different ANIP stations. The equation is $\delta^{18}O = 7.5\ \delta D - 3.2$. Both, slope and intercept are lower than corresponding values of the Global Meteoric Water Line, which is probably the result of sub-cloud evaporation during precipitation.

Local meteoric water lines of single stations using weighted isotope data are presented. These lines can be used as baseline data for future groundwater and surface-water investigations.

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Benedikt HAGER[1)2)*)] & Ulrich FOELSCHE[1)3)]

[1)] Institute for Geophysics, Astrophysics, and Meteorology, Institute of Physics (IGAM/IP), University of Graz, Graz A-8010, Austria;

[2)] now at: High Field MR Centre, Department of Biomedical Imaging and Image-Guided Therapy, Medical University of Vienna, Vienna A-1090, Austria;

[3)] Wegener Center for Climate and Global Change (WEGC), Graz A-8010, Austria;

[*)] Corresponding author, hager.benedikt@gmail.com

Appendix

Multiple regression model

A multiple regression model with two independent predictor variables has the following form:

$$Y=\beta_0+\beta_1X_1+\beta_2X_2+\varepsilon$$

Y is the dependent response variable ($\delta^{18}O$). The independent variables are X_1 and X_2, which in our case are temperature and precipitation amount. β_0, β_1 and β_2 are the regression coefficients and ε is the error term. The value of the dependent variable Y is a linear transformation of the predictors X_1 and X_2. Eventually, the fitted model can then be given as follows:

$$Y'=\beta'_0+\beta'_1X_1+\beta'_2X_2$$

where Y' is the fitted value and β'_0, β'_1 and β'_2 are the estimates of the regression parameters. The sum of squared residuals of the observed Y and the predicted Y' is thereby minimized.

Several conditions should apply to the data to allow the application of a linear regression.

Firstly, we tested for multicollinearity between the two predicting variables. Monthly temperature and precipitation amount values show co-linearity. The weather in Austria undergoes seasonal fluctuations, where higher temperatures are usually associated with higher precipitation amounts (i.e. summer) and, vice versa, lower temperature values with lower precipitation amounts (i.e. winter). This leads to moderate to low positive correlations between monthly temperature and monthly precipitation amounts for 11 ANIP stations. The average coefficient of determination for ANIP stations is $R^2 = 0.21$.The strongest correlation is found at the station in Graz ($R^2 = 0.38$) and the lowest at the station in Vienna ($R^2 = 0.06$). The average tolerance (tolerance = 1- R^2) is 0.79. Multicollinearity is indicated if the tolerance level is in the range of 0.1 or lower (Norman and Streiner, 2008), which means that in our case no multicollinearity problem is detectable.

Secondly, we tested for homoscedasticity using the Breusch-Pagan test (Breusch and Pagan, 1979). The test uses the framework of the Lagrangian multiplier test and it evaluates whether the error variances are a function of the predictor variables.

The p values are below 0.05 and therefore the null hypotheses of homoscedasticity are rejected. The heteroscedasticity partially weakens our regression models. However, we can still assume sufficient validity.