Processes affecting isotopes in precipitation of an arid region

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ABSTRACT

The isotopic composition of precipitation has been measured in samples simultaneously collected during individual precipitation events at two neighbouring high-altitude stations (Houxia at 2100 m a.s.l. and Gaoshan at 3545 m a.s.l.) in the Tianshan Mts., northwest China. The observed changes of $\delta^{18}O$ (δ^2H) and deuterium excess with surface air temperature, altitude and season have been evaluated to derive information on the effects of subcloud evaporation and moisture recycling on the formation of precipitation and its isotopic composition under arid climatic conditions. Consulting the long-term monthly averages of 'd' excess and temperature of the nearest GNIP station Wulumuqi, a striking similarity was found with the results of the two high-altitude stations concerning the relation between 'd' excess and temperature. The 'd' excess–temperature plot of the Wulumuqi data shows an hysteresis effect which appears to signify seasonal changes in the interplay between subcloud evaporation and moisture recycling. Finally, for the first time a negative altitude gradient of the d excess has been found for all stations including two more GNIP stations in northwest China but far away from the study area. This 'inverse altitude effect' may manifest a decrease of the recycled fraction in air moisture with altitude.

1. Introduction

The isotopic ratios of the chemical elements oxygen and hydrogen of the water molecule ($^{18}O/^{16}O$ and $^2H/^1H$, respectively) are powerful tools in studying hydrological and climatic processes. Such studies require a good understanding of the isotopic fractionation in processes controlling the isotopic composition of precipitation, the primary input to hydrological systems like surface water bodies, groundwater and glacier ice in polar and high mountain regions. These processes include condensation of atmospheric vapour, evaporation of water, sublimation of ice and recycling of atmospheric moisture. Recent studies have shown that there is still scope for improving the understanding of isotopic processes notably of those leading to observed variation of the deuterium excess [d excess = $\delta^2H - 8\delta^{18}O$ (Dansgaard, 1964)] in precipitation of polar and high mountain regions (e.g. Kreutz et al., 2003; Masson-Delmotte et al., 2008).

Evaluating measurements of the isotopic composition of ice core samples taken from a high-altitude glacier in the Tianshan Mountains, Kreutz et al. (2003) concluded that regional scale hydrological conditions, seasonal changes in the moisture source and recycling in the Caspian/Aral Sea region are responsible for the observed spatial and temporal variability of the d excess. As local processes of precipitation including moisture recycling and subcloud evaporation have notable effects on stable isotopes and d excess, explanations only with advected moisture can not provide a full picture of the observed isotopic variability. Furthermore, the effect of continental evaporation on local precipitation is still not clear in the vast arid regions.

To provide further evidence on the isotopic features of precipitation in northwest China, we have analysed samples taken from individual precipitation events at two neighbouring high-altitude stations in the Tianshan Mountains (Houxia, 2100 m a.s.l. and Gaoshan, 3545 m a.s.l.) in northwest China. Measuring the surface air temperature relative humidity and amount of precipitation during the precipitation events we were able to examine the relationship between these meteorological parameters and the isotopic composition of precipitation represented by the $\delta^{18}O$ and d excess values. A correlation with temperature has

been found and interpreted in terms of the interplay between sub-cloud evaporation and moisture recycling in forming the isotopic composition of precipitation in the study area. Furthermore, we have taken into account relevant data available for stations in northwest China through the IAEA-WMO Global Network for Isotopes in Precipitation (GNIP) (IAEA, 2006). Comparing the change of the d excess with temperature for all these stations new evidence could be found for the interplay between sub-cloud evaporation and moisture recycling in the formation of the isotopic composition of precipitation. Finally, a negative altitude gradient of the d excess ('inverse altitude effect') has been found which is suggested to be an indication of the contribution of moisture recycling to the formation of precipitation in this extremely arid region. The following summarizes the results of this study.

2. Study area

Individual precipitation events have been sampled at two selected meteorological stations located within the Wulumuqi River catchments in Eastern Tianshan, Xinjiang Uygur Autonomous Region of China (Fig. 1). Xinjiang region represents one sixth of China's land area. There are three major mountain chains that border the region, which are Altai Mts. in the north, Tianshan Mts. in the middle and Kunlun Mts. in the south (Fig. 1). In between these mountains, there are two large basins, namely Zhungeer Basin and Talimu (Tarim) Basin. Vast deserts exist in these two basins, for example, the area of Gurbantunggut

Desert accounts for 16.3% of the total area of Zhungerer Basin, and the area of Taklamakan Desert reaches to 63.7% of the total area of Tarim Basin.

There are five major air masses that influence the meteorological and pluviometric regime of Southeast Asia (Ren, 1985; Bryson, 1986; Winkler and Wang, 1993; Araguas-Araguas et al., 1998). For the Xinjiang area, the central Asia westerlies is dominant in all seasons (Araguas-Araguas et al., 1998; Tian et al., 2007), though in July, the polar air mass originated from the Arctic might reach northern Xinjiang (Dai et al., 2006), while the southwest monsoon is blocked by Tibetan Plateau (Tian et al., 2007).

Xinjiang belongs to typical continental arid climate, where the annual average ambient temperature ranges from about 7 to 10 °C. There is sporadic precipitation and most of it occurs in the mountainous areas. In Tianshan Mountains, evergreen vegetation grows between 1600 and 3400 m a.s.l. The mean annual temperature from 1959 to 2000 in the high mountain area (3693 m a.s.l.) is −5.2 °C, and the temperature is below 0 °C during 7–8 months. The average annual precipitation is around 450 mm. Precipitation is higher in summer than in winter. Snowfall accounts for about 30% of the total precipitation, which lasts from the end of November to next March, even to April sometimes. Evaporation in Xinjiang includes surface water evaporation and land surface evaporation. Surface water evaporation in the mountain is 800–1200 mm, and 1600–2200 mm in the basins; while the land surface evaporation is much less than it, with a range in the mountains is 100–300 mm, and in the basins is 10–100 mm,
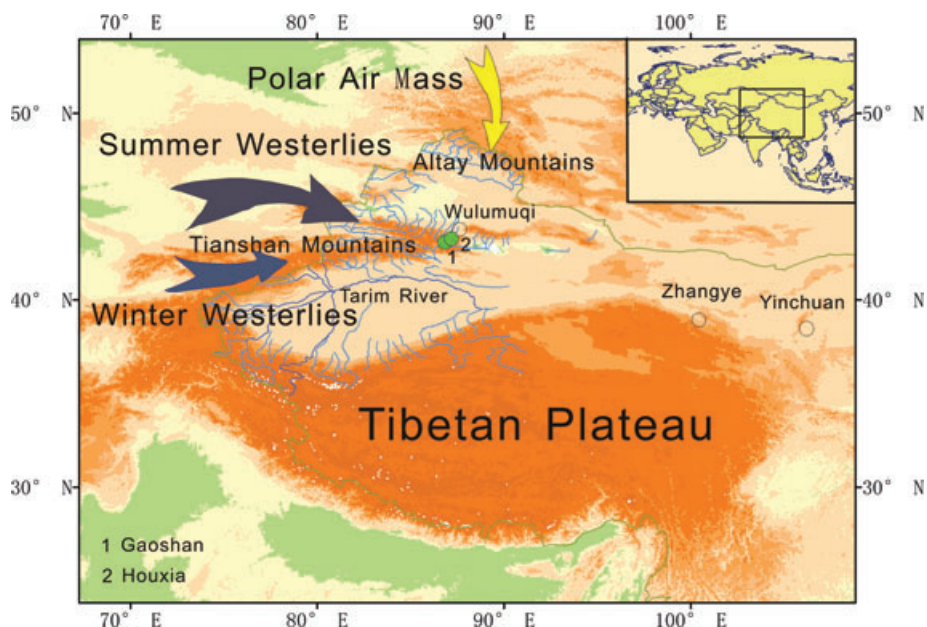

Fig. 1. Geographical distribution of mountains, deserts and endorheic basins in Xinjiang. Solid circles are our sampling sites, and open circles are selected GNIP stations. The inset illustrates the geographical location of the study area in the Euro–Asian continent. Sketch map showing the major air masses controlling precipitation patterns in Xinjiang. The elevation of Gaoshan and Houxia stations are 3545 and 2100 m a.s.l., respectively.

though in a few oasis cultivation zones it can reach 250–400 mm. The evaporated moisture experiences adiabatic cooling, mixing with westerlies and ultimately leads to precipitation.

There are plenty of glaciers in Xinjiang, which is one of the major recharging sources of rivers, accounting for 30.6%. Most rivers in Xinjiang are endorheic rivers that originate from the mountains and end in the terminal lakes. Significant seasonal variations result in the asymmetric distribution of intraannual discharge: discharge in summer accounts for more than 50% of the total volume; while discharge in winter only accounts for less than 10%. The discharge at the mountain-pass roughly represents the gross water resources in the basin. In the last decades, mountain-front discharge has increased by about 10% (Shi and Zhang, 1995; Chen et al., 2008). In order to predict future changes in water resources, it is necessary to gain a good understanding of the source of moisture and the relationship between discharge and air temperature.

The two sampling sites are Houxia meteorological station (87°11′E, 43°17′ N, 2100 m a.s.l.) and Gaoshan meteorological station (86°50′E, 43°06′N, 3545 m a.s.l.) near Glacier No. 1. Due to differences in elevation, the mean annual ambient temperature at Houxia station is higher than at Gaoshan station, 1.5 °C and –4.3 °C, respectively, and the annual precipitation, measured during the observation period 2003–2004 is 424 mm and 390 mm, respectively (Table 2).

3. Precipitation sampling and data collection

A total of 147 precipitation samples were collected at Houxia and Gaoshan stations (Fig. 1). All precipitation samples were event-based. At Houxia station, from May 2003 to July 2004, 58 precipitation samples were collected while at Gaoshan station, from April 2003 to July 2004, 89 precipitation samples were collected. All samples were immediately sealed in plastic bags

after collection and stored in the cold laboratory under –18 °C. When the samples are analysed, they were stored at 4 °C in the refrigerator to melt gradually to avoid evaporation. Meanwhile, the corresponding parameters, that is, amount of the precipitation, air temperature and humidity were also measured at the meteorological stations during sample collection.

All the precipitation samples were analysed in 2007 for $\delta^{18}O$ and δ^2H by MAT-253 using CO_2 equilibrium and chrome reduction methods, respectively, in the Stable Isotope Laboratory, Institute of Geology and Geophysics, Chinese Academy of Sciences. The precision was 0.02‰ and 0.2‰, for $\delta^{18}O$ and δ^2H, respectively. Results are reported as relative to the standard V-SMOW (Vienna Standard Mean Ocean Water).

4. Results and discussion

4.1. Local meteoric water line (LMWL)

A significant linear correlation ($R^2 = 0.98$) exists between the two parameters $\delta^{18}O$ and δ^2H (Fig. 2). Both slope (7.05) and intercept (0.6‰) of the linear regression line show the isotopic characteristics of precipitation in an arid region, which are smaller than both of the Global Meteoric Water Line (Craig, 1961; Rozanski et al., 1993) and the regional Meteoric Water Line for Southeast Asia (Araguas-Araguas et al., 1998). With reference to the GMWL, three groups of isotopic data can be distinguished: the first group comprises data points with low $\delta^{18}O$ values and plots above the GMWL, the second group with medium $\delta^{18}O$ values fits the GMWL and the third group with high $\delta^{18}O$ values are below the GMWL. Data points above the GMWL (deuterium excess above 10‰) represent mainly winter precipitation at low temperature and low absolute moisture content of the air. The data fitting the GMWL are located between the first and third group. The last group below the GMWL
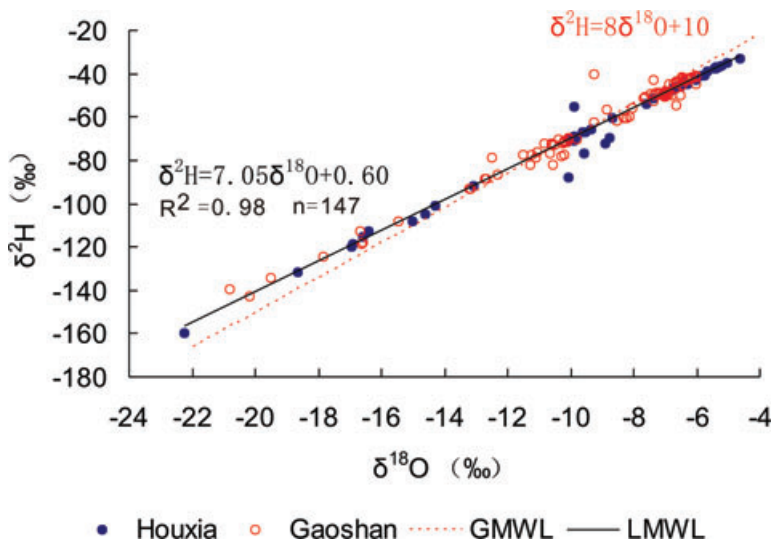

Fig. 2. Local meteoric water line for Eastern Tianshan, based on the data of individual sampling from May, 2003 to July, 2004 (LMWL). The isotopic data can be divided into three groups: above GMWL, on GMWL and below GMWL.
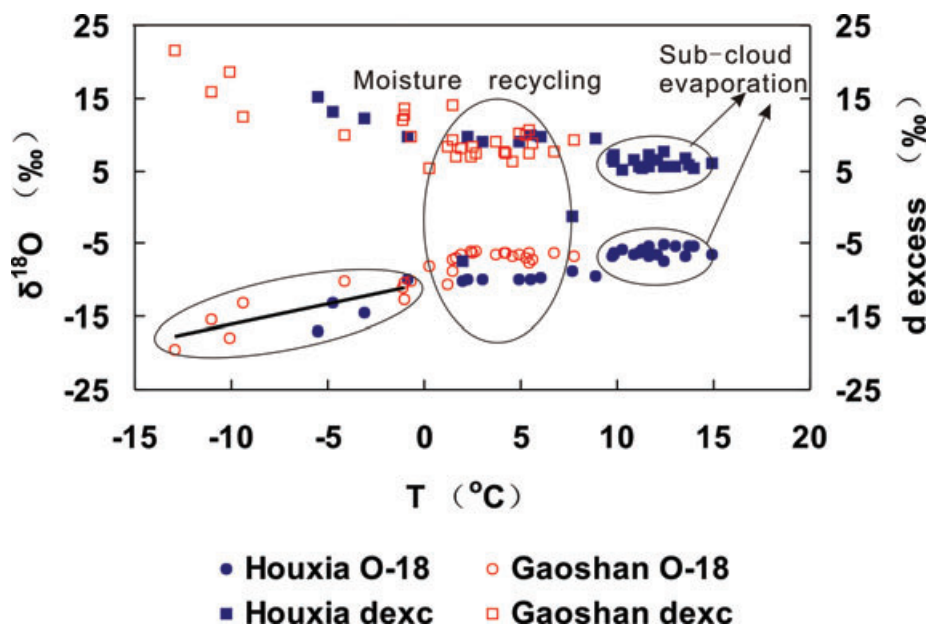
Fig. 3. Plot of temperature versus δ^{18}O and d excess for samples collected simultaneously at the two stations Houxia and Gaoshan. Three groups of isotopic data are distinguished representing three different processes during precipitation: adiabatic cooling, moisture recycling and subcloud evaporation.

signifies the effect of subcloud evaporation during the summer season (see below).

4.2. Oxygen-18 and deuterium temperature effect

Figure 3 contains data of those events for which simultaneous samples have been collected at both stations Houxia and Gaoshan; that is, these data represent air masses that crossed both stations.

Also this diagram allows distinguishing three groups of data: the first group is related to low temperatures, below 0 °C (snow), the second group to temperatures between 0 and 8 °C, the third group to higher temperatures between 8 and 15 °C. The first group shows a clear temperature effect. The linear relation between δ^{18}O and temperature points to adiabatic cooling of rising air masses in mountain terrains (Clark and Fritz, 1997; Gat et al., 2001). The nearly constant δ^{18}O values of the second group suggest that the enrichment of δ^{18}O caused by the temperature effect is compensated by recycling of evaporated moisture with accordingly lower values of δ^{18}O (e.g. Froehlich et al., 2008). The third group with generally higher δ^{18}O and lower d excess values at station Houxia appears to indicate that the isotopic enrichment due to subcloud evaporation over-compensates the isotopic depletion by moisture recycling.

The δ^{18}O–temperature coefficients for the temperature range below 0 °C (Type I, Table 1) are 0.66‰ °C^{-1} at Gaoshan station and 0.64‰ °C^{-1} at Houxia station. (The corresponding values for deuterium are also given in Table 2.) These values are between the values 0.45‰ °C^{-1} and 0.87‰ °C^{-1} that

Table 1. Isotopic temperature effect at the stations Houxia and Gaoshan. (Type I: samples with temperature below 0 °C; Type II: all the precipitation samples)

Types	Sites	δ^{18}O gradient (‰ °C^{-1}) (R^2)	δ^2H gradient (‰ °C^{-1}) (R^2)	Number of events
I	Houxia	0.64 (0.58)	4.57 (0.53)	12
I	Gaoshan	0.66 (0.58)	4.38 (0.58)	39
II	Houxia	0.52 (0.85)	3.65 (0.82)	58
II	Gaoshan	0.56 (0.77)	3.97 (0.78)	89

were found by Yao et al. (1999) for the stations Wulumuqi (918 m a.s.l.) and Daxigou (4200 m a.s.l.), respectively. This δ^{18}O (δ^2H)–temperature relationship is consistent with results derived from the Rayleigh model for equilibrium isotope fractionation. If the data of the whole temperature range are correlated, the temperature coefficients are lower, as shown in Table 1 (Type II).

4.3. Altitude effect

The isotopic composition of precipitation becomes gradually depleted when clouds rain out while rising along the slope of a mountain (Gonfiantini et al., 2001). Taking into account the adiabatic cooling with increasing altitude, this altitude effect can be related to the temperature effect. Under the atmospheric conditions in the study area, the altitude effect is observed only at

Table 2. Deuterium excess and relevant meteorological data of the sampling sites Houxia and Gaoshan and selected GNIP stations

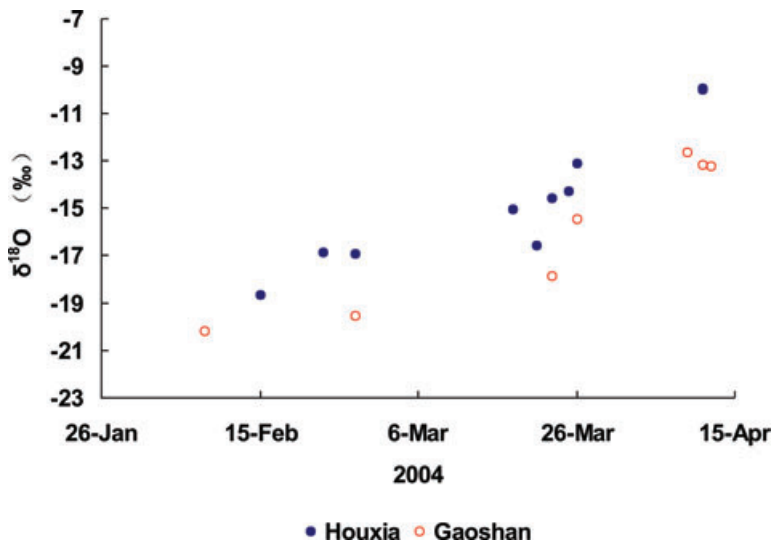| Station	Location		Altitude (m a.s.l.)	Mean annual temp. (° C)	Annual precipitation (mm)	Avg. d excess below 0°C (‰)	d excess temp coeff. (‰ K^{-1}) (R^2)
	Latitude	Longitude					
Gaoshan	43° 06′	86° 50′	3545	−4.3	390	12 ± 5	−0.47 (0.3)
Houxia	43° 17′	87° 11′	2100	1.5	424	14 ± 3	−0.49 (0.4)
Wulumuqi	43° 47′	87° 37′	918	7.5	306	19 ± 1	−0.43 (0.8)
Zhangye	38° 56′	100° 26′	1483	8.0	145	15 ± 5	−0.53 (0.8)
Yinchuan	38° 29′	106° 13′	1112	9.2	239	14 ± 2	−0.17 (0.3)

Fig. 4. Isotopic composition of precipitation samples collected simultaneously at stations Houxia (2100 m a.s.l.) and Gaoshan (3545 m a.s.l.) at surface temperatures below 0 °C. The altitude effect is observed only at temperatures below 0 °C.

temperatures below 0 °C (Figs 3 and 4). During the observation period, there were only 4 days at which precipitation occurred simultaneously at both stations with temperatures below 0 °C. For these events the measured difference in the isotopic composition between the two stations with different altitude (altitude effect) ranged from –0.16 ∼ –0.23‰/100 m for ^{18}O and –1.0 ∼ –1.6‰/100 m for ^{2}H. However, if also those data corresponding surface temperatures above 0 °C are taken into account, the altitude effect becomes lower, ranging from –0.10 to –0.18‰/100 m for δ^{18}O and –0.7 to –1.3‰/100 m for δ^2H, respectively. In any case, the values found in this study for the altitude effect are at the lower end of the range known from other investigations: –0.15‰/100 m to –0.5‰/100 m for δ^{18}O, and from about –1.0‰/100 m to –4.0‰/100 m for δ^2H (Clark and Fritz, 1997).

4.4. *Seasonal variation of $\delta^{18}O$ and deuterium excess*

The isotopic composition of the precipitation at the stations Houxia and Gaoshan is characterized by a pronounced seasonal variation with maximum values in summer of about –5‰ and –30‰ for δ^{18}O and δ^2H, respectively, and minimum values in winter of about –22‰ and –160‰, respectively. The d excess

changes in an opposite way, high values in winter and early spring (about 20‰) and low values in summer (about 5‰, some values below zero; Fig. 5). A similar seasonal variation of the d excess has been found in precipitation at Avalanche station (1775 m) in Western Tianshan and in a shallow ice core from the Tianshan Mountains of Kyrgyzstan, drilled at an altitude of 5100 m. Regional scale hydrological conditions, including seasonal changes in moisture source, transport and recycling in the Caspian/Aral Sea region, have been suggested to be responsible for the observed spatial and temporal variability and high values of the d excess (Aizen et al., 1996; Kreutz et al., 2003; Tian et al., 2007).

4.5. *Change of the deuterium excess with temperature*

In addition to the seasonal change of the d excess on which the paper by Tian et al. (2007) has been focused, we were able to examine the d excess–temperature correlation which sheds new light on the explanation of the seasonal variation of the d excess in the studied region.

Figure 6 shows the data for the individual precipitation events at Houxia and Gaoshan during 2003–2004 in comparison with the long-term monthly averages at the GNIP station
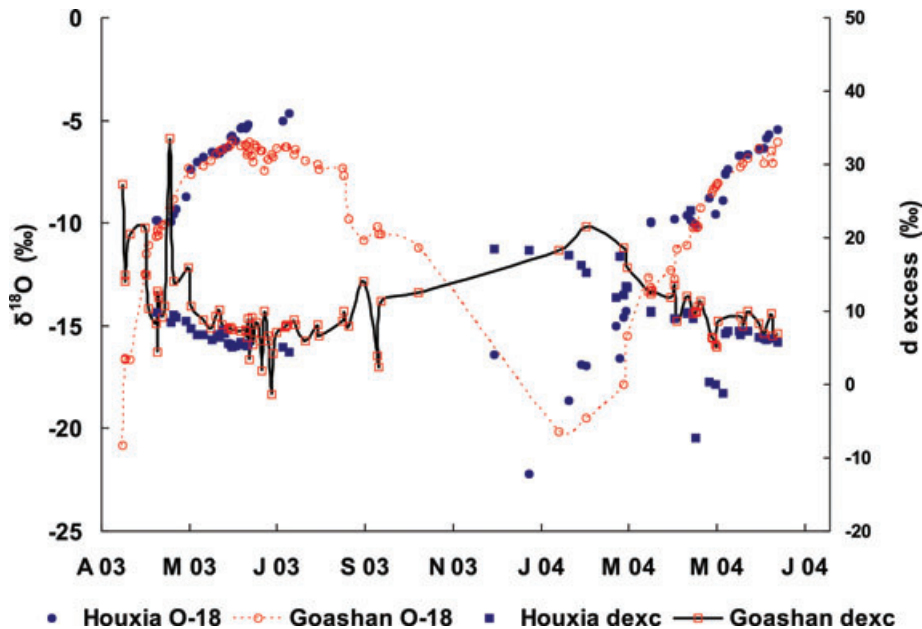
Fig. 5. Seasonal variation in δ^{18}O and d excess at Houxia and Gaoshan stations. Dashed and solid curves represent the variation of δ^{18}O and d excess, respectively.
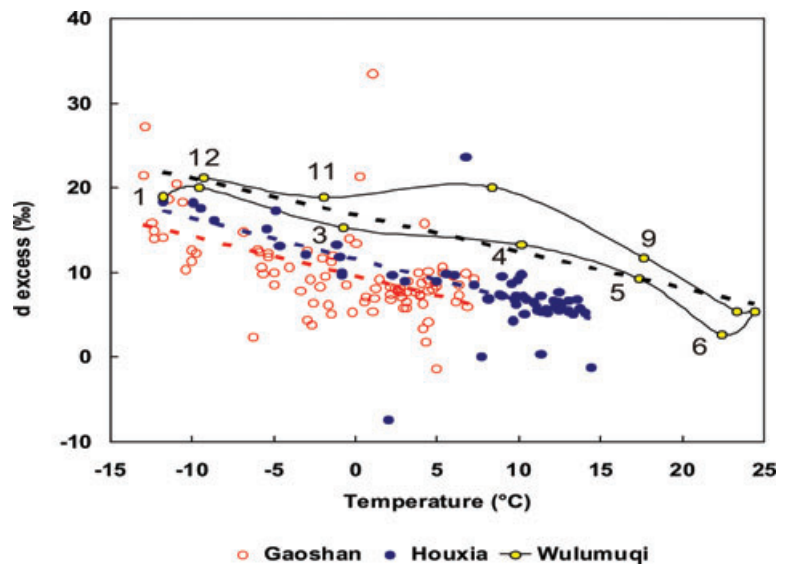

Fig. 6. Plot of all deuterium excess versus surface air temperature. The values of Houxia and Gaoshan represent single precipitation events while the values of the GNIP station Wulumuqi are long-term monthly averages. The numbers at the Wulumuqi points represent the month (1 January . . .12 December) of the corresponding long-term monthly averages.

Wulumuqi (Urumqi), which is next to the study area. Concerning the Houxia and Gaoshan data, there are a number of extreme deviations from the average behaviour indicating the high variability of the isotopic composition between individual precipitation events. The Wulumuqi monthly averages of d excess are generally above the values at the two high-mountain stations, exhibiting a hysteresis effect. A salient feature of Fig. 6 is the striking similarity in the change of the d excess with temperature and a general trend of the d excess with the elevation of the various stations. These findings can be interpreted as follows.

(1) A linear regression of the d excess versus temperature yields nearly the same slope for all three stations (Fig. 6, Table 2). This suggests that the decrease of the d excess with surface temperature is mainly controlled by subcloud evaporation. Kinetic isotopic fractionation during snow formation could in principle be considered for the temperature range below 0 °C, but measured data and model simulations (Jouzel and Merlivat, 1984; Ciais and Jouzel, 1994; Masson-Delmotte et al., 2008) suggest that the d excess is only affected by such kinetic fractionation at temperatures far below the minimum winter values reached at these three stations.
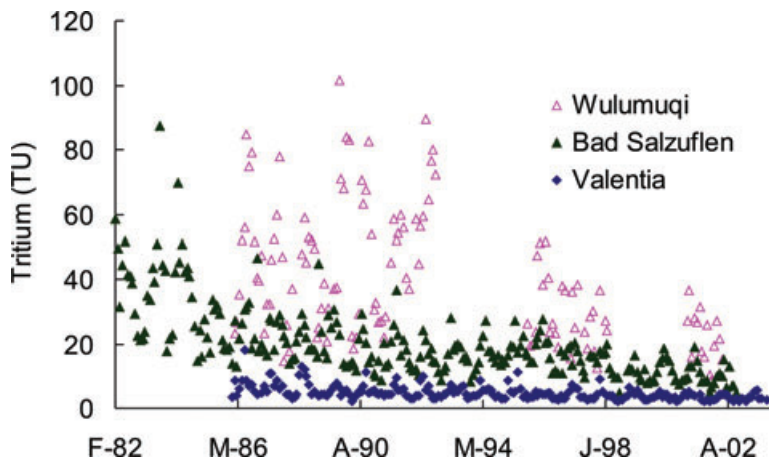
(2) The d excess appears to be nearly constant in the temperature range from about 0 and 8 °C, if the 'outliers' for Houxia and Gaoshan are not included. In this temperature range $\delta^{18}O$ has also been found to be nearly constant (Fig. 3), what is supposed to be an indication of moisture recycling. Obviously, in this temperature range the decrease of the d excess with increasing temperature due to subcloud evaporation is compensated by an increase due to recycling of evaporated moisture. It is known that recycling of moisture evaporated from soil surfaces causes the d excess to rise while the $\delta^{18}O$ and $\delta^{2}H$ values decrease (e.g. Froehlich et al., 2008). This recycling effect is clearly demonstrated by the hysteresis of the long-term monthly averages at Wulumuqi station. Although the temperature in October, for example, is about the same as in April, the d excess differs remarkably. Thus, this hysteresis effect suggests that from March to June recycling is lower than in the following period August–November. This explanation is supported by the observation that evaporation in summer (June–August) reaches the maximum through the year, accounting for about 40–52% of the annual evaporation (Li et al., 2006). Consequently, d excess increases gradually, and reaches the maximum in October (Fig. 6).

Further evidence for recycling of moisture evaporated from the ground over the region in northwest China has been given by the comparatively high tritium concentration of precipitation at the GNIP station Wulumuqi. Figure 7 shows that the tritium values in precipitation of Wulumuqi are distinctly higher than at two selected reference stations of the northern hemisphere, which are represented by the GNIP stations. Valentia (10°15′W, 51°56′N, 9 m a.s.l.) in Ireland and Bad Salzuflen (8°44′E, 52°6′N, 100 m a.s.l.) in Germany are selected to represent the tritium in the air mass of North Atlantic due to their locations. Apparently, the higher tritium values at Wulumuqi are caused by recycling of moisture evaporated from the ground of regions that still contains considerable amount of tritium deposited during past thermonuclear tests in the region.

(3) Finally, Fig. 6 clearly shows that the d excess at Wulumuqi is higher than at Houxia and Gaoshan stations. Although rather far from the study area, the values of the two additional GNIP stations located in the arid region of northwest China seem to fit into this peculiar relationship between the d excess and altitude (Table 2) characterized by a decrease of the d excess with altitude. This altitude effect of the d excess is just opposite to the one observed under more humid conditions where an increase of the d excess with the elevation of the station was found (Cruz-Sanjulian et al., 1992; Holko, 1994; Froehlich et al., 2008). This 'inverse altitude effect' suggests that in the vast arid area of northwest China moisture recycling is an important component of precipitation and that the recycled fraction in the air moisture decreases with altitude.

5. Conclusions

Processes underlying the isotopic temperature, altitude and seasonal effects in the vast desert region of northwest China have been addressed by isotopic analyses of samples simultaneously taken from individual precipitation events at two neighbouring high-mountain stations in the Tianshan Mts. These processes include equilibrium isotope fractionation during adiabatic rise of clouds during winter in a mountainous terrain, subcloud evaporation and recycling of moisture from the ground (soil and surface water). It was demonstrated that the d excess is a strong tool to unravel the interplay between subcloud evaporation and moisture recycling and to determine the relative contribution of these processes to the formation of precipitation under arid climatic conditions. The 'inverse altitude effect' of the d excess has been identified for the first time and discussed in terms of recycling of moisture formed by inland evaporation. An extension of such isotopic studies over a longer period and inclusion of some more stations may allow more quantitative determination of the various effects on the formation of precipitation in the arid region of northwest China.

6. Acknowledgments

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