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A 10-yr record of stable isotope ratios of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada

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ABSTRACT

Short-term (0.5–3 d) precipitation samples were collected from January 1992 to December 2001 in Calgary, Alberta, Canada, and the stable isotope ratios of hydrogen ($^2H/^1H$) and oxygen ($^{18}O/^{16}O$) for these samples were determined. The 10-yr amount-weighted average δ^2H and $\delta^{18}O$ values of precipitation were $-136.1‰$ and $-17.9‰$, respectively. Consistent with International Atomic Energy Agency (IAEA) established practice, the following local meteoric water line (LMWL) for Calgary was derived using amount-weighted monthly average δ^2H and $\delta^{18}O$ values: $\delta^2H = 7.68\ \delta^{18}O - 0.21$ ($r^2 = 0.96$, $n = 104$). The correlation equation between δ^2H and $\delta^{18}O$ values from individual samples was found to be $\delta^2H = 7.10\ \delta^{18}O - 13.64$ ($r^2 = 0.95$, $n = 839$), which is different from the LMWL, exhibiting lower slope and intercept values. A comparison of δ^2H and $\delta^{18}O$ correlation equations with temperature during precipitation events showed a trend of decreasing slopes and intercepts with increasing temperature. Our data suggest that this is caused by incorporation of moisture derived from evaporation from water bodies and soils along the storm paths and by secondary evaporation between the cloud base and the ground during precipitation events. These processes compromise the usefulness of d-excess values as an indicator for the meteorological conditions in the maritime source regions. The $\delta^{18}O$ temperature dependence at Calgary was found to be $\sim 0.44‰\ ^\circ C^{-1}$. The study shows that short-term sampling of individual precipitation events yields valuable information, which is not obtainable by the widely used monthly collection programs.

1. Introduction

Spatial and temporal variations of stable isotope ratios of hydrogen ($^2H/^1H$) and oxygen ($^{18}O/^{16}O$) in atmospheric vapor and precipitation are caused by equilibrium and kinetic isotopic fractionation mechanisms associated with condensation and evaporation processes during global water vapor circulation. Over the last five decades, isotopic investigations have contributed significantly to our understanding of atmospheric circulation patterns (Epstein and Mayeda, 1953; Gedzelman and Lawrence, 1982; Fritz et al., 1987; Jouzel et al., 1991; Lawrence and White, 1991; Edwards et al., 1996; Hoffman et al., 2000; Birks et al., 2002). Moreover, the stable isotope composition of hydrogen and oxygen for precipitation is an important input parameter for many hydrological studies, which focus on surface water (Gonfiantini, 1985; Telmer and Veizer, 2000; Gibson and Edwards, 2002), groundwater (Gat, 1981; Yonge et al., 1989) and their interactions. Hence the compilation of long-term records of stable isotope compositions of hydrogen and oxygen in precipitation is an important pre-requisite for atmospheric and hydrological studies in any given study region.

Global patterns of stable isotope compositions of hydrogen and oxygen in precipitation have been described by Rozanski et al. (1993) based on monthly average values from 379 stations belonging to the Global Network of Isotopes in Precipitation (GNIP) maintained by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO). However, this compilation does not include a station in the southern part of Alberta, Canada. Based on the measurements conducted within the Canadian Network for Isotopes in Precipitation (CNIP; http://www.science.uwaterloo.ca/~twdedwar/cnip/cniphome.html), a marked anomaly in Alberta with significantly lower annual average δ^2H and $\delta^{18}O$ values in comparison with other regions at similar latitudes is revealed. However, the extent and nature of this anomaly is not properly documented, since both GNIP and CNIP networks maintain no precipitation stations in southern Alberta, Canada (Fig. 1).

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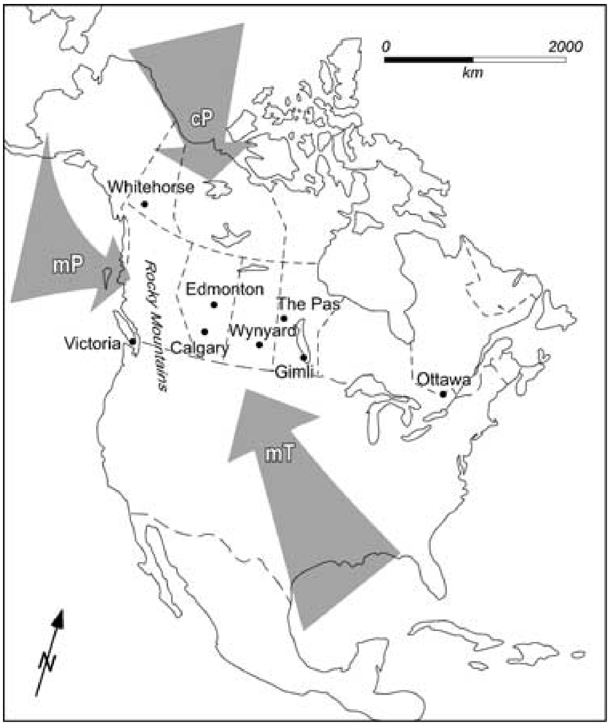

Fig 1. Map of Northern America indicating the location of Calgary in southern Alberta (Canada) and the locations of several other stations in Canada, for which stable isotope compositions of hydrogen and oxygen in precipitation have been determined within the GNIP or CNIP networks. Also shown are air masses, which influence the weather at Calgary.

It is well known that air masses tend to become progressively depleted in ^{2}H and ^{18}O during rainout of moisture on its way from the water vapor source region to a specific precipitation site. Dansgaard (1964) first proposed a series of relationships between stable isotope ratios of hydrogen and oxygen in precipitation with several parameters, such as latitude, altitude, amount of precipitation, distance from the coast (continentality) and surface air temperature. The relationships between the isotopic compositions of hydrogen and oxygen in precipitation with latitude (Lorius and Merlivat, 1977; Rozanski et al., 1982; Fisher, 1990), altitude (Taylor, 1972; Ehhalt, 1974; Rozanski and Sonntag, 1982), continentality (Salati et al., 1979; Sonntag et al., 1983; Ingraham and Taylor, 1991; Friedman et al., 1992), seasonality (Nativ and Riggio, 1990; Smith et al., 1992) and precipitation amount (Matsuo and Friedman, 1967; Yapp, 1982) have been well documented throughout the last four decades. Further investigations also showed that stable isotope ratios of hydrogen and oxygen in precipitation could be used to provide valuable information concerning sources of distinct air masses (Gedzelman and Lawrence, 1982; Lawrence et al., 1982).

Calgary (51.01°N, 114.01°W, 1049 m ASL) is located on the eastern side of the Canadian Cordillera in southern Alberta, Canada (Fig. 1). This area is characterized by a dry continental climate with long cold winters and short warm summers. In the time period between 1960 and 2000, the average annual precipitation in Calgary was approximately 400 mm and the average annual air temperature was about 1 °C. During this period, monthly average air temperatures varied between − 19.5°C and 17.7 °C in February and July, respectively (Environment Canada 1960–2001).

There are three major air masses influencing Calgary's weather (Reinelt, 1970; Raddatz, 1998; Lapp et al., 2002): (1) moist and unstable maritime air masses (mP), which originate in the Northern Pacific Ocean and reach the western coast of North America by several different trajectories, thereby dominating Calgary's weather patterns; (2) continental polar air masses (cP), originating in ice-covered regions in Northern Canada, which are responsible for the cold dry climate in Calgary's winter; (3) moist maritime tropical air masses (mT), which originate in the Gulf of Mexico and the Caribbean Sea but rarely produce rainfall over southern Alberta.

Continental cP air masses tend to dominate the relatively dry climate in the winter, whereas summer rainfall is typically caused by the invasion of maritime air masses and/or the water vapor from evapotranspiration of local origin. The Rocky Mountains located to the west of the study region (Fig. 1) cause the comparatively dry climate in Southern Alberta, since the mountains force the westerly maritime air masses to deposit most of their moisture on the western slopes of the continental divide. The air masses then descend the eastern slopes of the Rocky Mountains.

Owing to the geographic location of Calgary, stable isotope ratios of hydrogen and oxygen for atmospheric moisture in this area are subject to a marked continental effect, regardless of the respective source regions. Additionally, the isotopic composition of moisture derived from the Pacific Ocean is subject to an altitude effect resulting from the passage over the Canadian Cordillera (Yonge et al., 1989). Since atmospheric moisture at Calgary is derived from several different sources, high-frequency sampling of precipitation for isotope analysis is expected to reveal more detailed information than using monthly composite samples. Hence, we have sampled precipitation on a short-term basis since January 1992.

The objectives of this study were: (1) to establish a long-term record of stable isotope compositions of hydrogen and oxygen in precipitation at Calgary, Alberta, Canada; (2) to integrate the short-term data into monthly averages which could in turn be compared with the data in the IAEA-WMO/CNIP database; (3) to determine whether short-term records provide more insight than monthly records into the relationships of $\delta^{2}H$ and $\delta^{18}O$ values with meteorological and environmental parameters such as precipitation amount and air temperature.

2. Sample collection and methods

Since January 1992, precipitation (rain, sleet and snow) was collected at the Weather Station of the University of Calgary, Alberta, Canada (51.01°N, 114.01°W, 1049 m ASL). Collection was performed twice a day: one sample was collected from 08:00 am–15:00 pm and the second sample was collected either from 15:00 pm–08:00 am of the next day or from 15:00 pm on Friday—08:00 am on Monday of the following week. The samplers used were either an AES (former Atmospheric Environment Services, now Meteorological Service of Canada) rain gauge for rainwater or a Nipher gauge for snow to determine the amount of precipitation of each sample. Throughout the observation period from January 1992 to December 2001, 942 individual samples were collected.

δ^2H values were determined for all samples ($n = 942$). Determination of δ^2H was performed using H_2 generated by reduction of water over hot zinc metal at 490 °C in a sealed tube (Coleman et al., 1982). Isotope analysis was carried out with a dual-inlet isotope ratio mass spectrometer built with Micromass 602 components. δ^{18}O values were measured for all samples except for those collected in July and August of 1999 ($n = 919$), which were lost due to technical difficulties. Determination of δ^{18}O was performed by equilibration of CO_2 with water samples at 25 °C (Epstein and Mayeda, 1953). After isotopic equilibrium was reached, CO_2 gas was transferred into a dual-inlet isotope ratio mass spectrometer built with Micromass 903 components and the ^{18}O/^{16}O ratio was determined.

The conventional delta notation is used to express the stable isotope compositions of hydrogen and oxygen in the water samples

$$\delta[‰] = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \tag{1}$$

where R_{sample} and R_{standard} denote the ^{2}H/^{1}H or ^{18}O/^{16}O ratios in the sample and the standard material, respectively. The standard for both hydrogen and oxygen isotope measurements is V-SMOW established and distributed by the International Atomic Energy Agency (IAEA) in Vienna, Austria. Standardization of δ^2H and δ^{18}O measurements was achieved using the IAEA reference materials such as V-SMOW, GISP and SLAP for calibration, following the guideline of Coplen (1996), so that the δ^2H value of SLAP is −428‰ and its δ^{18}O value is −55.5‰. The uncertainty of δ^2H measurements was better than ±1.5‰, whereas that of δ^{18}O measurements was better than ±0.2‰.

In order to compare our isotope data obtained from short-term sampling (0.5–3 d) with monthly data from other stations belonging to the GNIP and CNIP precipitation networks, monthly and annually amount-weighted average δ^2H and δ^{18}O values were calculated from individual sample results as follows:

$$\delta^2\text{H}_{\text{monthly/annually}} = \frac{\sum P_i \delta^2\text{H}_i}{\sum P_i} \tag{2}$$

$$\delta^{18}\text{O}_{\text{monthly/annually}} = \frac{\sum P_i \delta^{18}\text{O}_i}{\sum P_i} \tag{3}$$

where P_i denotes the amount of each individual precipitation sample as measured at the Weather Station at the University of Calgary. The summations are either over all the precipitation events in one specific month or over all the precipitation events in one specific year, as in eqs. (2) and (3).

Values of average air temperature measured at ground-level during precipitation collection were calculated as follows:

$$T_{\text{average}} = \frac{\sum_{i=1}^{m} T_i}{m} \tag{4}$$

where m is the number of precipitation hours during one collection period. T_i is the average hourly air temperature measured at 1 m height above the ground in each precipitation hour and was obtained from Monthly Meteorological Summary published by Environment Canada (Environment Canada 1960–2001).

3. Results

3.1. Amount of collected precipitation

The 10-yr annual average precipitation collected in Calgary between 1992 and 2001 was 401 mm (Fig. 2a). Within the observation period, the annual precipitation was higher than the 10-yr annual average value in 1995, 1997, 1998 and 1999, whereas in the remaining years annual precipitation was below the 10-yr average value. 2001 was the driest year with 287 mm of precipitation and 1999 was the wettest year with 482 mm of precipitation.

The 10-yr monthly average precipitation amounts display a marked seasonal variation, with a strong summer maximum and a winter minimum (Figs. 2b and 2c). On average, approximately 70% of the annual precipitation occurred in the months May to August (280 mm), whereas the remaining 8 months receive only 30% of the annual precipitation (120 mm). June is the wettest month receiving an average of 94 mm precipitation, which represents 23% of the average annual rainfall, whereas December is the driest month with an average precipitation of 6.9 mm, accounting for only 1.7% of the average annual precipitation.

3.2. Individual sample δ^2H and δ^{18}O values

Individual sample δ^2H and δ^{18}O values of precipitation collected at Calgary between January 1992 and December 2001 are shown in Figs. 3a and 3b. There is a marked seasonal variation of δ^2H and δ^{18}O values with minima in the winter months and maxima in the summer months. Lowest values were typically observed in February, with δ^2H and δ^{18}O as low as −302.9‰ and −40.3‰, respectively; the highest values were typically observed in June, with δ^2H and δ^{18}O as high as −33.9‰ and −2.1‰, respectively.

3.3. Average monthly and annual δ^2H and δ^{18}O values

Monthly and annual amount-weighted average δ^2H and δ^{18}O values are summarized in Table 1 and amount-weighted monthly average values are displayed in Figs. 3c and 3d. A clear seasonality with lower δ^2H and δ^{18}O values in winter and higher values in summer is evident. The lowest amount-weighted monthly

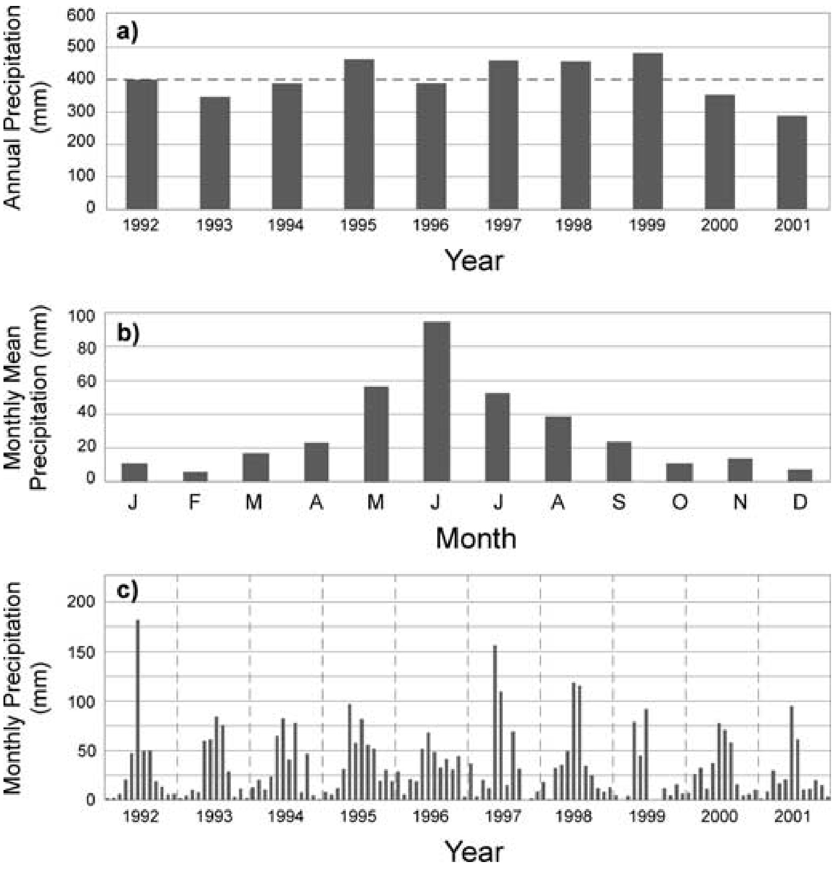

Fig 2. Distribution of precipitation amounts at Calgary (Alberta, Canada): (a) annual precipitation amounts from 1992 to 2001 with the dashed line indicating the mean precipitation amount in the 10-yr observation period (401 mm); (b) 10-yr (1992–2001) monthly average precipitation amounts; (c) monthly precipitation amounts from 1992 to 2001.

average δ^{18}O value was −31.2‰ (November 1993) and the highest monthly average δ^{18}O value was −9.7‰ (May 1998). The lowest amount-weighted monthly average δ^2H value was −260.2‰ (November 1993) and the highest one was −83.5‰ (June 1992).

Monthly amount-weighted 10-yr average δ^2H and δ^{18}O values are shown in Fig. 4. Maximum δ^2H and δ^{18}O values were observed in the months June to September with values around −125‰ and −16‰, respectively. Minimum δ^2H and δ^{18}O values were observed in January with values of −212.1‰ and −26.8‰, respectively.

The amount-weighted average annual δ^2H values varied between −149.5‰ (1996) and −112.3‰ (1992), whereas the amount-weighted average annual δ^{18}O values varied between −19.4‰ (1996) and −15.5‰ (1992). The amount-weighted 10-yr annual average δ^2H and δ^{18}O values were −136.1‰ and −17.9‰, respectively.

3.4. *Correlation between δ^2H and δ^{18}O values*

Figure 5a shows the correlation line between individual sample δ^2H and δ^{18}O values, with winter samples showing lower values at the left-hand side of the diagram and summer samples showing higher values at the right-hand side of the diagram. Figure 5b shows the correlation line between amount-weighted monthly average δ^2H and δ^{18}O values. Table 2 summarizes the regression equations for individual sample δ^2H and δ^{18}O values and amount-weighted monthly average δ^2H and δ^{18}O values for precipitation collected at Calgary. The correlation coefficients (r^2) for both equations in 1994 are lower than those obtained for the remaining years. We suspect that problems occurred during the storage of the 1994 samples and therefore have excluded the 1994 data set from further evaluations.

A significant difference between the δ^2H/δ^{18}O correlations derived from individual sample values and from monthly average values was observed (Table 2). The slopes of regression equations based on individual sample values (6.78–7.93) are generally lower than those based on monthly average values (7.13–8.52). Consequently the intercepts of regression equations based on individual sample δ^2H and δ^{18}O values, which ranged from −20.95‰ to 0.28‰, were lower than those obtained from monthly average δ^2H and δ^{18}O values, which ranged from −13.56‰ to 13.30‰.

4. Discussion

4.1. *δ^2H/δ^{18}O relationship*

Craig (1961) observed the following correlation between stable isotope ratios of hydrogen and oxygen in precipitation: δ^2H = 8

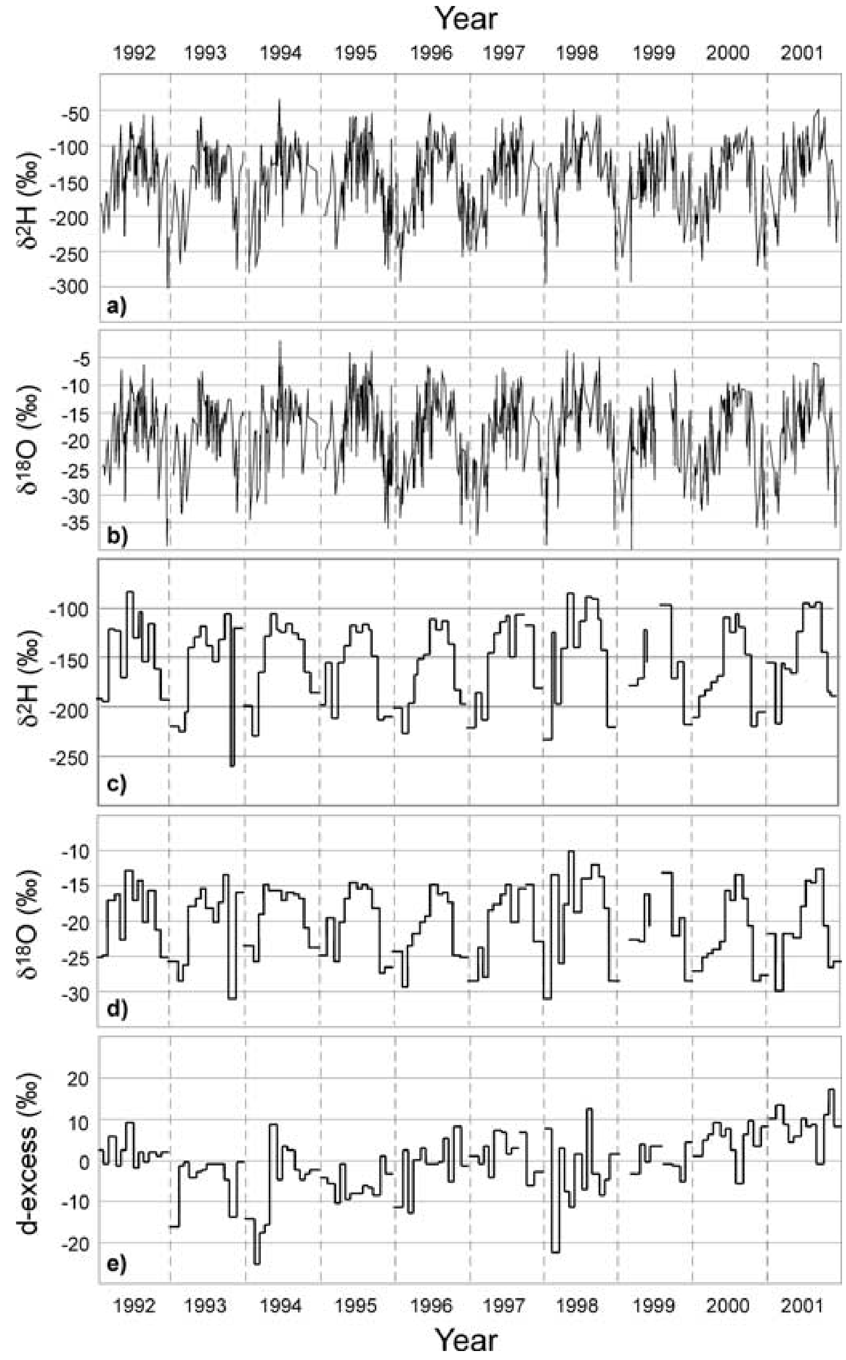

Fig 3. Time-series of δ^2H (a) and δ^{18}O values (b) for individual samples, amount-weighted monthly average δ^2H (c) and δ^{18}O values (d), and deuterium excess (e) for Calgary precipitation between January 1992 and December 2001.

δ^{18}O + 10. This global relationship, later defined as the Global Meteoric Water Line (GMWL), is reasonably well understood by introducing an "isolated air mass" model based on a Rayleigh fractionation mechanism. According to the model, the slope 8 of the GMWL is controlled by the ratio between isotope equilibrium fractionation factors of hydrogen and oxygen, while the intercept of 10 is controlled by evaporation processes in the water vapor source region (Craig, 1961). In 1993, Rozanski et al. (1993) published a refined global δ^2H/δ^{18}O correlation, using results from the IAEA/WMO GNIP database:

$$\delta^2\mathrm{H} = (8.20 \pm 0.07)\delta^{18}\mathrm{O} + (11.27 \pm 0.65)r^2 = 0.98n = 203. \tag{5}$$

Craig and Rozanski's results are essentially a global average of many local meteoric water lines (LMWL), each controlled by local geographic and meteorological factors, including water vapor sources, storm trajectories, evapotranspiration effects on local and synoptic scale, climatic conditions, precipitation

Table 1. Monthly and annual amount-weighted average δ^2H and δ^{18}O values for precipitation at Calgary, Alberta, Canada, from January 1992 to December 2001. Monthly and annual average values of air temperature at ground level and precipitation amounts are also shown.

	δ^{18}O (‰)	δ^2H (‰)	T (°C)	P (mm)
Jan-92	−25.1	−191.7	−1.0	1.5
Feb-92	−24.9	−194.2	−15.8	1.8
Mar-92	−16.7	−121.0	−1.4	5.8
Apr-92	−15.9	−123.1	1.1	20.2
May-92	−22.4	−170.4	3.6	46.5
Jun-92	−12.5	−83.5	11.3	181.5
Jul-92	−16.8	−130.4	12.1	49.2
Aug-92	−14.0	−103.9	14.4	49.4
Sep-92	−19.9	−153.9	3.9	18.4
Oct-92	−15.4	−115.2	2.3	12.8
Nov-92	−21.0	−161.0	−2.6	5.3
Dec-92	−25.1	−192.6	−13.4	5.8
Ann. ave of 1992	−15.5	−112.3	1.2	398.2
Jan-93	−25.7	−219.3	−12.0	1.3
Feb-93	−28.6	−224.7	−19.0	4.0
Mar-93	−26.3	−205.2	−6.9	9.7
Apr-93	−17.5	−139.6	3.0	7.1
May-93	−16.5	−129.2	7.8	59.1
Jun-93	−15.2	−118.1	10.0	60.8
Jul-93	−17.8	−137.7	11.2	83.6
Aug-93	−19.8	−153.8	10.6	75.1
Sep-93	−17.0	−131.7	5.0	28.3
Oct-93	−13.2	−105.3	−1.6	2.5
Nov-93	−31.2	−260.2	−8.9	10.9
Dec-93	−15.6	−119.9	−7.1	1.4
Ann. ave of 1993	−18.3	−142.6	−0.6	343.8
Jan-94	−23.4	−198.9	−17.0	12.4
Feb-94	−25.6	−229.2	−21.0	19.7
Mar-94	−18.7	−165.0	−5.4	10.0
Apr-94	−14.4	−128.1	−1.7	23.0
May-94	−15.2	−105.3	7.9	64.1
Jun-94	−15.2	−121.8	10.3	82.0
Jul-94	−16.8	−124.6	14.9	40.3
Aug-94	−15.5	−115.2	10.7	77.7
Sep-94	−16.1	−125.7	4.6	7.1
Oct-94	−16.5	−132.0	−1.3	46.0
Nov-94	−20.8	−164.7	−12.0	4.4
Dec-94	−23.5	−185.5	−19.0	0.4
Ann. ave of 1994	−16.5	−129.3	−2.4	387.1
Jan-95	−24.9	−198.2	−12.0	7.5
Feb-95	−19.3	−155.2	−11.0	4.9
Mar-95	−25.7	−212.0	−15.0	11.5
Apr-95	−20.0	−155.5	0.7	30.4
May-95	−16.6	−138.4	5.9	96.2
Jun-95	−14.2	−117.8	12.3	56.9
Jul-95	−15.1	−124.4	13.6	81.2
Aug-95	−14.3	−116.3	11.5	54.9
Sep-95	−14.9	−121.4	7.5	51.4
Oct-95	−18.0	−148.6	−0.9	19.0
Nov-95	−27.5	−213.0	−3.6	29.9
Dec-95	−26.4	−209.7	−16.0	18.5
Ann. ave of 1995	−17.4	−141.1	−0.7	462.3
Jan-96	−24.1	−200.7	−17.0	28.2
Feb-96	−29.4	−226.4	−15.0	5.1
Mar-96	−23.3	−196.0	−9.7	20.6
Apr-96	−21.7	−168.0	1.3	18.3
May-96	−20.1	−151.2	4.6	51.3
Jun-96	−19.0	−147.0	11.5	67.6
Jul-96	−14.5	−110.7	15.8	47.8
Aug-96	−15.9	−122.0	11.9	32.2
Sep-96	−15.6	−112.8	5.9	41.0
Oct-96	−17.0	−136.3	1.4	30.3
Nov-96	−24.8	−182.7	−14.0	43.7
Dec-96	−25.2	−197.5	−5.1	2.8
Ann. ave of 1996	−19.4	−149.5	−0.7	388.9
Jan-97	−28.6	−221.1	−15.0	36.4
Feb-97	−23.8	−185.6	−2.5	3.3
Mar-97	−27.9	−213.8	−10.0	19.9
Apr-97	−18.2	−145.2	−4.0	11.5
May-97	−17.5	−125.4	4.3	155.6
Jun-97	−16.0	−114.1	10.7	108.9
Jul-97	−14.4	−107.5	11.3	14.4
Aug-97	−19.8	−149.4	11.0	68.8
Sep-97	−15.0	−106.3	7.4	30.8
Oct-97	N.D.	N.D.	0	2.0
Nov-97	−14.4	−117.2	−1.8	1.1
Dec-97	−22.9	−180.7	−12.0	7.9
Ann. ave of 1997	−18.7	−137.7	0.0	460.6
Jan-98	−31.0	−232.9	−24.0	17.5
Feb-98	−12.9	−124.6	−10.0	0.2
Mar-98	−25.8	−197.4	−7.9	31.5
Apr-98	−17.2	−141.1	2.4	34.7
May-98	−9.67	−85.3	9.5	48.7
Jun-98	−18.4	−139.9	9.7	118.0
Jul-98	−13.7	−112.6	12.5	115.0
Aug-98	−13.6	−88.35	14.1	34.0
Sep-98	−11.5	−90.24	8.1	24.4
Oct-98	−13.3	−111.4	4.4	11.5
Nov-98	−17.8	−142.5	−3.6	7.7
Dec-98	−28.6	−220.7	−10.0	12.7
Ann. ave of 1998	−16.6	−129.9	0.5	455.9
Jan-99	−27.7	−209.3	−17.0	4.4
Feb-99	N.D.	N.D.	−10.0	5.0
Mar-99	−22.6	−178.7	−8.1	3.8
Apr-99	−22.7	−171.1	2.8	78.3
May-99	−15.9	−121.6	5.0	44.3
Jun-99	−20.6	−154.9	7.3	91.3
Jul-99	N.D.	−148.1	9.6	142.3
Aug-99	N.D.	−110.5	12.4	75.7
Sep-99	−12.7	−96.4	5.4	11.6
Oct-99	−22.0	−171.6	0.1	4.4

Table 1. (cont'd).

	δ^{18}O (‰)	δ^{2}H (‰)	T (°C)	P (mm)
Nov-99	−19.3	−154.4	−1.4	14.9
Dec-99	−28.6	−218.0	−5.9	6.1
Ann. ave of 1999	−19.1	−145.6	0.9	482.1
Jan-00	−27.2	−211.0	−19.0	6.6
Feb-00	−25.1	−189.0	−11.0	25.5
Mar-00	−24.5	−182.6	−4.5	31.8
Apr-00	−24.0	−174.7	−5.9	10.9
May-00	−22.7	−168.8	5.3	37.3
Jun-00	−15.5	−108.9	10.8	77.5
Jul-00	−16.7	−124.6	15.0	70.0
Aug-00	−13.1	−105.9	14.8	57.5
Sep-00	−16.6	−119.5	20.7	15.0
Oct-00	−20.5	−146.8	−0.8	4.1
Nov-00	−28.7	−219.5	−6.1	5.4
Dec-00	−27.6	−205.0	−15.0	9.9
Ann. ave of 2000	−18.7	−139.6	0.3	351.5
Jan-01	−21.6	−155.1	−9.6	1.0
Feb-01	−29.9	−217.4	−6.3	8.0
Mar-01	−21.5	−155.9	−2.5	29.3
Apr-01	−21.5	−161.3	4.1	16.2
May-01	−22.4	−166.1	9.7	20.4
Jun-01	−17.7	−123.3	14.0	94.3
Jul-01	−13.8	−95.0	16.4	60.6
Aug-01	−14.3	−98.3	15.7	10.1
Sep-01	−12.3	−93.59	10.6	10.7
Oct-01	−20.5	−144.6	5.7	19.5
Nov-01	−26.5	−185.0	−3.0	14.3
Dec-01	−25.6	−188.9	−8.3	2.8
Ann. ave of 2001	−18.5	−131.7	3.9	287.2

formation processes and secondary evaporation during rainfall. Hence, a LMWL at any given location might be quite different from the GMWL.

The local meteoric water line for Calgary, based on a 9-yr record (data from 1994 excluded) of amount-weighted monthly average δ^{2}H and δ^{18}O values, is

$$\delta^{2}\mathrm{H} = 7.68\delta^{18}\mathrm{O} - 0.21 \quad (r^{2} = 0.96, n = 104). \tag{6}$$

Equation (6) is similar to those from other stations in Western Canada such as Victoria, Edmonton, Wynyard and The Pas (Table 3), which are located at approximately similar latitudes as Calgary. The LMWLs for these stations are characterized by intercept values closed to zero, much lower than those of the GMWL (Rozanski et al., 1993) and LMWLs for stations in Eastern Canada (Table 3, Fritz et al., 1987). It was noted by Fritz et al. (1987) that it is difficult to decide a priori whether this is caused primarily by the difference in meteorological regimes over Eastern and Western Canada or as a result of local evaporation processes. Our short-term sampling procedure enabled us to address this issue in more detail (see below).

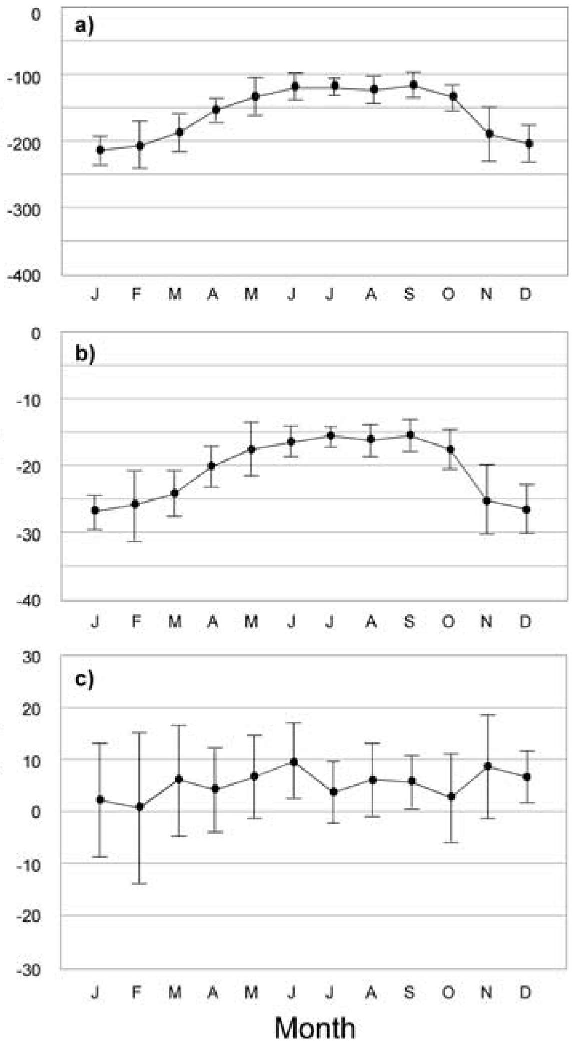

Fig 4. 10-yr (1992–2001) amount-weighted monthly average δ^{2}H (a) and δ^{18}O values (b), and d-excess (c) for Calgary precipitation with standard deviations.

The amount-weighted annual average δ^{2}H and δ^{18}O values for precipitation at Calgary were −136.1‰ and −17.9‰, respectively, and hence significantly lower than those for other Canadian stations at similar latitude (Table 3). Backtracking of air mass trajectories revealed that the moisture source of the majority of precipitation events at Calgary is the North Pacific Ocean. Hence, we conclude that a combination of continental and altitude effects is responsible for the low amount-weighted long-term average δ^{2}H and δ^{18}O values of precipitation at Calgary. We suggest that this feature should be reflected in future maps of isotope compositions for precipitation.

Interestingly, the correlation equation between individual sample values of δ^{2}H and δ^{18}O was found to be quite different from eq. (6), i.e. with lower values of slope and intercept:

$$\delta^{2}\mathrm{H} = 7.10\delta^{18}\mathrm{O} - 13.64 \quad (r^{2} = 0.95, n = 839). \tag{7}$$

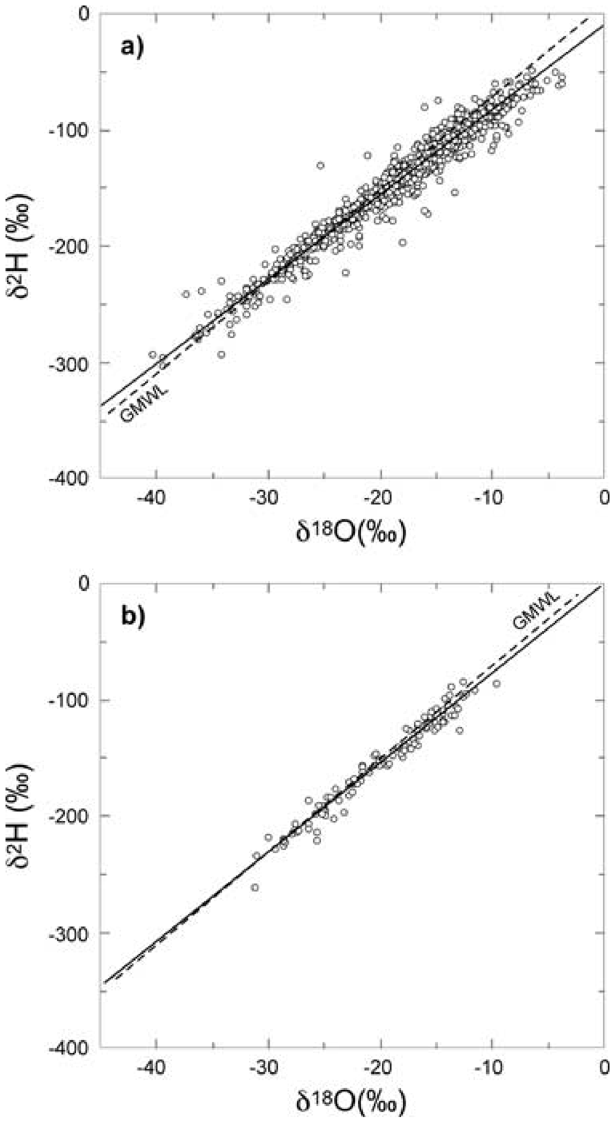

Fig 5. Correlation between δ^2H and δ^{18}O values for Calgary precipitation from January 1992 to December 2001: a) δ^2H and δ^{18}O values of individual samples ($n = 839$): $\delta^2\mathrm{H} = 7.10\,\delta^{18}\,\mathrm{O} - 13.64$ (solid line); b) Monthly amount-weighted average δ^2H and δ^{18}O values ($n = 104$): $\delta^2\mathrm{H} = 7.68\,\delta^{18}\,\mathrm{O} - 0.21$ (solid line). For comparison, the global meteoric water line (GMWL) is shown as a dashed line.

Table 4 summarizes the correlation equations between δ^2H and δ^{18}O values of individual precipitation samples at Calgary for each month. It is evident that the slopes and intercepts of the equations for the months April to August are generally lower than those in the remaining months (except October). This seems to indicate that air temperature (T) affects the correlation equation between δ^2H and δ^{18}O values. Since we had collected short-term samples (0.5–3 d), we were able to test this hypothesis by calculating the correlation equations between δ^2H and δ^{18}O values for different surface air temperature ranges. Precipitation collected at temperatures < -20 °C was characterized by a slope of 7.67 for the $\delta^2\mathrm{H}/\delta^{18}\mathrm{O}$ correlation, whereas the slope and intercept decreased continuously with increasing air temperatures (Table 5). Several known isotope effects may contribute to this phenomenon.

First, the values of the isotope equilibrium fractionation factors of hydrogen and oxygen for water condensation tend to decrease the slope of $\delta^2\mathrm{H}/\delta^{18}\mathrm{O}$ correlations slightly with increasing air temperature (Majoube 1971). However, it is evident from Table 5 that this effect is not sufficient to explain the observed variation of the slope for the $\delta^2\mathrm{H}/\delta^{18}\mathrm{O}$ relationship, which varies between 7.67 at lower ($T < -20$°C) and 6.62 at higher temperatures ($T > 10$°C).

Secondly, in the course of air masses moving over continental areas, the degree of mixing with water vapor originating from inland evaporation and plant transpiration is higher in summer than in winter. It has been pointed out by Zimmermann et al. (1967) and others that evaporation results in low slopes for the $\delta^2\mathrm{H}/\delta^{18}\mathrm{O}$ correlation while transpiration does not produce any significant isotopic fractionation during the process of vapor release from plants (Wershaw et al., 1966; Jacob and Sonntag 1991; Wang and Yakir, 2000). Thus, the observed trend of decreasing values of $\delta^2\mathrm{H}/\delta^{18}\mathrm{O}$ slopes in warm seasons may indicate the incorporation of moisture derived from evaporation of inland surface water bodies and soils, a process which plays a significant role in replenishing atmospheric moisture in southern Alberta, particularly in the summer months.

Thirdly, Calgary is characterized by a semi-arid climate. Evaporation of raindrops beneath the cloud base (secondary evaporation) in the summer time is known to induce additional isotope fractionation effects that reduce the slope of the $\delta^2\mathrm{H}/\delta^{18}\mathrm{O}$ correlation (Dansgaard, 1964). During rain events, water drops below the cloud base may become isotopically more enriched in the heavy isotopes ^{2}H and ^{18}O by kinetic isotope effects during evaporation as they fall towards the Earth's surface (Miyake et al., 1968; Steward 1975; Jouzel, 1986). Thus the stable isotope compositions of rainwater collected at ground level do not necessary represent those of the condensate at the cloud base (Jacob and Sonntag, 1991). Substantial ^{2}H and ^{18}O enrichment in raindrops due to secondary evaporation is best observed for light rain events or at the beginning of storms in an arid atmosphere. For example, the isotopic enrichment of heavy isotopes at the beginning of a single shower event is partly due to the evaporation of raindrops during the beginning of the rain process (Dansgaard, 1964). Gradual saturation of the air column beneath the cloud base occurs in the case of large amount of precipitation due to long-time rain events or heavy showers. Once air becomes saturated, evaporation stops and the enrichment mechanism for the heavy isotopes ^{2}H and ^{18}O in raindrops ceases to function. Thus, the in-cloud isotope signature will progressively characterize subsequent rains collected at ground level.

Part of the Canadian Prairies are characterized by a semi-arid climate and hence we tested the effects of secondary

Table 2. Correlation equations between (a) individual and (b) amount-weighted monthly average δ^2H and δ^{18}O values for the 10-yr period from 1992 to 2001 and for individual years.

Year(s)	(a) Individual values		(b) Monthly average values	
1992–2001	$\delta^2H = 7.13\delta^{18}O - 13.38$	$(r^2 = 0.95, n = 914)$	$\delta^2H = 7.73\delta^{18}O + 0.10$	$(r^2 = 0.96, n = 116)$
1992	$\delta^2H = 7.24\delta^{18}O - 9.62$	$(r^2 = 0.96, n = 98)$	$\delta^2H = 8.27\delta^{18}O + 13.30$	$(r^2 = 0.99, n = 12)$
1993	$\delta^2H = 7.93\delta^{18}O - 0.28$	$(r^2 = 0.94, n = 69)$	$\delta^2H = 8.52\delta^{18}O + 11.53$	$(r^2 = 0.98, n = 12)$
1994	$\delta^2H = 7.62\delta^{18}O - 7.99$	$(r^2 = 0.90, n = 80)$	$\delta^2H = 9.58\delta^{18}O + 27.60$	$(r^2 = 0.90, n = 12)$
1995	$\delta^2H = 6.95\delta^{18}O - 22.95$	$(r^2 = 0.93, n = 120)$	$\delta^2H = 7.60\delta^{18}O - 9.24$	$(r^2 = 0.99, n = 12)$
1996	$\delta^2H = 7.44\delta^{18}O - 8.88$	$(r^2 = 0.96, n = 110)$	$\delta^2H = 8.12\delta^{18}O + 6.96$	$(r^2 = 0.96, n = 12)$
1997	$\delta^2H = 7.11\delta^{18}O - 11.34$	$(r^2 = 0.94, n = 95)$	$\delta^2H = 8.08\delta^{18}O + 9.05$	$(r^2 = 0.98, n = 11)$
1998	$\delta^2H = 6.92\delta^{18}O - 17.90$	$(r^2 = 0.98, n = 100)$	$\delta^2H = 7.13\delta^{18}O - 13.56$	$(r^2 = 0.97, n = 12)$
1999	$\delta^2H = 6.78\delta^{18}O - 20.62$	$(r^2 = 0.93, n = 65)$	$\delta^2H = 7.52\delta^{18}O - 3.68$	$(r^2 = 0.99, n = 9)$
2000	$\delta^2H = 7.18\delta^{18}O - 9.02$	$(r^2 = 0.97, n = 99)$	$\delta^2H = 7.70\delta^{18}O + 5.62$	$(r^2 = 0.99, n = 12)$
2001	$\delta^2H = 6.83\delta^{18}O - 9.89$	$(r^2 = 0.95, n = 78)$	$\delta^2H = 7.38\delta^{18}O + 3.44$	$(r^2 = 0.99, n = 12)$

Table 3. Amount-weighted long-term average δ^2H and δ^{18}O values and correlation equations for amount-weighted monthly average δ^2H and δ^{18}O values for precipitation at stations maintained by the IAEA/WMO GNIP network. Data from Fritz et al. (1987) and GNIP website (http://www.iaea.or.at/programs/ri/gnipmain.htm*)*

Station	Location	Observation period	Average δ^2H value (‰)	Average δ^{18}O value (‰)	$\delta^2H/\delta^{18}O$ correlation equation	r^2
Western Canada						
Victoria	48.65°N, 123.43°W, 20m ASL	Monthly 1975–1982	−76.8	−10.2	$\delta^2H = 7.49\delta^{18}O - 1.56$	0.86
Canadian Prairies						
Calgary	51.01°N, 114.01°W, 1049 m ASL	Monthly 1992–2001	−136.1	−17.9	$\delta^2H = 7.68\delta^{18}O - 0.21$	0.96
Edmonton	53.57°N, 113.52°W, 671m ASL	Monthly 1960–1969	−130.7	−17.1	$\delta^2H = 7.67\delta^{18}O - 0.14$	0.98
Wynyard	51.77°N, 104.20°W, 561m ASL	Monthly 1975–1982	−116.8	−15.5	$\delta^2H = 7.63\delta^{18}O + 0.07$	0.99
The Pas	53.97°N, 101.10°W, 272m ASL	Monthly 1975–1982	−125.8	−16.5	$\delta^2H = 7.62\delta^{18}O + 0.62$	0.99
Gimli	50.62°N, 96.98°W, 223m ASL	Monthly 1975–1982	−104.2	−14.1	$\delta^2H = 7.80\delta^{18}O + 6.22$	0.98
Eastern Canada						
Ottawa	45.32°N, 75.67°W, 114m ASL	Monthly 1975–1982	−76.7	−11.0	$\delta^2H = 7.68\delta^{18}O + 9.50$	0.98

Table 4. Correlation equations for δ^2H and δ^{18}O values of individual samples for each month and monthly average temperatures.

Month	$\delta^2H/\delta^{18}O$ correlation equations	Monthly average temperature (°C)
January	$\delta^2H = 6.95\delta^{18}O - 21.88$ $(r^2 = 0.88, n = 49)$	−15.4
February	$\delta^2H = 6.68\delta^{18}O - 25.98$ $(r^2 = 0.94, n = 37)$	−10.8
March	$\delta^2H = 7.01\delta^{18}O - 18.33$ $(r^2 = 0.96, n = 68)$	−7.0
April	$\delta^2H = 6.34\delta^{18}O - 28.11$ $(r^2 = 0.96, n = 76)$	0.5
May	$\delta^2H = 6.58\delta^{18}O - 22.83$ $(r^2 = 0.89, n = 97)$	5.6
June	$\delta^2H = 6.47\delta^{18}O - 19.07$ $(r^2 = 0.90, n = 130)$	10.6
July	$\delta^2H = 6.52\delta^{18}O - 21.66$ $(r^2 = 0.86, n = 95)$	13.2
August	$\delta^2H = 6.42\delta^{18}O - 22.90$ $(r^2 = 0.85, n = 58)$	12.3
September	$\delta^2H = 7.46\delta^{18}O - 4.31$ $(r^2 = 0.92, n = 71)$	6.7
October	$\delta^2H = 6.57\delta^{18}O - 21.61$ $(r^2 = 0.90, n = 52)$	1.1
November	$\delta^2H = 7.11\delta^{18}O - 15.12$ $(r^2 = 0.94, n = 58)$	−6.5
December	$\delta^2H = 7.05\delta^{18}O - 17.79$ $(r^2 = 0.97, n = 48)$	−11.6

Table 5. Correlation equations for δ^2H and δ^{18}O values of individual precipitation samples collected in different temperature ranges at Calgary, Alberta, Canada. Also listed are the theoretical ratios between isotope equilibrium fractionation factors of hydrogen and oxygen ($^2\varepsilon_{v/l}/^{18}\varepsilon_{v/l}$) at these temperature ranges (Majoube, 1971).

Temperature range	δ^2H/δ^{18}O correlation equations	r^2	n	$^2\varepsilon_{v/l}/^{18}\varepsilon_{v/l}$
−30 to −20°C	$\delta^2H = 7.67\delta^{18}O - 9.53$	0.97	47	>8.8
−20 to −10°C	$\delta^2H = 7.35\delta^{18}O - 11.67$	0.98	77	8.6–8.8
−10 to 0°C	$\delta^2H = 7.18\delta^{18}O - 13.29$	0.97	168	8.5–8.6
0 to 10°C	$\delta^2H = 7.07\delta^{18}O - 14.79$	0.97	309	8.4–8.5
10 to 27°C	$\delta^2H = 6.62\delta^{18}O - 20.80$	0.98	238	<8.4

evaporation occurring in falling raindrops on the isotope composition of precipitation at Calgary. Table 6 summarizes the effect of secondary evaporation on the δ^2H/δ^{18}O correlation equation of Calgary precipitation for surface air temperatures >10°C. For small amount rain events (<5 mm), the slope of the δ^2H/δ^{18}O relationship was less than 7.1, indicating secondary evaporation effects on the raindrops. This effect was most pronounced for rain samples with amounts of <1 mm (slope = 6.08). For more intense rain events (5–10 mm), the slope of the δ^2H/δ^{18}O relationship increased to 7.56. It is interesting to note that the slope of the δ^2H/δ^{18}O relationship decreased to 6.91 for precipitation amounts >10 mm. Many of these rain events are thunderstorms or super cells that derive their moisture mainly from local evapotranspiration (Environment Canada 1960–2001). This indicates that the low slope in eq. 7 (7.10) is not only caused by secondary evaporation during small rain events (amount effect), but also by primary evaporation from inland water bodies and soils, particularly during the formation of thunderstorms, which result in large precipitation events.

The total amount of precipitation collected between May and August was 280 mm per annum, which represents about 70% of the average annual precipitation amount (401 mm). Out of the 380 samples collected in the months May to August between 1992 and 2001, 253 samples were from small amount events of less than 5 mm, accounting for only 61 mm of precipitation per year. There were 54 precipitation events with 5–10 mm, accounting for 52 mm per annum. The 73 precipitation events with more than 10 mm accounted for 167 mm per annum. The large number of precipitation events with amounts of less than 5 mm, which are often influenced by secondary evaporation (amount effect), are responsible for the low slope in the δ^2H/δ^{18}O relation using individual samples (eq. 7). However, these events contribute only 15% (61 mm) of the average annual precipitation (401 mm), and therefore have little effect on the δ^2H/δ^{18}O relation using amount-weighted values (eq. 6).

4.2. *Deuterium excess*

Dansgaard (1964) introduced the concept of deuterium excess, which is defined as $d = \delta^2H - 8\delta^{18}O$. The value of deuterium excess for precipitation in a specific atmospheric precipitation sample is believed to be mainly related to the meteorological condition at the source region from where the sample is derived, i.e. relative humidity in the atmosphere above the ocean, wind regime, ocean surface roughness as well as its temperature (Merlivat and Jouzel, 1979). Different air-sea conditions at the distinct water vapor sources result in a series of meteoric water lines with specific deuterium excess values (Gat, 1981). For this reason, the d-excess parameter has been used as a diagnostic tool to measure the contribution of water vapor from different sources to the atmosphere at a specific location. However it is also documented that d-excess values are partially related to the mixing of evapotranspiration water vapor fluxes from continental surfaces occurring along the storm track (Gat et al., 1994). Also, secondary evaporation during precipitation events has been shown to influence d-excess values (e.g. Fritz et al., 1987).

When precipitation in a particular location is derived mainly from a single vapor source, the monthly amount-weighted averages of d-excess values are typically lower in summer than those in winter (Rozanski et al., 1993). This apparent seasonality is interpreted as follows: (1) lower values of relative humidity at the source region during winter than during summer tend to enhance the kinetic isotope fractionation process during evaporation, which results in higher values of d-excess (Merlivat and Jouzel, 1979); (2) lower values of relative humidity and higher temperatures over continental precipitation sites in summer

Table 6. Amount-weighted average δ^2H, δ^{18}O, and d-excess values and the corresponding correlation equations for δ^2H and δ^{18}O values of individual precipitation samples collected at Calgary at temperatures > 10°C for different precipitation amount ranges.

Amount (mm)	Ave. δ^2H value (‰)	Ave. δ^{18}O value (‰)	d-excess (‰)	δ^2H/δ^{18}O correlation equations	r^2	n
0–1	−12.2	−103.7	−6.0	$\delta^2H = 6.08\delta^{18}O - 28.45$	0.89	60
1–2	−13.3	−109.2	−2.8	$\delta^2H = 7.04\delta^{18}O - 14.34$	0.94	26
2–5	−14.1	−111.8	1.0	$\delta^2H = 7.07\delta^{18}O - 13.28$	0.91	53
5–10	−16.7	−126.5	7.4	$\delta^2H = 7.56\delta^{18}O - 2.93$	0.93	23
10–60	−15.4	−116.7	6.8	$\delta^2H = 6.91\delta^{18}O - 10.73$	0.92	35

facilitate increased secondary evaporation of rain drops during their descent from the cloud base to the ground, which in turn decreases the d-excess value for the rain events in summer (Dansgaard 1964; Rozanski 1987); (3) additional non-equilibrium conditions occur during the formation of snow, which contributes to the higher d-excess in winter precipitation (Jouzel and Merlivat 1984).

The amount-weighted average d-excess values for Calgary precipitation for individual months are shown in Fig. 3e. Figure 4c displays the 10-yr amount-weighted monthly average values for d-excess including standard deviations. There appears to be no clear seasonality trend of d-excess values for precipitation at Calgary and the standard deviation of d-excess for each month is generally larger than the maximum variation of the mean values (7.56) throughout the year. Table 6 provides evidence that secondary evaporation between cloud base and ground results in a significant decrease of d-excess values for small precipitation events at temperatures >10 °C. Also, an admixture of water vapor from evapotranspiration over the continents along the storm paths may influence d-excess values, predominantly in the summer months. Therefore, we suggest that d-excess values for precipitation at Calgary do not solely reflect the meteorological conditions at the vapor source region. This is presumably also true for other stations in the Canadian Prairies (Fritz et al., 1987).

4.3. *Correlation between stable isotope ratios of oxygen and air temperature*

Since the beginning of isotope studies, the relationship between local meteorological parameters and stable isotope compositions of oxygen and hydrogen in precipitation has attracted much attention (Dansgaard, 1964; Jouzel, 1986; Yapp and Epstein, 1977; Rozanski et al., 1982).

Figure 6 shows the correlation between δ^{18}O values of individual samples and average temperature during precipitation events:

$$\delta^{18}\mathrm{O} = 0.46T - 19.35 \quad (r^2 = 0.59, n = 839). \tag{8}$$

The correlation between amount-weighted monthly average δ^{18}O values and temperature T is

$$\delta^{18}\mathrm{O} = 0.42T - 19.95 \quad (r^2 = 0.61, n = 104). \tag{9}$$

In eq. (9), the amount-weighted monthly average temperature is defined as

$$T = \frac{\sum P_i T_i}{\sum P_i} \tag{10}$$

where P_i and T_i denote the amount of each individual precipitation sample and the average air temperature measured at the ground during individual precipitation collection events (eq. 4), respectively. The summations are over all the precipitation events in one specific month.

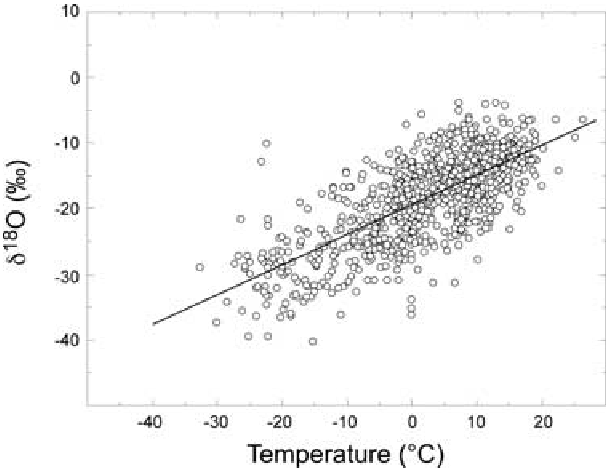

Fig 6. Correlation between δ^{18}O values of individual samples for Calgary precipitation and local air temperature for events between January 1992 and December 2001 ($n = 839$):$\delta^{18}\mathrm{O} = 0.46T$–19.35 (solid line). Temperature is the average value measured at ground level during the respective precipitation collection period (eq. 4).

Note that the IAEA/WMO GNIP network uses monthly average temperatures including time at which no precipitation occurred. If that practice is used for the Calgary data, then

$$\delta^{18}\mathrm{O} = 0.44T - 21.9 \quad (r^2 = 0.58, n = 104). \tag{11}$$

Equations (8), (9) and (11) are quite similar and it is suggested that each practice yields an acceptable correlation between δ^{18}O values and local temperature.

5. Conclusion

Stable isotope ratios of hydrogen and oxygen were evaluated for precipitation collected in the 10-yr time period between January of 1992 and December of 2001 at Calgary (Alberta, Canada) based on both the values for individual samples and the values of monthly amount-weighted averages. Amount-weighted annual δ^2H and δ^{18}O values of -136.1‰ and -17.9‰, respectively, are lower than those for other Canadian stations at similar latitude, since atmospheric moisture, which is mainly derived from the North Pacific Ocean, is subjected to pronounced continental and altitude effects. The local meteoric water line ($\delta^2\mathrm{H} = 7.68\delta^{18}\mathrm{O} - 0.21$) based on amount-weighted monthly average δ^2H and δ^{18}O values is markedly different from the regression equation, which is based on individual sample δ^2H and δ^{18}O values ($\delta^2\mathrm{H} = 7.10\delta^{18}\mathrm{O} - 13.64$). Our results suggest that this discrepancy is due to evaporation over the continent and secondary evaporation between the cloud base and the ground during precipitation events. Variations of regression equations between δ^2H and δ^{18}O values in different temperature ranges as well as secondary evaporation effects were only detectable using isotope data for short-term samples (0.5–3 d) rather than monthly amount-weighted average values.

Currently, attempts are being made to subdivide the data set of stable isotope ratios of hydrogen and oxygen according to air mass trajectories and hence specific vapor sources. It is anticipated that this will lead to a better understanding of the effect of evaporation on the isotopic composition of precipitation and its d-excess values. To clearly reveal the relationship between δ^2H and δ^{18}O values with distinctive source regimes, short-term sampling of precipitation events is essential. Important characteristics of stable isotope compositions of hydrogen and oxygen of precipitation will be lost during long-term (e.g. monthly) collection of precipitation samples due to the rapid change of atmospheric circulation and the high variability of meteorological parameters.

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