

DEUTERIUM EXCESS IN PRECIPITATION AND ITS CLIMATOLOGICAL SIGNIFICANCE

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ABSTRACT

The climatological significance of the deuterium excess parameter for tracing precipitation processes is discussed with reference to data collected within the IAEA/WMO Global Network for Isotopes in Precipitation (GNIP) programme. Annual and monthly variations in deuterium excess, and their primary relationships with $\delta^{18}\text{O}$, temperature, vapour pressure and relative humidity are used to demonstrate fundamental controls on deuterium excess for selected climate stations and transects. The importance of deuterium excess signals arising from ocean sources *versus* signals arising from air mass modification during transport over the continents is reviewed and relevant theoretical development is presented. While deuterium excess shows considerable promise as a quantitative index of precipitation processes, the effectiveness of current applications using GNIP is largely dependent on analytical uncertainty ($\sim 2.1\%$), which could be improved to better than 1% through basic upgrades in routine measurement procedures for deuterium analysis.

INTRODUCTION

The deuterium excess (or d-excess), defined by $d(\text{‰}) \equiv \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$ (Dansgaard, 1964), where $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are deuterium and oxygen-18 composition of water¹, respectively, has shown specific potential in climate studies for tracing past and present precipitation processes. D-excess is a measure of the relative proportions of ^{18}O and ^2H contained in water, and can be visually depicted as an index of deviation from the global meteoric water line (MWL; $d=10$) in $\delta^{18}\text{O}$ *versus* $\delta^2\text{H}$ space (Figure 1). While oxygen-18 ($\delta^{18}\text{O}$) and deuterium ($\delta^2\text{H}$) at moderate and high latitude continental areas are well correlated with the surface air temperature at precipitation site, the d-excess is correlated with the physical conditions (humidity, air temperature and sea surface temperature) of the oceanic source area of the precipitation (Merlivat and Jouzel, 1979). In addition, d-excess reflects the prevailing conditions during evolution and interaction or mixing of air masses *en route* to the

¹ δ values express isotopic ratios as deviations in per mil (‰) from the Vienna-SMOW (Standard Mean Ocean Water), such that $\delta_{\text{SAMPLE}} = 1000((R_{\text{SAMPLE}}/R_{\text{SMOW}})-1)$, where R is $^{18}\text{O}/^{16}\text{O}$ or $^2\text{H}/^1\text{H}$. Values cited herein are normalized on the SMOW-SLAP scale so that SLAP (Standard Light Arctic Precipitation) has a value of -55.5 ‰ in $\delta^{18}\text{O}$ and -428‰ in $\delta^2\text{H}$ (see Coplen, 1996).

precipitation site. Recently, the d-excess was demonstrated to be a useful, independent climatic parameter to calibrate atmospheric general circulation models (e.g. Jouzel et al., 1991, 1994, Ciais et al., 1995; Hoffmann et al., 2000) and to characterize atmospheric circulation in polar regions (Petit et al., 1991).

Despite these demonstrated advantages, the use of d-excess has some current drawbacks. Compared with the application of the individual isotopes of oxygen-18 or deuterium, d-excess variations can be complicated, and theoretical understanding of d-excess and related climatic controls has not yet been fully explored. Because changes in the d-excess depend on changes in both oxygen-18 and deuterium, the analytical uncertainty of this parameter can be relatively high in comparison with its natural variability. To date, the most definitive applications of the d-excess in climatological studies were achieved in studies of polar and high mountain glacier ice wherein analyses were performed in specialized laboratories capable of measuring d-excess with an uncertainty below one per mille (Johnson and White, 1989).

One prerequisite for widespread application of d-excess in climatology is improvement in routine analytical precision, primarily of deuterium measurements. Another prerequisite, which is the focus of this paper, is the development of an improved understanding of spatial and temporal variations in d-excess and their controls in present day precipitation. To demonstrate fundamental local, regional, and global patterns in the d-excess and its correlation with other climate parameters, namely $\delta^{18}\text{O}$, air temperature, and vapour pressure, we present a synthesis of long-term monthly and annual patterns observed for selected stations within the IAEA/WMO Global Network for Isotopes in Precipitation (GNIP) database. The synthesis, which also provides relevant theoretical development, underlines the nature of d-excess variations in modern precipitation and its climatic controls. As shown, the potential of the tracer justifies the need to improve basic analytical precision so that it can be fully exploited in future isotope-based climate research.

ANNUAL PATTERNS

The GNIP database comprises oxygen-18, deuterium and tritium values of monthly composite precipitation samples collected during 1961 to present from a network of 550 meteorological

stations which are irregularly distributed over the globe (Rozanski et al., 1993; Panarello et al., 1998). It also includes monthly mean values of air temperature, atmospheric vapour pressure and monthly precipitation amount. Minimum reported analytical uncertainty in oxygen-18 and deuterium measurements is 0.2 ‰ and 2 ‰, respectively although some laboratories (and therefore some stations or years) report lower values. Analytical uncertainty in d-excess for routine measurements is currently estimated at $u(d) = \sqrt{(u\delta^2H)^2 + 8 \cdot (u\delta^{18}O)^2} \approx 2.08 \text{ ‰}$, which is strongly dependent on the uncertainty in deuterium (2 ‰). Current uncertainty leaves obvious room for future improvement.

The annual averages of air temperature, vapour pressure, $\delta^{18}O$, δ^2H and deuterium excess of the GNIP stations are presented in Fig.2. Although there is a considerable scatter of the data, the plots reveal statistical correlations between some of these parameters, such as a curvilinear dependency between temperature (vapour pressure) and oxygen-18 and a linear dependency between the oxygen-18 and deuterium values. These statistical relationships have been extensively discussed in various reviews of the GNIP database (Dansgaard, 1964; Yurtsever and Gat, 1981; Rozanski et al., 1993).

Herein, special consideration is given to the d-excess (Fig. 2E and 2F). Despite the considerable scatter in the data presented in Fig.2F, a slight increase of the d-excess is visible between the cluster at 30 mbar and the one at about 15 mbar, and a notable decrease in d-excess is visible for vapour pressures below about 15 mbars. (It should be noted that there is certain equivalence in the dependency of the temperature and the vapour pressure, respectively, for the temperature range below 15°C. This “equivalence” is seen in the oxygen-18 plots of Fig. 2C and D, and it is founded on the apparent vapour pressure - temperature relationship manifested by Fig.2A). Fig.2F also illustrates the exceptionally high d-excess values recorded at stations receiving precipitation from the eastern Mediterranean, e.g. ISR (Israel), SAU (Saudi Arabia), and CYP (Cyprus). These high d-excess values reflect the specific conditions of the vapour formation over the eastern Mediterranean (Gat and Carmi, 1970). Annual average d-excess values below zero per mil are observed at stations with high temperature and/or low vapour pressure (e.g. VEN – Venezuela, MAL – Mali, CHA – Chad), where kinetic isotope fractionation processes, connected with the partial evaporation of the falling raindrops (Stewart, 1974), affect the d-excess of the collected precipitation.

Partial evaporation of the precipitation sample during the storage in the rain gauge under warm and dry atmospheric conditions may also be accountable for a portion of the observed decrease of the d-excess.

Three distinct data clusters are discernible on a plot of deuterium excess versus oxygen-18 (Fig. 2E). The first cluster includes stations with high oxygen-18 values and d-excess values ranging from about 5‰ to 15‰. These stations, with latitudes from 45 °S to 45 °N, mainly receive precipitation from tropical and subtropical oceanic source areas. A second cluster, characterized by about 3‰ lower oxygen-18 values and a d-excess ranging from about 5‰ to 12‰ is also discernible. This cluster is represented by stations located in the latitude band from 45° to 60° both of the northern and the southern hemisphere. The depletion in oxygen-18 relative to the first cluster points to the rainout effect of water vapour (Rayleigh distillation model) during poleward air mass movement. Mixing with water vapour evaporated from more northern (southern) oceanic areas may account for the observed slight depletion of the d-excess values. Stations receiving precipitation from the Mediterranean Sea region form the third cluster with deuterium excess values above 15‰ (Fig. 2E).

Two dashed lines with a slope of -4 have been plotted in Fig.2E. This value has been chosen because it corresponds to the estimated ratio between the change of d-excess and the change of oxygen-18 due to evaporation of falling raindrops (see below). As shown in Fig. 2E, clusters appear to be stretched along lines with this slope, indicating that sub-cloud evaporation is one of the major processes responsible for the observed spread of the d-excess.

Despite the considerable scatter in the global d-excess values, Fig. 2E suggests a slight overall increase of the d-excess with oxygen-18 of about $\frac{dd}{d^{18}\delta} = 0.1$ to 0.2 . With the relationship $\frac{dd}{d^{18}\delta} = \frac{d^2\delta}{d^{18}\delta} - 8$, which follows from the definition of the d-excess, the value of the slope $\frac{d^2\delta}{d^{18}\delta}$ in the $\delta^{18}O$ vs δ^2H plot would be between 8.1 and 8.2. This estimate is in good agreement with the value 8.2 ± 0.07 , which followed from a statistical evaluation of the GNIP data (e.g. Araguás-Araguás et al., 2000).

MONTHLY PATTERNS

While the spatial distribution of the long-term annual averages of the d-excess is characterized by a considerable statistical spread, the long-term monthly averages generally show a well-defined and systematic seasonal variation. For the northern hemisphere, the average d-excess over all stations usually reaches its maximum in December/January and its minimum in June/July (Fig. 3). In the southern hemisphere the seasonal variation of the d-excess shows a 6-month phase-shift. Fig. 3 also indicates that the amplitude of the seasonal variation is higher in the northern than in the southern hemisphere. This asymmetry seems to reflect the irregular distribution of land and sea at the two hemispheres. In summer, the relative humidity can reach lower values on land than on sea. Thus, on average, sub-cloud evaporation and consequently decrease of the d-excess is of stronger influence in the northern hemisphere.

The model of Merlivat and Jouzel (1979) allows a more quantitative description of the seasonal variation of the d-excess. It is based on the following relationship between the isotopic composition of the water vapour evaporating from the sea surface (δ_E) and the one of the atmospheric moisture above the sea (δ_{V0}):

$$\delta_E = (1-k) \frac{1/\alpha_e - h(1 + \delta_{V0})}{1-h} - 1 \quad (1)$$

For $\delta_E = \delta_{V0}$, the isotopic composition of the first-fraction precipitation in the oceanic source area, $1 + \delta_{P0} = \alpha_e(T_c) (1 + \delta_V)$ becomes:

$$\delta_{P0} = \frac{\alpha_e(T_c) (1-k)}{\alpha_e(T_s) (1-kh)} - 1 \quad (2)$$

where $\alpha_e(T_c)$ and $\alpha_e(T_s)$ are the equilibrium fractionation factors at condensation temperature (T_c) and sea surface temperature (T_s), respectively, h is the relative humidity related to the sea surface temperature, and k is a factor characterizing the kinetic isotope fractionation of the evaporation process. Merlivat and Jouzel (1979) obtained for a smooth regime $^{18}k = 6\%$ (for oxygen-18), and the ratio is $^{2}k/^{18}k = 0.88$. It should be noted that the condition $\delta_E = \delta_{V0}$ applies for a steady-state regime of the *whole* water cycle (Merlivat and Jouzel, 1979). For following it is also applied, since it is considered as a reasonable approximation for oceanic

source areas with high evaporation flux and smooth wind regime (e.g. in tropical and sub-tropical regions).

Using eq (2), the annual average d-excess values of first-fraction precipitation has been calculated for oceanic stations at which long-term measurements of the humidity, air temperature and sea surface temperature have been carried out (H. van Loon, 1984). Fig. 4 shows the calculated values as a function of the latitude of the corresponding marine observation stations. The wide spread of the values, especially for the North Pacific, is probably due to the large distance between the stations, and thus the different climatic conditions, even at comparable latitudes. It is also possible that the assumption on which eq. (2) is based, does not fully describe the complexity of the evaporation-condensation processes at the various stations. As far as the Indian Ocean is concerned, the data suggest lower d-excess values in equatorial regions and higher values in sub-tropical areas. Maximum values seem to be reached at latitude of around 30° , both in the southern and the northern hemisphere.

The same approach has been used to calculate the monthly mean d-excess of first-fraction precipitation at various stations in the North Atlantic, for which the long-term monthly averages of the required parameters are available. Fig. 5 demonstrates that the calculated d-excess values reach at all stations a maximum in winter and a minimum in summer. This result is in good agreement with the GNIP data (Fig. 3, curve for the northern hemisphere). Fig. 5 also indicates the strong influence of the relative humidity on the d-excess. At the stations 30°N and 40°N , the relative humidity is lower and the d-excess accordingly higher than at the more northern stations (55°N and 56°N). Finally, Fig. 5 reveals an important feature of these isotopic and climatological parameters, namely the phase shift between their seasonal variations. The maximum of the air temperature appears a few months later than the one of the relative humidity.

The phase shift between the seasonal variations of the various parameters gives rise to the hysteresis effect observed in the temperature *versus* relative humidity, $\delta^{18}\text{O}$ and d-excess relationships (Fig. 6). It should be noted that such hysteresis curves indicate that the observed isotopic pattern is dependent on the thermodynamic conditions in the atmosphere in the preceding months. While the phase shift between air temperature and relative humidity as

well as oxygen-18 is only a couple of months, the d-excess is nearly in anti-phase to the air temperature. It should be noted that the hysteresis curves in this figure would “degenerate” to straight lines, if the phase shifts were exactly zero months, for the relative humidity and for oxygen-18, or six months, for the d-excess. In fact, the phase shift between oxygen-18 and deuterium excess of first-fraction precipitation in the considered oceanic areas appears to be exactly 6 months, as shown by Fig.7. This plot also demonstrates that in oceanic areas the seasonal variation of oxygen-18 is rather small.

Considering the Rayleigh distillation model (Dansgaard, 1964), it is expected that the average oxygen-18 values become lower and the amplitude of the seasonal variation of oxygen-18 higher, when water vapour partially rains out at lower temperatures during the moisture transport away from the oceanic source area. This trend is verified by the GNIP data, as shown in Fig. 8 for the example of a transect from the Atlantic Ocean to the continental station in Vienna, Austria. It is interesting to note that over the large distance from the Azores to Gibraltar there is a rather small change in the isotopic composition of the precipitation compared to the short travel over continental regions up to Vienna. Furthermore, Fig. 8 indicates that there is a lower decrease of the d-excess maximum (winter season) with decreasing oxygen-18 than of the d-excess minimum (summer season). This trend, and particularly the very low d-excess in summer at Gibraltar indicate the effect of kinetic isotope fractionation due to partial evaporation of the falling raindrops. Stewart (1975) studied this process and provided a theoretical description. Assuming that the partial evaporation of the falling raindrop is not higher than about 20%, the following relationship can be derived from Stewart’s theory:

$$\frac{\Delta d}{\Delta^{18}\delta} \approx \frac{1 - 1/2 \alpha_k}{1 - 1/18 \alpha_k} - 8 \quad (3)$$

where $\alpha_k = \alpha_e (D/D')^{0.58}$, α_e is the equilibrium fractionation factor, and D/D' the ratio of the diffusion coefficients for the light and heavy isotope of oxygen and hydrogen, respectively. Using the values given by Stewart, the ratio of the change of the d-excess and the one of the oxygen-18 due to evaporation of falling raindrops is approximately:

$$\frac{\Delta d}{\Delta^{18}\delta} \approx -4. \quad (3a)$$

An example of the air mass evolution in North America and the distinctive imprints of $\delta^{18}\text{O}$ and d-excess is shown in Fig. 9 for a transect extending from Bermuda, located in the Atlantic Ocean, to Gimli Manitoba, and traversing the Great Lakes region. The progression in “continentality” of the air masses coming from the Bermudas is clearly labeled by the relationship of the long-term monthly means of $\delta^{18}\text{O}$ and temperature. In maritime areas (Bermuda and Hatteras), $\delta^{18}\text{O}$ is controlled by the rain amount compared to continental areas where it is strongly controlled by temperature effects (oxygen-18-temperature coefficient increases to about 0.5‰/°C). This behaviour, also observed in other regions (Araguás-Araguás et al., 1998), agrees with conclusions from measurements of vertical moisture and temperature profiles (Gaffen et al., 1992), namely that in tropical (and subtropical) areas the precipitable water is not a strong function of temperature but of vertical convection, whereas in humid (and continental) regions the precipitable water is controlled by horizontal advection and temperature.

The maritime character of the air mass over the Bermudas is also represented by the steep trend of d-excess versus oxygen-18 (Fig. 9b). The “degeneration” of the hysteresis at this station indicates that there is just a 6-month phase shift between oxygen-18 and d-excess. The deformation of the systematic transformation of the hysteresis curves at continental stations of the transect (Fig. 9b) suggests mixing of air masses of different origin. Principally, there are 4 sources of air moisture moving into the Great Lakes region. These are from Gulf of Mexico (dominating in summer), Pacific Ocean, Arctic region and the Atlantic Coast.

A striking feature of Fig. 9b is the increase of the d-excess by up to 5‰ at stations in the Great Lakes region, particularly in the fall (months 9 through 12) at Coshocton and Simcoe. This suggests enhanced continental water recycling (Gat et al., 1994), i.e., return of land surface evaporation water to the land surface as precipitation (Koster et al., 1993). A simple relationship between the change in d-excess, Δd , due to recycling and the recycling ratio, R (= relative amount of vapour evaporated from open water surfaces in the precipitation), can be derived as follows. Considering the isotopic composition of vapour evaporating from open water surfaces (e.g. Froehlich, 2000), assuming that the isotopic composition of the surface water corresponds with the one of the preceding precipitation, then a simple mass balance yields:

$$\Delta d = R(8^{18}C_k - 2C_k). \quad (4)$$

With the values of the kinetic fractionation coefficients ${}^2C_k = 14.3\text{‰}$ and ${}^{18}C_k = 12.4\text{‰}$ (Froehlich, 2000) the recycling ratio becomes $R = \Delta d/100$ (Δd in ‰). Thus, an increase of the deuterium excess by about 5‰ would correspond with a recycling from open water surfaces of about 5%. It should be noted that for the Great Lakes region the assumption made in deriving eq. (4) (isotopic composition of the surface water equal to the isotopic composition of the preceding precipitation) is not exactly realized. Nevertheless, the value of the recycling ratio estimated here for a d-excess increase of 5‰ is in good agreement with a more specific evaluation for the Great Lake region by Gat et al. (1994). Similarly, d-excess in the range of +20‰ for the Mediterranean indicates a recycling ratio close to 20%.

The GNIP data enable selecting numerous such transects across Europe, Africa and other continental regions. As demonstrated here, these transects provide insight into the long-term isotopic signals of the continental effect as atmospheric moisture evolves by progressive rainout and mixing processes over the continents. Transects crossing Germany and transects in mountainous regions can also be useful to study the evolution of the d-excess with increasing altitude (Froehlich, 1996; Gonfiantini et al., 2001). The systematic relationships between $\delta^{18}\text{O}$, d-excess and climatic parameters are useful for labeling and quantifying important air-mass regimes and seasonal fluctuations. These transects provide further information on the natural variability of the deuterium excess relevant for enhancing its use in climatic studies.

CONCLUSIONS

The database of the Global Network for Isotopes in Precipitation can be used to study the long-term annual and monthly averages of the deuterium excess in relation to oxygen-18 of precipitation and other climatic variables. Despite that uncertainty in the reported deuterium excess is currently quite high, variations both in the long-term annual and monthly averages of the deuterium excess are robust and systematic, suggesting significant potential of this parameter in climatic studies. The deuterium excess can be used as fingerprint of (1) the oceanic source area of the precipitation collected at a given station and (2) mixing of air

masses of different source, in particular, recycled air moisture. Relationships for estimating these effects are given in the paper. This also includes the effect on the deuterium excess of partial evaporation of falling raindrops under warm and dry conditions below the cloud base. The model of Merlivat and Jouzel (1979) of the formation of the isotopic composition of water vapour in the oceanic source area has been used to estimate the monthly variation of the isotopic composition and the deuterium excess in first-fraction precipitation at selected maritime observation stations. The results are in good agreement with data derived from the GNIP database and contribute to better understand the seasonal variations of the deuterium excess in precipitation. In the paper, advantage has been taken of deuterium excess versus oxygen-18 plots, which proved to be complementary and sometimes more “sensitive” (with regard to identification deuterium excess changes) than conventional deuterium versus oxygen-18 plots. Furthermore, hysteresis curves have been plotted to better demonstrate phase shifts between the seasonal variation of the deuterium excess and oxygen-18 and/or other climatic variables. Some regions with pronounced variations/phase shifts should be selected for further studies of long-term seasonal variations. With the advancement in using AGCMs for climate studies, experimental data on long-term seasonal variations of the isotopic composition and, thus, the deuterium excess in precipitation will be very useful for model validation.

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FIGURE CAPTIONSS.

FIGURE 1. Schematic plot of $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ showing the global meteoric water line (MWL; $d = 10$, slope = 8) of Craig (1961), local evaporation line (LEL; slope < 8), ocean water (SMOW) and relative changes in the d-excess (d). D-excess in precipitation increases in response to enhanced moisture recycling as a result of increased evaporate content. D-excess is reduced in the case where water is lost by evaporation.

FIGURE 2. Compilation of long-term annual averages of isotopic and climatic variables of the GNIP database.

FIGURE 3. Seasonal variation of deuterium excess in precipitation estimated from long-term mean monthly values of the stations included in the GNIP database.

FIGURE 4. Plot of annual average deuterium excess in first-fraction precipitation versus latitude of maritime stations. The climatic variables used for calculating the deuterium excess by eq.(2) are taken from Lon (1984).

FIGURE 5. Long-term monthly averages of climatic variables (air temperature and relative humidity related to sea surface temperature) taken from Lon (1984) for selected observation stations in the North Atlantic, and deuterium excess derived from these variables using eq.(2).

FIGURE 6. Hysteresis curves of monthly deuterium excess and oxygen-18 values calculated for first fraction precipitation and climatic variables for the observation station in the North Atlantic at 40°N and 60°W .

FIGURE 7. Monthly deuterium excess versus monthly $\delta^{18}\text{O}$ in first-fraction precipitation at selected maritime stations in the North Atlantic. The values are calculated by eq.(2) and using data published by Lon (1984).

FIGURE 8. Plot of monthly deuterium excess versus monthly $\delta^{18}\text{O}$ for precipitation collected at GNIP stations along a transect from the Punta Delgata, Azores, to Vienna, Austria.

FIGURE 9. Plot of monthly $\delta^{18}\text{O}$ versus temperature (a) and monthly deuterium excess versus $\delta^{18}\text{O}$ for precipitation collected at GNIP stations along a transect from the Atlantic Ocean at Bermuda to Gimli, Manitoba and crossing the Great Lakes region. MWL refers to the meteoric water line. Numbers denote months of year.

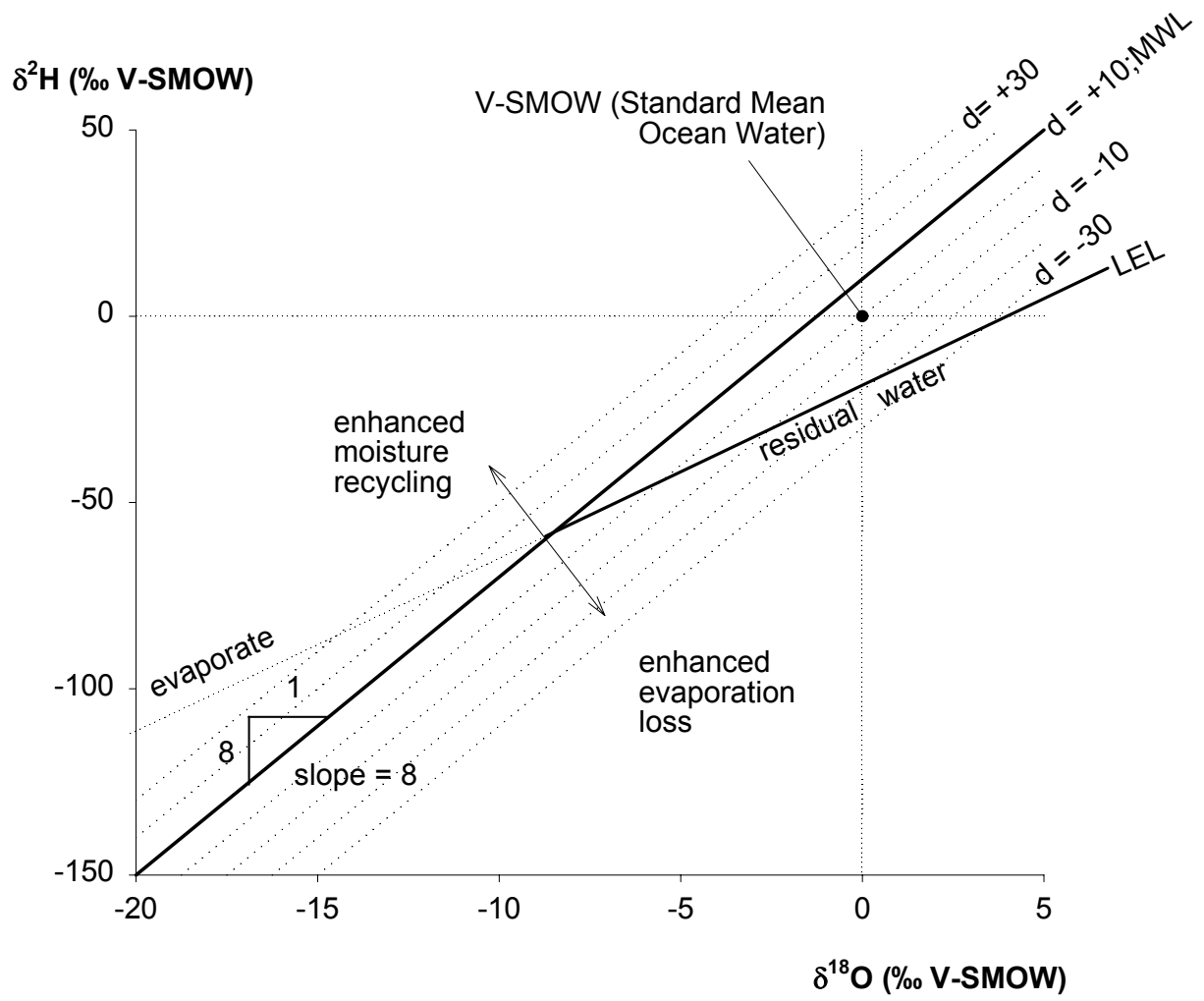


FIGURE 1.

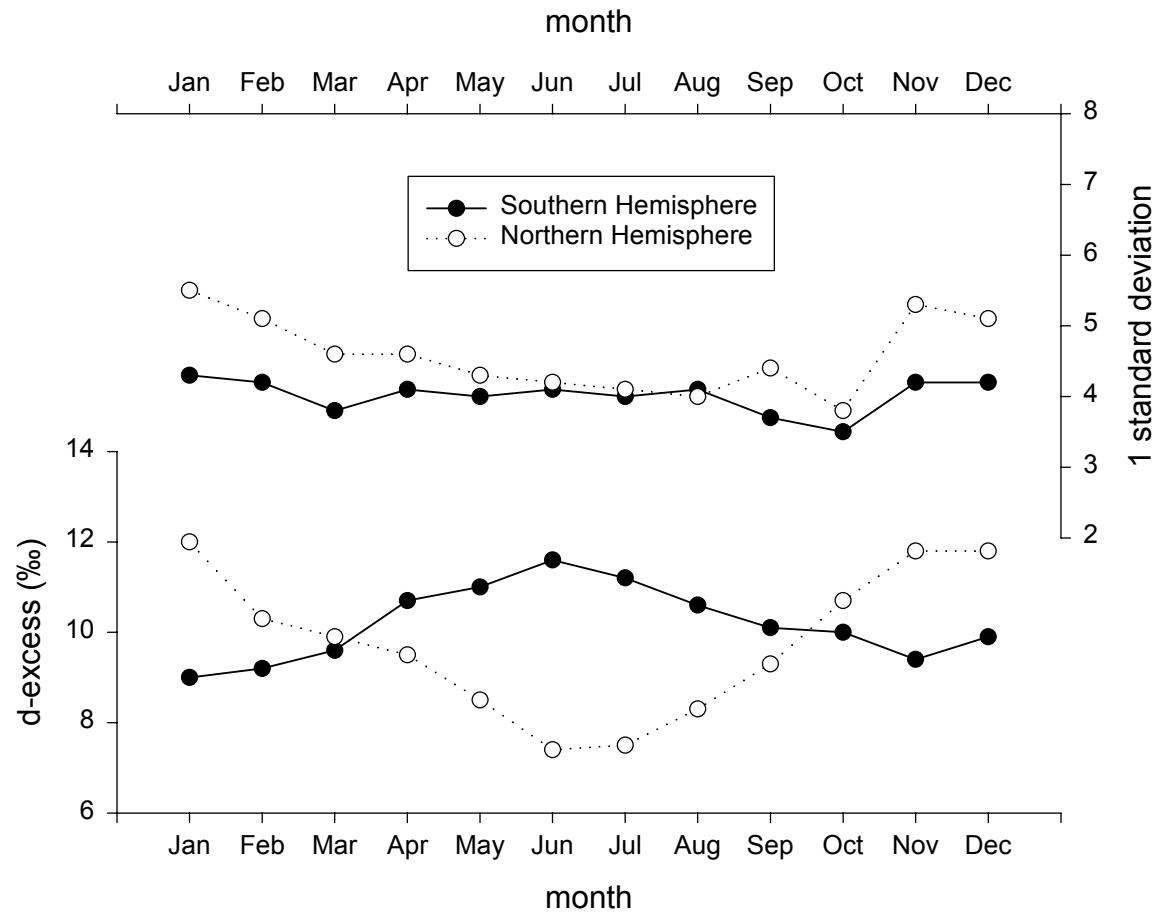


FIGURE 3.

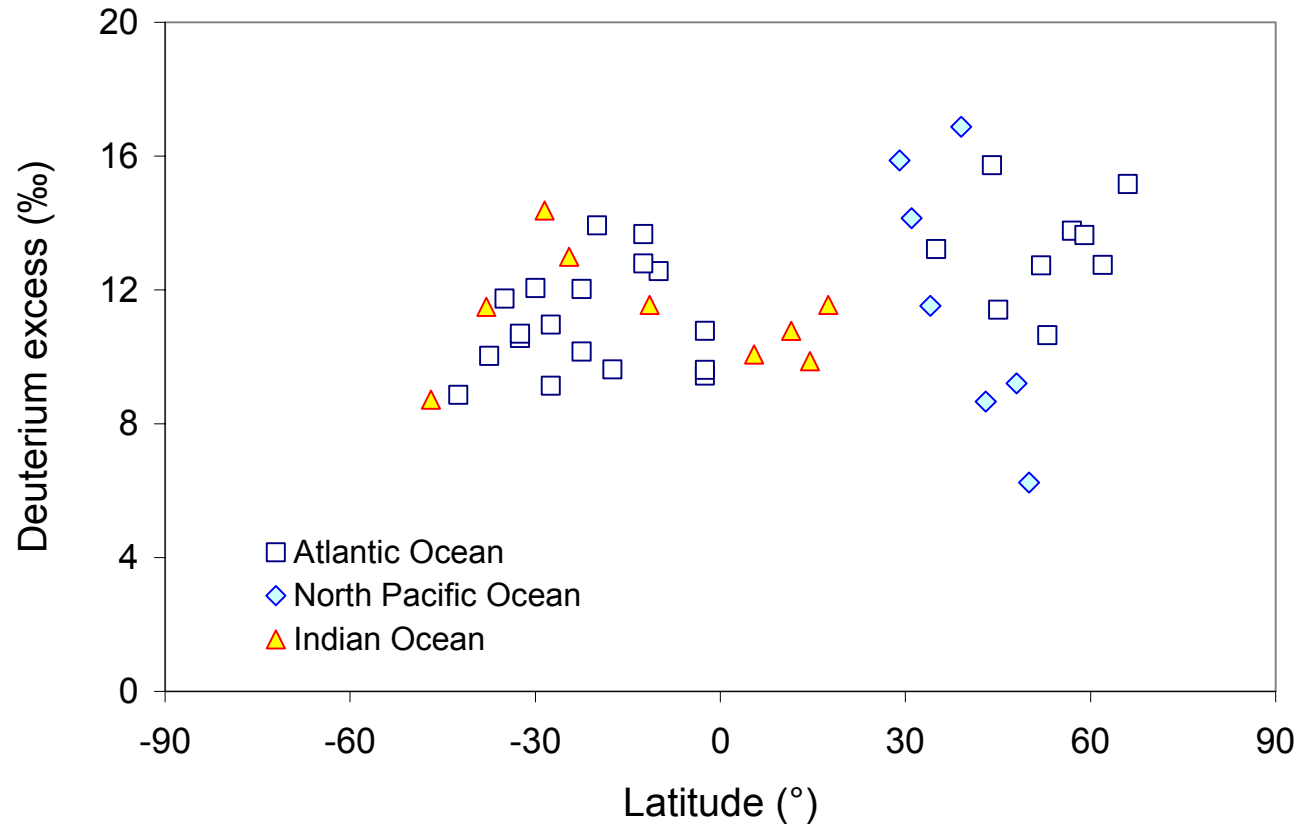


FIGURE 4.

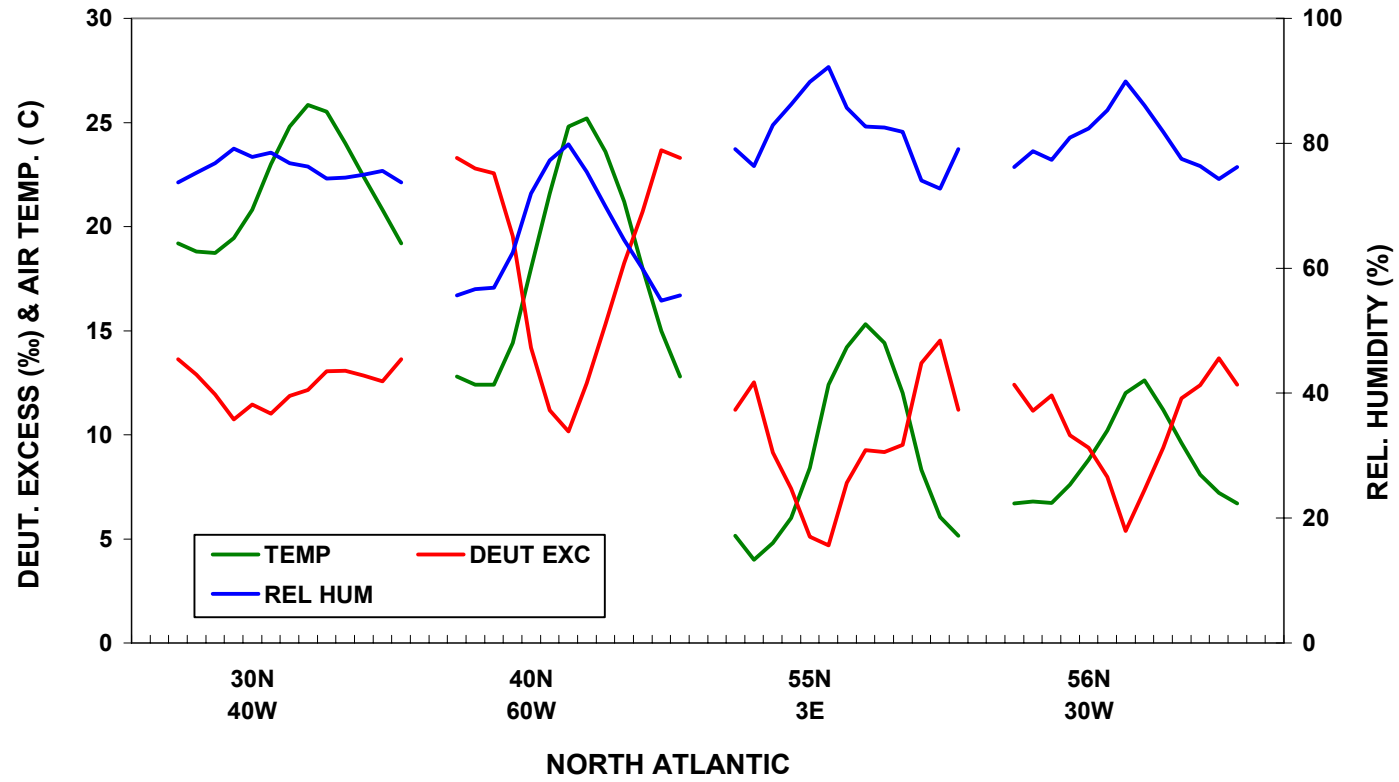


FIGURE 5.

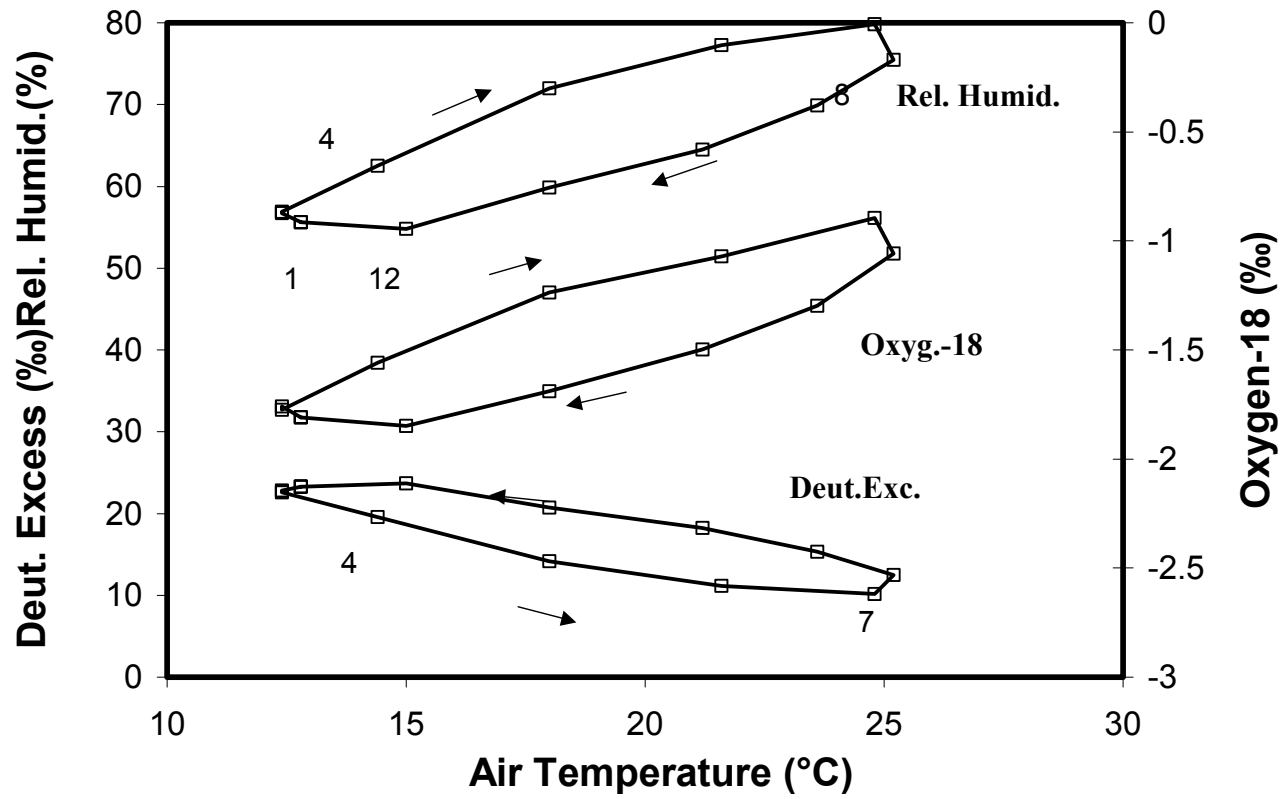


FIGURE 6.

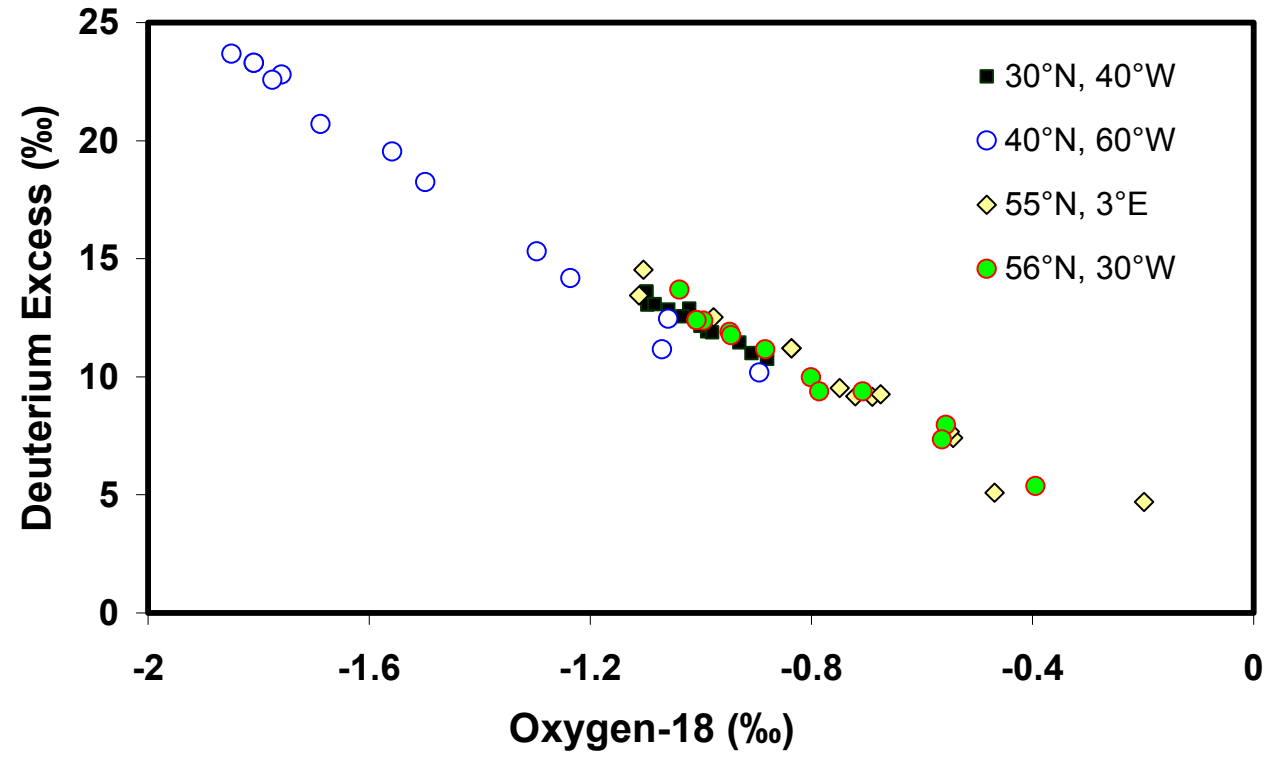


FIGURE 7.

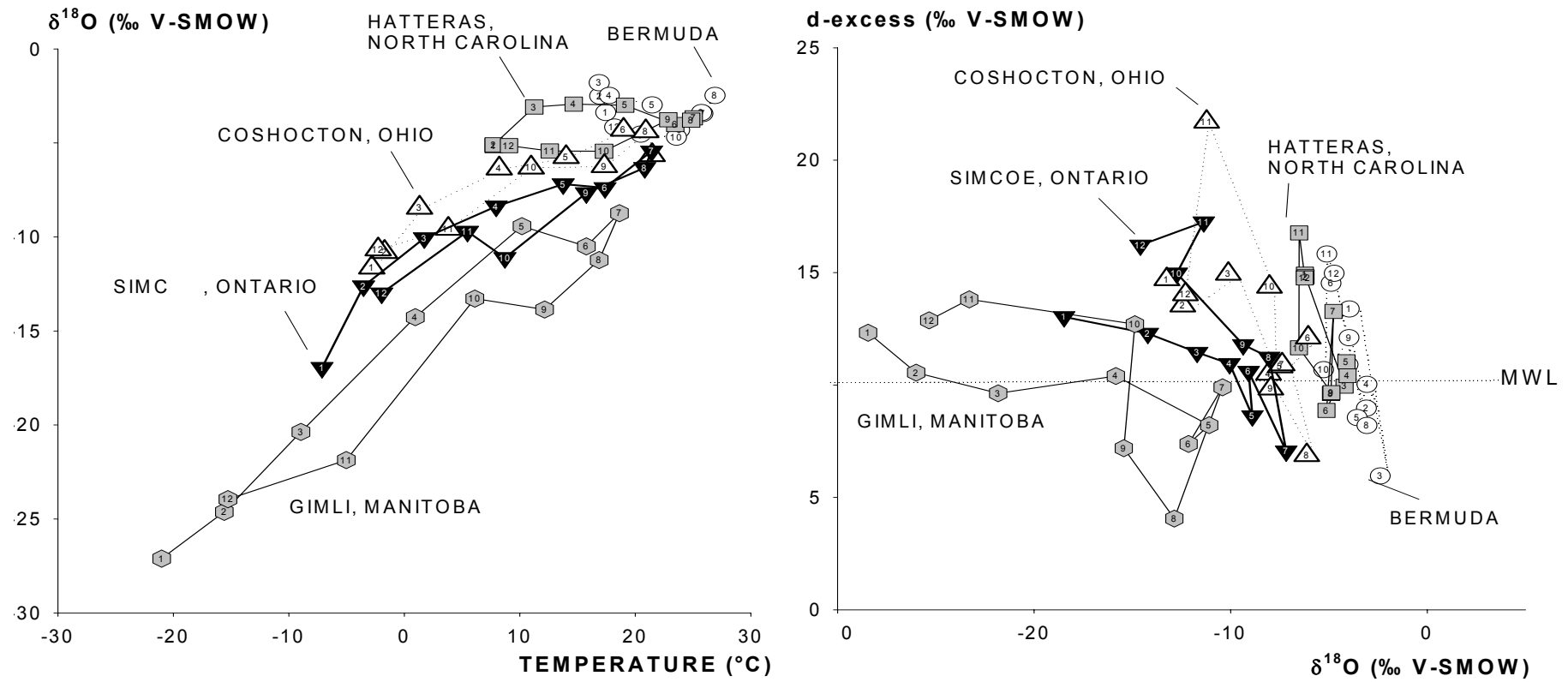


FIGURE 9.