Controls on Deuterium Excess Across Asia

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Abstract: Deuterium excess (d-excess) is a second-order stable isotope parameter measured in meteoric water to understand both the source of precipitation and the evolution of moisture during transport. However, the interpretation of d-excess patterns in precipitation is often ambiguous, as changes in moisture source and processes during vapor transport both affect d-excess in non-unique ways. This is particularly true in Asia where continental moisture travels a long distance across diverse environments from unique moisture sources before falling as precipitation. Here, I analyzed published d-excess records from meteoric water throughout Asia to better characterize what influences d-excess values. I conclude that, (1) an increase in d-excess values with elevation up the windward side of mountain ranges and a marked decrease in d-excess into their rain shadows are primarily related to subcloud evaporation as opposed to moisture source mixing; (2) high d-excess values (>10‰) associated with the eastern Mediterranean Sea are lowered across much of Central Asia by the addition of other moisture sources, both oceanic and recycled continental; (3) subcloud evaporation of raindrops is lowering d-excess values of precipitation (<10‰) throughout the relatively arid Tarim Basin, China; and (4) temporal changes in d-excess values of alpine glaciers do reflect spatio-temporal changes in moisture source, as these samples experience minimal variation in subcloud evaporation.

Keywords: stable isotope geochemistry; meteoric water; Central Asia; evaporation; hydrologic cycle; climate; paleoclimate

1. Introduction

While oxygen-18 ($\delta^{18}O$) and deuterium ($\delta D$) generally correlate with temperature at middle-to-high latitudes and with precipitation amount in many tropical regions, deuterium excess (d-excess) correlates with conditions at the oceanic source of precipitation [1], and is known to evolve during transport to the precipitation site [2]. Accordingly, d-excess is used to constrain both the source of precipitation and the conditions during vapor transport [3–6].

Deuterium excess (d-excess) is a function of the isotopic composition of oxygen ($\delta^{18}O$) and hydrogen ($\delta D$) in water (d-excess = $\delta D - 8 \times \delta^{18}O$) [7]. Isotopic ratios are expressed as $\delta$ values which are deviations in per mil (%) from a water standard (e.g., [8]). An “excess” of deuterium relative to $^{18}O$ in vapor (d-excess) occurs when water molecules diffuse across a density gradient during evaporation. A difference in the weight of a water molecule that contains deuterium ($H^1D^2O^{16} = 19$ g mol$^{-1}$) compared to heavy oxygen ($H^1H^1O^{18} = 20$ g mol$^{-1}$) results in more diffusive fractionation of heavy oxygen during evaporation. The more diffusion (kinetic fractionation) that occurs, the higher the deuterium excess observed in vapor (evaporated moisture).

The Global Network of Isotopes in Precipitation (GNIP) provides decades of d-excess data across the globe which is used to characterize the evolution of water through the hydrologic cycle [9,10]. The global average d-excess is 10‰ [11]. Synoptic-scale patterns of d-excess in meteoric water are significantly affected by the relative humidity (RH) at the vapor’s evaporative source [12,13], with the potential to constrain oceanic provenance. Higher d-excess values of vapor (and downwind...
precipitation) are observed when the RH is low over evaporating water bodies. This is why d-excess is generally higher in winter precipitation when the RH over oceans is low, and lower in summer precipitation when the RH over oceans is relatively high. Higher d-excess (>10‰) is also observed downwind of the eastern Mediterranean Sea, which exists in a relatively dry climate [14].

In addition, as raindrops fall through an unsaturated air column, evaporation occurs, lowering the d-excess values of raindrops that reach the ground [15,16]. This may obscure d-excess signatures that are related to the RH at the moisture source. Subcloud evaporation is reduced at high elevations where temperatures are low and raindrops fall a shorter distance. High-elevation precipitation in ranges surrounding the Tarim Basin, including the Himalaya, the Pamir, and Tian Shan (Figure 1), exhibit relatively high d-excess values (>15‰) which is attributed to both an eastern Mediterranean source and reduced subcloud evaporation [6,17], although the relative importance of each is not well understood.

Here, I compiled d-excess records from meteoric water across ranges in Asia to better characterize what causes changes in d-excess throughout the region. Spatial and temporal patterns show that both the moisture source and the local conditions influence d-excess values across the continent. I also documented patterns in d-excess along elevation transects to distinguish between the effect of subcloud evaporation and changes in moisture source in mountain precipitation. Lastly, I discussed how to more accurately interpret paleoclimate from d-excess in alpine glacier ice cores, and paleowater proxies from the rock record.

2. Empirical Observations of Deuterium Excess

Data presented in the following discussion are from the GNIP, supplemented by published data, particularly where GNIP spatial resolution is low (Supplementary Materials, Table S1). References are included therein.

2.1. Synoptic-Scale Spatial Patterns of Deuterium Excess

Synoptic-scale patterns of d-excess across Asia are widely interpreted to reflect changes in moisture source [6,17–20]. This is based on the observation that vapor derived from the eastern Mediterranean Sea has uniquely high d-excess values (~20‰) relative to the global average (~10‰; Figure 1). In Europe and Central Asia, higher d-excess values are often associated with this eastern-Mediterranean-derived precipitation that falls during later winter and spring. Conversely, low d-excess values (<10‰) are associated with summer precipitation derived from the Arctic, Indian, and Pacific Oceans. Annual weighted d-excess patterns in precipitation across Asia suggest Mediterranean influence extends eastward to Tehran, Kabul, and possibly Novosibirsk (all have mean d-excess values >10‰; Figure 1). Although Novosibirsk appears to be surrounded by relatively low d-excess values, it is likely part of the Mediterranean trend, as the interpolated surface to the southwest is influenced by a high number of relatively low values in the Tian Shan, which average ~8.1‰ (Supplementary Materials, Table S1). That said, with increasing distance eastward away from the Mediterranean, annual weighted d-excess gradually decreases, suggesting that westerly derived moisture is modified by local environmental conditions and/or mixing with moisture from other sources. For example, north of the Tibetan Plateau in the Tarim Basin, d-excess values of precipitation are <10‰ (Figure 1), likely due to enhanced subcloud evaporation of raindrops in this arid region [21]. This is consistent with low d-excess values of precipitation due to subcloud evaporation in the rain shadow of the Eastern Cordillera of South America, on the arid Andean Plateau [22].

Recycling of continental moisture also has an effect on the isotopic composition of both vapor and precipitation (e.g., [5,23,24]), and was shown to make up to 80% of precipitation in parts of Central Asia and the Tibetan Plateau [25–28]. The effect of local continental recycling is less predictable as it integrates the isotopic composition of surface water, which can be highly variable. That said, recycling may increase d-excess values of precipitation downwind, if accompanied by a progressive increase in the amount of recycled moisture and a decrease in relative humidity, as seen on the Tibetan Plateau [17].
2.2. Seasonal Patterns in Deuterium Excess

The observed pattern of d-excess values of precipitation becoming progressively lower east of the Mediterranean is also influenced by changes in the season of precipitation. Long-term weighted averages of d-excess in precipitation are generally low near the Arctic and Indian Oceans (Figure 1). Precipitation in those regions falls primarily during summer months, in contrast to the Mediterranean, where precipitation falls during the late winter and spring (Figure 2). This is consistent with global patterns of continental precipitation that show a seasonal change in d-excess from higher values in the winter to lower values in the summer [10]. For northern Asia, high relative humidity over the Arctic and Atlantic Oceans during the summer (Figure 3) results in relatively low d-excess values which extend westward across northern Europe (Figure 1). This seasonal distinction is also used to constrain the timing of evaporation for precipitation that falls in and around the Mediterranean Sea (e.g., [14,33,34]) and across Central Asia [20,35].
Figure 2. Map of the summer precipitation index, defined as the percentage of summer (May to October) precipitation over annual precipitation (1980–2010). Regions dominated by summer precipitation are closer to 100%, while regions dominated by winter precipitation are ∼0%. Seasonal precipitation data are from the National Oceanic Atmospheric Administration (NOAA) Earth System Research Laboratory’s (ESRL) Global Precipitation Climatology Centre (GPCC) full data reanalysis V6 combined at 1/4-degree resolution. The basemap is a hillshade raster image from Natural Earth.

Figure 3. Composite of Asia National Centers for Environmental Prediction (NCEP) / National Center for Atmospheric Research (NCAR) reanalysis data showing average relative humidity (RH) at 925 mb for summer months (A) and winter months (B) from 1980 to 2010. Note the high RH over the Indian Ocean in the summer compared to in the winter, and conversely, the low RH over Central Asia in the summer compared to in the winter. Image provided by the NOAA/ESRL Physical Sciences Division, Boulder Colorado [36,37].
A compilation of long-term averages of d-excess filtered by season suggests that the temporal evolution of d-excess is largely controlled by changes in RH over the oceans [12,13]. Across Asia, long-term d-excess averaged over winter months (November–April) minus summer months (May–October) is positive (average = 1.4‰), confirming that d-excess of meteoric water in the winter is generally more positive than in the summer (Figure 4). Conversely, the RH over the Indian and Arctic Oceans surrounding Asia is lower in the winter relative to in the summer (Figure 3). This is consistent with the interpretation that high RH over the oceanic source of vapor during the summer (Indian monsoon) minimizes evaporative diffusion, resulting in lower d-excess values in the summer vapor and precipitation [10]. It is also consistent with seasonal patterns of precipitation where high d-excess values are more associated with a wet winter and/or spring (Mediterranean), while low d-excess values are associated with wet summers (Siberia and the monsoon in India).

Across the Central-Asian interior, the difference between winter and summer d-excess is less pronounced. From the Tibetan Plateau northward to Siberia, summer d-excess is equal to or greater than winter d-excess. This may be due to a significant moisture contribution from continental recycling, as seasonal RH over land often shows the opposite trend to that observed over the oceans, with a higher RH in the winter relative to in the summer (Figure 3). In this case, evaporation of continental surface water during the summer under low-RH conditions might explain relatively high d-excess values in subsequent precipitation. An increase in the amount of continental recycled moisture inland has the potential to obscure unique oceanic moisture source signals.

Figure 4. Map of the difference between average winter and summer d-excess (winter–summer) where winter is defined as November–April, and summer is defined as May–October. Data are compiled from the GNIP [29], and are shown in Supplementary Materials, Table S1. Control points are shown as block dots, and represent an average of the total dataset available; therefore, years of integration vary from site to site. Seasonal averages were only calculated if at least 4/6 months were reported per season. This was not possible for sites with little-to-no seasonal precipitation (e.g., summer in Bahrain and Tashkent, or winter in Bombay and Central India). Interpolation was done using a spherical kriging algorithm in ArcGIS. The basemap is a hillshade raster image from Natural Earth.
2.3. Mountain-Scale Spatial Patterns in Deuterium Excess

The low spatial resolution of the GNIP station data in Central Asia precludes the interpretation of mountain-scale effects on d-excess. Studies that used a combination of data from precipitation, stream water, and ice cores in the Himalaya attributed relatively high d-excess values to moisture source partitioning by altitude, with relatively low-elevation precipitation in the Himalayan foothills brought by “monsoonal” southerlies sourced in the Indian Ocean (relatively low d-excess), and high-elevation snow brought by westerlies sourced in the Mediterranean Sea (relatively high d-excess) [6,18,38]. However, I argue that changes in d-excess with elevation observed across mountain ranges globally are more consistent with a universal process like subcloud evaporation rather than with moisture source mixing, which would likely be unique to each region.

In Asia, the effect of subcloud evaporation on d-excess is documented in river water up the windward (south) side of the Himalaya (Figure 5A). It is also observed in stream water up the north side of the Tian Shan (Figure 5B). In both cases, d-excess values increase with elevation up the windward side of the range. High-elevation raindrops evaporate less as they fall a shorter distance at colder temperatures in a wetter climate, resulting in a direct relationship between d-excess and elevation. The progressive orographic removal of moisture from an air mass (Rayleigh distillation) as temperature decreases is also predicted to increase d-excess values of precipitation downwind [39].

There is a sharp climatologic transition from the windward side of ranges into their rain shadow, which is often exceptionally dry. This transition normally occurs upwind of peak elevations, marked by a drop in precipitation. A transect across the Pamir Plateau shows this effect, as an initial decrease in d-excess values corresponds relatively well with a drop in precipitation, marking the beginning of a rain shadow upwind of peak elevations (Figure 5D). Downwind of the rain shadow, lower d-excess values and scattering are consistent with evaporation in an arid environment. In the case of Tibetan, Andean, and Pamir Plateaux, elevations remain high into the rain shadow (Figure 5A,C,D), so that temperatures and the cloud base stay low, both of which reduce subcloud evaporation. The Andes is the only transect shown that consists of precipitation samples (as opposed to surface water), and although the dataset is small, it does not show a reduction in d-excess or significant scattering in its rain shadow (Figure 5C). This suggests that surface-water evaporation is the dominant cause of d-excess variation on relatively arid plateaux, as surface-water samples are most affected. On the Tibetan Plateau, spatial patterns of surface-water d-excess generally correlate with precipitation (correlation coefficient = 0.44), and can be fully explained by Rayleigh distillation and evaporation, regardless of source [40]. For the Tian Shan, whose rain shadow is characterized by a drop in elevation (Figure 5B), a more significant decrease in d-excess is observed, likely because subcloud evaporation becomes significant. On the southern flank of the Tian Shan in the northern Tarim Basin (not shown in Figure 5), subcloud evaporation of raindrops was shown to average as much as 40%, resulting in a ~40‰ decrease in d-excess [21].

A similar trend is observed in precipitation samples down the western flank of the Andean Plateau into the hyperarid Atacama Desert of northern Chile [22,41].

Large-scale patterns of d-excess show that unique moisture sources do affect d-excess across Central Asia (Figure 1). However, within the continental interior, the effect is modest with d-excess variation less than 5‰ for sites of similar elevation but with different oceanic sources. Tashkent, Tajikistan (elevation = 445 m) receives moisture from the west (Mediterranean), and has an annual weighted d-excess of 13.1‰, while New Delhi, India (elevation 212 m) receives moisture from the Indian monsoon with an annual weighted d-excess of 8.7‰ (Supplementary Materials, Table S1). However, changes in d-excess associated with mountain ranges are much larger, varying by ~10‰ from low to high elevation (Figure 5). The influence of moisture source on d-excess across these ranges is likely minimal, as similar patterns of increasing d-excess values with elevation on the windward side of ranges is observed in precipitation up the Eastern Cordillera (northern Andean Plateau) in South America, where the source of moisture is not thought to vary (Figure 5C) [42]. The same phenomenon was also observed further south in Argentina [43], in the Pacific Northwest [44], and in the Alps [15,45]. This globally consistent pattern strongly suggests that elevated d-excess values observed at high
elevations throughout Asia are more related to a reduction in subcloud evaporation, rather than moisture source partitioning by elevation.

Figure 5. See Figure 1 for location of transects in Asia. (A) Elevation (latitudinal) transect from south to north up the Kali Gandaki in the Central Himalaya, showing d-excess values (black dots) of stream water samples published by Garzione et al. [46]. One stream-water sample’s anomalously high d-excess value was not included (sample # 99 kg 1 at 28.6‰). (B) Elevation (latitudinal) transect up the northern flank of the Tian Shan in Kyrgyzstan, showing d-excess values from stream-water samples [47]. (C) Elevation (longitudinal) transect up the eastern flank of the northern Andes (Eastern Cordillera), showing d-excess values from precipitation [39]. (D) Elevation (longitudinal) transect up the western flank of the Pamir Plateau in Tajikistan, showing d-excess values from stream-water samples [35]. For all transects, annual precipitation data (dashed curve) and elevation data (grey curve) are averaged over a 100-km swath perpendicular to the sampling transect. Precipitation data are from the GPCC with a resolution of 1/4 degrees [48]. Elevation data were generated from the National Aeronautics and Space Administration’s (NASA’s) Shuttle Radar Topography Mission (SRTM) at 30-arc-second (1/1200 degree) resolution [49].

3. Interpreting Paleoclimate from Deuterium excess

Deuterium excess was analyzed in paleowater preserved in ice cores from alpine glaciers throughout Asia. Temporal records from ice cores in Asia go back 10 s to 100 s of years, and show seasonal variability in d-excess, where high values are associated with Mediterranean-derived moisture and/or continental recycling, and low values are associated with Indian or Arctic Ocean-derived moisture and/or arid conditions that promote subcloud evaporation [5,50,51]. Because falling snow at high elevations does not evaporate much due to cold temperatures and a cloud base that is relatively close to the ground, seasonal changes in d-excess are more likely controlled by distinct moisture sources (oceanic and continental), as opposed to variations in subcloud evaporation. The observation that d-excess changes across mountain ranges by up to 5–10‰ (Figure 5) does not preclude the interpretation of moisture source from high-elevation snow. In fact, long-term changes in the dominant season of precipitation and balance of moisture source mixing for a given site were deduced from temporal records of d-excess evolution, regardless of the high spatial variability observed.
That said, caution should be exercised when interpreting changes in moisture source based on spatial variability across elevation transects, because subcloud evaporation is likely the main reason for these patterns. Kinetic effects during snow formation at extremely cold temperatures may also introduce variability [52].

Unlike ice, the rock record contains paleowater proxy material that can extend isotopic records back millions of years. Mineral proxies generally integrate environmental water over 100s to 10,000s of years, much longer than ice or modern water records. In addition, d-excess is not normally obtained from proxy material, as minerals are analyzed for either $\delta^{18}O$ or $\delta D$, whereas both are needed to calculate d-excess. There is a potential to combine proxies, such as $\delta^{18}O$ from carbonate and $\delta D$ from volcanic glass, to estimate ancient d-excess for a region (e.g., [53]), although considerable uncertainty is introduced by using different sample types for each element, as the number of variables that could affect results increases. That said, because d-excess is highly sensitive to mountain climatology, a multi-proxy approach may hold potential as a way of constraining the initiation of paleo-rain shadow development in and around the Tarim Basin, with implications for the timing of mountain formation and related geodynamic forcing mechanisms.

4. Conclusions

An analysis of d-excess across Asia suggests that the Mediterranean Sea significantly influences the isotopic composition of moisture in the Middle East, but its uniquely high d-excess source signal is lowered in much of Central Asia by the addition of other sources of moisture, both oceanic and recycled continental. Subcloud evaporation of raindrops is likely affecting d-excess in precipitation throughout the relatively arid Tarim Basin, where values are <10‰.

Consistent patterns of d-excess across mountain elevation transects on multiple continents suggest that an increase in values with elevation up the windward side of ranges and a marked decrease in d-excess into their rain shadows are primarily related to subcloud evaporation, as opposed to moisture source mixing, because the latter would likely be unique to each region. For the greater Himalaya, this elevation signal is likely accompanied by a change in the mixture of moisture sources from east to west, as westerlies become more influential [25,54]. Because d-excess is highly sensitive to local climate, data along elevation transects can be used to interpret the climatological transition from windward to lee (rain shadow) across catchments, which may be particularly useful where surface-water provenance is not well constrained.

Temporal changes in the d-excess values of alpine glacier ice core samples are likely to reflect spatio-temporal changes in the moisture source, as these samples experience minimal subcloud evaporation. However, water samples collected from a range’s rain shadow, from lower elevations, or with unknown provenance (as is the case for many paleowater proxy materials) should be interpreted with caution, as variable subcloud evaporation may significantly decrease d-excess values. When interpreting moisture source, focusing on the most positive d-excess values can help filter evaporative signals.

Supplementary Materials: The following is available online at http://www.mdpi.com/2076-3263/8/7/257/s1, Supplementary Table S1: Stable Isotope Data for Precipitation in Asia. This contains isotopic data used to create Figures 1 and 4.

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