

OXYGEN ISOTOPE CHANGES IN TROPICAL ICE, QUELCCAYA, PERU

P. M. Grootes and M. Stuiver

Quaternary Isotope Laboratory, University of Washington, Seattle

L. G. Thompson and E. Mosley-Thompson

Byrd Polar Research Center, Ohio State University, Columbus

Abstract. Low average $\delta^{18}\text{O}$ values and large seasonal variations in $\delta^{18}\text{O}$ in snow accumulating on the tropical Quelccaya ice cap in Peru can be quantitatively explained by a balance calculation of water vapor mass and isotopes. Important factors are (1) variations in air mass stability over the Amazon Basin, (2) the surface elevation of Quelccaya, and (3) seasonal changes over Quelccaya. Seasonal changes in evaporation of snow on the surface of the ice cap amplify the seasonal $\delta^{18}\text{O}$ cycle. Air circulation and air mass stability, rather than temperature, determine the seasonal $\delta^{18}\text{O}$ cycle at Quelccaya and, probably, at other low-latitude sites.

Introduction

The Quelccaya ice cap, Peru ($13^{\circ}56'\text{S}$, $70^{\circ}50'\text{W}$, elevation 5,670 m), is located in the easternmost glaciated mountain chain of the Peruvian Andes (Figure 1). Since 1976 it has been studied in detail for potential ice core paleoclimatic reconstruction [Thompson, 1980; Thompson et al., 1979, 1982, 1984 a, b, 1985, 1986]. Drilling to bedrock during the summer of 1983 yielded two long cores containing about 1500 years of accumulation [Thompson et al., 1985, 1986]. These cores have been analyzed for their microparticle content, conductivity, and the oxygen isotopic composition. Global significance of the record is clear from the correlation between the Quelccaya record and northern hemisphere temperature records from 1580 to 1975, showing the "Little Ice Age" [Thompson et al., 1986]. To interpret the oxygen isotope results of the long cores, the factors controlling the oxygen isotope signal preserved in this tropical ice cap must be identified.

Figure 2 shows three short Quelccaya $\delta^{18}\text{O}$ profiles. The oxygen isotopic composition is given as the relative deviation $\delta^{18}\text{O}$ of the isotopic abundance ratio $R = {}^{18}\text{O}/{}^{16}\text{O}$ of the sample from that of the standard mean ocean water (SMOW) of the International Atomic Energy Agency (IAEA) in Vienna (V): $\delta^{18}\text{O} = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}]$. The δ values are usually expressed in per mil units (‰). The most striking features in the oxygen isotopic composition of snow on Quelccaya are the strong ${}^{18}\text{O}$ depletion and the large seasonal cycle. The latter is surprising, in view of the small seasonal change in average surface temperature on Quelccaya (about 2°C ; Thompson et al., [1984a]). Moreover, ${}^{18}\text{O}$ depletion occurs during the wet southern hemisphere

summer and fall (November-April) and higher ${}^{18}\text{O}$ abundances are associated with winter precipitation (dry season). This seasonal ${}^{18}\text{O}$ pattern of the tropical Quelccaya ice cap is opposite to that frequently observed for middle and high latitudes, where the seasonal ${}^{18}\text{O}$ cycle correlates positively with the prominent summer-winter temperature cycle [Dansgaard, 1964; Rozanski et al., 1982].

The $\delta^{18}\text{O}$ record in the Quelccaya ice reflects (1) atmospheric processes between the oceanic source of water vapor and Quelccaya that determine the isotopic composition of snow deposited on the ice cap, and (2) local conditions determining how the depositional isotope signal is modified during firnification. The focus of this paper is on understanding the $\delta^{18}\text{O}$ signal deposited. For this reason, we discuss air circulation over Quelccaya, and the ${}^{18}\text{O}$ depletion that results from water vapor loss from the air in a Rayleigh condensation model. Isotopic alteration during firnification is briefly discussed.

Air Circulation Over Quelccaya

The location of Quelccaya on the crest of the Andes at 5670 m places it near the atmospheric 500-mbar level, which stands in this area around 5850 m [Chu and Hastenrath, 1982]. From June to September (winter), winds on Quelccaya are predominantly from the west or the northwest, while during the rest of the year winds are quite variable, with an increasing prevalence of tropical easterlies in summer [Thompson et al., 1984a].

In summer and fall (November-April), winds on Quelccaya are strongly influenced by the South American heat-low developed between about 15° and 30°S , 60° and 68°W just east of the Andes [Schwerdtfeger, 1976; Van Loon, 1972]. This low-level convergence brings humid, unstable Amazon air masses into central Brazil, near the Andes, on north to northwesterly winds [Ratisbona, 1976; Taljaard, 1972] (Figure 1). The Amazon air mass brings abundant precipitation. At the 500-mbar level the rising air leads to a divergence [Van Loon, 1972] and easterly flow across the Andes and Quelccaya. It forces westerlies connected with the southern polar vortex back to just south of the tropic [Ratisbona, 1976]. Abundant wet season (summer-fall) precipitation falls on Quelccaya from thunder-storms in these uplifted air masses.

In winter the low-level continental heat low is replaced by a small high-pressure cell. Westerly winds strongly predominate above 5000 m at the crest of the Andes, south of 10°S [Ratisbona, 1976]. These winds block airflow from the Amazon Basin to Quelccaya. The increasing importance of the west winds south of 10°S is mirrored by the increase with

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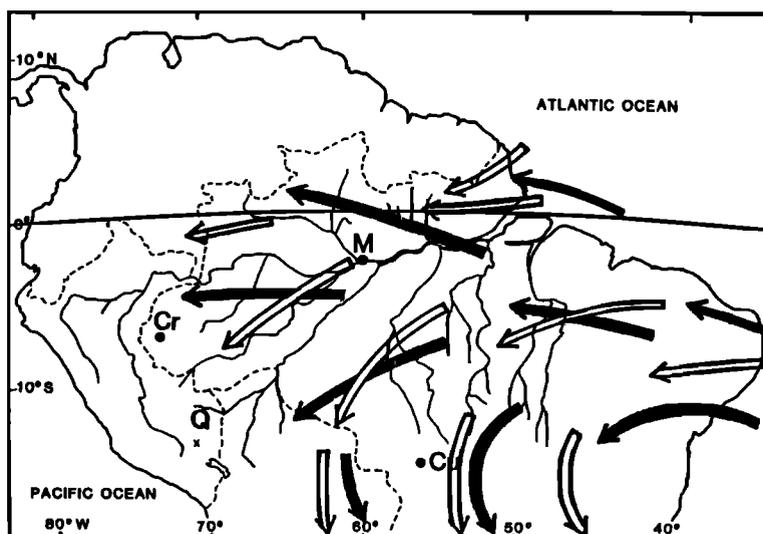


Fig. 1. Average low-level (1-3 km) flow patterns over southern tropical South America in summer (open arrows) and winter (solid arrows) [from Taljaard, 1972]. Q indicates Quelccaya; Cr, Cruzeiro do Sul; Cu, Cuiaba; M, Manaus.

latitude of the concentration of annual rainfall over the altiplano of southern Peru and Bolivia in the 6-month period November-April (summer-fall) [Johnson, 1976]. Field observations on Quelccaya over many dry seasons indicate that winter precipitation falls from convective disturbances in the lower-level air masses to the east that occasionally break through the westerly flow [Thompson et al., 1984a]. With the disappearance of the continental heat low in winter, a large part of central Brazil, extending to the Andes, comes under the influence of dry stable air and easterly winds from the Atlantic

anticyclone [Ratisbona, 1976; Taljaard, 1972] (Figure 1). Winter rainfall in this area is low or absent.

Field observations and the airflow pattern over tropical South America (Figure 1) thus indicate that the water vapor source areas for the isotopically quite different summer and winter precipitation on Quelccaya are both located over the tropical Atlantic Ocean to the east. The observed large $\delta^{18}\text{O}$ changes can be reconciled with the common source area and the small difference between average summer and winter temperature on Quelccaya by a balance calculation for water vapor mass and isotopes.

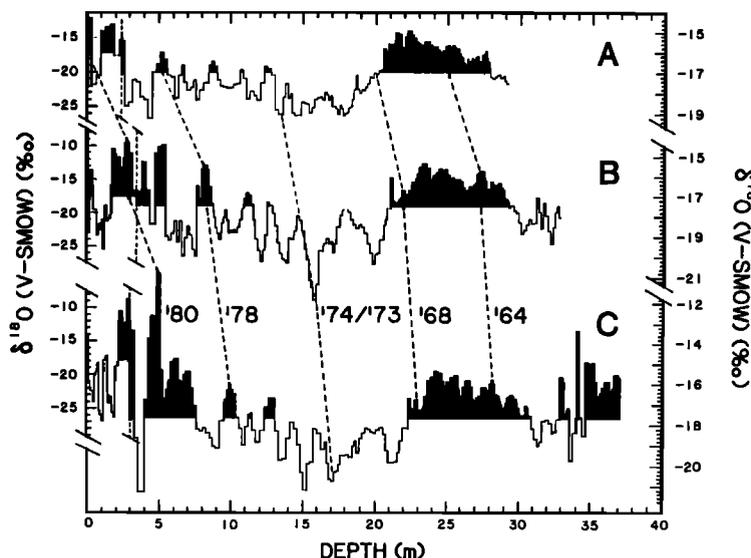


Fig. 2. Oxygen isotopic composition $\delta^{18}\text{O}$ as a function of snow depth on the Quelccaya ice cap, Peru. (a) Composition of 1980 crevasse wall and core samples; (b) 1981 core samples; and (c) 1982 core samples. The large-amplitude $\delta^{18}\text{O}$ cycle at the top of each profile is plotted on the $\delta^{18}\text{O}$ scale on the left. The remainder of the profile, to the right of the vertical dashed line, uses the right-hand scale. Shaded areas indicate $\delta^{18}\text{O}$ above average for each profile (Figure 1a, -17.1‰ ; Figure 1b, -17.6‰ ; Figure 1c, -17.7‰). Site A is a crevasse profile 1 km east of the summit at 5600 m above sea level. A time scale derived from dust layer snow stratigraphy is used for the time correlation.

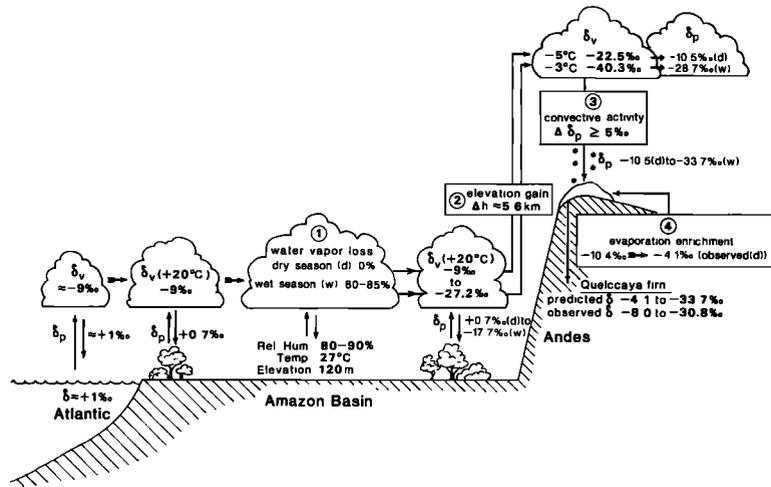


Fig. 3. Oxygen isotopic composition of atmospheric water vapor and precipitation from the tropical Atlantic Ocean across the Amazon Basin to Quelccaya. The ^{18}O depletion accompanying net water vapor loss from the air is calculated using a Rayleigh condensation equation (equation (1)). Step 1), Water vapor depletion over the Amazon Basin varies from 0% (dry season) to 85% (wet season), resulting in a seasonal $\delta^{18}\text{O}$ change in precipitation of up to 18.4‰ ; Step 2), a 5.6 km increase in surface elevation from the Amazon Basin to Quelccaya results in a $\delta^{18}\text{O}$ decrease in precipitation of about 11‰ ; Step 3), strong convection in summer showers can increase the range of the seasonal $\delta^{18}\text{O}$ cycle by at least 50‰ (-10.5 to -33.7‰). Enrichment of ^{18}O at the surface during the dry season may produce snow with $\delta^{18}\text{O} = -4.1\text{‰}$. The observed range of $\delta^{18}\text{O}$ values in snow pits (-8.0 to -30.8‰) and its phase agree with the predicted range of -4.1 to -33.7‰ .

Atmospheric Water Vapor Mass and Isotope Balance

The change of the isotopic composition of atmospheric water vapor, accompanying loss of water vapor from the air (precipitation minus evapotranspiration), is treated as a Rayleigh process [cf. Dansgaard, 1964; Rozanski et al., 1982]. This assumes that condensation occurs under equilibrium conditions and that the condensate is removed immediately. The relationship between the fraction F of the original amount of water vapor remaining in the air and the change in isotopic composition it has undergone is then given by the Rayleigh equation:

$$R/R_0 = F^{\alpha-1} \tag{1}$$

Here R and R_0 are the current and the original isotopic abundance ratio $^{18}\text{O}/^{16}\text{O}$ of the water vapor, respectively, and α is the isotopic fractionation factor of the water liquid-vapor (or ice-vapor) equilibrium. For comparison with the ^{18}O depletion observed in precipitation, the isotope ratio of the precipitation (R_p) has to be calculated from that of the vapor (R_v) via $R_p = \alpha R_v$. For convenience both isotope ratios are converted into their relative deviation δ from a standard (V SMOW) using:

$$\delta_v = F^{\alpha-1}(1 + \delta_{v0}) - 1 \tag{2}$$

$$\delta_p = \alpha(1 + \delta_v) - 1 \tag{3}$$

Here subscripts v and p indicate vapor and precipitation, and v_0 refers to the original water vapor. In the original water vapor over the ocean, $\delta_{v0} \approx -9\text{‰}$ for ^{18}O .

The Rayleigh process is an oversimplification of what goes on in a convective cloud system. Realistic

cloud models that consider various size water droplets and ice crystals as well as an admixture of outside air have been developed [e.g., Federer et al., 1982]. These models are, however, unsuitable to describe the effect that seasonal changes in water vapor balance over a large geographic area, such as the Amazon Basin, have on the monthly average isotopic composition of precipitation.

Dall'Olio et al. [1979] studying isotopic composition of precipitation in the Amazon Basin, and Rozanski et al. [1982], dealing with the same problem in Europe, used a Rayleigh process with the temperature at the 850-mbar level (corresponding to the average cloud base level) as the effective condensation temperature. This choice of temperature reflects the influence (through vapor and isotope exchange) of the lower region of the convective system on the isotopic composition of precipitation. Dall'Olio et al. [1979] found qualitative agreement between the calculated and the observed seasonal $\delta^{18}\text{O}$ cycle in precipitation in the Amazon Basin [cf. Salati et al., 1979]. Rozanski et al. [1982] obtained the correct δD change with increasing distance from the ocean in Europe (continentality effect) as well as realistic seasonal changes (temperature effect). The Rayleigh process apparently can provide an adequate description for our purposes. We use it to show that the observed $\delta^{18}\text{O}$ values in snow on Quelccaya can be obtained from water vapor from a single source area, that is, the tropical Atlantic Ocean. For the discussion we consider separately (1) the Amazon Basin up to the Andes, (2) the altitude effect, and (3) fractionation over Quelccaya. The results are summarized in Figure 3.

The Amazon Basin

The hydrometeorology of the Amazon Basin has been studied extensively to define the role of the

tropical rain forest in the hydrological cycle [e.g., Salati et al., 1979; Salati and Vose, 1984]. The influx of oceanic water vapor is only about half of the amount of rainfall over the Amazon Basin [Marques et al., 1977]. The remaining rainfall is water recycled through evapotranspiration of the tropical rain forest [Molion, 1975; Villa Nova et al., 1976; Salati et al., 1979; Lettau et al., 1979; Leopoldo et al., 1982]. In evapotranspiration, water is carried to the point of evaporation (leaf and/or soil surfaces) by plant vessels or soil capillaries. Therefore heavy isotope enrichment at the evaporating surface cannot reach the bulk of the water reservoir by mixing, and evapotranspiration proceeds without isotope fractionation [Eriksson, 1965].

In summer and fall (November-April), precipitation from convective showers over central Brazil, especially the Amazon Basin, may be double or triple the evapotranspiration of the rain forest [Dall'Olio et al., 1979]. The net water vapor loss from the air results in depletion of the heavy isotopes in the water vapor remaining and in precipitation. During June-August, rainfall is low or absent. No depletion of water vapor or isotopes occurs as precipitation is recycled by evapotranspiration.

To obtain the range of ^{18}O depletions of water vapor in air that passed over the Amazon Basin from the tropical Atlantic Ocean to the Andes, we need not repeat Dall'Olio's modeling. We can use in the Rayleigh equation (equation (1)) directly his estimates of the fraction F of the original amount of water vapor that leaves the Basin during different seasons (15-20% during the rainy period, close to 100% in the dry spring [Salati et al., 1979]). For α we use 1.00979, its value at 20°C calculated from Majoube [1971a]. This value is associated with the 850-mbar level at about 1500 m altitude near the cloud base [Salati et al., 1979; Rozanski et al., 1982; Saxena and Eriksson, 1985]. The relatively constant average temperature (27°C) and relative humidity (80-90%) in large parts of the Amazon Basin [Ratisbona, 1976] suggest that α can be taken constant from ocean to Andes. Equations (1) and (2) predict that the 15-20% of water vapor remaining during the wet season will be depleted in ^{18}O by 18.2-15.5‰, while depletion during the dry winter is virtually zero (Figure 3, see step 1).

The tropical ocean surface, source of the water vapor, has a $\delta^{18}\text{O}$ value of $\approx +1\text{‰}$ [Craig and Gordon, 1965]. Therefore the first rain to fall over the ocean will have a similar composition. The calculated seasonal variation in $\delta^{18}\text{O}$ in precipitation is from +0.7‰ (no vapor loss) to -17.7‰ (85% vapor loss). The calculated $\delta^{18}\text{O}$ range agrees with the range of monthly average $\delta^{18}\text{O}$ in precipitation observed at IAEA/World Meteorological Organization southwestern stations (Figure 1): Cuiaba, +5.2 to -15.8‰ over the years 1961-1982 [International Atomic Energy Agency, (IAEA) 1969, 1970, 1971, 1973, 1975, 1979, and IAEA unpublished results for the years 1976-1982], and Cruzeiro do Sul -2.0 to -14.9‰ over the years 1972-1975 (E. Salati, personal communication, 1984). The minimum $\delta^{18}\text{O}$ values correspond with F values of 0.18 and 0.20, respectively, compared with the estimated values of 0.15 to 0.20 used in our calculation. The high $\delta^{18}\text{O}$ value ($>+1\text{‰}$) at Cuiaba is attributable to enrichment in ^{18}O as raindrops fall through undersaturated air below the clouds during the dry season [Dansgaard, 1964; Stewart, 1975], an effect neglected in our model. A contribution of iso-

topically light wet season precipitation, stored in groundwater, to dry season evapotranspiration can lead at inland stations to dry season $\delta^{18}\text{O}$ values lower than those calculated [cf. Rozanski et al., 1982], since the calculation assumes that the isotopic composition of the water vapor recycled by evapotranspiration is the same as that of contemporaneous local precipitation. Calculated minimum $\delta^{18}\text{O}$ values are likely to be more extreme than the monthly means reported for $\delta^{18}\text{O}$ in precipitation at the IAEA/World Meteorological Organization stations. The seasonal alternation of abundant rains with light rain or drought, caused by the alternating dominance of humid unstable and dry stable air masses, respectively, results in a seasonal $\delta^{18}\text{O}$ cycle near the Andes with a phase and amplitude similar to the observed seasonal isotope cycle on the Quelccaya ice cap.

The "Altitude Effect"

As air rises, either in a convection cell or at a mountain range, it undergoes adiabatic cooling. This leads to precipitation and to depletion of the heavy isotopes. The isotopic "altitude effect" is independent of the source of the water vapor. The airflow patterns and field observations indicate that its isotopic change should be added to that occurring over Brazil just east of the Andes.

We use again the Rayleigh model (equation (1)) to calculate the ^{18}O depletion of the atmospheric water vapor and its precipitation. The calculation takes air at 27°C and 80-90% relative humidity in the Amazon Basin [Ratisbona, 1976] and cools it (adiabatically) to -3° to -5°C and 100% relative humidity at about 5700 m altitude (the elevation of Quelccaya) in temperature steps of 1°C. The fraction F of the original amount of water vapor remaining in the air ($F \leq 1$; equation (1)) is calculated as the ratio of saturated water vapor pressure to water vapor pressure without condensation. Empirical vertical profiles of average atmospheric temperature and pressure are used to calculate these quantities in an approach similar to that of Jouzel and Merlivat [1984] for precipitation in East Antarctica. The use of measured profiles eliminates the need to estimate the relative importance of adiabatic and isobaric cooling. The saturation pressure of water vapor in the air is obtained from the average temperature profile of the atmosphere over the east slope of the Andes in Peru and Ecuador [Johnson, 1976] and from tables of water vapor pressure as a function of temperature [Chemical Rubber Company, 1965]. The temperature profile used extrapolates to about -5°C at 5680 m, close to the average annual temperature of -3°C on the 5670 m Quelccaya ice cap [Thompson et al., 1984a]. The water vapor pressure after uplift without condensation follows from the pressure distribution of the tropical (15°N) supplemental standard atmosphere [Sissenwine, 1969]. Average values of α over each 1°C interval are calculated from Majoube [1971a].

We consider two sets of conditions for the $\delta^{18}\text{O}$ altitude effect: (1) a dry season with no ^{18}O depletion over the Amazon Basin, 80% relative humidity, and cooling from 27°C to -5°C; and (2) a wet season with 85% of the water vapor lost in the Amazon Basin, 90% humidity, and cooling from 27°C to -3°C. The altitude-related decrease in $\delta^{18}\text{O}$ in precipitation on Quelccaya defined by conditions (1) and (2) is

11.2‰ and 11.0‰, respectively. The altitude effect is thus practically independent of the seasons.

Values of α and vapor pressure for the liquid phase were also used below 0°C. This implies formation of snow by freezing of condensation droplets in the cloud. The direct transition from vapor to ice has a larger fractionation factor α [Majoube, 1971b] and therefore produces heavier snow from the same water vapor. This is at least partly offset by kinetic isotope fractionation at the surface of the ice crystal which favors the light isotopes [Jouzel and Merlivat, 1984]. Near 0°C both freezing of droplets and ice formation from vapor will occur, and for our calculation, which extends only to -3°C (or -5°C), the simplification of considering only liquid condensation will be allowed.

The combined effect of isotopic fractionation over the Amazon Basin and the altitude effect is a seasonal $\delta^{18}\text{O}$ cycle in precipitation, with values from -10.5‰ during the dry season to -28.7‰ during the wet summer and fall (November-April) (Figure 3; step 2). Measured $\delta^{18}\text{O}$ values in fresh snow of -13.8‰ in June 1981 and of -11.3, -11.1, and -10.4‰ in the June/July 1983 dry season agree with the calculated value. The altitude effect of about 11‰ and the predominance of wet season snow, isotopically light because of ^{18}O depletion over the Amazon Basin, cause the low average $\delta^{18}\text{O}$ values in Quelccaya snow.

Fractionation Over Quelccaya

Precipitation on Quelccaya falls from convective showers. Intense summer insolation [Johnson, 1976] results in strong uplift and cooling of the air in summer showers and in the precipitation of a larger fraction of the available atmospheric water vapor than in winter. This leads, as can be seen from (1) to (3), to both lower average and minimum $\delta^{18}\text{O}$ values in the summer snow. The seasonal insolation differences may thus amplify the seasonal $\delta^{18}\text{O}$ cycle already present in the water vapor reaching Quelccaya. The potential effect of shower intensity on the average δ value is demonstrated by the $\delta^{18}\text{O} = -9\text{‰}$, measured in precipitation from a particularly heavy shower at Manaus where most "normal" rain storms gave $\delta^{18}\text{O} = -4\text{‰}$ (E. Salati, personal communication, 1984). The last precipitation to fall from such a storm is strongly depleted in ^{18}O to produce the low average $\delta^{18}\text{O}$ value. The snow on Quelccaya will not only preserve the low average $\delta^{18}\text{O}$ of a summer shower but, until isotopic smoothing occurs, will also preserve the extreme depletion of its final precipitation. Even if just the average $\delta^{18}\text{O}$ value is considered, a summer shower with intense convection could produce snow with $\delta^{18}\text{O} = -33.7\text{‰}$, instead of the -28.7‰ calculated for the initial wet season precipitation over Quelccaya, based on Amazon Basin depletion and altitude (Figure 3; step 3).

Modification of the Depositional Isotope Signal

The isotopic composition of snow deposited on Quelccaya, discussed above, undergoes significant changes during firnification. At the surface these lead to ^{18}O enrichment and amplify the seasonal cycle. At greater depths, water vapor transport

and/or meltwater percolation increasingly smooth the isotopic signals. Firnification smoothing is outside the scope of this paper and will be discussed only briefly at the end.

Mass Loss and Isotopic Enrichment at the Surface

Hastenrath [1978] concluded from the approximate balance between daily totals of incoming shortwave and outgoing longwave radiation for the central part of the Quelccaya ice cap that nearly no energy was available for ablation. Yet the strong diurnal variation in incoming shortwave radiation (zero at night, up to a maximum of over 1000 Wm^{-2} during the day) and the fairly constant outgoing longwave radiation [Hastenrath, 1978] result in a strong diurnal temperature cycle in the upper firn. During the day, radiation energy is available near the surface of the firn for melting and evaporation. Energy loss at night cools the upper firn and sends a winter cold wave into the firn. The measured diurnal dry season temperature cycle (average of several 24-hour cycles) is from -2.6° to -20.6°C at 2 cm below the surface and from -9.4° to -11.2°C at 30-cm depth. Below 50 cm the diurnal temperature variations become insignificant, and temperatures increase with depth (-5.3° to -5.6°C at 1.0 m; -1.1° to -1.5°C at 2.8 m) to 0°C between 15- and 43-m depth [Thompson et al., 1984a, and unpublished data, 1984]. During the 1983 field season, meltwater was observed in the upper 6 cm of firn, but not at or below 12 cm depth. No data are available for conditions during the wet season. Modification of the isotope signal at and near the surface will occur mainly in the dry season, since a heavy cloud cover and frequent precipitation during the wet season will tend to reduce the diurnal temperature cycle as well as evaporation loss. Moreover, rapid accumulation will leave wet season snow near the surface for only a short time.

Isotopic enrichment of the surface layer of firn grains caused by evaporation fractionation can be distributed throughout the firn grains by isotopic diffusion [Whillans and Grootes, 1985]. Yet for rapid evaporation the speed of solid diffusion limits the enrichment that can be obtained. Meltwater, present near the surface mostly on grain surfaces, is well mixed and allows stronger average isotopic enrichment. Strong surface cooling during the night results in freezing of the meltwater and in transport of water vapor depleted in ^{18}O from underlying warmer layers to the surface. Large hoar-frost crystals can regularly be seen. Freezing occurs with isotopic fractionation, the ice being about 3‰ heavier than the water from which it forms [O'Neil, 1968; Souchez and Jouzel, 1984] and about 15‰ heavier than water vapor [Majoube, 1971b]. The result of freezing and sublimation is ice depleted in ^{18}O at the surface of the firn and on the outside of firn crystals. Enrichment of ^{18}O occurs inside the snow crystals and at some depth (5-20 cm) beneath the snow surface. Mass loss to the air during the day will first eliminate the outer ^{18}O depleted layers. Percolation of meltwater, enriched in ^{18}O by evaporation, during the day may add to the enrichment of the immediate subsurface layers. The large diurnal temperature cycle on Quelccaya with day temperatures at the surface near freezing during the dry season thus favors ^{18}O enrichment of the upper firn layer between the infrequent dry season snow showers. It

should be noted that even when dry season precipitation is lost by evaporation, dry season isotopic enrichment will create a layer with higher $\delta^{18}\text{O}$ values near the surface.

The ^{18}O enrichment is evident in a series of samples of surface snow on Quelccaya taken at various times after a fresh snowfall during June/July 1983. The samples show $\delta^{18}\text{O}$ increasing with time over a 12-day period from a value of -10.4 to -4.1 ‰. Evaporation enrichment of ^{18}O may thus be responsible for $\delta^{18}\text{O}$ values higher than those predicted by the altitude effect, like the -8 ‰ observed in a snow pit [Thompson et al., 1984a].

The Quelccaya Seasonal $\delta^{18}\text{O}$ Cycle

The possible range of $\delta^{18}\text{O}$ values in near-surface firn on the Quelccaya ice cap, estimated from measurements and from the four isotope fractionation steps discussed above, is from -4.1 to -33.7 ‰ (Figure 3; step 4). This range exceeds the observed seasonal extremes of -8 and -30.8 ‰ measured in Quelccaya snow pits [Thompson et al., 1984a]. The seasonal $\delta^{18}\text{O}$ cycle observed on Quelccaya is thus compatible with a common source for both winter and summer snow (the tropical Atlantic Ocean) and with the small seasonal temperature differences.

Of the four fractionation steps, only the change with altitude is well defined. An increase in relative humidity in the Amazon Basin from 80 to 90% decreases δ_p by 1.1 ‰ and 2°C cooling on Quelccaya likewise decreases δ_p by 1.1 ‰. This is the typical range of humidity and temperature observed. In the change from wet season to dry season, the two effects almost cancel. The calculated δ_p change over the Amazon Basin depends critically on the choice of the fraction F of the original water vapor leaving the Basin. A decrease in F from 0.20 to 0.15 increases depletion by 2.7 ‰. The minimum $\delta^{18}\text{O}$ values reported for Cuiaba and Cruzeiro do Sul point toward 0.15 as a reasonable choice to determine the maximum range of δ values. The local $\delta^{18}\text{O}$ depletion that may occur in the last phase of a wet season intense thundershower over Quelccaya is quite uncertain. This is not particularly serious for our range estimate, since the extra range of 2.1 ‰ needed to match the -28.7 ‰ from steps 1 and 2 with the observed -30.8 ‰ is well within realistic limits. Thus the Quelccaya $\delta^{18}\text{O}$ values can be described by our model.

We can use our model in reverse to derive the average atmospheric water vapor balance from observed average Quelccaya $\delta^{18}\text{O}$ values. The average $\delta^{18}\text{O}$ of the three profiles in Figure 2 is -17.5 ‰. Since we calculated $+0.7$ ‰ for coastal precipitation, the depletion is 18.2 ‰. Assuming negligible influence of dry season snow and surface enrichment on the annual average $\delta^{18}\text{O}$ value leads to an 18.2 ‰ total depletion, of which 11 ‰ is due to the wet season altitude effect (water vapor remaining: $F = 0.32$). If the additional 7.2 ‰ depletion occurs over the Amazon Basin, then an average of about 48% of the original water vapor reached the Andean foothills near Quelccaya during the period 1960-1980, and about 15% of it reached the ice cap. If no depletion were to occur over the Amazon Basin and the full 7.2 ‰ were caused by depletion over Quelccaya,

then the 7.2 ‰ depletion would require a remaining fraction of 46% and the final fraction at Quelccaya would also be 15%. Evidently, the ^{18}O depletion is little affected by the geographical location of the depletion. Weighted average annual $\delta^{18}\text{O}$ values at Manaus and Cuiaba of -5.68 ‰ and -5.26 ‰, respectively [International Atomic Energy Agency, (IAEA), 1981] suggest $F = 0.52$ at Manaus and $F = 0.54$ at Cuiaba. Thus most of the depletion leading to the average $F = 0.48$ calculated from Quelccaya firn must have occurred over the Amazon Basin. If isotopically heavy dry season snow makes a non negligible contribution to the total accumulation on Quelccaya and/or if near-surface enrichment increases the annual average $\delta^{18}\text{O}$, the wet season F values will have to be lower.

Firnification

Considerable smoothing of the $\delta^{18}\text{O}$ signal between the surface and the firn-ice transition at about 20-m depth reflects present climatic conditions on Quelccaya. Percolation of meltwater was not observed at or below 12-cm depth and thus does not contribute to isotopic smoothing at depth under the winter weather conditions observed. Therefore diffusion of water vapor in the pore spaces is mainly responsible for vertical mixing and the smoothing of the isotopic signal [Johnsen, 1977; Whillans and Grootes, 1985]. Smoothing is rapid at temperatures near freezing, as found on Quelccaya, as a result of the relatively high water vapor pressures. The observed diurnal temperature cycle creates strong and varying temperature gradients in the upper 50 cm of firn. In conjunction with dynamic pressure fluctuations in the firn [Clarke et al., 1987], these gradients accelerate vapor mass transport and isotopic mixing near the surface. The presence of meltwater near the surface and the diurnal temperature cycle detectable down to about 50 cm indicate that firnification conditions in the upper meter of firn may vary rapidly with weather conditions on the ice cap and that smoothing by percolating meltwater cannot be excluded, based on the limited field observations available.

More data are needed to obtain a quantitative understanding of the smoothing process and to determine, for example, what caused a section with less $\delta^{18}\text{O}$ variability and higher average $\delta^{18}\text{O}$ values like the one between about 20- and 30-m depth in Figure 2. Possible causes include (1) less wet season precipitation; (2) wet season precipitation less depleted in ^{18}O , and (3) increased dry season smoothing and evaporation enrichment. These causes may become separable based on differences that they generate in the $\delta\text{D}/\delta^{18}\text{O}$ relation, the microparticle content, and the chemical content of the ice.

Large seasonal $\delta^{18}\text{O}$ fluctuations are present in the cold ice below 43 m [Thompson et al., 1986]. Evidently, smoothing varies with time and was substantially less in the past under cooler conditions (Little Ice Age).

Conclusions

The main factors influencing the isotope record on Quelccaya are (1) the duration and relative strength of the continental heat low over South America determining the Quelccaya wet season; (2)

the atmospheric water vapor balance over central Brazil, especially over the Amazon Basin; (3) the surface elevation of the ice cap; and (4) the local climate over the ice cap, influencing both the isotopic signal deposited and its subsequent modification during firnification.

Interpretation of the large changes in $\delta^{18}\text{O}$ on Quelccaya in terms of surface temperature change gives unrealistic results. A seasonal $\delta^{18}\text{O}$ cycle of about 20‰ would require on Quelccaya a wet season/dry season temperature difference of 20° - 25°C, instead of the observed annual range of 2°C [Thompson et al., 1984a].

Understanding of the quantitative relationships between isotopic smoothing and local climate is needed before changes in the isotope record related to smoothing, like those observed at Quelccaya between the upper 43 m and the cold ice below it, can be interpreted properly. The oxygen isotope profile of the Quelccaya ice cap records past changes in the seasonal pattern of large scale airflow and air mass stability, as well as changes in local climate that affect firnification. The same holds probably true for other low-latitude isotope records and, to some extent, also for mid-latitudes.

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References

- Chemical Rubber Company, Handbook of Chemistry and Physics, 46th ed., pp. D93-D94, Cleveland, Ohio, 1965.
- Chu, P. S., and S. Hastenrath, Atlas of Upper-Air Circulation Over Tropical South America, University of Wisconsin, Madison, 1982.
- Clarke, G. K. C., D. A. Fisher, and E. D. Waddington, Wind pumping: A potentially significant heat source in ice sheets, The Physical Basis of Ice Sheet Modelling, edited by E. D. Waddington and J. S. Walder, IAHS Publ., 170, 169-180, 1987.
- Craig, H., and L. I. Gordon, Deuterium and oxygen-18 variations in the ocean and marine atmosphere, in Stable Isotopes in Oceanographic Studies and Paleotemperatures, edited by E. Tongiorgi, Consiglio Nazionale delle Ricerche, Rome p. 9-130, 1965.
- Dall'Olio, A., E. Salati, C. T. Azevedo, and E. Matsui, Modelo de fracionamento isotópico da água na bacia Amazônica: Primeira aproximação, Acta Amazonica, 2, 675-687, 1979.
- Dansgaard, W., Stable isotopes in precipitation, Tellus, 16, 436-468, 1964.
- Eriksson, E., Deuterium and oxygen-18 in precipitation and other natural waters. Some theoretical considerations, Tellus, 17, 498-512, 1965.
- Federer, B., N. Brichet, and J. Jouzel, Stable isotopes in hail stones, I, The isotopic cloud model, J. Atmos. Sci., 39, 1323-1335, 1982.
- Hastenrath, S., Heat-budget measurements on the Quelccaya ice cap, Peruvian Andes, J. Glaciol., 20, 85-97, 1978.
- International Atomic Energy Agency, Environmental Isotope Data No. 1: World Survey of Isotope Concentration in Precipitation (1953-1963), Tech. Rep. Ser., 96, IAEA, Vienna, Austria, 1969.
- International Atomic Energy Agency, Environmental Isotope Data No. 2: World Survey of Isotope Concentration in Precipitation (1964-1965), Tech. Rep. Ser., 117, IAEA, Vienna, Austria, 1970.
- International Atomic Energy Agency, Environmental Isotope Data No. 3: World Survey of Isotope Concentration in Precipitation (1966-1967), Tech. Rep. Ser., 129, IAEA, Vienna, Austria, 1971.
- International Atomic Energy Agency, Environmental Isotope Data No. 4: World Survey of Isotope Concentration in Precipitation (1968-1969), Tech. Rep. Ser., 147, IAEA, Vienna, Austria, 1973.
- International Atomic Energy Agency, Environmental Isotope Data No. 5: World Survey of Isotope Concentration in Precipitation (1970-1971), Tech. Rep. Ser., 165, IAEA, Vienna, Austria, 1975.
- International Atomic Energy Agency, Environmental Isotope Data No. 6: World Survey of Isotope Concentration in Precipitation (1972-1975), Tech. Rep. Ser., 192, IAEA, Vienna, Austria, 1979.
- International Atomic Energy Agency, Statistical Treatment of Environmental Isotope Data in Precipitation, Tech. Rep. Ser., 206, IAEA, Vienna, Austria, 1981.
- Johnsen, S. J., Stable isotope homogenization of polar firn and ice, Isotopes and Impurities in Snow and Ice, IAHS Publ., 118, 210-219, 1977.
- Johnson, A. M., The climate of Peru, Bolivia, and Ecuador, in World Survey of Climatology, vol. 12, Climates of Central and South America, edited by W. Schwerdtfeger, pp. 147-188, Elsevier-Science, New York, 1976.
- Jouzel, J., and L. Merlivat, Deuterium and oxygen-18 in precipitation: Modeling of the isotope effects during snow formation, J. Geophys. Res., 89, 11,749-11,757, 1984.
- Leopoldo, P. R., W. Franken, and E. Salati, Balanco hídrico de pequena bacia hidrográfica em floresta amazônica de terra firme, Acta Amazonica, 12, 333-337, 1982.
- Lettau, H., K. Lettau, and L. C. B. Molion, Amazonia's hydrologic cycle and the role of atmospheric recycling in assessing deforestation effects, Mon. Weather Rev., 107, 227-239, 1979.
- Majoube, M., Fractionnement en oxygène 18 et en deutérium entre l'eau et sa vapeur, J. Chim. Phys., 68(10), 1423-1436, 1971a.
- Majoube, M., Fractionnement en ^{18}O entre la glace et la vapeur d'eau, J. Chim. Phys., 68(4), 625-636, 1971b.
- Marques, J., J. M. dos Santos, N. A. Villa Nova, and E. Salati, Precipitable water and water vapor flux between Belem and Manaus, Acta Amazonica, 7, 355-362, 1977.
- Molion, L. C. B., A climatonic study of the energy and moisture fluxes of the Amazonas basin with considerations of deforestation effects, Ph.D. thesis 133 pp., Univ. of Wis., Madison, 1975.

- O'Neil, J. R., Hydrogen and oxygen isotope fractionation between ice and water, *J. Phys. Chem.*, **72**, 3683-3684, 1968.
- Ratisbona, L. R., The climate of Brazil, in *World Survey of Climatology*, vol. 12, *Climates of Central and South America*, edited by W. Schwerdtfeger, pp. 219-293, Elsevier-Science, New York, 1976.
- Rozanski, K., C. Sonntag, and K. O. Münnich, Factors controlling stable isotope composition of European precipitation, *Tellus*, **34**, 142-150, 1982.
- Salati, E., and P. B. Vose, Amazon Basin: A system in equilibrium, *Science*, **225**, 129-138, 1984.
- Salati, E., A. Dall'Olio, E. Matsui, and J. R. Gat, Recycling of water in the Amazon Basin: An isotopic study, *Water Resour. Res.*, **15**, 1250-1258, 1979.
- Souchez, R. A., and J. Jouzel, On the isotopic composition in δD and $\delta^{18}O$ of water and ice during freezing, *J. Glaciol.*, **30**, 369-372, 1984.
- Saxena, R. K., and E. Eriksson, Hydrometeorological interpretation of isotopic data on atmospheric moisture and precipitation, *Ann. Glaciology*, **7**, 181-184, 1985.
- Schwerdtfeger, W., Introduction: The atmospheric circulation over Central and South America, in *World Survey of Climatology*, vol. 12, *Climates of Central and South America*, edited by W. Schwerdtfeger, pp. 1-12, Elsevier-Science, New York, 1976.
- Sissenwine, N., Standard and supplemental atmospheres, in *World Survey of Climatology*, vol. 4, *Climate of the Free Atmosphere*, edited by D. F. Rex, pp. 5-44, Elsevier-Science, New York, 1969.
- Stewart, M. K., Stable isotope fractionation due to evaporation and isotopic exchange of falling water drops: Applications to atmospheric processes and evaporation of lakes, *J. Geophys. Res.*, **80**, 1133-1146, 1975.
- Taljaard, J. J., Synoptic meteorology of the southern hemisphere, *Meteorology of the Southern Hemisphere*, edited by C. W. Newton, *Meteorol. Monogr.*, **13**, 139-213, 1972.
- Thompson, L. G., Glaciological investigations of the tropical Quelccaya Ice Cap, Peru, *J. Glaciol.*, **25**, 69-84, 1980.
- Thompson, L. G., S. Hastenrath, and B. M. Arno, Climatic ice core records from the tropical Quelccaya Ice Cap, *Science*, **203**, 1240-1243, 1979.
- Thompson, L. G., J. F. Bolzan, H. H. Brecher, P. D. Kruss, E. Mosley-Thompson, and K. C. Jezek, Geophysical investigations of the tropical Quelccaya Ice Cap, Peru, *J. Glaciol.*, **28**, 57-69, 1982.
- Thompson, L. G., E. Mosley-Thompson, P. M. Grootes, M. Pourchet, and S. Hastenrath, Tropical glaciers: Potential for ice core paleoclimatic reconstructions, *J. Geophys. Res.*, **89**, 4638-4646, 1984a.
- Thompson, L. G., E. Mosley-Thompson, and B. M. Arno, El Niño-Southern Oscillation events recorded in the stratigraphy of the tropical Quelccaya Ice Cap, Peru, *Science*, **226**, 50-53, 1984b.
- Thompson, L. G., E. Mosley-Thompson, J. F. Bolzan, and B. R. Koci, A 1500-year record of tropical precipitation in ice cores from the Quelccaya Ice Cap, Peru, *Science*, **229**, 971-973, 1985.
- Thompson, L. G., E. Mosley-Thompson, W. Dansgaard, and P. M. Grootes, The "Little Ice Age" as recorded in the stratigraphy of the tropical Quelccaya Ice Cap, *Science*, **234**, 361-364, 1986.
- Van Loon, H., Pressure in the southern hemisphere, *Meteorology of the Southern Hemisphere*, edited by C. W. Newton, *Meteorol. Monogr.*, **13**, 59-86, 1972.
- Villa Nova, N. A., E. Salati, and E. Matsui, Estimativa da evapotranspiração na Bacia Amazônica, *Acta Amazonica*, **6**, 215-228, 1976.
- Whillans, I. M. and P. M. Grootes, Isotopic diffusion in cold snow and firn, *J. Geophys. Res.*, **90**, 3910-3918, 1985.

P. M. Grootes and M. Stuiver, Quaternary Isotope Laboratory, University of Washington, Seattle, WA 98195.

E. Mosley-Thompson and L. G. Thompson, Byrd Polar Research Center, Ohio State University, Columbus, OH 43210.

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