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ON THE VARIATIONS OF THE ISOTOPIC COMPOSITION
OF PRECIPITATION AND OF GROUNDWATER
DURING THE QUATERNARY AS A CONSEQUENCE
OF CLIMATIC CHANGES
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

The present publication includes most of the papers presented at the Advisory Group Meeting on the Variations of the Isotopic Composition of Precipitation and of Groundwater during the Quaternary as a Consequence of Climatic Changes, which was held in Vienna at the IAEA Headquarters from 25 to 28 November 1980. J.R. Gat, of the Weizmann Institute of Science, Rehovot, Israel, chaired the meeting, which was attended by 26 participants from 13 countries and one international organization in addition to the participants of the hosting organization. The list of participants is given at the end of this book.

The scope of the meeting was two-fold, that is to evaluate the use of isotope techniques for palaeoclimatological investigations, and for the identification of palaeogroundwater.

In recent years, considerable progress has been made in the comprehension of isotopic variations of precipitation. A number of models have been proposed to explain the isotopic composition of precipitation in different climatic conditions. Therefore, if one knows the isotopic composition of precipitation in the past – which can be obtained from polar ice cores, freshwater carbonates and organic matter – one should be able to formulate hypotheses on past climates. From the opposite point of view, knowing the climatic conditions occurring now and in the past at a given place, one should be able to evaluate the present and the past isotopic composition of precipitation.

The palaeoclimatic changes discussed at the meeting were limited to those that occurred during the late Pleistocene and the Holocene, i.e. the period beginning with the last glaciation approximately 70 000 years ago. This period is the one investigated in the most detail and the best known by other methods. In addition it is probably during humid periods which occurred within this time that some large aquifers in arid areas were recharged. Thus we come to the second of the objectives listed above, which has important hydrogeological aspects and practical implications.

One of the major hydrogeological problems in arid areas is whether groundwater is recent or not, i.e. whether there is modern recharge and how this can be distinguished from water recharged thousands of years ago; therefore, the identification of palaeogroundwater with isotope techniques is a major contribution to the evaluation of groundwater resources in many arid countries. This has practical implications, for instance on the exploitation rate of groundwater resources, with consequences on the present and future living conditions of local populations. Any activity in this field is therefore important for many developing countries and is in line with the conclusions and the recommendations formulated at the United Nations Water Conference in Mar del Plata in 1976.

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CONTENTS

ISOTOPIC COMPOSITION OF NATURAL WATERS AND CLIMATE (Section 1)

ISOTOPIC COMPOSITION OF ORGANIC SUBSTANCES (Section 2)

ISOTOPIC COMPOSITION OF SEDIMENTS (Section 3)

ISOTOPIC COMPOSITION OF PALAEOGROUNDWATERS (Section 4)

ISOTOPIC COMPOSITION OF NATURAL WATERS AND CLIMATE

(Section 1)

PRECIPITATION, GROUNDWATER AND SURFACE WATERS

Control of climate parameters on their isotopic composition and their utilization as palaeoclimatological tools

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Abstract

PRECIPITATION, GROUNDWATER AND SURFACE WATERS: CONTROL OF CLIMATE PARAMETERS ON THEIR ISOTOPIC COMPOSITION AND THEIR UTILIZATION AS PALAEOCLIMATOLOGICAL TOOLS.

The isotopic composition of precipitation is correlated with climatic parameters such as mean temperature and humidity both in the source areas of the atmospheric moisture and along the storm trajectories. However, additional meteorological variables such as seasonal distributions of rainfall, convection patterns in the cloud and intensity, duration and intermittency of rain influence the isotopic composition. It is shown in this context that the isotopic composition of Negev and Sinai palaeowaters is consistent with the notion of summer rains in this area arising from Atlantic-based storm centres.

1. INTRODUCTION

The reconstruction of palaeo-environments on the basis of the isotopic composition of environmental materials such as lake sediments [1, 2], speleothems [3], land snails [4], glacier ice [5] or palaeowater sources [6, 7] relies in the final analysis on some correlation between the isotopic composition of meteoric waters and climate parameters such as temperature and humidity. Because of the complexity of the meteorological system, we have no choice but to use the isotopic pattern of the present-day meteoric water cycle as the primary guideline. However, one is then severely limited in interpretative capability because the available isotope/climate correlations are essentially space correlations for the relatively stable meteorological regime of today; this we would then transpose into a time correlation for meteorological patterns that differed from the present ones. One must recognize, moreover, that the isotopic data of the IAEA precipitation network (on which our picture of isotopes in the present water cycle is based) pertain to monthly composite samples. These climatically averaged values may hide synoptic or other meteorological variability.

Obviously only a detailed understanding of the rules of isotope fractionation in the meteoric water cycle and a truthful model of the pattern of moisture movement will allow one to extrapolate safely from the present water cycle to any palaeoclimate scenario.

It is rather well established that isotope fractionation in the hydrologic cycle comes about as a result of phase transitions: evaporation and, conversely, the condensation of vapour to liquid or ice. The sites of these changes are the ocean/air interface (and to a lesser extent the land/air boundary) and the cloud systems. Turbulent motions in clear air result in the mixing of vapour of different isotopic compositions but without any further isotope fractionation. The flow of groundwaters and, to a lesser degree, of rivers also seems to be essentially conservative with respect to isotopic composition.

2. CONTROL OF THE D-PARAMETER BY SOURCE CHARACTERISTICS OF ATMOSPHERIC VAPOUR

The natural evaporation process takes place into an under-saturated atmosphere and the ensuring isotope fractionation depends primarily on the degree of undersaturation [8, 9]; however, there is also a hidden temperature dependence, since the humidity is measured in this process relative to the saturated vapour pressure at the water surface, the latter, of course, being a function of temperature.

As a general rule, the lower the humidity the larger the isotopic fractionation (depletion) of the vapour and also the resultant deuterium excess, expressed [10] as $d = \delta D - 8\delta^{18}O$. This latter value is thus implanted in the air mass as the vapour is formed and apparently does not change much when precipitation is subsequently wrung out of the air by cooling.

Precipitation in the marine environment (in island and coastal stations) shows surprising variability in its isotopic composition and the d-excess parameters; in particular the correlation between ^{18}O and deuterium values is much poorer in the marine environment than is the case for inland precipitation. (A good correlation can be expected when the data closely follow the meteoric water line, i.e. when the isotopic changes represent differing degrees of rainout from air masses of similar origins, and also in arid regions where the ^{18}O versus deuterium regression line is the result of an evaporative process, so that isotope data fall along a well defined evaporation line.) The correlation coefficient (r^2) of the monthly deuterium versus monthly ^{18}O data of precipitation in the different IAEA network stations [11] averages 0.79 and 0.84 for island and coastal stations respectively, compared to 0.91 for continental (inland) stations. Evidently each storm engenders its own isotopic character, depending on the conditions at the air/sea boundary. The characteristic d-parameter value of the various climate zones represents an averaging of such local isotopic compositions and is established by larger-scale mixing of the precipitating air masses as the storms move overland and become detached from their vapour sources.

What are these characteristic values of the d-parameter? Traditionally a deuterium excess of d = 10‰ is assigned to meteoric waters of the European and North-American continents as well as to most high latitude regions including Antarctica; the vapour source for this precipitation is the mid-latitude regions of the Atlantic and the Pacific. Rain in the tropics also shows a similar d-value, as illustrated by the isotopic composition of the Amazon River, namely $\delta^{18}O = -5.55‰$, d = 9.8‰ [12]. Indeed the annually averaged data from all IAEA network stations follow the meteoric line correlation rather closely, with a correlation coefficient of r = 0.977 and standard error of estimate of $\delta_D = \pm 3.3‰$, which defines the scatter of data along the line [13]; the temperature (which controls the position of the data points on the meteoric water line) is thus the dominant meteorological variable. Exceptional source regions are inland seas, notably the eastern Mediterranean where one encounters a deuterium excess of d > 15‰ (22‰ on the average, with some values as high as 35‰ [14]). The latitudes south of the Tropic of Capricorn in Africa and Oceania are also characterized by d-values of 14–16‰.

The monsoonal rains on the Indian subcontinent again show a d-value of 10‰, but there are indications that somewhat lower values (d ∿ 5‰) apply for precipitation in the Sinai and southern Negev that originates from the Indian Ocean.

A closer look at the yearly cycle of the isotopic data from most network stations (except for those situated in the tropical area) shows not only the expected change in the (correlated) degree of depletion of the heavy isotopes between summer and winter, but also a seasonal cycle in the d-values, with lower values during the summer months. In some of the stations such a pattern is mainly the result of increased evaporation from falling rain droplets during summer; however, more generally such an effect is due to differences in the air/sea interaction parameters of the oceanic source regions between summer and winter. In any event the European winter precipitation is characterized by d-values of between d = 11‰ and 12‰, whereas lower d-values apply to the summer rains; the annual value is fixed as the weighted mean between the winter and summer data.

3. DEPLETION OF HEAVY ISOTOPES IN PRECIPITATION: FACTORS CONTROLLING THE LOCATION OF DATA ALONG METEORIC WATER LINES

On a global scale the depletion of the heavy isotopic species along the meteoric water line follows a Rayleigh type law [10, 15]. This law, in a way, is an expression of the overriding temperature dependence and applies because the removal of moisture (by rainout) from the atmosphere comes about by cooling. This law accommodates the well known altitude, inland and latitude effects [10]. Only the so-called amount effect is not simply related to the rainout mechanism [15].

If one looks at the isotopic data of precipitation samples in more detail, it becomes clear that additional meteorological factors related to rainfall and cloud structure come into play. These factors are not satisfactorily accounted for in the simple isotope models such as the Rayleigh models.

The conceptional basis for interpreting worldwide isotope data has been the rapid equilibration between raindrops and the ambient air, as a result of which the rain forgets the in-cloud isotopic composition. The isotopic content of the precipitation is accordingly determined to a large degree by the properties of the surface air, with an isotope fractionation factor appropriate to the near-surface temperature. The depletion in heavy isotopes of the precipitating weather system as a whole is dictated (from material balance considerations) by the removal of equilibrium rain from the ambient air mass. This situation holds for rains of moderate intensity but does not apply strictly in the case of light rains (when evaporation effects dominate). It also holds for very intense showers, first because the relaxation length for exchange is long for larger raindrops [16] but also because the surface moisture is then swamped by the larger amounts of water in the rain, as will be presently discussed; the process of equilibration is, of course, quite irrelevant when the precipitation appears as either snow or hail.

However, even admitting a local vapour/rain equilibrium, the crucial question to be considered is the relationship between the isotopic composition of the atmospheric moisture under the cloud and that of the large-scale, average, air-mass composition. The answer to this question involves a balancing of the water transport by air motions (advection, turbulent exchange in the vertical or horizontal) with that by the falling raindrops. Factors such as the intensity of updrafts or downdrafts as well as the duration and intensity of rain have to be considered. As an example, one finds on the coast of the Amazon basin a range of isotopic compositions in marine rains of close to 15‰ in ^{18}O [12]; the more negative δ-values are obtained when large-scale vertical motions are engendered in the precipitation zone due to the location of the inter-tropical convergence zone (ITCZ) in that region. Similarly there are differences between the isotopic composition of rain that results from the orographic lifting of marine air and that produced by frontal activity; once again this is the consequence of different degrees of mixing between the surface air and air from higher altitude layers, the latter being influenced by the cloud processes (and hence yielding water that is more depleted in the heavy isotopic species). Note, however, that to the extent that the in-cloud phase transitions (vapour/liquid/ice) are indeed equilibrium processes, one would then not expect major changes in the value of the d-parameter as rainout occurs, except for the effect produced by evaporation from the falling rain droplets and the recycling of air into which such evaporation has occurred [17].

In continental areas, where the precipitating air masses are detached from the marine vapour sources, the degree of re-evaporation (the continental water balance) obviously affects the continental precipitation and its isotopic composition, in particular the inland gradient of the depletion of the heavy isotopic species. Re-evaporated moisture redresses the water loss from the atmosphere by rainout; the extent to which the isotopic composition of the water is then also restored depends critically on the isotope fractionation associated with the re-evaporation flux. Evapotranspiration and evaporation from a closed evaporation basin that has reached an isotopic steady state with regard to inflow and evaporation will return the water to the atmosphere essentially unfractionated; thus a reduced inland isotope gradient is observed and no change in the value of the d-parameter is to be expected. Evaporation from surface waters that is accompanied by the fractionation of isotopic species results, however, in the addition to the atmosphere of vapour with a higher deuterium excess than the original precipitation; a positive inland gradient of the d-value is indeed observed in the tropical regions, such as the Amazon basin and in central Africa [10, 12]. An effect opposite to the one just described, namely an inland reduction of the d-excess, will be found in more arid regions simply due to the dominance of evaporation losses from the falling droplets themselves (i.e. it is an expression of decreasing humidity).

In summary we can state that the mean isotope composition of precipitation at any station is a function of a great number of meteorological variables, some of which are not usually considered in the characterization of climate. Foremost the data depend on synoptic patterns that relate the precipitating systems to the oceanic source region; also the water balance of the air mass along the storm path has to be considered with regard to the rainout pattern (temperature controlled) on the one hand and on re-evaporation effects on the other. Further influences are exerted by the seasonal distribution of rain, cloud types and their convective patterns and intensity, duration and intermittency of rainshowers.

It follows that a change in the air circulation pattern, climate parameters or the nature of rainfall can result in a change of the isotopic composition of precipitation. Moreover, in areas that are influenced by weather of different origins and character (climate transition zones) it suffices that the relative weight of such different storms is shifted in the annual average so that a marked shift in the yearly isotopic content of the precipitation can be observed.

4. SURFACE AND GROUNDWATERS

The effect of the transition from precipitation to groundwaters on isotopic composition has been described in the literature [18–20]. The distortion of isotopic composition during recharge is relatively small and rarely exceeds ± 1‰ in $\delta^{18}O$. The most common cause for such a change is the evaporative loss of water from the surface, especially from bare soil, before recharge occurs. This effect, naturally, is climatically controlled and assumes prominence under more arid conditions. Another factor that may influence isotopic composition is the selective utilization of only part of the rainfall for recharge or runoff, the selection occurring on the basis of season, rainfall intensity or the contribution of snowfall and snowmelt to the water yield.

Open surface waters, such as lakes, are enriched in heavy isotopes relative to the waters that feed them; the degree of enrichment depends on the fraction of water lost by evaporation, i.e. on the water balance. The latter is a function of climate, on the one hand through its dependence on the water yield of the watershed and precipitation amounts and on the other hand because of the dependence of the evaporation flux on the saturation deficit, i.e. the humidity gradient. Just as lake levels respond to climatic change and can serve as climate monitors [21], similarly isotope composition responds to changes in the environment, especially the degree of aridity [22].

5. ISOTOPIC COMPOSITION OF METEORIC AND PALAEOWATERS IN THE LEVANT AND THE NORTH AFRICAN DESERT: INTERPRETATION IN TERMS OF CLIMATE PATTERNS

The Mediterranean climate is associated with a well defined precipitation pattern of winter rains, related to the cyclonic activity engendered or intensified within the Mediterranean basin. This climate dominates the situation in the eastern Mediterranean area and over the land masses further to the east [23]. In most cases the Mediterranean moisture is picked up in the Tyrrhenian basin or in the eastern Mediterranean between the Greek mainland and Cyprus by very cold (= dry) air from Europe; the transport to the east occurs along a number of preferred storm tracks, each with a more or less pronounced marine trajectory [23].

The Mediterranean winter precipitation shows a deuterium excess of around d = 20‰ [22, 24]; in this arid region one must exercise judgement to exclude data from months with little rain whose isotopic composition might be distorted by evaporation. The moderate isotopic depletion in the coastal regions of the Levant ($\delta^{18}O$ values range between −4‰ and −6.5‰) is commensurate with a vapour origin within the area. More detailed analysis, however, shows differences in isotopic compositions during different rain events that apparently are correlated with the storm trajectory. For rainshowers in the Negev Desert, the air masses which approach from the south to southwest are significantly more depleted in heavy water isotopes than the rain derived from storms coming from the west [25].

I. Carmi (private communication) considered rain data from the northern half of Israel and suggests that these fall into two groups whose isotopic contents differ one from the other by at least 1 to 2‰ in ^{18}O; the more depleted rains also show, on the average, higher d-excess values. Shifts in the average isotopic composition at any station from year to year are due to differences in the relative abundance of these two water types.

One must further recognize the presence of European air masses (d = 10‰) to the north of the area and that air masses of low d-values are found to the south. The latter appear to originate from the Indian Ocean with characteristically very low tritium values. The range of isotopic values found in recent meteoric waters of the area is summarized in Fig.1.

As shown in Fig.1, the isotope compositions of Pleistocene or early Holocene palaeowaters (identified as such by their low ^{14}C content (2 to 6% of modern carbon and "O tritium" age) from southern Israel and adjacent countries stand out quite notably relative to these more recent water sources. The most striking difference is the location of these data close to the worldwide meteoric water line, actually with a range of d-values between 3‰ and 10‰, d = 7‰ on the average [20, 26]. Furthermore, the degree of depletion in the heavy isotopic species is quite moderate ($\delta\,^{18}O$ ranges from about −7‰ to −9‰) when compared either with data from southern Europe (extrapolated to an equivalent easterly longitude) or with palaeowaters in the western (Egyptian) desert [27].

In attempting an interpretation of the isotopic composition of palaeowaters in terms of the possible changes in climate or rain patterns, we are bound by the two climate scenarios characteristic of this period and region [28]: (1) a colder period with moderate rains just before the last glacial peak or during the Pleistocene-Holocene transition and (2) a warm, humid climate phase some 4500–7000 years ago. The ^{14}C ages of the palaeowaters under discussion would assign these to the Pleistocene, but as the interpretation of carbon ages of groundwaters is open to some doubt we have to keep an open mind as to the period of recharge for these waters.

During the colder periods of the Pleistocene one would expect a reduced role of the Mediterranean as a vapour source; this is indeed suggested by the absence of the large d-excess in the palaeowaters that is characteristic of the Mediterranean climate waters. Were these waters then of Atlantic origin and transported into the Levant by the southward-displaced storm tracks, thus dumping that precipitation in the Mediterranean space which nowadays accounts for the precipitation in eastern Europe, the Balkans and northern Turkey?

Sonntag et al. [27] indeed interpreted the isotopic data of the northern African (Saharan) palaeowaters in terms of a westward drift of Atlantic winter air masses over northern Africa, establishing there a continental gradient that is of similar magnitude to that of the present winter precipitation over Europe. (These air masses evidently formed with a d-value of d = 5‰, presumably owing

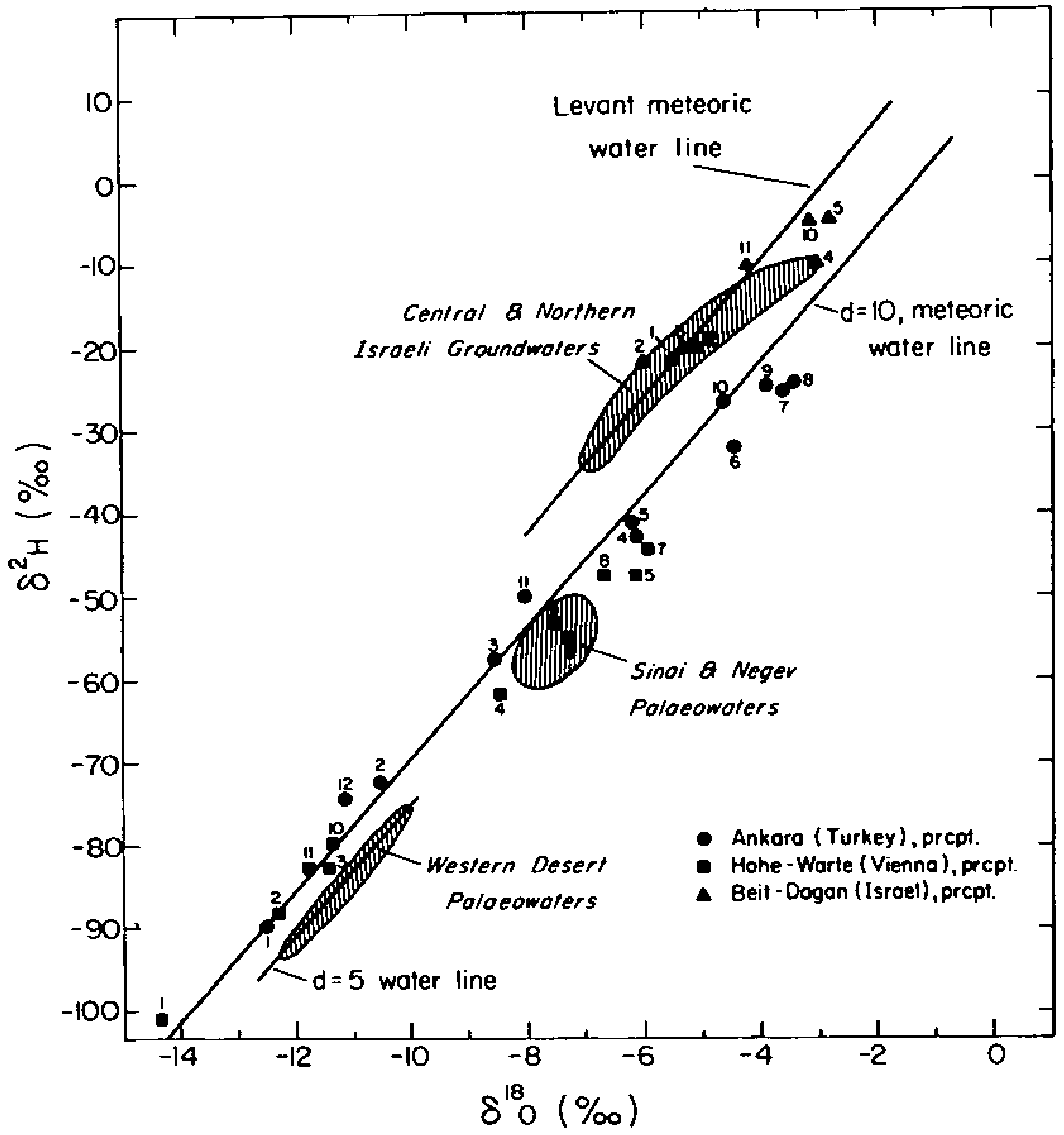

FIG. 1. Isotopic composition of modern meteoric waters and of palaeowaters in the eastern Mediterranean Sea area. The averaged monthly precipitation data (1963–1978) from Ankara, Vienna and Beit-Dagan are shown as reported in Ref. [11]; numbers 1–12 refer to calender months. Furthermore we indicate the range of groundwater sources of the modern and palaeohydrologic cycle in the Levant [24]; data from palaeowaters of the western desert (Egypt) as reported in Ref. [27] are given for comparison.

to a reduced saturation deficit, i.e. 10‰ over the ocean [29].) The palaeowaters of the Negev and Sinai, however, cannot be fitted into such a scheme, as their depletion in ^{18}O falls short by at least 5‰ relative to the prediction of the western-drift model. It can be argued, of course, that the difference between expected and observed isotopic composition was made up by the additional input of vapour from the Mediterranean, which although being cooler than at present might still have been effective as a partial source of vapour. Application of the Rayleigh rainout model shows that this local contribution would have had to account for about 43% of the water. It seems difficult to reconcile such a large contribution with the stability of the air/sea system over the Mediterranean during that period.

During a colder period, when the destabilizing influence of the Mediterranean is not operative, there is no reason to expect the same winter rain regime that is characteristic of the present-day Mediterranean climate. One should then consider the possibility of summer precipitation. If we now take the summer precipitation of southeastern Europe as our model, we find, for example, that the mean April–September rains in Vienna have an isotopic composition of $\delta^{18}O = 6.8‰$. (The only available and appropriate data in the IAEA network are those from station Hohe Warte, Vienna, Austria, and Ankara, Turkey; the Ankara value is $-5.45‰$ but here evaporation effects may have to be taken into account.) In relation to this number the palaeowater isotope data fall smoothly into place, considering a southward displacement of storm tracks of the Atlantic air masses and the longitude of the Levant. In other words, the stable isotopic composition of palaeowaters is consistent with a notion of spring, summer or fall precipitation from storms that originate in the Atlantic. One can note that the deuterium excess of the summer precipitation in western Europe is similar to that of the north African palaeowaters [27] and the Negev.

On the grounds of the isotopic data one cannot rule out an alternative possibility, namely that the vapour origin of the palaeowaters was the Indian Ocean. However, the predominance of such waters in our area would be inconsistent with model predictions of the Pleistocene atmospheric circulation.

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RELATIONSHIPS BETWEEN CLIMATIC CHANGES AND VARIATIONS IN ISOTOPIC COMPOSITION OF GROUNDWATER, PRECIPITATION AND ORGANIC SOIL MATTER IN THE QUATERNARY PERIOD

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Abstract

RELATIONSHIPS BETWEEN CLIMATIC CHANGES AND VARIATIONS IN ISOTOPIC COMPOSITION OF GROUNDWATER, PRECIPITATION AND ORGANIC SOIL MATTER IN THE QUATERNARY PERIOD.

Examples are given of isotopic investigations of groundwaters in the southern Urals, South Turkmenia and South Kazakhstan which were recharged in the Holocene and Pleistocene Epochs. From the variations in the isotopic composition of the groundwaters, the authors deduce climatic changes that occurred in these regions. Some 9000–13 000 years ago, the mean annual temperatures in the southern Urals were 5°C lower than they are today. In South Turkmenia, temperatures rose sharply 12 000 years ago, and in South Kazakhstan the climate grew colder 14 000 years ago. Climatic variations in the Spitsbergen region are interpreted on the basis of results from studies of ^{18}O variations measured in ice core samples reaching to a depth of 213 m. The investigations cover the period from 1200 to the present. Palaeoclimatic interpretations are given of variations in the composition of stable carbon isotopes occurring in organic matter sampled from the flood-plain deposits formed by small rivers flowing through various bioclimatic regions. Future applications of this technique are also discussed.

1. VARIATIONS IN ISOTOPIC COMPOSITION OF PLEISTOCENE GROUNDWATERS

Pleistocene groundwaters were discovered during a study of artesian water flow through a relatively impervious formation in the Shadrinsk region (southern Urals). It has been established that a quantitative assessment of groundwater flow through an impervious formation can be based on a study of the distribution of deuterium and ^{18}O in interstitial water through the cross-section of the impervious layer [1, 2].

In the Shadrinsk region, isotopic data were used to study the groundwater flow through a marl and clay bed approximately 130 m thick separating Cretaceous and Palaeogene aquifers. Deuterium and chlorine ion concentrations were examined in the interstitial water through the cross-section of the layer. The results of these measurements are shown in Table I and Fig.1.

The marl-clay bed lies at a depth (from the earth's surface) of 98–220 m. The deuterium content of the water in the Cretaceous (lower) and Palaeogene (upper) horizons is −99 ± 3‰ and −109 ± 3‰ respectively. The chlorine ion concentration in the lower horizon varies by 1.2 ± 0.2 g/L; in the water of the upper horizon it varies with depth, reaching 0.90 ± 0.06 g/L at the bottom. The data in Table I and the graph in Fig.1 show that the sectional distribution of deuterium is at a minimum at a depth of H = 148 m and at a maximum at a depth of H = 118 m. The peak in the chlorine ion distribution occurs at a mean depth of 138 m. Given that there is an overpressure of approximately 5 atm in the lower horizon, it may be assumed that water flows from the Cretaceous horizon to the Palaeogene. If that is the case, the minimum in the deuterium distribution across the bed is due to the presence in the Cretaceous horizon of 'light' water formed at the beginning of the Holocene by the melting of glaciers and snow in a recharge area associated with the Ural Mountains. The maximum δD value may be attributed to the low filtration rates during the glaciation era when there existed a sub-permeable bed of permafrost rock in the recharge area, which led to diffusion salting of the lower water-bearing stratum and to the inflow of certain quantities of water of marine origin to the syngenetic Lower-Cretaceous sedimentary bed. The peak in the chlorine ion distribution curve also indicates that, during the unfavourable recharge conditions prevailing in the last Pleistocene glaciation, salting of the confined aquifer occurred. Carbon-14 dating has revealed waters 9000–13 000 years old in the watersheds of the region under investigation, and the isotopic composition of these waters ($\delta D = -121 \pm 5‰$, $\delta^{18}O = -12.9‰$, tritium content ~2 TU) differs considerably from the modern values ($\delta D = -110 \pm 4‰$, $\delta^{18}O = -11.2 \pm 0.3‰$, tritium content up to 40 TU). It may, therefore, be concluded that the recharge of the aquifer began 9000–13 000 years ago. This conclusion is not in contradiction with the generally accepted data on the overall rise in temperatures

TABLE I. DEUTERIUM AND CHLORINE ION SECTIONAL DISTRIBUTION THROUGH AN IMPERVIOUS CLAY–MARL BED IN THE SHADRINSK REGION (SOUTHERN URALS)

Sampling depth (m)	δD (‰)	$[Cl^-]$ (g/L)
98.8–99.0	−109 ± 3	0.8
111.8–112.0	−108 ± 3	1.0
113.8–114.0	−98 ± 3	–
117.8–118.0	−88 ± 3	1.2
127.8–128.0	−99 ± 3	1.6
137.8–138.0	−97 ± 3	–
140.8–141.0	−110 ± 3	1.6
147.8–148.0	−115 ± 3	1.6
156.8–157.0	−107 ± 3	–
157.8–158.0	−105 ± 3	1.3
166.8–167.0	−101 ± 3	–
167.8–168.0	−107 ± 3	1.2
176.8–177.0	−100 ± 3	1.3
208.8–209.0	−99 ± 3	1.2

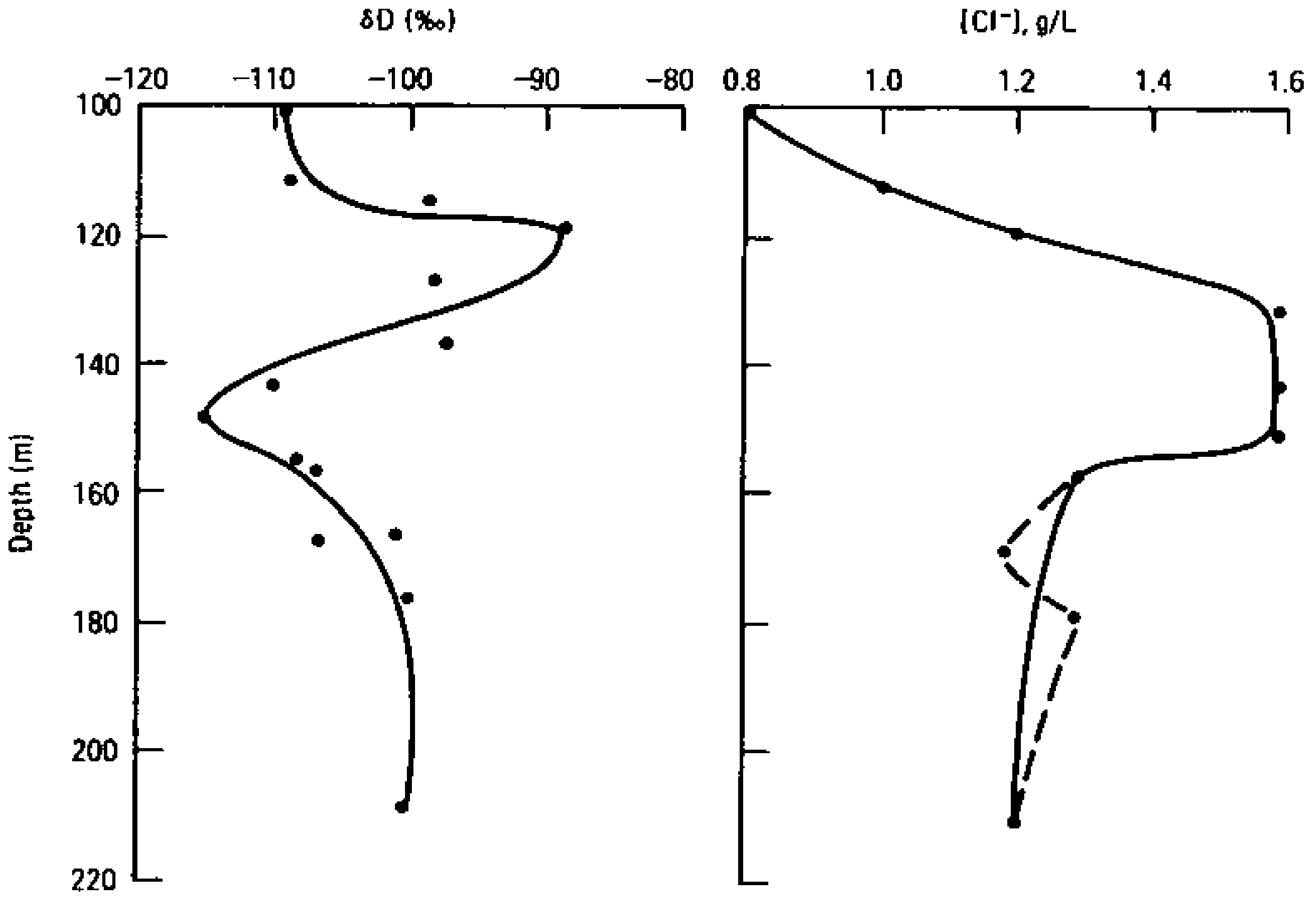

FIG. 1. Variations in δD values and chlorine ion concentrations over the cross-section of a watertight clay-marl bed (Shadrinsk region, southern Urals).

TABLE II. ISOTOPIC AND CHEMICAL COMPOSITION OF GROUNDWATERS IN THE BAKHARDEN DEPOSIT

Sampling point	Sampling depth (m)	Water temperature (°C)	Chemical composition of water	pH	H_2 (mg/L)	HCO_3^- (mg/L)	δD (‰)	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)	Radiocarbon age of water (a)
Borehole 3	30	19.5	$M_{0.5}\frac{SO_4 46 HCO_3 46 Cl 8}{Mg 35 Ca 34 Na 31}$	7.4	–	238	–69	–9.2	–6.0	Modern
Borehole 16	400	30.5	$M_{1.8}\frac{SO_4 65 Cl 19 HCO_3 16}{Na 59 Mg 22 Ca 19}$	7.7	–	256	–71	–10.8	–2.8	8 000
Borehole 17	800	30.3	$M_{2.2}\frac{SO_4 68 Cl 18 HCO_3 14}{Na 66 Mg 23 Ca 12}$	7.7	–	281	–70	–9.0	–2.8	5 500
Borehole 18	1200	38.5	$M_{2.4}\frac{SO_4 67 Cl 28 HCO_3 15}{Na 57 Ca 24 Mg 19}$	6.7	25	354	–71	–11.4	–2.5	5 000
Borehole 19	1600	38.3	$M_{3.7}\frac{SO_4 71 Cl 18 HCO_3 10}{Na 55 Ca 28 Mg 27}$	7.0	60	342	–73	–8.9	–4.0	12 000
Borehole 20	2000	49	$M_{4.9}\frac{SO_4 71 Cl 20 HCO_3 8}{Na 54 Ca 30 Mg 16}$	7.3	80	378	–104	–11.5	–9.0	17 000

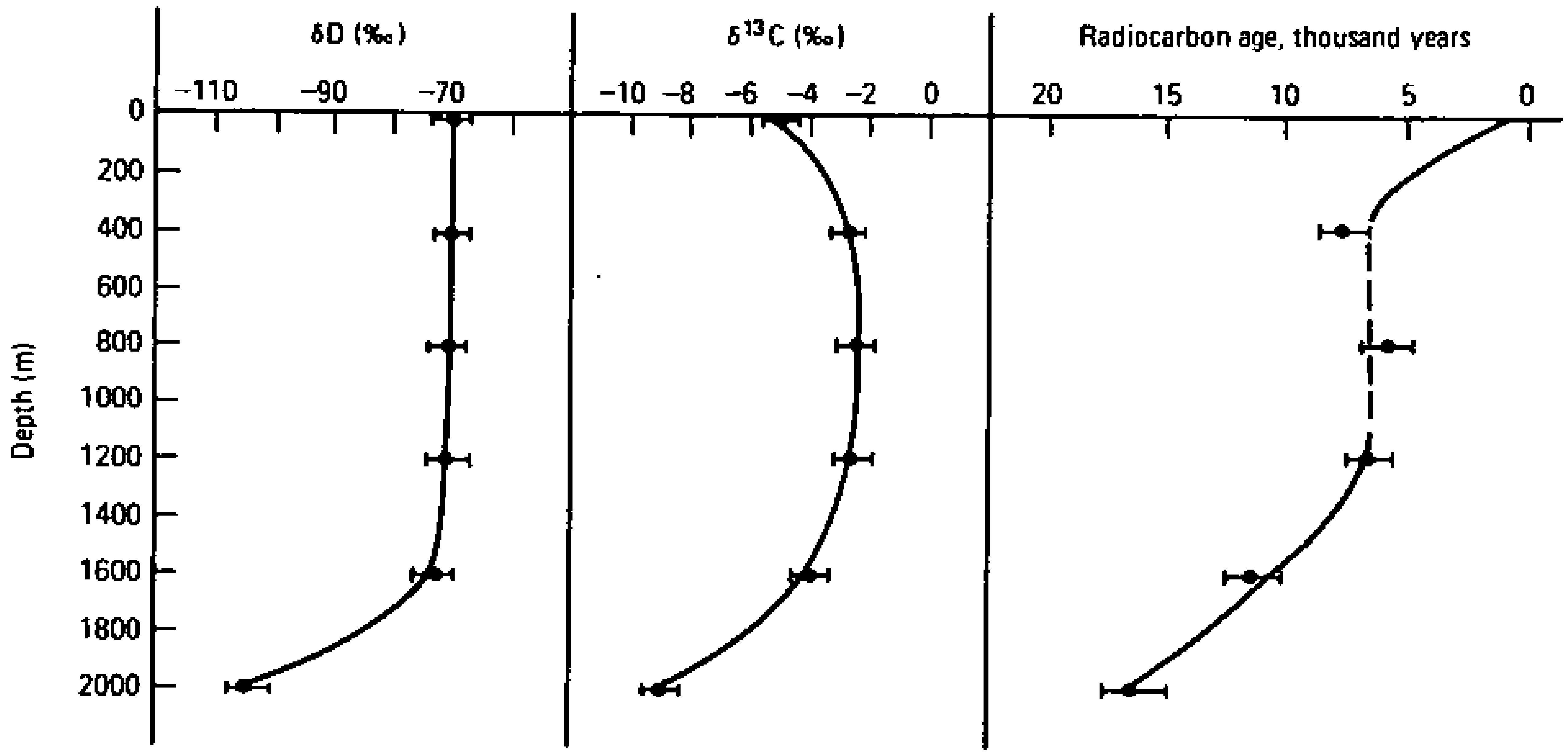

FIG. 2. δD and $\delta^{13}C$ variations and water age/depth distribution in the Bakharden mineral water basin (South Turkmenia).

during the Holocene about 10 000 years ago [3]. Assuming that the recharge of the lower (K_2) confined aquifer began about 10 000 years ago, it is not difficult to calculate the flow rate from the data on deuterium distribution: the result is 0.7 cm/year ($\sim 2 \times 10^{-5}$ m/day). The peak in the chlorine ion distribution lags typically about 20 m behind the deuterium peak over that period, i.e. the clay-marl bed acts as a chromatographic column, and the chlorine ion cannot be used as an indicator of water movements in clay beds.

With allowance for diffusion 'blurring' of the deuterium minimum on the distribution curve, the deuterium content of the water flowing into the Cretaceous stratum at the beginning of the Holocene can be estimated at $\delta D = -125 \pm 5‰$. Given that the temperature gradient for variations in the isotopic composition of atmospheric precipitation is ~3.0‰ per 1°C, we may conclude that, during the accumulation of glaciers and snow cover in the recharge area of the aquifers under investigation (the southern spurs of the Ural Mountains), the mean annual temperatures were about 5°C lower than they are today.

In our study of the conditions in which the mineral waters of the Bakharden deposit associated with the Predkopetdag deep fault (South Turkmenia) were formed, we analysed data on the hydrogen, oxygen and carbon isotopes present in the groundwaters. The results are listed in Table II and shown in graph form in Fig.2.

The groundwaters of the deposit are associated with a carbonaceous-terrigenous bed of the Malm-Neocomian Epoch. In the upper confined aquifers, δD and $\delta^{18}O$ values of −70‰ and −10‰ respectively are typical and are close to the characteristic values for modern atmospheric precipitation in the recharge

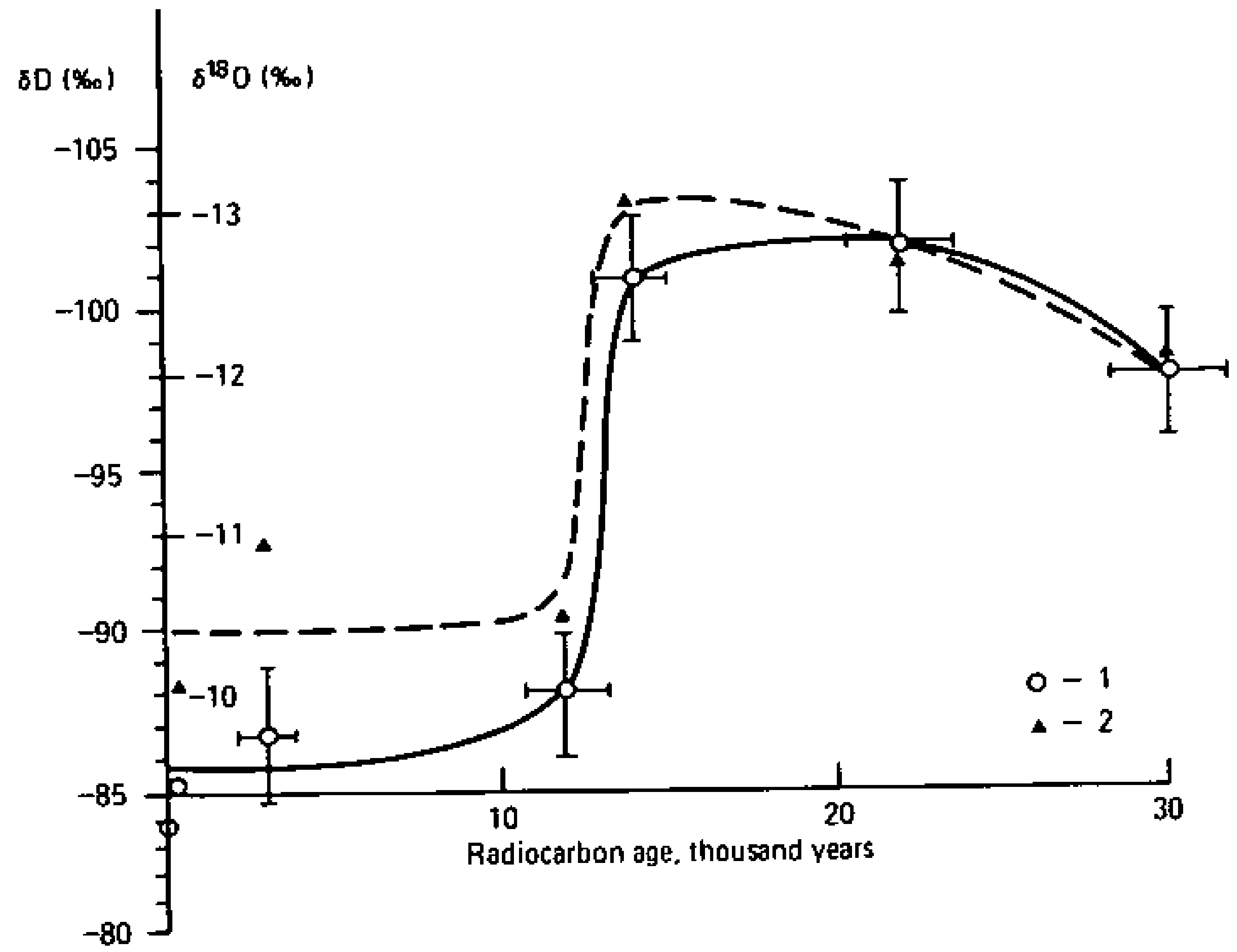

FIG.3. Relationship between δD and $\delta^{18}O$ values and variation in the radiocarbon age of groundwaters in South Kazakhstan: 1 = deuterium; 2 = ^{18}O.

area. Waters discovered at a depth of ~2000 m on the other hand show much lower deuterium concentrations (δD = −104‰). These waters probably flowed into the Malm-Neocomian aquifer complex during the last Pleistocene glaciation. Radiocarbon dating of these waters, with corrections for the isotopic and chemical composition of carbon from the carbonate system, yields an estimated age of approximately 17 000 ± 3000 years. Table II and Fig.2 show that temperatures in the area under investigation rose sharply about 12 000 years ago.

There are two possible reasons why the isotopic composition of carbonate-system carbon in the groundwater becomes lighter with depth: (1) a change in the photosynthetic type of modern vegetation (Hatch-Slake cycle) compared with the plants that grew in the pluvial Pleistocene period (Calvin cycle); (2) the occurrence in the carbonate system of 'light' carbon from dissolved organic matter as a result of sulphate reduction processes. The second explanation seems the more plausible since the variation in the $\delta^{13}C$ values is parallel with the increase in the hydrogen sulphide content of the aquifers under investigation.

The effect of the pluvial period on the formation of groundwaters in central Asia is being traced in the Syr-Dar'ya, Chu-Sarysu and Ili artesian basins (South Kazakhstan). Figure 3 illustrates the variation in the isotopic composition of groundwaters associated with the Upper-Cretaceous terrigenous-sedimentary bed as a function of the water's radiocarbon age corrected for dissolved carbonate components. Figure 3 shows that in the Pleistocene from 30 000 to 20 000 years ago the climate grew colder in the region under investigation and that this

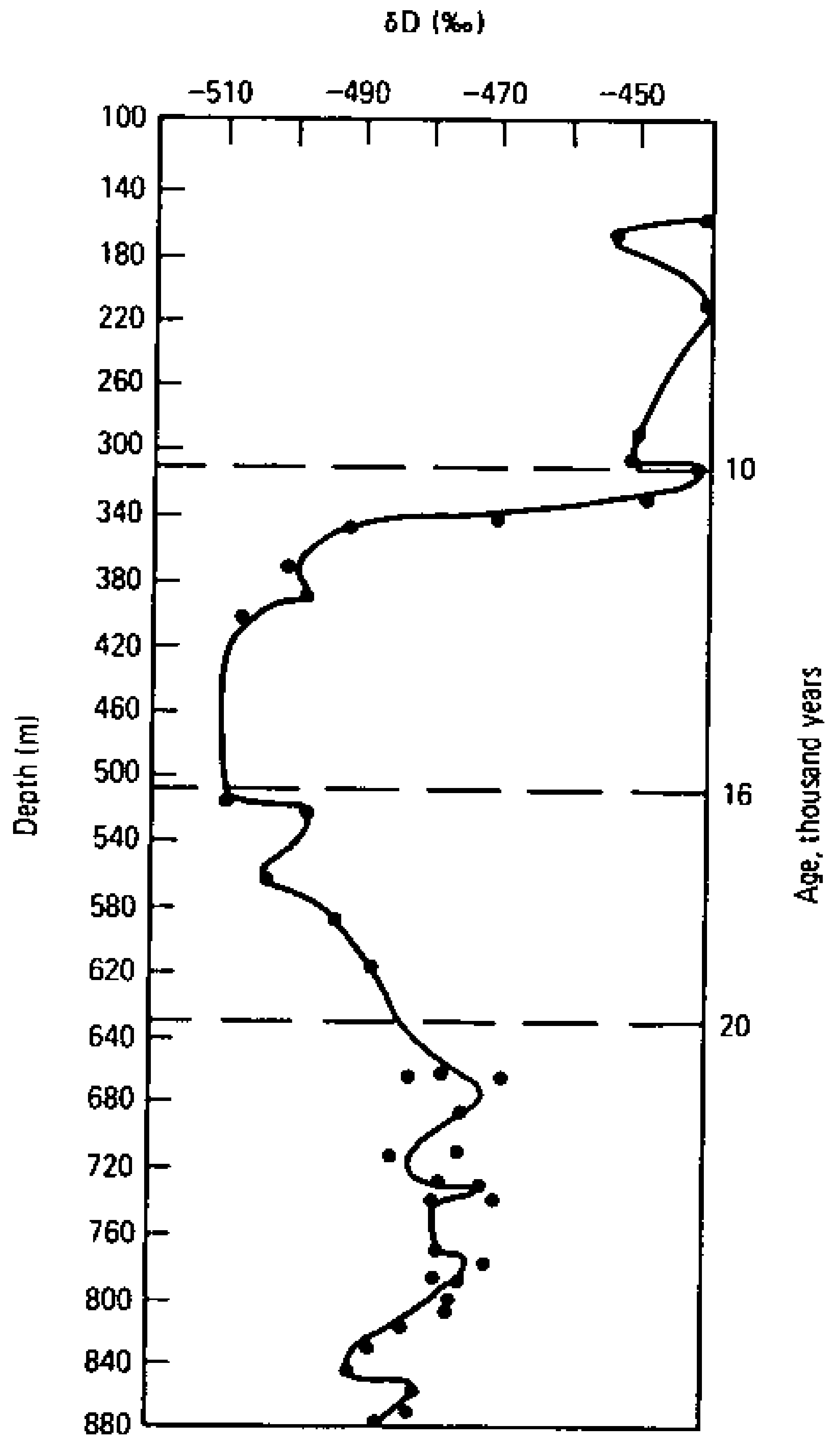

FIG.4. Variations in the isotopic composition of an Antarctic ice core with depth at the Vostok station.

trend continued up to about 14 000 years ago. The climate then grew warmer rather rapidly between 14 000 and 12 000 years ago, after which the climatic conditions in the region under investigation became similar to those prevailing today. In all probability, the change in climate at the end of the Pleistocene was of a global nature; this is confirmed by an analysis of the isotopic composition of ice core samples from the Vostok Station (Antarctica) which were supplied by N.I. Barkov. The results of this analysis are shown in Fig.4. The age scale of the ice core is plotted according to the data provided by Gordienko and Kotlyakov [4]. Figure 4 shows that at the end of the Pleistocene (about 20 000 years ago) the climate cooled down, the lowest temperatures being reached about 16 000 years ago. By comparing the Antarctic isotope data quoted in this paper with those obtained from the Byrd Station [5], from Greenland [6], from South Kazakhstan and from South Turkmenia (Fig.3), we

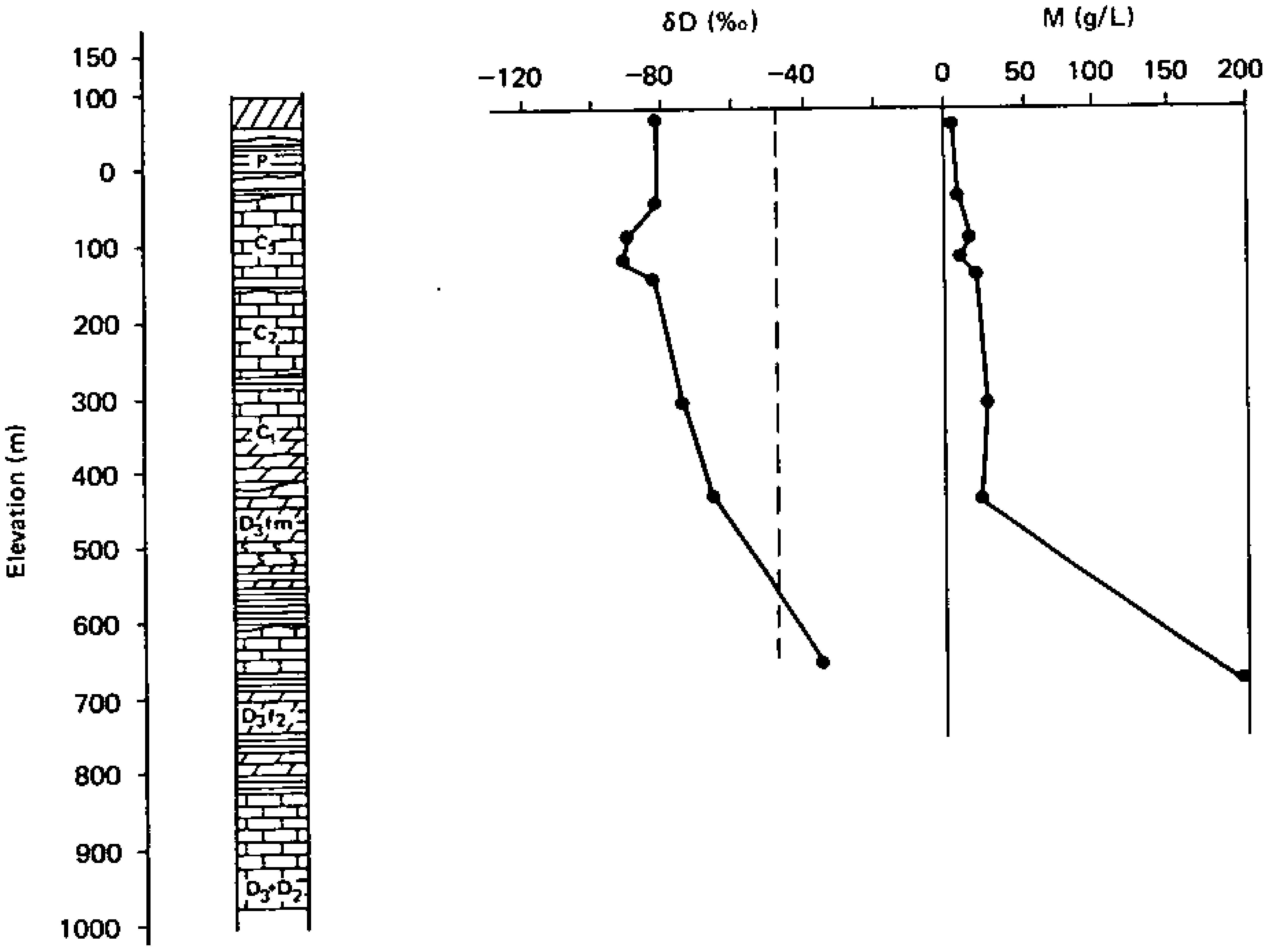

FIG.5. Hydrogeological section, variations in the deuterium content and mineralization of groundwaters in the Kashin area (Moscow region).

may conclude that there was a virtually simultaneous change in climatic conditions throughout the globe; this finding ties in with other ideas now published in the literature [7].

The influence of the last Pleistocene glaciation is revealed in the isotopic and chemical composition of the groundwaters in the Moscow artesian basin. A study of the hydrogeological cross-section of this basin in the Kashin region has revealed some tendency towards 'lighter' water in respect of hydrogen isotopic composition (Fig.5) in the salt and brackish waters of the Upper-Carboniferous deposits (at a depth of 180–200 m), a result which is also in agreement with the reduced mineralization of these groundwaters.

A study of groundwaters in the Gdov and Strel'nin horizons (Proterozoic) in the Baltic region has shown that the water around Tallin has an abnormally light isotopic composition ($\delta D = -159‰$, $\delta^{18}O = -19.5‰$) which is quite unlike that of the modern phreatic waters ($\delta D = -88‰$, $\delta^{18}O = -9.8‰$) but similar to modern atmospheric precipitation in the Mirnyj region (Yakutsk ASSR) (see Fig.6). The mean annual temperatures are now +4.5°C in the Baltic region and −8°C in the Mirnyj region, so we may conclude that, when these aquifers were being recharged, the mean annual temperatures in the

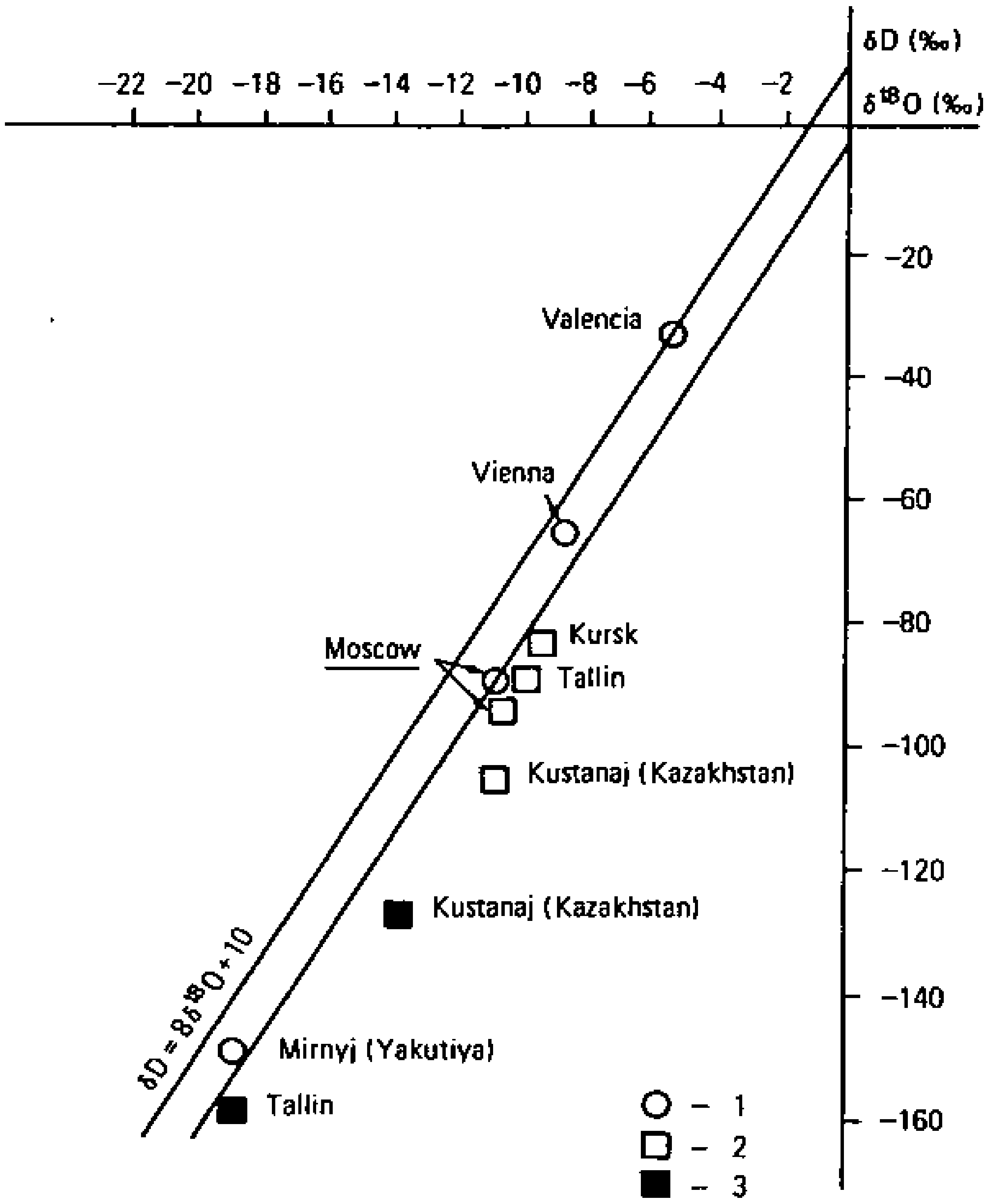

FIG.6. δD – $\delta^{18}O$ relationship for various regions of the European continent: 1 = atmospheric precipitation; 2 = modern groundwaters; 3 = ancient groundwaters with a radiocarbon age of ~10 000 years.

Baltic region were about 13°C lower than they are today. It is also probable [8] that the Gdov and Strel'nin aquifers were recharged at the end of the Pleistocene during the deglaciation of the Baltic basin when a single Baltic glacial lake was being formed. The isotopic composition of the Scandinavian ice sheet may, therefore, be rounded to $\delta D = -160‰$ and $\delta^{18}O = -20‰$. These values differ somewhat from the estimated average isotopic composition of the North American ice sheet ($\delta^{18}O = -15‰$) [9].

The mean annual temperatures during the glacial accretion in Scandinavia in the Valdai glaciation were probably somewhat lower than the present-day temperatures in the Mirnyj region. That being the case, the variation in the $\Delta\delta D/\Delta_t$ and $\Delta\delta^{18}O/\Delta_t$ values during the evolution of the climatic conditions may be estimated at 5–6‰ per 1°C and 0.6–0.7‰ per 1°C respectively. These estimates are close to the values obtained by Dansgaard [10], who analysed the correlation between isotopic composition and mean annual temperatures of surface air for various regions of the world. In Fig.6 data from readings taken over a number of years also reveal a continental effect for Vienna and Moscow

TABLE III. REGRESSION ANALYSIS OF AVERAGE MONTHLY $\delta D - t$ AND $\delta^{18}O - t$ RELATIONS IN ATMOSPHERIC PRECIPITATION FOR VARIOUS REGIONS OF THE WORLD

Station	Meteorological data			Number of months of observation	$\delta D = A_1 + B_1 t$			$\delta^{18}O = A_2 + B_2 t$		
	Average annual precipitation (mm)	Vapour pressure (mbar)	Mean annual temperature (t°C)		$A_1 \pm \Delta A_1$	$B_1 \pm \Delta B_1$	r_1	$A_2 \pm \Delta A_2$	$B_2 \pm \Delta B_2$	r_2
Teheran	208	7.6	17	77	−43 ± 6	1.8 ± 0.4	0.46	−6.9 ± 1.0	0.27 ± 0.06	0.48
Vienna	660	8.5	10	123	98 ± 3	2.9 ± 0.2	0.77	−13.6 ± 0.4	0.42 ± 0.03	0.76
Moscow	575	6.5	4	92	−101 ± 2	2.4 ± 0.2	0.89	−12.6 ± 0.3	0.34 ± 0.03	0.82
Barrow	110	1.7	−12	66	−113 ± 7	1.9 ± 0.4	0.55	−13.4 ± 1.2	0.27 ± 0.07	0.41
Nord	150	1.1	−18	63	−133 ± 7	2.8 ± 0.3	0.75	−17.0 ± 1.1	0.40 ± 0.05	0.74
Mean value for Vienna, Moscow, and Nord Stations						2.7			0.39	

(the weighted annual averages for δD and $\delta^{18}O$ are shifted to the right of the 'normal' Craig dependence).

The isotopic composition of the groundwater (readings taken over a ten-year cycle in the Moscow region) does not match the isotopic composition of atmospheric precipitation, although it does bear a close resemblance. This is likely due to the fact that atmospheric precipitation during the cooler seasons of the year is the dominant factor in groundwater recharge and also to some variation in the isotopic composition of the infiltrating moisture owing to evaporation from the zone of aeration. Evaporation processes are most prominent in a semi-arid region (Kustanaj in North Kazakhstan). Moreover, in this region the difference between the δD and $\delta^{18}O$ values for underground water with a radiocarbon age of 10 000–15 000 years and those for modern groundwaters is typically less than in the Tallin region.

Let us consider whether palaeotemperatures can be calculated in terms of the isotopic composition of the water by referring to the correlation between isotopic composition and the average monthly temperatures of the surface air in a given region, as was done, for instance, by the authors of Ref. [11]. The parameters of such a dependence, based on published data and on our own measurements, are set out in Table III, where it is shown that the rates of variation in the isotopic composition of atmospheric precipitation at different stations, expressed as a function of the average monthly temperature, differ considerably from the data published by Dansgaard. When the average air temperatures during the Valdai glaciation in the Baltic region are calculated from the temperature gradients shown in Table III, the values are 28–30°C lower than they are today; this finding is in contradiction with the results of independent research reported by Kind [3]. The global climatic changes during the glacial periods probably also gave rise to changes in moisture transfer processes, and this was then reflected in the temperature gradients associated with changes of isotopic composition over time.

2. VARIATIONS IN ISOTOPIC COMPOSITION OF PRECIPITATION IN THE ARCTIC REGION

During isotope and geochemical investigations on the island of Spitsbergen in 1975, a borehole 213 m deep was sunk to the underlying bed in an ice divide between the Groenfjord and Fritof glaciers in the western part of the island. The ice divide was at a height of 450 m above sea-level. The mean rate of accumulation of precipitation between 1951 and 1975 was 75 cm per year, a result obtained by reference to levels of enhanced radioactivity. Isolation of seasonal layers in the top 12 m on the basis of the oxygen isotope profile indicated an average annual rate of accumulation of 49 cm.

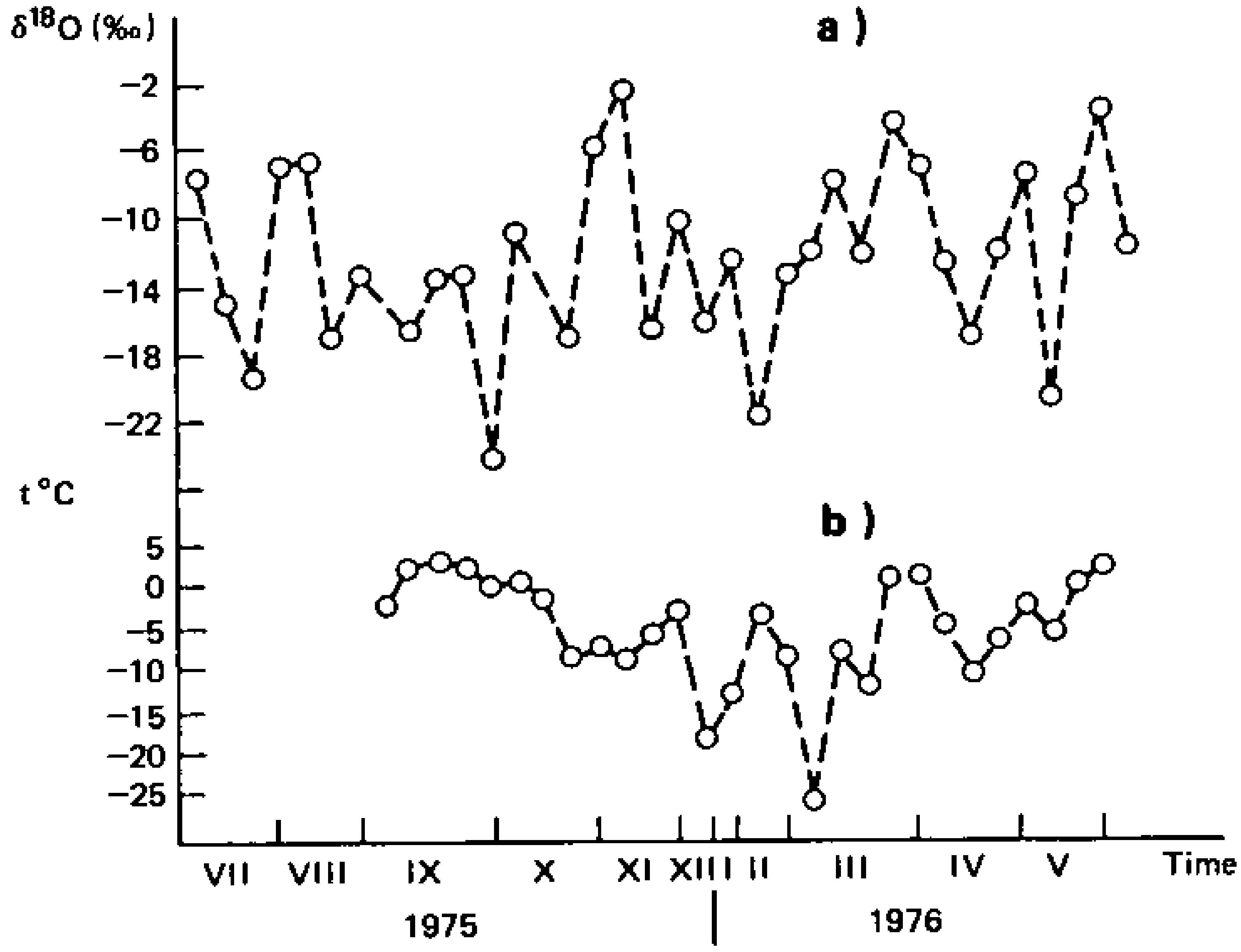

FIG. 7. $\delta^{18}O$ variations in precipitation at the Barentsburg weather station over the period 07.1975–05.1976 (a), and the corresponding variations in temperature (b).

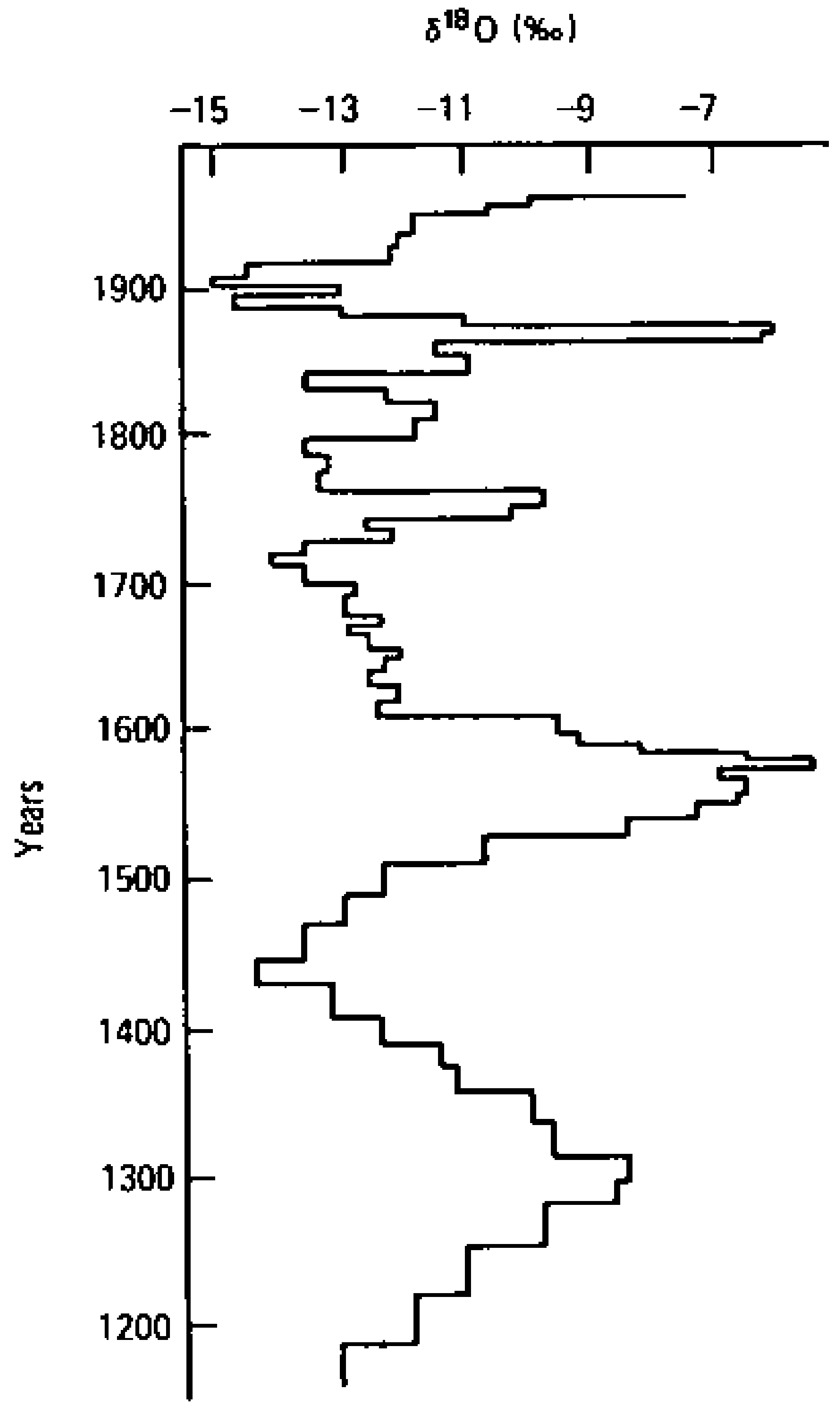

FIG. 8. $\delta^{18}O$ variations across a firn-ice bed in the Groenfjord-Fritof ice divide (Spitsbergen).

Investigation of atmospheric precipitation sampled at the Barentsburg weather station did not show a constant relationship between variations in isotopic composition and the precipitation temperature [12]. The data for the period 1975–1976 are plotted in Fig.7, which shows three peaks in the $\delta^{18}O$ distribution reflecting local variations in the formation of precipitation. Similar phenomena were observed at other stations on the island. However, the average long-term data show good agreement between the isotopic data and the temperature at which the precipitation was formed in this region.

Figure 8 shows a profile of oxygen isotope variations with the depth of the borehole. The isotopic data are expressed as mean $\delta^{18}O$ values over a ten-year period. A steady-state model [13] was used to date the results.

The graph shows a series of palaeoclimatic changes in the isotopic composition of the core. The rise in temperature that began in the 1930s is in good agreement with the data from the Green Harbour and Barentsburg weather stations. Compared with the data concerning other regions in the northern hemisphere, the warmer period began later in the region under investigation. The data are in closest agreement with the results obtained from core studies at the Crête station in Greenland and with meteorological data from Iceland [14]. In many regions of the Arctic the peak in the temperature rise curve occurs between the 1930s and 1950s. The data show that right up to 1975 there was no sign that the climate in the western part of Spitsbergen was growing cooler. According to data from the Barentsburg weather station, the mean annual temperatures began to fall somewhat in the 1960s. However, there was still no drop in the water temperature in the Greenland Sea.

The so-called 'little ice age' that extended from the 17th to the 19th century stands out clearly in Fig.8. The $\delta^{18}O$ value during that period corresponds to the conditions prevailing during the first decades of the 20th century, when the average air temperatures measured at weather stations on the Isfjord coast were 2–3°C lower than they are today.

The relatively cold period from the 17th to the 19th century was interrupted by two brief periods when the climate grew warmer, the second of which occurred during the 1870s. The data indicate that the warmer period that occurred in the middle of the 18th century was not as intensive, but it was also detected in the core samples taken at the Camp Century station as well as a few decades earlier in England and Iceland. The non-synchronous nature of the climatic variations in the various regions of the Arctic basin obviously reflects not so much an overall fluctuation in temperature but rather the influence of temperature redistribution due to the movements of water masses in the basin.

Figure 8 shows that throughout the 16th century the climate grew considerably and consistently warmer, and this result is supported by data from other points in the region. The duration of the warm period, as measured at the Groenfjord-Fritof ice divide, may be compared with the results from the Camp Century station [15].

The analysis of the last core section was subject to considerable dating errors, which made interpretation difficult. Nevertheless, there is a clear indication of a warmer period beginning in the 13th century and reaching a peak in about 1300.

We have recently measured the ^{18}O content of a core sample taken from a depth of 556 m in the Vavilov ice cap. The investigations cover a period of 70 000 to 100 000 years. The data, which are now being prepared for publication, yielded some extremely interesting results that should shed light on the climatic changes occurring during that period in the Arctic region under investigation.

3. PALAEOCLIMATIC RECONSTRUCTION BASED ON CARBON ISOTOPE VARIATIONS IN ORGANIC SOIL MATTER

In addition to the well-developed techniques of oxygen palaeothermometry established by Yuri, Epstein and other researchers, another method for reconstructing palaeotemperatures based on an analysis of carbon isotope variations in organic matter has been formulated in recent years.

Sackett et al. [16] and Wong and Sackett [17] discovered that the $\delta^{13}C$ value in marine phytoplankton was a function of the temperature of the sea-water; as the water temperature rose by 1°C, the carbon in the plankton underwent heavy isotope enrichment of 0.25–0.36‰. Stuiver observed a similar dependence in freshwater organisms, analysing the organic matter found in lake sediments from various geographical areas [18].

The variation in carbon isotopes in surface vegetation is influenced not only by the temperature but also by the humidity of the air. For tropical vegetation the biochemical fractionation factor is at a maximum, and the organic matter shows the strongest enrichment in the light isotope of carbon. In arid regions we observe the strongest enrichment in the heavy carbon isotope.

Data published by various authors show that there is a $\delta^{13}C$/temperature correlation of 0.2–0.4‰ per 1°C for trees. The link with humidity was observed only at the lower limit of the forests and has not been determined quantitatively [19, 20].

We have begun to study how carbon isotope variations in organic soil matter can be used for the purpose of palaeoclimatic reconstruction. The first results are set out below.

In our studies we used samples of organic matter taken from genetically monotypic sections of alluvial deposits formed by small rivers flowing through various geographical regions and associated with specific bioclimatic belts, i.e. forest, steppe and sub-tropical (dry and humid) (Table IV).

TABLE IV. $\delta^{13}C$ VARIATIONS IN ORGANIC MATTER FROM FLOOD-PLAIN SECTIONS OF SMALL RIVERS

Bioclimatic belt	Mean annual temperature (°C)	Annual precipitation (cm)	No. of samples from flood-plain sections	Sampling depth (m)	$\delta^{13}C_{org}$ (‰) (PDB)
		Zapadnaya Dvina			
Forest, temperate	3	61.2	1	0–0.1	–43.6
			7	0.6–0.7	–37.7
			14	1.3–1.4	–38.8
			20	1.6–1.7	–39.8
			21	1.9–2.0	–40.6
		Eruslan			
Steppe, dry	4.2	39.0	1	0–0.08	–39.9
			3	0.16–0.24	–37.0
			7	0.32–0.40	–34.6
		Istisu			
Dry subtropical	15	124.7	1	0–0.1	–33.5
			4	0.18–0.24	–24.5
			6	0.30–0.36	–25.5
			9	0.48–0.54	–39.3
			15	0.84–0.90	–39.7
		Supsa			
Humid subtropical	13.8	215.4	1	0–0.1	–34.5
			3	0.2–0.3	–34.9
			9	0.8–0.9	–38.7
			15	0.14–0.15	–41.3
			20	1.6–1.7	–38.2
		Ehsheri (sea)			
	13.4	234	1	0–0.1	–35.4
			3	0.2–0.3	–37.0
			7	0.6–0.7	–36.9
			9	0.8–0.9	–39.9
			10	0.9–1.0	–37.1

The alluvial deposits mainly consist of organic and mineral suspensions accumulated from fairly large areas during the flood season. The deposits are supplemented at low water by the meadow and forest vegetation that grows naturally on the flood plain.

The alluvial sections have three characteristics of importance to us: (1) they display very little discrete structure because each new flood deposit is superimposed on the previous one; (2) the organic matter occurring in the alluvial sections of small rivers provides an average sample of the organic matter found in the corresponding bioclimatic belt; and (3) the flood plains from which the samples are taken constitute 'live' geomorphological units that are not affected by epigenetic processes, so the complex structure of these sections is preserved over time.

In order to ensure maximum representativeness of the data, the entire ground was sampled by means of a vertical-section trenching technique, each sample covering a specific depth not exceeding 5–10 cm.

The forest bioclimatic belt, i.e. a zone of temperate and humid climate, is represented by a flood-plain section in the upper reaches of the Zapadnaya Dvina near Toropets. The alluvial deposits reach a depth of 2 m in this area and are underlain by typical lake sediments.

In the steppe bioclimatic belt, i.e. where the climate is dry, we took samples from an alluvial section 0.4 m deep in the upper reaches of the Eruslan river (a tributary of the Volga near Saratov). This section is underlain by fluvial sand deposits.

The dry sub-tropical belt is represented by an alluvial section of the Istisu river in the Lenkoran' region of Azerbajdzhan. The section is 0.80 cm deep and is laid down on pebble-boulder fluvial deposits.

In the same sub-tropical belt but in a humid sub-tropical region, we took samples from an alluvial section in the lower reaches of the Supsa river, which flows into the Black Sea near Batumi. The section is 1.7 m deep. The black-earth alluvial deposits are underlain by clays exhibiting a strong hydrosulphuric odour, indicating that they are of marine origin.

To draw a comparison with continental sections, we also analysed samples of Black Sea sediments taken from a submarine canyon situated in the extension of the Ehsheri river valley into the sea. The canyon bottom lies about 67 m from the surface in an area where the average sea depth is 15–20 m. The length of the drill-core pipe permitted the benthic deposits to be sampled to a depth of 1 m.

The geologic data indicate that the flood-plain sections belong to the Holocene, the lower layers being about 10 000–11 000 years old.

We should emphasize that only the initial results of our investigations are reported in this paper. Not all the samples have undergone isotopic analysis; instead, we have selected two or three samples to represent the upper, middle and lower parts of each section.

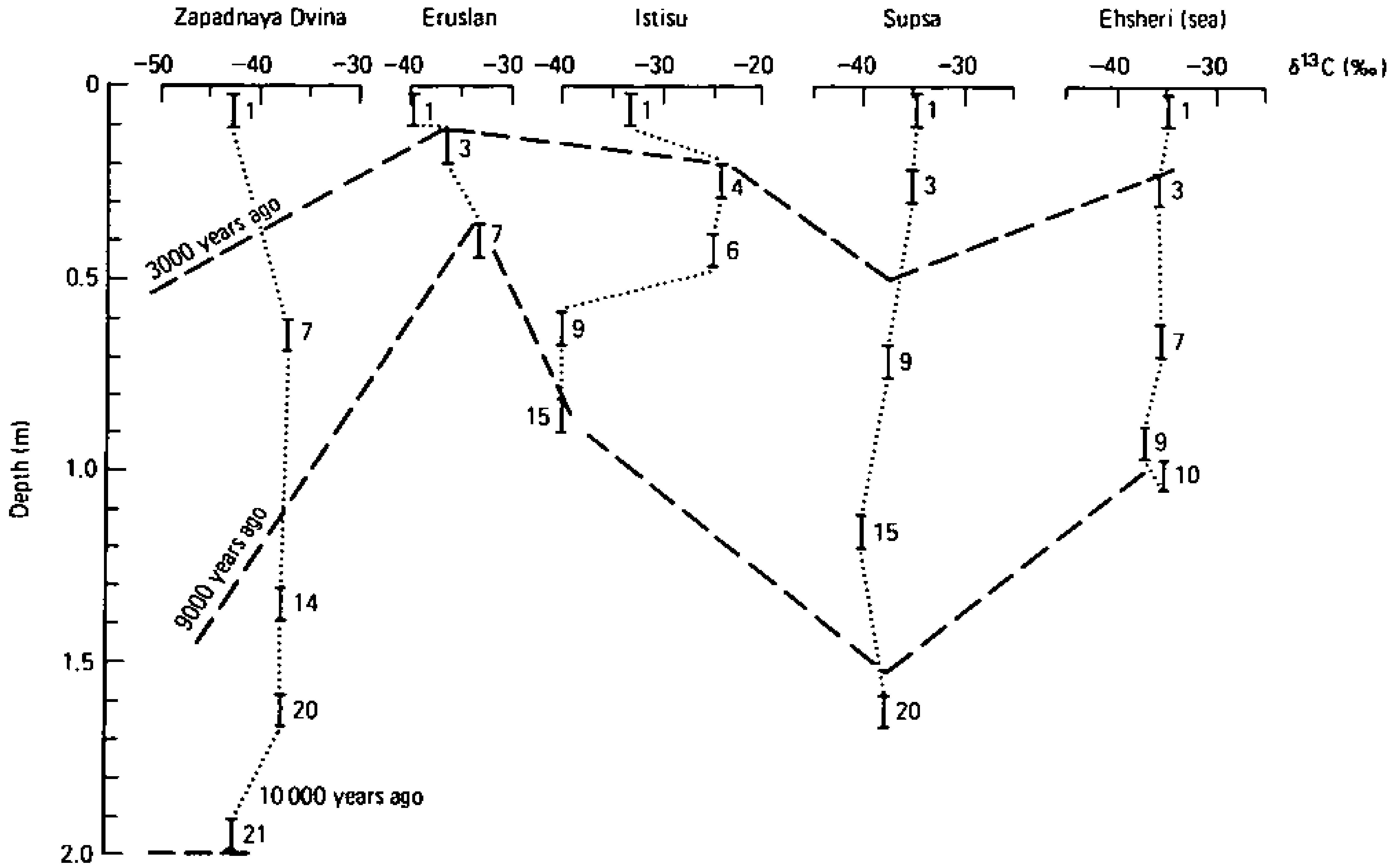

FIG. 9. $\delta^{13}C$ variations with depth recorded in samples of organic matter taken from flood-plain sections in various bioclimatic zones. The figures denote the sample number (see Table IV).

The soil samples were first boiled in hydrochloric acid for one hour and then washed twice with distilled water to separate out the carbonate component. The organic matter was further broken down by a 'wet' method; approximately 300 g of the sample were placed in a round-bottomed flask from which the air was evacuated over a two-hour period by means of an oil pump. The sample was then treated with a mixture of concentrated sulphuric acid and potassium bichromate and left at room temperature for 24 hours, after which the carbon dioxide gas released was collected in a liquid nitrogen trap. To remove any gaseous impurities and moisture, the CO_2 sample was chilled three times in alternate mixtures of dry ice + acetone (t ~ −70°C) and liquid nitrogen (t ~ −196°C). The clean CO_2 sample was then sent for carbon isotope measurements on a GD-150 mass spectrometer.

The results shown in Table IV are expressed in $\delta^{13}C$ values versus PDB standard with an accuracy of ±0.8‰ allowing for the reproducibility of the chemical treatment.

The results of the organic matter carbon isotope analyses are shown in Table IV and plotted against the sampling depth in Fig.9.

In order to compare our carbon isotope results with palaeoclimatic fluctuations during the Holocene in Europe, we referred to a record of mean

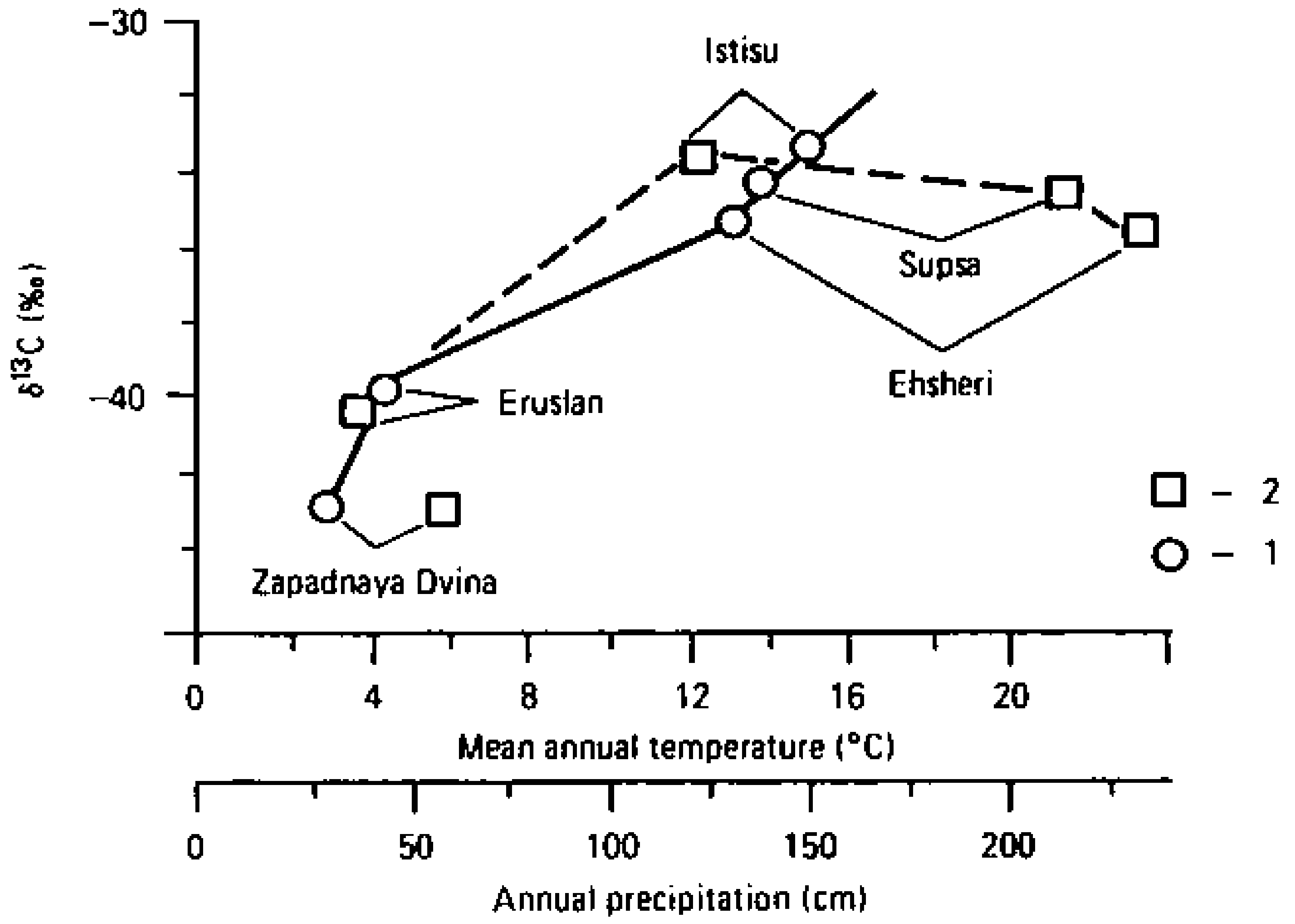

FIG.10. $\delta^{13}C_{org}$ variations in the modern upper layers of flood-plain sections, plotted against the mean annual temperature (1) and humidity (2) of the corresponding bioclimatic zone.

summer temperatures based on the oxygen isotope composition of carbonate shells found in lake sediments on the island of Gotland (Baltic Sea) [21]. In our view, this record provides the most accurate and detailed palaeotemperature scale for Europe. It comprises the following major periods:

(1) From 11 000 to 9000 years ago when there was a transition from the Pleistocene glaciation to the warmer Holocene with temperatures 2–3°C lower than they are today;
(2) From 9000 to 3000 years ago when there was a general rise in temperatures with maximum summer temperatures 2–3° higher than they are today;
(3) From 3000 to 2000 years ago when temperatures dropped ~2°C to their present level;
(4) From 2000 years ago to the present day when modern temperatures have prevailed.

Based on these major periods, which included some minor fluctuations, we divided the flood-plain sections into three parts. We assumed that each bioclimatic belt had its own but, on average, constant sedimentation rate and broke each section down into a lower layer roughly corresponding to the period from 10 000 to 9000 years ago, a middle layer corresponding to the period from 9000 to 3000 years ago and an upper layer corresponding to the period from 3000 years ago to the present. These time boundaries are shown by the broken lines in Fig.9.

Figure 9 shows that, for modern organic matter from the upper layer down to a depth of 15 cm, $\delta^{13}C$ varies from −43 to −33.5‰ and increases steadily by 9.5‰ as we go from a temperate climate to a dry sub-tropical climate. However, if $\delta^{13}C_{org}$ is compared with the modern mean annual air temperature, we see that the variation does not follow a regular pattern; during the transition from the temperate forest climate to the steppe climate, the temperature gradient is 3‰ per 1°C, but in the transition from the steppe to the dry sub-tropical climate the gradient becomes ~0.6‰ per 1°C (Fig.10). This is normal since the type of vegetation occurring in each bioclimatic belt depends not only on the temperature conditions but also on the availability of moisture. With a given availability of moisture, the dominant type of vegetation is to a large extent determined by the range of summer and winter air temperatures. Therefore, to establish a possible interrelationship between temperature and the isotopic composition of the organic matter occurring in the various climatic regions, it is more correct to refer to the mean annual temperatures.

In Fig.10, variations in the carbon isotope composition of organic matter sampled from the modern upper layers are plotted against the mean annual temperature and humidity prevailing at the given location. Figure 10 shows an almost linear relationship between $\delta^{13}C_{org}$ and temperature, whereas the humidity dependence is more complex. In the low temperature region (3–4°C), as the humid forest climate changes to a dry steppe climate, the carbon isotope effect amounts to 0.17‰ per 1 cm reduction in annual humidity. In the region of high mean annual temperatures (13–15°C), as the dry sub-tropical climate changes to a moister climate, the carbon isotope effect drops to 0.01‰ per 1 cm reduction in humidity. In the intermediate region significant changes both in temperature (4–13°C) and moisture (60–125 cm/a) occur simultaneously. It is impossible to separate these two parameters in order to evaluate the effect of each on biogenic fractionation ($\delta^{13}C$) because there is no analytic interrelationship between mean annual temperatures (t°C) and the amount of precipitation (P_{cm}). We can, therefore, discuss only the overall isotopic effect. In dry conditions where the steppe climate changes to a dry sub-tropical climate, the temperature gradient is 0.6‰ per 1°C increase in temperature, to be compared with –0.84‰ per 1°C in humid conditions where the temperate climate changes to a humid sub-tropical climate; in other words, as moisture increases, plants react more sharply to temperature variations. To put it another way, when moisture conditions are favourable, plants are more sensitive to changes in temperature. In humid conditions, the bioseparation effect produced by each 1°C increase in temperature is equivalent to that produced by a nearly 1.5°C increase in temperature in dry conditions (0.84:0.6 = 1.4). There is a physical explanation for this, since high moisture damps temperature variations, and the oscillations that do occur have the same effect as a much greater increase in temperature in drier conditions.

Both our data and those published in the literature show that humidity and temperature have differing effects on the separation factor. An increase in humidity leads to an increase in fractionation, whereas an increase in temperature reduces fractionation. As regards isotopic effects, this process brings about a reduction in $\delta^{13}C$ in organic matter in the first instance and an increase in the heavy isotope content in the second instance. Since we have observed that the carbon isotope content in the modern samples becomes progressively heavier as we move from north to south through the bioclimatic belts, temperature rather than moisture must be the decisive factor in biological fractionation over the given humidity and temperature range.

If we now consider the variation of $\delta^{13}C_{org}$ in our flood-plain samples with depth or, what is the same thing, with age, we are struck by the distinct and everywhere observable variations in the carbon isotope content of the samples dating from 3000 to 9000 years ago. In the Zapadnaya Dvina, Eruslan and Istisu sections, the atomic weight of carbon tends to be higher than in the modern samples. The maximum values occurring in these sections are 5.9, 5.3 and 9‰ respectively; these results tie in well with the general rise in temperature that has been established by various geological and isotopic methods. If we use the maximum temperature gradient that has just been calculated on the basis of modern samples (~0.8‰ per 1°C), we find that the mean annual temperature prevailing in the various belts during the Holocene was 7°, 6.3° and 10.7° higher than it is today. This variation is far greater than the increase in mean summer temperatures in Europe for the same period (3000 to 9000 years ago) quoted in Ref. [21], i.e. 2–3°C. The only reasonable explanation for this difference between mean annual and mean summer temperatures is that the increase in mean annual temperatures was mainly due to an increase in winter temperatures compared with summer temperatures. This means that the warmer climate during the Holocene was reflected in essentially milder winters and a shorter seasonal temperature span. These trends can only be the result of a general increase in humidity, which fits in with the idea of high ocean levels during the interglacial period.

On the basis of the same line of reasoning, the 8°C reduction in mean annual temperatures in the Supsa river section at the beginning of the Holocene compared with the period from 3000 years ago to the present should be regarded as a sign of much lower winter temperatures and possibly a general increase of 2°C in summer temperatures. Consequently, the climate on the Caucasian coast at the beginning of the Holocene, some 8000 years ago, must have been more continental with sharp seasonal drops in temperature. The ^{13}C concentration found in the Lower-Holocene organic matter in the Supsa section matches the $\delta^{13}C_{org}$ value in the Zapadnaya Dvina section during the Holocene peak (~3000 years ago). If such a comparison is permissible, we may assume that the climate on the Caucasian coast about 8000 years ago was similar to the mild continental climate prevailing in the northern latitudes when temperatures were at their highest.

The $\delta^{13}C$ variations in the Supsa flood-plain section indicate that the continental climate began to grow milder 8000 years ago and became more like a moist, marine climate. By 3000 years ago, the climate was similar to the conditions we know today. If we consider the conclusions drawn by Deuser from his study of carbonates and organic matter in Black Sea sediments [22], we can establish a link between the general climatic trends on the Caucasian coast and the hydrology of the sea. According to Deuser, up to 9000 years ago the Black Sea was a closed, inland water body containing fresh water. The comparatively low humidity and proximity of the high mountains may have given rise to considerable seasonal fluctuations in temperature. Some 9000 years ago, as a result of a general rise in the ocean level, salt water began to flow into the Black Sea after it was connected to the Mediterranean Sea and to the world ocean. The Black Sea reached its present level and degree of salinity 3000 years ago, as is borne out by our own data, i.e. $\delta^{13}C_{org}$ in the Supsa flood-plain section has remained at its present level over the past 3000 years.

The variation in $\delta^{13}C_{org}$ with depth in the coastal marine canyon in the Ehsheri river region (Fig.9) is entirely synchronous with the isotopic fluctuations in the Supsa river section. This result indicates first that the organic matter in the benthic deposits near the coast is of continental origin and, hence, that the submarine canyon is most likely to be an extension of the Ehsheri river valley. Second this result shows that the climatic variations during the Holocene were common to the whole (or at least to the southern part) of the Black Sea coast.

4. CONCLUSIONS

The following conclusions may be drawn from our investigations.

(1) The variations in the carbon isotope composition of organic matter occurring in the flood-plain sections are on the whole consistent with the climatic changes during the Holocene Epoch (~10 000 years ago).

(2) The $\delta^{13}C$ values recorded in the organic matter sampled from the modern upper layers of the sections reflect both the mean annual temperatures and the general humidity prevailing in the various bioclimatic belts. Temperature is the main parameter governing the isotopic composition of the organic matter. However, since we cannot separate the effects of these two environmental parameters, we have calculated the overall isotopic effect over a natural mean annual temperature range of +4°–+15°C and over a moisture range of 40–215 cm per year. The overall effect is 0.6–0.8‰ per 1°C temperature rise.

(3) By using the calculated coefficient for maximum $\delta^{13}C_{org}$ shifts during the period from 3000 to 9000 years ago, we estimate that the mean annual

temperatures in the various climatic belts were about 7–10°C higher than they are today. We compare these temperatures with the mean summer values obtained by Mörner and Wallin [21] using an oxygen isotope thermometer and we thus assume that the variation in climatic conditions during the Holocene was mainly due to an increase in winter temperatures and to a decline in the continental climate.

(4) The reduction in mean annual temperatures during the Lower-Holocene which was observed in the sections from the Black Sea coast (Supsa, Ehsheri) is connected with the particular history of the Black Sea as established by Deuser from isotopic investigations of benthic deposits. The transition from continental climatic conditions to a moist, marine climate, which ended about 3000 years ago, corresponds with the change in the Black Sea from a freshwater lake to a saltwater body forming part of the general Atlantic Ocean system.

Further investigations in the same direction will allow us to draw more precise and more extensive conclusions.

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DEPENDENCE OF $\delta^{18}O$ AND δD IN PRECIPITATION ON CLIMATE

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Abstract

DEPENDENCE OF $\delta^{18}O$ AND δD IN PRECIPITATION ON CLIMATE.

Different kinds of comparisons of $\delta^{18}O$ with temperature are discussed, mainly for European stations from the IAEA/WMO network. Anomalies (deviations from mean monthly values) of $\delta^{18}O$ are significantly correlated to temperature anomalies, but this correlation explains only about 10–20% of the overall isotopic variability. According to the Rayleigh condensation model, $\delta^{18}O$ and δD directly depend on the degree of rainout f which is given by the ratio between the water vapour mixing ratios at the sampling station and in the vapour source region. The observed relation between δD and f at Valentia, Stuttgart and Vienna, taking the Azores as representing the vapour source region, is in remarkably good agreement with the Rayleigh model.

1. RAYLEIGH CONDENSATION MODEL

Although stable isotope analyses have become a standard tool in hydrological and palaeoclimatic studies, the climatological causes of the variations of $\delta^{18}O$ and of δD are not yet fully understood. For this reason, it is not possible at present to interpret isotope records stored in polar ice and other materials in a quantitative way, for instance in terms of temperature. The review of Dansgaard [1] is still valid as a comprehensive summary of observed ^{18}O and deuterium variations in precipitation, and the Rayleigh condensation model, although strongly simplifying the natural processes, is still being generally used (sometimes in a modified way) for explaining these variations. Different kinds of systematic stable isotope variations were empirically found by Dansgaard and others. For temperate latitudes, particularly temperature, continentality and altitude are parameters that influence $\delta^{18}O$ and δD.

A major part of the stable isotope variability can be explained by rainout of the heavy isotopes during the continuing condensation of precipitation from a moist air mass. This has been represented as a Rayleigh condensation process, whereby isotopic equilibrium and immediate removal of the condensate without any further interaction with the vapour are assumed. For an infinitesimal condensation step, this can be written as

$$f\,dR_v = (\alpha - 1)R_v\,df \tag{1}$$

where R_v = isotope ratio ($^{18}O/^{16}O$ or D/H) of the vapour
f = remaining fraction of vapour mass
α = isotope fractionation factor between condensate and vapour ($\alpha > 1$).

Equation (1) can be integrated if it is approximated by using instead of the (variable) fractionation factor some mean value $\bar{\alpha}$; the result is

$R_v = R_{vo} f^{\bar{\alpha}-1}$, and for the condensate:

$$R_c = \alpha R_{vo} f^{\bar{\alpha}-1} \tag{2}$$

or $$\delta_c = \alpha(1 + \delta_{vo}) f^{\bar{\alpha}-1} - 1 \tag{3}$$

R_{vo} and δ_{vo} indicate the isotopic composition of the original vapour.

According to the Rayleigh model, the isotopic composition depends on the degree of condensation f, on the initial vapour composition R_{vo} and, through the fractionation factor α, on temperature. Since α does not vary strongly with temperature (except for a discontinuity at the liquid-ice transition), the direct dependence of δ on temperature is relatively weak.

The Rayleigh model does not take into consideration post-condensational changes of raindrops and snowflakes, i.e. evaporation and vapour exchange, or mixing of vapour masses of different origin. The first process in general tends to enrich the heavy isotopes, especially ^{18}O, in rain. The second process occurs, for instance, when evapotranspiration adds water vapour to an air mass moving over the continent. If the added vapour has the same composition as the last-condensed precipitation, there will be no net isotopic change, compared to the pure Rayleigh case (Fig. 1(b)). (In Figs 1(b) and 1(c), f refers to the total vapour mass present, including added vapour, rather than to the residual of the original vapour only.) Since evapotranspiration does not involve isotopic fractionation, this situation may occur when the evapotranspired water is from rain from the same season.

If, however, isotopically different vapour is added to the atmosphere, the relation δ–f will be affected. This case can be expected in summer in temperate latitudes, when vapour from isotopically light winter precipitation is admixed (Fig. 1(c)). If the liquid water content of a cloud is taken into account, the Rayleigh Eqs (2) and (3) have to be changed by replacing $(\bar{\alpha} - 1)$ by $(\bar{\alpha} - 1)/(1 + \bar{\alpha}L) \simeq (\bar{\alpha} - 1)/(1 + L)$, where L = relative amount of liquid cloud water [2, 3]. This means that the slope of the curve $\delta(f)$ is simply reduced by the factor $1/(1 + L)$.

Eriksson [4] pointed out that condensation by mixing leads to a smaller decrease of δ than condensation under Rayleigh conditions, and he found that

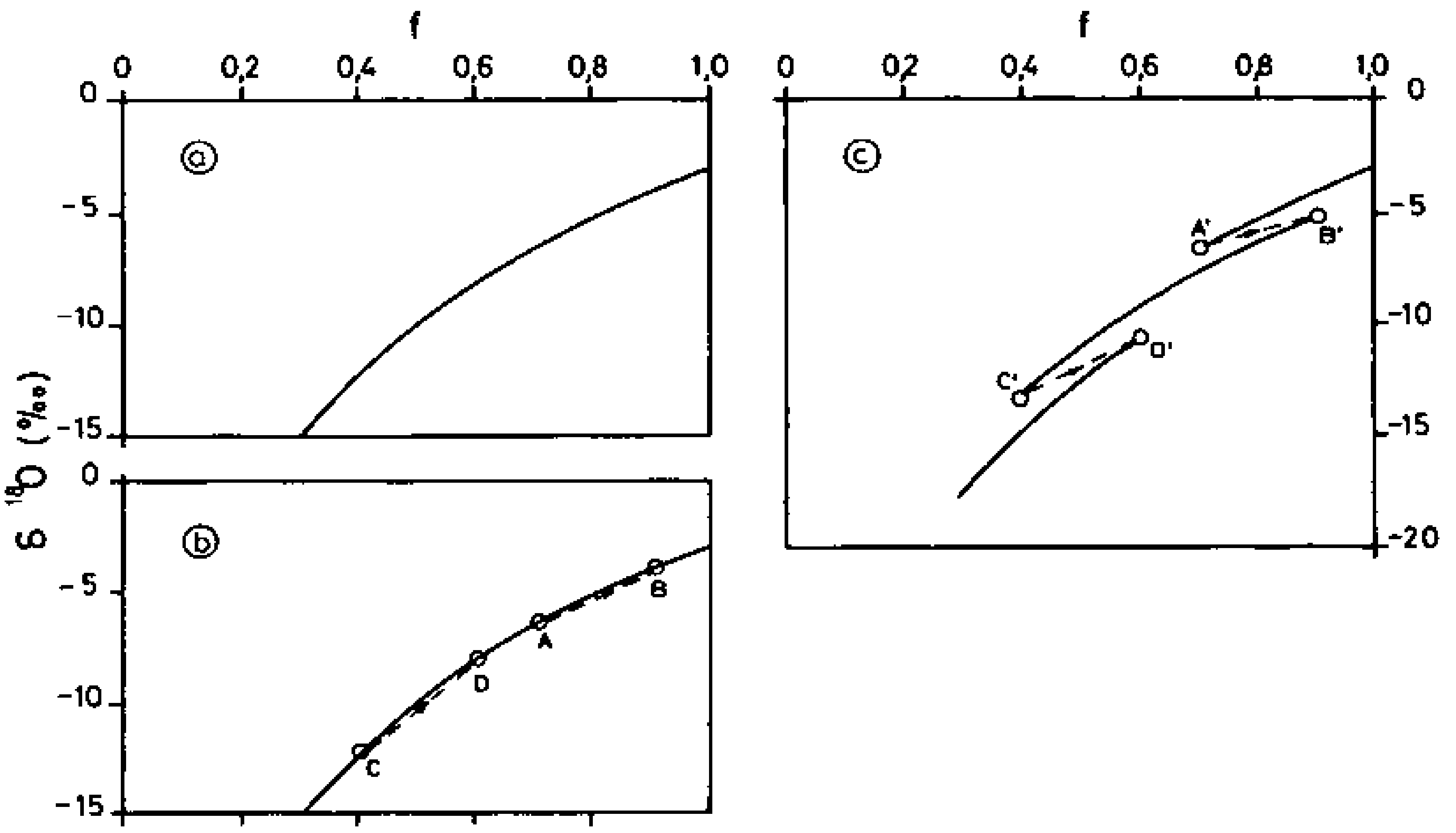

FIG.1. Depletion of ^{18}O in precipitation with progressing condensation according to the Rayleigh model. f = amount of water vapour relative to original amount. Fractionation factor $\alpha = 1.010$. (a) Simple Rayleigh condensation. (b) Admixture of vapour of same $\delta^{18}O$ as previously outrained condensate: net effect is not different from case (a). f = 1 → A: Rayleigh condensation; A → B: vapour is added; B → C: Rayleigh condensation; C → D vapour is added; etc. (c) Similar to (b), but $\delta^{18}O$ of added vapour is 5% lower than $\delta^{18}O$ of previous condensate.

under some special assumptions, the δ–f relation follows a law analogous to the Rayleigh formula, but $(\sqrt{\bar{\alpha}} - 1)$ replacing $(\bar{\alpha} - 1)$. For the actual formation of clouds, condensation by mixing of air masses of different moisture content plays an insignificant role, so this case is of no practical importance for precipitation.

As already mentioned, the direct influence of temperature on the rainout of the heavy isotopes is of minor importance only. There is a large indirect effect, because condensation is in general an effect of cooling, so the remaining fraction of vapour f is related to temperature. The variation of f, and therefore of δ, with temperature depends on the type of cooling. For $\delta_v \simeq 0$, we get from Eq. (1) and the relationship $(d\delta_c/dT) \simeq (d\delta_v/dT) + (d\alpha/dT)$ that:

$$\frac{d\delta_c}{dT} \simeq \frac{\alpha - 1}{f}\,\frac{df}{dT} + \frac{d\alpha}{dT} \qquad (4)$$

For isobaric cooling, f is proportional to the vapour pressure e, hence $(1/f)(df/dT) = (1/e)(de/dT)$. At 10°C, $(1/e_s)(de_s)/(dT) = 0.067°C$ (e_s = saturation vapour pressure), $\alpha - 1 = 10.7‰$ and $d\alpha/dT = -0.10‰/°C$ for $^{18}O/^{16}O$, hence $d\delta_c/dT \simeq 0.62‰/°C$ for isobaric cooling. Here T denotes condensation temperature, which is, in general, lower than surface temperature; a better measure than surface temperature is dew-point temperature. For moist-adiabatic cooling, $d\delta/dT$ is lower because air expands while cooling; thus for a given decrease of vapour pressure, a larger temperature decrease is necessary. For an estimate it is convenient to start from the water vapour mixing ratio m (g water per kg air). If p is the barometric pressure and M_w and M_{air} are the molecular weights of water and air, then

$$m = \frac{e}{p} \quad \frac{M_w}{M_{air}}$$

$$\text{and} \quad \frac{df}{f} = \frac{dm}{m} = \frac{de}{e} - \frac{dp}{p} \tag{5}$$

The moist-adiabatic lapse rate is, for 10°C and 1000 mbar, −0.53°C per 100 m [5]; the corresponding decrease of saturation vapour pressure (with 6.7% per degree) is −3.6% per 100 m of height increase. Barometric pressure changes by −1.2% per 100 m. Thus, from Eq. (5), $(1/f)(df/dT) \simeq (-3.6\% + 1.2\%)/(-0.53°C) = 4.4\%/°C$, and from Eq. (4), $d\delta_c/dT \simeq 0.38‰/°C$. For deuterium, the temperature coefficients estimated in the same way are 5.2‰/°C for isobaric and 2.9‰/°C for adiabatic cooling.

In nature, condensation is most effective when caused by uplift of air, that is by moist-adiabatic cooling. This type of cooling applies for vertical isotope profiles. If, however, horizontal variations between different stations at about the same altitude are considered, conditions vary approximately in an isobaric way.

2. VARIATION OF $\delta^{18}O$ WITH TEMPERATURE

We can consider three different ways to compare $\delta^{18}O$ and temperature (cf. Fig. 2): (1) changes of annual mean values at a fixed location, (2) short-term (seasonal) variation at a fixed location and (3) long-term mean values at different stations. The model relationships are derived for condensation temperatures, but since these are not generally available, comparison is commonly made with surface temperature (which naturally is not an ideal substitution). Relationships (1) to (3) have been discussed earlier for several stations in Switzerland [6]. Here, the discussion is extended to other stations from the IAEA/WMO network, data for which were taken from a magnetic tape supplied by the IAEA (same data as in [7] and from Ref. [8].

If one is interested in interpreting isotope records in terms of palaeoclimate, comparison (1), between long-term changes of $\delta^{18}O$ and temperature, is the most appropriate. Data (weighted annual means of $\delta^{18}O$ versus arithmetic means of

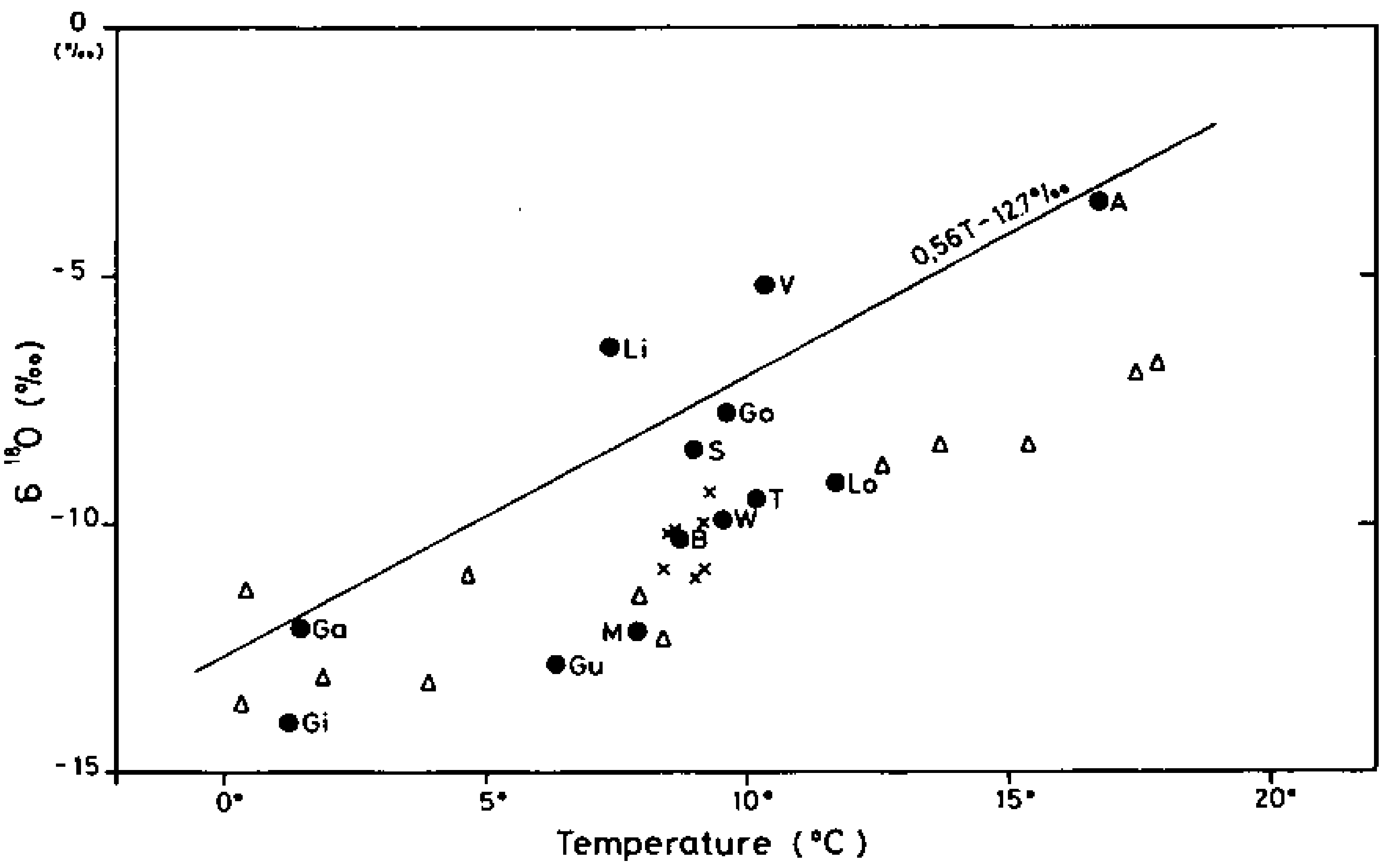

FIG.2. Mean $\delta^{18}O$ values versus mean temperatures: X arithmetic mean values for individual years at Bern, Δ mean monthly values (arithmetic) for Bern. ● Long-term annual arithmetic mean $\delta^{18}O$ versus temperature for European stations. A: Azores, B: Bern, Ga: Grønnedal, Gi: Grimsel, Go: Groningen, Gu: Guttannen, Li: Lista (Norway), Lo: Locarno, M: Meiringen, S: Stuttgart, T: Thonon (France), V: Valentia (Ireland), W: Vienna. B, Gi, Gu, Lo and M are locations in Switzerland.

temperature, from Ref. [8]) for a number of stations in temperate and high latitudes, for which results exist for at least 8 years, have been statistically tested for correlation (Table I). Significant correlation with a confidence level of at least 90% is found at only 4 out of 14 stations; the corresponding temperature coefficients (slopes of the regression lines) are between 0.40 and 1.9‰ per degree. At 3 more stations, correlation is significant at low confidence levels of between 80 and 90%, one of them (Gough, Ireland) with a negative temperature coefficient; at the remaining 7 stations, annual means of $\delta^{18}O$ are not correlated to temperature in any significant way. This result is deceptive with respect to palaeoisotope records because we cannot deduce a temperature coefficient for their interpretation. It does not mean, however, that there is no correlation on a longer term between climate and $\delta^{18}O$ in precipitation, because the statistics cover only a few years. The lack of correlation between annual mean temperature and $\delta^{18}O$ is illustrated for Bern in Fig. 2. (The crosses in Fig. 2 represent arithmetic means, while weighted means were used for Table I. Qualitatively, the correlation is not different for the two kinds of mean annual values.)

The annual cycles of $\delta^{18}O$ and temperature cover a large range of 'climates', and there is a rather good correlation between the two parameters when mean monthly values are considered, as illustrated in Fig. 2 for Bern (triangles). Also,

TABLE I. WEIGHTED ANNUAL MEANS OF $\delta^{18}O$: CORRELATION WITH TEMPERATURE

Linear regression: $\delta^{18}O = a\,T(^\circ C) + b$

Station		r[a]	s[b]	a	b	n[c]
Reykjavik	(64°N)	0.514	>80%	(0.37)	(−9.5)	8
Lista	(58°N)	0.283	–			8
Groningen	(53°N)	0.378	>90%	0.40	11.7	13
Stuttgart	(49°N)	−0.390	–			8
Vienna[d]	(48°N)	0.176	–			12
Thonon	(46°N)	0.290	–			13
Chicago	(42°N)	0.082	–			9
Teheran	(36°N)	0.704	>97.5%	1.75	−43.8	10
Windhoek	(23°S)	0.590	>95%	1.91	−42.0	13
Pretoria	(26°S)	−0.132	–			13
Gough, Ireland	(40°S)	−0.426	>80%	(−0.36)	(0.2)	11
Invercargill	(46°S)	0.542	>80%	(2.03)	(−21.8)	10
Argentine Island	(65°S)	0.602	>95%	0.58	−8.9	13
Halley Bay	(75°S)	−0.333	–			10

[a] r = correlation coefficient.

[b] s = statistical significance (two-sided) [7].

[c] n = number of years; only years for which $\delta^{18}O$ represents $\gtrsim$95% of the total annual precipitation were considered.

[d] 1960 is not included in the analysis because $\delta^{18}O$ is suspiciously high.

between $\delta^{18}O$ and temperature of individual monthly samples the correlation is highly significant, in general with a confidence level of higher than 99.9% (Table II(a)). For the coastal stations Valentia (Ireland) and Grønnedal (Greenland), the correlation coefficients r are much lower than for the continental locations, which can be related to the smaller overall variability of $\delta^{18}O$ at maritime stations. The temperature coefficients for the continental stations studied are, with one exception, between 0.35 and 0.43‰/°C, and they are also in this range for most other extra-tropical continental stations of the IAEA/WMO precipitation network [8]. The one exception is Meiringen, in the Swiss Alps, located in a valley surrounded by high mountains; here, $\delta^{18}O$ is influenced orographically [6].

TABLE II. REGRESSION ANALYSIS OF MONTHLY PRECIPITATION SAMPLES

(a) $\delta^{18}O$ versus temperature, (b) $\delta^{18}O$ anomaly versus temperature anomaly. Correlations for a and b are all significant at the >99.9% level, except for Grønnedal (a, s > 99%; b, not significant at the 80% level) and Meiringen (b, s > 99%). Regression model $\delta^{18}O = aT + b$. For b the means and therefore the intercept are zero by definition of the anomaly. (Data for Valentia, Stuttgart, Vienna and Grønnedal (1962–65, 73–74) are from IAEA tape; for Bern, Meiringen and Locarno (1971–78) are our own measurements [6].)

(a) $\delta^{18}O$ versus temperature

Station	r^2	a	b
Valentia	0.184	0.23	−7.6
Stuttgart	0.546	0.37	−11.7
Vienna	0.618	0.43	−13.7
Bern	0.540	0.35	−13.7
Meiringen	0.630	0.53	−16.5
Locarno	0.676	0.40	−14.2
Grønnedal	0.138	0.21	−12.4

(b) Anomalies of $\delta^{18}O$ versus anomalies of temperature

Station	r^2	a	n
Valentia	0.224	0.69	59
Stuttgart	0.166	0.43	71
Vienna	0.166	0.52	69
Bern	0.140	0.50	96
Meiringen	0.089	0.45	99
Locarno	0.160	0.53	76
Grønnedal	0.026	(0.21)	55

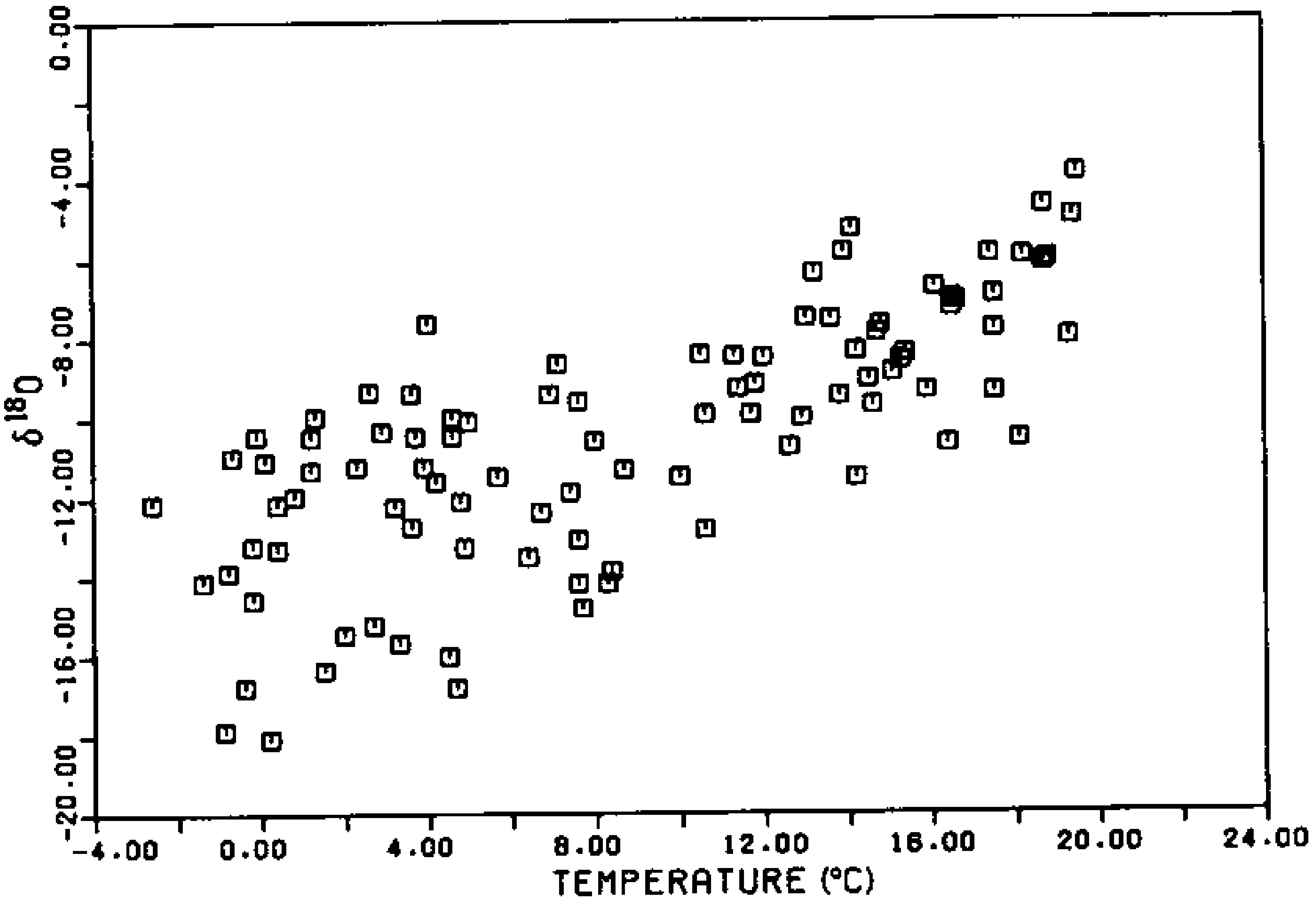

FIG.3. $\delta^{18}O$ versus temperature for monthly precipitation samples of Bern, 1971–1978.

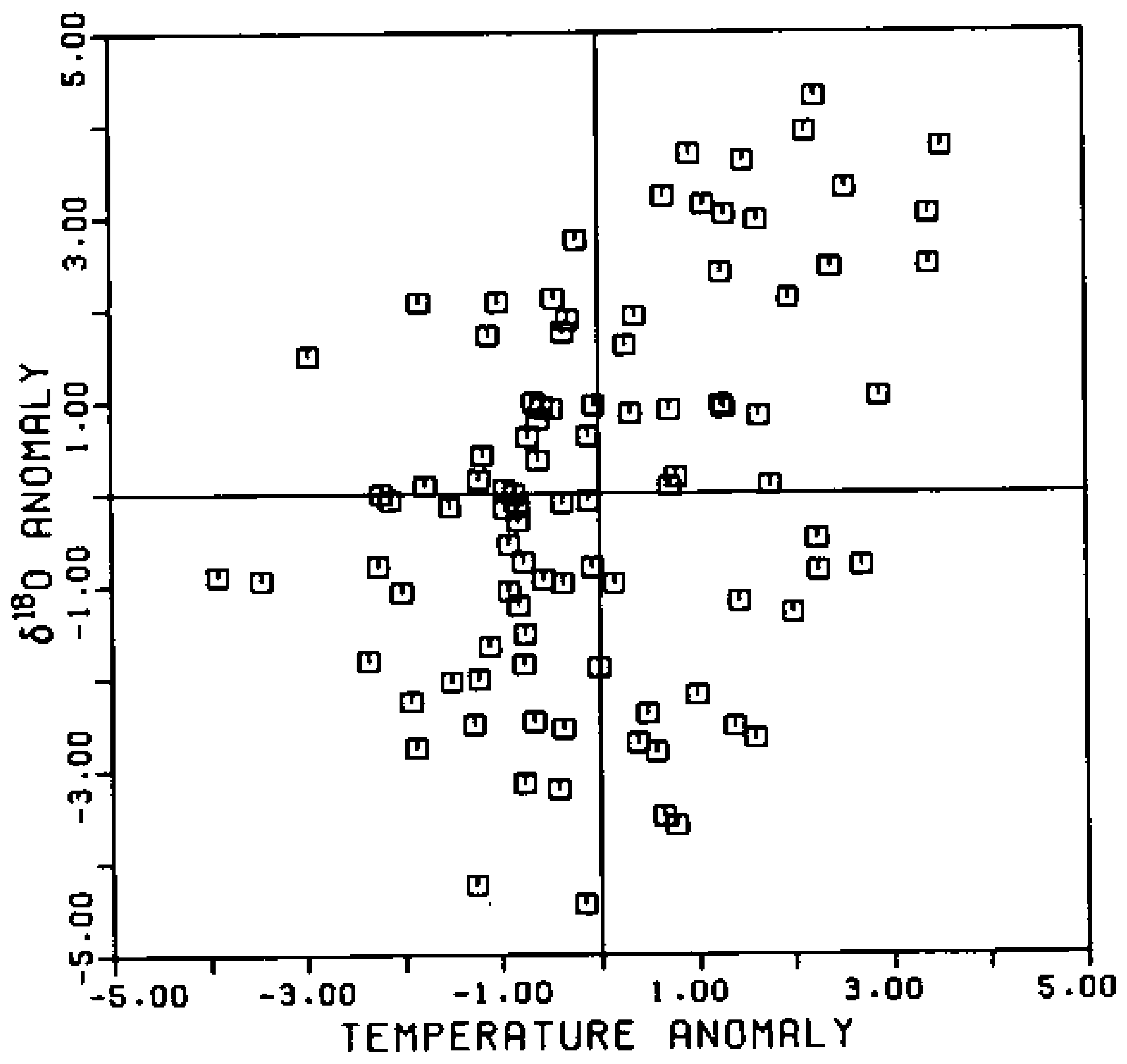

FIG.4. $\delta^{18}O$ anomalies versus temperature anomalies for monthly precipitation samples at Bern. Anomaly is defined as deviation of the values for the individual month from the long-term monthly mean value.

In spite of the highly significant correlation, variation of temperature can account for only 54 to 68% of the seasonal δ^{18}O variability at continental stations, and for 14 and 18% at the two coastal stations of Table II (a) (coefficient of determination, r^2). This is expressed in a δ^{18}O-temperature plot by a high standard deviation around the regression line (standard error of estimate) of e.g. 2.1‰ for Bern (Fig. 3).

To study the influence of temperature in more detail we removed the mean seasonal trends from the monthly data by considering anomalies, that is the deviations from the mean values for that month. (For instance, the temperature anomaly for January 1975 is defined as T (Jan 75) – $\overline{T}$ (Jan).) In this way one can see whether, e.g. in an unusually cold January, δ^{18}O is actually lower than generally in January. The results are given in Table II (b) and plotted for Bern in Fig. 4. Except at Grønnedal, there is a statistically significant correlation for all considered stations including Valentia, but temperature explains only between 9 and 22% of the overall variability of isotopic anomalies. Figure 4 illustrates the large scatter well enough. For palaeoclimatic work on ice cores this means that a detailed interpretation of δ^{18}O records in terms of temperature is not justifiable, at least not in temperate latitudes.

For long-term mean values of coastal stations, Dansgaard [1] found the well known relation $\delta^{18}O = 0.70T - 13.7‰$. This relation is valid for temperatures below about 10°C. For stations in the temperature range 0 to 20°C, van der Straaten [9] determined the mean relation

$$\delta^{18}O = 0.56T - 12.7‰$$

which is indicated by a line in Fig. 2, where long-term annual mean values for European stations are also given (full circles). The effect of continentality is clearly visible in Fig. 2. Thus, δ^{18}O decreases systematically from Valentia (V in Fig. 2) through Groningen (Go) and Stuttgart (S) to Vienna (W), totally by nearly 5‰, although all four stations have similar mean temperatures (between 9.0 and 10.3°C).

The relation between mean values at different stations is not directly comparable to climatic variations because precipitation at different stations may originate from different vapour source regions and be influenced by regional geographical features such as orography.

According to the Rayleigh model, isotopic composition should be compared with the temperature difference between the water vapour source region and the precipitation sampling station, rather than just with temperature at the latter. In general, water vapour transport over Europe is from the west to the west-southwest [10], so the IAEA/WMO station on the Azores (Ponta Delgada) probably represents well the major vapour source region for Stuttgart and Vienna; for Valentia, the source region may be somewhat more to the north. The isotopic composition of rain can be influenced by evaporation. Since this effect is less important for deuterium than for ^{18}O, we will now consider deuterium data. In Fig. 5, mean monthly δD-values for Valentia, Stuttgart and Vienna (based on all data available on the IAEA data tape) are plotted versus the temperature difference ΔT between the Azores and the station considered. This comparison implies the assumption that the initial vapour composition in the source region is approximately constant throughout the year.

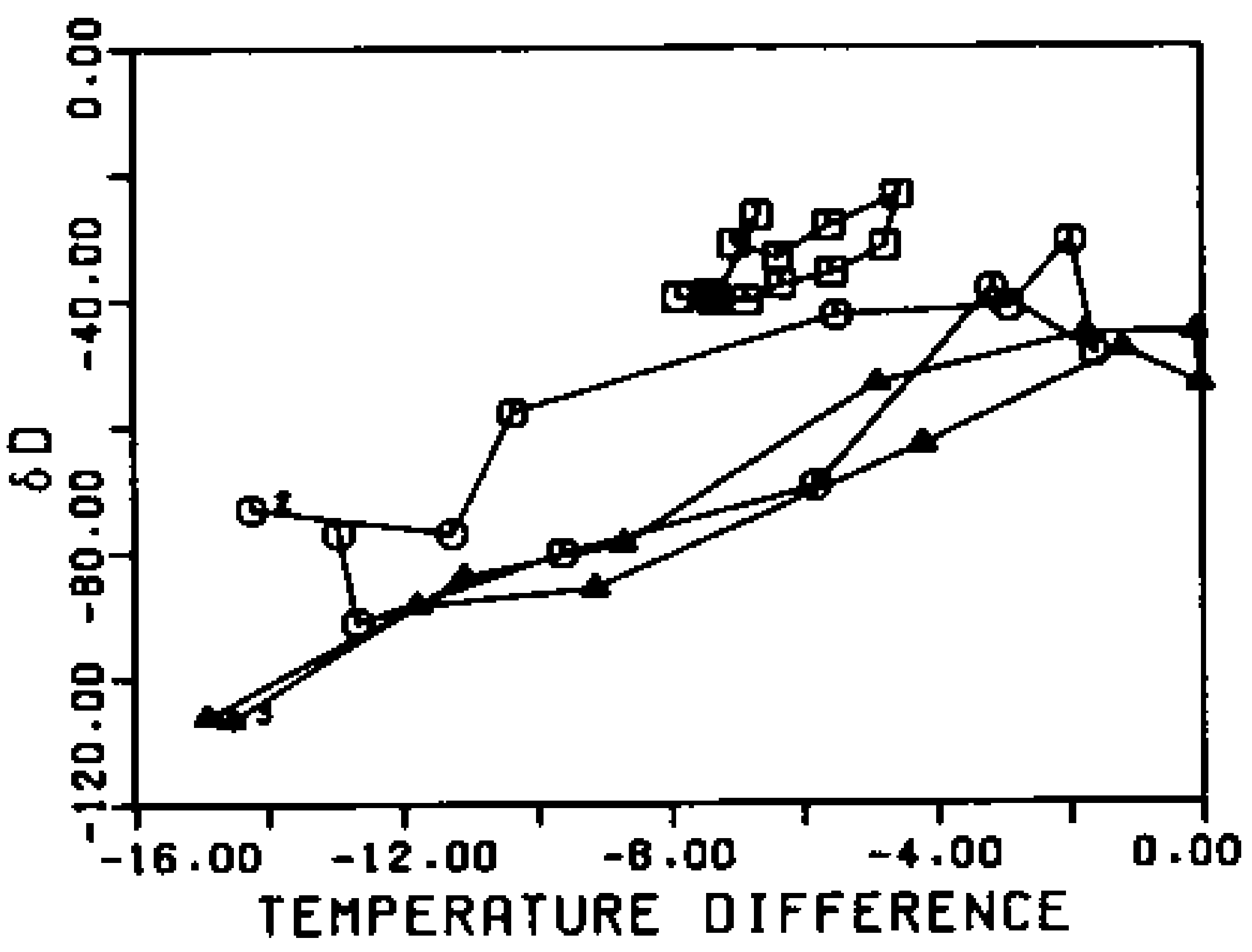

FIG.5. Mean monthly δD for Valentia (□), Stuttgart (0) and Vienna (▲), plotted versus the corresponding temperature differences between sampling station and Ponta Delgada, Azores (which is assumed to represent the vapour source region).

The corresponding regression lines have slopes of 4.4, 3.6 and 4.0‰/°C for Valentia, Stuttgart and Vienna, which are lower than the value of 5.2‰/°C derived above for isobaric cooling from the Rayleigh model. Part of this difference may be a consequence of the fact that in summer, relative humidity is lower on the continent than on the Azores and the difference of dew-point temperatures smaller than the difference of air temperatures. From Fig. 5 we further observe that the mean monthly data pairs (ΔT, δD) do not fall on one line but describe a loop at all these stations, with higher δD for the same temperature difference in the second half than in the first half of the year. Again, this is connected to relative humidities.

3. ANOTHER LOOK AT THE RAYLEIGH MODEL

According to the Rayleigh picture, the isotopic composition directly depends on the remaining vapour fraction f. For this reason Eriksson [4] compared mean annual values of $\delta^{18}O$ and precipitable water in the air column for a large number of stations. Rozanski et al. [11] considered seasonal variations at European stations, calculating f from an atmospheric water balance.

The degree of rainout can also be calculated directly as the ratio between the water vapour mixing ratios at the sampling station and in the vapour source region, or, from Eq. (5)

$$f = \frac{e}{e_0} \cdot \frac{p_0}{p} \tag{6}$$

In contrast to temperature, mixing ratios are not affected by adiabatic uplift of air as long as there is no condensation; thus mixing ratios and values for f determined from surface data can be considered representative for cloud-base conditions and therefore to be valid estimates of the remaining vapour fraction.

If we again take the Azores as representative for the vapour source region for Europe, then we can calculate f from the monthly data for vapour pressure e given on the IAEA tape and in the data lists [7], and the constant factor p_0/p, the ratio between the barometric pressures at the Azores and at the precipitation station considered. Figure 6 is a representation of mean monthly values of δD versus f for Valentia, Stuttgart and Vienna; for calculating f, only months for which δD was measured were considered. The correlation δD with f is good, mainly for Vienna, for which more data pairs (147) were available than for Stuttgart (75) and Valentia (60). In Fig. 6(b), a Rayleigh model curve is also shown which is given by the expression $\delta = \alpha(1 + \delta_0)f^{\bar{\alpha}-1} - 1$, (Eq. (3)). It was fitted to the Vienna data by considering δ_0 as an adjustable parameter (see Appendix 1). The slope of the model curve is prescribed, and the fact that at all three stations the mean slope of the δD-f data agrees remarkably well with the Rayleigh slope indicates that the actual fractionation processes for D/H are, on the average, well represented by the Rayleigh condensation model. The agreement of the Vienna data with the model is actually nearly perfect, except for the month of June (right-most data point in Fig. 6(b)), which has relatively low δD. Re-evaporation of isotopically light winter precipitation over the continent in summer (cf. Fig. 1) or a non-negligible liquid-water content in clouds would cause smaller slopes; in view of the small difference between observed and model-predicted slopes, and also of the reasonable values δ_0 for initial condensate, there is no reason for assuming that these effects would be of major importance. (For $\delta^{18}O$, evaporation of raindrops may, however, exert a non-negligible influence.)

The continental effect is still present but lower than in a δD-temperature plot: for T = 10°C, the regression lines for the latter [8] are distant by 12‰ between Vienna and Stuttgart and by 24‰ between Stuttgart and Valentia, while the best-fit Rayleigh curves (see below) for the two pairs of stations are

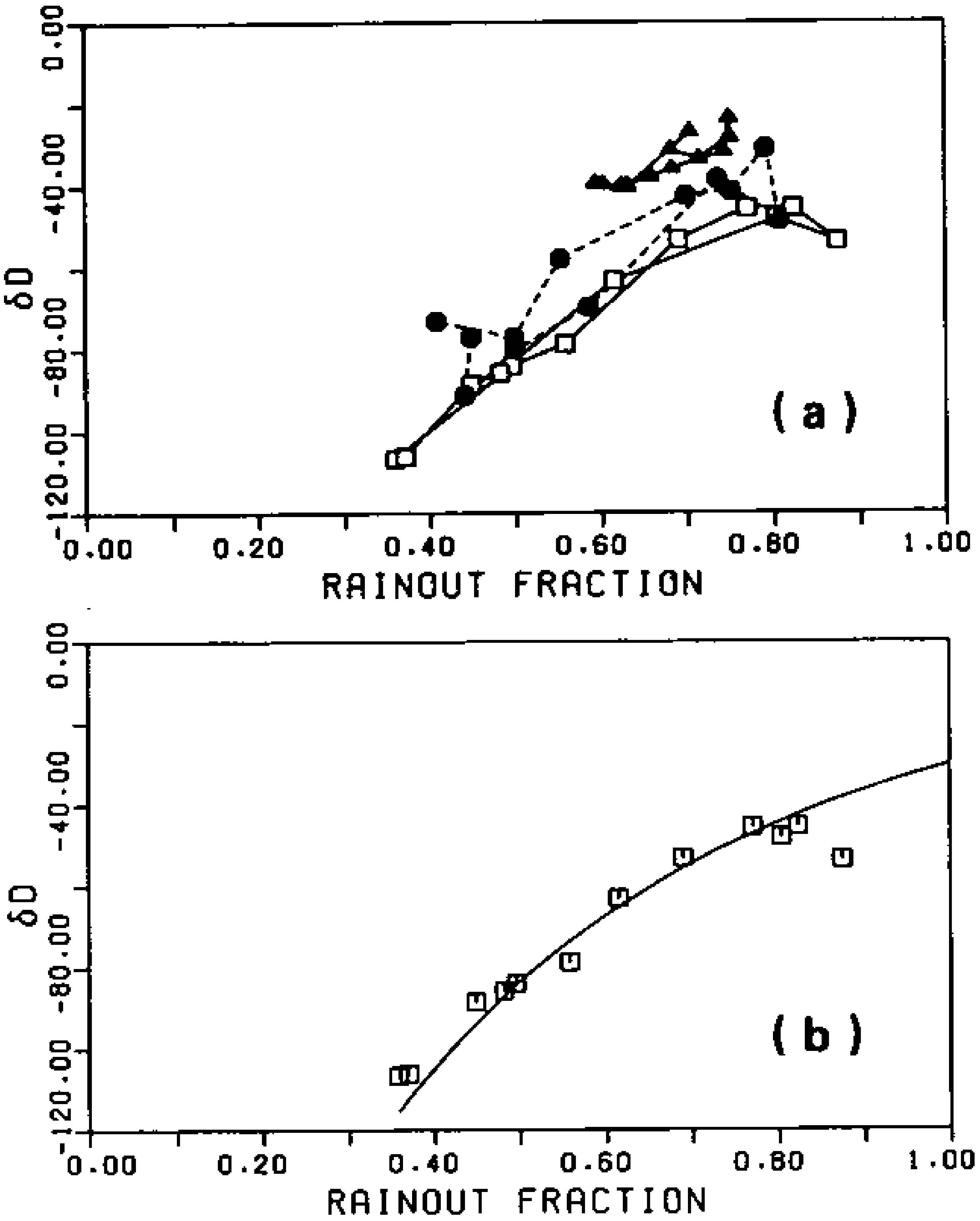

FIG.6. Mean monthly δD as a function of remaining water vapour amount f assuming that the Azores represent the vapour source region. f is calculated as the ratio of water vapour mixing ratios of sampling station and Azores (see text).
(a) Data for Valentia (▲), Stuttgart (●) and Vienna (□).
(b) Comparison of observed data for Vienna (□) with the relation predicted from the Rayleigh model (solid line).

only 10 and 13‰ distant for f = 0.6. The reason is that relative humidities are lower at Stuttgart and Vienna than at Valentia, so for a given temperature, f is smaller for the continental stations than at the coast.

The values δ_0 for the composition of first condensate, obtained by fitting the Rayleigh curves, are –30, –20 and –6‰ for Vienna, Stuttgart and Valentia and agree roughly with a mean annual δD of about –18‰ for precipitation at the Azores. The fact that δ_0 is different for the three stations indicates that their vapour source regions are not exactly identical. In the source region for precipitation at Valentia, absolute humidity is probably lower that at the Azores by 10 to 20% (and the actual f correspondingly higher), that is, the source region is cooler than the Azores and presumably nearer to Valentia. Thus, the 'continental' effect, causing lower δ-values on the continental stations than at Valentia for similar temperatures, is a combined effect of different relative humidities and different vapour source regions.

The seasonal cycles of temperature and relative humidity at the Azores and the three precipitation stations are different. This causes a seasonal phase shift between temperature and remaining vapour fraction f which expresses itself in loops in the δD-ΔT plots (Fig. 5), while such loops are absent or not clearly discernible in the δD-f plots (Fig. 6).

It must be emphasized that the assumption that the Azores are representative for the vapour source region can be valid in a statistical sense only. In a δD-f plot of individual monthly data, there is approximately as much scatter as in a δD-temperature plot (Fig. 3). This is not surprising, since the origin of air masses bringing precipitation to Europe is quite variable. In order to study the isotopic composition of individual monthly or daily samples, a detailed analysis of air mass origin would be necessary.

4. CONCLUSIONS

The mean seasonal deuterium variations at Valentia, Stuttgart and Vienna closely follow the Rayleigh condensation model, if the remaining vapour fraction is calculated from vapour mixing ratios at the precipitation stations and in the source region. Therefore, it should be possible to analyse palaeoisotope records in a quantitative way. This can, however, not be done in terms of the temperature at the site of observation alone, because surface temperatures and relative humidities at the observation site and in the vapour source region are all important. Shifts of vapour source regions and changes of relative humidity and of sea surface temperature must therefore be included in the interpretation of stable isotope records.

While mean $\delta^{18}O$ and δD values, averaged over sufficient time, are well correlated to temperature, there is a large scatter in the δ-temperature relation for individual or monthly precipitation samples. Extreme caution is therefore necessary when trying to interpret short-term isotopic fluctuations in terms of temperature.

Appendix I

FIT OF A RAYLEIGH MODEL CURVE TO OBSERVATIONS

n data pairs (f_i, δ_i) are given. The curve to be fitted is given by

$$\delta_c = \alpha(1 + \delta_{vo}) f^{\alpha - 1} - 1 = \frac{\alpha}{\alpha_0}(1 + \delta_{co}) f^{\bar{\alpha} - 1} - 1$$

and δ_{co} has to be determined so as to minimize the sum of squares of the deviations $[\delta_c(f) - \delta_i]$.

From mean monthly data for the stations considered, the following relationship between $\bar{T}$ and f was determined: $\bar{T} \simeq 40f - 11.6$°C ($\bar{T}$ = monthly average temperature between the Azores and the precipitation stations). $\bar{\alpha}$ was estimated from $\bar{T}$ using the analytical expression by Majoube [12].

For $T \simeq 10$°C, $\alpha/\alpha_0 \simeq \exp[-0.0012(T - T_0)]$; on the other hand, from the temperature dependence of the saturation vapour pressure, $F \simeq \exp[0.067(T - T_0)]$. In summary

$$\delta_c \simeq (1 + \delta_{co}) f^{\bar{\alpha} - 1.018} - 1$$

From the least-squares fit δ_{co} is obtained as

$$\delta_{co} = \frac{\Sigma(1 + \delta_i) r_i}{\Sigma r_i^2}$$

where

$$r_i = f_i^{\bar{\alpha} - 1.018}$$

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STABLE ISOTOPIC COMPOSITION OF PRECIPITATION AND CLIMATIC VARIABILITY

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Abstract

STABLE ISOTOPIC COMPOSITION OF PRECIPITATION AND CLIMATIC VARIABILITY.

By assuming that the atmospheric vapour mass originates from the oceanic regions at low latitudes and by using a simple Rayleigh model, several observations on the yearly averages and the seasonal fluctuations of $\delta^{18}O$ and $\delta^{2}H$ of precipitation can quantitatively be explained as a function of temperature. The theory presented is mainly a simplified review of earlier work. Based on this model the prediction seems warranted that during climatic variations the isotopic composition varies according to the presently observed latitudinal temperature effect of: $d\delta^{18}O/dt = (0.62 \pm 0.10)‰/°C$ and $d\delta^{2}H/dt = (5.1 \pm 0.9)‰/°C$, depending on the temperature range.

1. INTRODUCTION

Before being able to discuss the temperature dependences of $\delta^{18}O$ and $\delta^{2}H$ in precipitation in detail, we have to review earlier calculations. For explaining the stable isotopic composition of precipitation on a global scale, a combined model is applied consisting of two processes: (1) the formation of an atmospheric vapour mass in the regions with the highest surface ocean temperatures and (2) the progressive condensation of the vapour during transport to higher latitudes with lower temperatures. The first process has been discussed by Craig and Gordon [1] and Merlivat and Coantic [2]. The second process has essentially been applied by Dansgaard [3]. A more detailed discussion has been given by Merlivat and Jouzel [4]. We will restrict ourselves to a simplified version of the overall process.

2. EQUATORIAL EVAPORATION PROCESS

This process is described by a two-box model [1, 2]: (1) the ocean water having a constant isotopic composition, R_{l0}, for oxygen as well as hydrogen isotopes and (2) the atmospheric vapour over the high temperature surface ocean water ('thermal

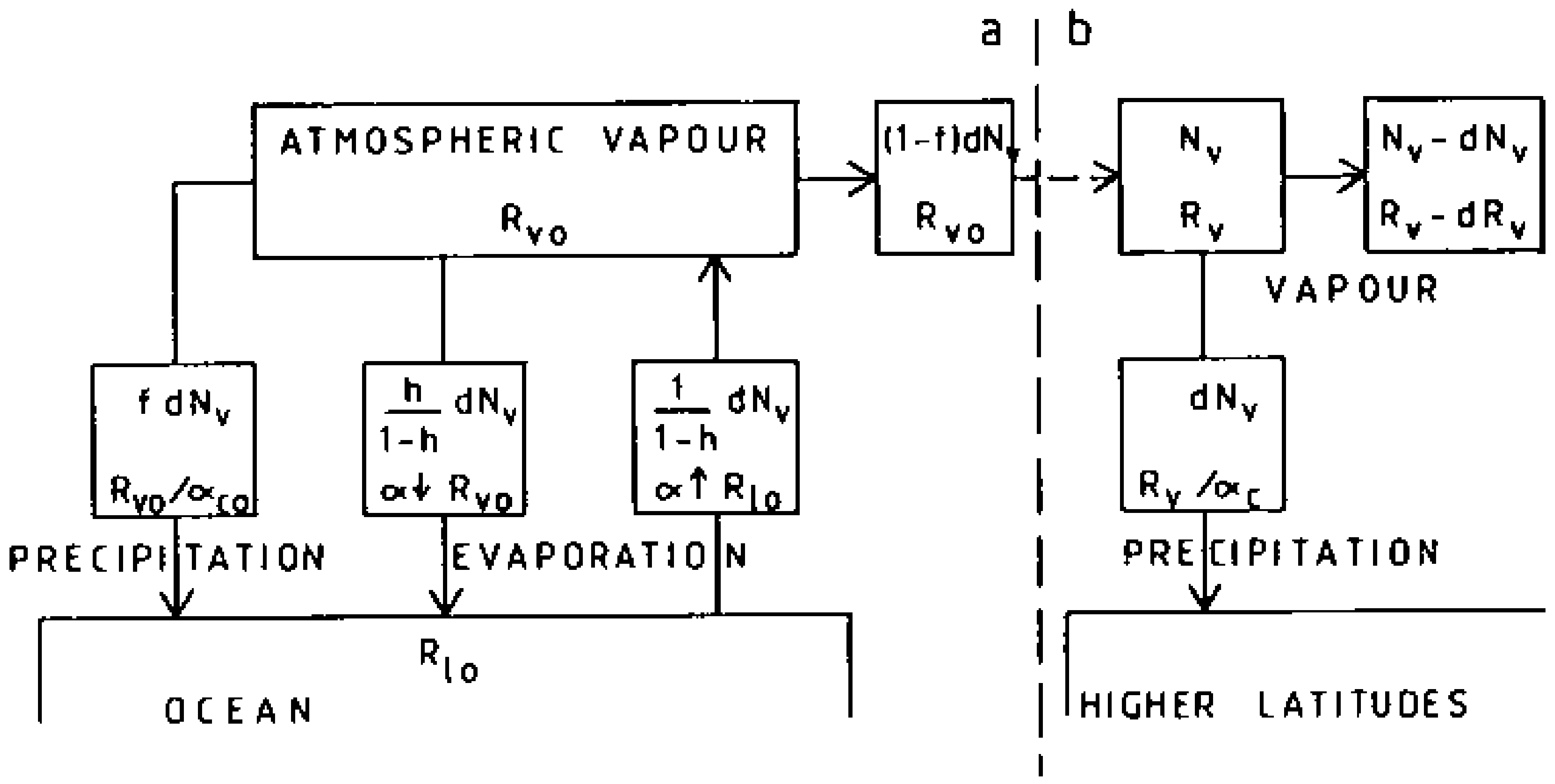

FIG.1. Schematic representation of (a) the equatorial evaporation process [1] *and (b) the temperature induced Rayleigh depletion due to precipitation at higher latitudes* [3]. *(a) The net amount of evaporating water (dN_v) at a relative humidity h is balanced by precipitation in the vapour source region (fraction f) and transport of vapour to higher latitudes ($1-f$). (b) The vapour condensation to rain is considered to occur under isotopic equilibrium conditions (α_c).*

equator'). Water evaporates from the ocean with a kinetic fractionation factor $\alpha\uparrow$, whereas vapour condenses back into the ocean with a kinetic fractionation $\alpha\downarrow$. Since the relative humidity of the air is below unity, there is a net transport of water into the atmopshere. These two partial processes are denoted by *exchange*. A fraction f of the vapour mass thus formed condenses directly into precipitation in the source region. The remaining vapour is transported to higher latitudes. The following model serves to calculate the isotopic composition of this vapour, R_{v0}.

A schematic diagram of the two-box model is presented in Fig. 1a. The simplification with respect to the detailed treatment by Craig and Gordon [1] is that the laminar layer resistance in the liquid is taken as zero. The two kinetic fractionation factors $\alpha\uparrow$ and $\alpha\downarrow$ are simply related to the isotopic equilibrium fractionation of water vapour with respect to liquid water at the *evaporation temperature*

$$\alpha_l(v) = \alpha_0 = \alpha\uparrow/\alpha\downarrow \qquad (1)$$

The isotopic ratios of the water and the vapour are respectively R_{l0} and R_{v0}.

The net evaporated water (= net added vapour dN_v to the air) at a relative humidity h_0 has an isotopic ratio of

$$\frac{\alpha\uparrow R_{l0}\,\frac{1}{1-h_0}\,dN_v - \alpha\downarrow R_{v0}\,\frac{h_0}{1-h_0}\,dN_v}{dN_v} = \frac{\alpha\uparrow R_{l0} - h_0\alpha\downarrow R_{v0}}{1-h_0} \qquad (2)$$

A fraction f of the vapour is considered to precipitate in the vapour source region. This precipitation is assumed to be in isotopic equilibrium with the vapour from which it condenses and thus to have an isotopic ratio = R_{v0}/α_{c0}, where α_{c0} refers to the *condensation temperature* over the region of evaporation. The transport of the remaining fraction of the vapour 1 − f goes without fractionation. The condition of dynamic equilibrium is then expressed by

$$\frac{\alpha\!\uparrow\! R_{l0} - \alpha\!\downarrow\! h_0 R_{v0}}{1 - h_0} = R_{v0}\left[\frac{f}{\alpha_{c0}} + (1 - f)\right] \tag{3}$$

The treatment by Merlivat and Jouzel [4] does not include the local precipitation term, i.e. f = 0.

Using Eq. (1) and noting that R_{l0} about equals mean ocean water (= V-SMOW), the isotopic composition of the equatorial oceanic vapour is

$$\delta_{v0} = \frac{R_{v0}}{R_{l0}} - 1 = \frac{\alpha_0}{h_0 + \frac{1}{\alpha\downarrow}\left[\frac{f}{\alpha_{c0}} + (1 - f)\right](1 - h_0)} - 1 \tag{4}$$

The net fractionation between the ocean water and the atmospheric vapour thus is

$$\alpha_k = \frac{R_{v0}}{R_{l0}} = \frac{\alpha_0}{h_0 + \frac{1}{\alpha\downarrow}\left[\frac{f}{\alpha_{c0}} + (1 - f)\right](1 - h_0)} \quad . \tag{5}$$

The value of the kinetic fractionation during condensation $\alpha\downarrow$ can, in principle, be determined by laboratory experiments [2, 5–7]. However, the experimental conditions, especially concerning the degree of turbulence in the air over the ocean surface, cannot be reproduced realistically. In fact, both the calculated and the experimentally determined $\alpha\downarrow$ values appear to be larger than the natural fractionation values. By taking the evaporation temperature = 25°C and the condensation temperature in the source region = 20°C and using the equilibrium fractionation values (Eq. (11)) of Majoube [8] for calculating α_0 and α_{c0} respectively, and assuming $h_0 = 0.85$, the natural observations can be explained by taking $1/\alpha^2\!\downarrow = 1.010$ and $1/\alpha^{18}\!\downarrow = 1.008$ [1]. For f varying between 0 (no precipitation in the vapour source region) and 1 (no vapour transport to higher latitudes), the resulting isotopic composition of the atmospheric vapour varies as (observed values of Ref. [1] within brackets):

$-75‰ > \delta^2H_{v0} > -87‰$ (−75 to −100‰)

$-10.5‰ > \delta^{18}O_{v0} > -11.9‰$ (−11 to −14‰)

3. TEMPERATURE INDUCED DEPLETION AT INCREASING LATITUDES

In this model [3] we assume that as the equatorial vapour mass is transported to higher latitudes and thus to lower temperatures, condensation to precipitation has to occur in order to maintain the vapour at saturation pressure at the prevailing air temperature. The Rayleigh condensation model is based on the assumption that the precipitation condensing from an atmospheric vapour mass is in isotopic equilibrium with the vapour. Because at thermodynamic equilibrium between vapour and water the latter has a higher ^{18}O and ^{2}H content, the remaining vapour is progressively depleted in the heavy isotopes. Figure 1b presents the simple box model. N_v is the number of abundant, isotopically light molecules and R_v is the isotopic ratio ($^2H/^1H$ or $^{18}O/^{16}O$). In the case of the removal of dN_v molecules and taking into account the accompanying fractionation factor α_c, the mass balance for the rare isotopic molecules gives

$$(R_v - dR_v)\,(N_v - dN_v) = R_vN_v - \frac{R_v}{\alpha_c}\,dN_v$$

or, neglecting the products of differentials,

$$\frac{dR_v}{dN_v} = (1/\alpha_c - 1)\,\frac{R_v}{N_v}$$

Here we assume that the number of isotopically light molecules N_v equals the total amount of molecules. The general solution for this equation is

$$R_v/R_{v0} = (N_v/N_{v0})^{1/\alpha_c - 1} \qquad (6)$$

The change in R_v as a function of the condensation temperature is

$$\frac{dR_v}{dT} = \frac{dR_v}{dN_v}\,\frac{dN_v}{dT} = (1/\alpha_c - 1)\,\frac{R_v}{N_v}\,\frac{dN_v}{dT}$$

The relative change in the amount of vapour equals the relative change in the (saturated) vapour pressure p_v:

$$dN_v/N_v = dp_v/p_v$$

where the relation between vapour pressure and temperature for the isobaric condensation process can be derived from the law of Clausius-Clapeyron:

$$p_v = C\exp(-D/T) \qquad (7)$$

where $D = \ell/G$; ℓ is the molar heat of evaporation, G is the gas constant and C is an integration constant. From this we have

$$dN_v/N_v = (D/T^2)dT$$

Furthermore, we conveniently write the dependence of the fractionation of water vapour relative to liquid water as

$$\alpha_c = A \exp(-B/T) \tag{8}$$

The use of this temperature relation is a refinement of the calculation by Dansgaard [3], who inserts an average α_c value over the temperature range between equator and precipitation area.

The temperature dependence of R_v now is

$$\frac{dR_v}{dT} = R_v \frac{D}{T^2}\left(\frac{1}{A}\, e^{B/T} - 1\right)$$

Integration and application of the boundary condition at the equator $T = T_0 \rightarrow R_v = R_{v0}$, gives

$$R_v/R_{v0} = \exp D\left[1/T - 1/T_0 - \frac{1}{AB}\,(e^{B/T} - e^{B/T_0})\right] \tag{9}$$

4. LATITUDINAL VARIATION OF δ VALUES WITH TEMPERATURE

The isotopic ratio of the precipitation condensing from this vapour is $R_c = R_v/\alpha_c$, where α_c now refers to the condensation temperature. The δ value relative to V-SMOW (= R_{l0}) then is

$$\delta_c = \frac{R_c}{R_{l0}} - 1 = \frac{R_c}{R_v} \cdot \frac{R_v}{R_{v0}} \cdot \frac{R_{v0}}{R_{l0}} - 1 = \frac{\alpha_k}{\alpha_c}\frac{R_v}{R_{v0}} - 1$$

The kinetic condensation process is considered to be a diffusional process and, consequently, temperature independent, i.e. $d\alpha{\downarrow}/dt = 0$. Using Eq. (4), Eq. (5) and Eq. (9) we finally have

$$\delta_c = \frac{1 + \delta_{v0}}{\alpha_c} \exp D\left[1/T - 1/T_0 - (1/\alpha_c - 1/\alpha_{c0})/B\right] - 1 \tag{10}$$

where δ_{v0} is given by Eq. (4).

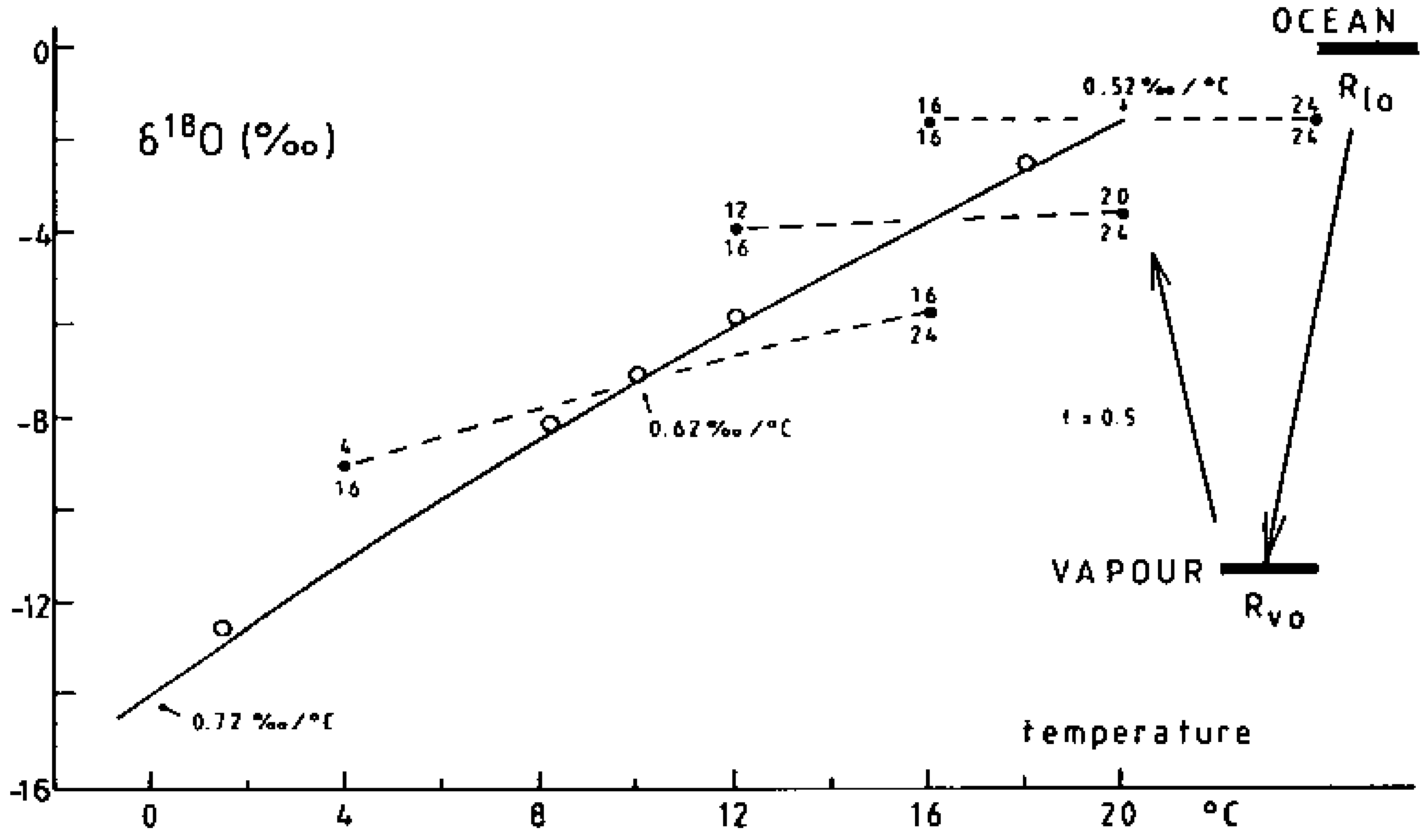

FIG.2. Calculated (Eq. (10)) oxygen isotopic composition (versus V-SMOW) of precipitation depending on the temperature (full line) [4]. *Equatorial evaporation is considered to take place at an ocean surface temperature of 25° C, the first precipitation at 20° C in the vapour source region. Seasonal variations are drawn by dashed lines, where the condensation respectively in the precipitation area and at the vapour source region is indicated for winter and summer conditions (cf. t and t_0 respectively of Eq. (10)); f is taken to be 0.5. The fractionation for the transition of R_{lo} to R_{vo} (Fig. 1) is calculated from Eq. (5). The open circles refer to actual annual precipitation data (IAEA) from high to low temperature: the Azores, Valentia, Groningen, Bergen and Grønnedal.*

A best exponential fit to the data from Majoube [8] over the range 0–30°C ($\alpha_c = Ae^{-B/T}$) is

$$\begin{aligned} \alpha^2{}_c &= 1.272\ \exp(-94.54/T) \qquad (\pm\ 0.5‰) \\ \alpha^{18}{}_c &= 1.0161\ \exp(-7.545/T) \qquad (\pm\ 0.05‰) \end{aligned} \qquad (11)$$

By making a least-squares fit of ln p_v against 1/T in the temperature range 0 to 30°C, D in Eq. (7) is calculated to be 5349 K, equivalent with a molar heat of evaporation of 44.5×10^3 J/mol. For values of $1/\alpha^2\downarrow = 1.010$ and $1/\alpha^{18}\downarrow = 1.008$ and for estimated values of $f = 0.5$ and $h_0 = 0.85$ we can now calculate the curves that are to be compared with the observed latitudinal variations in yearly δ_c values versus temperature (curve for $\delta_c{}^{18}O$ in Fig. 2). It has to be emphasized, however, that in our calculation t refers to the condensation (equilibrium) temperature, whereas the observed δ_c values are related to the average surface air temperatures. Apart from this possible phase shift, the slopes of the curves will not be affected. If we assume that the yearly average temperature in the source region of the vapour is 25°C and that condensation in this region

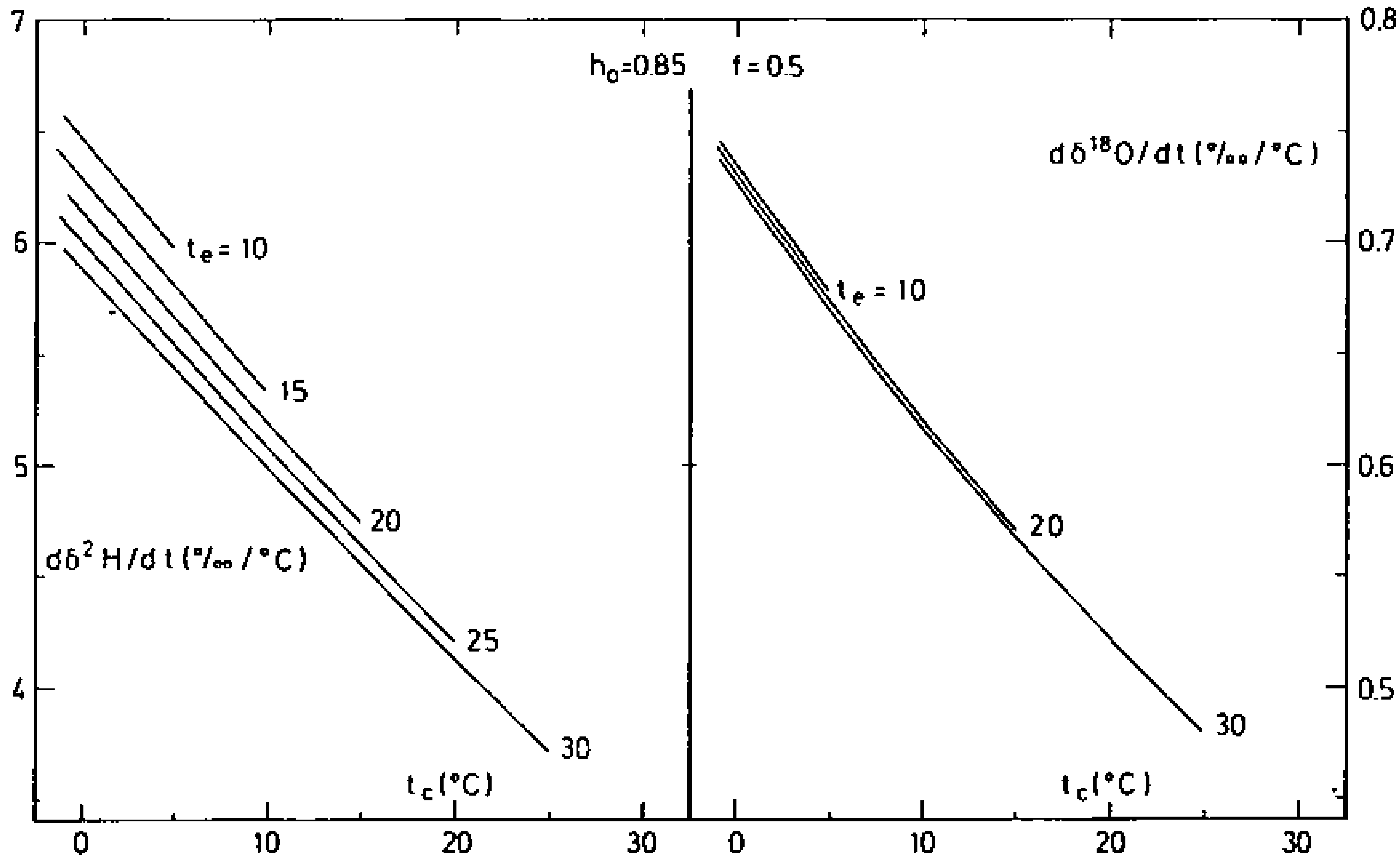

FIG.3. Temperature dependence of δ^2H and $\delta^{18}O$ in precipitation as a function of the condensation temperature (t_c) (slope of Fig. 2), for varying evaporation temperatures (t_e) of the surface ocean water. For simplicity evaporation temperature and condensation temperature over the vapour source region differ by 5°C. The dependence of the figures on h_0 and f is extremely small. It is seen that the temperature dependence of $\delta^{18}O$ at a certain condensation temperature hardly depends on the evaporation temperature. All temperatures are in °C.

takes place at a 5°C lower cloud temperature, the agreement between calculated and observed values is extremely good, especially in the upper temperature range (surprisingly, considering the simplicity of the model).

At lower temperatures, that is, at higher latitudes, the discrepancy between calculated and observed values seems to become more significant. This is not surprising, because the ocean evaporation and exchange at the higher latitudes has not been taken into account. Moreover, the air mass movements are more irregular. One shortcoming of our treatment is that no specific difference between condensation temperature and earth surface temperature has been introduced. This, however, does not influence the temperature dependences of the isotopic effects, which is the main aim of our discussion.

From Eq. (10) we can now specially derive the *temperature dependence* of the δ_c values (see also Fig. 3):

$$\frac{d\delta_c}{dt} = (1 + \delta_c)\frac{D}{T^2}\,(1/\alpha_c - 1)$$

(i.e. contribution of Rayleigh depletion for $^{18}O \cong +0.7‰/°C$)

$$-\,(1 + \delta_c)\frac{B}{T^2}$$

(i.e. contribution of temperature dependence of $\alpha_e \cong -0.1‰/°C$)

Using the same values of the constants as in Fig. 2, this numerically comes to the *latitudinal, yearly average temperature dependence:*

$$d\delta^2H_c/dt = 6.0 - 0.09\ t \qquad (‰/°C)$$
$$d\delta^{18}O_c/dt = 0.72 - 0.010\ t \qquad (‰/°C) \qquad (13)$$

where t is the condensation temperature in °C. The resulting values nicely agree with the IAEA magnetic tape data averaged for stations with $0° < t < 18°C$.

$$\delta^2H_c = (4.9 \pm 0.6)\ t - 97‰$$

$$\delta^{18}O_c = (0.56 \pm 0.09)\ t - 12.7‰$$

The numerical values added in parentheses with Eq. (12) respectively refer to the temperature dependence due to the Rayleigh depletion and to the temperature dependence of the fractionation factor α_c. The latter is seen to be relatively small and opposed to the total effect.

5. RELATION BETWEEN δ^2H AND $\delta^{18}O$

According to Craig [9] the yearly averages of temperature and δ_c values of the precipitation obey a linear relation, generally referred to as the *meteoric water line:*

$$\delta^2H = s\delta^{18}O + d \qquad (14)$$

where most meteoric waters agree with s = 8 and d = 10‰. The slope s and the ordinate intercept d can be deduced in a simple quantitative manner [1]. According to Eq. (6),

$$\ln R_v^2/R_{v0}^2 = \ln(1 + \delta^2H) \cong \delta^2H = (1/\alpha_e^2 - 1)\ln N_v/N_{v0}$$

$$\ln R_v^{18}/R_{v0}^{18} \cong \delta^{18}O = (1/\alpha_e^{18} - 1)\ln N_v/N_{v0}$$

so that changes in δ^2H and $\delta^{18}O$ along the meteoric water line are simply related by the two fractionations:

$$\frac{\Delta\delta^2H}{\Delta\delta^{18}O} \cong \frac{1/\alpha_e^2 - 1}{1/\alpha_e^{18} - 1} \cong 8$$

A more accurate calculation should be based on Eq. (12), while the slope is given by

$$s = \frac{d\delta^2H_c}{d\delta^{18}O_c} = \frac{d\delta^2H_c/dt}{d\delta^{18}O_c/dt} \qquad (15)$$

The numerical values of the calculated slope vary from 8.25 at 0°C and 8.05 at 20°C, very close to the slope of 8 reported in Refs [1, 3, 9]. The ordinate intercept can now be calculated from

$$d = \delta^2H_c - \frac{d\delta^2H_c}{d\delta^{18}O_c}\,\delta^{18}O_c \qquad (16)$$

Figure 4 shows the dependence of s and d on h_0, t_e, f and t_c. Using the same values of constants and parameters ($h_0 = 0.85$, $f = 0.5$, $t_0 = 20°C$ and an evaporation temperature = t_0 + 5°C), the resulting d values range from +10.4‰ at 0°C and + 9.6‰ at 20°C, so that the theoretically derived *meteoric water line* is presented by

$$\delta^2H_c = (8.15 \pm 0.1)\delta^{18}O_c + (10.0 \pm 0.4)‰ \qquad (17)$$

Higher values of the intercept can be explained by assuming a lower relative humidity in the evaporation area. For instance, by taking $h_0 = 0.6$, the equation is

$$\delta^2H_c = (8.1 \pm 0.1)\delta^{18}O_c + (20.3 \pm 0.6)‰ \qquad (18)$$

Similar values have been observed by Gat and Dansgaard [10] in the eastern Mediterranean.

6. SEASONAL VARIATIONS OF δ-VALUES WITH TEMPERATURE

The seasonal variations of δ^2H and $\delta^{18}O$ values of precipitation with temperature should essentially be smaller than the latitudinal variations of yearly average values. For understanding this phenomenon we again have to consider Eq. (10). The fact is that during winter not only is the condensation temperature T smaller than during summer, but also T_0, the prevailing average temperature in the region of evaporation. In this way the local effect of the temperature change is partly compensated. During winter over the northern hemisphere the highest temperatures are found south of the equator. The water vapour from this region, however, is not easily transported to the northern hemisphere. Consequently, the

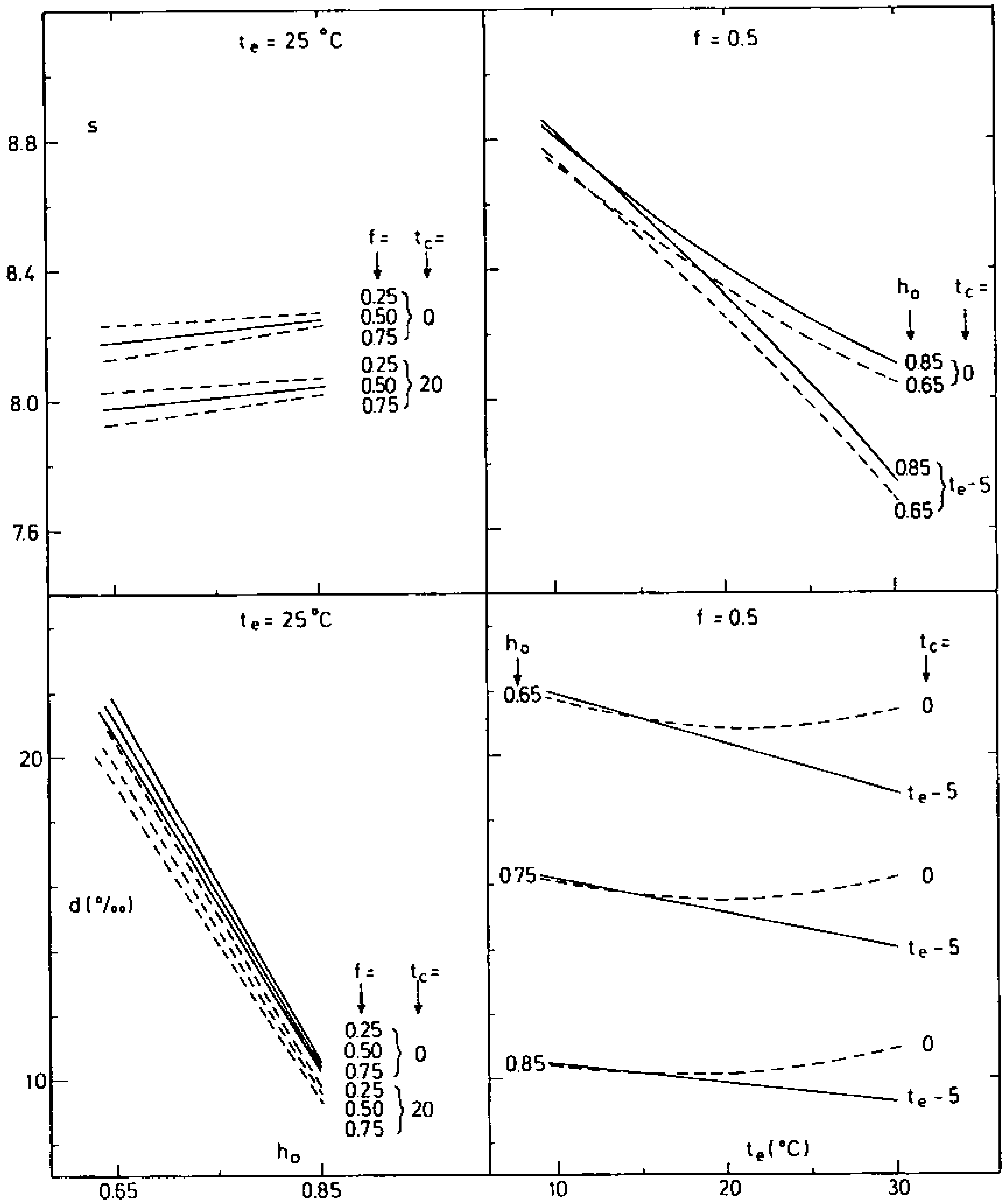

FIG.4. Dependence of the slope (s) and the intercept (d) of the meteoric water line ($\delta^2H = s\delta^{18}O + d$) on relative humidity ($h_0$) and surface ocean evaporation temperature (t_e) in the vapour source region. Lines are drawn for different values of the fraction of vapour condensed to rain in the vapour source region (f) and of the condensation temperature (t_c). All temperatures are in °C.

effective evaporation region for the northern hemisphere has a lower T_0 value than during summer.

In Fig.2 three examples are given for seasonal variations. The upper horizontal line with $d\delta^{18}O_c/dt = 0‰/°C$ refers to a tropical island in the zone of evaporation: $t = t_0$ during summer as well as winter. The middle line reflects the condition of a parallel change of t and t_0, whereas the lower curve is considered to be representative for most mid- and high-latitude stations: the summer/winter temperature transition is more pronounced than that in the evaporation area.

Calculated values for seasonally varying temperature in the above three cases show that the slope of the $\delta^2H/\delta^{18}O$ plot is not generally 8 as in the case of the yearly averages. Especially if the relative humidity is allowed to change, slopes of 4.5 to 5.0 can be explained. In fact, these smaller slopes are indeed observed [7]:

$$\begin{aligned} &\text{23 tropical to polar islands:} && s = 5.8 \pm 1.2 \\ &\text{51 coastal stations:} && s = 6.6 \pm 1.0 \\ &\text{33 continental stations:} && s = 6.8 \pm 0.8 \end{aligned} \qquad (19)$$

7. EFFECT OF CLIMATIC CHANGES ON δ^2H AND $\delta^{18}O$

The model calculations, confirmed by observation, show that global variations in δ^2H and $\delta^{18}O$ are mainly due to the temperature difference between the region of evaporation and the precipitation area. Consequently, in order to be able to predict or explain the average isotopic composition of regional precipitation in the past in terms of regional temperature changes, we have to answer the main question: how is the average temperature of the equatorial belt over a period of years related to climatic changes (ice ages) at higher latitudes.

It seems reasonable to assume that the temperature changes in this region of evaporation are small compared with the high-latitude changes. Consequently, it is the most reasonable to assume that temperature changes induce isotopic changes, about equal to the presently observed latitudinal temperature effect (see Eq. (13)):

$$\begin{aligned} d\delta^2H/dt &\cong (5.1 \pm 0.9)‰/°C \\ d\delta^{18}O/dt &\cong (0.62 \pm 0.10)‰/°C \end{aligned} \qquad (20)$$

slightly depending on the actual temperature range.

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DEUTERIUM AND ^{18}O IN PRECIPITATION

A global model from oceans to ice caps

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Extended Synopsis

On a worldwide basis, the deuterium and ^{18}O content of precipitation (rain or snow) decreases with decreasing mean surface temperature. Usually the two isotope ratios are linearly related ($\delta D = 8\delta^{18}O + 10$). The empirical laws derived from these observations, which are of very great use in all the isotopic studies developed in the glaciological field, received a first theoretical basis from a simple Rayleigh distillation model.

From a global evaporation-precipitation-runoff cycle, we propose a more general model (for both isotopes), taking into account the fractionation effects occurring at the air/sea interface and during the atmospheric processes leading to the formation of rain and snow. The isotopic effects taking place during evaporation are modelled from experiments conducted in a large air/sea simulating facility and the water cycle is described by a three-phase cloud model allowing for the coexistence of liquid and ice and partial or total removal of precipitation at each step.

We first studied the liquid phase down to a minimum value of −20°C [1]. We have demonstrated, in particular, that the $\delta D-\delta^{18}O$ relationship corresponds very well to the general linear form $\delta D = s\delta^{18}O + d$, the slope s and the intercept d being practically independent of the atmospheric processes. This is why a linear relationship is experimentally well observed over a large range of conditions. On the other hand, we have shown that s and d mainly depend on the physical characteristics of the air/sea interface. A very important result is that the d-value is primarily governed by the relative humidity of the air mass at its oceanic origin, indicating that the d-index is a potential tool for reconstructing the palaeohumidity of the ocean surface.

In a first approach, the model failed to explain the $\delta D-{}^{18}O$ slope observed for snow precipitation (the calculated values lying around 6). Then, considering that snow is formed in a supersaturated environment (over ice), we introduced the concept that a kinetic fractionation effect exists at vapour deposition. It results in excellent agreement between experimental data and theoretical δD and $\delta^{18}O$ curves for very reasonable values of supersaturation.

This new idea is of major importance for the relation between isotopic content (D or ^{18}O) and temperature of formation of the precipitation over the ice caps. Thus, the ^{18}O temperature gradient is lowered by 40% when this kinetic effect is taken into account (from 2 to 1.2‰/°C). This satisfactorily explains the low gradients measured in successive traverses in Antarctica and gives very good confidence in the use of these spatial gradients to interpret isotopic curves as obtained from ice cores [2] in terms of surface palaeotemperatures.

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$^{18}O/^{16}O$ RATIO OF WATER IN A LOCAL ECOSYSTEM AS A BASIS OF CLIMATE RECORD

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Abstract

$^{18}O/^{16}O$ RATIO OF WATER IN A LOCAL ECOSYSTEM AS A BASIS OF CLIMATE RECORD.

The $^{18}O/^{16}O$ ratio of local precipitation depends on the geographical position of the observation site and on the climate there, mainly on the mean annual temperature. This report summarizes long-term observations of the $^{18}O/^{16}O$ ratio in the different components of the ecosystem in Jülich, Federal Republic of Germany: precipitation, groundwater, air humidity, water transport system of plants and leaf water. The $^{18}O/^{16}O$ ratio of water in the leaves is determined by the isotopic composition of the precipitation (groundwater) and of the water vapour in the air, as well as by the relative humidity. The isotopic composition of water in the leaves, and consequently the photosynthetic products built up there, should reflect the status of the local climate.

1. INTRODUCTION

During the natural global cycle of water the isotopes of hydrogen and oxygen are fractionated. The large oceanic water reservoir has a very constant isotopic composition. Remarkable differences are observed only near the melting polar ice sheets and in surface layers with large evaporation rates [1–3]. At the continents the IAEA network for the collection and measurement of precipitation samples [4] demonstrates the large differences of isotope ratios in dependence on the geographical position of the stations. The data often have been used to construct a worldwide pattern, e.g. Refs [5, 6]. Generally the ^{18}O content decreases from the equatorial toward the polar regions.

The first impression is a close correlation between the $^{18}O/^{16}O$ ratio and mean annual temperature, but other mechanisms are known to be effective also. For example, the rain precipitates during the flow of air from the sea over mountains and across land areas. Therefore one cannot expect a simple linear correlation between ^{18}O content and temperature, valid at all geographical positions [5–7].

Temperature alone may be an indicator of climate, but it is only one of the important environmental parameters. One should distinguish between changes of climate and changes of mean annual temperature. Conversely, a change of the mean isotope ratio in precipitation really indicates a change of local climate, maybe only from dry to humid conditions.

Usually the time necessary to detect changes or even averages is very long. Short-term statistical variations are within the same order of magnitude as long-term tendencies. The cellulose of tree rings, a material easy to date, should preserve the average of the isotopic composition of water of its year of growth. It is built up freshly each year and consists of carbon, hydrogen and oxygen only. Other materials are introduced later and usually with different isotope ratios.

We assume that the cellulose, which is synthezised in a certain solution, has a predictable isotopic content, which means that the cellulose of a tree ring should preserve the isotopic content of water during the time or its formation. In a first step one must test the constancy of the $^{18}O/^{16}O$ ratio of water in plants and in the whole ecosystem as the basis for further interpretations. We have observed $^{18}O/^{16}O$ ratios of water samples in Jülich and in the neighbourhood. For an easy comparison of the different kinds of water flows and pools we use the concept of the ecosystem.

2. FLOW OF WATER IN AN ECOSYSTEM

An ecosystem [8] includes all of the organisms and the physico-chemical conditions of the environment in a limited area. A flow of energy leads to a defined trophic structure and a cycling of material between the different participants, mainly between producers, consumers and decomposers.

Even above bare land areas a purely physically driven water cycle will be observed. Rain and other precipitations infiltrate the soil downwards to the groundwater or flow away as surface waters. The exchange of water between the liquid phase at the bottom and the vapour in the air should result in an average ^{18}O content of the air humidity.

If the land is covered by organisms, the large plants (the trees) play an important role. The consumers and decomposers depend on the primary production of plants and can be neglected. The plants absorb the main part of the energy inflow into the ecosystem, but their yield of solar irradiation is only 1%. The energy inflow is used for the transpiration: e.g. in the Federal Republic of Germany about 40% of the precipitation is fed back into the atmosphere by the transpiration of plants [9]. The flow of carbon dioxide is negligible compared to the turnover of water by the leaves. The exchange of gases (water, carbon dioxide) happens via the large surface of the leaves. The transport of water from the root via the xylem to the leaves is a mass flow without a separation of the isotopes. The most interesting processes are located in the leaves: the photosynthesis of sugars and the exchange of water vapour between leaf and air. Transpiration is influenced by biological mechanisms (structure of leaf, aperture of stomata), but the isotope fractionation during that process is a purely physical event. The large diurnal variation under field conditions [10–12] and the rapid equilibration under defined laboratory conditions confirm this idea.

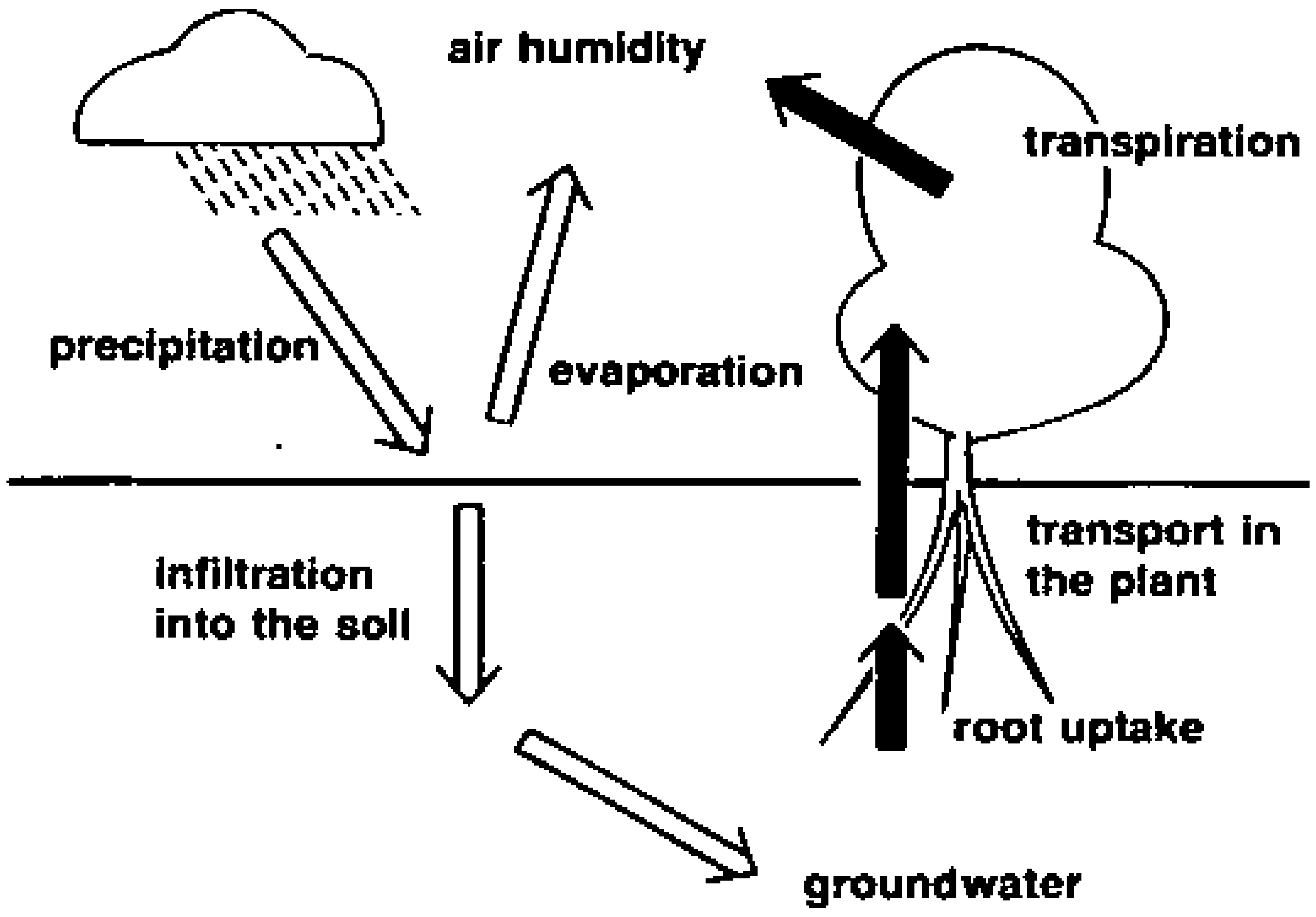

FIG. 1. Scheme of the water fluxes in an ecosystem. The non-biological components of the local water cycle are indicated by open arrows, the water flow through the biomass by black ones.

The application of $^{18}O/^{16}O$ ratios for climatological studies necessitates studies of the different water pools in the ecosystem at least during one season or year. This paper reports the techniques of sampling and measuring the $^{18}O/^{16}O$ ratio of water from different materials, describes our results from the local ecosystem in the area of the Nuclear Research Centre Jülich (KFA), and summarizes their importance for the interpretation of the $^{18}O/^{16}O$ ratios in the cellulose of tree rings. The discussion follows the scheme of the non-biological and biological water cycles in an ecosystem (see Fig. 1).

3. COLLECTION OF SAMPLES

Except for special observations the samples have been collected in the area of the Nuclear Research Centre Jülich (KFA). The KFA is situated within a forest in the plain of river Rur near the Eifel hills.

Precipitation in Jülich is collected in a large vessel each month and mixed well afterwards. Groundwater samples from the whole area of the Federal Republic of Germany were mailed to us in tight vessels and measured in a random manner to avoid systematic errors. After the measurements of all the samples a selected set was measured again, to ensure correct storage and to neglect systematic errors of the series of samples.

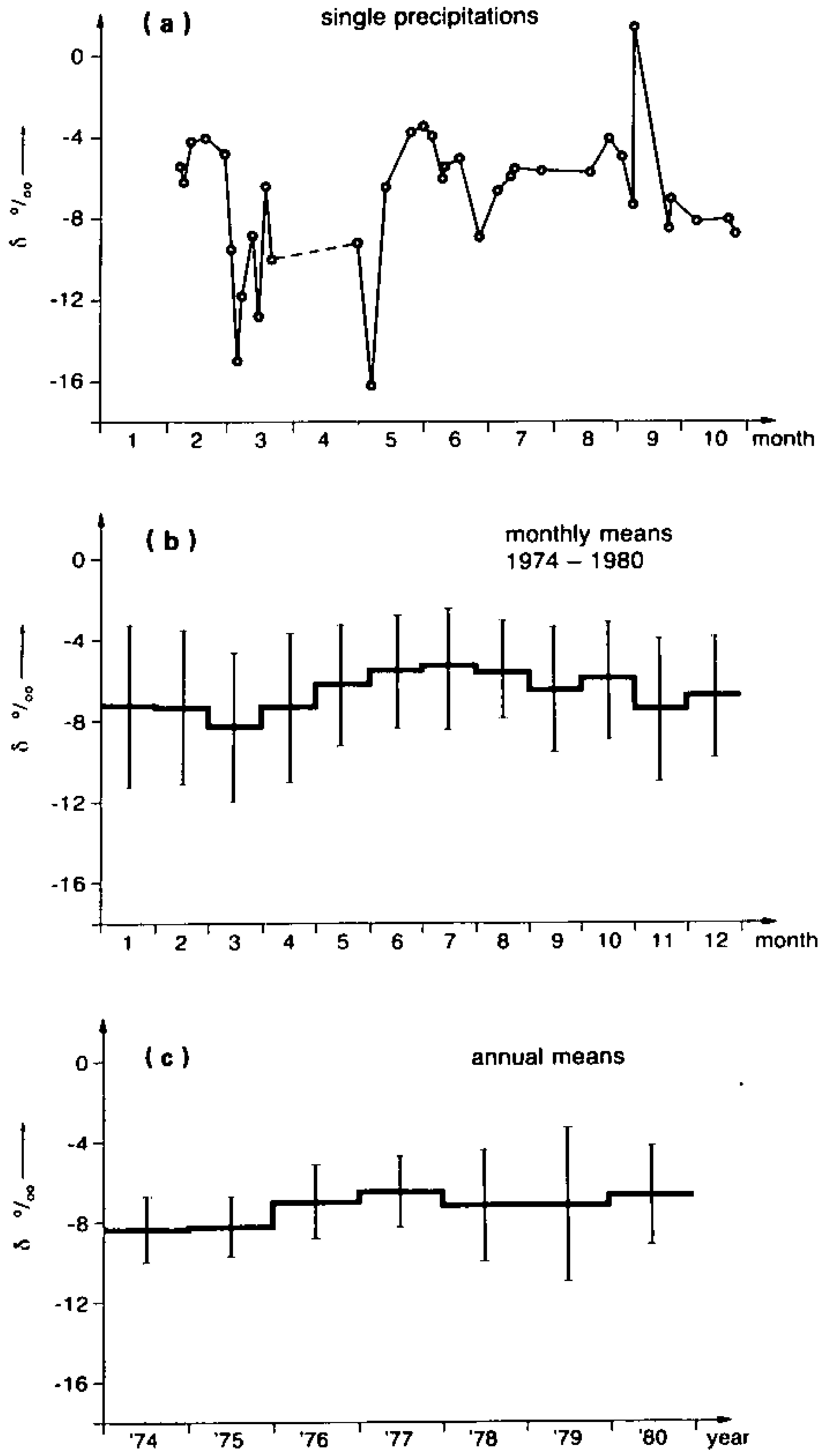

FIG. 2. $^{18}O/^{16}O$ ratio of precipitation samples collected in Jülich, Federal Republic of Germany.

(a) $^{18}O/^{16}O$ ratio of single precipitation during 1974.

(b) Monthly means of the $^{18}O/^{16}O$ ratios of precipitation from 1974 to 1980. The standard deviations are marked by vertical lines.

(c) Annual means from 1974 to 1980. The standard deviations of the monthly averages are given as vertical lines.

Plant material is enclosed immediately in gas-tight glass vessels and stored at −18°C. Water vapour is frozen out of an air stream of 24 L/h into a trap cooled at −61°C. The long-term observation was made on working days from 8 to 12 a.m.

In the former experiments the water from plants was distilled under vacuum conditions from the material at room temperature into a trap cooled by a dry ice/acetone mixture or even by liquid nitrogen. In the present observations the frozen material is evacuated rapidly and brought directly into contact with carbon dioxide overnight.

The ^{18}O^{16}O ratio of water is measured mass spectrometrically after an exchange of gaseous carbon dioxide and liquid water. The exchange is completed overnight. The purified carbon dioxide is introduced into the inlet system of the mass spectrometer and compared directly to a standard carbon dioxide gas. The double inlet and the double collector system (V.G. Micromass 602) enables one to measure oxygen isotope ratios with a reproducibility of at least ±0.1% (as δ-value). The isotope ratios are given as δ-values compared to Vienna-SMOW [13].

4. OXYGEN ISOTOPE RATIO OF LOCAL PRECIPITATIONS AND OF GROUNDWATER

Figure 2 summarizes our results of the oxygen isotope ratio of precipitations in Jülich. Figure 2(a) demonstrates the large differences between single precipitations even within one day and during one precipitation event. If the precipitation is collected monthly, the scattering diminishes (Fig.2(b)). During the spring, especially in March, a significant minimum is observed every year. The comparison of averages of the annual precipitation in Jülich (Fig.2(c)) supports our idea of a relatively constant isotope ratio at one location.

The groundwater in Jülich corresponds closely to the ^{18}O/^{16}O ratio of precipitation. During the last decade no distinct changes of the oxygen ratio of groundwater from different wells in Jülich have been reported [14, 15]. The precipitations infiltrate the soil column and are mixed during their way down to the groundwater layer. The oxygen isotope ratio of this water reservoir represents a long-term average of the local precipitation, at least in Jülich.

Nine hundred samples of the municipal water supply have been measured to construct a general pattern of the oxygen isotope ratio in the groundwater of the Federal Republic of Germany. Figure 3 demonstrates a decrease of the oxygen isotope ratio from the coastal to the interior regions. The large number of stations enables us to select special local effects, e.g. the use of filtrated river water, and to describe the general pattern. In the northwestern coastal regions the influence of sea water can be seen clearly. Towards the interior the 'continental' and the 'altitude effect' result in a decreasing ^{18}O content. Neither effect, the precipitation

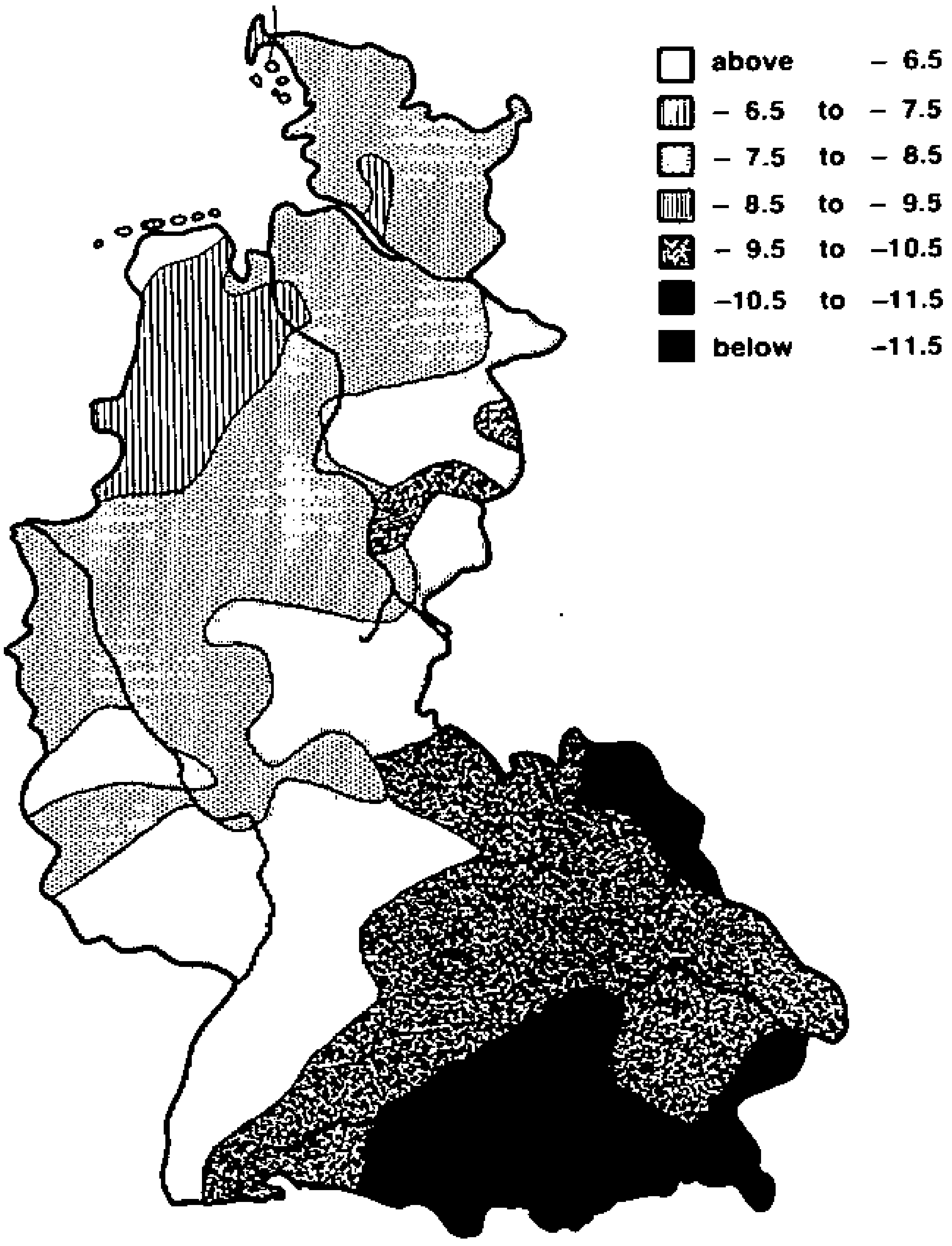

FIG.3. Regional pattern of the $^{18}O/^{16}O$ ratio in the area of the Federal Republic of Germany. The map demonstrates the decreasing ^{18}O content from north to south as a result of a combined altitude and continental effect.

of rain during the flow of air masses across the hills in the middle and across the mountains in the southern part or the subsequent precipitation during the flow of air from the sea to the continental parts, can be distinguished easily. The oxygen isotope ratio pattern is the result of the whole weather situation, i.e. of the 'climate'.

5. OXYGEN ISOTOPE RATIO OF AIR HUMIDITY

Measurements of the isotope ratio in air humidity during one or more days demonstrated that its mean δ-value is predictable also. Sudden jumps of the isotope ratio are usually caused by sudden changes of the weather conditions or are due to technical errors because of an incomplete trapping of the water vapour.

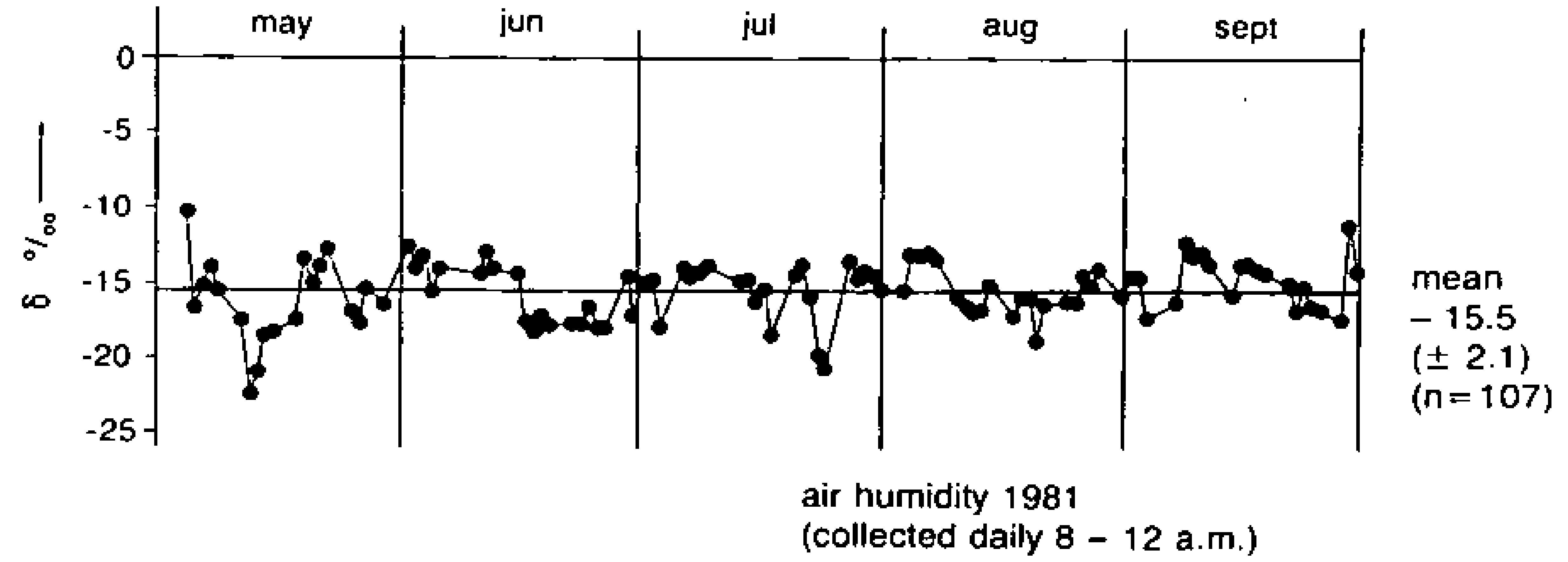

FIG. 4. $^{18}O/^{16}O$ ratio of air water vapour, collected during the growth period in Jülich in 1981 daily from 8 to 12 a.m. (10 m above soil level).

During days with constant weather conditions the oxygen isotope ratio of the humidity is constant during the whole day and does not vary at different heights above ground level in a dense beech forest [12]. The last statement is important, for there is no indication up to now that the transpiration of trees can influence the isotope ratio of water vapour in a dense forest.

Long-term measurements of the oxygen isotope ratio of air humidity near Chicago [16] give results comparable to ours. The climatic conditions also seem to be very similar. The measurements suggest a simple model: the air humidity at a location is in an equilibrium with the liquid phase of the soil water. Naturally, this assumption is too simple, but it confirms in a first approach our results of the oxygen isotope ratios in the air water vapour during the growth period of natural vegetation from May to September 1981 in Jülich (Fig.4). For further considerations one may assume a constant δ-value of the local precipitation and a defined δ-value of the humidity, in our case corresponding to the equilibrium between gaseous and liquid phase.

6. FRACTIONATION OF OXYGEN ISOTOPES DURING THEIR TRANSPORT WITHIN THE PLANT

The uptake of water by the roots is not accompanied by a fractionation of the oxygen isotope of water, for the diffusion of water is a very rapid process. In the xylem one observes a mass flow, which empirically does not result in an isotope fractionation. Therefore one must know the isotope concentration of water flowing into the leaves, the water of the twigs. It should reflect the mean $^{18}O/^{16}O$ ratio of precipitation and of soil water, respectively.

Measurements of an annual cycle of the oxygen isotope ratio in the twig water are shown in Fig.5. During the active period of the plants the water in the twigs really reflects the isotope composition of the local precipitation and of

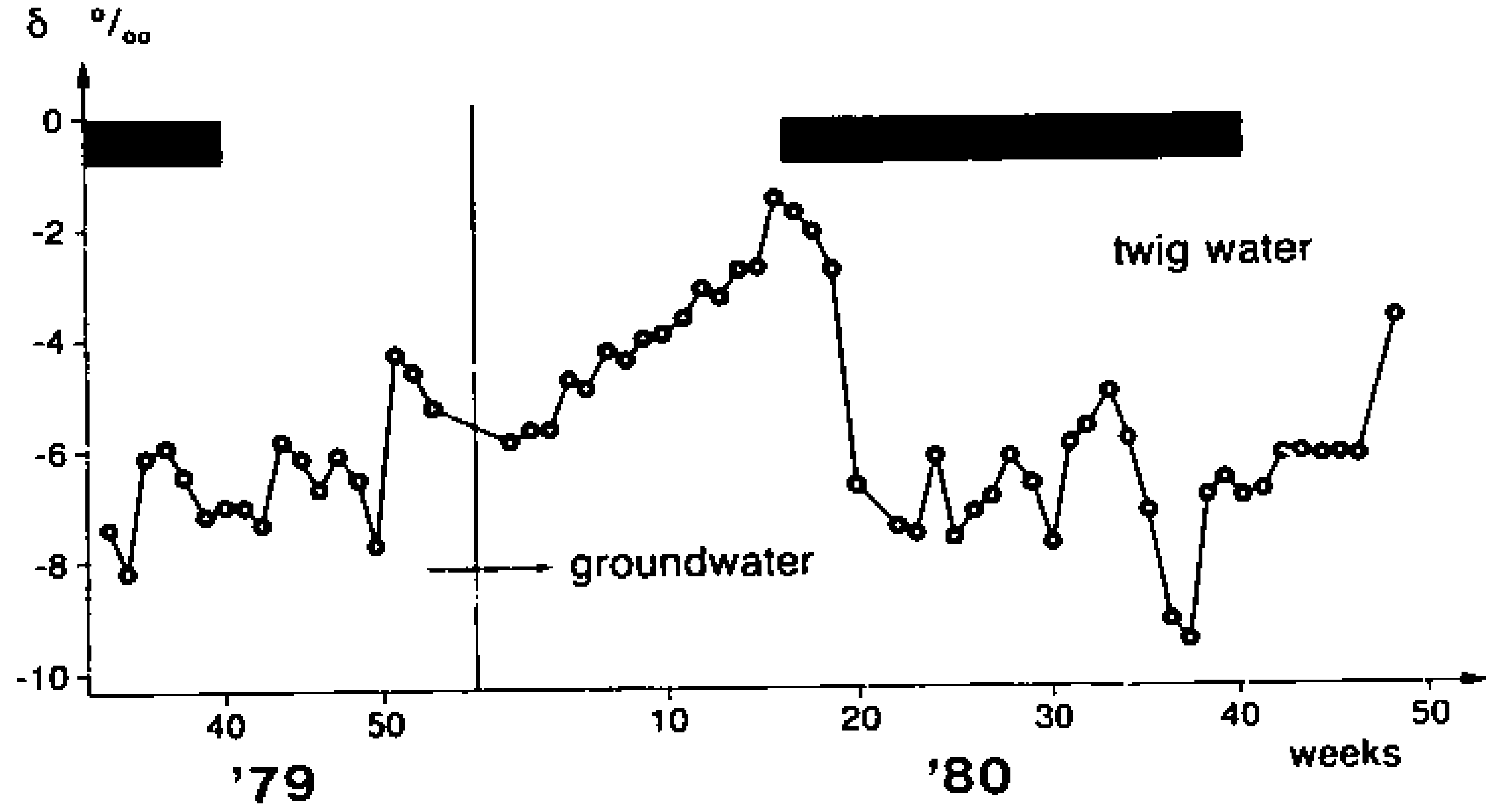

FIG.5. $^{18}O/^{16}O$ ratio of water in twig segments of seven different species (two oaks, a willow, a birch, an alder, a hickory, an ash, a beech) in the forest around the Nuclear Research Centre Jülich (KFA). The growth period during the summer months is indicated by large horizontal lines. During the growth period an intensive flow of water supplies the plant with water from the soil continuously. During the rest, if the plants have lost their leaves, the water evaporates via the bark, resulting in an increase of the δ-value of twig water. The arrow "Jül I" indicates our local standard, i.e. the local groundwater.

soil water. Only during the periods of rest, in winter and in early spring, the water loss of the twigs results in an increasing enrichment of ^{18}O. But directly after the start of biological activity, transpiration leads to an intensive flow of water through the xylem tissue. The resulting $\delta^{18}O$ values of twig water then reflect again the isotopic composition of soil water. Figure 6 compares the oxygen isotope concentration of twig water from two plants: the willow *Salix spec.*, a shrub that develops its leaves early in the spring to use the irradiation before the big oak trees *(Quercus robur)* develop their leaves. One can see that the onset of plant activity is combined with an intensive uptake of water from the soil and a reset of the δ-values. Generally the water in the transport system of plants has the isotope composition of soil water. Trees especially drain the water out of the soil by their large root systems, which 'averages' the oxygen isotope content of different water layers in the soil volume.

7. OXYGEN ISOTOPE RATIO OF LEAF WATER

The water flows from the xylem via the intracellular space and the water volume of the cells to the stomata, where the main exchange between leaf water and air humidity actually happens. As a result of the transpiration, one expects an increased ^{18}O content of the water remaining in the leaf. This fact alone is not too surprising but the changes of the $^{18}O/^{16}O$ ratio during every day are really remarkable [11, 12].

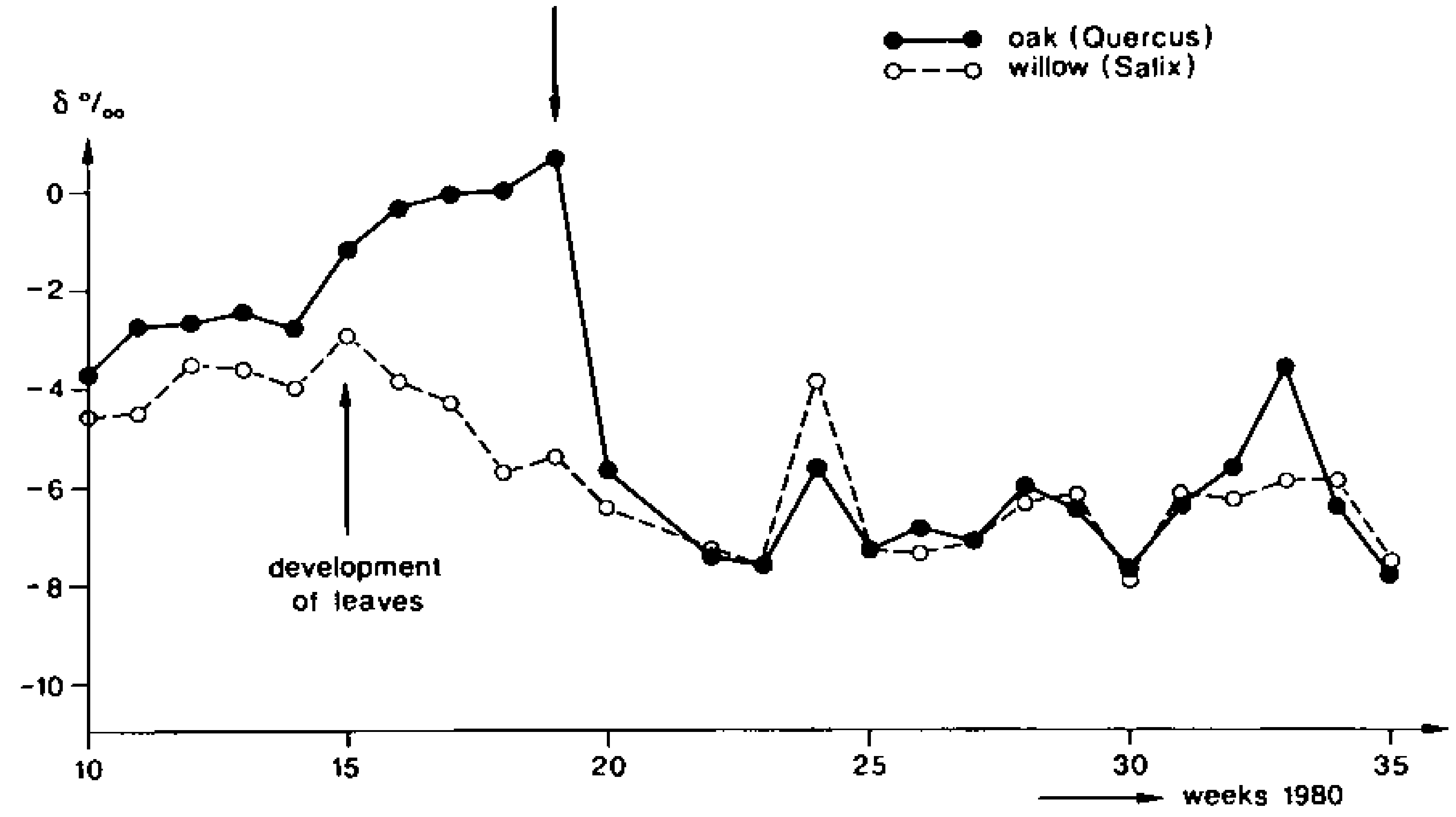

FIG. 6. The δ(^{18}O) values of twig water of two species are compared. The willow develops its leaves early in the spring, the oak much later. Directly after the start of an intensive water turnover the δ-value of twig water represents the mean isotopic composition of precipitation and soil moisture.

Figure 7 demonstrates the $^{18}O/^{16}O$ ratios of oak leaves collected from five trees at the border of a forest clearing. Therefore the branches are oriented in different directions. The result can be compared to the observations of three ecosystems (beech forest, fir forest, meadow) [12]. In the experiment reported here also no significant differences between the five plants can be seen. The temperature and the relative humidity during this day show the common course. The $^{18}O/^{16}O$ ratio of air water vapour was measured simultaneously.

Figure 8 reports the $^{18}O/^{16}O$ ratios of leaf water and the data of temperature and relative humidity of air. These samples and data were collected usually once a week, at 2.00 p.m., during the growth period 1981. The general trend of an inverse correlation of temperature and relative humidity of the air can be seen during May. The same correlation between temperature and $^{18}O/^{16}O$ ratio of leaf water as shown in Fig.7 can be observed in this long observation. But from a physical point of view a simple correlation between temperature of air and $^{18}O/^{16}O$ ratio of leaf water cannot be explained by any mechanism known today.

The leaf can be described as a flat water sheet of constant volume that exchanges its water rapidly between the liquid and the gaseous phase. Deviations from this simple hydrological model, which should include differences between various species, can be explained by geometrical and irradiation effects. In an experiment the surface of wet filter papers has been covered by a network of metallic tissue. Only 50% of the surface was covered. This is a very rough simulation of the stomatal function. As a result an enhancement of the $^{18}O/^{16}O$

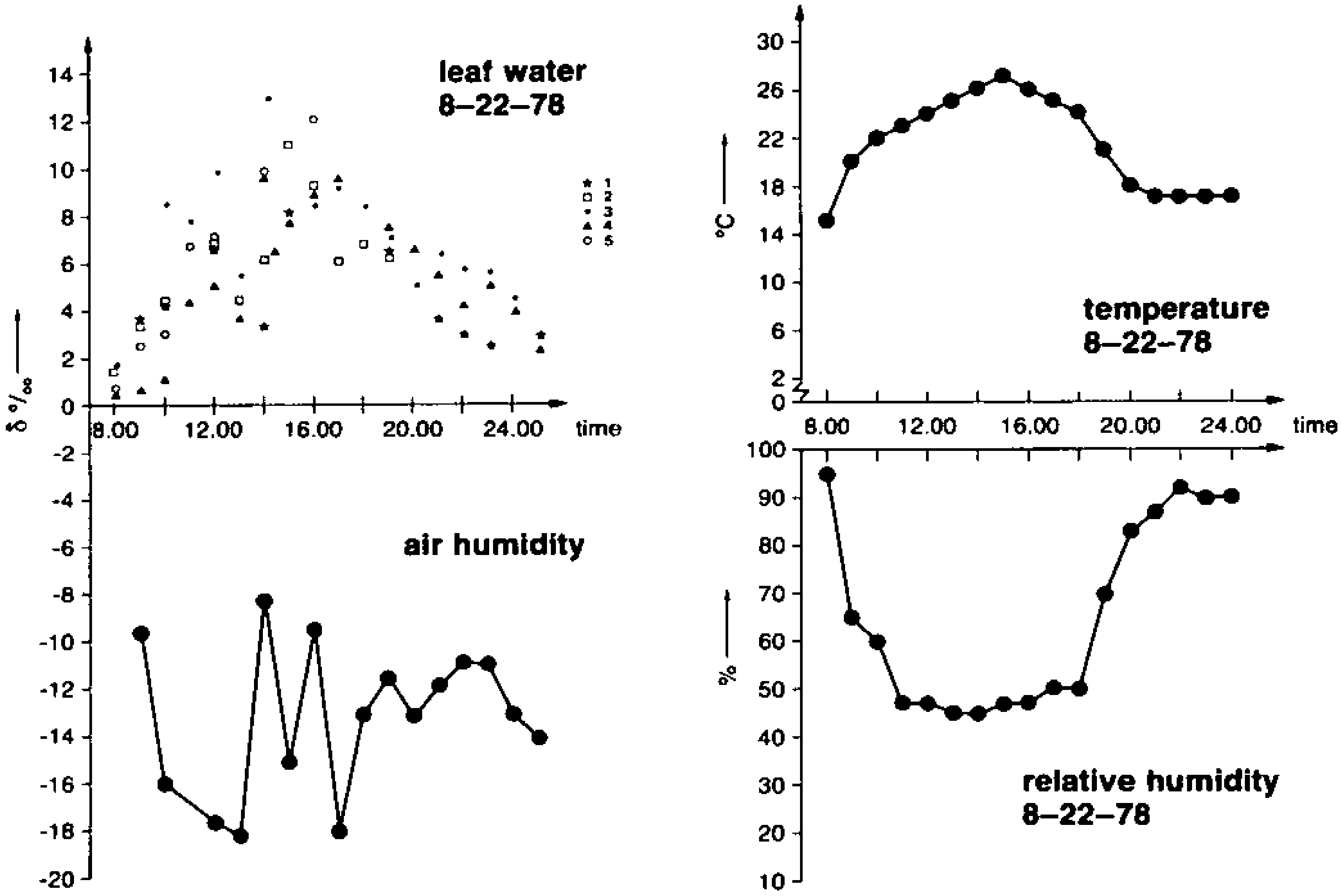

FIG.7. $^{18}O/^{16}O$ *ratio of leaf water and air humidity in comparison to the temperature and relative humidity of air samples of various oak leaves collected simultaneously at the border of a rectangular forest clearing from five trees. The branches are oriented into different directions. The δ-values of leaf water do not vary markedly. The scattering of the oxygen isotope ratio in the water vapour of air could be due to the special weather conditions. The diurnal course of temperature and relative humidity of air corresponded to the general experience under our local conditions.*

ratio by 1‰ (as δ-value) was observed. A simulation of an increase of leaf temperature above the environmental level also enhanced the $^{18}O/^{16}O$ ratio; we observed positive differences of 5°C under natural conditions by direct (thermocouple) and indirect (infrared camera) measurements. The enrichment in the liquid phase depends on the temperature conditions of the boundary layer [17]. An increase in the temperature of water corresponds to a fall of the relative humidity of the surrounding air. These effects may be the explanation of the parallels of the diurnal $^{18}O/^{16}O$ ratio curves of three species at the same site under identical environmental conditions [12]. The three species differ especially in the geometry of their photosynthetic organs (needles, leaves), and possibly also in their leaf temperature.

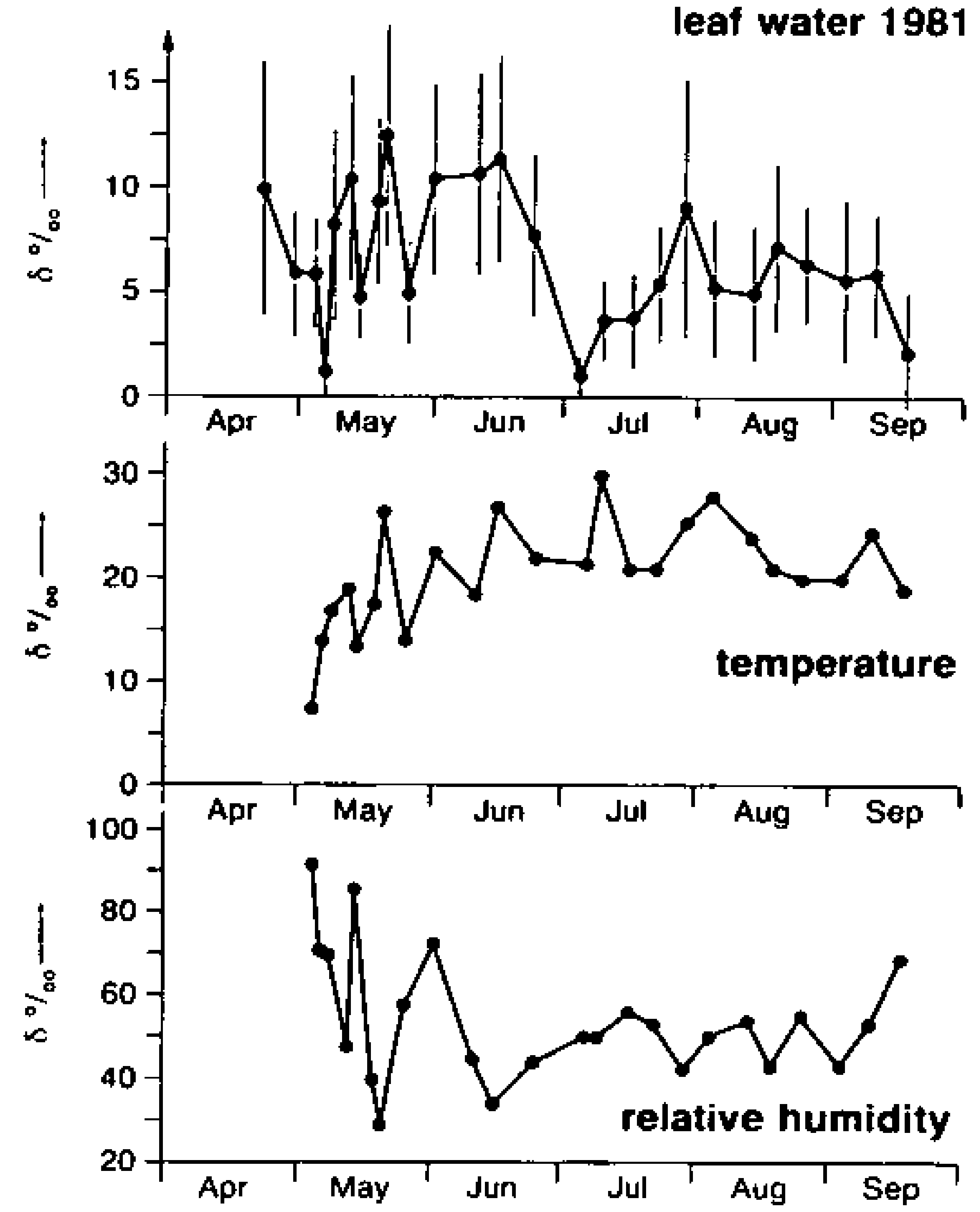

FIG.8. $^{18}O/^{16}O$ ratio of leaf water, temperature and relative humidity of air at 2 p.m. during the growth period. Usually one set of samples per week has been collected. The δ-values of eight different species are summarized. The variation is given as standard deviation by vertical lines. Especially during May 1981 the inverse correlation between air temperature and relative humidity is clearly demonstrated.

Figure 7 could suggest a simple correlation between temperature and $^{18}O/^{16}O$ ratio, as reported earlier [12]. But the model of the isotopic fractionation during the evaporation of water seems to be empirically and theoretically conclusive [18–20]. The formula, which describes stationary conditions, is given as:

$$\delta_\ell = \delta_s(1-h) + \epsilon_{eq} + \epsilon_k + (\delta_a - \epsilon_k)h$$

where δ = isotope ratios, related to Vienna-SMOW
ϵ = constant fractionation constants ($\epsilon = \alpha - 1$).
Index (ℓ, s, eq, k, a): leaf water, soil water, equilibrium, kinetic, air humidity;
h: relative humidity of air ($1 \geqslant h \geqslant 0$).

In the climate box sudden changes of the environmental conditions, especially of the relative humidity of air, were simulated. The $^{18}O/^{16}O$ ratio of the leaf water responded very rapidly [21]. Therefore one can assume that the actual ^{18}O content of leaves really reflects the environmental conditions close to stationary state. The actively transpiring leaves exchange their water volume very rapidly with the water vapour of the surrounding air.

TABLE I. INFLUENCES OF CLIMATE ON THE $^{18}O/^{16}O$ RATIO OF LEAF WATER

Soil and groundwater	Air water vapour	Relative humidity
Annual mean temperature Distance from sea Altitude above sea level Geographical position Humid/arid conditions	Equilibrium (?) Geographical position	Temperature Humid/arid conditions

The validity of the equation can be tested by the results shown in Figs 4 and 8. The mean $^{18}O/^{16}O$ ratio of leaves during the growth period 1981 is 6.4 ± 3.5‰. The mean relative air humidity from April to September was 53 ± 18%; the mean oxygen isotope ratio in the air water vapour is −15.5 ± 2.1‰. The isotope ratio of the soil water is represented by the local groundwater (oxygen isotope ratio: −7.7‰).

The equilibrium value at 20°C (average during the observation period: 20.5°C) is taken as 9‰ [22], the kinetic fractionation as 16‰. If one uses these data and their limits (standard deviations), one gets the following results.

(1) The mean values of all parameters necessary result in a 'theoretical $^{18}O/^{16}O$ ratio' of +4.7‰ (empirically observed +6.4‰).

(2) If one takes the limits of the $^{18}O/^{16}O$ ratio of the air water vapour into consideration, the 'theoretical $^{18}O/^{16}O$ ratio' will lie between +5.8 and +3.6‰.

(3) If only the limits of the relative humidity are taken into account, the resulting theoretical $^{18}O/^{16}O$ ratios are +9.0 and 0.4‰, now including the mean result of leaf water under field conditions. On the other hand the observed $^{18}O/^{16}O$ ratio of leaf water has a standard deviation of ±3.5‰ (δ-value); the limits therefore are +9.9 and +2.9‰.

Generally the value observed actually may lie within the limits predicted by the hydrological equation, but it is 1.7‰ higher than expected. This could be due to an enhanced leaf temperature or even to the microclimatic difference between the tree and the meteorological station. The temperature and relative humidity were taken from the results of our conventional weather station (2 m above ground, closed basket). The ϵ_k value must be tested carefully also, especially for biological material of different species.

One should not discuss the results only on the basis of a simple linear correlation between temperature and $^{18}O/^{16}O$ ratio. The value of leaf water is empirically found and represents the mean local oxygen isotope ratio. A change of this ratio must indicate a change of the local climate conditions.

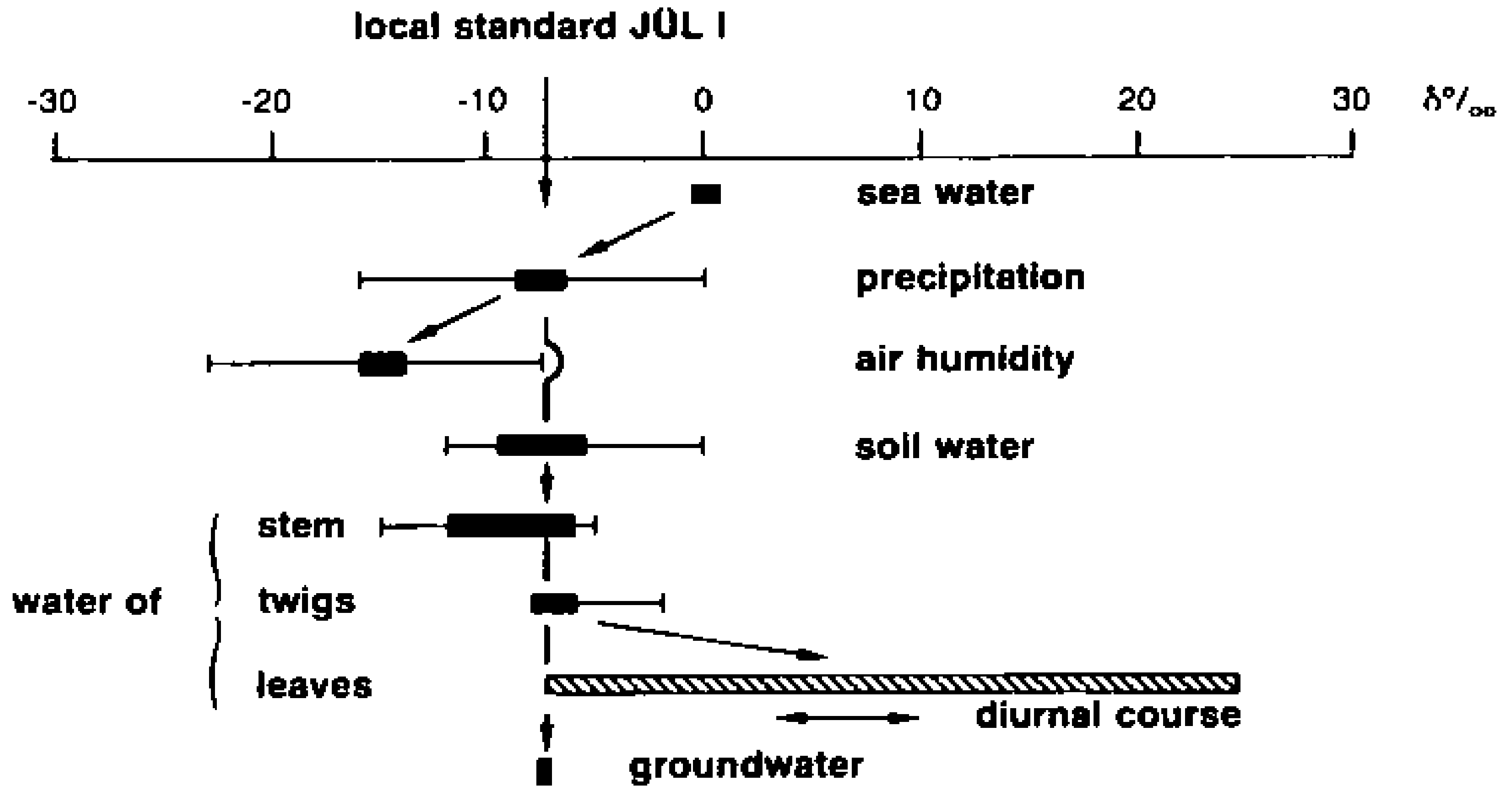

FIG.9. Schematic summary of the $^{18}O/^{16}O$ ratios of water samples from the local ecosystem in Jülich. The black lines symbolize the usual range of scattering, the horizontal lines limit values of extreme scattering.

The $^{18}O/^{16}O$ ratio of leaf water can be used as an indicator of variations, but not as a relative scale of temperature. Similar experiences are known from the $^{18}O/^{16}O$ data of cellulose from tree rings.

8. CONCLUSIONS

The hydrological formula, given above, describes the influences of the environmental parameters on the $^{18}O/^{16}O$ ratio of leaf water and consequently on the ^{18}O content of the cellulose of tree rings. According to the formula, the $^{18}O/^{16}O$ ratio of leaf water depends on the local climate.

(1) The $^{18}O/^{16}O$ ratio of local precipitation and of the soil and groundwater is governed by the climatological situation. Seasonal variations can be seen; in central Europe we observe routinely an ^{18}O minimum in March, but generally the water of different precipitations is mixed well during its way down through the soil column into the groundwater. The water, which is transported in the xylem of trees to the leaves, represents the $^{18}O/^{16}O$ ratio of local precipitation. This $^{18}O/^{16}O$ ratio of xylem (twig) water is the basic value of the ^{18}O content in leaf water.

(2) The $^{18}O/^{16}O$ ratio of air water vapour is important for the description of the influence of the exchange between air humidity and leaf water. Under our climatic conditions there seems to be an equilibrium between liquid and gaseous phase. At last the difference between the $^{18}O/^{16}O$ ratio of the mean annual precipitation and the long-term mean of air water vapour confirms this idea. The $^{18}O/^{16}O$ ratio should be measured by special programmes, which include different types of climate in various geographical positions.

(3) The relative humidity of the air is a very important parameter. It describes the extent of exchange between leaf water and the water vapour of the air, i.e. the enrichment of ^{18}O in the leaf water in relation to the other oxygen isotope concentrations of the water in the local ecosystem. Under our climatic conditions the temperature and the relative humidity of the air are inversely correlated. An increase of the temperature results in a decrease of the relative humidity of the air and consequently the $^{18}O/^{16}O$ ratio of leaf water is enhanced. Table I summarizes the climatological influences on the $^{18}O/^{16}O$ of leaf water.

Figure 9 includes a schematic view of the level and variation of the $^{18}O/^{16}O$ ratios in our local ecosystem. Our experience during one decade has shown us that during long periods of observation one is able to predict the results with diminishing scattering. Therefore, the $^{18}O/^{16}O$ ratio preserved by the cellulose of the datable tree rings should reflect the long-term trend of the local climate, at least of remarkable changes.

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ISOTOPIC COMPOSITION OF ORGANIC SUBSTANCES

(Section 2)

$^{18}O/^{16}O$ RATIOS IN LEAF WATER AND CELLULOSE OF AQUATIC AND TERRESTRIAL PLANTS

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Abstract

$^{18}O/^{16}O$ RATIOS IN LEAF WATER AND CELLULOSE OF AQUATIC AND TERRESTRIAL PLANTS.

Different experiments and measurements performed on terrestrial and aquatic plants to point out relationships between ^{18}O content of cellulose and environmental factors have shown the following. (1) There is a linear correlation between cellulose and mesophyll water δ's. (2) The variations of the isotopic composition of cellulose with the environmental conditions are induced essentially by the mesophyll water $\delta^{18}O$ changes controlled themselves by the plant transpiration process; $\delta^{18}O$ variations of leaf water appear then as the principal intermediary in the relations linking $\delta^{18}O$ of plant cellulose to the growth medium. (3) The correlations between cellulose and mesophyll water δ's obtained for aquatic and terrestrial plants are different: for aquatic plants $\delta^{18}\text{cellulose} = 0.65\ \delta_{LW} + 25.4$; for terrestrial plants $\delta^{18}\text{cellulose} = 0.39\ \delta_{LW} + 21.6$. This difference is interpreted as a consequence of the isotopic exchange process of CO_2 with leaf water, which is complete in the case of aquatic plants (fixation of dissolved CO_2) and probably incomplete in the case of terrestrial plants (fixation of atmospheric CO_2). (4) In both correlations, the slope values are less than 1; this result shows that variations of ^{18}O content of cellulose cannot be completely interpreted as a simple isotopic equilibrium process between water and CO_2 or photosynthesis products.

1. INTRODUCTION

The use of $^{18}O/^{16}O$ ratio in organic material as a palaeoclimate indicator implies a good knowledge of the processes controlling the variations of this ratio. Studies have established some correlations between the ^{18}O content of plant cellulose and various environmental or biological factors such as temperature [1–4] and relative humidity and $\delta^{18}O$ of water supplied [5, 6]. To account for these observed relationships, several theoretical models have been proposed.

(1) The temperature effect is to be related directly to an isotopic fractionation during photosynthesis reactions, thermodynamically depending upon temperature [3]. According to this model we can write

$$\delta^{18}O\ \text{cellulose} = a \cdot t + C \qquad (1)$$

with t = temperature and a and C = constants.

(2) Oxygen atoms incorporated in cellulose derive from water and carbon dioxide in proportions of one-third and two-thirds respectively. According to this model, the relationship describing the $\delta^{18}O$ variations in plant cellulose should be expressed in different ways for aquatic and terrestrial plants.

(a) for aquatic plants

$$\begin{aligned}\delta^{18}\text{O cellulose} &= 0.33\ \delta^{18}\text{O}(\text{H}_2\text{O}) + 0.67\ [\delta^{18}\text{O}(\text{H}_2\text{O}) + \epsilon] \\ &= \delta^{18}\text{O}(\text{H}_2\text{O}) + 0.67\ \epsilon \qquad (2)\end{aligned}$$

with $\epsilon = 41‰$ at 25°C

(b) for terrestrial plants

$$\begin{aligned}\delta^{18}\text{O cellulose} &= 0.33\ \delta^{18}\text{O}(\text{H}_2\text{O}) + 0.67 \times 41 \\ &= 0.33\ \delta^{18}\text{O}(\text{H}_2\text{O}) + 27.5 \qquad (3)\end{aligned}$$

In this last case, non-equilibrium is assumed for oxygen isotopes between H_2O and CO_2 in cells.

(3) The oxygen isotopic composition of CO_2 does not influence the ^{18}O content of cellulose [7, 8] which depends, therefore, uniquely upon the $^{18}O/^{16}O$ ratio of water used during photosynthesis. Two interpretations are proposed to account for this assumption: (a) carbon dioxide undertakes a complete exchange with water in cells prior to its fixation, and (b) isotopic exchange occurs during hydration of carbonyl groups of intermediate compounds of cellulose photosynthesis. This model involves an identical relationship between the ^{18}O content in cellulose and in mesophyll water for the two categories of plants (aquatic and terrestrial). This relationship may be written as

$$\delta^{18}\text{O cellulose} = \delta^{18}\text{O (mesophyll water)} + \text{C} \qquad (4)$$

with C = 27.5‰.

In fact, experiments performed under controlled conditions where only one parameter was varied at a time have shown a negligible effect of temperature but a large effect of relative humidity and $\delta^{18}O$ of irrigation water. Both effects of relative humidity and isotopic composition of irrigation water suggest that the isotopic composition of cellulose is related essentially to the ^{18}O content of water in leaf mesophyll and that environmental factors affect especially the isotopic composition of this water following the fractionation processes induced by plant transpiration.

The aim of the present study is to determine and compare the relationships between the ^{18}O content in leaf mesophyll water and in cellulose in terrestrial and aquatic plants.

2. METHOD AND MATERIAL

2.1. Isotopic analysis

Oxygen-18 content in cellulose extracted from leaves by a standard procedure [9] was analysed using a pyrolysis method [10]. The water contained in a small fragment of leaf mesophyll was also isotopically analysed by the same method, modified and adapted for analysis of microquantities of water [11, 12].

The results are given in the well known δ notation:

$$\delta = \left(\frac{R_E}{R_S} - 1\right) \cdot 1000$$

where R_E and R_S refer to $^{18}O/^{16}O$ ratio in sample and in standard, respectively. The standard is the mean ocean water (SMOW).

2.2. Material

Aquatic plants were collected from different aqueous media selected for the slight seasonal variations of the isotopic composition of their water and from an aquarium with water of known $\delta^{18}O$. The ^{18}O contents were determined both in mesophyll water and in cellulose.

For terrestrial plants, we studied on bean plants *(Phaseolus vulgaris)* grown under controlled conditions (temperature, relative humidity, $\delta^{18}O$ of irrigation water): (1) the effect of relative humidity and isotopic composition of irrigation water on the $^{18}O/^{16}O$ ratios of the plant cellulose, (2) the effect of these parameters on the isotopic enrichment of the mesophyll water and (3) the relative isotopic enrichment of water in different parts of the plant.

3. RESULTS

3.1. $\delta^{18}O$ of cellulose in aquatic plants

Table I shows the $\delta^{18}O$ values of cellulose in various species growing in waters of different $\delta^{18}O$. These values range from 17‰ to 30.8‰ when the water δ's

TABLE I. $\delta^{18}O$ OF WATER AND CELLULOSE OF AQUATIC PLANTS

Location	Plants	$\delta^{18}O$	
		Water	Cellulose
Lac Léman (Alps)	*Potamogeton crispus*	−12.7	16.5
	Myriophyllum spicatum		17.6
	Elodea canadensis		16.9
	Ranunculus aquatilis		17.3
Lac d'Aydat (M. Central)	*Elodea canadensis*	−8.9	19.9
	Potamogeton crispus		20.1
Passy/Eure (Eure)	*Callitriche capillaris*	−7.3	20.8
	Alisma trivialis		21.1
Fontaine s/jouy (Eure)	*Polygonum amphibium*	−7.4	20.1
Manche (Abbeville)	*Ulva lactuca*	−0.2	25.2
	Enteromorpha intestinalis		24.8
Manche (Roscoff)	*Ulva lactuca*	−0.4	24.8
Pacific ($\mathrm{N^{elle}}$ Calédonie)	*Ulva lactuca*	+0.2	25.6
Méditerranée (Agde)	*Ulva lactuca*	+1.7	26.6
	Enteromorpha intestinalis		26.9
Aquarium	*Potamogeton sp.*	+8.1	30.7

vary from −12.4‰ to +8‰. Measurements performed on water in leaves and in aqueous media show no difference in the ^{18}O content. This result is consistent with those of Refs [5, 13]. A good correlation appears between cellulose and water δ's. The least-squares fit to the data points gives

$$\delta^{18}O\ (\text{cellulose}) = 0.65\ \delta^{18}O(H_2O) + 25.4 \qquad (5)$$

with a correlation coefficient r = 0.99.

3.2. $\delta^{18}O$ of cellulose in bean plants

The results (Table II) show an appreciable influence of relative humidity and isotopic composition of water supplied on the variations of the $^{18}O/^{16}O$ ratios of

TABLE II. $\delta^{18}O$ OF BEAN PLANT CELLULOSE RELATED TO THE $\delta^{18}O$ OF IRRIGATION WATER AND TO RELATIVE HUMIDITY

$\delta^{18}O$ of soil water	Relative humidity	$\delta^{18}O$ of cellulose
−12.41	0.6	24.7
− 6.08		25.8
+11.80		28.9
+23.10		29.7
− 6.08	0.1	30.8
	0.35	28.5
	0.75	24.3
	0.95	21.4

cellulose in bean plants. When all other parameters are maintained constant over time, the increase of relative humidity induces a decrease in $\delta^{18}O$ of cellulose. The equation describing these variations can be written as

$$\delta^{18}O\ (\text{cellulose}) = -10.92h + 32.12 \tag{6}$$

with r = 0.98.

Variations in the $\delta^{18}O$ of irrigation water (under constant relative humidity) also cause variations in the $\delta^{18}O$ of cellulose following the relationship

$$\delta^{18}O\ (\text{cellulose}) = 0.15\ \delta^{18}O\ (\text{irrigation water}) + 26.68 \tag{7}$$

with r = 0.96.

3.3. Distribution of water $\delta^{18}O$ in different parts of a bean plant

Different studies on ^{18}O in leaf water [14–18] showed a noticeable isotopic enrichment of water in leaves with transpiration. The analytical procedure used in the course of our work allows $\delta^{18}O$ determination of water in very small fragments of plant material (less than 10 mg). This technique offers, thus, the opportunity to investigate precisely the distribution of the $^{18}O/^{16}O$ ratios of water in

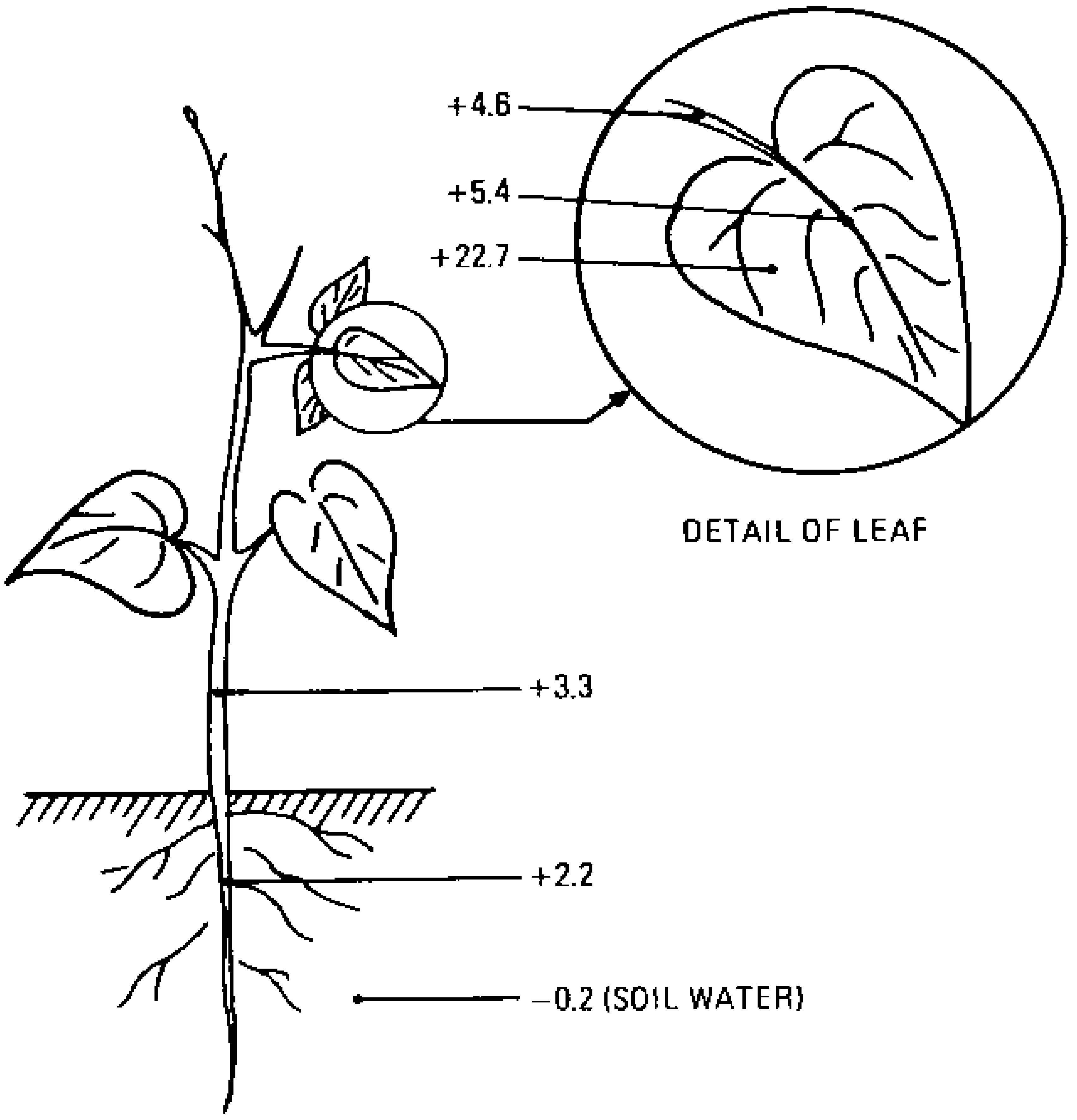

FIG. 1. $\delta^{18}O$ of water in different parts of a bean plant.

different parts of a plant and even in different parts of a single leaf. From the data shown in Fig. 1, three important results can be noted:

(1) Water in all parts of the plant is more or less enriched in ^{18}O with respect to the soil water.

(2) In the same leaf, there is a great isotopic difference between water in nervures and water in mesophyll.

(3) The ^{18}O content of water in mesophyll is appreciably higher than expected from previous data obtained by researchers who analysed the water in whole leaves.

3.4. Relative humidity and light/dark effect on the $\delta^{18}O$ of mesophyll water

Bean plants were placed under different relative humidities and the isotopic composition of the mesophyll water was determined twice a day: in the morning, after a dark period and in the afternoon, after a light period.

Relative humidity appears to be an important factor in the isotopic variations of mesophyll water. The data (Fig. 2) confirm the experimental results of Ref. [19], which gives the following relationship:

$$\delta_{LW} \cong -32h + 28 \qquad (8)$$

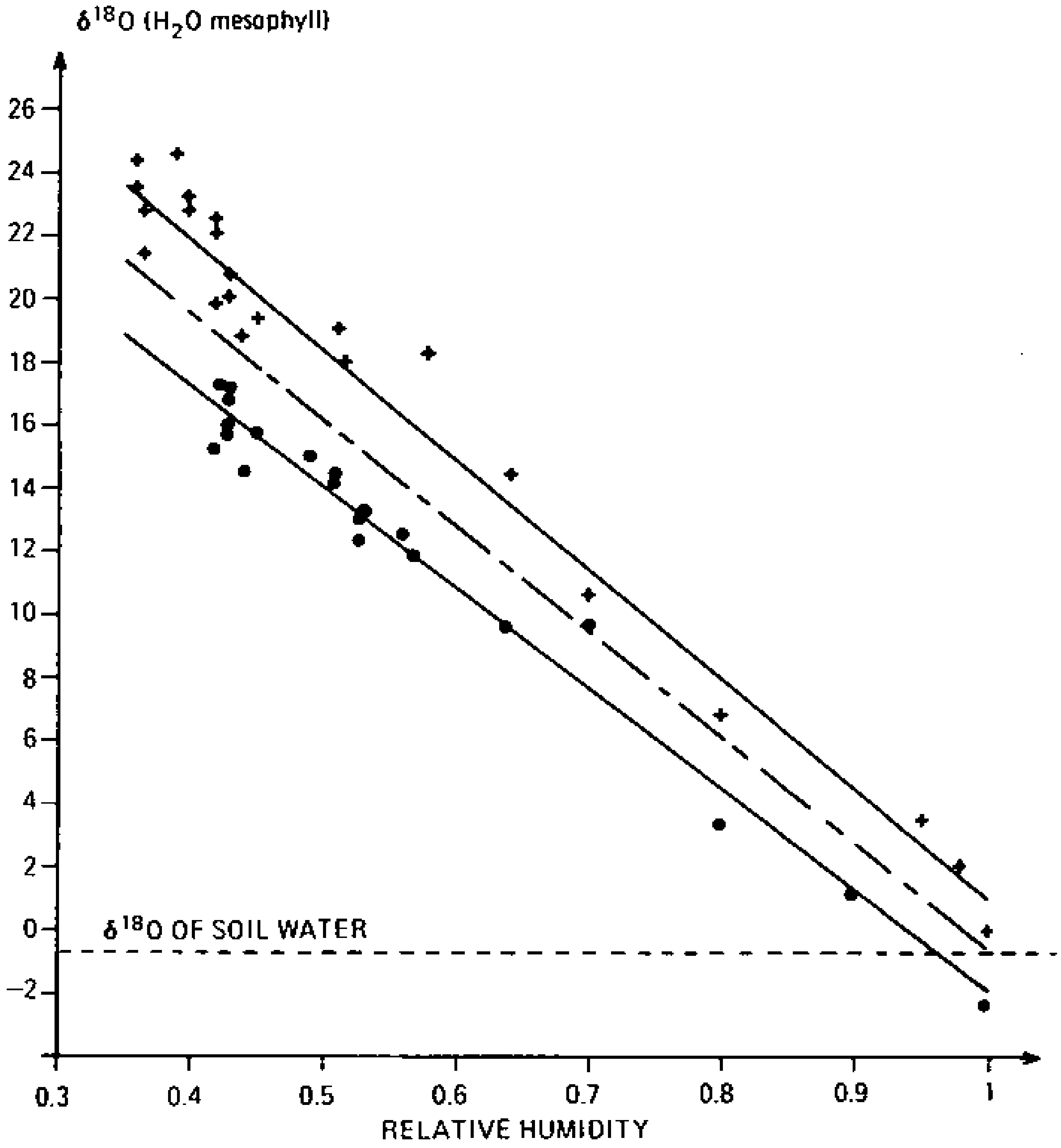

FIG. 2. $\delta^{18}O$ variations of mesophyll water in a bean plant with respect to relative humidity (● = $\delta^{18}O$ in the morning; + = $\delta^{18}O$ in the afternoon).

In addition to this humidity effect our results show a significant difference (about 3 to 4‰) in mesophyll water δ's when determined in the morning or in the afternoon under the same relative humidity. Analysis every 3 hours during 24 hours under constant conditions (temperature, relative humidity, $\delta^{18}O$ of soil water) evidenced this variation related to a light/dark effect (Fig. 3).

Thus, the mesophyll water δ's versus relative humidity relationship can be expressed as

$$\delta^{18}{}_{LW} = -32.2h + 30.2 \qquad (r = 0.97) \qquad (9)$$

(in morning)

$$\delta^{18}{}_{LW} = -35h + 35.9 \qquad (r = 0.96) \qquad (10)$$

(in afternoon)

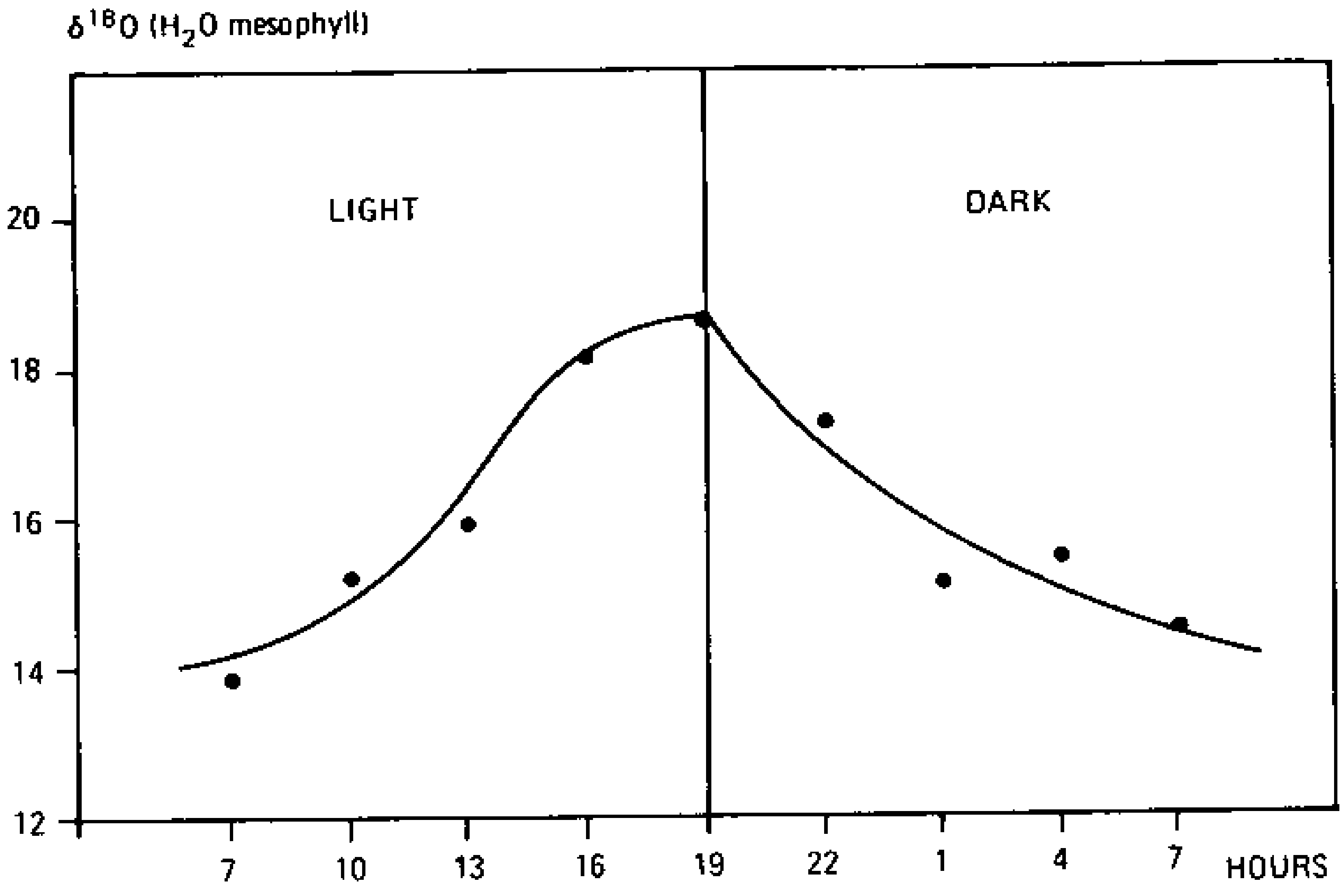

FIG.3. Light/dark effect on the $\delta^{18}O$ of mesophyll water under constant relative humidity.

Considering all points, we obtain the equation of the median line

$$\delta^{18}{}_{LW} = -33.6h + 33 \qquad (r = 0.96) \qquad (11)$$

representing the mean variation of the $^{18}O/^{16}O$ ratios in mesophyll water with relative humidity. The parameters of this last equation are slightly different from those found earlier, and this is probably due to the difference in the kind of water analysed: whole leaf water in earlier experiments and only mesophyll water in ours.

4. DISCUSSION

To compare the relationship between ^{18}O content of cellulose and mesophyll water in aquatic and terrestrial plants, the mean values of ^{18}O content in mesophyll water of the bean plants during their growth under different experimental conditions must be known.

These values can be estimated by calculation, if the four following parameters are known: temperature, relative humidity, $\delta^{18}O$ of irrigation water and $\delta^{18}O$ of atmospheric water vapour.

4.1. Theoretical considerations

In general, a leaf can be compared to a system evaporating water at a constant or non-constant level (e.g. the leaf water content can be considered as constant or not constant during transpiration). Under a given temperature, the isotopic composition of the water in such a system is a function of three variables: relative humidity, $\delta^{18}O$ of atmospheric water vapour and $\delta^{18}O$ of input water. The relationship between these parameters and the ^{18}O content of evaporating water can be calculated [15, 20–22].

Evaporation is generally considered as a diffusion process described by Fick's law

$$\phi_E = \Gamma(C_s - C_A) \qquad (12)$$

where ϕ_E, Γ, C_A and C_S are evaporation flux, profile coefficient [23–25] vapour concentration in air and saturated vapour concentration.

Two equations can be written for the two isotopic species ^{16}O and ^{18}O:

$$J = \Gamma(C_S - C_A) \qquad (\text{for } ^{16}O) \qquad (13)$$

$$J' = \Gamma'(C'_S - C'_A) \qquad (\text{for } ^{18}O) \qquad (14)$$

The $\delta^{18}O$ of the evaporation flux can be computed from these equations [21, 22]

$$R_E = \frac{1}{\alpha_k}\left[\frac{\frac{1}{\alpha_e} R_L - R_A h}{1 - h}\right] \qquad (15)$$

where $R_E = J'/J = {}^{18}O/{}^{16}O$ ratio in ϕ_E and $\alpha_k = \Gamma/\Gamma'$ = kinetic fractionation factor.

$$\alpha_e = \frac{R_L}{C'_S/C_S} = \frac{R_L}{R_V} = \text{equilibrium fractionation factor}$$

(R_L and R_V stand for $^{18}O/^{16}O$ ratios in liquid and in vapour phases);
$R_A = C'_A/C_A = {}^{18}O/^{16}O$ ratio in air water vapour; $h = C_A/C_S$ = relative humidity.

The isotopic ratios can be expressed in ∂ notation: $\partial_x = (R_x/R_s) - 1$ (R_x and R_s refer to the $^{18}O/^{16}O$ ratios of the sample and the standard).

Equation (15) is then

$$\partial_E = \frac{1}{\alpha_k} \cdot \left[\frac{\frac{1}{\alpha_e}(\partial_L + 1) - h(\partial_A + 1)}{1 - h}\right] - 1 \qquad (16)$$

Rearranging and neglecting the products of small quantities, we then obtain

$$\partial_E = \frac{\partial_L - \epsilon_e - \epsilon_k - h(\partial_A - \epsilon_k)}{1 - h} \qquad (17)$$

(with $\epsilon_e = \alpha_e - 1$ and $\epsilon_k = \alpha_k - 1$)

or in δ per mille notation:

$$\delta_E = \frac{\delta_L - \epsilon_e - \epsilon_k - h(\delta_A - \epsilon_k)}{1 - h} \qquad (18)$$

(where δ's and ϵ's are expressed in ‰).

The differential equation describing the water $\delta^{18}O$ evolution over time in an evaporating system is

$$d(V \cdot \delta_L) = (\phi_a\,\delta_a - \phi_E\,\delta_E)dt \qquad (19)$$

where V is the water bulk in the system and ϕ_E and ϕ_a are evaporation and input water fluxes; δ_E and δ_a refer to the isotopic composition in ϕ_E and ϕ_a.

$$dV = (\phi_a - \phi_E)dt$$

and $V = (\phi_a - \phi_E)t + V^0$

hence $$\frac{d\delta_L}{dt} = \frac{\phi_a \cdot \delta_a - \phi_E \cdot \delta_E - (\phi_a - \phi_E)\delta_L}{V^0 + (\phi_a - \phi_E)t} \qquad (20)$$

TABLE III. $\delta^{18}O$ OF BEAN PLANT CELLULOSE RELATED TO THE $\delta^{18}O$ OF LEAF WATER CALCULATED USING EQ. (23), WITH $\epsilon_k = 24$‰, $\epsilon_e = 9$‰ AND $\delta_A = -9.7$‰

$\delta^{18}O$ (cellulose)	24.7	25.8	28.9	29.7	30.8	28.5	24.3	21.4
$\delta^{18}O$ LW	7.8	10.3	17.5	22.0	24.2	17.3	6.2	0.7

Taking into account the δ_E value (Eq. (18)) and integrating this differential equation, we obtain

$$\delta_L = \delta_L^0 \left(\frac{V^0 + D\cdot t}{V^0}\right)^x + \left[\frac{q\delta_a(1-h) + h(\delta_A - \epsilon_k) + \epsilon_e + \epsilon_k}{q(1-h)+h}\right]$$

$$\times\left[1 - \left(\frac{V^0 + D\cdot t}{V^0}\right)^x\right] \qquad (21)$$

with $x = \dfrac{\phi_a - h\cdot\phi_E/(1-h)}{\phi_a - \phi_E}$

$D = \phi_a - \phi_E$

$q = \phi_a/\phi_E$

This equation represents the general form of the particular equations describing the variations of the isotopic composition of a water body in different evaporating conditions:

(1) constant level systems ($\phi_a = \phi_E$)
(2) decreasing level systems ($\phi_a < \phi_E$)
(3) increasing level systems ($\phi_a > \phi_E$)
(4) Rayleigh's distillation ($\phi_a = 0$ and $h = 0$)

As for the constant level system (which is the model assumed for a transpiring leaf), Eq. (21) becomes, when ϕ_a tends towards ϕ_E,

$$\delta_L = \delta_L^0\, e^{-ft} + [(1-h)\delta_a + h(\delta_A - \epsilon_k) + \epsilon_e + \epsilon_k](1 - e^{-ft}) \qquad (22)$$

with $f = \dfrac{\phi_E}{V(1-h)}$

The curve corresponding to this equation allows one to observe the evolution of leaf water $\delta^{18}O$ over time when one of the parameters (e.g. h, δ_a, δ_A) changes.

Under given conditions of growth, the isotopic composition of leaf water tends, with time, to a steady-state level given by the equation

$$\delta_{eq} = (1-h)\delta_a + \epsilon_e + \epsilon_k + h(\delta_A - \epsilon_k) \qquad (23)$$

which is the limit for δ_L in Eq. (22) when t increases.

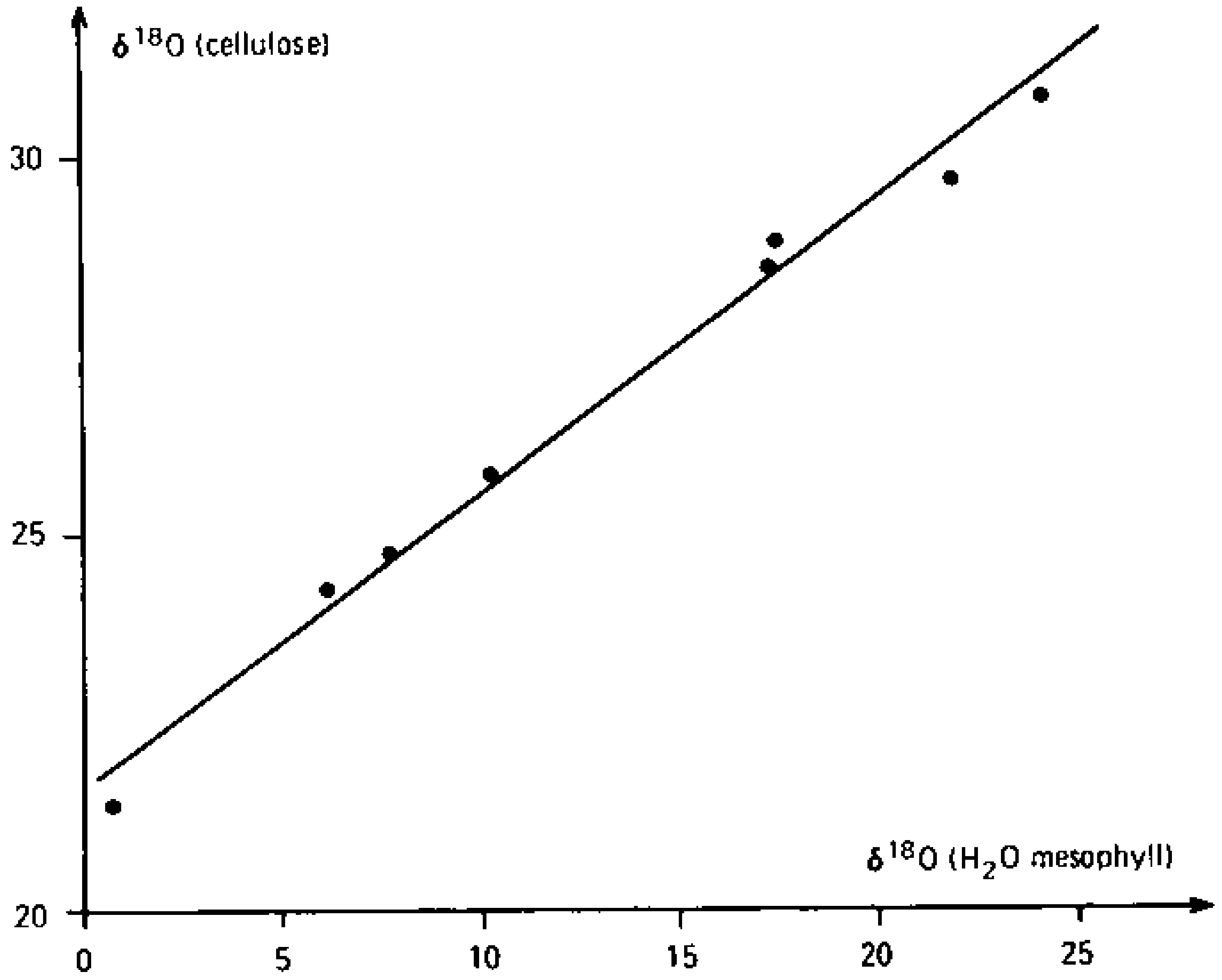

FIG. 4. *$\delta^{18}O$ variations of bean plant cellulose with respect to the mesophyll water $\delta^{18}O$.*

We retrieve, thus, the equation giving the isotopic composition of leaf water at the equilibrium level [16, 17, 26].

This equation can be used to estimate the isotopic composition of leaf water when plants grow under controlled conditions. For this we need to know ϵ_K and δ_A. The values of these parameters can be computed from Eqs (11) and (23). We thus find $\epsilon_K = 24‰$ and $\delta_A = -9.7‰$. The kinetic fractionation factor value obtained is consistent with values found earlier.

With regard to the $\delta^{18}O$ of atmosphere water vapour exchanging with leaf water, there is a significant difference (5–6‰) between the value computed from Eqs. (11) and (23) and the $\delta^{18}O$ measurements performed on air water vapour in our laboratory (mean $\delta^{18}O = -15.6‰$; number of measurements $n = 15$).

The calculated δ_A value represents, in fact, the $\delta^{18}O$ of the vapour layer exchanging effectively with leaf water. Vapour in this layer originates from the local atmospheric water vapour and from the vapour yield by the leaf itself. This last vapour fraction is more enriched in ^{18}O than is the local vapour, which may explain the difference between calculated and measured δ_A value.

Knowing ϵ_K and δ_A values, we can now use Eq. (23) to calculate the leaf water $\delta^{18}O$ of bean plants grown under controlled conditions (Table III). These data fit a line (Fig. 4).

$$\delta^{18}(\text{cellulose}) = 0.39\ \delta^{18}_{LW} + 21.6$$

A comparison of this line with that obtained for aquatic plants (Eq. (5)) points out an appreciable difference between the variations characterizing the isotopic composition of cellulose with respect to the leaf water ^{18}O for aquatic and for terrestrial plants. This result does not confirm either of the two models quoted in the introduction of this paper. Indeed, if we assume a complete isotopic exchange between CO_2 (or oxygen deriving from CO_2) and leaf water, we should find (1) the same equation for both plants, aquatic and terrestrial, and (2) a slope value of 1 for the line corresponding to this equation.

On the other hand, if we assume that oxygen in cellulose derives only from H_2O and CO_2 in the proportion of x and y, the slope of the aquatic plant line in that case also must be 1 because dissolved CO_2 taken up by aquatic plants is in isotopic equilibrium with medium water, and theoretically we can then write

$$\begin{aligned}\delta^{18}\text{cellulose} &= x \cdot \delta^{18}H_2O + y\,\delta\,CO_2 + C\\ &= \delta^{18}H_2O + y\epsilon + C \qquad (24)\end{aligned}$$

with ϵ = fractionation factor between H_2O and dissolved CO_2.

The slope values of the lines obtained from experimental data fall far short of what may be expected from the theoretical models mentioned above. In fact, our experimental results suggest that in the case of terrestrial plants, the CO_2 absorbed does not equilibrate isotopically with leaf water prior to its fixation but in the case of aquatic plants, the CO_2 absorbed is in isotopic equilibrium with the medium water. This explains the difference between the slopes of the lines obtained for aquatic and terrestrial plants.

The fact that the slope value is lower than unity for the regression lines of both plants suggests that oxygen in cellulose derives not only from CO_2 and H_2O but also from molecular oxygen of air fixed or exchanged during respiration and photorespiration processes.

According to this hypothesis, the isotopic composition of cellulose should vary as

$$\delta^{18}(\text{cellulose}) = x\,\delta^{18}(\text{LW}) + y\,\delta^{18}(CO_2) + z\,\delta^{18}(O_2) + C$$

where x, y and z refer to the proportions of oxygen in cellulose deriving from the three sources: leaf water, carbon dioxide and air oxygen.

This model is a simple way to account for the observed results. Its accuracy has to be verified, however, by different experiments, particularly by growing plants in ^{18}O enriched atmosphere.

Whatever the origin of oxygen atoms incorporated in cellulose, the leaf water $\delta^{18}O$ remains the unique source of variations affecting the isotopic composition of cellulose under natural conditions, since the $\delta^{18}O$ of atmospheric O_2 or CO_2 can be considered as constant values (23.5‰ and 41‰ respectively). For aquatic plants, the $\delta^{18}O$ of dissolved carbon dioxide is also dependent upon the water isotopic composition. Subsequently, the ^{18}O content of cellulose reflects essentially the leaf water $\delta^{18}O$ which appears, therefore, as the principal factor linking the isotopic composition of cellulose to environmental conditions.

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STABLE ISOTOPE STUDIES ON ORGANIC MATERIAL

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Extended Synopsis

Two examples are given of comparison between ^2H values of fossil samples of plants and climatic records. Figure 1 shows the deviation of ^2H content in ^{14}C-dated Dutch peat and in wood from Alpine regions (Baumkirchen, Austria [1–3], and Switzerland [4]) from δ^2H values[1] of comparable recent samples as a function of age. The δ^2H values of the fossil samples have been corrected according to the formula of Schiegl [5] that relates to the empirical fact that a 1% change in the carbon content of the total sample is associated with an alteration in the ^2H content of 2.8 δ^2H‰. The resulting curve was compared with a temperature curve [6] obtained from glacier positions in the Alps and from alterations of the timber line in the Tauern mountains and in the Ötz valley in Austria and with the $\delta^{18}O$ values of the ice core of Camp Century in Greenland [7]. The correlation of the ^2H values with the curve from Ref. [6] is surprisingly good, better than with the ^{18}O values of the ice core, which is probably due to the large distance between these regions and the difference between their respective climates.

The second example is δ^2H measurements performed on the Wurmian slate coal deposit in the region of the eastern Isar glacier (Federal Republic of Germany). The 20–30 cm slate beds investigated were from Breinetsried and Höfen with ^{14}C ages of the 65 000 years and 45 000 years BP respectively [8]. They are associated with interstadials of the early glacial or the middle pluvial glacial epoch. The pollen spectra of Breinetsried and Höfen are much the same.

Stephan [9] concludes from these spectra that these time periods, as far as the history of the forest is concerned, could be described as 'pine age with spruce' and 'inhospitable climatic conditions'. It is assumed that the growth of the peat layers of Breinetsried started at the end of an interstadial. Such a conclusion cannot be drawn for the Höfen profile. Table I shows the ^2H content of various samples

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[1] The δ value is the relative ‰ deviation of the isotope content of the water sample from the isotope content of a standard water (V-SMOW).

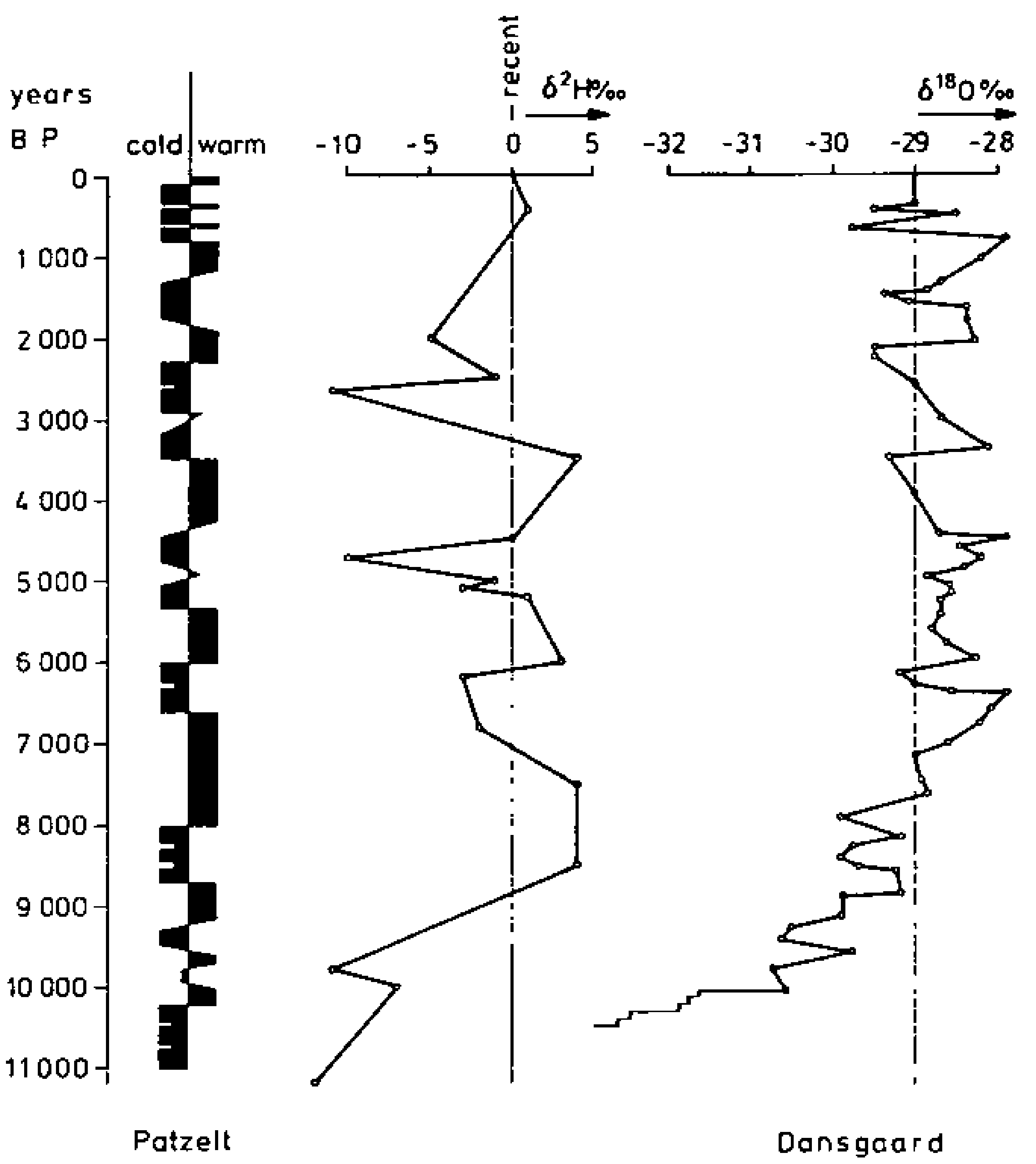

FIG. 1. Deviation of δ^2H values of fossil Dutch peat and of woods from Alpine regions (Baumkirchen, Austria, and Switzerland) from δ^2H values of comparable recent samples as a function of age in comparison with a temperature curve obtained from glacier and timber line positions in the Alps and with the $\delta^{18}O$ values of the Camp Century ice core.

in both profiles. The δ^2H values are corrected to the carbon content of the uppermost layer using Schiegl's formula [5]. A marked increase in the ^{2}H content can be seen from top to bottom for both profiles. Converted into temperatures this means that it was warmer at the beginning of the peat formation. For Breinetsried this corresponds with the results of pollen analyses mentioned earlier. If one uses the δ^2H temperature relation found [5] from ^{2}H measurements and pollen analyses on peat samples of different ages, the temperature gradient for both slate coal deposits corresponds at 2 to 3°C. Using the same formula, a comparison of the ^{2}H contents of the slate coal with that of recent peat or a recent pine from a neighbouring region (Penzberg, Federal Republic of Germany) shows that for both deposits the temperature at the time of the formation of the uppermost layer must have been about 4 to 5°C lower than it is at present. This is at least qualitatively consistent with conclusions drawn from pollen spectra for a relatively cool climate at the time in the Alpine foothills [9].

TABLE I. δ^2H VALUES OF ^{14}C-DATED SLATE COAL DEPOSIT PROFILES WITH CALCULATED TEMPERATURE DIFFERENCES AGAINST TODAY

Probe		Layer (cm from top)	^{14}C model age (years BP)	δ^2H (‰)	$\delta^2H_{corr.}$ (‰) [5]	Temperature difference against today (°C) [5]
Type	Location					
Pine	Penzberg		Recent	−103	−103	–
Peat	Penzberg		Recent	−116	−102	–
Slate coal	Höfen	0.0 – 1.0	45 000	−129	−129	−4.0
		7.0 – 8.0		−130	−122	−2.0
		9.0 – 10.5		−132	−123	−2.3
		13.5 – 14.5		−128	−121	−1.8
Slate coal	Breinetsried	1.5 – 3.0	65 000	−119	−119	−5.0
		7.5 – 9.0		−122	−118	−5.0
		15.0 – 16.5		−119	−115	−4.0
		21.0 – 22.5		−130	−116	−4.0
		30.0 – 31.5		−126	−111	−2.0

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OXYGEN ISOTOPIC COMPOSITION OF MAMMAL BONES AS A POSSIBLE TOOL FOR PALAEOCLIMATIC STUDIES

*First results**

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Abstract

OXYGEN ISOTOPIC COMPOSITION OF MAMMAL BONES AS A POSSIBLE TOOL FOR PALAEOCLIMATIC STUDIES: FIRST RESULTS.

Oxygen isotope measurements of the phosphate in mammal bones are suggested as a potential tool for palaeoclimatic studies. For this purpose it is necessary to demonstrate experimentally the existence of quantitative relationships between the $^{18}O/^{16}O$ ratio of the environmental water, the $^{18}O/^{16}O$ ratio of the body water and the $^{18}O/^{16}O$ ratio of the phosphate in bones. To check this point albino rats were reared under controlled conditions. They were fed with semi-dry food containing water of known and constant isotopic composition and supplied first with drinking water whose $\delta^{18}O$ was about $-6‰$ and then with ^{18}O enriched water. After the drinking water was changed, the $\delta^{18}O$ of the rats' blood water changed very quickly. Steady-state conditions were established after about one week. The $\delta^{18}O$ of the blood water under steady-state conditions for different isotopic values of drinking water has also been measured. The oxygen isotopic composition of water from human blood samples collected in different areas with different $\delta^{18}O$ of the environmental water has also been measured. These preliminary studies indicate that the suggested relationship between $\delta^{18}O$ of the environmental water and $\delta^{18}O$ of body water does exist at least in some cases and is probably characteristic for each species of mammals. The $\delta^{18}O(PO_4^{3-})$ values measured on a first group of human bones from different latitudes indicate that this variable varies over a wide range, according to latitude, i.e. according to the average values of the environmental water. The results obtained are consistent with the starting hypothesis and further research in this direction looks quite promising.

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1. INTRODUCTION

The possibility of using the oxygen isotopic composition of phosphate from fossil mammal bones for detailed palaeoclimatic studies was suggested long ago by Longinelli [1]. Such a possibility was based on the following considerations.

(1) The body temperature of mammals is not affected by changing climatic conditions because it is constant within each species and internally controlled, with the exception of pathological conditions.

(2) About 65% of the weight of a mammal body is made up of water. The isotopic composition of this water should be fairly constant in specimens of the same species. The isotopic composition of the body water of mammals should be related to: (a) average isotopic composition of ingested water (drinking water plus water in food), (b) physiological processes characteristic of each species (metabolic processes, total amount of metabolic water produced during synthesis of organic compounds, total amount of CO_2 produced by the organisms, etc.) and (c) isotopic mass balance between inhaled and exhaled water vapour.

(3) The precipitation of the calcium phosphate of mammal bones should take place, in specimens of the same species, under the same physical-chemical conditions. Consequently, independent of the existence of equilibrium or non-equilibrium conditions, a quantitative relationship should exist between the oxygen isotopic composition of the phosphate of bones and the oxygen isotopic composition of the body water.

(4) Since the variables reported under point 2(b) should be, on the average, characteristic of a species and not of individuals, variables 2(a) and 2(c) should be the only ones to determine the oxygen isotopic composition of bone phosphate. This means that, finally, the average isotopic composition of environmental water (to which atmospheric water vapour is also normally related) should be the only, or at least the main, variable to determine the isotopic composition of mammal bones. In fact, at least in the case of wild animals living under natural conditions, the isotopic composition of the water ingested with food is in turn closely related to that of the environmental water.

(5) It is well known [2, 3] that the average isotopic composition of meteoric water in a certain area is directly related to the annual average ground temperature. Climatic variations (changes in average annual temperature) should directly affect the average isotopic composition of meteoric water, higher temperatures causing isotopically heavier precipitations and lower temperatures causing isotopically lighter ones. This should be a general rule even though it is known that the quantitative relationship given by Dansgaard [3] is not always applicable.

From these considerations it may be concluded that it should be possible to establish a quantitative relationship between the oxygen isotopic composition of phosphate in mammal bones and the average annual temperature of the period during which the phosphate was precipitated, provided that the previous hypotheses are correct. The most important points to be checked are: (1) the existence of a quantitative relationship between $\delta^{18}O(H_2O)$ in the blood and $\delta^{18}O$ of environmental water and (2) the constancy of the $\delta^{18}O(H_2O)$ in the blood of different specimens of the same species. The first results obtained are reported here.

2. SAMPLES STUDIED AND RESULTS OBTAINED

The easiest way to obtain information on these two points is to rear small mammals in the laboratory under controlled conditions and to check the relationship between the $\delta^{18}O(H_2O)$ in their blood and the $\delta^{18}O$ of total intaken water. A few papers have been already published on this subject [4–7]. While Gleason and Friedman [5] only studied the variability of the D/H ratios of body water, the others studied the problem in terms of total energy and material balance or in terms of a qualitative relationship with environmental conditions. Consequently, it is not possible to draw detailed information from their data. We reared albino rats in the laboratory and supplied them with semi-dry food containing about

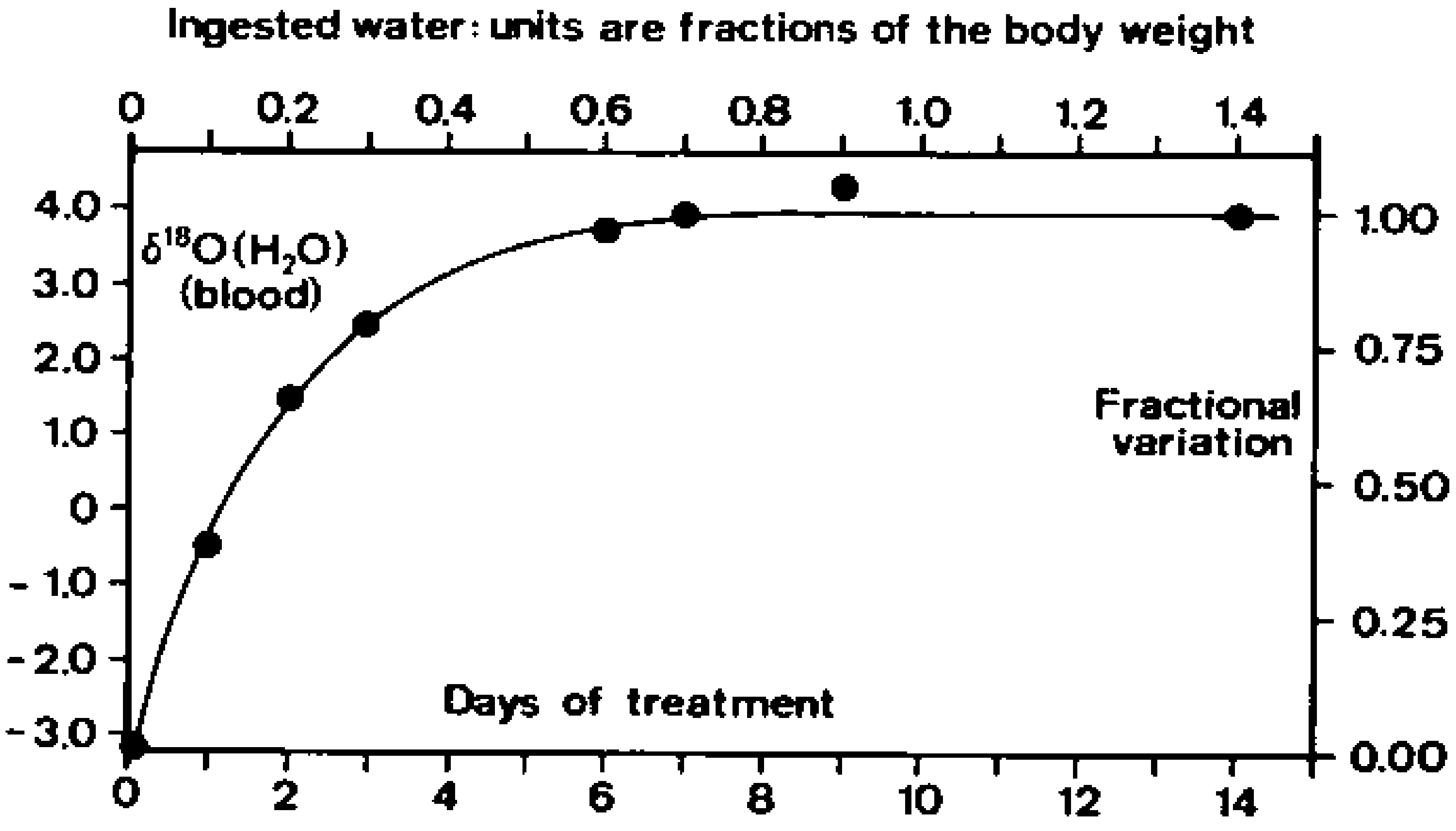

FIG. 1. Oxygen isotopic composition of water in the blood of groups of rates (average values) versus the number of days of treatment with ^{18}O *enriched water. The isotopic variation is given also as a fraction of the overall variation and the days of treatment are reported also as amount of ingested water expressed as a fraction of the body weight.* $\delta^{18}O$ *of the initial water was−6‰;* $\delta^{18}O$ *of enriched water was + 10‰ (isotopic composition of total ingested water).*

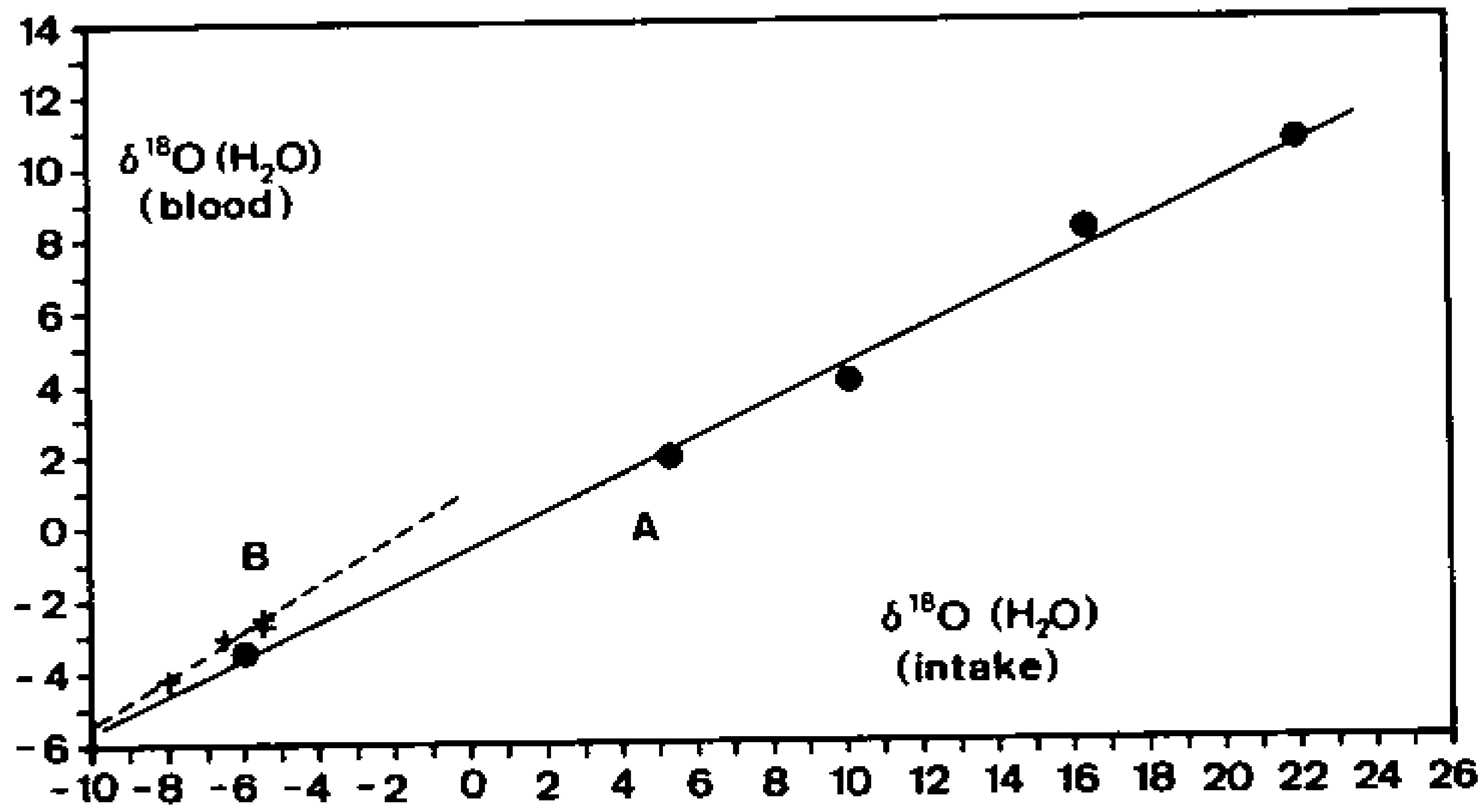

FIG.2. Oxygen isotopic composition of water taken in (rats) and of environmental water (human beings) versus oxygen isotopic composition of the water in the blood (steady-state conditions). Black dots are reared rats, crosses are human beings.

15% water of known isotopic composition (about −7‰) and with drinking water of known isotopic composition. The $\delta^{18}O(H_2O)$ of their blood was checked periodically and found to be fairly constant with time (a few months). The $\delta^{18}O$ of the drinking water was then suddenly changed and the isotopic composition of blood water was checked almost daily on groups of three rats per day. Measurements were made after distilling the blood samples (about 5 to 8 mL) *in vacuo* to dryness, heating the dry residue to about 250°C to remove water totally and equilibrating the water samples thus obtained with CO_2 following well established techniques [8]. The standard reproducibility of the samples (distillation plus equilibration) was of the order of ±0.1 to 0.15‰ (1σ).

After the $\delta^{18}O$ of the drinking water was changed, a large change of the $\delta^{18}O(H_2O)$ in the rats' blood was apparent; steady-state conditions were reached within a few days. The typical curve of the variation of the $\delta^{18}O(H_2O)$ in the blood is shown in Fig.1. The equation of the curve that fits the experimental points is

$$y = \frac{e^{4x} - e^{-4x}}{e^{4x} + e^{-4x}}$$

The factor 4 in the equation is due to the fact that the response is very fast in rats and is related, very likely, to the high value of the ratio between the weight of the water taken in daily and the body weight (under the conditions we used, equal to about 0.1). The half-time in going from one steady-state isotopic condition to another is 1.4 d. This time is considerably smaller than that which

TABLE I. $\delta^{18}O(H_2O)$ FROM BLOOD OF HUMAN BEINGS

No. of samples	Location	Age	$\delta^{18}O(H_2O)$ from blood (total range)	$\bar{M}\ \delta^{18}O(H_2O)$ from blood	$\delta^{18}O$ of local rain-water
9	Petralia	45–71	−3.7 to −5.2	−4.2	~ −8.0
10	Palermo	21–62	−2.4 to −3.6	−2.7	~ −5.5
8	Pisa	20–50	−2.6 to −3.4	−3.1	~ −6.5
8	Cagliari	22–65	−2.5 to −2.9	−2.6	~ −5.5

can be calculated from the results obtained by Lee and Lifson [4], about 2.6 d, and that obtained by Gleason and Friedman [5] in the case of D/H ratios, about 3 d. The reason for these differences is not clear; it may be due to differences in the production and isotopic composition of metabolic water and metabolic CO_2 related to different diets.

In the case shown in Fig.1 it should be noted that, while the overall variation of the $\delta^{18}O$ of the intaken water was about 16‰ (drinking water plus water in the food) the corresponding variation of the $\delta^{18}O(H_2O)$ in the blood was 7.2‰, that is, slightly less than half of the total isotopic change of the ingested water. As already suggested [9] this fractionation may be ascribed to several physiological processes although we presently have no experimental evidence for explaining this effect in detail. However, from the point of view of the possibility of using these data for palaeoclimatic studies, we can, as a first approximation, postpone the interpretation of these results, even though the production of metabolic water and metabolic CO_2 seems to be the most likely process.

The experiment was then repeated with different groups of rats, reared under the same conditions and supplied with drinking water of different isotopic composition until isotopic steady-state conditions were obtained. The $\delta^{18}O(H_2O)$ values in their blood are shown in Fig.2 against the $\delta^{18}O$ values of the total intaken water. (All isotopic results reported here are given versus V-SMOW standard [10].) Least-squares treatment of the reported results gives the following equation:

$$y = 0.506x - 0.64$$

which clearly indicates that, in the case of rats under the conditions we used, the variation of the $\delta^{18}O(H_2O)$ in their blood is about half of the total $\delta^{18}O$ change of the intaken water. The slope of the reported equation can probably vary slightly, according to different chemical and isotopic composition of the food and, consequently, of the metabolic water produced.

We wanted then to check the constancy of the $\delta^{18}O(H_2O)$ in the blood of different specimens of the same species. In the case of rats reared in the laboratory with the same food and the same water, the overall range of the δ values is rather narrow and of the order of ±0.2 to 0.3‰ under isotopic steady-state conditions. We then carried out measurements on blood samples drawn from human beings, both males and females. Groups of eight to ten samples were collected in four different places in Italy: Palermo, Petralia, Cagliari and Pisa. The results obtained are reported in Table I. Fairly large variations occur within each group. In the case of human beings these variations can very likely be ascribed to different nutritional conditions. In fact, one expects great variations in the diets of individuals and even greater variation in the beverages they use, with quite different $\delta^{18}O$ values, such as beer, wine, water, fruit juice, milk, etc. However, apart from the range of values within each group and despite the limited number of measurements made, it appears that environmental conditions are reflected in the isotopic composition of water in the blood, in agreement with the results obtained from rats. Least-squares treatment of these results (Fig.2) gives the equation $y = 0.624x + 0.87$. The difference between the slope of this equation and that of the equation obtained from rats is fairly large and of particular interest from the point of view of their use for palaeoclimatic studies. In fact, the larger the difference between the slopes of the equations for different species, the smaller the error resulting from conversion of the isotopic experimental data into average environmental temperatures.

We also ran a first group of oxygen isotope measurements of human bones and teeth coming from different areas under different climatic conditions to get an idea of the possible range of these values and of the possibility of some sort of correlation between the $\delta^{18}O(PO_4^{3-})$ values and the $\delta^{18}O$ of environmental water. Isotopic measurements on bones were carried out according to the technique described by Longinelli [11, 12]. The results obtained are reported in Table II.

The average isotopic values of meteoric water cannot be reported since, obviously, the location of the samples in rather vague and fairly large variations do exist, within the same area, between different locations. However, a general qualitative relationship between $\delta^{18}O(PO_4^{3-})$ and climatic conditions does exist, causing lighter isotopic values in cold areas and heavier ones in warm areas, according to the general trend of the average isotopic composition of rain-water with latitude and average temperature.

3. CONCLUSIONS

Several hypotheses have to be checked experimentally and with a number of measurements of statistical significance before the proposed method for detailed

TABLE II. OXYGEN ISOTOPIC COMPOSITION OF PHOSPHATE IN HUMAN TEETH AND BONES

Sample No.	Location	Sample	$\delta^{18}O(PO_4^{3-})$ (SMOW)
1	Lappland	Rib	+14.1
2	Lappland	Rib	+14.7
3	Finland	Nose	+15.5
4	Finland	Tibia	+15.7
5	Tierra del Fuego	Rib	+14.5
6	USA (Massachusetts)	Tooth	+15.7
7	USA (Washington)	Tooth	+15.0
8	USA (Texas)	Tooth	+16.7
9	USA (Mississippi)	Tooth	+17.2
10	Italy	Tibia	+18.8
11	Italy	Tibia	+16.8
12	Italy	Rib	+17.6
13	Libya	Rib	+18.2
14	Somaliland	Rib	+21.1
15	Somaliland	Tibia	+22.3
16	Somaliland	Tibia	+21.9

palaeoclimatic studies can be used. However, the first data obtained on this subject are strongly in favour of the feasibility of the proposed research. The conclusions that can be drawn from these data are that:

(1) a direct relationship does exist between the average oxygen isotopic composition of environmental water and the oxygen isotopic composition of the water in the blood of some species of mammals; and

(2) the oxygen isotopic composition of the phosphate of human bones seems to vary proportionally to latitude and climate, which means proportionally to the average isotopic composition of environmental water.

From these preliminary data and considerations, the development of detailed research in this direction seems to be a highly promising endeavour.

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ISOTOPIC COMPOSITION OF SEDIMENTS

(Section 3)

ISOTOPIC COMPOSITION OF PALAEOWATERS AS INFERRED FROM SPELEOTHEM AND ITS FLUID INCLUSIONS

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Abstract

ISOTOPIC COMPOSITION OF PALAEOWATERS AS INFERRED FROM SPELEOTHEM AND ITS FLUID INCLUSIONS.

Speleothem precipitated in the deep interior of karstic caves is commonly found to have been deposited in isotopic equilibrium with the water from which it was precipitated. The temperature of deposition can in such cases be determined from the oxygen isotopic fractionation between the calcite and the water. For this purpose the composition of the water can be determined from analyses of the water trapped as fluid inclusions in the stalagmites, flowstones and other speleothems. However, because of the possibility of isotopic exchange between the calcite and the oxygen of the water, D/H ratios of the inclusions have been used to infer the original $^{18}O/^{16}O$ ratio, assuming a relation between oxygen and hydrogen isotope ratios comparable to that existing at present in both meteoric precipitation and drip waters in caves. Some shift in the position of the meteoric water line is inferred to have occurred during glacial periods, however, as shown by measurements of ice cores from Antarctica. If account is taken of this shift, then palaeotemperatures for Wisconsin stage speleothems are found to be consistent with their ages relative to the time scale of the glacial stage. Variations in δD of meteoric palaeowaters can be directly inferred from fluid inclusion data; using the uranium series dates on the host speleothem, it is possible to reconstruct the history of the isotopic composition of rain and snow at a site over the past 300 000 years. During the last two glacial stages in North America, precipitation was on the average about 12‰ lighter than its modern value at each site.

1. INTRODUCTION

Speleothems are deposits, usually of calcite, which have formed by chemical precipitation from vadose seepage waters entering through the roof or walls of limestone caverns. As these deposits grow, small quantities of seepage water are trapped within them. Since it is possible to date such formations by various means, including uranium series disequilibrium methods [1], stable isotope analyses of both calcite and fluid inclusions present complementary data for palaeoclimate records at a given site. However, to demonstrate the validity of

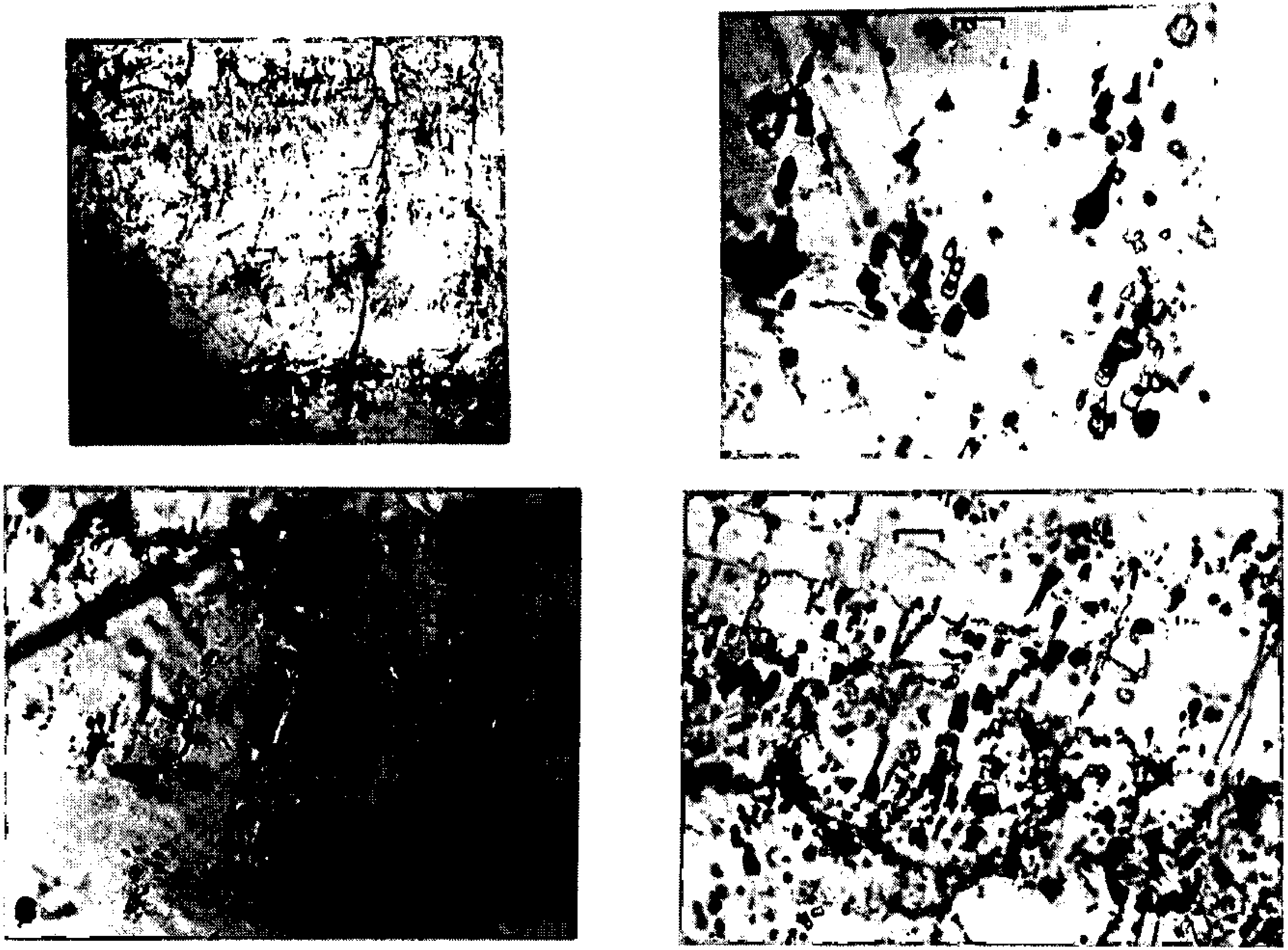

FIG.1. Fluid inclusions of various types in stalagmites and flowstones. Scale bar is 30 μm long.

such records it is necessary to show first that fluid inclusions are equivalent to seepage waters which in turn represent meteoric waters falling at that site, and second that the speleothem calcite formed in isotopic equilibrium with its parent seepage water.

2. NATURE OF THE SAMPLES

Deposition of speleothem calcite is brought about by the outgassing of CO_2 as seepage water encounters cave air of considerably lower pCO_2. This process supersaturates the water with calcite, which then precipitates. In some cases, but more rarely, other minerals may be deposited. One of the conditions for the suitability of any material to be used in palaeoclimate studies is that isotopic equilibrium be established. In the case of calcite, slow outgassing of CO_2 occurring in air of 100% humidity results in this condition. If CO_2 loss is rapid, as in draughty conditions and for less than 100% humid air, then the water and calcite precipitated from it experience kinetic isotope effects which make the samples unusable for palaeoclimate studies. Deposits formed at isotopic equilibrium can be recognized by characteristic patterns of C and O isotopic composition along growth layers [2].

Speleothems occur in a variety of morphologies but stalagmites and flowstones are the most useful for analysis. Occurring as regular, continuous sequences of stratigraphic layers, both stalagmites and flowstones have the advantage that their layering has greater lateral extent than in other deposits. This allows tests for isotopic equilibrium and replicate analyses to be made. Flowstones, although exhibiting the greatest lateral growth by far, tend to accrete up to 50 times slower than stalagmites.

The presence of fluid inclusions in speleothem is revealed by a milky tan to white colour (see Fig. 1). This, at least, is the case for speleothems containing fluid inclusions above a size of 10 μm. However, some of our recent results indicate that even transparent calcite crystals invariably contain some water. How this water is lodged in the structure is under investigation. The range of water content by weight appears to be between 0.05 to 0.50% in all speleothem studied so far.

3. EXTRACTION OF FLUID INCLUSIONS

Care is taken to choose speleothem that is quite pure, avoiding such water-bearing contaminants as clay minerals and natural organic substances. The choice is generally not difficult since most deep-cave deposits are composed of remarkably pure calcite. Structural water, held in other minerals such as hydromagnesite, if present, is not likely to contribute significantly to the total water content since only trace amounts exist in speleothem [3].

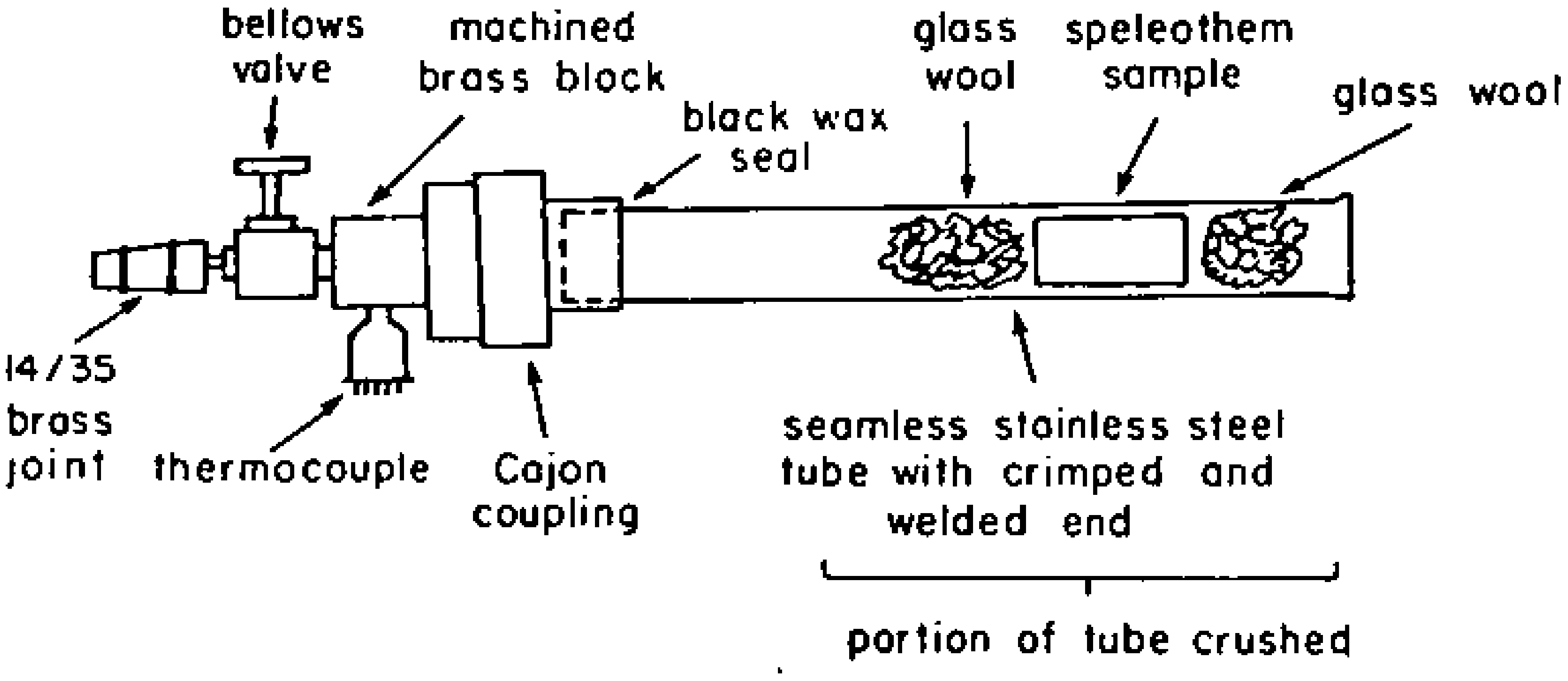

FIG.2. Apparatus for extraction of fluid inclusions by crushing.

Until recently, fluid inclusion water was released by crushing the sample in a stainless steel tube under vacuum [4]. The vapour was subsequently frozen onto a cold finger held at liquid nitrogen temperatures (see Fig. 2). Recent work now suggests that this procedure, in some cases, may not completely release the trapped water (Section 8 deals with this in more detail). As a result, we have adopted the method of heating the sample in a furnace so that CO_2 and H_2O are generated under vacuum at 700°C. The mixture is pumped through a spiral trap held at CO_2/methanol temperatures (−78.5°C), allowing CO_2 to be pumped from the system while the water remains frozen (see Fig. 3). The sample is heated until no further CO_2 is liberated and the pressure falls to about 10^{-4} torr. At this point the water is presumed to have been completely released from the sample, which by now is converted to CaO. The furnace is then isolated to prevent any back reaction with CaO when the water is transferred to the uranium furnace. Here the water is reduced to hydrogen for mass spectrometric analysis.

4. USE OF STABLE ISOTOPES IN SPELEOTHEM

Palaeoclimatic records can be obtained from speleothem in a variety of ways. Oxygen isotopic analyses of either calcite or water yield sequences of data open to palaeoclimatic interpretation. If coexisting calcite and water phases are analysed then absolute temperatures can be determined [5, 6]. A major objection to using the $\delta^{18}O$ of the water arises because of the possibility of isotopic exchange between water and calcite as the deposition site changes temperature with time. Because hydrogen is absent from the calcite phase, a way of avoiding the problem is to measure D/H ratios in the fluid inclusions. Their initial isotope ratio should be preserved because no exchange is possible. The initial oxygen isotope ratios are then inferred from the Craig-Dansgaard meteoric water line [7, 8] or some other established relationship of this kind. Even if such a relationship is not

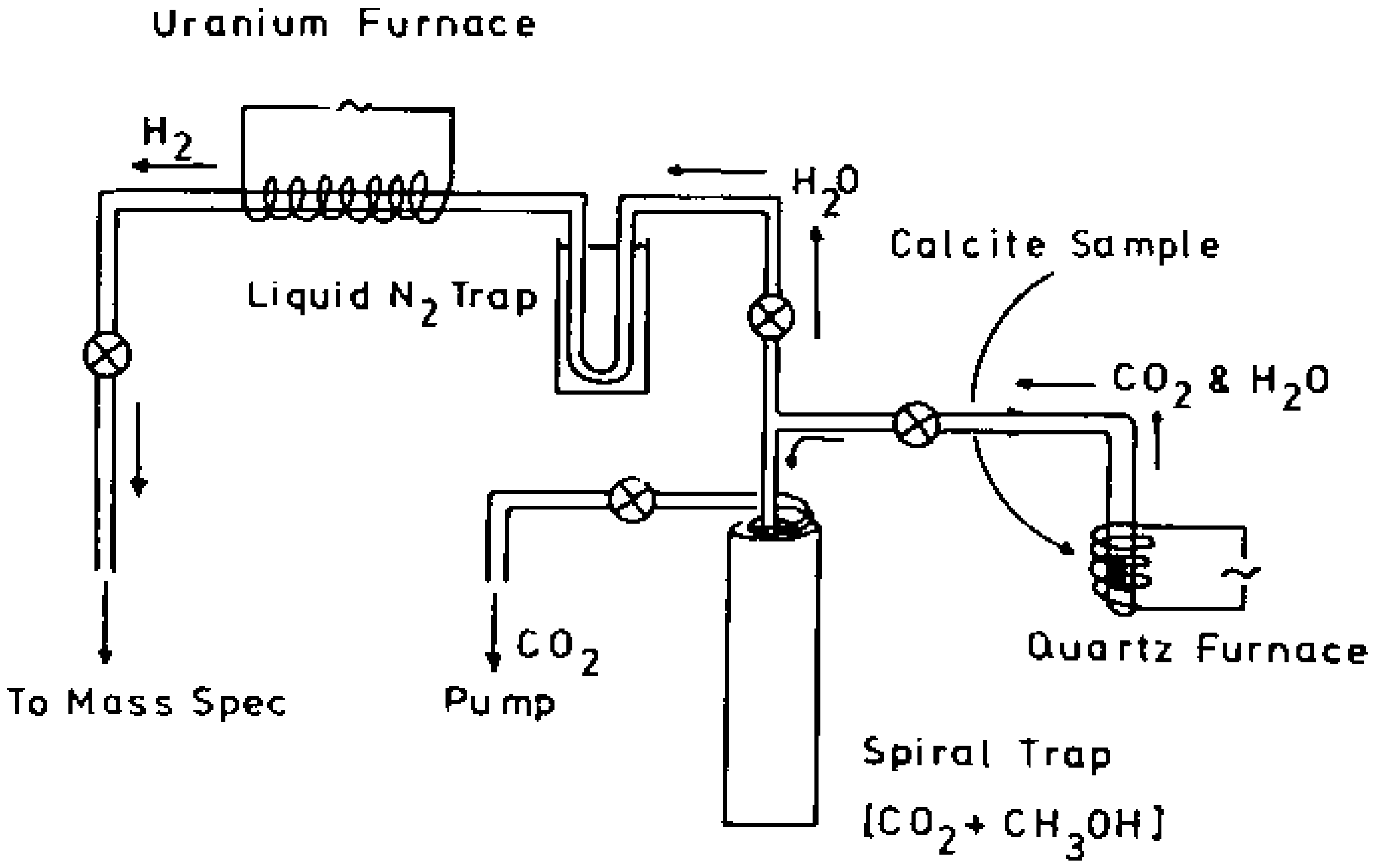

FIG.3. Apparatus for extraction of fluid inclusions by heating.

determinable, the δD sequence alone can be used as a measure of variation of meteoric water through time. Interpretations of isotopic sequences are discussed in Section 7.

Using this relation between δD and $\delta^{18}O$ of meteoric waters, Schwarcz et al. [4] showed that one could infer the sign of the derivative $d(\delta^{18}O_c)/dT$ where $\delta^{18}O_c$ is the isotopic composition of calcite and T is the temperature of the cave (equivalent to average surface T). Harmon et al. [9] presented several such sequences of $\delta^{18}O_c$ for the past 20 000 years; in general $\delta^{18}O_c$ was found to decrease with increasing T. However, Gascoyne et al. [10] have found one site, on Vancouver Island, Canada, at which the opposite trend was inferred to have occurred based on the observation that $\delta^{18}O_c$ decreased over the interval from 60 to 30 ka BP, a period during which temperatures in this area were known to have decreased.

5. RELATION BETWEEN METEORIC AND SEEPAGE WATER

Meteoric waters are highly variable both in amount and isotopic composition throughout the year and indeed can be highly variable within a single storm [11]. Summer precipitation is generally enriched in ^{18}O and D compared to winter precipitation.

Data from Mammoth Cave, Kentucky [12] indicated a response of oxygen isotopic variations in the cave seepage water to corresponding variations in meteoric precipitation, with a lag of around two weeks and with considerable damping of the amplitude of $\delta^{18}O$ excursions. However, the study was based on relatively few data. A subsequent detailed study of three North American cave

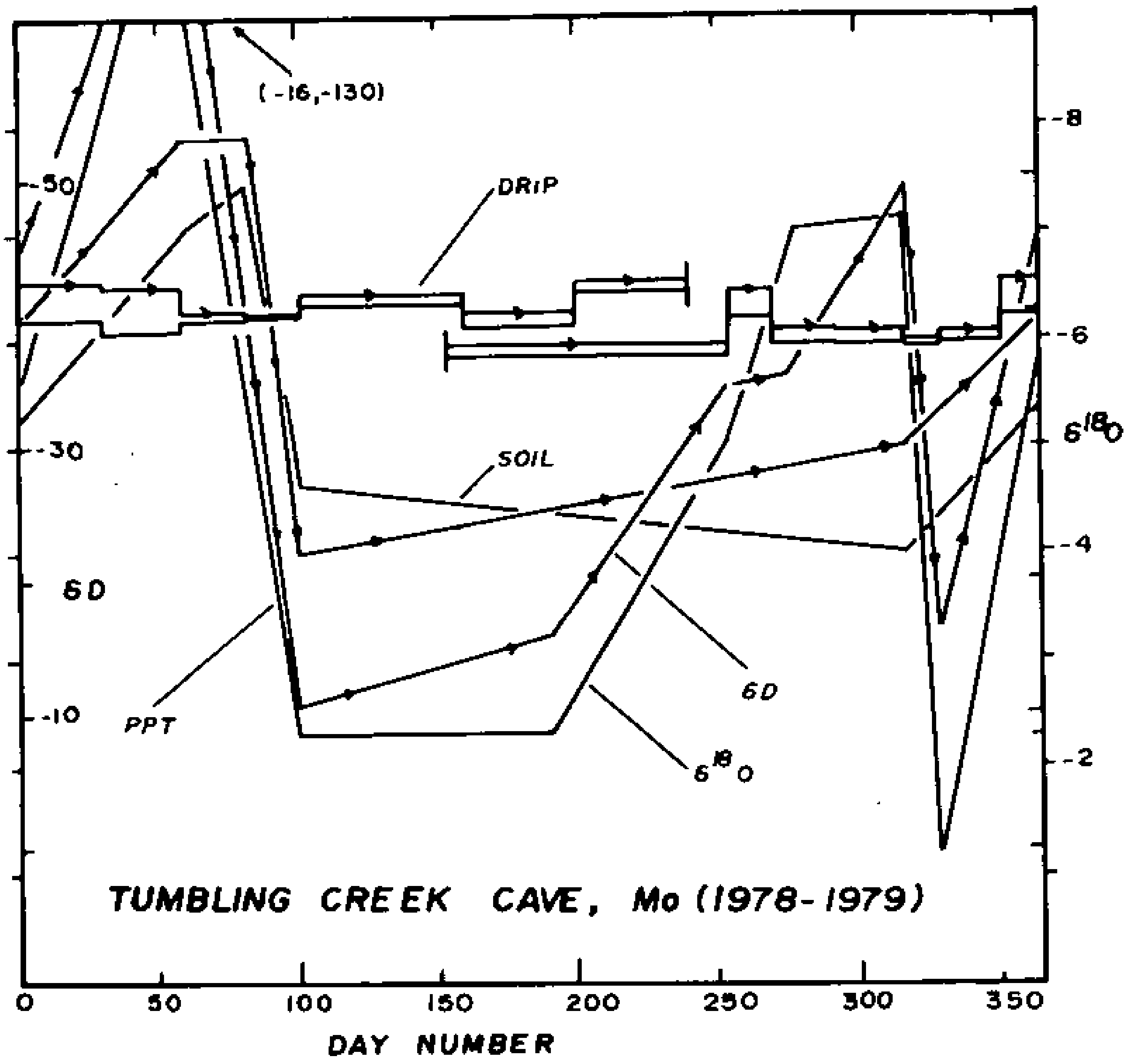

FIG.4. Variation in δD and $\delta^{18}O$ of meteoric precipitation (PPT), soil water, and seepage water (DRIP) in and above Tumbling Creek Cave, Missouri, during one year. The record begins in October 1978. Note that lighter values are toward top of figure.

sites indicates isotopic homogenization in the vadose zone with considerable damping within the soil at depths of less than a metre (Fig. 4). Moreover, even though flow rates of seepage water responded almost instantaneously to intense rainfall on the surface, the isotopic signal remained unchanged. This phenomenon is attributed to piston flow of the water [13], in which meteoric water passing into an aquifer causes resident isotopically homogenized water to be pumped out as seepage water. Each increment of meteoric water added to the system is completely mixed well before the water reaches the zone of seepage. A study of well sites and soil in Pennsylvania supports this contention [14].

In one sense a lack of isotopic variation is unfortunate since a highly detailed study of speleothem might reveal yearly variations in fast growing deposits such as are formed in tropical caves; such annual variations in $\delta^{18}O_c$ might provide a corroborative dating method. But in another sense such monotony is rather fortunate. Cave temperatures represent two to three year average surface temperatures for a given site [15]. Seepage also represents homogenization of

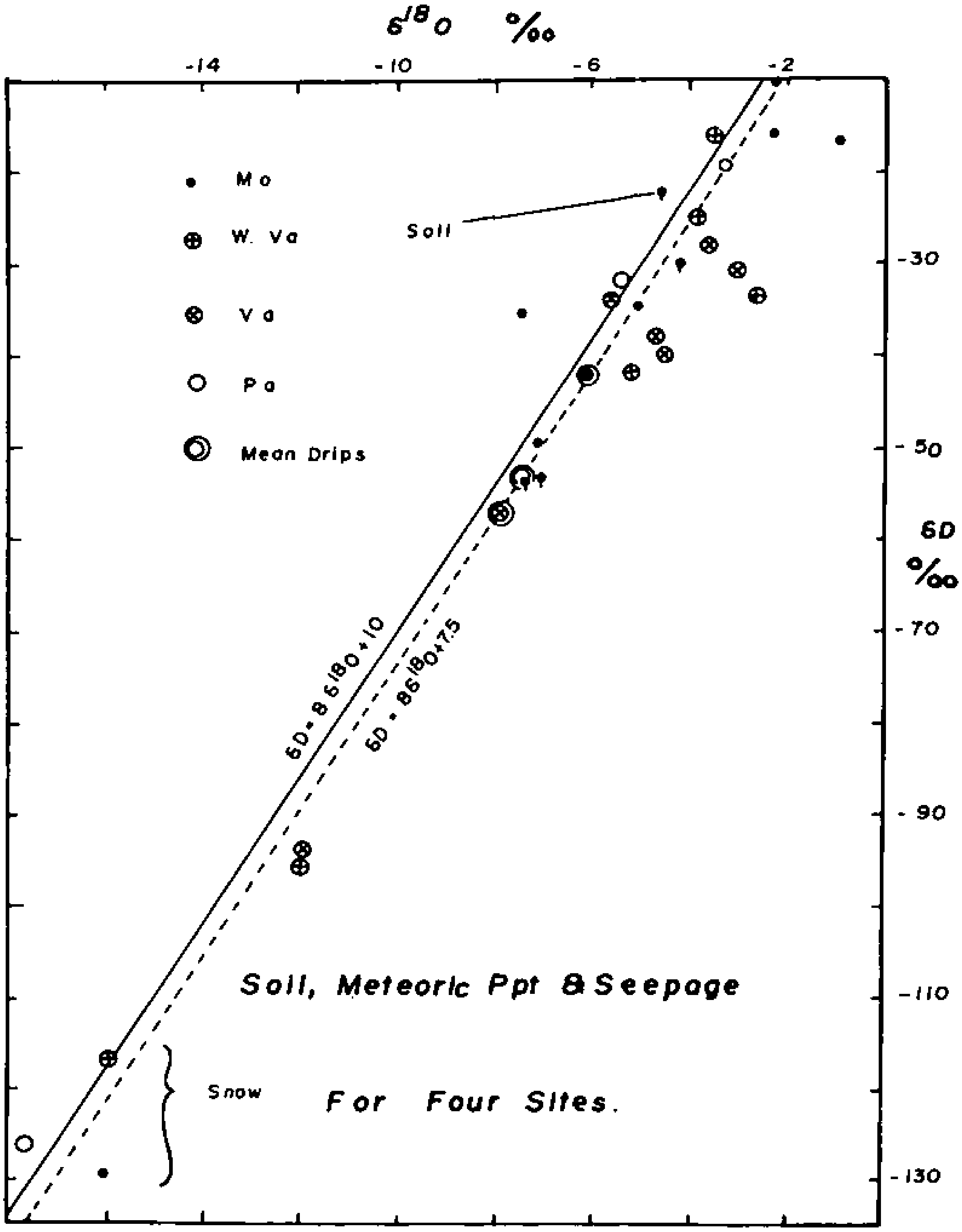

FIG.5. Variation in δD and $\delta^{18}O$ of meteoric water from cave sites in Missouri (Mo.), West Virginia (W. Va.), Virginia (Va.), Pennsylvania (Pa.) and average seepage waters at these sites.

meteoric water over at least one year. Thus, any changes seen in the palaeowater record would have resulted from secular changes in the multi-year average of the isotopic composition of meteoric water through the Pleistocene. A further problem which is avoided is that a lack of isotopic variation in seepage negates the possible effect of seasonal variation in the rate of deposition of calcite (due to changes in water chemistry) and hence a concomitant bias towards some isotopic composition other than the mean.

Isotopically, seepage waters lie close to the meteoric water line (see Fig. 5). There is a growing body of evidence that the meteoric water line is not universal

TABLE I. ISOTOPIC DATA AND CALCULATED ISOTOPIC TEMPERATURES FROM MODERN DEPOSITS

Locality	Isotopic ratios for stalagmite fluid inclusion seepage			Isotopic temperature (°C)		Measured cave temperature (°C)	Extraction procedure
	$\delta^{18}O_{Ct}$	$\delta D_{f.i.}$	δD_{seep}	$T_{f.i.}$	T_{seep}		
Iowa	24.10	−55.6	−52.2	10.6	9.0	8.8	C
W. Virginia	23.64	−60.9	−59.4	10.7	10.0	10.8	C
Missouri	24.78	−47.9	−40.8	10.5	14.0	15.0	C
Pennsylvania	24.06	−50.0	−53.6	11.0	9.3	10.0	D
Iowa	24.58	−54.0	−52.2	7.0	7.9	8.8	D
Jamaica	26.22	− 8.8	–	24.0	–	22.0	D
New York State	23.13	−64.5	−67	7.6	8.8	8.5	D

Ct = Speleothem calcite; f.i. = Fluid inclusion; seep = Seepage water; C = Crushing; D = Decrepitation.
Isotopic temperatures calculated from $10^3 \ln \alpha_{C\text{-}W} = 2.7 \times 10^6 T^{-2} - 2.89$.
$\delta^{18}O$ (water) calculated from $\delta D = 8\delta^{18}O + 10$.

and varies both spatially and temporally. The consequences of this are examined in more detail in Section 8.

6. MODERN FLUID INCLUSIONS AND SEEPAGE WATER

A good way to test whether fluid inclusions are in fact aliquots of parent seepage water is to examine modern equilibrium deposits of speleothem. At the same time the isotopic thermometer can be tested against present cave temperatures. The results in Table I suggest some success in this direction both from crushing and decrepitation experiments. However, in some cases results from the former have yielded anomalously low temperatures (see Section 8).

Analysis of modern deposits does not resolve the problem that fossil fluid inclusion could have altered post-depositionally. The calcite might have recrystallized, some inclusions may have leaked or later seepage water might have penetrated the deposit, exchanging with older waters. Petrological studies [16] indicate that fluid inclusions fill isolated and disconnected cavities whose integrity can be recognized in unaltered samples. Decrepitation experiments suggest that water also lies in sites other than these microscopically resolvable fluid inclusions. In spite of this, all speleothems exhibit a fine structured isotopic profile displaying variations in δD of considerable magnitude and giving some assurance that post-depositional homogenization has not taken place.

7. PALAEOWATER RECORD

Equilibrium speleothems have been found which have grown or are growing within a period from 0 to 300 ka BP. Older, as yet undatable samples have been studied and the record may be extended considerably with palaeomagnetic or ESR measurements to include most of the Pleistocene, but the abundance of accessible deposits decreases with increasing age. However, given that fluid inclusions do record meteoric precipitation and that their isotopic integrity is maintained through time, a considerable palaeowater record exists within caves over the continents of the world.

Previous data [9] indicate a dependence of δD on temperature smaller than that determined for modern rainfall (Table II). This is not surprising since the former dependence reflects secular changes in δD, due to changes in climate, while the latter is a short-term response to seasonal changes in temperature.

The factors controlling secular change in δD include (1) temperature difference between site of precipitation and source [8]; (2) isotopic composition of sea water due to growth of continental glacial ice [17]; (3) conditions of evaporation, precipitation and runoff at the source of atmospheric water vapour

TABLE II. δ^0_w TEMPERATURE EFFECT FOR EIGHT NORTH AMERICAN IAEA PRECIPITATION SITES

(Data from IAEA World Precipitation Survey, 1969, 1970)

Location	Latitude (°N)	Longitude (°W)	Ts-Tw	$\delta^0_w s$-$^0_w w$	$d\delta^0_w/dT$ (‰/°C)	$d\delta D/dT$ (‰/°C)
Chicago, Illinois	47°47′	87°47′	18.5	7.3	0.39	3.12
Edmonton, Alberta	53°34′	113°31′	19.3	7.6	0.39	3.12
Fort Smith, N.W.T.	60°	111°58′	23.4	4.0	0.17	1.36
Whitehorse, Yukon	60°43′	125°04′	16.9	3.1	0.18	1.44
Bermuda	32°37′	64°68′	6.9	0.06	0.01	0.08
Waco, Texas	31°62′	97°22′	13.0	1.3	0.30	2.4
Flagstaff, Arizona	35°12′	111°39′	16.9	5.6	0.33	2.64
Veracruz, Mexico	19°20′	96°13′	5.7	1.7	0.30	2.40

Ts = average summer temperature (May-October).
Tw = average winter temperature (November-April).
$\delta^0_w s$ = average δ^0_w of summer precipitation.
$\delta^0_w w$ = average δ^0_w of winter precipitation.
$d\delta^0_w/dT$ = $(\delta^0_w s - \delta^0_w s)/(Ts - Tw)$.
$d\delta D/dT$ = $8d\delta^0_w/dT$.

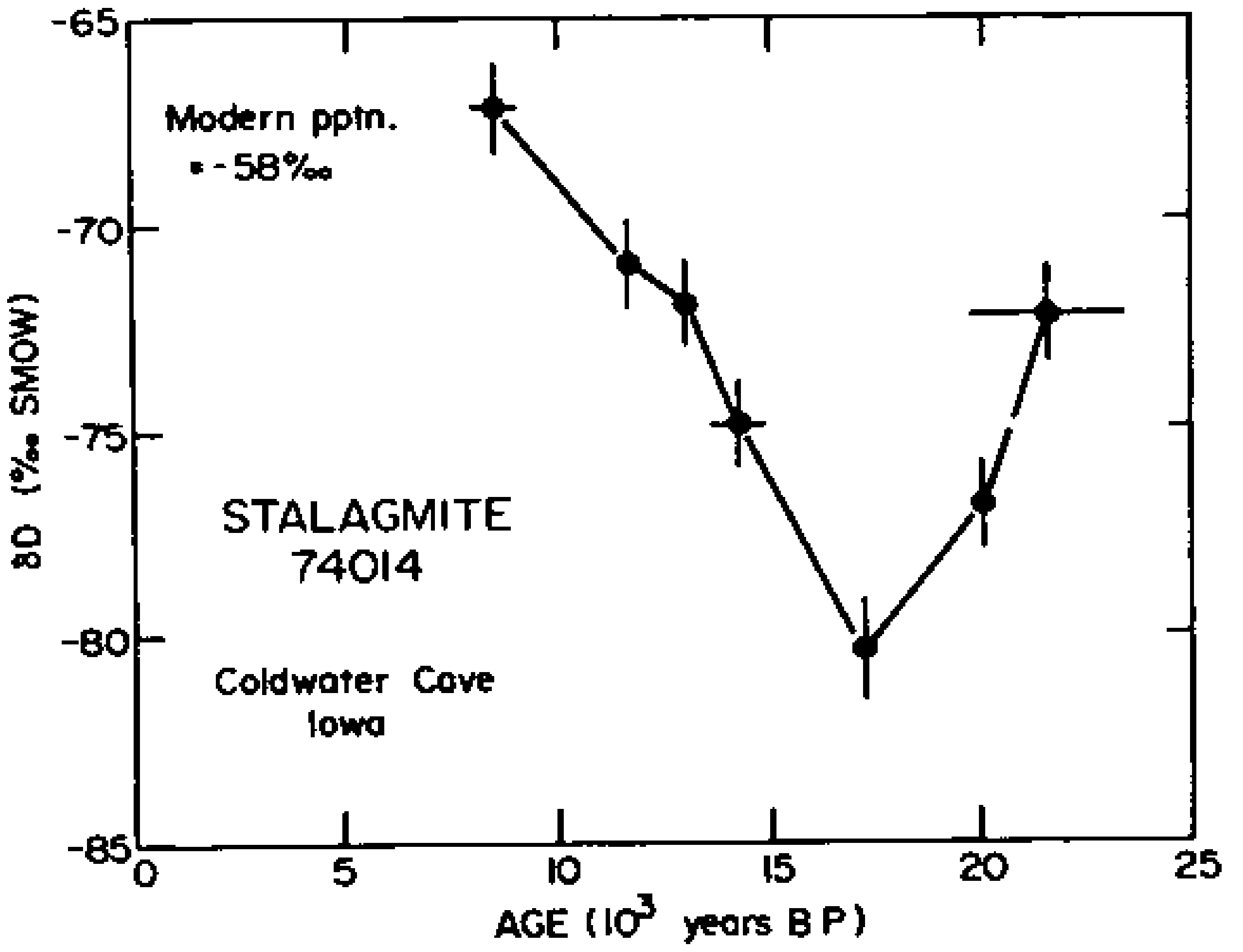

FIG.6. Variation in δD of fluid inclusions obtained by crushing of stalagmite from Coldwater Cave, Iowa (from [15]).

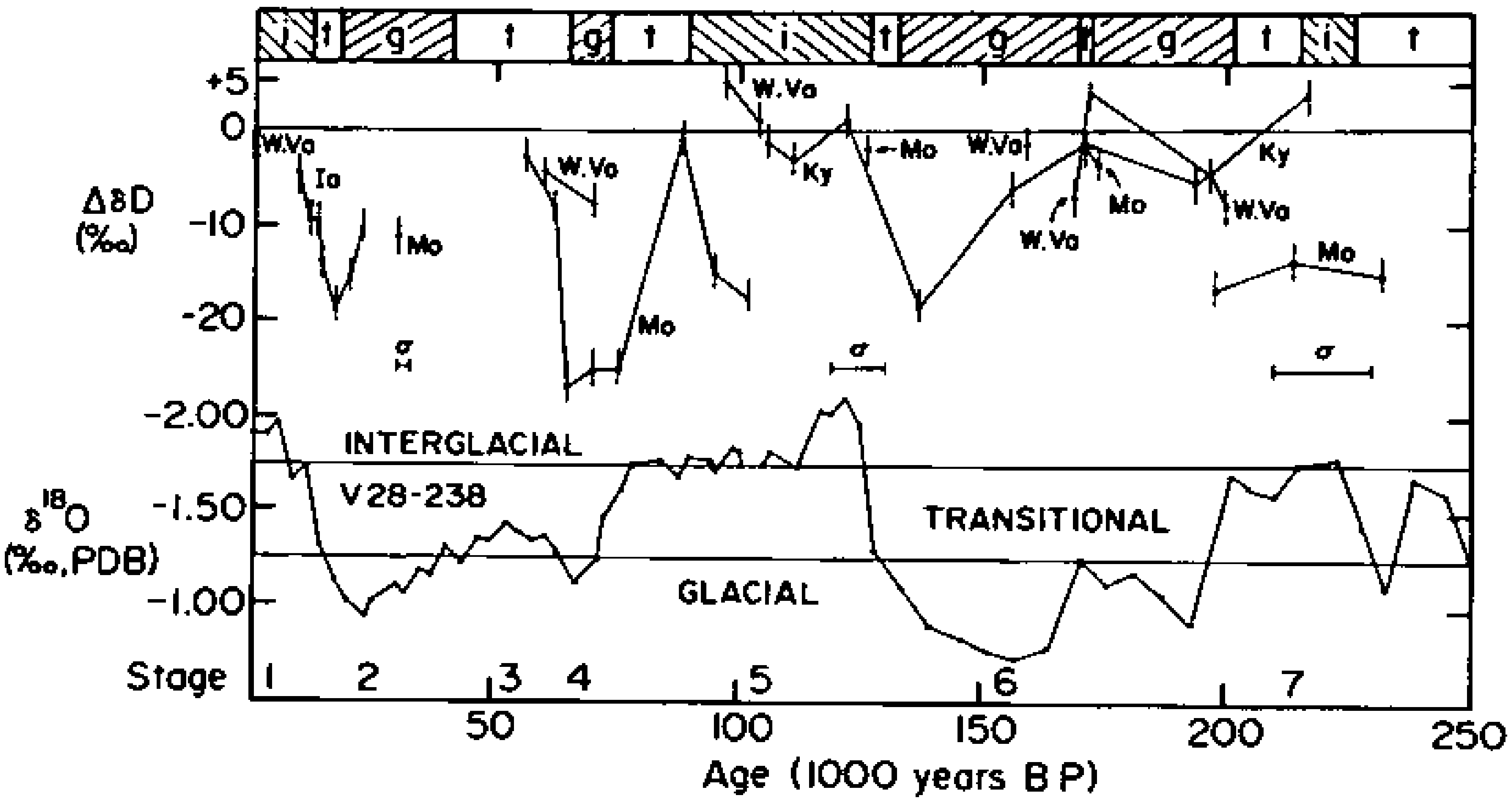

FIG. 7. Temporal variation in $\Delta\delta D$, the difference between modern δD of cave seepage and δD of fluid inclusions, for speleothems from caves in West Virginia (W. Va.), Iowa (Ia.), Missouri (Mo.), and Kentucky (Ky.). For comparison, the variations in $\delta^{18}O_f$ of foraminifera from deep sea core V28–238 (Ref. [17]*) are shown. Interglacial (i), transitional (t) and glacial (g) periods are defined by excursions of $\delta^{18}O_f$ below, within, or above the interval (−1.75‰, −1.25‰) respectively (from Ref.* [9]*).*

([18–20]); and (4) distance and path travelled by water vapour from which the precipitation condensed.

This preliminary work partly answers a very interesting question as to whether there has been any change in D/H ratios of meteoric precipitation throughout the Pleistocene. Figure 6 depicts variations in δD at a cave site in the driftless area of Wisconsin over the end of the last glaciation. This curve reached a minimum at about the time of both maximum ice volume on the continents and local ice advance at the site. These and other data are shown in Fig. 7 along with changes in $\delta^{18}O$ of planktonic foraminifera over the same interval. The latter serve as an index of global ice volume and therefore of climate. The foraminifera curve has been used to divide up the last 200 ka into three types of climatic stages: glacial, interglacial and intermediate. In Table III the D/H data have been summarized for each period with respect to modern seepage at the given site. In general D/H ratios are lighter by 12‰ corresponding to a shift in oxygen of about 1.5‰, although total shifts at any given site vary considerably more. This reduction in isotopic ratios during glacial advances is consistent with most current climatic models (see [9] for a review).

8. PALAEOTEMPERATURES

As mentioned in Section 4 isotopic analyses of coexisting calcite and water allow depositional temperatures to be calculated. Thus, calcite analyses of samples

TABLE III. AVERAGE VALUES OF DIFFERENCE IN δD BETWEEN FLUID INCLUSIONS AND MODERN METEORIC PRECIPITATION FROM SITES IN NORTH AMERICA (from Ref. [9])

Sample locality	Average difference (‰) i	 m	 g
Iowa	− 3	−14	−18
West Virginia	− 4	− 5	− 7
Missouri	−10	−24	−31
Kentucky	− 3	− 5	−13
Average (all sites)	− 5	−12	−17

i = interglacial; m = intermediate; g = glacial.
All data obtained by crushing.

studied permit the determination of absolute temperatures. Unfortunately, when this is done some temperatures at the coldest part of glacial stages fall below zero, an obvious impossibility since calcite cannot form in a sub-zero environment. A possible way around the dilemma is to ask whether the meteoric water line generally true for today held during the past, particularly during the extreme conditions of full glaciations.

The calculation of temperature requires that the $\delta^{18}O$ in the water phase be inferred from δD measurements according to a relationship of the form

$$\delta D = 8\delta^{18}O + d_0 \tag{1}$$

where normally d_0 is taken to be +10‰. The latter value is not valid everywhere on the planet even now (for example, [21–23]), so it is perhaps not unreasonable to expect a change in the past. Measurements of glacial ice cores from the Antarctic ([24], Fig. 8) showed that during the Wisconsinan d_0 was much smaller; their data can be fitted with a line with the equation

$$\delta D = 7.9\delta^{18}O \tag{2}$$

which corresponds to a δ_0 value of 4‰ (assuming a mean $\delta^{18}O$ of −40‰) whereas modern snow at the site gives a d_0 value of 10‰. Our work on the Byrd 71SW core suggests similar relationships (Fig. 9) for that period. Current studies by Merlivat [25] and others point to a shift in d_0 from 4.1 to 8.8‰ for ice ranging in ages from Holocene to about 29 ka BP. Merlivat and Jouzel [20] have been given a theoretical argument that the slope of the δD-$\delta^{18}O$ data correlation line should

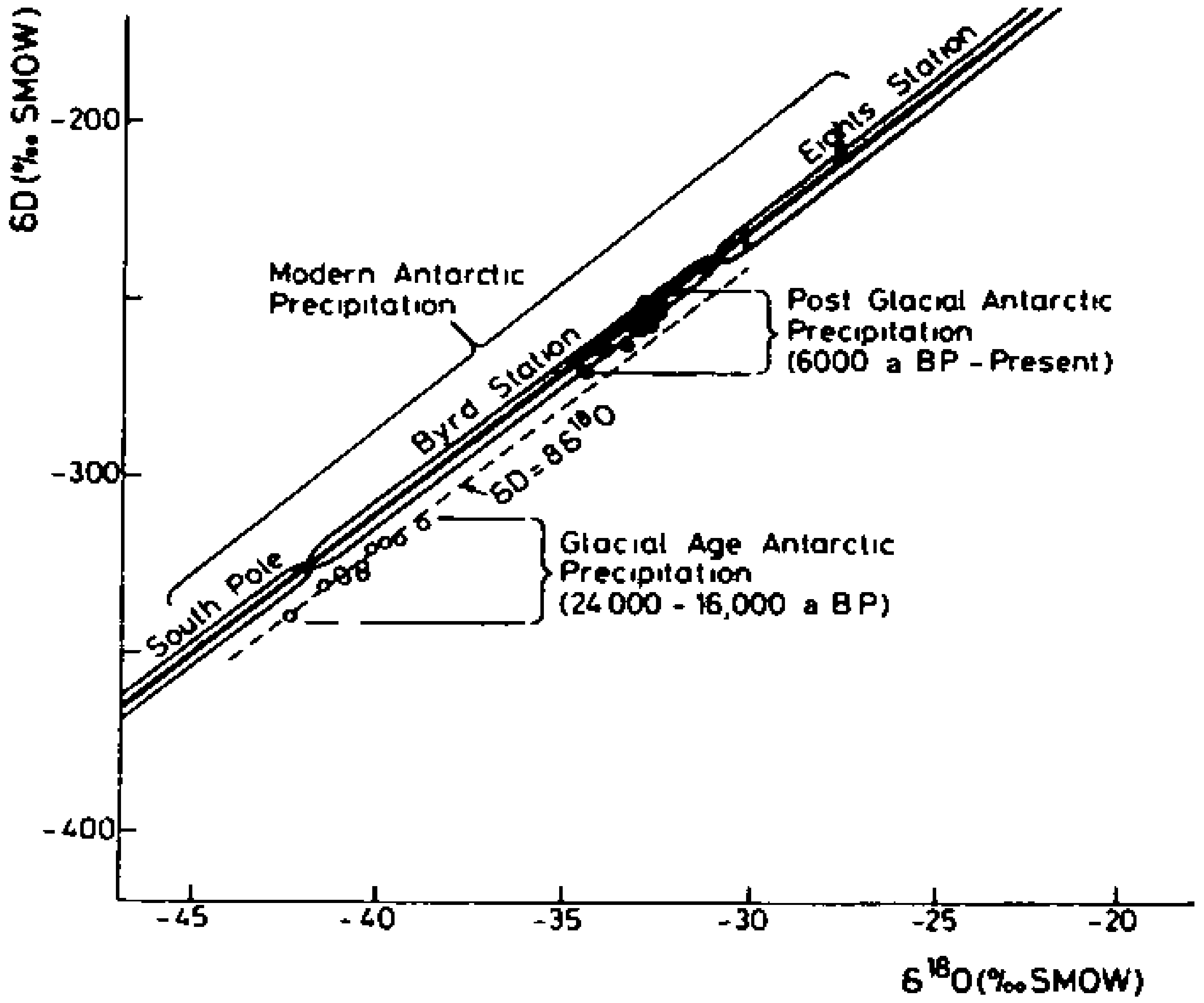

FIG.8. Relation between $\delta^{18}O$ and δD of snow and ice from Antarctica, as reported in Ref. [24]. Individual data points were read from separate graphs of $\delta^{18}O$ versus depth in that reference.

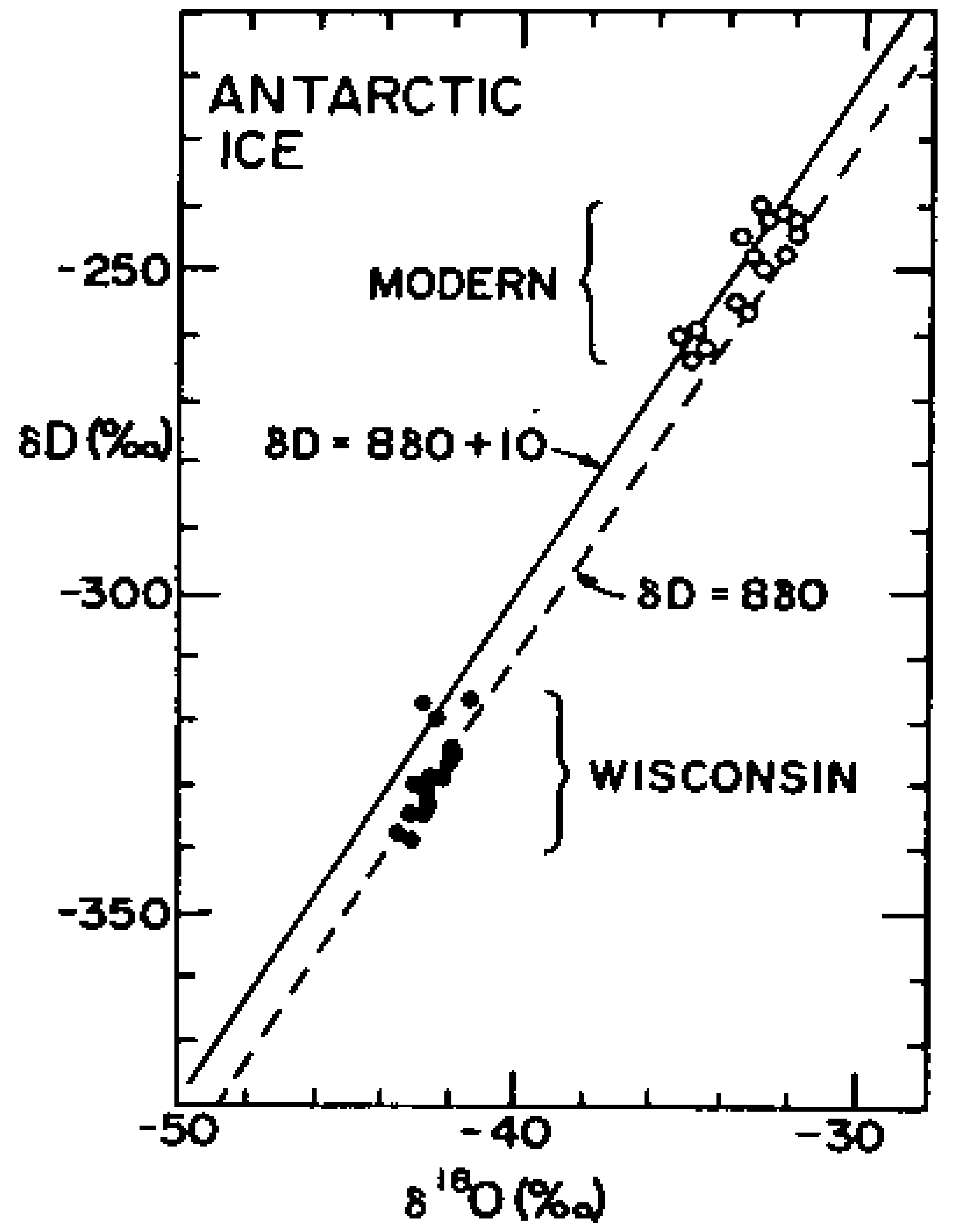

FIG.9. Relation between $\delta^{18}O$ and δD for the deep core Byrd 71 SW ("Wisconsin") and modern firm from Byrd Station, Antarctica. The lines for d_0 = 10 and 0 are shown for reference only.

TABLE IV. ISOTOPE AND PALAEOTEMPERATURE DATA FOR FLUID INCLUSIONS COMPARED FROM TWO EXTRACTION PROCEDURES

Locality	No. of analyses	$\delta D_{f.i.}$ (‰)	Palaeo-temperature (°C)	Mode of extraction	Age (ka)
BERMUDA	11	− 8.57 (± 2.5)[a]	+20.3(± 1.5)	D	110
(Government Quarry Cave)	11	− 46.5 (± 11.3)	− 2.4(± 6.0)	C	
IOWA[b]	1	− 54.0 (± ?)	+ 7.0(± ?)	D	Modern
(Cold Water Cave)	2	− 62.1 (± 5.1)	+ 3.2(± 3.0)	C	
VANCOUVER ISLAND	3	−103.2 (± 1.5)	+ 3.6(± 0.9)	D	50
(Cascade Cave)	3	−110.1 (± 8.1)	0.0(± 3.2)	C	
U.K.	4	− 37.1 (± 0.6)	+ 4.5(± 0.4)	D	95
Lost John's Cave	2	− 87.7 (± 24.5)	−18.0(± 12.2)	C	

D = Decrepitation; C = Crushing; $\delta D_{f.i.}$ = hydrogen isotope ratios of fluid inclusions (w.r.t. SMOW); [a] Range of values. [b] Data also included in Table I.

not have been strongly affected by changes in global climate. They show, however, that changes in humidity over the oceans during the Pleistocene could account for the changing deuterium excess (d_0), while these climatic changes should have little effect on the slope. If a d_0 value of +4‰ is assumed in computing palaeotemperatures from the data of Harmon et al. [9] then almost all temperatures become positive [26]. It is also possible that crushing of the calcite results in incomplete extraction of fluid inclusion water preferentially releasing isotopic light water, which could also account for some low temperatures. However, where crushing has been found not to yield acceptable data, the data are extremely inconsistent and give palaeotemperatures that are clearly anomalously low (Table IV). Unfortunately, at the present time it is not possible to be absolutely sure of the validity of crushing data. A detailed petrological study of samples may resolve the ambiguity because speleothems possessing certain fabrics might lend themselves to crushing in which 100% extraction is achieved. However, if decrepitation by heating can be shown to yield reliable results then it would be a faster, less tedious method for future use.

9. PALAEOTEMPERATURES FROM DECREPITATION EXPERIMENTS

The results of heating modern calcite have been presented in Table I. They are generally encouraging, with 'palaeotemperatures' falling within 2°C of the present cave temperatures and hydrogen isotopic compositions of waters falling within 3‰ of the seepage water.

Other temperatures calculated from fossil speleothem, assuming integrity of the inclusions, can be used to check warming and cooling trends as inferred from sequences of $\delta^{18}O_c$ data (Section 4). Note that $\delta^{18}O_c$ may increase or decrease with temperature depending on the relative magnitudes of the temperature dependence of $\delta^{18}O$ of meteoric water and the isotopic fractionation factor between water and calcite. While the latter is constant at about −0.25‰/°C, the former varies from values of about +0.7‰/°C in coastal areas to values around 0.2‰/°C in some continental areas. Furthermore, secular changes of $\delta^{18}O$ of sea water and of paths of water vapour masses over continental areas can have affected the secular shift in $\delta^{18}O$ of precipitation, and thus $\delta^{18}O_c$ [22]. Some palaeoclimatic information can be gotten from such $\delta^{18}O_c$ sequences by comparing them with $\delta^{18}O_c$ of modern calcite at the site providing the record passes through a complete glacial cycle. Relative warming and cooling trends can then be assigned to peaks and troughs in the records, since presumably modern or interglacial temperatures are always higher than those during glacial intervals.

The decrepitation data lead to some ambiguous results (Table IV). Data from Vancouver Island [10] (Fig. 10) show a nice progression downwards of $\delta^{18}O$ (calcite) during the middle of the Wisconsinan, suggesting that $\delta^{18}O_c$ was decreasing with falling temperature. The decrepitation data back this contention, yielding a temperature lower than 4°C for the 50 ka BP period and suggesting an appropriate isotopic shift in precipitation at that time to values 15‰ lighter than modern precipitation. Results from Victoria Cave, England, are also encouraging. A sample was taken from the top of a small stalagmite lying inside a massive block of flowstone. Going up the stalagmite axis, $\delta^{18}O$ (calcite) fell steadily to more negative values until growth temporarily ceased at about 250 ka BP. The water shows an appropriate isotope shift to values 8‰ lighter than those of modern seepage water [21] and the isotopic temperature gives a value of around zero when growth would be expected to stop.

Less encouraging are the data from Lost John's Cave, England. The top of a stalagmite at 95 ka was thought to have been deposited at a lower temperature than the base at 115 ka according to the $\delta^{18}O_c$ interpretation ($d\delta^{18}O_c/dT < 0$). Fluid inclusion data suggest the reverse with temperatures for the top and base being 4.5°C and 2.7°C respectively. In addition the base contains water indistinguishable from modern precipitation whereas the inclusions in the top of this stalagmite are about 7‰ heavier. The increase in δD may be attributable to the increase in δD of sea water during the transition to a glacial period.

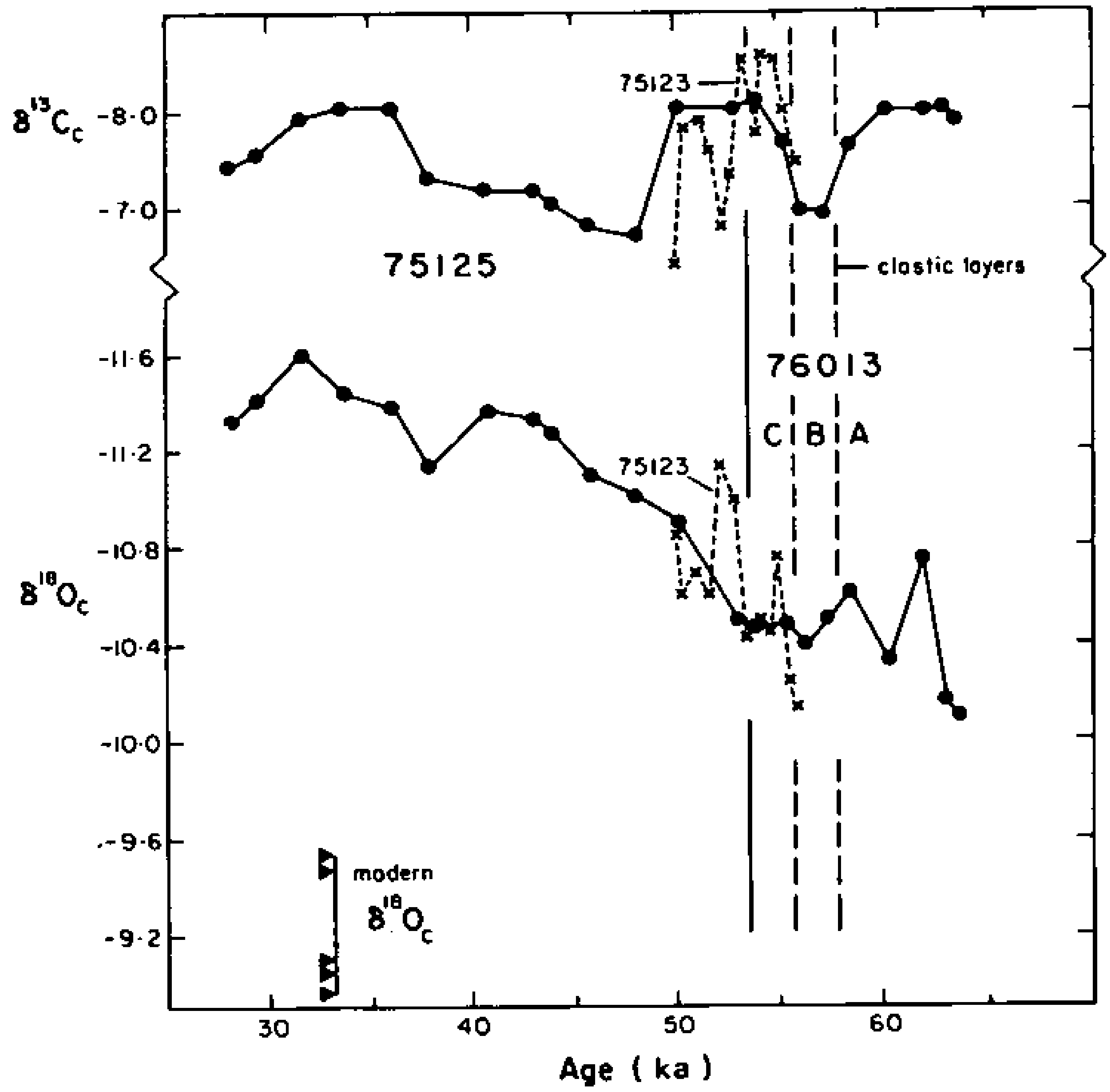

FIG.10. Oxygen isotopic composition of a series of three stalagmites deposited in Cascade Cave, Vancouver Island. Smooth decrease in O^{18}/O^{16} ratio from 63 to 28 ka occurred synchronously with cooling climate. No marked shift in carbon isotopic composition accompanied this change. From unpublished data of M. Gascoyne et al.

However, this implies that the temperature effect on δD of precipitation is negligible, which is unlikely. The sample is being studied in more detail as are the others.

The samples from Government Quarry Cave, Bermuda, are from a single layer in a flowstone deposited about 110 ka BP, during the last interglacial. Temperatures inferred from the D/H measurements are comparable to those observed in the cave today.

10. PRECISION OF ANALYSES

All D/H measurements were made on a home-made Nier-McKinney type mass spectrometer designed by C.E. Rees. Procedures for extraction by decrepitation were developed in our laboratory. Instrumental precision (replicate analyses of the same gas) is around ±0.6‰. Replicate analyses of standard water samples (1–2 μL) passed through an on-line uranium furnace were around ±1.2‰. The precision of replicate flowstone analyses, made on a geographically wide selection of samples, is better then 2.5‰ (1σ). Combining the precision of fluid inclusion analyses (±2.5‰) and that of $\delta^{18}O_c$ analyses (±0.1‰) yields a precision in palaeotemperature determination of ±1.5°C providing that there are no errors in the choice of a meteoric water line for conversion from δD to $\delta^{18}O$ of the water.

11. FUTURE WORK

Clearly further work must be done to characterize the nature of fluid inclusions. Currently we are carrying out petrological studies using both SEM and transmitted light microscopes, as well as heating experiments. In the latter, variation in the isotopic composition of water released at successively higher temperatures may reveal the presence of water (or OH^- ions) bound at other sites in the calcite crystals besides fluid inclusions, e.g. bound as structural water. DTA studies will determine if phase changes such as decarbonation or dehydration are taking place during decrepitation.

The wide distribution of speleothem and the existence of additional possible dating methods such as ESR and palaeomagnetism, potentially capable of extending the time range, could allow us to establish a global pattern of D/H variation through the Pleistocene. In arid regions such as north Africa and parts of western Asia caves occur less commonly. Furthermore, deposits within the caves may be fed intermittently and may have been deposited under conditions of less than 100% humidity. Such deposits are unlikely to have been formed at isotopic equilibrium. During pluvial periods in these areas, conditions may have more closely resembled those of present-day temperature regimes and higher humidity may have permitted equilibrium deposition, but at moderately high temperatures which would have encouraged rapid growth. Should this be the case then detailed records might be obtained from such sites of the alternation through time between periods of arid (interpluvial) and moist temperature (pluvial) climate. During periods of equilibrium deposition, palaeowater samples might be obtained from fluid inclusions for comparison with groundwaters supposed to have been recharged during pluvial stages. Thus, providing that the isotopic systematics of fluid inclusions can be worked out in more detail, there is great potential for using speleothem as a climatic recorder throughout the Pleistocene.

ACKNOWLEDGEMENTS

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ISOTOPE AND OTHER PHYSICO-CHEMICAL PARAMETERS OF PALAEOLAKE CARBONATES

Tools for climatic reconstruction

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Abstract

ISOTOPE AND OTHER PHYSICO-CHEMICAL PARAMETERS OF PALAEOLAKE CARBONATES: TOOLS FOR CLIMATIC RECONSTRUCTION.

Mollusc shells from a palaeolake core in south-west Switzerland have been studied for mineralogy, geochemistry and isotopic composition. Criteria for interpretation (e.g. the palaeotemperature scale, relations between ^{18}O content of water and climatological factors) are discussed. A very good relation between mean annual temperature and the growth temperature of molluscs is established. Conclusions relative to the evolution of the palaeolake fit palaeontological data very well.

1. INTRODUCTION

Peri-alpine and more generally juxtaglacial lake sediments provide records of important variations that are linked to changes in climatic characteristics of their catchment area. Isotope studies on carbonate recovered from cores have already provided useful information (Keith et al. [1], Serruya et al. [2], Stuiver [3], Fritz et al. [4], Eicher et al. [5, 6], Mörner et al. [7], Blanc et al. [8]). Changes in ^{18}O and ^{13}C content which can be at last qualitatively correlated with climatic changes have not yet been quantitatively interpreted, e.g. as changes in temperature, due to the complexity of factors in the continental areas and the fast response of sedimentary parameters at the difference of marine media, where modifications are largely buffered by the mass of water which is very important respective to lakes.

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TABLE I. OXYGEN ISOTOPIC COMPOSITION OF *Lymnea peregrinea* AND *Planorbis corneus* GROWN UNDER CONTROLLED CONDITIONS

t (°C)	$\delta^{18}O_c - \delta^{18}O_w$ (‰)	
	Lymnea	*Planorbis*
26.5	−0.04	−0.65
21.5	−0.28	+1.51
15.0	+0.77	+2.50
6.5	+3.33	–

In this paper we present some attempts to discuss isotopic, chemical and mineralogical characteristics of some lacustrine carbonates in the palaeoclimatic perspective. Such attempts are preliminary but may guide further investigations.

2. OXYGEN ISOTOPE FRACTIONATION BETWEEN H_2O ($\delta^{18}O_w$) AND CARBONATES ($\delta^{18}O_c$)

Thermodependence for this fractionation has been studied theoretically by McCrea [9] and Bottinga [10] and experimentally by McCrea [9] and Epstein et al. [11, 12]. Craig [13] has proposed the classical equation:

$$t = 16.9 - 4.206\,(\delta^{18}O_c - \delta^{18}O_w) + 0.13\,(\delta^{18}O_c - \delta^{18}O_w)^2$$

Some authors, such as Naidin et al. [14] and Van Donk and Mathieu [15], have used different formulas.

We have carried out experiments on various molluscs characteristic of the peri-alpine lakes in order to test their response to temperature and isotope composition of the water. *Lymnea peregrinea* and *Planorbis corneus* were grown in controlled water at station temperatures. Unfortunately, *Valvata piscinalis*, found in the palaeolake cores, could not be grown. Details are given by Lemeille [16]. Results are shown in Table I, for which the following relation holds:

$$t°C \simeq 23.2 - 4.19\,(\delta^{18}O_c - \delta^{18}O_w)$$

At 26.5°C, *Lymnea* presented reverse coiling; at 6.5°C, *Planorbis* did not survive.

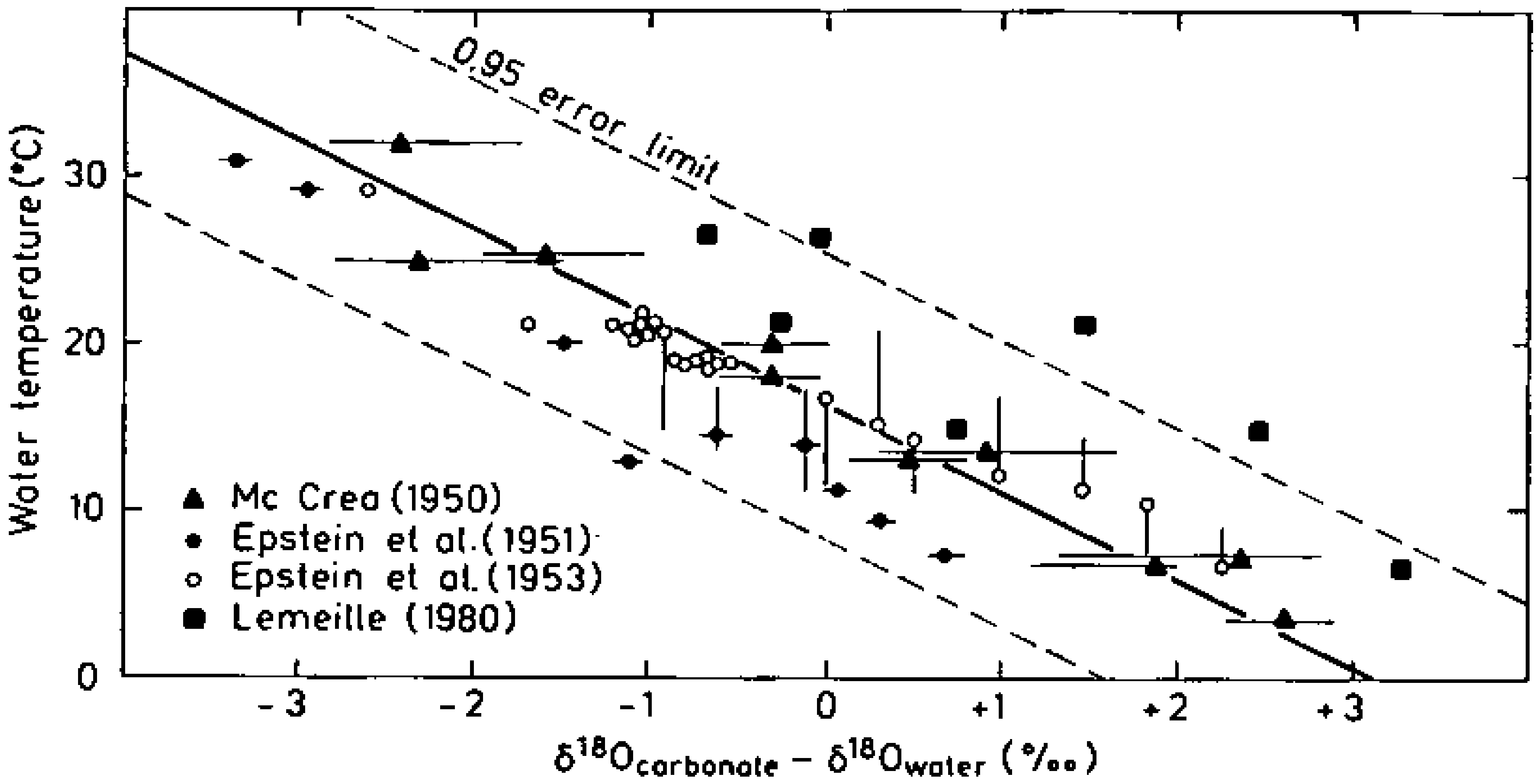

FIG. 1. Water temperature versus the oxygen isotopic composition of carbonate and mother water.

The slope of the regression lines between $\delta^{18}O$ of shell aragonite with temperature and the isotope composition of water fit Craig's formula rather well, but the intercept differs. It is well known from studies by marine palaeothermometrists (Grazzini [17] and others), that so-called vital effects affect the isotopic response of carbonate-growing organisms to local conditions. This may be due to differences in the kinetics of carbonate deposition and/or to differences in the biochemical reactions linking water ^{18}O content with the deposited carbonate.

Moreover, Tarutani et al. [18] have stated that calcite and aragonite present a different isotopic fractionation:

$$\delta^{18}O_{\text{ARAGONITE}} - \delta^{18}O_{\text{CALCITE}} = 0.6‰ \text{ at } 25°C$$

From all these observations, it can be seen that an indetermination of about 5°C exists (Fig. 1) in the temperature estimation due to the imprecision of the palaeotemperature relations.

A general approximative relation is:

$$t = t_0 - (4.2 \pm 0.2)(\delta^{18}O_c - \delta^{18}O_w)$$

or in a differentiate form:

$$\Delta(\delta^{18}O_c - \delta^{18}O_w) = -(0.24 \pm 0.01)\Delta t \qquad (1)$$

A special difficulty arises in the study of continental carbonate. It comes from the isotopic composition of lake water, which is not as well buffered as

TABLE II. MAJOR CLIMATOLOGICAL PARAMETERS AND ISOTOPIC COMPOSITION OF PRECIPITATION IN FIVE STATIONS IN THE ALPS

1971–1978	Thonon	Bern	Meiringen	Guttanen	Grimsel
Altitude (m)	380	572	632	1055	1950
Mean annual temperature (°C)	10.10	8.80	7.90	6.30	1.20
Weighted mean ^{18}O in precipitation (‰)	−9.9	−10.0	−11.7	−12.8	−14.4
Temperature coefficient for seasonal ^{18}O variations (‰/°C)	0.40	0.35	0.53	0.55	0.44
Mean annual precipitation (mm/a)	921	964	1271	1650	2091

marine water during climatic changes because of the small water storage, even for the biggest lakes, compared to the sea. It is not easy to make approximations for lake water during climatic changes.

Moreover, lake waters do not reflect exactly the isotope composition of precipitations because of effects such as evaporation, which enriches water in the heavier isotopes, or the integration of waters coming from various catchment areas located at various altitudes, with various residence times, etc.

3. ISOTOPE COMPOSITION OF PRECIPITATIONS ($\delta^{18}O_R$)

Dansgaard [19] has established for the coastal and polar regions the well known relation between the annual mean composition of rains ($\delta^{18}O_R$) and the mean annual air temperature (t_a):

$$\delta^{18}O_R = 0.695\ t_a - 13.6‰$$

Förstel et al. [20], using the IAEA world statistics, have given:

$$\delta^{18}O_R = 0.38\ t_a - 11.79‰$$

For the northern Alps (Grimsel, Guttanen, Meiringen and Bern stations: Siegenthaler and Oeschger [21]; and Thonon: Blavoux [22]: Table II) the following holds:

$$\delta^{18}O_R = 0.525\ t_a - 15.36‰$$

For the five stations above, the altitude of which lies between 380 and 1950 m, the overall variation coefficient of ^{18}O with t_a is:

$$\frac{\Delta\delta^{18}O_R}{\Delta t_a} = +0.52‰/°C$$

For each station, it lies between 0.35‰/°C and 0.55‰/°C, with a mean value of 0.45‰/°C. The discrepancy between this last value and 0.52‰ shows that factors other than temperature are responsible for the ^{18}O content of rains. Some authors, especially Gat [23] and Siegenthaler [24], quote:

(1) conditions prevailing in the regions where oceanic water vapour forms (temperature, relative humidity, $\delta^{18}O$ of surface sea water),
(2) history of the water vapour from its origin to the precipitation area (mixing with other air masses, evaporation and exchange in the clouds, rain intensity, amount effect).

In the following discussion we will use:

$$\Delta\delta^{18}O_R = 0.45\,(\pm 0.08)\Delta t_a \qquad (2)$$

4. RELATION BETWEEN $\delta^{18}O_R$ AND $\delta^{18}O$ OF LAKE WATER ($\delta^{18}O_L$)

Lake water cannot be considered as the same as input water from rain and tributaries because evaporation processes enrich the evaporating water body in heavy isotopes. The enrichment is a function of the evaporation flux relative to the water budget. Measurements made on small lakes in temperature areas by Stuiver [3], Fritz and Poplawski [25] and Eicher and Siegenthaler [5] show enrichment of lake waters to be some ppt relative to the input water.

For small lakes the water balance of which has not changed (as proved by the absence of changes in sedimentology), it may be considered as a first approximation that variations of the lake water follow variations in the rain (≡ input) water:

$$\Delta\delta^{18}O_L \simeq \Delta\delta^{18}O_R \qquad (3)$$

5. A POSSIBLE RELATION BETWEEN ANNUAL TEMPERATURE (t_a) AND GROWTH TEMPERATURE (t_s)

The temperature calculated from the palaeotemperature equation is not the mean annual temperature but rather a weighted mean of summer temperatures,

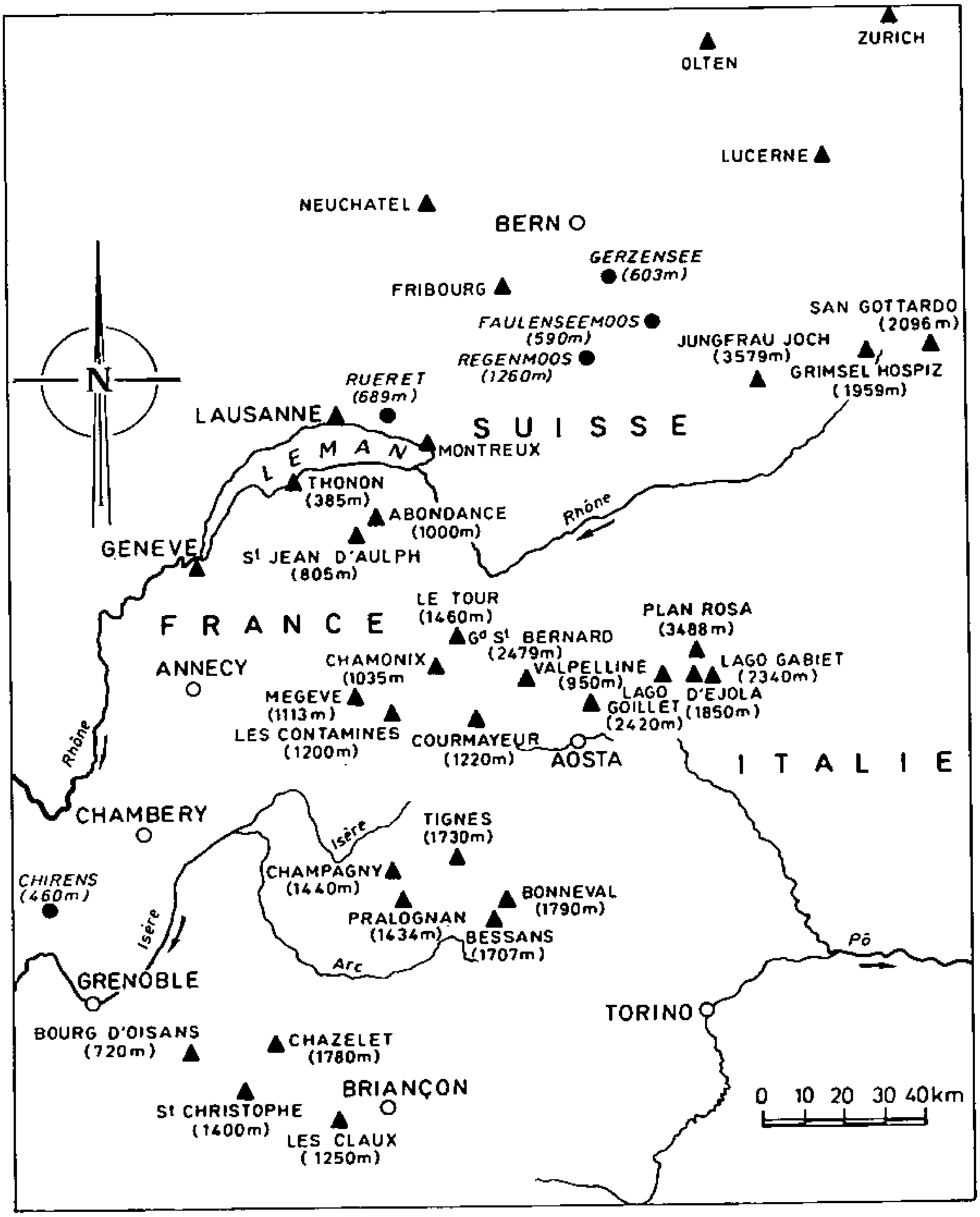

FIG.2. Map showing the location of Le Rueret, just north of Lake Leman.

when molluscs are able to grow their carbonate. As it is yet unknown what the possibilities of molluscs are in this field, it is not possible to tell if the lower limit for carbonate growth is 10°C or more.

We have tried to find a relation between annual and summer temperatures for the region surrounding Lake Leman. Statistics from 34 stations (Gaudet [26]) from Mt. Rose (4300 m) to Thonon (370 m, the lowest) were used (Fig. 2), and

TABLE III. CORRELATION BETWEEN THE AVERAGE VALUES OF TEMPERATURE IN SUMMER AND IN THE YEAR FOR THE REGION SURROUNDING LAKE LEMAN

$t_s \geqslant$ (°C)	n	t_0	Relation: $t_s = t_0 + \alpha t_a$ (α)	r
18	8	14.0	0.46	0.60
17	13	13.4	0.48	0.79
16	16	12.9	0.48	0.66
15	19	11.1	0.63	0.93
14	21	10.9	0.63	0.96
13	26	10.4	0.63	0.96
12	29	10.0	0.61	0.96
11	29	10.0	0.60	0.96
10	29	9.1	0.68	0.94

plots for the mean temperature observed above a pre-established limit (from 10°C to 18°C) were drawn against the mean annual temperature for each station (see Table III).

It can easily be seen that there is in each case a rather good linear correlation and moreover that the slopes of the lines are almost the same. Therefore, considering with some certitude that molluscs do not grow carbonates below 10°C, a typical relation for the Leman region can be written, using data between 11°C and 15°C:

$$\Delta t_{\text{summer}} \simeq (0.62 \pm 0.01)\Delta t_{\text{annual}} \tag{4}$$

One should keep in mind that this relation holds *only* for the north-western Alps, under the present climatic conditions (zonal wind directions from west to east etc.) and that it is certainly different for areas with more oceanic or continental settings.

6. POSSIBLE COMBINATION OF THE ABOVE RELATIONS

From Eqs (1)–(4), one can get

$$\Delta t_{\text{summer}} \simeq (2.0 \pm 0.7)\Delta\delta^{18}O_{\text{carbonate}} \tag{5}$$

This relation could be used to interpret variations observed in Holocene palaeolakes of north-western Alps.

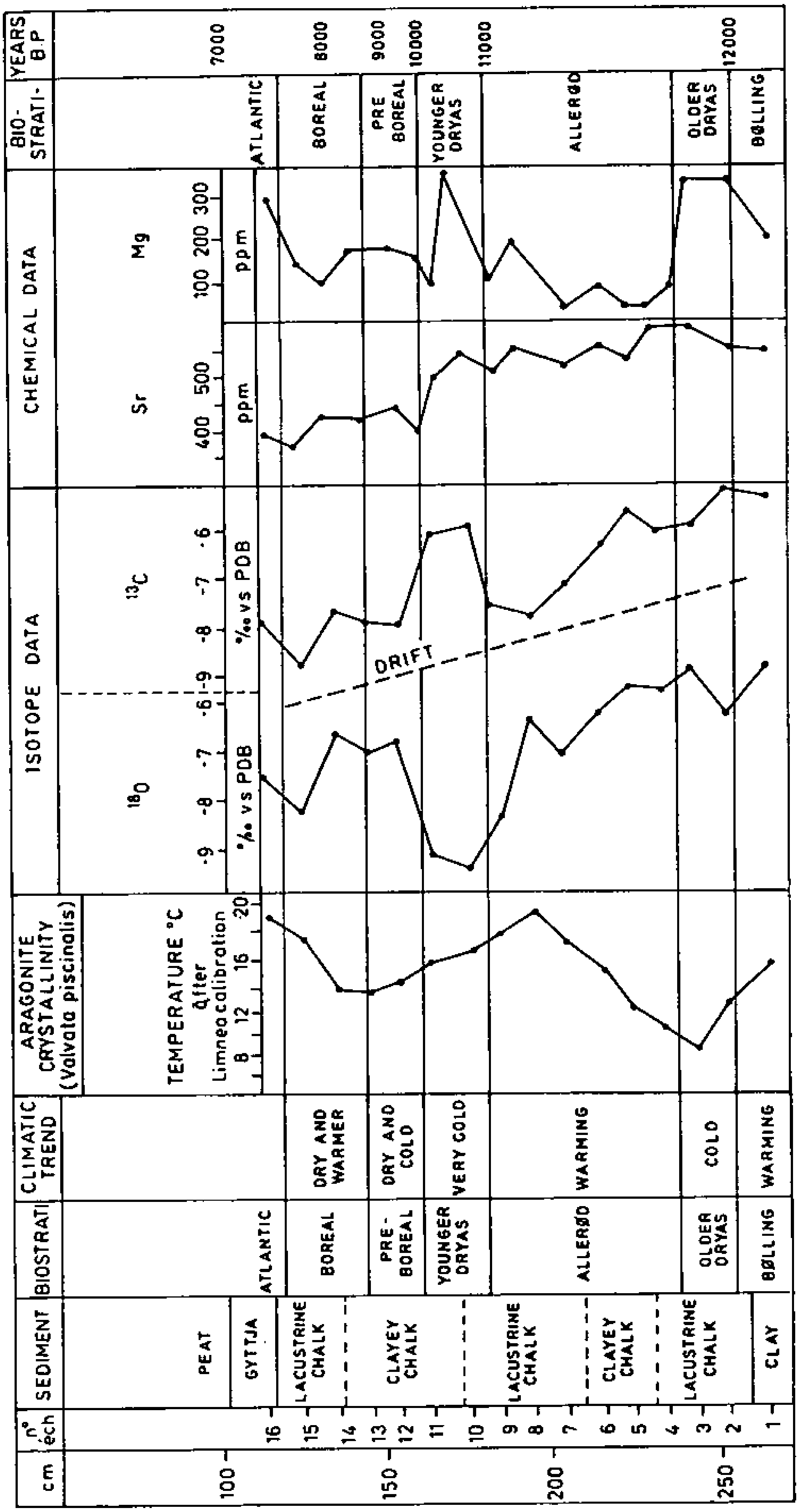

FIG.3. Isotope data and chemical data versus depth in a core from Le Rueret.

New experimental data will be used in the study of a small palaeolake at Le Rueret (Switzerland) (Fig. 2), where a core was sampled and studied for palynological and malacological studies by Arn [27] (Fig. 3). We have picked out the shells of *Valvata piscinalis*, a mollusc which grows a pure aragonite shell. This choice was based on the idea that aragonite is very unstable in most media and, after the death of the animal, it is either dissolved or replaced by secondary calcite. Pure aragonite samples could then be considered as having preserved their original characteristics.

It can be easily seen from Fig. 3 that the ^{18}O record of aragonite presents two characteristics: (1) a general drift from –6‰ to –8‰, from about 12 000 a BP (Bölling) to the beginning of Atlantic (7500 a BP) and (2) a big drop of 3‰ corresponding to the Younger Dryas episode, between 11 000 and 10 000 BP. This 3‰ accident should indicate a lowering of summer temperature of about 6°C. This, in fact, corresponds to Arn's conclusion [27].

It is not possible, however, to consider that the general drift in ^{18}O corresponds to a negative shift in temperature from 12 000 BP to 7000 BP, since it is well known that Bölling, Allerφd and Atlantic climates were not very different from the present climate. We must, therefore, consider the possible effect of evaporation which was not taken into account in the preceding discussion. As time went on, the lake was filled with sediments and, after 7000 BP, became a marsh, then dried. As the evaporation flux is proportional to the surface of a lake, it is possible that changes in its morphology modified the influence of evaporation (consider also that aerial vegetation progressively invaded the lake and certainly modified the evaporation effect). It does not seem possible to give a quantitative evaluation of such an effect.

These isotopic data have been compared with those obtained by Eicher and Siegenthaler [5] for the whole carbonate fraction (Gerzensee and Faulenseemoos), by Eicher [28] on Regenmoos, and Tourbière de Chirens by Eicher et al. [6]. All sites (Fig. 2) show the following features:

(1) *Oldest Dryas (Ia):* cold and dry climate (tundra landscape) with pioneer plants (willow, Hippophae, Juniperus).

(2) *Bölling (Ib), Older Dryas (Ic), Allerφd (II):* for step Ib warming begins with a phase with Juniperus followed by the extension of birch. For step Ic, Juniperus disappears and is replaced by pines. In step II is the climax for pines.

As for oxygen isotopes, an abrupt shift of 3‰ is also observed at the Ia/Ib limit, followed by a small constant diminution of about 1‰. Pollen analysis does not point to a cooling evolution but on the contrary to warming at the end of this period (Allerφd). The same was observed at Le Rueret.

All of this period (from 13 000 a to 11 000 a BP) corresponds to the end of the melting of the Alpine Würmian ice-cap and this regional phenomenon may be linked to the observed ^{18}O slow change.

(3) *Younger Dryas (III)* (from 10 800 a to 10 300 a BP): during this period, pine forest becomes less dense, with an increase of grass. Lang [29] estimates the cooling to be from 3.5°C to 5°C. The lowering of $\delta^{18}O$ is between 2 and 3‰, which, according to relation (5), would correspond to a temperature lowering of 4°C to 6°C. It is remarkable that such a shift, not only for the cooling but also for the warming, lasted less than one century.

(4) *Preboreal (IV) and boreal (V):* the forest becomes denser and the birch comes back. Hazels, elms, oaks and limes appear during the boreal and the pine diminishes.

The $\delta^{18}O$ evolution differs from place to place, probably due to variations in the infilling process of lakes, with the subsequent consequences on evaporation.

TABLE IV. CARBON ISOTOPIC COMPOSITION OF *Lymnea peregrinea* AND *Planorbis corneus* GROWN UNDER CONTROLLED CONDITIONS

t (°C)	$\delta^{13}C$ (‰ versus PDB)	
	Lymnea	*Planorbis*
26.5	−16.08	−15.00
21.5	−12.94	−13.81
15.0	−10.86	−10.04
6.5	−8.32	–

7. THE $\delta^{13}C$ RECORD

Along with the $\delta^{18}O$ of aragonite, the $\delta^{13}C$ was also measured on the molluscs grown in controlled conditions and gave a good relation with temperature (Table IV).

$$\delta^{13}C \simeq -0.38t - 5.3 \qquad r = 0.98 \ (n = 7)$$

or

$$\Delta^{13}C \simeq -0.38\Delta t \tag{6}$$

which confirms Stuiver's observations [3].

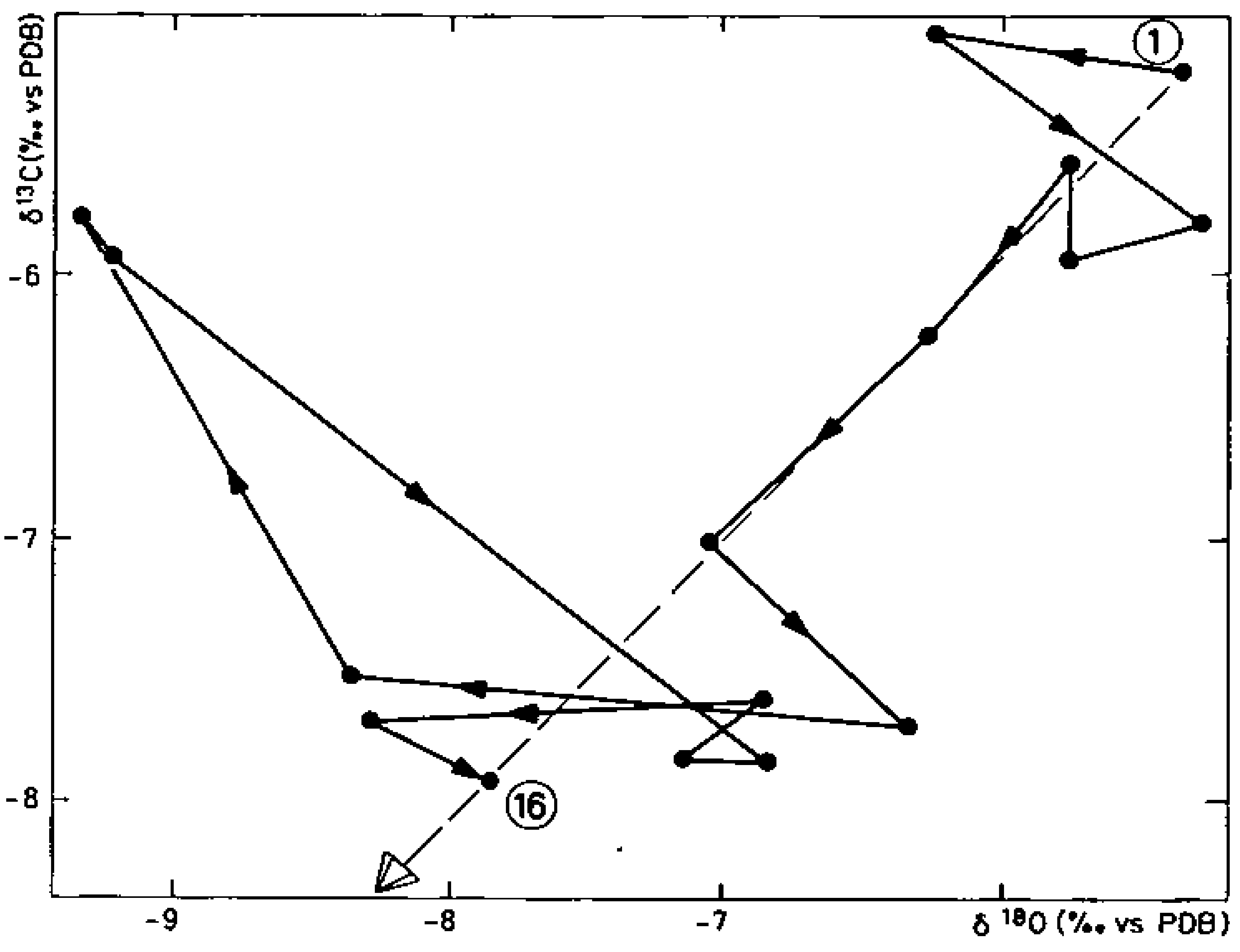

FIG.4. Isotopic changes of aragonite in the core from Le Rueret.

It is clear that at warm temperatures, aquatic vegetation, which is used by the molluscs for their food and which produces carbon with low $\delta^{13}C$ content, grows more easily in the controlled aquariums. Therefore, more low ^{13}C carbon is incorporated in the aragonite shells. The ethological difficulties for the growth of molluscs forbid controlling the relative importance in food for molluscs of locally produced carbon and of carbon coming from the general atmospheric reservoir ($\delta^{13}C \simeq -8$‰). It is therefore certain that the above relation cannot be used, as presented here, in a general way.

Coming back to the Le Rueret samples (Fig. 3), we observe two different phenomena, as for $\delta^{18}O$: (1) general drift from −5‰ to −8.5‰ and (2) a 2‰ positive accident correlated again with the Younger Dryas episode. The co-variation between $\delta^{18}O$ and $\delta^{13}C$ of aragonite is shown in Fig. 4.

During cold episodes, the lacustrine vegetation is scarcer and therefore contributes less to the ^{13}C budget of carbonates, which show higher $\delta^{13}C$ values since the atmospheric component becomes more important. As for the general drift, the same explanation as for $\delta^{18}O$ may hold. As the lake becomes shallower, vegetation colonizes it more and more. Carbon dioxide from its decay and its use by molluscs contribute more and more low ^{13}C carbon to the carbonate budget of the lake.

Figure 4, for Le Rueret, presents interesting features: (1) the general drift tendency holds for most samples and the general gradient $\delta^{13}C/\delta^{18}O$ is approximately 1, and (2) the Younger Dryas accident shows a negative correlation.

TABLE V. TEMPERATURE VARIATIONS EVALUATED FROM ISOTOPIC DATA

Sample	$\Delta t \simeq -2.6\,\Delta\delta^{13}C$		$\Delta t = 2.0\,\Delta\delta^{18}O$	
	$\Delta\delta^{13}C$	Δt estimated	$\Delta\delta^{18}O$	Δt estimated
1	0	0	0	0
2	+0.6	−1.6	−1.1	−2.2
3	−0.2	+0.5	+0.4	+0.8
4	−0.1	+0.3	+0.1	+0.2
5	+0.3	−0.8	+0.2	+0.4
6	−0.1	+0.3	0	0
7	−0.6	+1.6	−0.6	−1.2
8	−1.2	+3.2	+0.2	+0.4
9	−1.7	+4.6	−1.6	−3.2
10	+1.1	−2.9	−2.4	−4.8
11	+1.1	−2.9	−2.2	−4.4
12	−0.6	+1.6	+0.3	+0.6
13	−0.4	+1.1	+0.2	+0.4
14	0	0	+0.6	+1.2
15	−0.9	+2.4	−0.7	−1.4
16	0	0	0	0

The small anomaly corresponding to Older Dryas seems significant for the isotope changes. It is inviting to try to go further using the above relations.

If one considers as the $\delta^{18}O$ excess and the $\delta^{13}C$ excess the deviations of isotope values from the main drift tendency on the isotope record (from samples #1 to #16), it can be seen that two forms of co-variation occur: a positive correlation with slope 1 for samples which determine the drift tendency and a negative one for the others. For those, the slope is about −1; this is not very different from the slope which could be deduced from a pure thermic dependency as shown by relations (5) and (6), which give

$$\Delta\delta^{13}C \simeq -0.76\,\Delta\delta^{18}O$$

An attempt to calculate temperature variations using relation (6) on the so-called $\delta^{13}C$ excess gives values shown in Table V. Although estimations

TABLE VI. ISOTOPIC AND CHEMICAL VARIATIONS WITH DEPTH OF *Valvata piscinalis*

Valvata piscinalis					
Depth (cm)	Sample no.	$\delta^{18}O$ (‰ versus PDB)	$\delta^{13}C$ (‰ versus PDB)	Sr (ppm)	Mg (ppm)
105	16	−7.8	−8.1	400	300
115	15	−8.3	−8.7	350	140
125	14	−6.8	−7.6	450	100
135	13	−7.2	−7.8	450	180
145	12	−6.9	−7.9	470	180
155	11	−9.2	−6.1	400	160
165	10	−9.5	−5.8	500	100
175	9	−8.3	−7.5	600	380
185	8	−6.3	−7.8	550	100
195	7	−7.3	−6.9	600	200
205	6	−6.2	−6.3	620	50
215	5	−5.8	−5.7	600	80
225	4	−5.8	−5.8	680	50
235	3	−5.4	−5.7	680	80
245	2	−6.2	−5.1	600	340
265	1	−5.3	−5.4	600	200

appear too high, the general tendency fits well with Arn's deductions. The numerical coefficient in (6) is certainly overestimated.

The same attempt with $\delta^{18}O$ excess and relation (5) shows common features with the temperatures estimated from $\Delta\delta^{13}C$ but also gross discrepancies. It is clear that those could be used to discuss further secondary effects (e.g. evaporation) which were not considered above. The scarcity of data for the Rueret example precludes further reflections on the subject.

8. TRACE ELEMENT CHEMISTRY

Some trace elements were measured by flame photometry in the aragonite samples (Table VI). Only magnesium and strontium contents appear to show

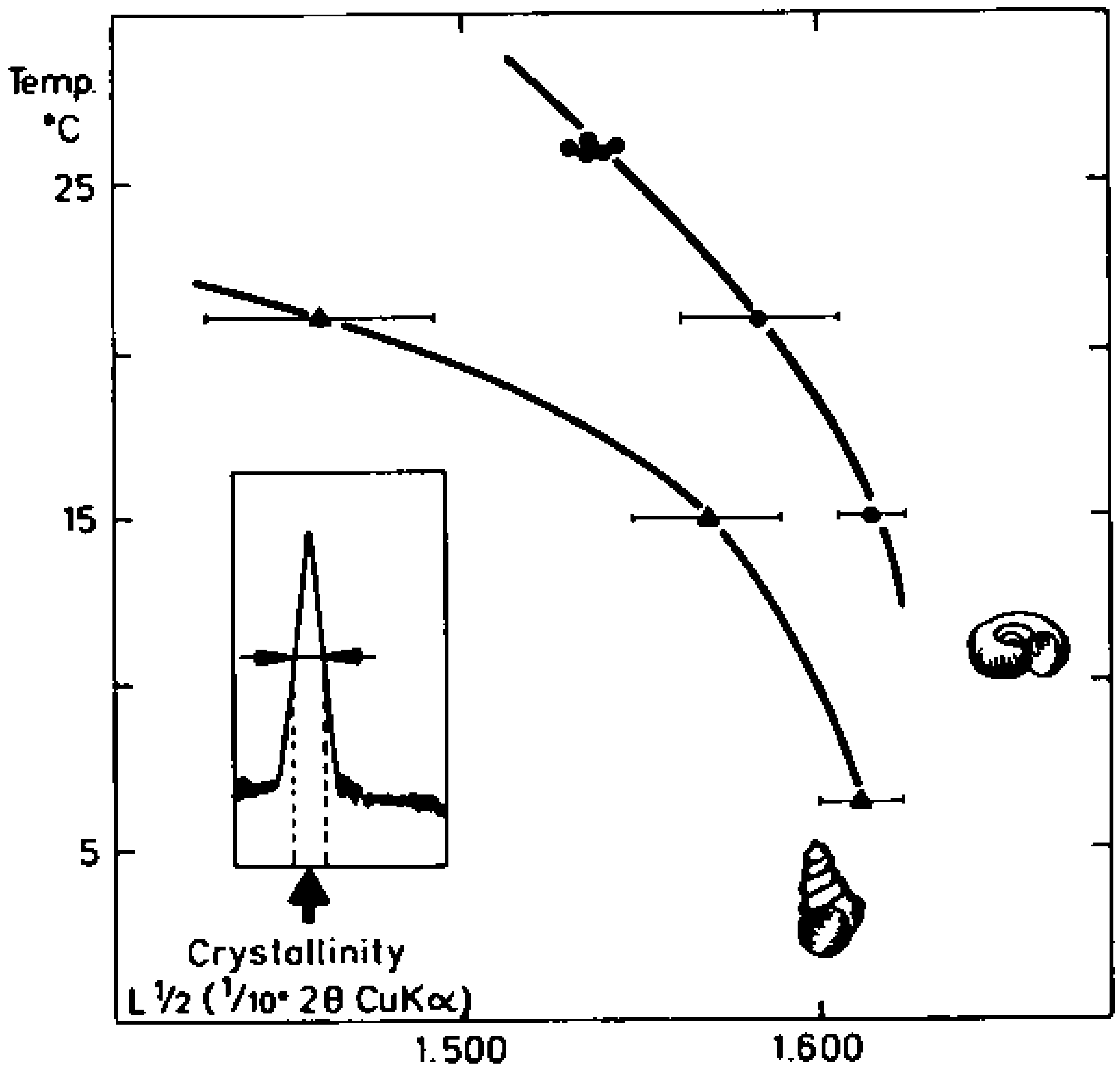

FIG.5. Crystallinity as a function of temperature for two different species of gastropods (Lymnea peregrinea *and* Planorbis corneus).

significant changes, especially strontium. This shows a good correspondence with ^{18}O (Fig. 3): the same drift with time and a significant diminution after the Younger Dryas event.

Strontium is known to be easily integrated in the aragonite crystals, and a temperature effect has been calculated (Kinsman [30]). For magnesium, no precise information exists. An augmentation in magnesium content seems to appear with colder events. It is possible that climatic events that modify the ratio of physical erosion and chemical alteration, especially in relation with the vegetal cover of the lake area, slightly change the chemical composition of the lake water. The partition coefficient between calcium and rarer cations in aragonite certainly changes also with temperature.

On the whole, trace element chemistry seems an interesting tool to investigate lacustrine palaeoclimatology.

9. MINERALOGY OF SHELLS

The gastropods *Lymnea peregrinea* and *Planorbis corneus* grown during the experiments are made of pure aragonite. This was submitted for X-ray analysis crystallinity measurement. Crystallinity will be defined here as the width at half-height of the 111 diffraction peak of aragonite, using X-ray diffraction techniques perfected in the laboratory. Results (Fig. 5) show that (1) at a given temperature each species is characterized by a proper crystallinity value and (2) each species displays a clear relation with temperature. These results show the role played by the metabolism in the work-out of the shell and show that the higher the temperature (in the investigated field) the better the crystallinity. The latter relation agrees with the fact that aragonite is stable at higher temperatures than is calcite.

Similar measurements were carried out on Le Rueret *Valvata piscinalis* shells. This species, used because it is the only one present throughout the core, is not documented for the temperature dependence of its crystallinity. Nevertheless, because it is purely aragonitic and morphologically similar to *Lymnea peregrinea,* we tentatively used the temperature calibration curve of the latter. Results (Fig. 3) show a rather good agreement with the climatic variations known from palynological studies. Influences other than temperature clearly intervene in the crystallinity of aragonite and should be investigated further.

10. CONCLUSION

It appears that many geochemical parameters, in connection with ^{13}C and ^{18}O measurements on mollusc shells, may be helpful for palaeolake reconstitutions. Strontium and magnesium carbonate contents appear interesting to investigate further. Carbonate crystallinity seems a promising tool to develop. It appears also that useful relations may be established to interpret isotopic variations, at last on a regional scale.

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$^{18}O/^{16}O$ RATIOS OF THE PORE WATER OF BALTIC SEA SEDIMENTS

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Abstract

$^{18}O/^{16}O$ RATIOS OF THE PORE WATER OF BALTIC SEA SEDIMENTS.

Two cores of Baltic Sea sediment were collected in 1975. The $^{18}O/^{16}O$ ratio of the water enclosed in the sediment (pore water) was measured after the separation of the liquid from the solid phase. The results may support the discussion about the history of the Baltic Sea. At the top of the core the $^{18}O/^{16}O$ ratio of the water represents the oxygen isotope composition of the sea water above. Towards the deeper parts of the sediment, independently of the salt content, the $^{18}O/^{16}O$ ratio decreases towards values observed in the precipitation of the surrounding land areas.

1. INTRODUCTION

The Baltic Sea has changed since the glacial age from marine to fresh water conditions several times [1]. In certain intervals the dissolved oxygen of the deeper water layers disappears. Many organisms cannot survive this change from aerobic to anaerobic conditions. This change does not depend on pollution only, but mainly on the hydrological situation of the Baltic Sea.

The Baltic Sea is an extended, relatively flat basin [2] connected to the open sea only by narrow, flat channels. The water of the Baltic Sea today is mainly supplied by the fresh water of the rivers that drain off the surrounding land areas. Simultaneously ocean water from the North Sea, a part of the Atlantic Ocean, is introduced into this system by exchange processes. This cold water of high salinity is deposited into the bottom layers. The bottom relief of the Baltic Sea is a series of subsequent basins. The water of higher salinity is transported from one basin to another and covers large bottom areas of the Baltic Sea. There are no continuous mixing processes to supply the deeper layers with oxygen. The oxygen is consumed near the bottom by the biological decomposition of the material produced in the surface layers. Intensive mixing can only be enforced by storms, more or less statistical events.

In the sediment layer the salt content of the pore water does not necessarily represent the history of changes from fresh water to marine conditions, for this salinity is mainly the result of the decomposition of deposited organic materials.

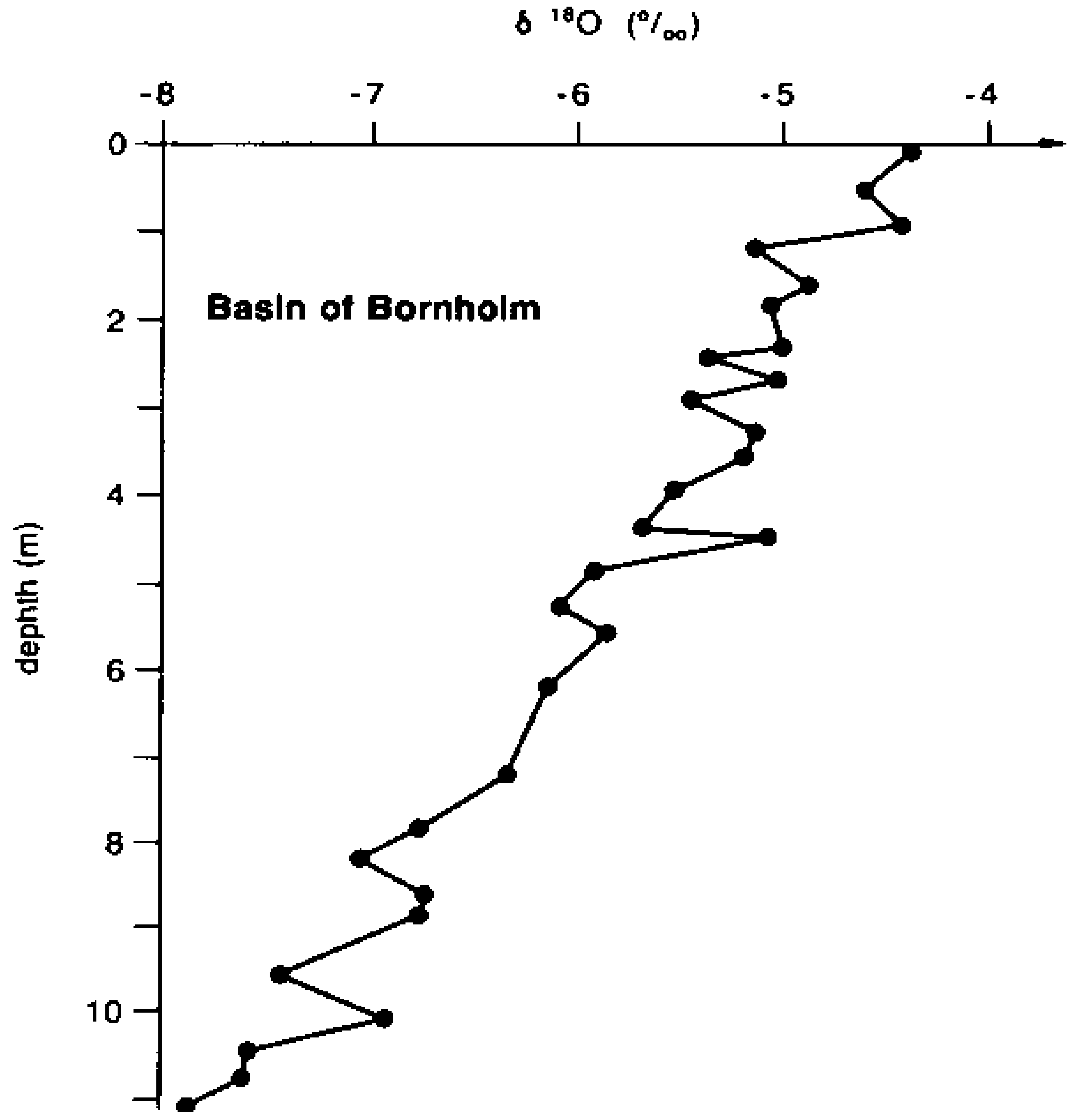

FIG.1. $^{18}O/^{16}O$ ratio of pore water in a sediment core from the basin near Bornholm (Denmark).

Therefore, in addition to fossils and stratigrafic observations one should have other support for a description of Baltic Sea history, or at least for the critical examination of results of stratigrafic and chemical analyses. This paper reports $^{18}O/^{16}O$ ratios of pore water from two cores of the Baltic Sea.

2. MATERIAL AND METHODS

The two cores were collected during May 1975 on board the research vessel Meteor during its cruise from Gdansk (Poland) via Bornholm (Denmark) to Kiel (Federal Republic of Germany). Mr. Kögler was responsible for the collection of the cores (stations 267 and 301 of 'Baltic 75') and Mr. Suess (also from the Geological-Palaeontological Institute of the University Kiel) supplied us with the water samples. He gained the solution by pressure filtration through a filter membrane at 4°C. The fluid was redistilled under vacuum to avoid the influence of the high salt content and the precipitations. Overnight 1 mL of each sample was exchanged with a defined amount of carbon dioxide. The $^{18}O/^{16}O$ ratio of carbon dioxide is compared to a laboratory standard gas and given as δ-value related to Vienna-SMOW [3, 4].

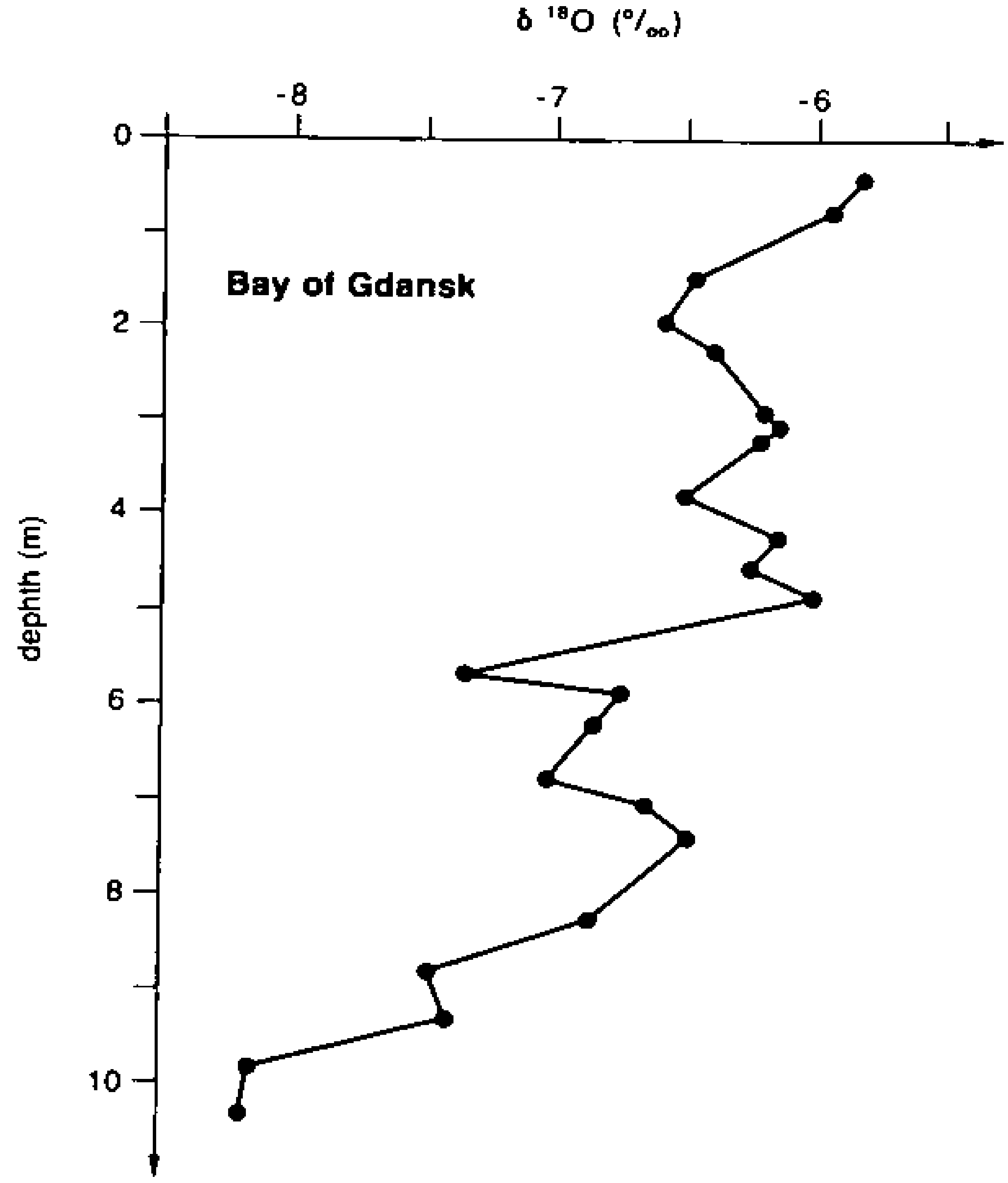

FIG. 2. $^{18}O/^{16}O$ ratio of pore water in a sediment core from the bay of Gdansk, Poland.

3. RESULTS AND DISCUSSION

The $^{18}O/^{16}O$ ratios of pore water in the two cores are given in Figs 1 and 2. One must keep in mind the hydrological situation. The oceanic water can be considered as a volume of relativelz constant ^{18}O content. According to the definition [3, 4] its δ-value is close to 0, while the δ-value of the precipitation and the river water from the surrounding land areas ranges between −6 and −12‰, average −8‰. Our results confirm the idea that the mixing of sea and fresh water in the Baltic Sea must result in a close correlation between salinity and $^{18}O/^{16}O$ ratio. In our case we have estimated the chlorinity instead of only the total salinity. The water samples were taken from different stations and in various depths during the whole course from Gdansk to Kiel. The correlation is demonstrated in Fig.3. The straight line equation is

$$\delta = 0.46 \cdot Cl - 8.9 \ (‰)$$

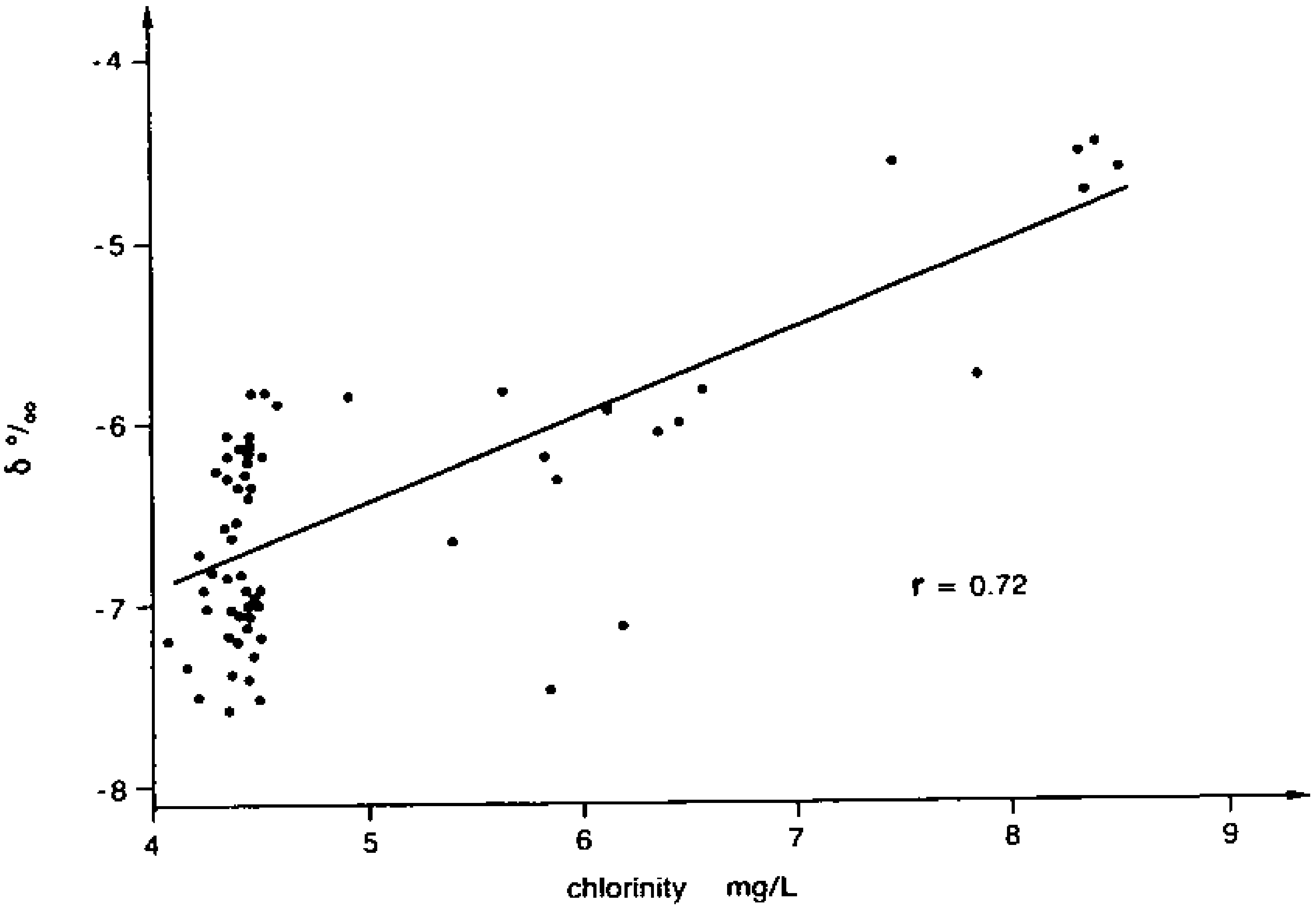

FIG. 3. Correlation between chlorinity and $^{18}O/^{16}O$ *ratio in water samples of the Baltic Sea, collected during May 1975 en route from Gdansk (Poland) to Kiel (Federal Republic of Germany).*

where δ: $^{18}O/^{16}O$ ratio of water related to Vienna-SMOW [4], Cl: chlorinity in % related to a Mediterranean Sea Standard (supplied to us by the Institute of Marine Research, University of Kiel).

The mean δ-value of inflowing fresh water results, if one extrapolates toward a salinity of zero. The δ-value of −8.9‰ seems to be too negative, but one must take into account that the main inflow results from the northern parts of the Baltic Sea and consequently has more negative δ-values. As an important result of the correlation study between chlorinity and $^{18}O/^{16}O$ ratio the mean δ-value of the inflow results as −8.9‰, in accordance to the IAEA data network [5].

The $^{18}O/^{16}O$ ratio of the top sedimental layers reflects the local oxygen isotope concentration in the bottom layer of the Baltic Sea water. The basin of Bornholm is closer to the inflow of sea water than the bay of Gdansk, where the fresh water influence is more dominant. The decrease of the $^{18}O/^{16}O$ ratio from the top towards the deeper parts of the core can be described by a straight correlation (see Table I). The $^{18}O/^{16}O$ ratio of the top layer is given as the right term of the equation.

TABLE I. LINEAR REGRESSION OF THE $^{18}O/^{16}O$ RATIO IN PORE WATER VERSUS THE DEPTH OF THE SEDIMENT CORE (d). THE EQUATIONS OF THE STRAIGHT LINE AND THE COEFFICIENTS OF REGRESSION (r) ARE GIVEN

Core origin	Straight line equation (‰)	Regression coefficient (r)
Bornholm Basin	$-0.29 \cdot d - 4.38$	−0.98
Bay of Gdansk	$-0.18 \cdot d - 5.73$	−0.83

Towards the deeper layers the $^{18}O/^{16}O$ ratio decreases, surprisingly, towards a value of about −8‰ in both cases (according to the regression equation at 10 m −7‰). This δ-value is close the $^{18}O/^{16}O$ ratio of precipitation in the surrounding area.

4. CONCLUSION

The decrease of the $^{18}O/^{16}O$ ratio in the two sediment cores of the Baltic Sea indicates that the water within the deeper layers must originate from fresh water sources, and despite its salt content it cannot be of marine origin.

The $^{18}O/^{16}O$ ratio profile could be the result of two processes:

(1) The $^{18}O/^{16}O$ ratio of present pore water preserves the δ-values of the past. The profile then would be the result of a long-term shift from fresh water to brackish water conditions.

(2) The $^{18}O/^{16}O$ ratio is the result of diffusion processes between a fresh water layer in the deeper parts of the sediment and the brackish water in the bottom layers of the Baltic Sea.

Both limiting cases may help to interpret other results from the sediments of the Baltic Sea bottom. The water of pure oceanic sediments does not show such large variations. A simple correlation of δ-variations to changes of the temperature using the correlation of Dansgaard [6] would indicate a fall in temperature between 5° (core near Bornhom) and 3°C (core near Gdansk).

ACKNOWLEDGEMENTS

This paper was initiated during a stay on board the research vessel Meteor in May 1975. The whole idea is the result of discussions with the members of the Geological-Palaeontological Institute of the University Kiel.

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PALAEOCLIMATIC STUDIES USING FRESHWATER DEPOSITS AND FOSSIL GROUNDWATER IN CENTRAL AND NORTHERN CANADA

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Abstract

PALAEOCLIMATIC STUDIES USING FRESHWATER DEPOSITS AND FOSSIL GROUNDWATER IN CENTRAL AND NORTHERN CANADA.

Sediments in post-glacial lakes in southern Ontario (Canada) often comprise molluscs and marls, i.e. carbonates whose oxygen isotopic composition can be used to estimate ^{18}O shifts in precipitations as a consequence of climatic changes. On the basis of available results, it is estimated that the last major climatic improvement which occurred ~10 000 a B P caused only a minor ^{18}O shift ($< 3‰$) and that large shifts obtained on molluscs are the result of glacial meltwater contributions. Similarly, pore fluids in post-glacial clays and tills in the area show the presence of meltwater. A third type of water analysed is permafrost from northern Canada, where ^{18}O differences of up to 10‰ are recorded between active and inactive frost. These differences are not the result of isotope effects occurring during freezing but reflect water of different origin. However, the presence of glacial meltwater is not excluded. Work on cores from an ice-free corridor should confirm or deny this assumption.

1. INTRODUCTION

The use of ^{18}O and ^{13}C in palaeoclimatological research is based on the observation that the isotopic composition of aquatic habitats changes in response to modifications of climate. It has also been recognized that the isotopic response is much greater in terrestrial environments than in marine ones. Yet virtually all systematic work has been done on marine organisms because the number of variables that enter into the interpretation of terrestrial data is much larger. However, with the increased concern about short-term variations of climate, especially in response to man's activities, there has been a renewed interest in studies of terrestrial environments.

In this short note we report on some basic observations of isotope analyses made in a number of investigations carried out in recent years or still in progress in different environments. The data were obtained primarily in southern Ontario (Canada) and in the Canadian Arctic and often form a component of larger projects.

Samples involve not only molluscs and marls from lakes and ponds but also groundwaters from very impermeable clays and tills of known age and from ground from the permafrost regions of northern Canada. It also must be emphasized that the mollusc and marl studies often involve a number of different approaches and that isotope analyses are one of several tools. For example, wherever possible, pollen analysis work is done, mollusc assemblages are characterized on the basis of habitat, geochemical studies are done on water and sediment samples, and most palaeoclimate projects include fossil beetle analyses. It is only through this combination of different techniques that we feel confident about interpretations made with respect to climate and palaeohydrology of surface water systems.

2. ^{18}O AND ^{13}C IN FRESHWATER MOLLUSCS

Most post-glacial lake deposits in southern Ontario contain an abundant mollusc fauna whose isotopic composition reflects the habitat in which they existed. The oxygen isotopic composition of a lake or pond is controlled not only by the local precipitations but also by the physiography of the drainage basin and the runoff generated within it and by general climatic parameters. Modern lakes in southern Ontario are thus much more controlled by evaporation effects than by any other parameter, whereas northern lakes tend to reflect local groundwater compositions and precipitations. Similarly, habitat variations have a profound influence on the carbon budget of a system and its isotopic composition. Since many molluscs obtain a significant portion of the carbon in their shells from the aquatic environment rather than from their food [1], their carbon isotopic compositions may be quite variable. No simple, straightforward interpretation is usually possible.

It is thus important to document that, despite the strong local influences, meaningful and interpretable isotope data can be obtained and that they are constant for any given environment. Figure 1 compares a number of different mollusc species which were separated from sediments in central Lake Erie [2]. Little species dependency is visible for the ^{18}O data but it is pronounced in the ^{13}C abundances. However, the differences are systematic and the results suggest that equilibrium conditions were obtained for both isotopes. The equilibria may not be those of simple water-aqueous, species-solid carbonate systems but could include minor biological factors. This may provide a partial explanation for the systematically different $\delta^{13}C$ values of the different mollusc species. It also must be mentioned that not all mollusc species are equally well suited for such studies. For example, gastropods such as *Helisoma* and *Gyraulus* live near the water surface or at pond margins and thus in environments where local environmental parameters fluctuate to the extreme. Other gastropods (such as *Lymnaea* or *Valvata*) or bivalves (e.g. *Pisidium* or *Sphaerium*) are found in more central environments and are thus much more likely to have representative isotopic compositions.

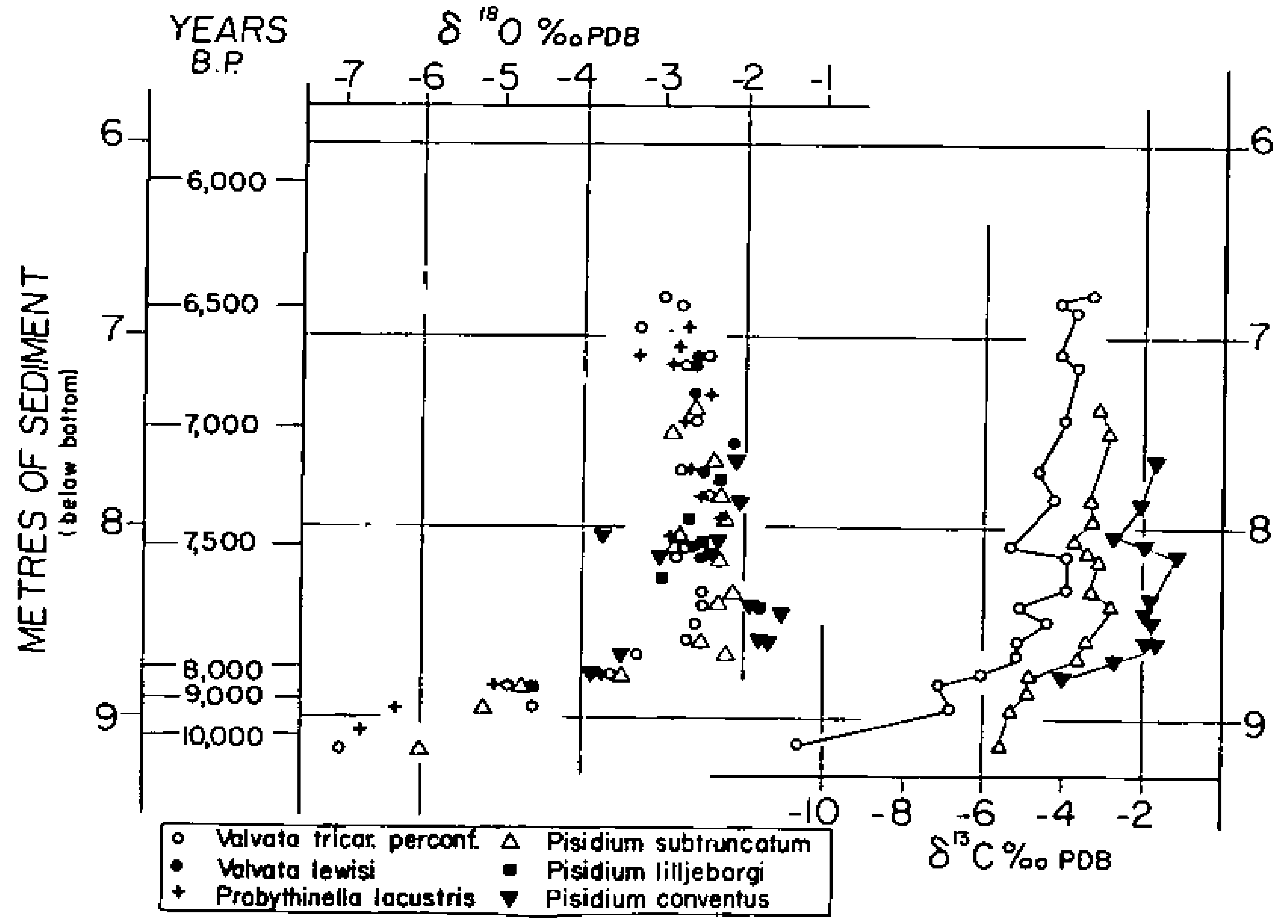

FIG. 1. Comparison of $\delta^{18}O$ and $\delta^{13}C$ of different mollusc species from central Lake Erie. Ages are inferred on the basis of pollen data.

The Lake Erie core mentioned earlier has provided so far the most complete record of isotopic changes in terrestrial environments in North America. The amplitudes of the variations are remarkable (Figs 1 and 2) and are much larger than could be expected in a marine milieu. Carbon-14 ages and ages inferred from pollen data show that these shifts are related to major climatic changes. However, it is not clear whether they are the consequence of changing precipitations or changing hydraulic regimes. Both ^{18}O increases at ~12 700 B.P. and 10 000 B.P. could, for example, be explained by a decreasing significance of glacial meltwaters in the drainage system. A distinction between the two has little significance for the recognition of timing of climatic changes but is important if the magnitude of climatic changes is to be discussed. The latter is not possible unless we can show that secondary phenomena are of no importance, especially, however, the inflow of glacial meltwaters and evaporation effects.

Present research programmes focus thus on small ponds and lakes with local drainage systems in an attempt to analyse systems where isotope changes are dominated by precipitation effects. This then should permit quantifying the climate changes in terms of changes in average annual temperatures. Our preliminary results as well as data published by Stuiver [3] on similar systems seem to suggest that, indeed, the isotope variations associated with climatic changes are

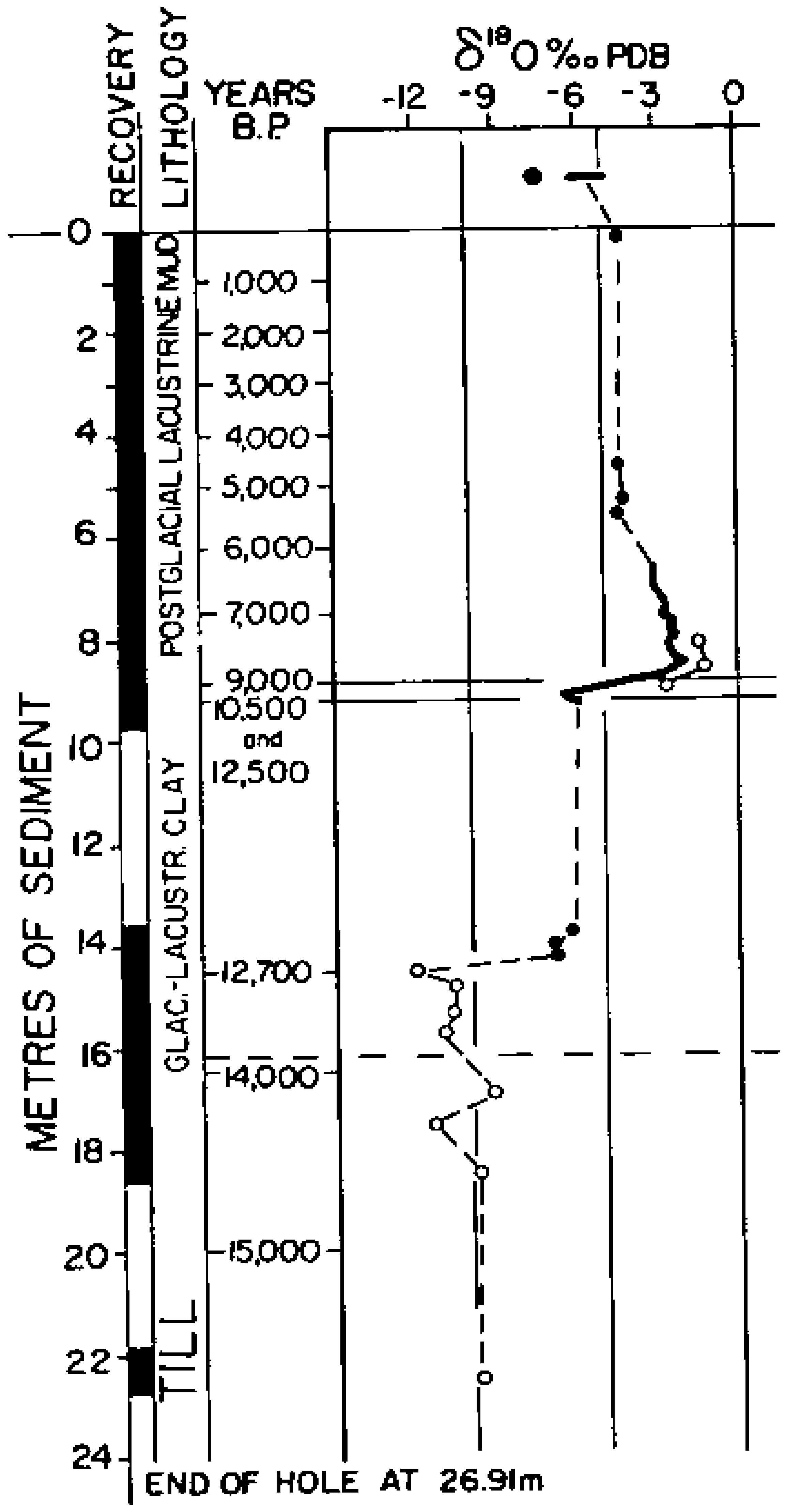

FIG. 2. Variation in the ^{18}O composition of molluscs and ostracods from central Lake Erie. Ages are inferred on the basis of pollen data (from Ref.[2]).

smaller in such restricted environments than the regional drainage systems connected to early Lake Erie. Thus the climatic improvement $\sim$10 000 years ago seems to be characterized in most small systems by an ^{18}O increase of 1–3‰ rather than the 5–6‰ found in Lake Erie. To further test this and to eliminate the influence of evaporation effects which can be very important in small lakes and ponds a programme has been initiated in which samples from river banks that contain datable mollusc deposits are collected and analysed. No results are yet available.

3. MARL DEPOSITS

Many lakes and ponds in southern Ontario precipitated calcium carbonate during one time or another; many still do. The formation of this material occurs either abiotically if the pCO_2's of inflowing groundwaters are very high and if

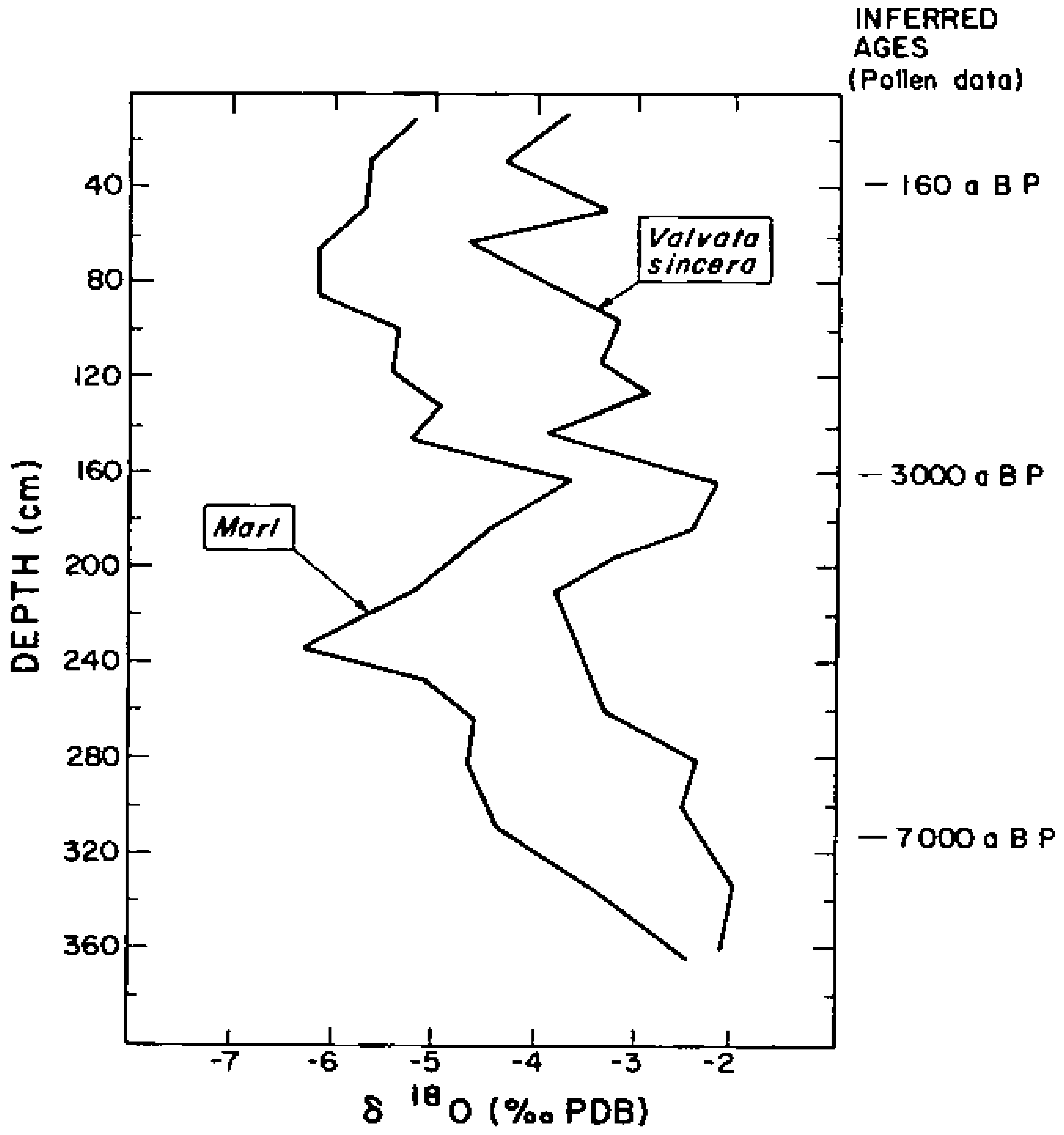

FIG.3. ^{18}O *contents in marls and the mollusc* Valvata sincera *from a core obtained from the sediments of Little Lake, Puslinch, Ontario.*

these waters are calcite saturated or if it is the consequence of CO_2/HCO_3^- removed by aquatic plants. In both cases it is likely that an ^{18}O equilibrium with the water is maintained and that the ^{18}O values observed in the marls reflect those of the water. This has been discussed and applied extensively by researchers in Switzerland [4, 5] and remarkably strong variations are noted whenever climatic changes occurred.

Similar changes, although possibly less sharp, are observed in samples from southern Ontario. The data base available to date is limited but Fig.3 shows a preliminary plot of results obtained [6] on marls from a small pond (Little Lake, Puslinch, Ontario, < 1 km^2 surface area) in which continuous marl deposition has occurred since about 10 000 a B.P. The decrease in δ^{18}O from a climate maximum that occurred at ~9000 B.P. to an ^{18}O minimum at about 5000 B.P. is clearly visible and is followed by an increase until about 3000 B.P. Modern lake water has δ^{18}O values of about -6‰ during summer months and marl values closely reflect this composition, indicating that marl deposition occurs primarily when water temperatures are above 10°C. If we assume that the hydraulic and temperature regimes did not vary dramatically during marl deposition throughout the history of this lake, then we can deduce that the oldest marls were deposited in a water which had about 2–3‰ higher $\delta^{18}O$ values than the modern lake. Furthermore, if the changes were entirely due to the modification of rainfall, then this would reflect 1.5 to 2.0°C higher average annual temperatures than today's. This is not an unreasonable change in temperature and corresponds to observations made on molluscs in Lake Erie [2].

Noteworthy, as shown in Fig.3, is that the mollusc data parallel the marl curve, attesting not only to the preservation of primary compositions but also to the suitability of both types of material for palaeo-environmental studies. The systematic differences observed between marl and mollusc $\delta^{18}O$'s are probably a function of environmental differences, primarily temperature of deposition. However, to aid understanding of these, current investigations focus on the aspect of climate changes and resulting ^{18}O variations in water and calcium carbonate and also attempt to pay attention to the genesis of marl [6] especially since inorganic marls may well precipitate during a greater portion of a year (and thus over much wider temperature regimes) than biogenic marls or molluscs.

4. ^{18}O IN 'FOSSIL' WATER

Isotope hydrogeologists have long insisted that it is possible to recognize old water and that groundwater dating can be used to define its age. In many instances groundwaters of age exceeding 10 000 years are found and where differences in ^{18}O and ^{2}H contents from modern waters are noted, this is quoted as additional proof. However, many studies are open to criticism because either the hydrogeology or the geochemistry of the waters is poorly understood and, as a result, it is very difficult to obtain from groundwaters information on palaeoclimates and thus the isotopic compositions of palaeoprecipitations of specific time periods.

For this reason it is interesting to consider data obtained from waters in glacio-lacustrine clay and till deposits of southern Ontario. At six different sites we have found water that is isotopically very distinct from modern surface waters and occurs at depths not exceeding 50 m. Desaulnier et al. [7] described the geology, hydrology and geochemistry of four sites.

The age of these deposits varies between about 15 000 and 10 000 a B.P. and physical hydrology data suggest that the water in which they were deposited should still be present because they are nearly impermeable to moving fluids. The $\delta^{18}O$ and $\delta^{2}H$ data substantiate this since the deep waters are 7–9‰ lower in ^{18}O than modern surface waters. These waters must be older than about 10 000 years because since then precipitation has had annual average isotope contents similar to or slightly more positive than modern precipitations. Considering the

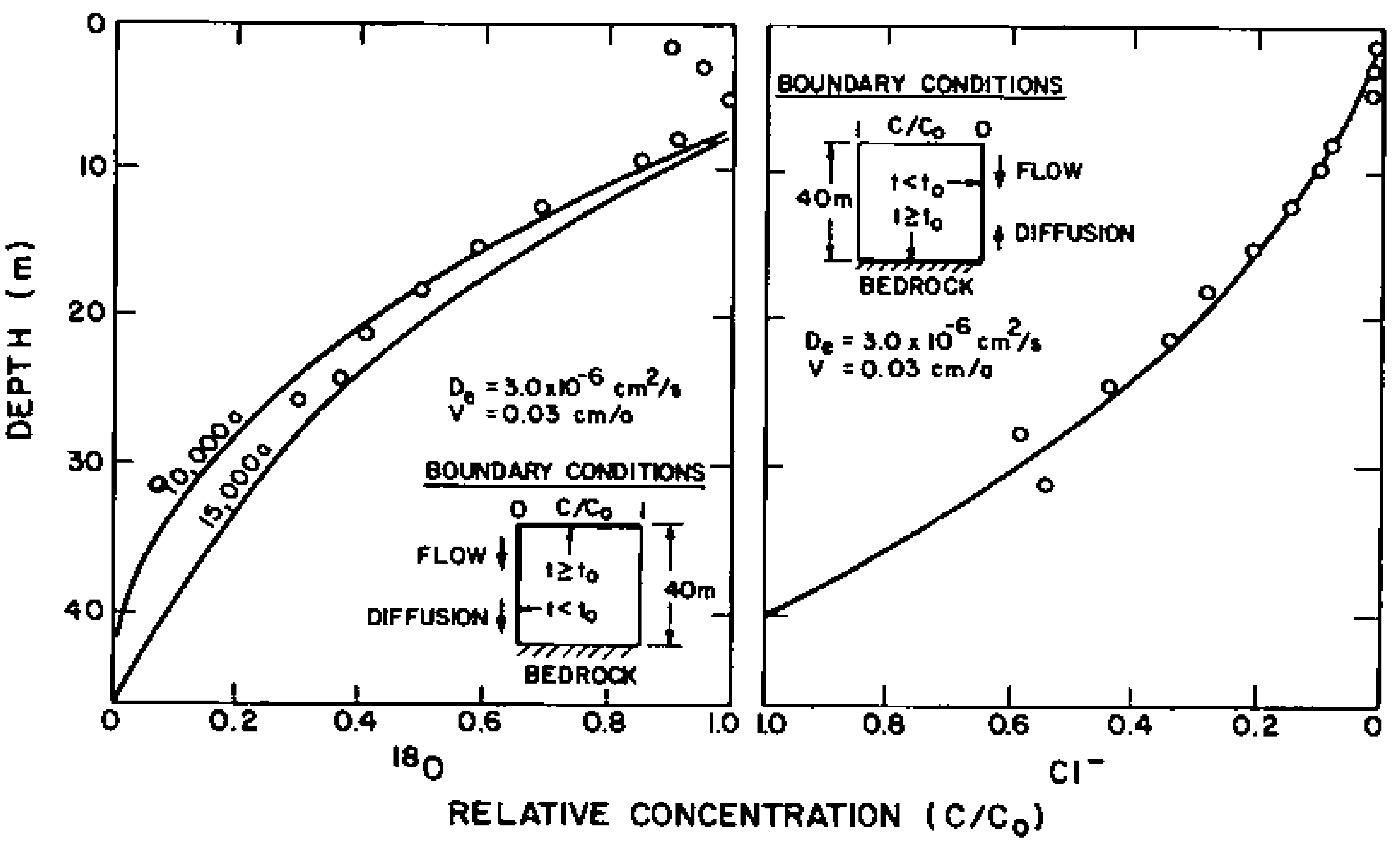

FIG.4. Relative ^{18}O *and chloride contents in waters from a glacio-lacustrine clay/till sequence at Sarnia (Ontario). At* C/Co = 0 *the* $\delta^{18}O = -18‰$ *and* $Cl^- = 0$ mol/L; *at* C/Co = 1 *the* $\delta^{18}O = -10‰$ *and* $Cl^- = 20.3 \times 10^{-3}$ mol/L.

genesis of the deposits one would suggest that glacial meltwaters are present and that, therefore, the 7–9‰ ^{18}O shift is not only a function of changing precipitation in response to climatic improvements. This then enhances the arguments presented above and possibly also the major changes observed in the molluscs of Lake Erie, which then are at least in part the result of changing meltwater contributions.

Near-surface waters in these deposits have modern compositions and the change with depth is very gradual. This distribution of ^{18}O and a similar pattern for the Cl^- contents in these fluids have been modelled and it can be shown that the movement of water and its dissolved load is essentially diffusion controlled [7]. Results are shown in Fig.4, where relative concentrations are plotted versus depth. (The $\delta^{18}O$ at 0 concentration corresponds to −18‰ and to −10‰ at a concentration 1.) A fit is obtained for both $\delta^{18}O$ and Cl^- at about 10 000 years. A steady-state distribution has been reached for Cl^- after that time. At this site $\delta^{18}O$ of the water in the aquifer below the clays has a $\delta^{18}O = -18‰$ but much higher Cl^- content than modern water. Thus the ^{18}O profile is controlled by diffusion and flow in the direction of the hydraulic gradient, which is down, whereas Cl^- diffuses against flow and, therefore, shows a concave distribution.

Carbon-14 measurements were also done on a number of samples [7] and after geochemical corrections are applied ages between 8000 and 10 000 a B.P.

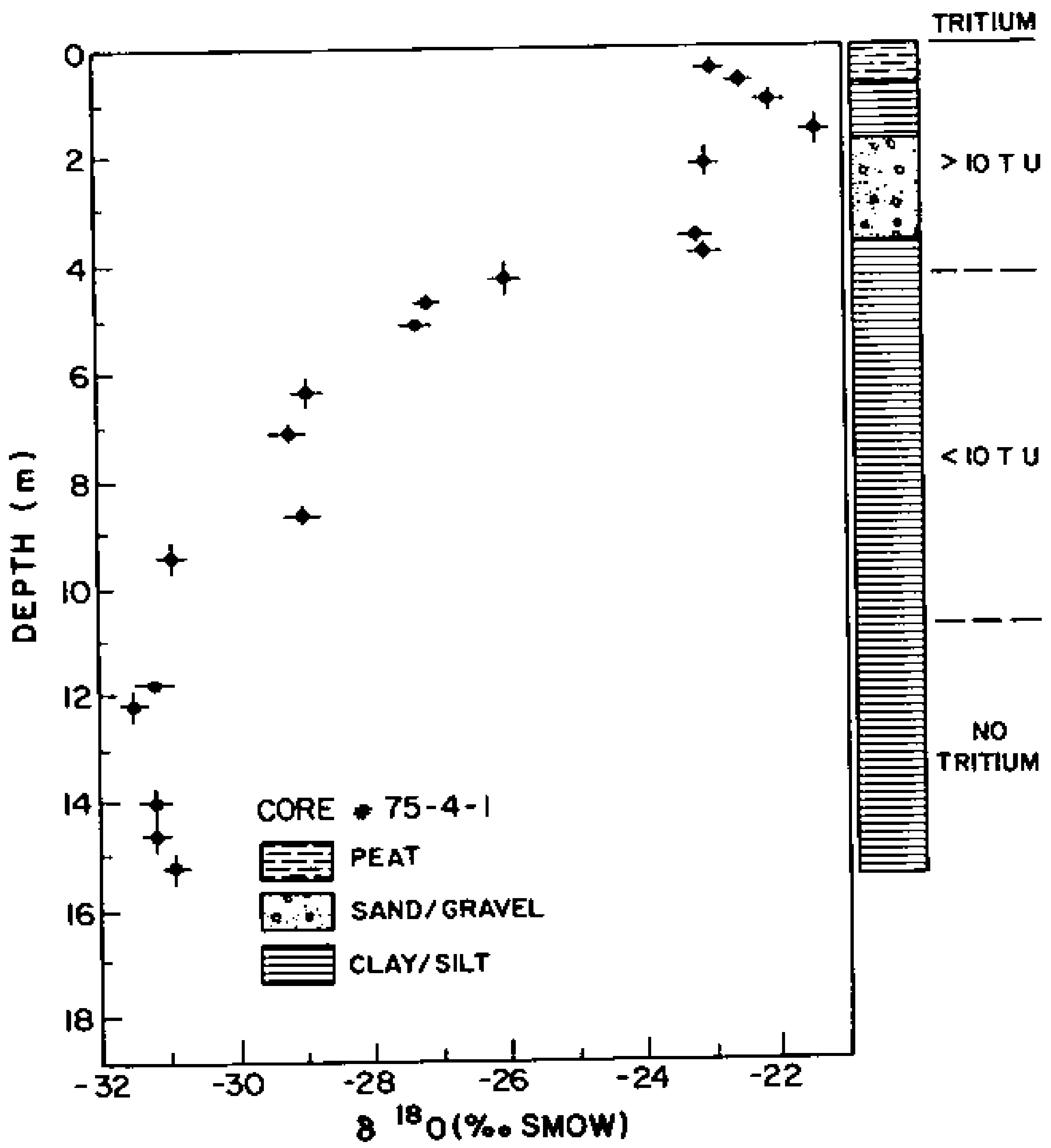

FIG.5. ^{18}O contents in permafrost waters from a core from the Mackenzie Valley, Canada. Tritium concentrations are those observed at other, nearby locations (from Ref. [8]).

are obtained for the deep, low ^{18}O waters. It is further interesting to note that all samples plot on the local meteoric water line for $\delta^{18}O$ versus $\delta^{2}H$. This signifies that evaporation in proglacial lakes of this area was not important.

5. ^{18}O AND ^{2}H IN PERMAFROST

Isotope investigations in glacial ice sheets have provided a wealth of information on climatically dependent variations of the isotopic composition of palaeoprecipitations. Similarly, in areas of permafrost hydrogeological records are frozen in place and can yield information on the palaeoclimatology of a region. Core samples from a number of drilling projects in northern Canada were analysed for their ^{18}O and ^{2}H contents [8, 9] (Fig.5).

As a general observation one notes a decrease in $\delta^{18}O$ with depth. In the uppermost section the high $\delta^{18}O$ values are associated with tritium and thus represent modern waters or the most active permafrost, i.e. the zone in which hydrogeological processes are active during summer months. The intermediate section may represent a mixing zone leading to water with considerably lower ^{18}O and ^{2}H contents.

Laboratory experiments show that this large isotope shift (observed in most cores) to δ^{18}O values as low as $-31.5‰$ is not related to isotope effects during freezing of water in a soil column but reflects waters which infiltrated during colder climatic conditions and/or are related to glacial meltwaters. It is speculated that the existence of permafrost beneath the ice sheet of the Wisconsin glacial is unlikely [10]. The growth of permafrost would then have occurred after the retreat of the ice. By 10 000 a B.P. the Mackenzie Valley was completely ice-free [11] and glacial lakes, which covered the valley floor during the existence of ice dams further north, were draining. Subsequent permafrost aggradation locked the water of the saturated sediments in place. Corrected ^{14}C ages on the spring waters near the site of core 75–19–3 are on the order of 2000 to 4000 a B.P. Their δ^{18}O values are close to values observed in active permafrost,and local shallow groundwaters add support to the suggestion that the water in the permafrost with lower δ^{18}O values was formed before that time, possibly during colder climatic conditions [8]. At this time we cannot attach a finite age to these deeper waters but it is worthwhile to note that Hillaire-Marcel et al. [12] estimate that during the last glaciation the average composition of the Laurentian ice sheet was close to $-31‰$, a value which agrees well with the low $-^{18}$O permafrost waters described here. We thus suspect that again glacial meltwaters played a role in the formation of these groundwaters. However, this assumption will be tested on cores which have now been collected in the glaciation-free area of Canada's Yukon.

6. CONCLUSION

The isotopic composition of post-glacial lakes in southern Ontario with regional drainage systems is apparently strongly dependent on the presence of glacial meltwaters. Therefore, mollusc and marl data may show isotope shifts in response to climatic improvements which do not reflect changing isotope contents in precipitations and thus cannot necessarily be used for palaeoclimatic studies that involve palaeotemperature determinations. Only samples from smaller ponds distant from retreating glaciers could prove useful.

Glacial meltwaters are also still present in groundwaters locked into glacio-lacustrine clays and tills and it appears that such runoff waters also played an important role in the formation of groundwaters in areas where permafrost has frozen such fluids into place. Isotope techniques are thus well suited to the investigation of the hydrogeological properties of these deposits and for the distinction of active and inactive permafrost but again yield only limited quantitative palaeoclimatic information. However, these studies provide us with important elements for the discussion of data obtained in more restricted environments.

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ISOTOPIC COMPOSITION OF PALAEOGROUNDWATERS

(Section 4)

STABLE ISOTOPIC EVIDENCE FOR PALAEO-RECHARGE CONDITIONS OF GROUNDWATER

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Abstract

STABLE ISOTOPIC EVIDENCE FOR PALAEO-RECHARGE CONDITIONS OF GROUNDWATER.

The palaeoclimatic influences on recharge form an important part of the evaluation of aquifer resources, particularly in arid and semi-arid areas where the magnitude of present recharge may not be well understood. Initially the factors affecting the isotopic composition of groundwater in temperate areas are examined, and it is clear that the isotopic relationship between precipitation and recharge is not yet fully understood. Palaeogroundwater studies in the United Kingdom illustrate phenomena such as mixing that require the application of several isotopic and chemical techniques to resolve the age and composition of palaeo-recharge. Studies in northern African regional aquifers have demonstrated the significance of episodic recharge as a function of climatic change and also the importance of carbon isotope data on dissolved and solid phases. In contrast, the recharge history of southern African aquifers is not well understood, in particular the magnitude of the active recharge component and its isotopic composition.

1. INTRODUCTION

The stable isotopic composition of groundwaters has been used for the investigation of two closely related topics: the variation of palaeoclimatic conditions during the recharge history of the aquifer, and the evaluation of aquifer resources for which the past pattern of recharge provides evidence for present behaviour. In essence, the problem is two-fold: the inference of both groundwater age and palaeoclimatic indicators from the isotopic (and chemical) evidence. For detailed palaeoclimatic indications, there is no doubt that groundwaters with all the concomitant problems of mixing and potential modifications do not present a tool of discrimination comparable to that of speleothems and ice cores. However, these powerful palaeoclimatic indicators, along with the many other methods available to the Quaternary investigator, provide the framework in which the important subject of aquifer recharge and evaluation may be tackled. This paper considers the hydrogeological significance of variations in stable isotopic composition of water.

A logical starting point for this subject is the relationship between the isotopic compositions of precipitation and groundwater recharge across the range of present-day environment that might be considered as analogues of past environments and climatic conditions.

2. ISOTOPIC COMPOSITION OF MODERN RECHARGE

The difficulties encountered in relating modern groundwater compositions to seasonal patterns of recharge and precipitation composition suggest a cautions approach to historical extrapolation from palaeogroundwater composition to that of past rainfall. Studies of rainfall/groundwater relationships in areas with temperate climates have demonstrated the potential dependence of this isotopic relationship on land use and vegetation [1, 2] inasmuch as these influence the time and rate of infiltration. Although the isotopic composition of infiltration under such conditions is found to be similar (if not identical within the statistical constraints imposed by rainfall variability) to that of overall average precipitation, it has been suggested that this might reflect the composition of precipitation during seasons of maximum infiltration [3]. Thus, selective infiltration might be compensated for within the seasonal fluctuations of precipitation composition. Research is currently in progress at the Wallingford Stable Isotope Laboratory to investigate these factors in greater detail by means of detailed monitoring of both precipitation and infiltration moisture. These studies are expected to shed more light on the processes affecting unsaturated zone moisture that were inferred from earlier studies by Zimmerman et al. [4]. Initial results from a research site on the Chalk aquifer of eastern England demonstrate a bias towards heavier isotopic composition in lysimeter drainage and saturated zones relative to average rainfall (Fig. 1), although caution must be applied when considering data from only one annual cycle [3, 5].

The possibility of extreme modification of isotopic composition is clearly far greater in the case of infiltration under semi-arid and arid conditions. The effect of surface evaporation from soil or sand on the isotopic composition of initial infiltration moisture has been demonstrated by Zimmerman et al. [4], and the further possibility of modification of precursor precipitation as a result of evaporation from raindrops has been illustrated by Dinçer et al. [6]. The contributions of these processes and that of selective infiltration have been identified in groundwaters of the coastal plains and more arid inland areas of Israel [7, 8]. More recently, some very important observations by Levin et al. [9] on the detailed fluctuations of rainfall and flash flood composition in the Negev have demonstrated the occurrence of abnormally depleted isotopic compositions in storms leading to flash floods.

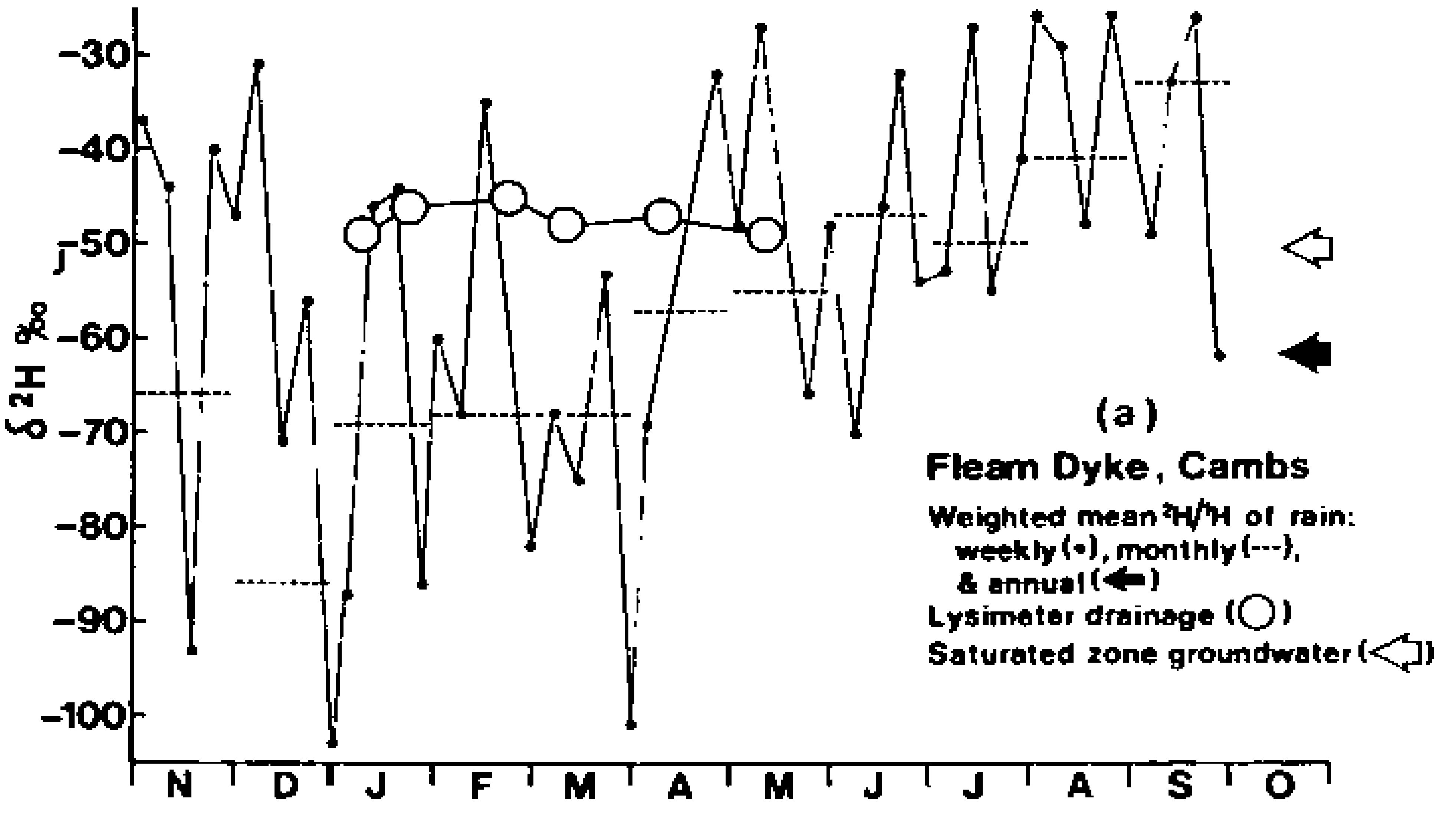

FIG.1a. Weighted mean $^2H/^1H$ of rainfall at Fleam Dyke research site, Cambridgeshire, for 12 month period over 1979–80. Weekly, monthly and annual means calculated from daily sampling and analysis. $^2H/^1H$ of drainage from an in situ lysimeter, 5 m deep, and also of water from saturated water table at 16 m depth is shown.

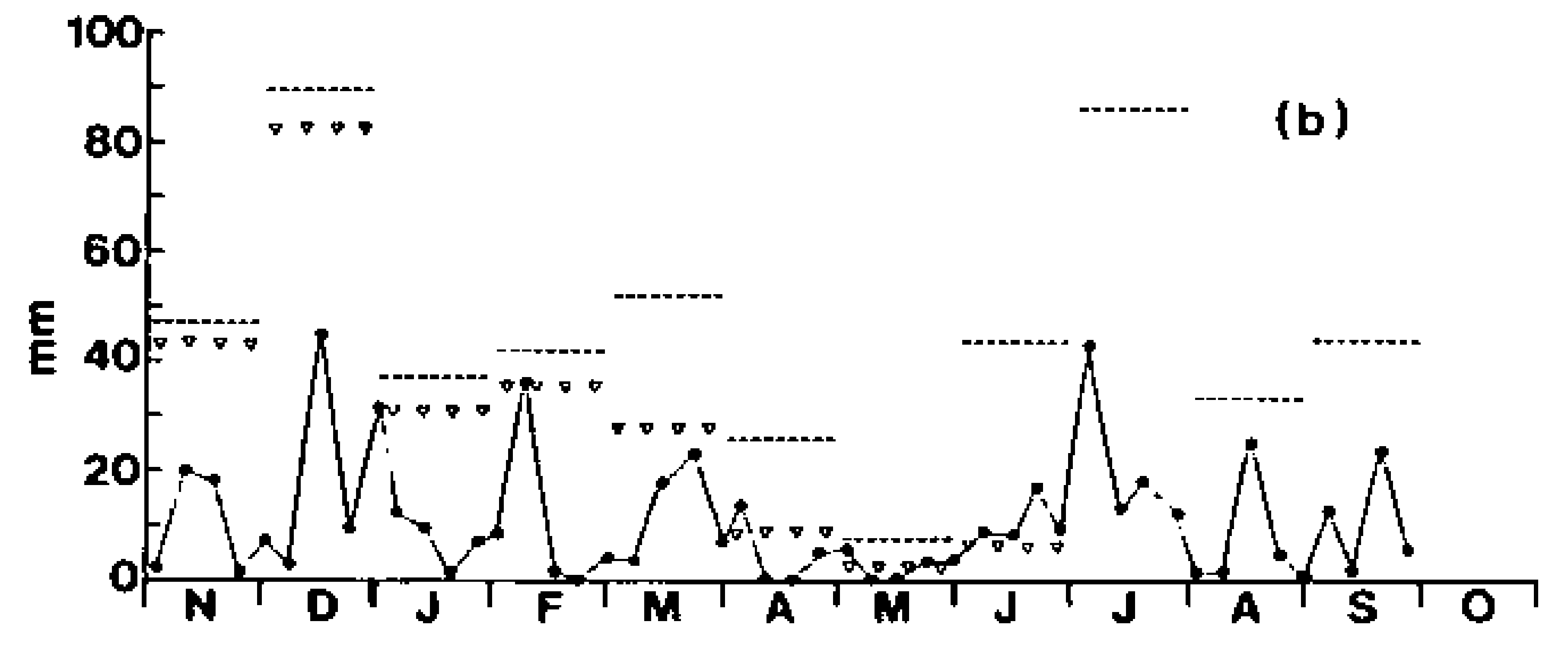

FIG.1b. Rainfall distribution over same period, showing weekly (●) and monthly (-----) totals. Calculated infiltration is also shown (∇ ∇).

The concept of episodic aquifer recharge from flash flood events in arid areas therefore introduces the possibility of modern groundwaters having relatively depleted isotopic composition, modified to a greater or lesser extent by surface or near-surface evaporation. It seems that the recognition of palaeogroundwater solely on the grounds of lighter isotopic composition, i.e. recharge under cooler conditions, cannot be regarded as definitive in arid climates, and may indeed be overlooking important evidence for the mechanism of present-day recharge.

3. CLIMATIC INFLUENCE ON ISOTOPIC COMPOSITION OF MODERN PRECIPITATION

The two commonly used indications of climatic conditions found in the isotopic composition of precipitation are the $\delta^{18}O$ and δ^2H values themselves, and the deuterium-excess parameter, d, defined by $d = \delta^2H - 8\delta^{18}O$ [10]. The slope relating δ^2H and $\delta^{18}O$, which has been established as predominantly a function of isotope fractionation at the ocean/water vapour interface, is close to 8 for normal conditions of evaporation and subsequent equilibrium condensation during cloud formation [11]. However, slopes for the $\delta^{18}O$-δ^2H relationship in precipitation outside the expected range (around 8) are indicative of secondary atmospheric processes affecting the observed composition of precipitation at or near the ground surface. Merlivat and Jouzel [11] have further demonstrated that, under normal evaporation and condensation conditions, the d-parameter is predominantly a function of humidity in the source region at the ocean surface.

It is within this theoretical framework of evaporation and condensation processes and by analogy with present-day precipitation that the $\delta^{18}O$-δ^2H relationships in palaeogroundwaters permit inferences of climatic conditions. It is important, however, that secular and geographical variations in present-day precipitation and infiltration be distinguished; geographical variations may

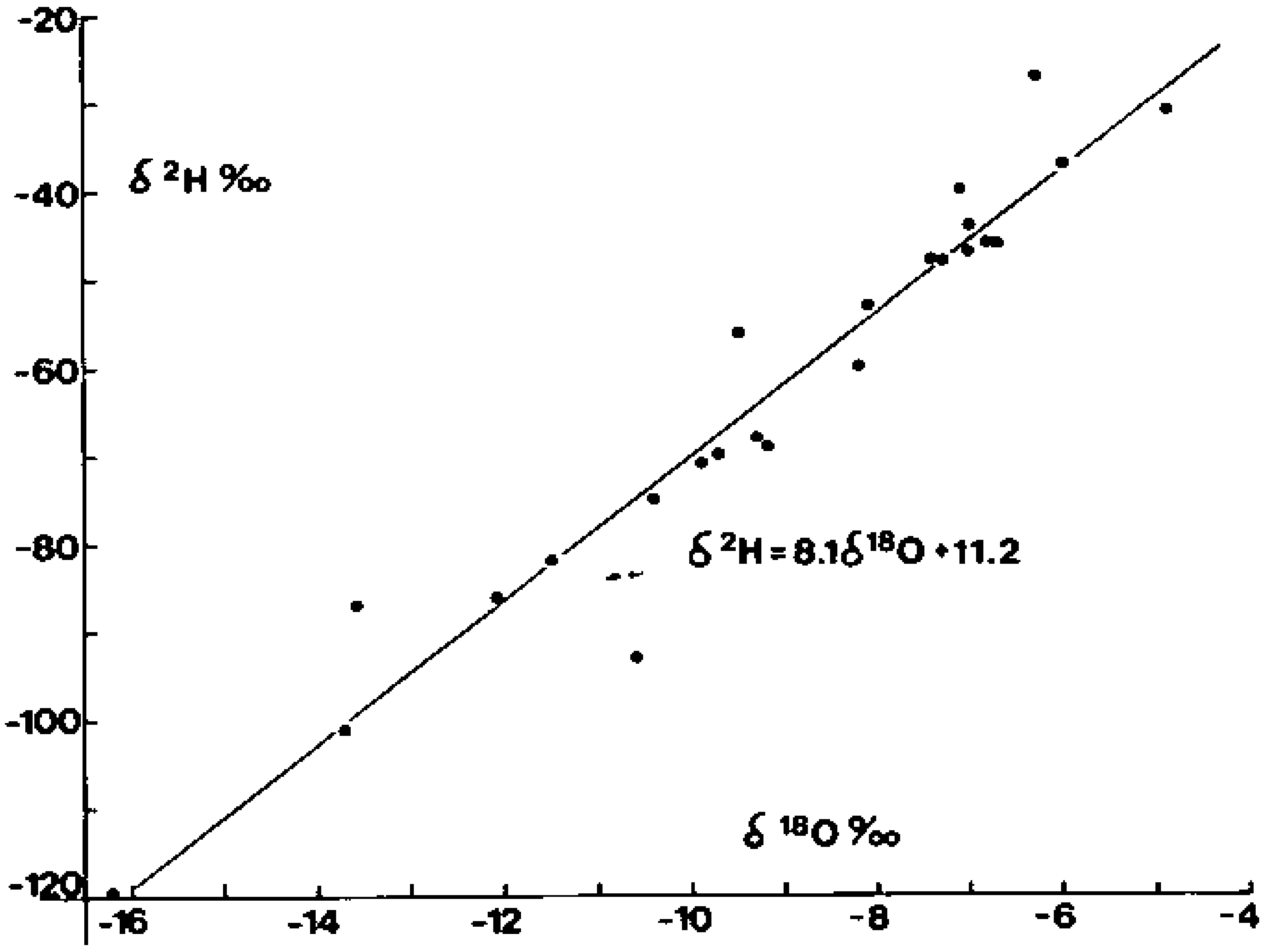

FIG.2. δ^2H versus $\delta^{18}O$ for weekly weighted mean isotopic composition of rain at Fleam Dyke (see Fig. 1a). Regression line is shown ($r^2 = 0.93$).

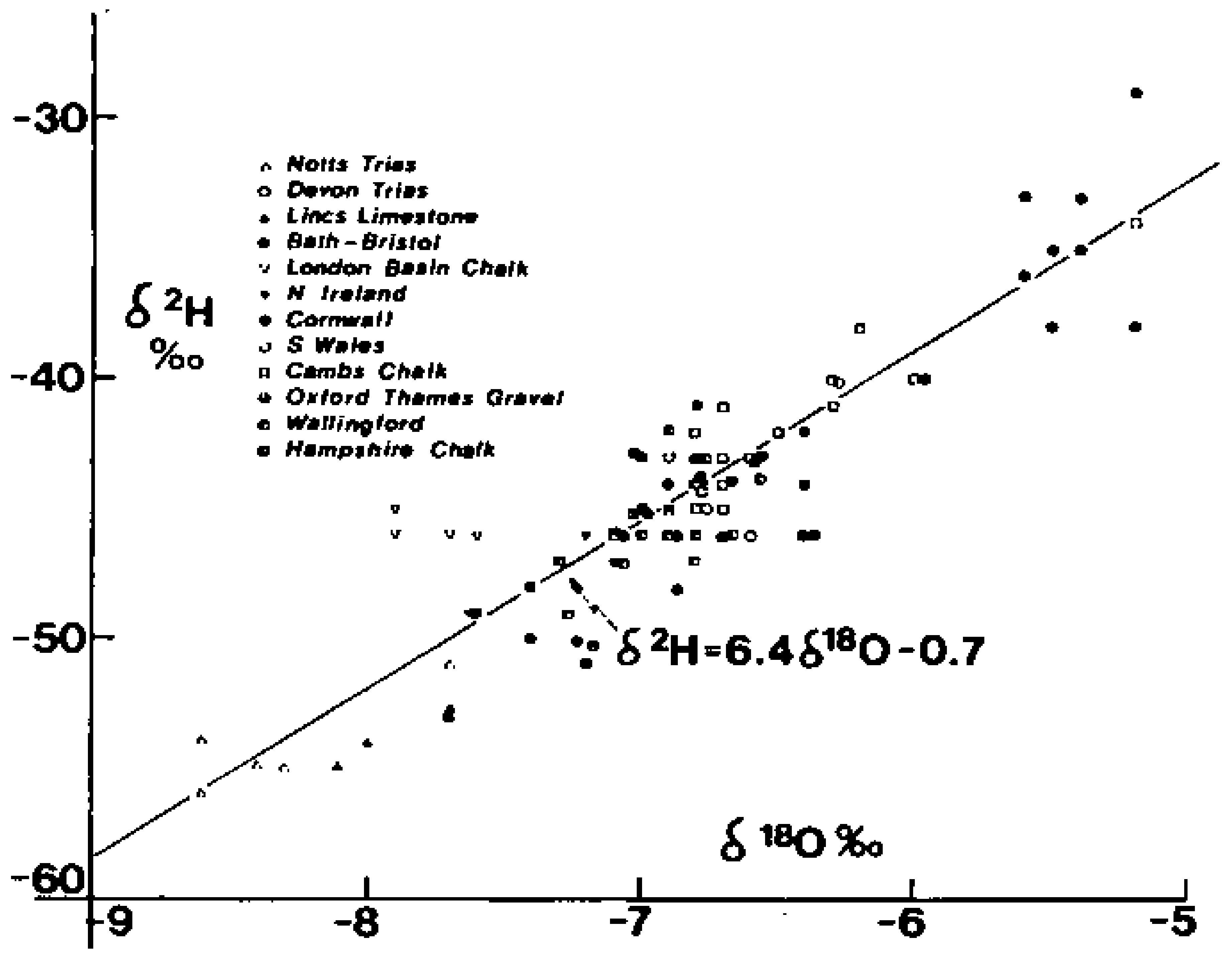

FIG.3. δ^2H versus $\delta^{18}O$ plot of isotopic compositions of modern groundwater in the UK demonstrating geographic variation. Regression of all points is shown ($r^2 = 0.83$). All analyses at IGS Wallingford laboratory.

reflect local influences as well as changes in climatic conditions in the source region. For instance, the $\delta^{18}O$-δ^2H relationship for weekly rainfall samples at the research site in eastern England seems to exemplify the control of slope and d-parameter by source region temperature and humidity (Fig. 2), as described. The slope and d-parameter are coincidentally identical to those reported by Dansgaard [10] for geographical variation of weighted mean annual precipitation at continental stations over the northern hemisphere. However, secular variation given by the IAEA/WMO monthly samples from individual European stations gives slopes consistently below 8, in the range 4.2 to 7.5 [11]. From their analysis of these monthly data, Evans et al. [12] suggest a $\delta^{18}O$-δ^2H relationship of $\delta^2H = 6.9\ \delta^{18}O - 0.3$ as probably the best representation of precipitation over the UK. This is not in agreement with the short-term fluctuation reported above and illustrates the necessity of distinguishing short-term and long-term fluctuations, as well as secular from geographical variation.

The geographical variation of isotopic composition of recently recharged UK groundwaters is shown in Fig. 3. The slope represented by these samples is in fair agreement with that previously reported for a smaller group of similar samples [12]. This relationship was compared with that inferred for long-term variation of precipitation [12]. It would seem that the slope of these geographical and long-term variations should not be interpreted as having direct climatic significance in the way that slope and intercept of short-term variations can be interpreted. Similar considerations should be applied when interpreting palaeogroundwater isotopic data.

The variation of $\delta^{18}O$ and $\delta^{2}H$ values themselves is attributed to change in temperature of condensation [10], assuming that oceanic source region parameters (temperature, humidity) are constant [11]. Dansgaard [10] derived a temperature coefficient for $\delta^{18}O$ of 0.70‰/°C from a wide range of global annual mean precipitation measurements, and this value has been widely quoted in studies dealing with both present-day geographical variations in precipitation composition and secular variations in palaeowater compositions. However, some localized studies of geographical variations in precipitation composition have suggested a wider range of temperature coefficients depending on local circumstances. A coefficient of 0.45‰ $\delta^{18}O$/°C is inferred for central Europe [5] and 0.23‰/°C has been suggested for north-west Europe. It should be noted that the derivation of such coefficients for condensation temperature implies that source region conditions are assumed to be constant. Dansgaard [10] interprets the global temperature coefficient to be the result of progressive condensation and rain-out during isobaric cooling of a moist air mass. The smaller coefficients from more localized data suggest a more complex behaviour, including the effect of evaporation from falling raindrops [5] and the occurrence of adiabatic cooling [10].

In summary, the influences of the many climatic factors controlling the isotopic composition and $\delta^{18}O$-$\delta^{2}H$ relationships in modern precipitation must act as analogues with which we compare isotopic patterns in palaeowaters. However, as Siegenthaler and Oeschger [5] emphasize, the coefficients from short-term seasonal variation may be quite different from long-term climatic variation and therefore caution is required in this extrapolation.

4. PALAEOGROUNDWATERS

The derivation of both relative and absolute ages for groundwater bodies relies on deduction from the hydrogeological evidence available as well as analytical determination by one or more of the isotopic techniques available. The former is inevitably important since the hydraulic regime dictates the evolution of the real system in terms of mixing of recharge from different sources and of different ages, leakage from other water sources, and so on, and therefore the real significance of groundwater ages. Conversely, deduction of palaeoclimatic influences on the composition of water at recharge (elemental chemistry, inert gas contents, stable isotopic composition) is limited by the same mixing phenomena. Dispersive mixing of water from different recharge conditions or of different ages but within the same hydrogeological unit will result in an averaging effect and loss of fine detail in any interpretation; this must be an inevitable

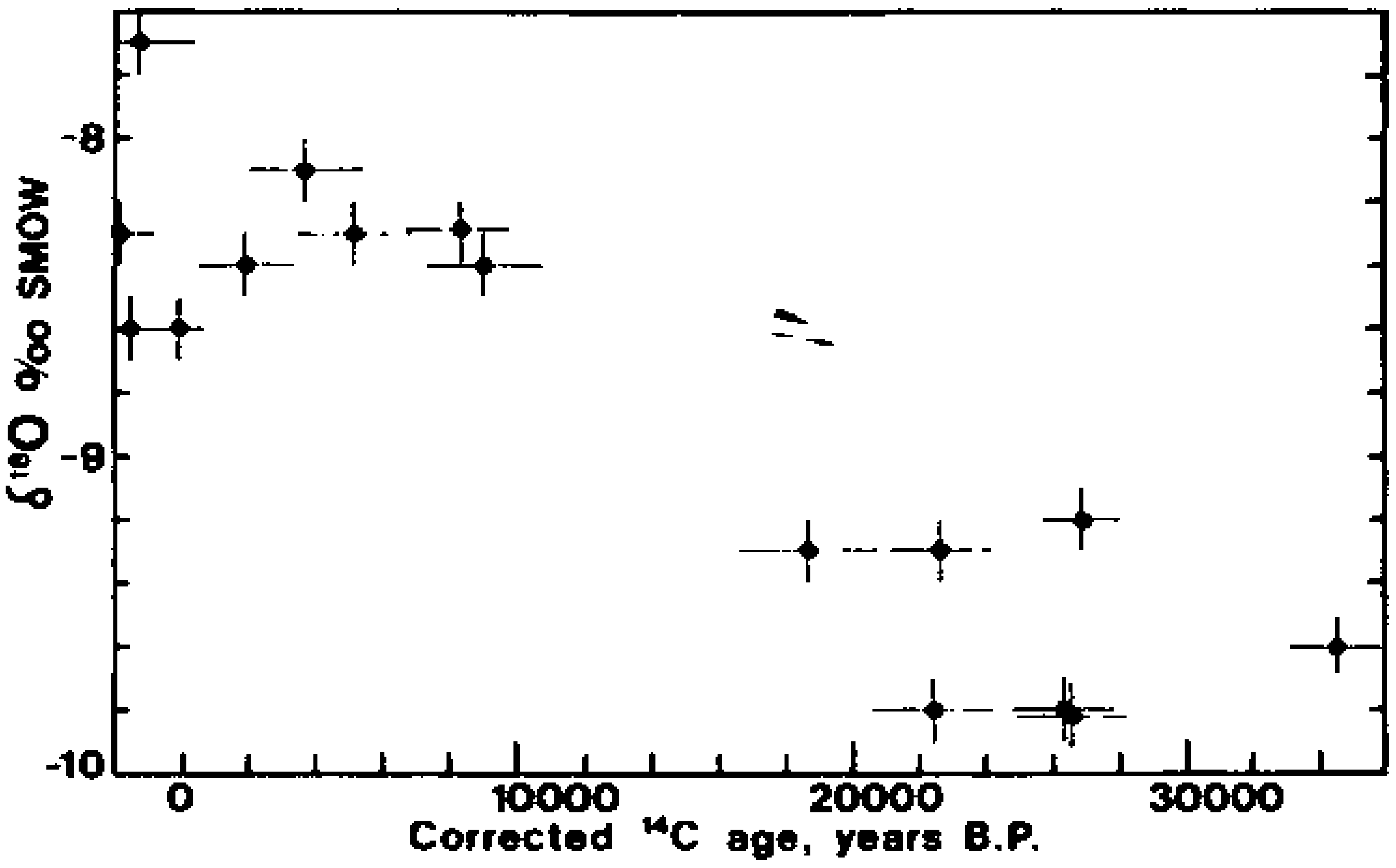

FIG.4. $^{18}O/^{16}O$ of East Midlands Triassic aquifer groundwater as a function of corrected ^{14}C age (see Ref. [14]*).*

phenomenon in any water mass of considerable age and particularly so in the more permeable formations that are usually the subject of aquifer studies. Mixing of water from different hydrogeological regimes, i.e. leakage, is a different matter and causes a loss of, or a false, signal [13]. It is becoming increasingly clear from the results of regional aquifer studies that isotopic methods must be applied to the solution of these mixing problems and the resolution of age patterns.

4.1. Aquifers in the United Kingdom

The hydrochemistry and isotope hydrology of the East Midlands Triassic sandstone aquifer reveals a systematic pattern in the groundwater that is related to recharge history [14]. The pattern of heavy-isotope-depleted groundwater with increasing age (Fig. 4) is typical of other studies in temperate countries of the northern hemisphere and has been interpreted to indicate the colder conditions of recharge prior to the last glacial maximum about 18 000 years ago. In this case, the interpretation is supported by an apparent interruption in the groundwater age spectrum, corresponding to the shift in $\delta^{18}O$ values and attributed to the reduction or cessation of infiltration during periglacial conditions. The stable isotopic composition of the older Triassic aquifer groundwater is significantly more depleted than that of groundwater of apparently comparable age in the Chalk of the London Basin [15].and also in the Lincolnshire Limestone aquifer [16] (Fig. 5). The disparity might be accounted for by real palaeoclimatic differences, and therefore a temperature difference of up to 7°C could be inferred if the smaller temperature coefficient [12] is applied. However, it seems more likely that the apparent disparity arises from the uncertainties that are inherent in the interpretation of groundwater radiocarbon ages in the three cases. In the latter two

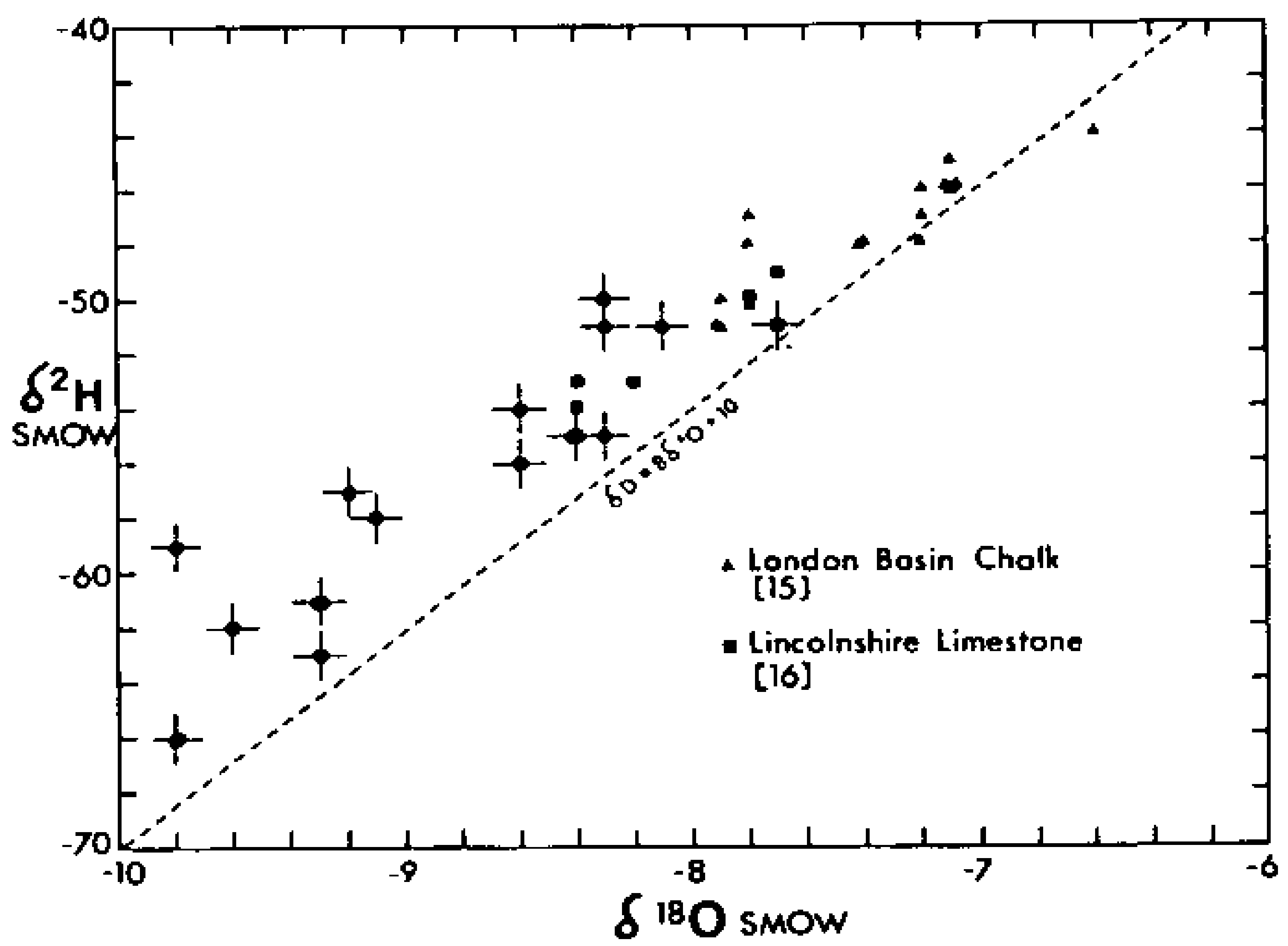

FIG.5. δ^2H versus $\delta^{18}O$ for groundwater samples from East Midlands Triassic aquifer, UK (from Ref. [14]). Regression line through these data is $\delta^2H = 6.6\delta^{18}O + 1.3$ ($r^2 = 0.83$). Data from groundwater samples with similar range of ^{14}C contents from London Basin Chalk (Smith et al. [15]) and Lincolnshire Limestone (Downing et al. [16]) aquifers are also shown.

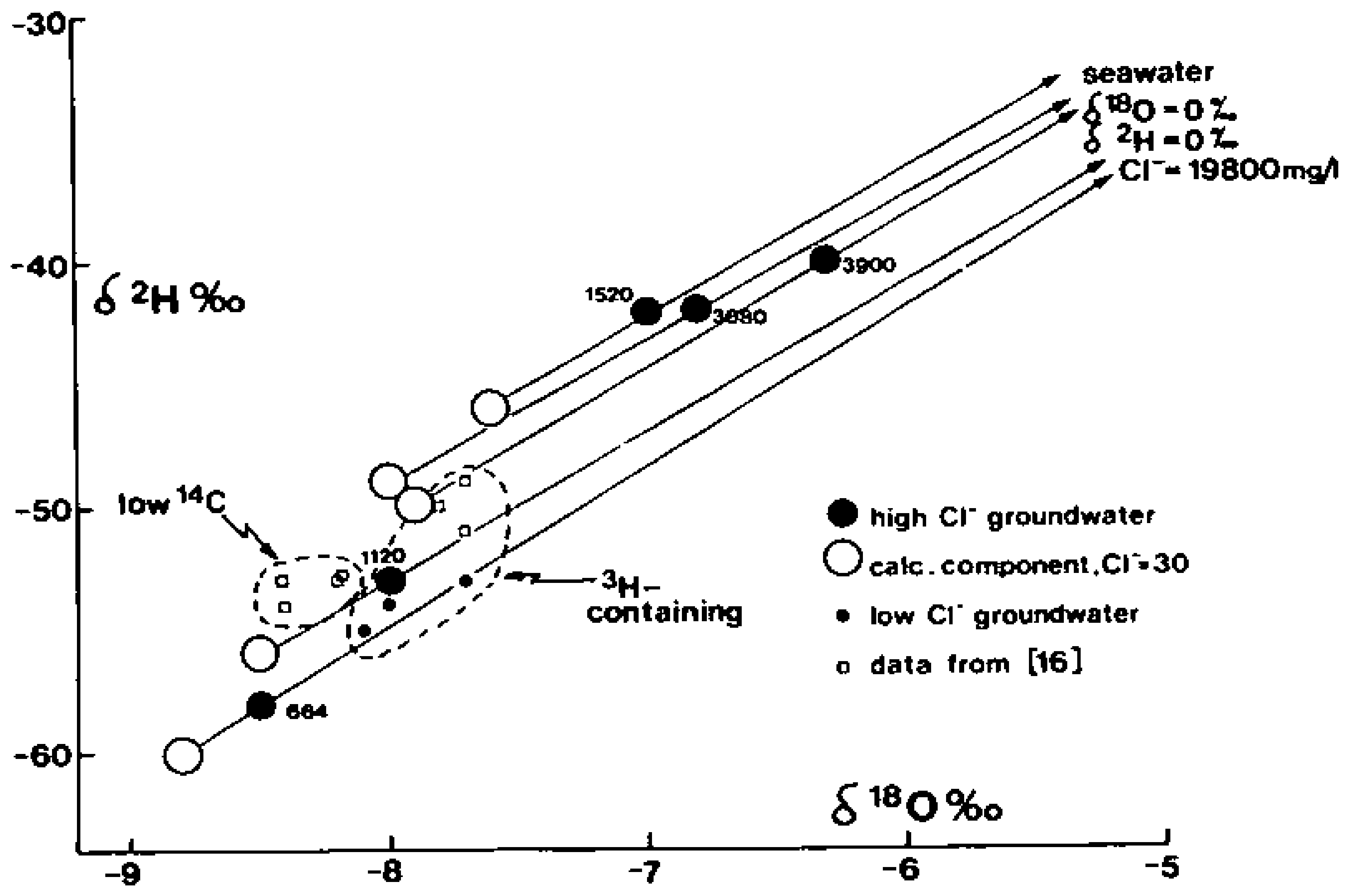

FIG.6. Illustration of mixing model by which isotopic and chemical composition of Lincs Limestone groundwater evolves. Solid points are data measured at IGS Wallingford laboratory with chloride concentration in $mg \cdot L^{-1}$. Open circles represent isotopic composition of fresh component, assuming groundwater is a two-component mixture between connate seawater as shown (pre-Pleistocene seawater was probably somewhat lighter than this) and meteoric water with $Cl^- = 30\ mg \cdot L^{-1}$.

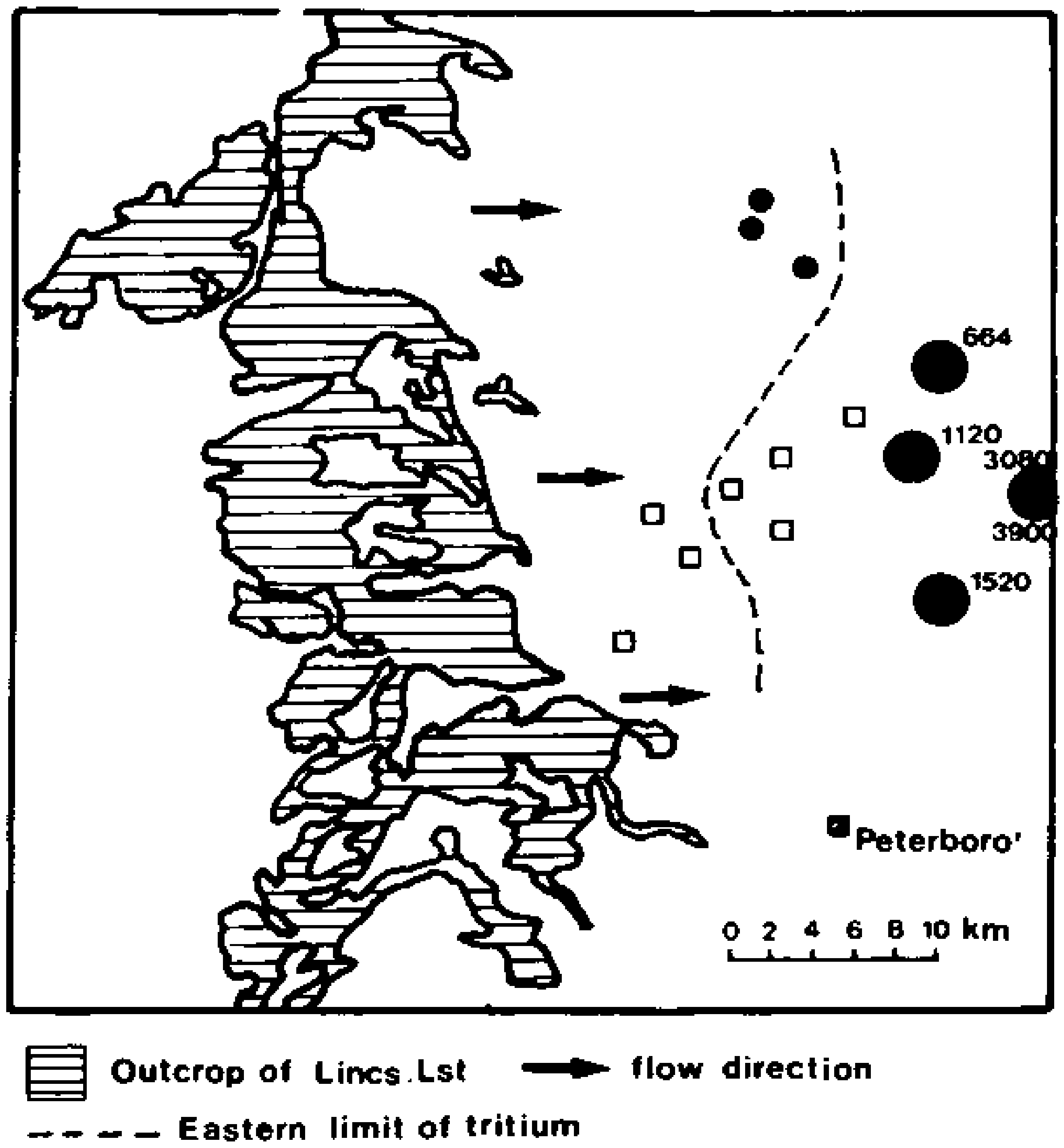

FIG. 7. Outline map of Lincs Limestone aquifer and location of sample points in confined aquifer. Symbols as in Fig. 6.

aquifers, down-gradient groundwater has very low negative $\delta^{13}C(HCO_3^-)$ values approaching isotopic equilibrium with the aquifer matrix carbonate, thereby introducing large errors into ^{14}C corrections; groundwater may have quite different maximum ages in the three aquifers. In the Triassic sandstone aquifer, the pattern of inert gas and stable isotope changes is reasonably consistent with independent palaeoclimatic records and lends some weight to the age interpretation [14]. The $\delta^{18}O$-δ^2H relationship between groundwaters of all ages in the East Midlands Triassic (Fig. 5) has slope and d-intercept very similar to those of the geographical variation of recently recharged groundwater (Fig. 3). Therefore, an analogy between the climatic factors giving rise to regional variations in modern precipitation composition and the palaeoclimatic changes causing secular change in groundwater composition is supported in this specific case.

The importance of mixing to the chemical and isotopic composition of very old, down-gradient groundwater has been impressively demonstrated in the case of the Lincolnshire Limestone aquifer, where the contents of both Cl^- and ^4He have been interpreted to represent a gradual mixing of very old connate water with the more rapidly moving water contained in fissures [17]. In this case the

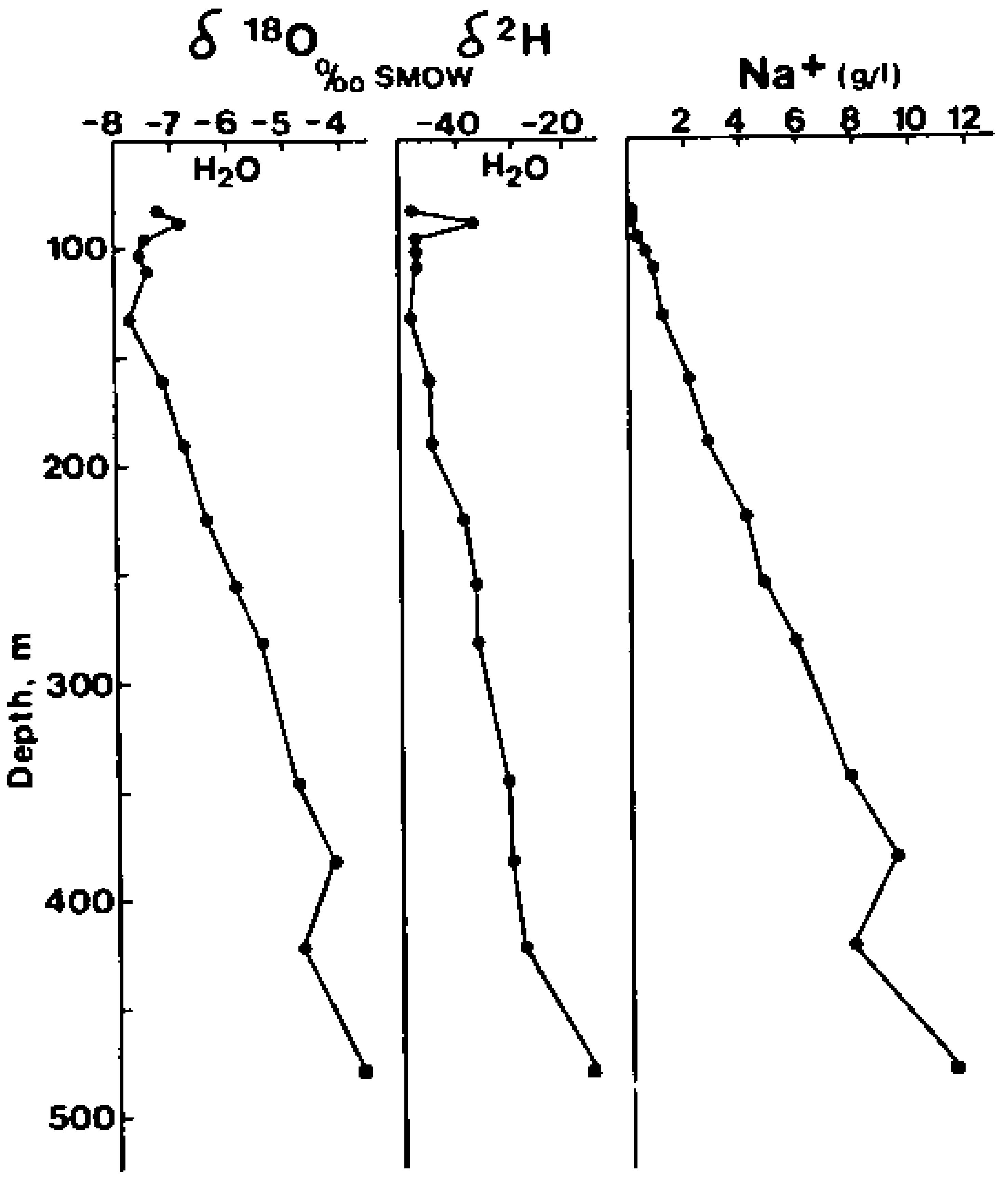

FIG.8. Depth profiles of isotopic and chemical composition of interstitial water from chalk in eastern England, illustrating mixing between connate seawater and meteoric water (Ref. [19]*).*

composition of the mixture between the two components clearly has no palaeoclimatic significance of its own, although it is possible to resolve the mixtures into two end-member components: a connate seawater and a fresh groundwater whose age extends back to that of Pleistocene recharge. The isotopic composition of the fresh component calculated from available analyses of pumped water indicates two groupings (Fig. 6): one similar to low-chloride, tritium-containing groundwater in the aquifer [16, 18] and the other being isotopically lighter and similar to the low-chloride, low-radiocarbon groundwater found in an intermediate location in the confined aquifer [16] (Fig. 7).

A predominantly diffusion-controlled mixing process is also found to operate in the interstitial solution retained in the sub-micron-scale voids of the English Chalk formation. Chalk is a micritic limestone which provides one of the most important UK aquifers in the more shallow, fissured parts of the formation. The interstitial solution is found to become more saline with depth, approaching the composition, modified by diagenesis, of the original connate seawater. This gradient in salinity is accompanied by an increasingly heavy isotopic composition of water (Fig. 8), and it can be demonstrated that the chemical and isotopic depth profiles are best described by a diffusion process modified by the additional effects of advection of meteoric water in the shallow part of the formation [19].

4.2. Aquifers in northern Africa

A major study of the groundwater contained in the Sirte and Kufra basins of the Libyan Sahara has revealed chemical and isotopic distinctions among waters recharged during the Late Pleistocene [20]. The important conclusion from this study is that the chemical and isotopic evidence is entirely consistent with the concept of episodic large-scale recharge corresponding to humid phases, or pluvials. The older pluvial inferred represents the major phase of palaeo-recharge across northern Africa and correlates with the Weichselian period of glacial advance over more northern latitudes (38 000–14 000 a BP). This phase of recharge is found in many aquifers in the region: those of Saudi Arabia [21], Qatar [22], the north-western Sahara [23, 24] and the eastern Mediterranean [25, 26]. In addition, evidence is found for a more recent humid episode in northern Africa. Groundwater beneath a relict wadi line is chemically and isotopically distinct and its radiocarbon content suggests an age around 8000 a B P [20]. Similarly distinct groundwater is found in the Grand Erg Occidental aquifer of the north-western Sahara [23].

The interpretation of the palaeoclimatic significance of the isotopically distinct groundwaters must also take account of the varying modification of palaeo-recharge composition as a result of evaporation. Evaporative enrichment in heavy isotopes along a slope of about 4.5 is apparent in the Kufra and Sirte Basins [20] as well as in the Grand Erg palaeo-recharge [23] and this feature has been used to identify recharge to the Continental Intercalaire by leakage from the overlying Grand Erg in the northern Sahara [24] (Fig. 9a). The evaporative modification is itself indicative of climatic conditions under which recharge took place. The data for the Kufra and Sirte Basins appear to suggest that evaporative enrichment increased with time (Fig. 9b), which is interpreted as indicating a gradual shift towards convective influences on rainfall in the Late Pleistocene and Early Holocene [20]. A similar model of monsoonal summer rainfall subjected to evaporation was proposed for the recharge to the Grand Erg [23].

The pattern of stable isotope compositions in the fossil (> 20 000 a BP) groundwaters of northern Africa has been compared with the pattern in present-day European groundwaters and attributed to a continental effect whereby the maritime influence from the west was dominant but with higher source region humidity than at present, giving rise to small d-excess [27]. However, Edmunds and Wright [20] infer a common source to the south for Pleistocene and Holocene rainfall. This is based on the interpretation of Kufra and Sirte groundwaters having had a common isotopic composition of recharging precipitation prior to evaporative modification and the comparison of this composition with the ranges of compositions found for present-day monsoonal rains in western Africa (Fig. 9). Thus the stable isotope data have been interpreted to be compatible with two alternative models for the dominant climatic conditions responsible for aquifer recharge, both models being based on analogies with present-day conditions. It

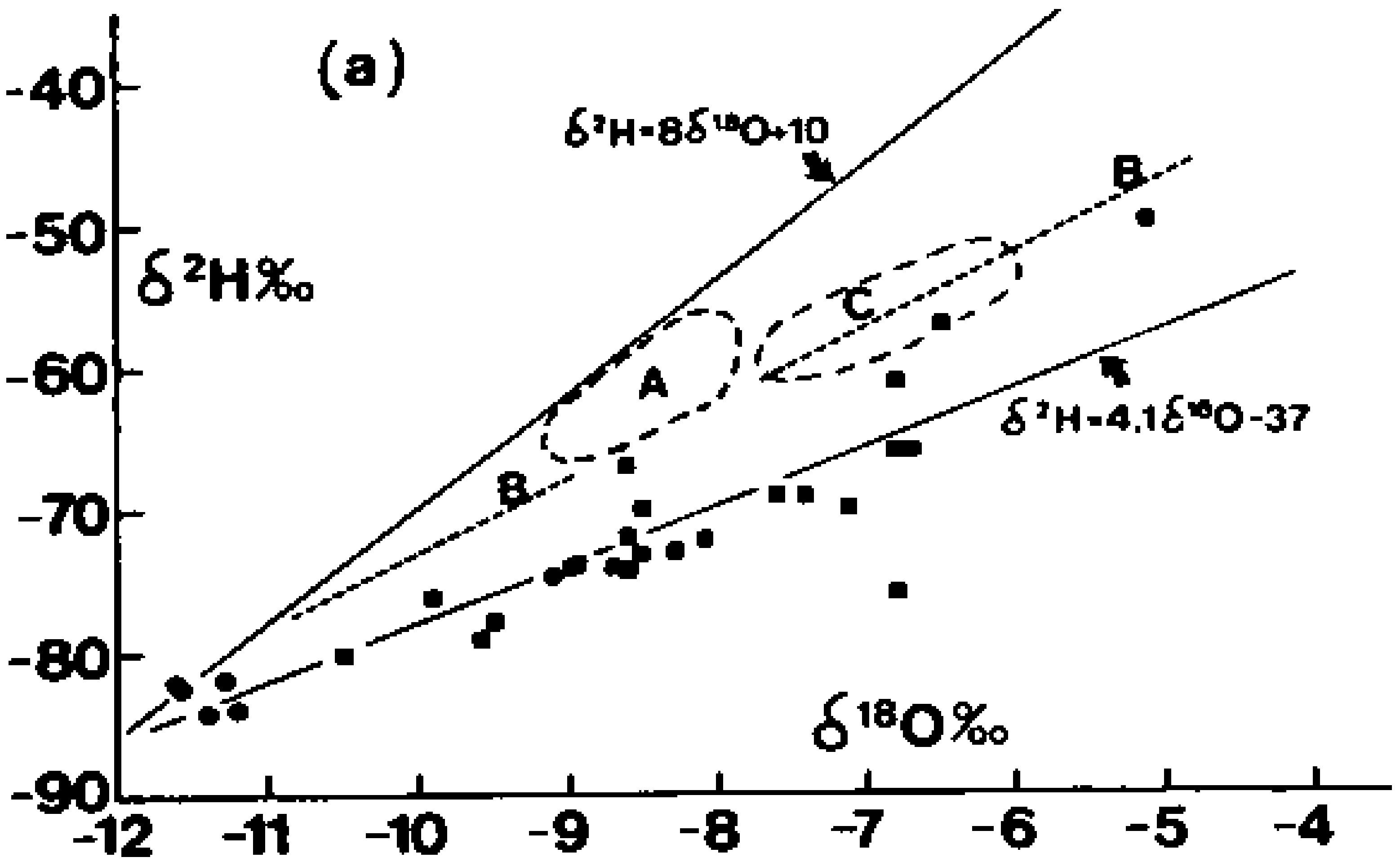

FIG.9a. *δ^2H versus $\delta^{18}O$ for groundwater samples from the Kufra (●) and Sirte (■) basins in Libya (Ref.* [20]*). Also shown are the data fields for groundwater from the eastern (A) and western (C) Continental Intercalaire aquifers demonstrating mixing in the latter of water from the Grand Erg (falling along line B) (Ref.* [24]*).*

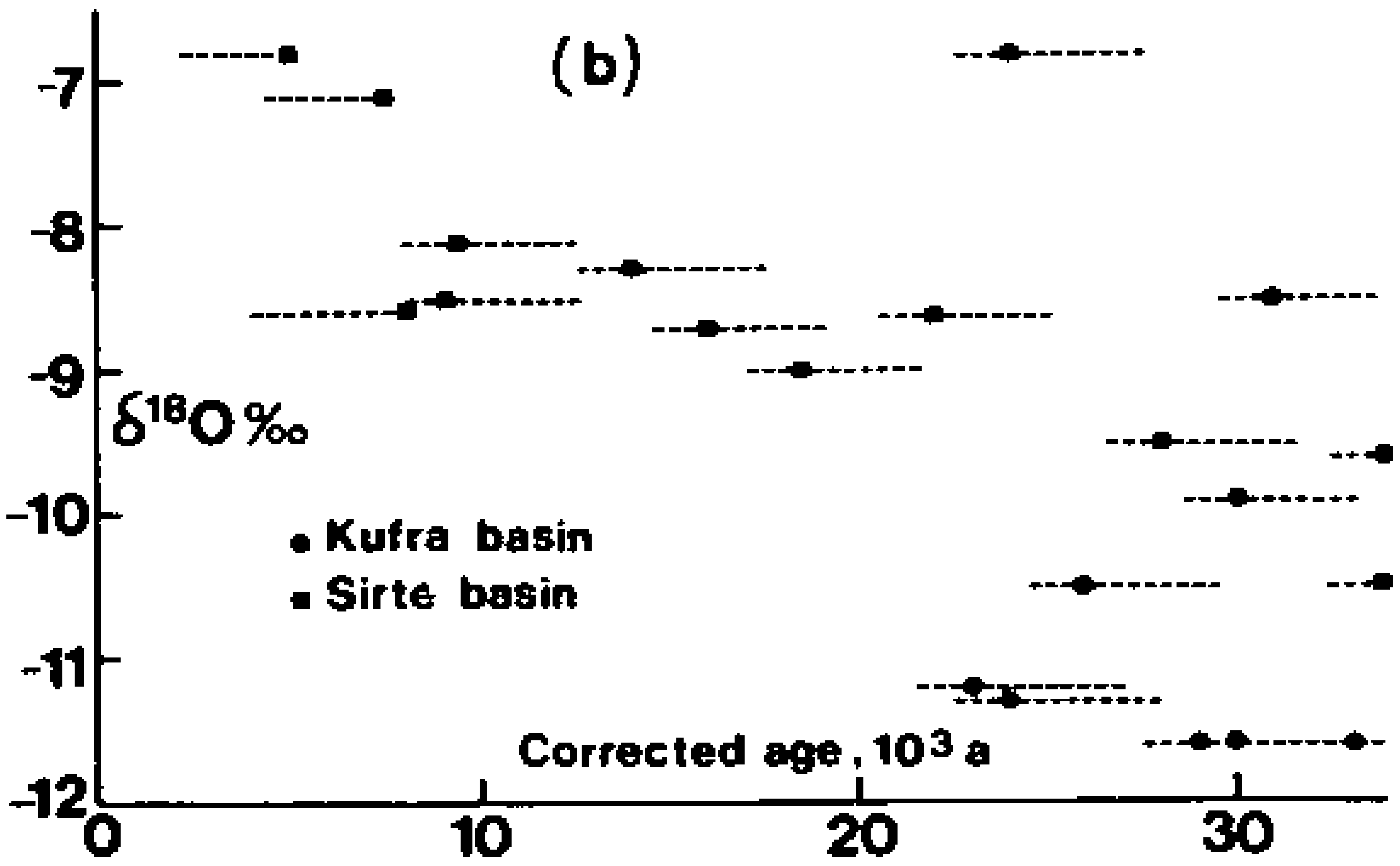

FIG.9b. Correlation between $\delta^{18}O$ and 'corrected' ^{14}C age in groundwaters of the Kufra and Sirte basins, Libya (Ref. [20]*).*

is possible that both processes might have contributed to rainfall over the 34 000–13 000 a BP period if the cyclonic circulation and zone of inter-tropical rain both moved southwards as has been suggested [28].

Further powerful evidence for palaeoclimatological changes can be found in stable carbon isotope data on the groundwater and also on calcrete. The $\delta^{18}C$ values for groundwaters attributed to the two distinct recharge episodes in Libya are quite different, with the more ^{13}C-enriched groundwater ($\delta^{13}C = -3.2‰$) being the younger and the late-Pleistocene groundwater having $\delta^{13}C$ between −5.6 and −11.7‰ [20]. The distinction between the two groups is interpreted to result from fundamental differences in the evolution of dissolved inorganic carbon.

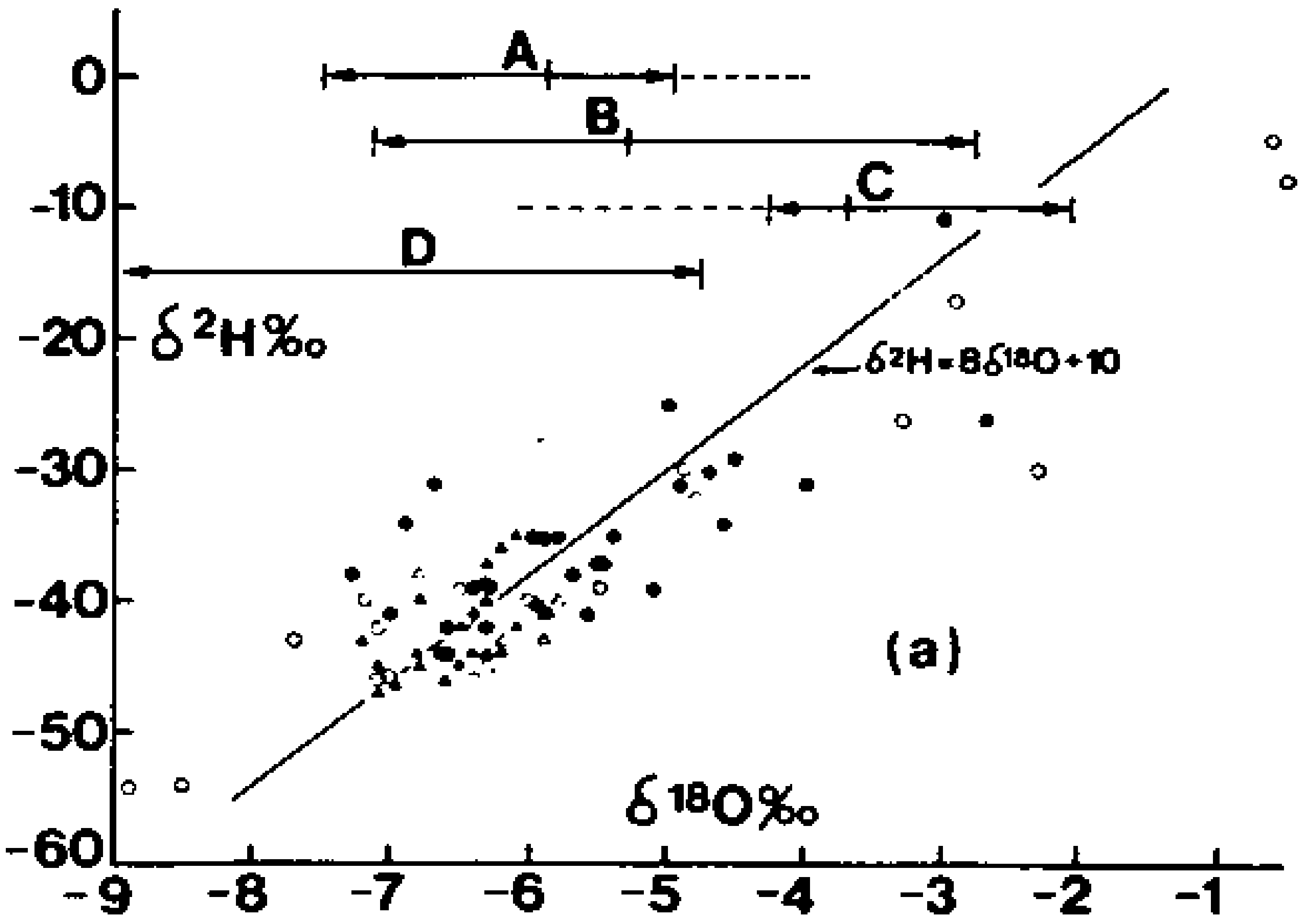

FIG.10a. δ^2H versus $\delta^{18}O$ for groundwater samples from Karoo (solid symbols) and other aquifers (open symbols) in the Kalahari region of Botswana (average rainfall in range 250–550 mm·a^{-1}). Sources of data are Mazor et al. [30] (● and ○) and Mazor et al. [31] (▲ and △). The ranges of weighted annual mean and overall weighted mean $\delta^{18}O$ for rainfall at Salisbury (A; 863 mm·a^{-1} average rainfall), Windhoek (B; 370 mm·a^{-1}) and Pretoria (C; 746 mm·a^{-1}) are also shown (data source [36]), and also the range of δ^{18}O reported for Namibian groundwaters of various ages (D; [33]).

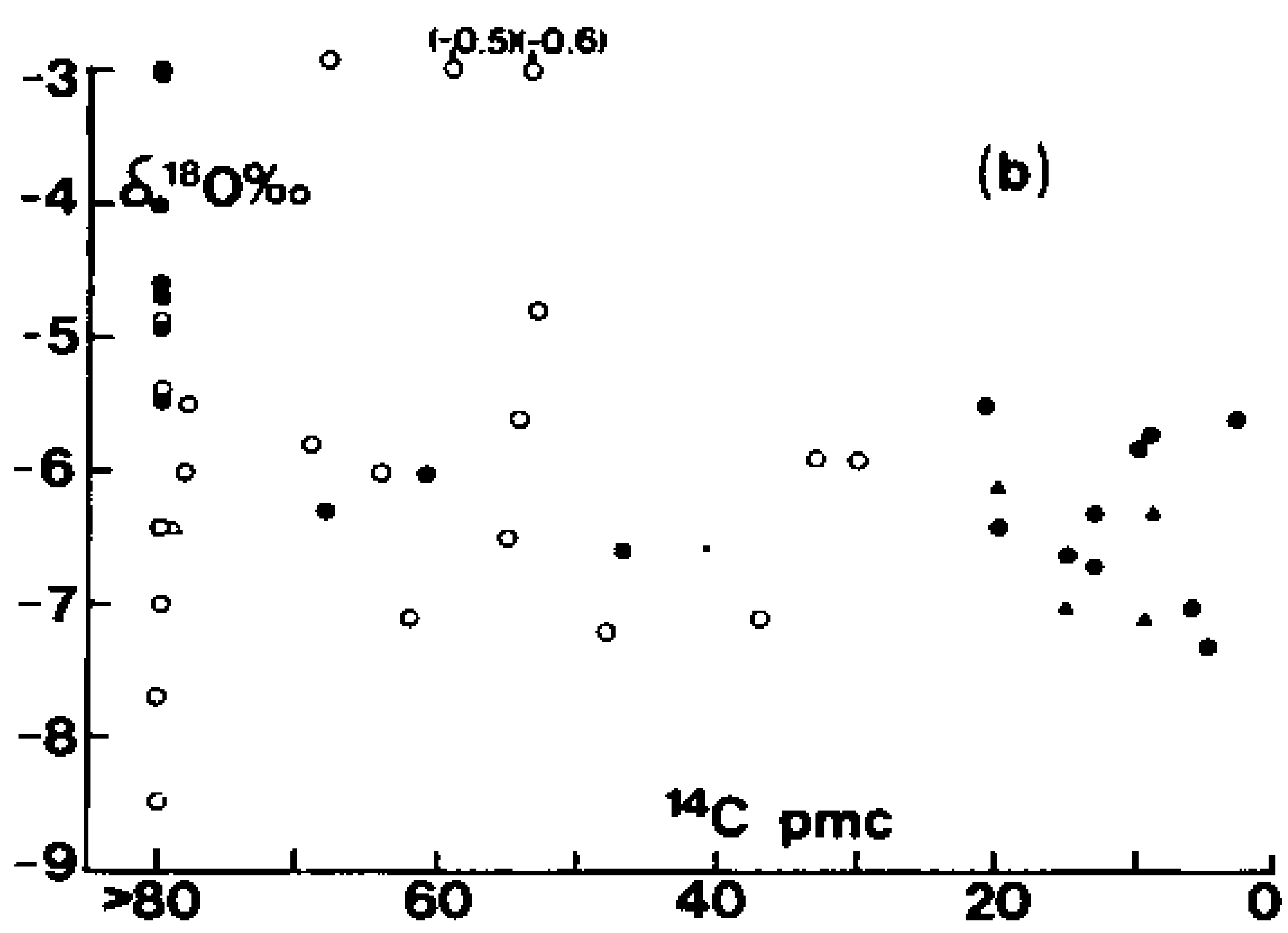

FIG.10b. $\delta^{18}O$ versus ^{14}C concentrations for Kalahari groundwaters [30, 31]. Symbols as in Fig. 10a.

The ^{13}C-enriched composition results from a predominance of inorganic carbon sources, i.e. atmospheric CO_2 and calcrete carbonate. Major calcrete formation would have taken place in the arid phase intervening between the two humid phases, when the water table was probably higher than at present. Calcrete formation itself is not only an important palaeoclimatic indicator and subsequent influence on the chemistry of infiltrating water, but it must also be an important factor in modifying the recharge mechanism when in the massive form as is found in the Kalahari formation in Botswana [29].

4.3. Aquifers in southern Africa

The pattern of palaeo-recharge to regional aquifers in southern Africa is much less clear than for those in northern Africa. The relative significance of episodic recharge accompanying gross climatic change against continuous but small-scale recharge is still not understood for these fossil groundwaters. Active recharge has been established for water table aquifers occurring in the aeolian Kalahari Beds in some parts of Botswana [30, 31] and also in South Africa [32]; however, the recharge history of the underlying aquifers, particularly those of the Karoo formation, is much less clear. No overall correlation is found between ^{14}C content and stable isotope composition, although quite a wide range of compositions (e.g. −8.5 to −3‰ $\delta^{18}O$) is found; the greatest scatter of isotopic composition is found among the modern groundwaters with high ^{14}C (> 80 pmc) and frequently positive tritium (Fig. 10b). However, groundwater in the Karoo aquifers does show some shift in isotopic composition with age, with the heavier isotopic compositions being found in the water table aquifers at the periphery of the Kalahari and the lighter compositions around −5.5 to −7.5‰ $\delta^{18}O$ occurring in the confined Karoo aquifers beneath Kalahari Beds cover (Fig. 10b).

Mazor et al. [31] argue in favour of a common source for both unconfined shallow aquifers and the semi-confined Karoo aquifer on the grounds of similar isotopic compositions in their study at Orapa (see Fig. 10a). The common source was suggested to be direct infiltration with minimal isotopic modification due to intermediate evaporation. It is possible that some of the isotopically heavier groundwaters sampled from water table conditions in the earlier general study by Mazor et al. [30] have suffered evaporative modification, shifting them to the right of the meteoric water line (Fig. 10a). The grouping of isotopic compositions between −5.5 and −7.5‰ $\delta^{18}O$ has been used as evidence for selective infiltration of heavy rainfall events with lighter-than-average compositions, by comparison with Pretoria rainfall (C in Fig. 10a) [30]; a similar argument was used in the case of Namibian groundwaters (D and B in Fig. 10a) [33]. However, the range and average of isotopic composition of modern precipitation over the Kalahari area are not known and therefore the exact relationship between compositions of rain and groundwater in Botswana is uncertain (note the much ligher composition of rain at Salisbury[1] – A in Fig. 10a). In summary, doubt remains as to whether palaeo-recharge to southern African aquifers can in general be identified by distinct stable isotopic composition, although the young groundwater found under water table conditions in the Karoo seems to be distinct from the bulk of the Karoo groundwater, which is old and low in ^{14}C. It may be that groundwater dominated by recent recharge and therefore with high ^{14}C is found only in atypical water table conditions, e.g. where superficial cover is thin or absent, which could explain the large variation in isotopic compositions (Fig. 10b). The pattern of stable isotopic composition against ^{14}C content, in contrast to the northern Africa case, does not on its own indicate recharge episodes in the palaeogroundwater, as distinct from continual recharge at very low rates during the late Pleistocene and Holocene.

The palaeoclimatic evidence suggests that a period of aridity in which sand dunes were active was terminated by a humid period commencing about 17 000 a BP [34, 35]. This humid period resulted in the formation of numerous small lakes in depressions caused by deflation action of the preceding arid phase [35]. It is therefore probable that major recharge to the sub-Kalahari aquifers occurred during this wet phase, corresponding to the late glacial phase of the northern hemisphere (17 000–15 000 a BP). This may account for the bulk of the Karoo groundwater such as that represented at the right of Fig. 10b with < 20 pmc ^{14}C. Lancaster [35] suggests that the increased precipitation fell as summer rains originating from a more southerly position of the ITCZ, by analogy with present years of abnormally heavy rainfall which correlate with persistence of the ITCZ at its southerly limit. It is these years of abnormally heavy rainfall that tend to show the relatively lighter annual average isotopic compositions for the regional stations of the IAEA/WMO monitoring network [36]. This model supports the proposal that sub-surface recharge is biased towards lighter isotopic composition relative to average precipitation as a result of selective infiltration [30, 33] but also implies an absence of secular change in this isotopic composition. There is no evidence for a humid phase early in the Holocene to correspond with that seen in northern Africa, and relative aridity seems to have been re-established by that time in the Kalahari region.

The massive calcretes that are widespread within the Kalahari Beds may owe their formation to the recession of the water table following the return to arid conditions. Two profiles through these calcretes, up to 20 metres thick, in the southern Kalahari have $\delta^{13}C$ values in the range -7 to $-9‰$ versus PDB, and other measurements have found $\delta^{13}C$ between -5 and $-6‰$ [30]. The range of $\delta^{13}C$ measured for dissolved bicarbonate in groundwater is between -13 and $-6‰$ [30], but there are no low negative $\delta^{13}C$ values such as those found in northern Africa for the early Holocene recharge and attributed to inorganic carbon reactions including calcrete dissolution [20].

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[1] Now Harare, capital city of Zimbabwe.

5. SUMMARY

(1) Although the value of stable isotopic compositions of groundwaters for palaeoclimatological reconstruction is limited, the importance of understanding past recharge regimes places emphasis on understanding the hydrochemical and isotopic evolution of groundwaters.
(2) The relationship between isotopic compositions of precipitation and groundwater recharge is still not completely understood even under present-day temperature conditions.
(3) The influences of mixing and leakage within the aquifer upon the isotopic signal must be considered. Hydrochemistry and other isotopic and inert gas measurements are applicable techniques.
(4) The isotopic record in the northern African aquifers provides evidence for episodic recharge. Comparison of various features of the isotopic compositions with proposed palaeoclimatic models permits estimates of the long-term significance of present-day recharge.
(5) Isotopic features of secondary climatic evidence such as calcretes are important lines of evidence and are particularly relevant in regard to their influence on recharge mechanisms.
(6) The recharge history of southern African aquifers is not well understood. Groundwater, and therefore its isotopic composition in the regional semi-confined aquifers, is dominated by palaeo-recharge. The significance of modern recharge in various environments, and whether its isotopic composition is distinct from that of older groundwater with which it is mixing, require further investigation.

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ISOTOPIC COMPOSITION OF GROUNDWATER IN THE SOUTHERN SAHARA

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Abstract

ISOTOPIC COMPOSITION OF GROUNDWATER IN THE SOUTHERN SAHARA.

In the southern Sahara, the ^{18}O and deuterium contents of old groundwater, i.e. groundwater with low ^{14}C content, are definitely lower than those of modern precipitation and of young groundwater, i.e. groundwater with high tritium and/or ^{14}C. In addition, there is a tendency of ^{18}O and deuterium of old groundwater to decrease towards the north because of a continental effect. On the contrary, modern waters seem to become enriched in heavy isotopes as aridity increases, that is, in the northern and eastern directions.

1. INTRODUCTION

The application of environmental isotope techniques to the study of Sahara desert groundwaters started in the early 1960s when isotope hydrology was still in its initial stages of development. It was immediately understood that isotope techniques are particularly useful when applied to arid zone hydrology. However, the majority of studies have been carried out in the northern and central Sahara, for which a selected list of papers is given in Refs [1–14]. Only a few isotope investigations have been performed in the southern Sahara and in the Sahel, that is, say, south of the 20th parallel. Here, the Lake Chad basin, the Bara basin and the Khartoum area in Sudan have been investigated in some detail, but most of the results have been discussed in various reports not easily accessible to the scientific community [15–19].

At present, groundwater studies with isotope techniques are being performed in the southern Sahara and in the Sahel by the Section of Isotope Hydrology of the IAEA, namely in Mali, Niger and the Sudan. Part of the isotopic data so far accumulated for projects now under way as well as from those done in the past are used in this paper, together with precipitation data from the IAEA/WMO global network. The subject of this paper, in fact, is the comparison of the isotopic composition of precipitation and of recent groundwater with that of old groundwater in the region of the Sahara between the latitudes of 20° and 10°N, with

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TABLE I. MEAN STABLE ISOTOPE PRECIPITATION DATA OF THE IAEA/WMO AFRICAN STATIONS IN THE NORTHERN TROPICAL BELT

				Mean yearly data					Mean data for August		
Station and country	Latitude	Longitude	Altitude (m a.s.l.)	Precipitation (mm)	Temperature (°C)	Relative humidity (%)	δD	$\delta^{18}O$	Precipitation (mm)	δD	$\delta^{18}O$
Bamako, Mali	12°38′N	8°02′W	332	1099	28.1	52	−27.5 (14)	−4.06 (15)	334	−38.6 (14)	−6.25 (15)
Kano, Nigeria	12°03′N	8°32′E	481	872	26.1	45	−23.5 (6)	−3.75 (8)	311	−35.9 (6)	−5.62 (8)
N'Djamena, Chad	12°08′N	15°02′E	295	646	27.9	46	−19.9 (11)	−3.70 (13)	257	−32.3 (10)	−5.61 (12)
Faya Largeau, Chad	18°00′N	19°10′E	234	16	28.7	26	−11.8 (3)	−1.27 (2)	11		
Geneina, Sudan	13°29′N	22°27′E	805	549	24.2	37	−8.5 (7)	−1.92 (9)	230	−19.1 (6)	−2.95 (9)
Khartoum, Sudan	15°36′N	32°33′E	380	164	28.7	32	−9.2 (8)	−2.03 (8)	72	−15.9 (7)	−2.93 (7)
Addis Ababa, Ethiopia	9°00′N	38°44′E	2360	1089	16.8	61	+1.4 (6)	−1.47 (8)	236	−15.1 (8)	−3.58 (9)

N.B. The figure in brackets below the δ-values is the number of years for which the isotopic measurements are available.

the aim of obtaining information on the climatic conditions that occurred in the past.

The major geological and hydrogeological outlines of the southern Sahara are similar to those occurring in the north. The Pre-Cambrian crystalline basement outcrops at a latitude of about 20°N to form the mountain ranges of Ahaggar, Aïr and Tibesti, and, more to the south-east, that of Marra. Elsewhere, the basement is overlain with sedimentary formations of age ranging from Palaeozoic to Quaternary, gently dipping to the south. The main water-bearing formations are the Palaeozoic deposits (predominantly porous sandstones), the Nubian Sandstone of Middle Cretaceous age (practically equivalent to the so-called Continental Intercalaire), the Eocene-Oligocene deposits (mainly sand and clay inter-bedded, known also as Continental Terminal) and the Quaternary alluvial and aeolian deposits.

South of the 13th parallel the basement outcrops again. Here, the groundwater is contained in the weathered rocks at shallow depth and in the network of fractures that extends to considerable depth in the crystalline rock.

The climatic conditions range from arid to hyper-arid in the north (with less than 20 mm of mean precipitation per year and frequent years with no precipitation at all) to Sudano-Sahelian in the south, with a long dry season (October to May) and a shorter rainy season (June to September). In this latter area the yearly mean precipitation ranges from 400 to 1000 mm.

2. ISOTOPIC DATA

2.1. Precipitation

The weighted mean contents of deuterium and ^{18}O of precipitation at seven African stations in the northern tropical belt are given in Table I. Also the mean values of the most rainy month (August) are included. The isotopic composition of recent groundwater is supposed to lie between these two values, perhaps closer to that of August. (The values of Faya Largeau are, however, doubtful, due to the short period of observation and the extreme aridity of the site.)

Values for mean precipitation, temperature and relative humidity are taken from Ref. [20]; isotopic values are from [21] and from IAEA files on isotopes in precipitation.

2.2. Groundwater

Table II includes the mean stable isotope composition of selected groundwater samples from seven areas in the southern Sahara indicated in Fig. 1. These

TABLE II. MEAN VALUES OF THE STABLE ISOTOPE COMPOSITION OF GROUNDWATER IN THE SOUTHERN SAHARA

	Mali West	Niger West	Niger North	Chad basin	Chad North	Sudan Bara	Sudan Khartoum
Precipitation[a] (mm/a)	1099	636	164	450	16	418	164
Young groundwater							
$\bar{\delta}^{18}O$‰	−5.08	−4.18	−3.12	−5.28	-1.27^{b}	−3.27	−2.59
σ_1	0.60	0.45	–	0.99		0.65	0.83
$\bar{\delta}D$‰	−33.5	−26.0	−19.2		-11.8^{b}	−22.5	−8.0
σ_1	3.8	2.8	–			6.6	7.1
n	20	4	2	26		25	4
Old groundwater							
$\bar{\delta}^{18}O$‰	−6.89	−7.35	−7.43	−6.66	−9.62	−6.65	−9.49
σ_1	–	−0.60	0.69	0.78	–	0.89	0.75
$\bar{\delta}D$‰	−49.6	−51.5	−57.3			−50.9	−69.3
σ_1	–	4.2	2.7			6.6	6.4
n	2	7	13	17	3	6	5
Difference young-old							
$\delta^{18}O$‰	1.81	3.17	4.31	1.38	8.35^{c}	3.38	6.90
δD‰	16.1	25.5	38.1			28.4	61.3

[a] Precipitation values are from [20] and refer to the following stations: Bamako for Mali West, Niamey for Niger West, Agadès for Niger North, average of 7 stations (Zinder, N'Guigmi, Mainé Soroa, Maiduguri, Mao, N'Djamena, Moussoro) for Chad basin, Faya Largeau for Chad North, El Obeyd for Sudan Bara and Khartoum for Sudan Khartoum.

[b] Precipitation values of Faya Largeau (see Table II).

[c] Using precipitation value for the young groundwater.

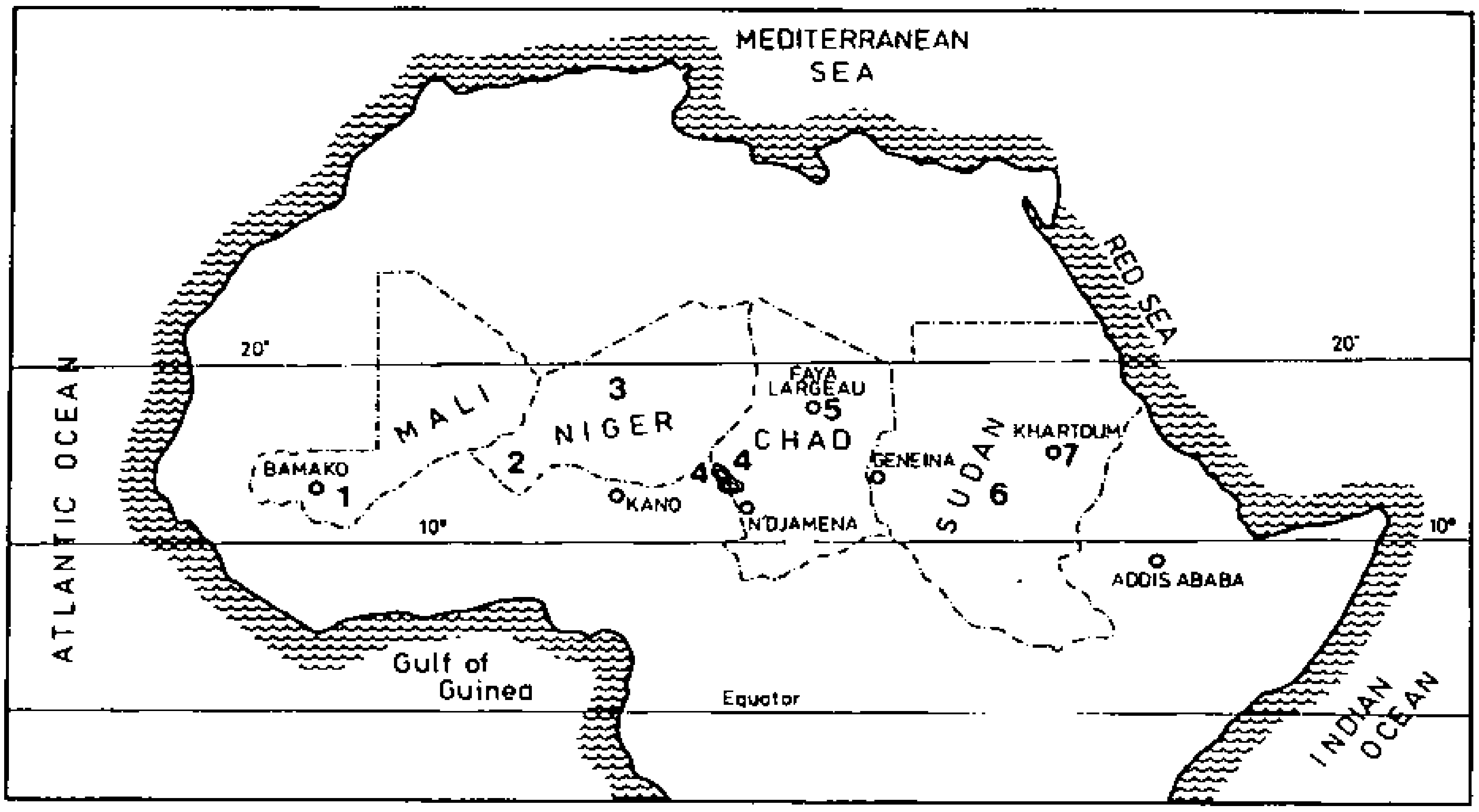

FIG. 1. Map of Africa showing the stations of the IAEA/WMO network in the northern tropical belt, for which the isotopic composition of precipitation is known (Table I) and the areas in southern Sahara for which isotopic data on groundwater are available (Table II). Code: 1, Mali West; 2, Niger West; 3, Niger North; 4, Chad Basin; 5, Chad North; 6, Sudan Bara; 7, Sudan Khartoum.

areas are: the basin of Bamako in Mali (No. 1 of Fig. 1), Niamey-Dallol Maori in western Niger (No. 2), Agadès-Arlit in northern Niger (No. 3), the Chad basin around Lake Chad (No. 4), Faya Largeau in northern Chad (No. 5), the Bara basin (No. 6) and Khartoum (No. 7) in Sudan. The isotope values derive from current IAEA projects and from Refs [16, 18] for Chad and [19] for Sudan. For each area the samples have been subdivided into two groups: the young groundwater and the old groundwater.

The term 'young' refers to groundwater that has been recharged within the last two or three millennia, during which the climatic conditions have always been similar to the present ones, according to current knowledge. Therefore, the ^{14}C content of this groundwater should be high and, for very recent samples, the tritium content too should be well above the detection limit.

Of the 81 samples considered young, the ^{14}C analyses are available for only 34. Of these, 33 have ^{14}C content well above 50% of modern and 1 (from the Bara basin) contains only 42% of modern; however, the $\delta^{13}C$ value (−2.5‰ versus PDB) indicates a rather extensive isotopic exchange with the aquifer matrix and, consequently, the age computed from ^{14}C using a correction method based on ^{13}C only [13] is recent. Among the remaining 47 samples, 29 have a tritium content of 2 TU or more and therefore contain recent water (although in principle values of 2–20 TU may also result from mixing of modern and old water) and 18 have been considered young on the basis of hydrogeological considerations only.

The great majority of the young groundwater samples derive from unconfined, shallow Quaternary aquifers. Only 15 derive from other aquifers: 10 from the Palaeozoic aquifer outcropping in the Bamako basin (9 of them have a ^{14}C content higher than 80% of modern and one has 65%), 4 having high tritium from the Nubian Sandstone in Niger and Chad and 1 with high tritium and high ^{14}C from the Chad formation.

Only groundwater samples from sites distant from Lake Chad or from the Nile in the Khartoum area have been used for the computations of Table II. These surface water bodies have an isotopic composition strongly affected by evaporation and, in addition, derive from precipitation and runoff over large basins with prevailing climatic conditions quite different from those of the sampled areas. Both Lake Chad and the Nile significantly affect the isotopic composition of groundwaters near them, which then do not reflect that of local recharge from precipitation.

The mean isotopic composition so computed for young groundwater in the Chad basin is $\delta^{18}O = -5.28$, which is very close to the value of August precipitation in N'Djamena and to the most negative δ-values observed in sand dune groundwater in the vicinity of Lake Chad [15, 17]. Also the computed mean isotopic composition of young groundwater in the Khartoum area corresponds quite well to that of local precipitation; in this case, however, the contribution of the river cannot be excluded on isotopic grounds because the wells selected are at a distance of 10 km or more from the right bank of the Blue Nile, the isotopic composition of which is similar to that of precipitation at Khartoum [19], especially during the high flow period from late summer to autumn when evaporation effects may become negligible. The Blue Nile derives, in fact, from the Ethiopian highlands, where the isotopic composition of precipitation is also similar to that at Khartoum, as can be seen in Table I (Addis Ababa).

The term 'old' is used for groundwater that has been recharged more than about 6000 years ago, when climatic conditions were generally more humid than the present ones. All the samples of this type selected for the present discussion, therefore, must have a low ^{14}C content and should obviously not contain any appreciable amount of tritium.

The ^{14}C measurement is available for 49 of the 53 groundwater samples selected. In 44 cases the ^{14}C content is below 5% of modern, which produces an age well above 20 000 years with the computation method using the $\delta^{13}C$ value for correction. In the 5 remaining cases the ^{14}C content ranges from 12.7 to 39.2% of modern and the computed age from 6000 to 10 000 years. The other 4 samples for which the ^{14}C measurement is not available (but all of them have a tritium content below 1 TU, although this is a necessary but insufficient condition to classify them as old) have been included in this group on hydrogeological grounds.

All the samples but two included in the old groundwater group derive from deep wells exploiting the following aquifers: Cambrian (Mali), Carboniferous (Niger North), Nubian Sandstone or Continental Intercalaire (Niger West, Chad, Sudan Bara and Sudan Khartoum), Continental Terminal (Chad) and the Plio-Quaternary Chad formation. The two remaining samples are from a spring and from a nearby shallow well in northern Chad, which drain water from the Tertiary aquifer.

Also for old groundwater samples there is the risk that some of them may contain water isotopically modified by evaporation before infiltration. This can occur especially in the Chad basin, considering that Lake Chad has been much wider in the past. For instance at about 7000 a BP the lake extended from 19° to 10°N with a surface area that reached at the moment of its maximum expanse approximately 500 000 km^2, that is, 25 times the surface of the modern lake [22]. However, the evaporation effect, if any, on the isotopic composition of Chad basin groundwater seems to be negligible, as can be inferred from the few pairs of δD-$\delta^{18}O$ values available.

3. DISCUSSION

The histogram of Fig. 2 includes all the $\delta^{18}O$ values measured in groundwater samples from the southern Sahara, which can be classified either young or old from their ^{14}C or tritium content or from hydrogeological considerations. The histogram clearly shows that young groundwater is, as a whole, enriched in heavy isotopes as compared with old groundwater. The reason for such a difference in isotopic composition, which parallels that observed in the northern Sahara, is the climatic change with a drastic decrease of precipitation that occurred during the Holocene.

Much more instructive, however, is the series of histograms of Fig. 3, where the $\delta^{18}O$ values have been plotted separately for each area. The various histograms appear in the figure in order of decreasing precipitation (or of increasing aridity) from the top. The following facts can bė observed from Fig. 3 and Table II:

(1) There is, in general, very good agreement between the isotopic composition range of precipitation and that of young groundwater, as should be expected if the latter is locally recharged.

For the Chad basin, however, the $\delta^{18}O$ distribution in young groundwater is clearly skewed towards the more negative values. This indicates simply that some of the samples, included in the group on the basis of their tritium content, consist of mixtures of young and old groundwater. In some cases this conclusion could

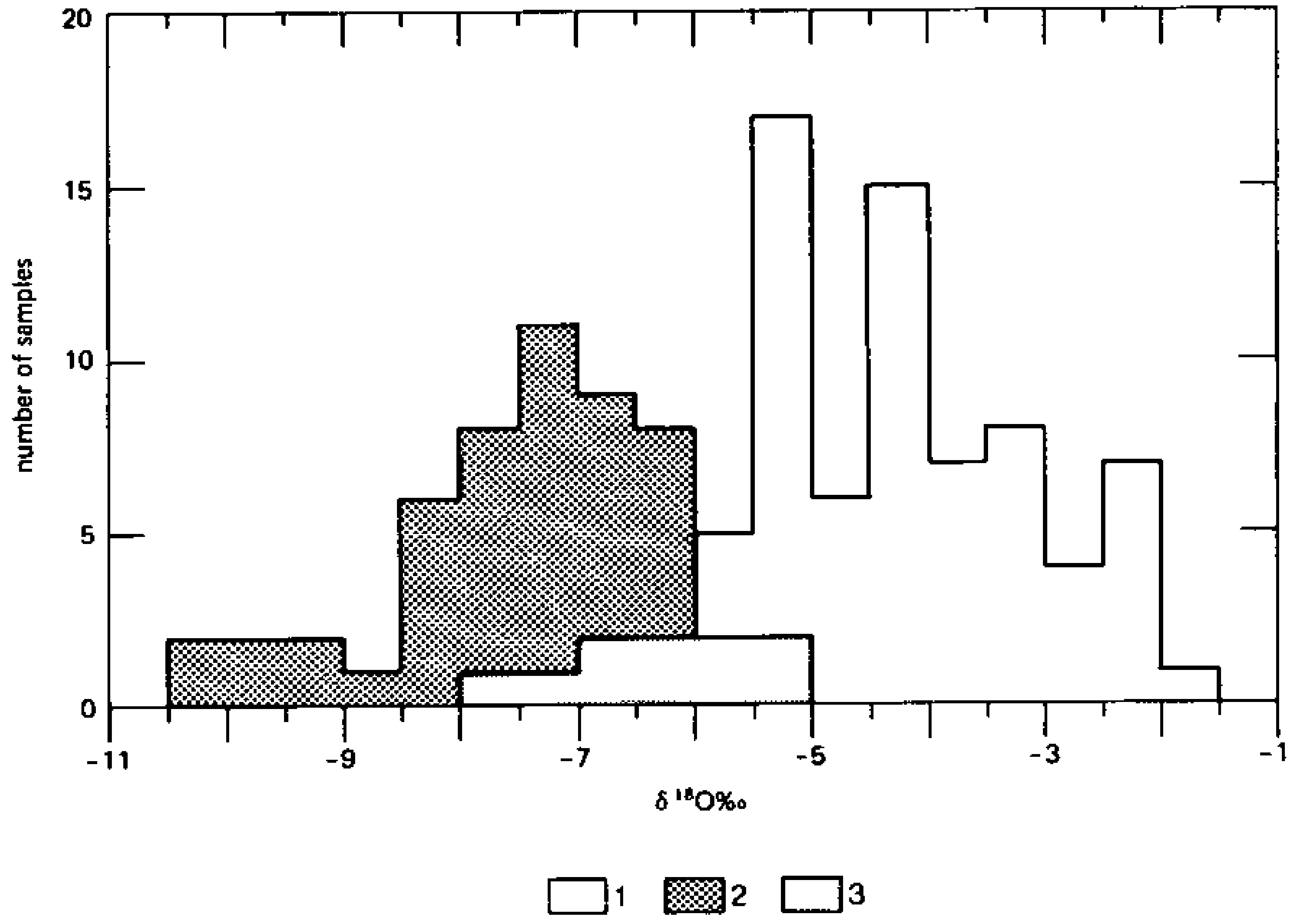

FIG. 2. Histogram showing the ^{18}O distribution in all groundwater samples used for this paper: (1) young groundwater; (2) old groundwater; (3) area common to both groups.

perhaps have been anticipated on hydrogeological grounds, e.g. for the three samples with the most negative $\delta^{18}O$ values and tritium concentrations of few TU (no ^{14}C value available) that derive from wells in the Continental Intercalaire located on the north of Zinder (Niger), in the western part of the Chad basin. Here, the Continental Intercalaire outcrops and the occurrence at shallow depth of mixtures of old and young groundwater can also be inferred from comparison with deep wells.

(2) There is a tendency of the heavy isotope content of precipitation and of young groundwater to increase slightly as aridity increases. In the case of Faya Largeau (Chad North) precipitation this enrichment can be attributed to evaporation during rainfall, as indicated by the low deuterium excess (Fig. 4). Less clear in other cases is the reason for the heavy isotope enrichment, the deviations from the meteoric water isotopic line, if any, being much less important. The trend observed is practically the reverse of that which should be produced by the so-called continental effect, by which the heavy isotope content should rather decrease in the northern and eastern directions.

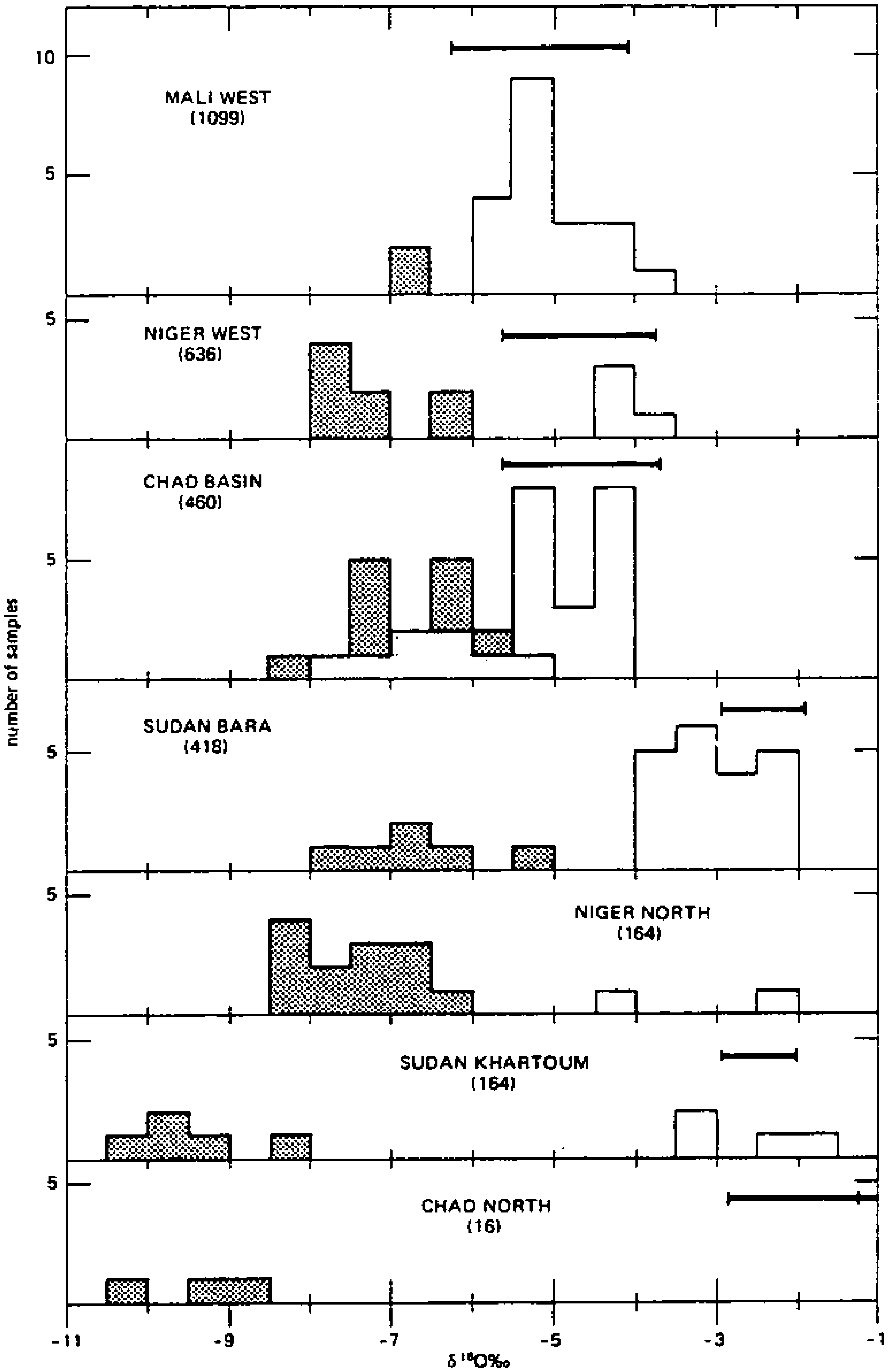

FIG.3. Histograms showing the ^{18}O distributions in groundwater in each area of Table II. The figures in brackets are the mean annual precipitation in mm, as reported in Table II. The bars show the range of isotopic composition of precipitation at each site given by the weighted mean annual value and the weighted mean value of the most rainy month (August). The following stations have been used: Bamako for Mali West, Kano for Niger West, N'Djamena for Chad Basin, Geneina for Sudan Bara, Khartoum for Sudan Khartoum and Faya Largeau for Chad North. Although Kano and Geneina are rather distant from the areas for which they have been used as reference, they are at about the same latitude and in very similar climatic and meteorological situations.

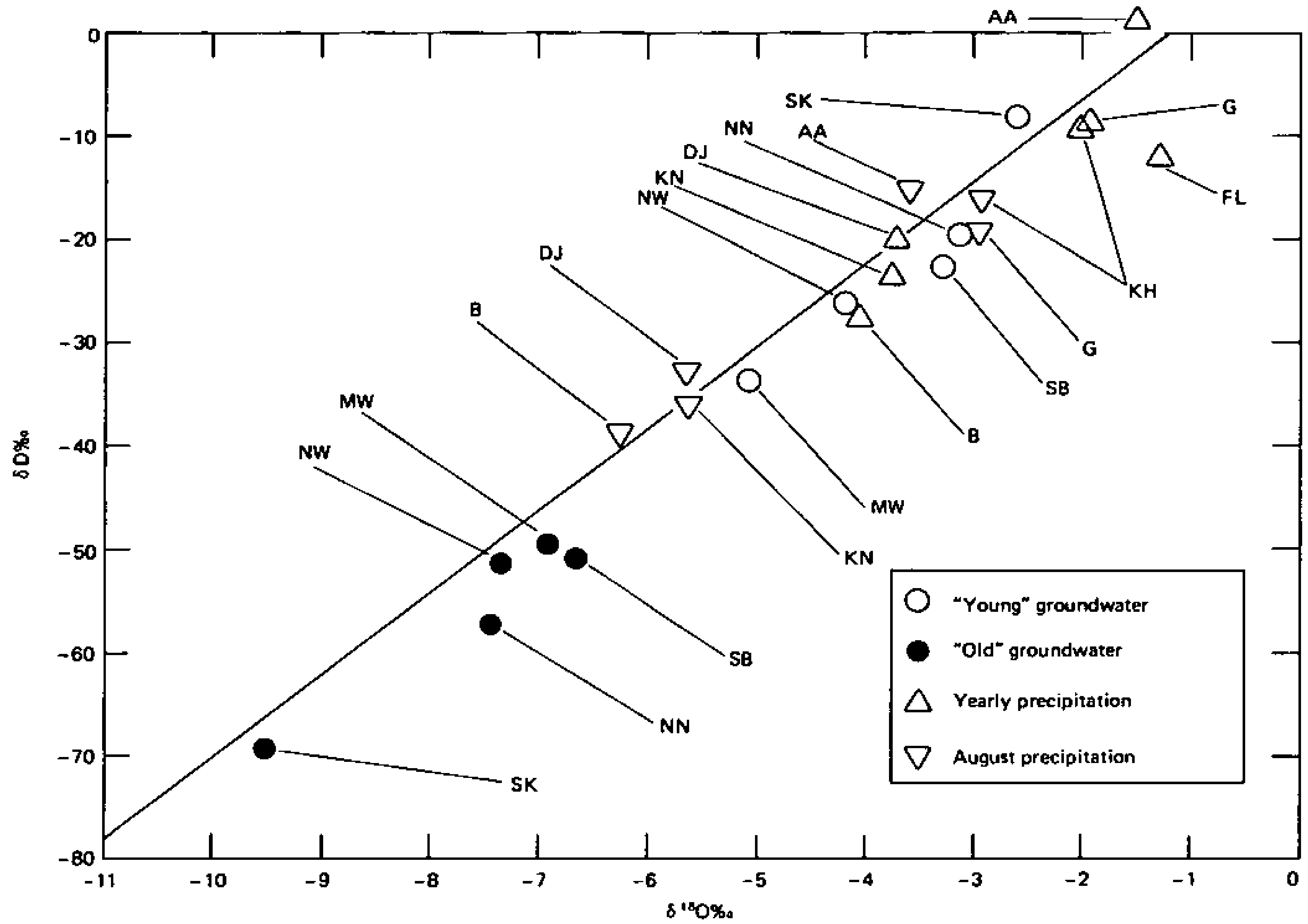

FIG.4. Deuterium-^{18}O plot of precipitation and groundwater mean values of Tables I and II. Code: AA, Addis Ababa; B, Bamako; DJ, N'Djamena; FL, Faya Largeau; G, Geneina; KH, Khartoum; KN, Kano; MW, Mali West; NN, Niger North; NW, Niger West; SB, Sudan Bara; SK, Sudan Khartoum.

(3) The old groundwater shows a reverse tendency with respect to that of young groundwater, with $\delta^{18}O$ and δD values that become more negative in the direction of presently increasing aridity. This is particularly evident, however, only for the most northern areas, i.e. Niger North, Sudan Khartoum and Chad North. This trend can be attributed to the south-north continental effect occurring on the isotopic composition of past precipitation, during the northwards displacement of the monsoon front.

The west-east component of such a continental effect seems much less effective than the south-north one, contrary to that observed in the northern Sahara [10]. In fact, there is no significant variation in the isotopic composition of old groundwater between Mali West, Niger West, the Chad basin and Sudan Bara. Probably the reason for such a difference between the northern and the southern Sahara is the following: in the northern Sahara, the major source of atmospheric moisture in the past was the Atlantic, with only a limited contribution from the Mediterranean, and therefore a strong west-east continental isotope effect was produced on the precipitation. In the southern Sahara, the moist air masses derived from the Atlantic on the west, the Gulf of Guinea in the south and the Indian Ocean in the south-east; it seems reasonable, therefore, that the south-north component of the continental isotope effect should have prevailed on the west-east component.

To some extent, the meteorological conditions in the ancient southern Sahara can probably be compared with those occurring now in the Indian subcontinent: here, the moist air masses derive from the Arabian Sea to the south-west and, in a minor proportion, from the Gulf of Bengal to the south-east. Therefore a noticeable south-north variation of isotopic composition of precipitation should occur, and the longitudinal variation should be much smaller.

(4) In a δD-$\delta^{18}O$ plot (Fig. 4) some of the old groundwater values lie below the present world meteoric water line. Such a deviation, which has also been observed in northern Sahara groundwater, would reflect more humid climatic conditions on a global scale according to current isotopic models of precipitation [23].

In conclusion, in the southern Sahara, as in the northern Sahara, the isotope composition of old groundwater recharged during the late Pleistocene and the early Holocene reflects the humid climatic conditions prevailing at that time. Therefore, also in the southern Sahara the stable isotope composition of groundwater can be used to identify recent recharge and to distinguish between it and old groundwater: needless to say, this considerably enhances the usefulness of the isotopic tool in groundwater resources investigations in arid areas.

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STABLE ISOTOPE STUDIES ON PALAEOWATERS

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Extended Synopsis

Four examples are given for ^{2}H and ^{18}O content of water samples taken from aquifers with groundwaters formed during the last ice age and the subsequent post-glacial epoch or during a pluvial period in the same time span.

In Libya, isotope investigations were carried out in the course of regional hydrogeological studies in the area of the north-eastern extension of the Hamada al Homra basin and its extreme eastern part including the Hun Graben [1]. Carbon-14 model ages of all investigated groundwaters extend from 8000 a up to maximum detectable ages (≈ 35 000 a). The δ^2H-δ^{18}O relation[1] allows classification of the groundwaters into two groups. In Group I, characterized by relatively low ^{14}C model ages (<20 000 a), there are δ^{18}O values from −5.8 to −7.5‰ and δ^2H values from −35 to −50‰ scattered around the line δ^2H-8 δ^{18}O + 10, corresponding to the meteoric water line in middle Europe. Group II, with high ^{14}C model ages (>20 000 a), comprises considerably lower δ-values (see Fig. 1) and Refs [1–5]) situated on the line $\delta^2H = 8\,\delta^{18}O + 4$.

In Saudi Arabia, various environmental isotope studies were performed as part of a combined sedimentological, hydrogeological, hydrochemical, geomorphological and climatological project in the central and eastern Arabian peninsula [5]. Also in this region, two isotopically different types of groundwater have been found: samples taken from shallow Wadi aquifers (e.g. from Wadi Hanifah near Riyadh) contain bomb tritium and show, as expected for recent waters, a similar δ^2H-δ^{18}O relation as of precipitation in the eastern Mediterranean region [6] with an intercept of d = 23‰. In contrast, old waters (^{14}C model ages >30 000 a) from karst springs in the oases Al Qatif (east cost) and Al Hasa (70 km inland from the east coast) show a relation of $\delta^2H = 8\,\delta^{18}O + 2$ with

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[1] The δ-value is the relative ‰ deviation of the isotope content of the water sample from the isotope content of a standard water (V-SMOW).

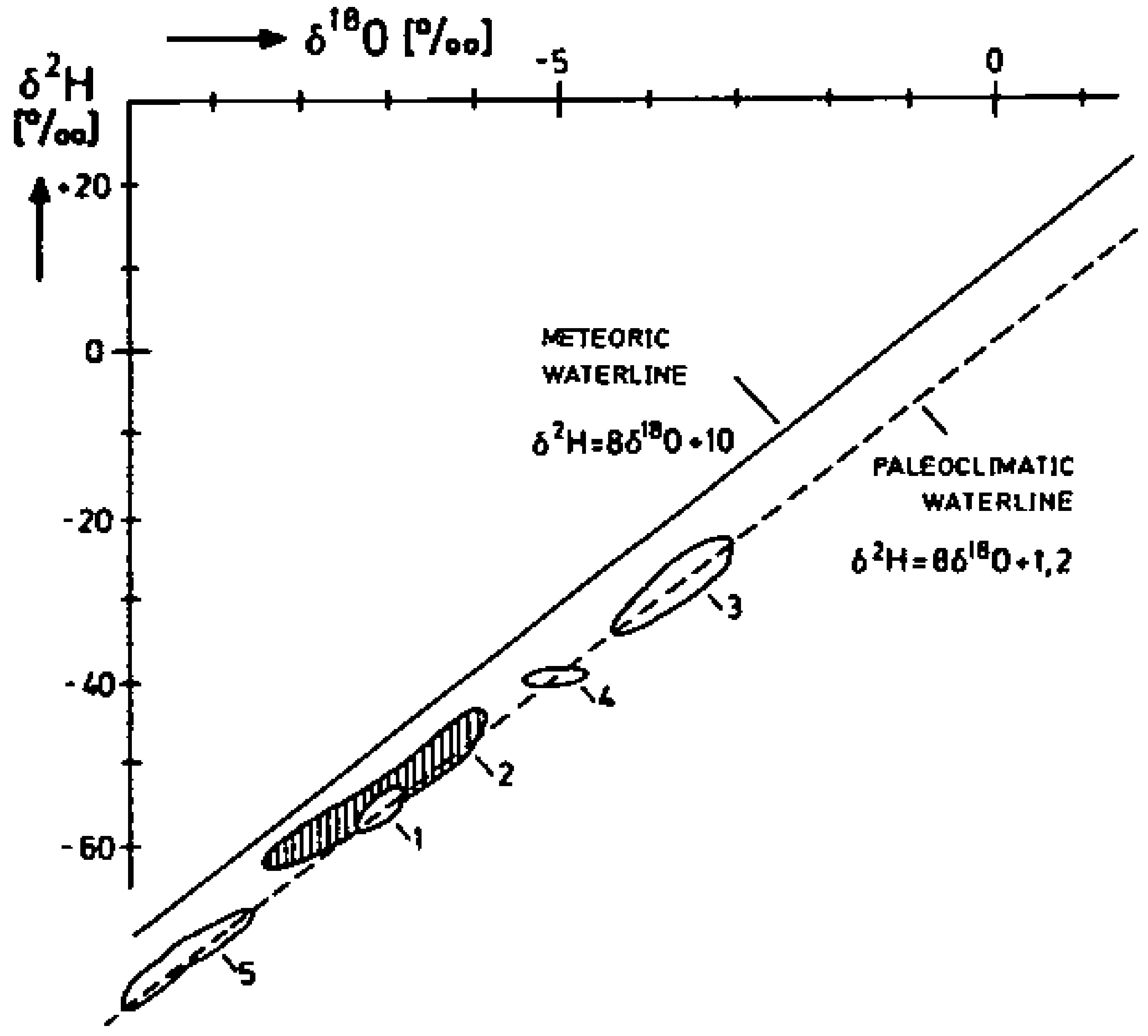

FIG.1. δ^2H-$\delta^{18}O$ relation of palaeowaters in desert areas between North Africa and Saudi Arabia. 1: Algeria, 2: Continental Intercalaire, 3, 4: Saudi Arabia, 5: Libya.

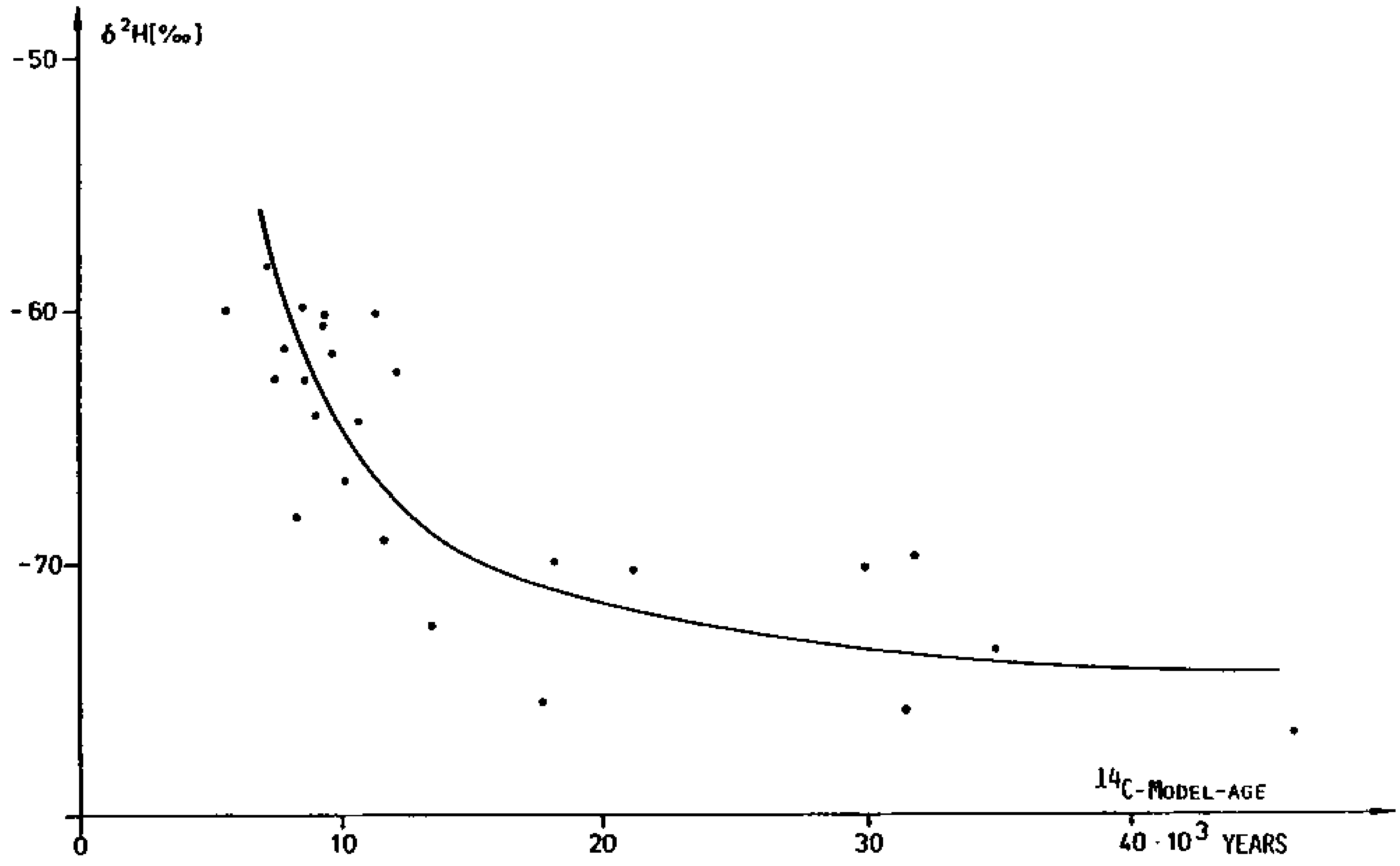

FIG.2. ^2H contents of deep artesian groundwaters in the Styrian basin in relation to their uncorrected ^{14}C ages.

relatively low δ-values. Figure 1 summarizes the ^{2}H and ^{18}O contents of the old Libyan and Saudi Arabian groundwaters in relation to similar results from groundwaters in Algeria and in the Continental Intercalaire aquifer, which also show a low intercept. Using a theoretical model [7], this intercept in the δ^2H-δ^{18}O relation indicates a palaeohumidity of the air over the ocean of more than 90% compared to 80% computed for modern conditions.

The next two examples show that not only in arid regions but also in middle European aquifers groundwaters with lower intercepts than measured in modern precipitation exist.

In the region of Munich and Augsburg (Federal Republic of Germany) groundwaters within the strata of the upper freshwater molasse have ^{14}C model ages[2] of 12 000 years and an intercept of the δ^2H-δ^{18}O relation of 6‰ (see also [8]). The δ-values are 10 to 15 δ^2H‰, 1 to 1.5 δ^{18}O‰ lower than in the precipitation of today. The lower δ-values are significant if one assumes that the fossil waters probably originate from summer precipitation, which in times of permafrost could possibly only infiltrate, whereas today the recharged groundwater is primarily from winter precipitation.

In the region of the Styrian basin in Austria, the ^{2}H content of deep artesian groundwaters was measured [9]. The ^{2}H content generally decreases with the depth of the sample well. In deep wells values of ^{2}H content occur that are lower than the monthly mean ^{2}H values of the precipitation measured in the highest deviations of the catchment area. The assignment of ^{2}H values according to age for several waters (Fig.2 and Ref.[10]) leads to the conclusion that these waters with low δ-values are Pleistocene waters.

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