

$\delta^{13}\text{C}$ of Loess Organic Matter as a Potential Proxy for Paleoprecipitation

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Received September 24, 1999

Paleoprecipitation reconstructions on the basis of pollen are well known, but they do not provide high temporal resolution for glacial periods. High-resolution paleoprecipitation reconstructions for the last glaciation based on the isotopic record organic matter in loess from Nussloch (Rhine Valley, Germany) are consistent with paleoprecipitation inferred from peat in the same area using an independent method. Thus, $\delta^{13}\text{C}$ of loess organic matter can be used as a proxy for paleoprecipitation. © 2001 University of Washington.

Key Words: carbon isotopes; loess; organic matter; paleoprecipitation; Weichselian.

INTRODUCTION

Studies of past high-frequency climatic variability require sedimentary sequences. Peat bogs and lacustrine deposits provide good records of local vegetation changes during wet interglacial periods, while loess sequences with high accumulation rates are well suited for the study of dry, cold glacial periods. For the Rhine Valley of northwestern Europe, malacological (Rousseau, 1987) and pedological (Antoine *et al.*, 1999, and

in press) studies show that vegetation contemporaneous with loess deposition is open vegetation, e.g., tundra or cold steppe. In the same area, isotopic records of loess organic matter indicate that throughout the last climatic cycle, vegetation predominantly followed a C3 photosynthetic pathway (Hatté *et al.*, 1998; Hatté, 2000). Furthermore, preliminary studies (Lin *et al.*, 1991; Wang *et al.*, 1997; Hatté *et al.*, 1998) performed on loess deposits suggested that the carbon isotopic composition of organic matter ($\delta^{13}\text{C}_{\text{org}}$) can be used as a record of vegetation sensitivity to climatic stress. For northwestern Europe, Hatté *et al.* (1998) show that $\delta^{13}\text{C}_{\text{org}}$ variations correspond to changes in the global concentration and isotopic composition of atmospheric CO_2 superposed on fluctuations in water availability.

On the other hand, studies of vegetal physiology performed on plants following the C3 photosynthetic pathway, exhibit quantitative relationships between environmental changes and the isotopic composition of plants. According to Farquhar *et al.* (1989), O'Leary (1981), and Tieszen (1991), parameters influencing isotopic composition of C3 plants ($\delta^{13}\text{C}_{\text{p1}}$) are light, temperature, isotopic composition and concentration of atmospheric CO_2 , and water availability.

(1) Yakir and Israeli (1995) reported that light variations have a significant influence on $\delta^{13}\text{C}_{\text{pl}}$ only in the case of large variations, such as a doubling of light intensity. They do not present an important contribution on $\delta^{13}\text{C}_{\text{pl}}$ in a natural system.

(2) The control of temperature changes on plant $\delta^{13}\text{C}$ is poorly constrained. It is difficult, in a natural environment, to separate its influence from others parameters. O'Leary (1988) observed a positive relationship between $\delta^{13}\text{C}$ in trees and temperature in a natural environment, and a negative one under control-room conditions.

(3) As shown by different models, the effect of changes in isotopic composition of atmospheric CO_2 ($\delta^{13}\text{C}_{\text{atm}}$) on $\delta^{13}\text{C}_{\text{pl}}$ is direct and quantitative (Farquhar *et al.*, 1989).

(4) A negative relationship between CO_2 concentration and $\delta^{13}\text{C}$ in plants has been shown by several authors (Krishnamurthy and Epstein, 1990; Van de Water *et al.*, 1994; Feng and Epstein, 1995; Pasquier-Cardin *et al.*, 1999). All agree with the coefficient established by Feng and Epstein (1995), a decrease of $2.0 \pm 0.1\%$ in $\delta^{13}\text{C}_{\text{pl}}$ for an increase of 100 ppm in atmospheric CO_2 concentration.

(5) Likewise, a negative relationship relates isotopic composition of plants to water availability: $\delta^{13}\text{C}_{\text{pl}}$ becomes less and less negative when aridity increases (O'Leary, 1981, 1988; Garten and Taylor, 1992; Schleser, 1995; Stewart *et al.*, 1995; Heaton, 1999). However, great variability exists between coefficients established by different authors because of the extreme influence of other parameters, e.g., soil texture and type, vegetation type, and precipitation range and distribution. Water availability results in a complex balance among precipitation, annual distribution, evaporation, water runoff, and drainage. It is difficult to tie efficient water for plant growth directly to precipitation. Nevertheless, Stewart *et al.* (1995) exhibits a coefficient for eastern Australian climate covering a large range of precipitation (350 to 1500 mm) and including open vegetation. They measured a decrease of $0.33 \pm 0.07\%$ per 100-mm increase in precipitation.

In northwestern Europe, the isotopic composition of loess organic matter is close to the isotopic composition of the original plants and exhibits a great predominance of C3 plants that recorded climatic changes qualitatively during the last climatic cycle. The $\delta^{13}\text{C}$ record in C3 plants can be calibrated for several important climatic parameters. The aim of this paper is to apply the quantification of climatic parameters influencing $\delta^{13}\text{C}_{\text{pl}}$ to the $\delta^{13}\text{C}$ record of loess organic matter and then to determine if $\delta^{13}\text{C}_{\text{org}}$ constitutes a paleoprecipitation proxy.

HYPOTHESIS

Considering the complexity of organic matter fossilization in loess and the plant record of environmental changes, simplifications need to be made in order to use loess organic matter $\delta^{13}\text{C}$ as a paleoprecipitation proxy.

(1) As mentioned above, vegetation contemporaneous with loess deposition was open vegetation, such as tundra or cold

steppe. This type of vegetation is associated with a weak rhizosphere and a very high accumulation rate common to loess deposits, thereby reducing considerably the effect of organic matter turnover responsible for mixing old and recent organic matter. Thus, unlike soils and paleosols, in which an important organic matter turnover distorts the isotopic composition of plants during pedogenesis, it can be assumed that $\delta^{13}\text{C}_{\text{org}}$ is equal to the $\delta^{13}\text{C}$ of plants contemporaneous with loess deposition, at least for the last glacial period (ca. 75,000–15,000 yr B.P) in northwestern Europe. The $\delta^{13}\text{C}$ of loess organic matter therefore mirrors climatic and environmental variations recorded by $\delta^{13}\text{C}$ in the original vegetation at the time of deposition.

(2) Due to poor control of temperature on plant $\delta^{13}\text{C}$, and because our study will consider only the glacial period and not the transition between glacial and interglacial phases, the influence of temperature will be neglected. Thus, as a second approximation, only the isotopic composition and concentration of atmospheric CO_2 and water availability will be taken into account as influencing the $\delta^{13}\text{C}$ of C3 plants.

(3) As a third approximation, we will consider that all effects are additive.

(4) We will apply a coefficient of $-2.0 \pm 0.1\%/100$ ppm between CO_2 concentration and plant $\delta^{13}\text{C}$.

(5) During glacial periods, temperatures were not high enough to produce significant evaporation. The depositional environment permits us to reject significant water loss through runoff. A majority of C3 vegetation under cold temperatures could exist only with water availability all year long. Thus, we assume that during the last glaciation, there is a linear correlation between water use efficiency for plants and precipitation. Consequently, we will consider that plant $\delta^{13}\text{C}$ records annual precipitation.

(6) There is a big range of published coefficients relating precipitation or humidity to plant $\delta^{13}\text{C}$. We adopt here the coefficient measured by Stewart *et al.* (1995) in Australia because his study covers a wide range of precipitation (including the low values expected for the glacial period in northwestern Europe) and includes open vegetation (like tundra or steppe areas of the last glaciation).

(7) Global records of concentration and isotopic composition of atmospheric CO_2 have been measured in air bubbles in the Vostok (Antarctica) ice core (Leuenberger *et al.*, 1992; Petit *et al.*, 1999). CO_2 concentration measurements are available for the last 400,000 yr (Petit *et al.*, 1999), with a temporal resolution of ca. 1400 yr. Intermediate values of CO_2 concentration ($[\text{CO}_2]$) are obtained by linear interpolation between measured points. CO_2 isotopic data are not numerous and are unequally distributed from today to 42,000 yr B.P. (Leuenberger *et al.*, 1992). Thus, intermediate values are obtained by linear interpolation between measured values, and for the oldest period of the last glaciation, the last measured value, -6.7% , is adopted.

(8) Finally, all coefficients given in the vegetal physiology literature are values characterizing changes between two states.

In order to obtain absolute paleoprecipitation, one reference state must be defined. This value will have no influence on relative changes of precipitation between two consecutive intervals, as between stadial and interstadial intervals or between two oxygen isotope stages (OIS). We choose here as reference state the preindustrial period for which most parameters are well constrained and not disturbed by the anthropogenic effect. Again, this choice will have no effect on the signal magnitude, and will be responsible only for a small translation of all the values obtained for lower or higher paleoprecipitation. The following values are used here: $\delta^{13}\text{C}_{\text{pl}0} = -26\%$ (mean value proposed by O'Leary, 1981); $\delta^{13}\text{C}_{\text{atm}0} = -6.41 \pm 0.02\%$ and $[\text{CO}_2]0 = 281.1 \pm 1.7$ ppmv (Leuenberger *et al.*, 1992); $P0 = 692$ mm (considering that the anthropogenic influence had no repercussion on precipitation and that preindustrial precipitation equals present rainfall; Leemans and Cramer, 1991)

With the proposed hypothesis and these approximations, the following equation can be written,

$$\delta^{13}\text{C}_{\text{org}} - \delta^{13}\text{C}_{\text{pl}0} = (\delta^{13}\text{C}_{\text{atm}} - \delta^{13}\text{C}_{\text{atm}0}) - 0.02 * ([\text{CO}_2] - [\text{CO}_2]0) - 0.0033 * (P - P0), \quad (1)$$

from which a precipitation factor can be extracted as

$$P = 692 - 1/0.0033 * [(\delta^{13}\text{C}_{\text{org}} + 26) - (\delta^{13}\text{C}_{\text{atm}} + 6.41) + 0.02 * ([\text{CO}_2] - 281.1)]. \quad (2)$$

SITE, FIELD PROCEDURE, AND METHODS

The Nussloch section is located on the eastern side of the Rhine graben at $49^\circ 21' \text{N}$, $8^\circ 43' \text{E}$ (Fig. 1). The geomorphic setting is characterized by the wide alluvial Rhine plain with a steep slope on the eastern side, which would have been exposed to the prevailing winds from the northwest to north during the

last glacial maximum. During Weichselian time, this site was favored for loess accumulation due to its location at the border between the upper valley slope and the plateau, thus allowing development of series of loess dunes separated by troughs (the “gredas” of L ger (1990)). A schematic log is presented in Fig. 2 (for further information on sedimentology and stratigraphy, see Antoine *et al.* (1999, and in press).

The chronology of this loess sequence is based on several optically simulated luminescence (OSL) and thermoluminescence (TL) ages, and on ^{14}C ages of macrorests (wood, bone, gastropod shells) and loess organic matter (Hatt  *et al.*, 1999; Hatt , 2000). This sequence shows a very high accumulation rate during the last glacial maximum (Fig. 2). More than 8 m of loess accumulated between 24,000 and 18,000 yr B.P., an interval falling within OIS 2. However, sediments from the beginning of the early Weichselian are missing due to a hiatus.

The outcrop, accessible in a quarry, was sampled at 5- to 10-cm intervals, depending on sedimentological and pedological variations. Sediments were decarbonated with HCl 0.6 N, and total organic carbon was analyzed for isotopic ratio and carbon content. Carbon isotope ratios were obtained with a dual-inlet VG Optima mass spectrometer coupled to an elementary analyzer (Carlo Erba NA1500), and $\delta^{13}\text{C}$ values are expressed in per mil versus PDB standard, with an absolute precision of 0.1‰. The $\delta^{13}\text{C}_{\text{org}}$ record is presented in Fig. 2 as a function of depth.

RESULTS

Due to low temporal resolution of global records used for paleoprecipitation, we chose to estimate paleoprecipitation from a smoothed $\delta^{13}\text{C}_{\text{org}}$ record with a 1000-yr step. The paleoprecipitation reconstruction obtained for the Nussloch loess sequence using Eq. (2) is shown in Fig. 3 and Table 1.

The best way to answer the question “could $\delta^{13}\text{C}_{\text{org}}$ constitute a paleoprecipitation proxy?” would be to compare our results to others obtained independently on the same sequence. Unfortunately, such reconstructions are not available for the Nussloch sequence. We can, however, compare our results with paleoprecipitation data obtained in a neighboring section (La Grande Pile) through a palynological study (Guiot *et al.*, 1989). This sequence differs from our record in several aspects: first, the accumulation rate for the 75,000–15,000 yr period is much lower and does not permit a high-resolution study. Second, La Grande Pile is located on the other bank of the Rhine Valley and south of Les Vosges mountains; thus it does not offer the same exposure to climatic events. Third, La Grande Pile, in contrast to Nussloch, does not have a precise chronology, and error margins on the age-scale can reach 5000 years. Nevertheless, considering the error margins on paleoprecipitation for both records, the estimates obtained are broadly consistent and show equivalent variations with more pronounced variations in Nussloch than in La Grande Pile. Several climatic events are recognizable in both records (gray bars in Fig. 3).

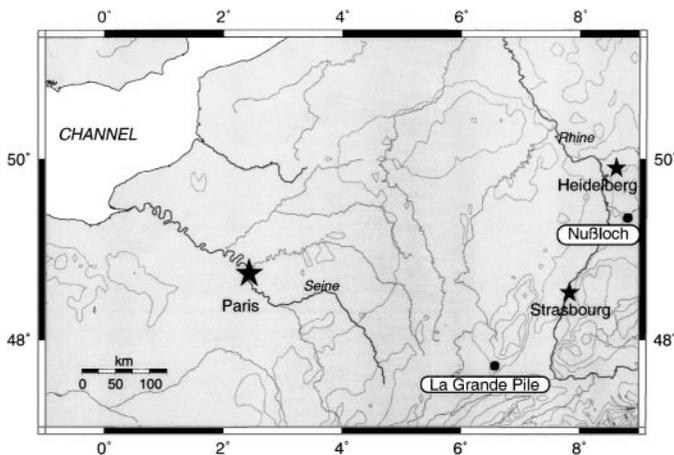


FIG. 1. Map showing Location of Nussloch and La Grande sites.

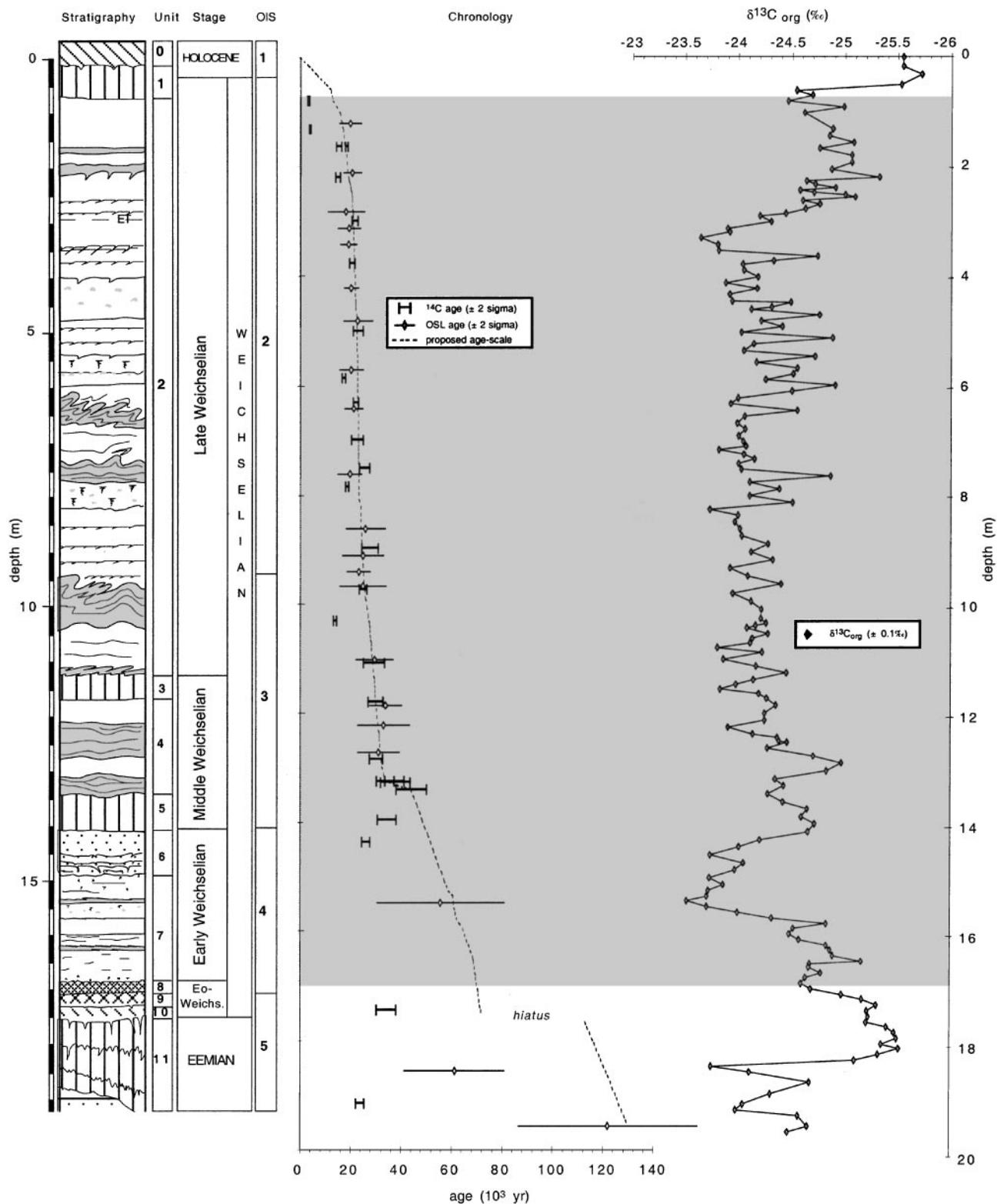


FIG. 2. Chronostratigraphy, chronology, and isotopic record of the Nussloch loess sequence. In the left column is a chronostratigraphic log with simplified descriptions presented relative to the chronozones (0 and 1: Humic horizon and BT horizon of the surface soil; 2 and 4: Typical calcareous loess with tundra gley horizons and cryoturbations; 3 and 5: Horizons of boreal leached soils; 6: Aeolian sands; 7: Sandy loess with tundra gley horizons; 8: Steppe soil; 9: Gray forested soil; 10: Colluvium; 11: BT horizon of the Eemian soil.). In the center are the ^{14}C ages (calibrated or corrected following the study of Kitagawa and Van der Plicht (1998)), the OSL ages, and the proposed chronology. In the right column is $\delta^{13}\text{C}_{\text{org}}$ vs depth. The gray zone outlines the period for which paleoprecipitation is estimated.

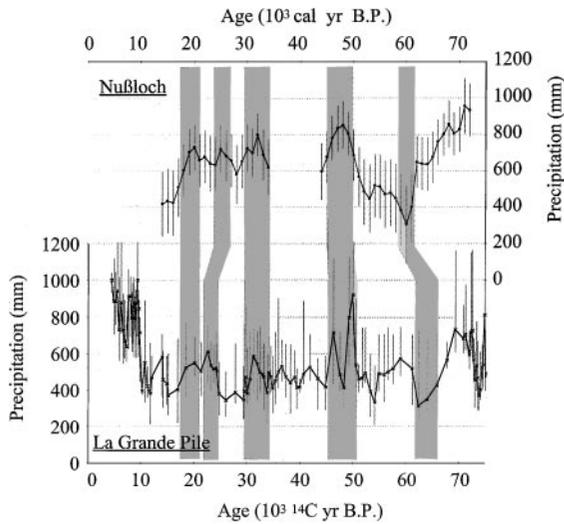


FIG. 3. Paleoprecipitation reconstruction obtained for Nussloch and La Grande Pile. Paleoprecipitation reconstruction obtained from a smoothed isotopic record of Nussloch (upper part) and the palynological record of La Grande Pile (modified from Guiot *et al.* (1989); present precipitation 1000 mm) (lower part). The range of variations in the Nussloch Paleoprecipitation reconstruction is represented by dotted lines. La Grande Pile estimations are presented with error margins for each point. The gray bars emphasize correlations between the two records.

The most important difference between the two records is the higher values of precipitation obtained by the isotopic method for the period 35,000–18,000 yr B.P., if we assume the same level of rainfall at 60,000 yr B.P. Two explanations are possible for this difference. The first is inherent in the modern analog method used for paleoprecipitation reconstruction in the La Grande Pile record. Due to lower concentration of CO_2 during the glaciation than today, C_3 plants did not have the same responses to drought as they do today. There is no good modern analog for the vegetation of glacial periods. Cowling and Sykes (1999), supported by Williams *et al.* (2000), show that glacial climates inferred from the pollen-based reconstructions may appear drier than they actually were. This could explain an underestimation of paleoprecipitation through the palynological method for the whole glaciation. The second explanation is the presence of cryoturbation features in the loess. These features are associated with permafrost and then with the continuous presence of water in soils (Van Vliet-Lanoë, 1998). The presence of pedogenetic water weakens our hypothesis, as all the available water is meteoritic water. This produces a small overestimation of paleoprecipitation through the isotopic record for periods with significant permafrost, because soil water is counted in our balance as meteoritic water. Nevertheless, the precipitation estimates based on the isotopic method agree with the paleoprecipitation record of Guiot *et al.* (1989) from the La Grande Pile.

Our first attempt to obtain a paleoprecipitation reconstruction using $\delta^{13}\text{C}$ permits us to define two periods, corresponding to

OIS 2 and 4, as the driest of the last glaciation. The beginning of OIS 3 appears to have been very wet, and wetter than today. However, the open vegetation associated with these wet conditions points to cold temperatures.

TABLE 1
Values of Smoothed Isotopic Record of the Nussloch Loess Sequence, CO_2 Concentration, and Isotopic Composition Used for Paleoprecipitation Estimations. (Presented with Error Margins in the Last Two Columns)

Age (10^3 yr)	$\delta^{13}\text{C}_{\text{org}}$ (‰) ± 0.1‰	CO_2 (ppm) ± 2 ppm	$\delta^{13}\text{C}_{\text{atm}}$ (‰) ± 0.1‰	P (mm)	ΔP
16	-24.7	250	-7.0	315	179
17	-24.9	246	-6.9	402	161
18	-24.9	238	-6.9	495	144
19	-25.0	226	-6.8	597	126
20	-24.8	215	-6.8	621	124
21	-24.3	203	-6.7	551	143
22	-24.2	194	-6.8	570	141
23	-24.2	193	-6.9	532	150
24	-24.0	194	-6.7	527	151
25	-24.1	194	-6.5	612	132
26	-24.1	195	-6.7	575	140
27	-24.2	196	-6.8	550	145
28	-24.1	197	-6.9	474	161
29	-24.2	199	-6.7	545	145
30	-24.2	200	-6.5	617	130
31	-24.2	200	-6.6	591	135
32	-24.7	199	-6.7	691	114
33	-24.5	198	-6.9	581	138
34	-24.4	201	-7.0	512	151
44	-24.3	206	-6.9	490	155
45	-24.4	199	-6.9	569	140
46	-24.6	191	-6.9	672	121
47	-24.6	183	-6.9	727	126
48	-24.7	183	-6.9	745	130
49	-24.7	191	-6.9	699	118
50	-24.5	199	-6.9	579	138
51	-24.1	203	-6.9	462	162
52	-23.9	206	-6.9	379	178
53	-23.8	207	-6.9	342	186
54	-24.0	205	-6.9	412	172
55	-24.0	202	-6.9	408	173
56	-23.8	201	-6.9	366	183
57	-23.8	201	-6.9	373	181
58	-23.7	202	-6.9	343	187
59	-23.7	210	-6.9	277	199
60	-23.6	218	-6.9	200	213
61	-23.9	218	-6.9	295	193
62	-24.7	216	-6.9	542	141
63	-24.6	213	-6.9	533	143
64	-24.5	209	-6.9	530	145
65	-24.6	206	-6.9	570	138
66	-24.8	204	-6.9	652	121
67	-24.9	201	-6.9	694	114
68	-25.0	197	-6.9	750	127
69	-24.7	193	-6.9	698	117
70	-24.8	192	-6.9	722	122
71	-25.2	193	-6.9	851	150
72	-25.2	196	-6.9	827	143

CONCLUSION

In order to extract the paleoprecipitation record from the $\delta^{13}\text{C}$ of loess organic matter, we made many simplifications and hypotheses. In spite of the simplifications, a paleoprecipitation reconstruction can be obtained, and it agrees well with rainfall estimates obtained in a nearby area using an independent method. It is now possible to answer in the affirmative the question “can $\delta^{13}\text{C}_{\text{org}}$ in loess constitute a paleoprecipitation proxy?”

ACKNOWLEDGMENTS

We are very grateful to Dr. J. Guiot for providing paleoprecipitation reconstruction data obtained for La Grande Pile. We thank Heidelberger Zement AG for permitting us to work in their quarries. Valuable comments from Dr. Jim Channel helped improve the English. The work was supported by CEA and CNRS, by the EC Environment Program BIMACEL (EV5V-CT93-0298), and by CNRS PNEDC and VARIANTE funding. We thank Leon Follmer and one anonymous reviewer for helpful suggestions and comments. This is LSCE (Laboratoire des Sciences du Climat et de l'Environnement) contribution 2000-0500 and ISEM contribution 2000-078.

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