δ\textsuperscript{13}C variations of loess organic matter as a record of the vegetation response to climatic changes during the Weichselian

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ABSTRACT
This paper presents high-resolution records of 13C/12C ratios of organic matter from two loess sequences in northwestern Europe. Our analysis is the first attempt to use organic matter δ\textsuperscript{13}C as a record of the response of vegetation to climatic variations in an area where climatic changes were not strong enough to induce a radical change in vegetation cover. Over the last climatic cycle, the vegetation of the Rhine Valley showed a strong predominance of C3 plants. Thus, the small δ\textsuperscript{13}C variations, with an amplitude of only 1.5‰ to 3‰, are interpreted as corresponding to fluctuations in water supply and atmospheric CO\textsubscript{2} concentration variations rather than to the ratio of C4 to C3 vegetation. Furthermore, loess sequences accumulated at high rates and allow high correlation with climatic proxy data, like the Greenland Ice Sheet Project 2 (GISP2) δ\textsuperscript{18}O and the variations in CO\textsubscript{2} concentration recorded in the Vostok ice core. The δ\textsuperscript{13}C constitutes a reliable and complementary proxy to study small climatic stresses endured by vegetation during the Weichselian in northwestern Europe. Moreover, by using absolute age control and correlations between global (Vostok-CO\textsubscript{2}) or semi-global (GISP2-δ\textsuperscript{18}O) climate effects, δ\textsuperscript{13}C values of organic matter in loess sequences offer a new tool to establish a refined chronology in continental sequences.

INTRODUCTION
Loess sequences have been intensively studied to analyze Quaternary climatic changes by using, for example, paleopedology (Haesaerts, 1985; Antoine et al., 1994), sedimentology (Sommé et al., 1986), magnetic susceptibility (Kukla, 1987), malacology (Puisségur, 1978; Rousseau and Wu, 1997), or stable isotopes (Lin et al., 1991; Frakes and Jianzhong, 1994; Wang et al., 1997). In this paper, we use the 13C/12C ratio of organic matter in loess sequences as a record of the vegetation response to climatic changes. The type of vegetation contemporaneous to continental deposits mostly depends on climatic conditions. Changes of vegetation cover can thus be characterized by variations of carbon isotope ratios (δ\textsuperscript{13}C) of the organic matter in the continental sedimentary deposits.

During photosynthesis, plants discriminate against uptake of \textsuperscript{13}C because of differences in chemical and physical properties due to its heavier mass. The light isotope (\textsuperscript{12}C) is more stable chemically and diffuses more easily. Isotopic fractionation is a combination of all individual fractionations existing at each step of CO\textsubscript{2} uptake (diffusion, dissolution, carboxylation, and respiration) and depends on the type of vegetation and on the plant environments (O’Leary, 1981). Carbon isotope fractionation by plants also depends on the atmospheric CO\textsubscript{2} concentration and on the humidity level. All these metabolic responses to CO\textsubscript{2} content and/or moisture level indicate that the carbon isotope composition of plants reflects climatic variations.

Although degradation of organic matter is not homogeneous and can produce changes in the isotopic composition of stable carbon, δ\textsuperscript{13}C of organic matter deposited in sediment acts as a record of the vegetation cover (Lin et al., 1991; Lee-Thorp and Beaumont, 1995; Wang et al., 1997). During loess accumulation, because pedogenesis is reduced and organic matter is buried rapidly without a real effect of turnover, the isotopic signal might only slightly altered. However, in a soil profile there could occur downward translocation of the soluble organic matter that could then be complexed with clays or older humic material (Head et al., 1989). Thus, organic matter can be younger than the loess in which it is contained.

Two loess sequences located in the Rhine valley have been investigated for carbon isotope studies. The Achenheim sequence (France) is located in the Rhine graben (48.5°N, 7.5°E). This thick loess sequence, over Rhine and Vosges alluvial sandy deposits, was deposited during the middle and late Pleistocene, with the upper 18.3 m corresponding to the last climatic cycle (Sommé et al., 1986; Rousseau et al., 1998a). The Nußloch sequence (Germany) is located in the right bank of Middle Rhine valley (49.3°N, 8.8°E). The geomorphologic setting is characterized by a wide alluvial plain and an abrupt slope. During the Weichselian Pleniglacial, loess accumulated at the junction between the slope and the plateau, producing series of loess dunes (Léger, 1990). Several thermoluminescence (TL) dates for the Achenheim (Rousseau et al., 1998a) and forNußloch (Zöller et al., 1998) sequences are available (Fig. 1). Two 14C dates complete the Nußloch absolute chronological markers: (1) 12.9 ± 0.1 k.y. B.P. (GISP-96244), obtained on organic matter from snail shells, was corrected by using the Stuiver and Reimer calibration (1993), the calibrated age ranges between 14.8 and 15.7 k.y. B.P. (2) 31.8 ± 0.4 k.y. B.P. (GIS/LSM-10442), obtained on wood, was corrected by using magnetic calibration (Laj et al., 1996), the corrected age ranges between 30.6 and 36.2 k.y. B.P. Some well-established correlations with the northwestern European loess stratigraphy (Fig. 1) involving paleopedological, sedimentological, and periglacial level marks and tephratigraphy are used too: Eemian BT (following the European conventional usage) and early-glacial humic soils complex (Antoine et al., 1994), the Marker II of the central European soil complexes (Kukla, 1977; Rousseau et al., 1998b), the Eltville tephras (Zöller et al., 1988), and the Nagelbeek tongue horizon (Juvigné et al., 1996).

Both sequences were sampled at intervals of 5–10 cm. Between 1 and 2 g samples of sediment were collected and, after decarbonation, were analyzed isotopically and for organic carbon contents. In both sequences, carbonate contents range between 3% (in the Eemian BT) and 30%–40% (in loess sediment). Carbon organic contents were determined with an elementary
analyzer (Carlo Erba NA 1500) and are expressed in weight percent, with a relative precision of 1 wt%. Carbon isotope ratios, obtained from a VG Optima mass spectrometer, are expressed as $\delta^{13}C = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000$ (‰) where $R = \frac{^{13}C}{^{12}C}$, and the standard (std) is the Pee Dee belemnite (PDB) in per mil with an absolute precision of 0.1‰.

Organic carbon content records in Achenheim and Nußloch are reported in Figure 1. In Achenheim, organic carbon content varies between 0.86% and 0.10%, with higher values for the Achenheim I soil complex (around 0.4%) and lower values for the loess (around 0.2%). The record of Nußloch shows very low and constant values of organic carbon content. It remains lower than 0.1%, except for soils at around 12, 14, and 16 m, where organic carbon content reaches 0.3%. In loess sediment, no correlation is observed between organic carbon content and $\delta^{13}C$ values (Fig. 1). $\delta^{13}C$ variations range from 1.5‰ to 3‰; mean values are –24.5‰ in Achenheim and –24.3‰ in Nußloch. Although the degradation of organic matter can produce alteration of the isotopic signal, these $\delta^{13}C$ values result from the degradation of vegetation with a predominance of C3 plants. These plants grow in temperate environments and have $\delta^{13}C$ values of about –26‰ (O’Leary, 1981). In Achenheim and Nußloch, past climates were not arid enough to support plants with the C4 photosynthetic pathways; such plants prefer high temperature, strong insolation, and/or water stress and show $\delta^{13}C$ values of about –14‰ (O’Leary, 1981). Our results differ from those obtained for the Chinese Loess Plateau, where variations of the $^{13}C/^{12}C$ ratio of loess carbonate (Lin et al., 1991; Frakes and Jianzhong, 1994) or of loess organic matter (Lin et al., 1991; Wang et al., 1997) have been interpreted in terms of transition between C4 vegetation and C3 plants. In that case, when climatic changes were strong enough to induce such a transition, the $\delta^{13}C$ record shows an amplitude higher than 9‰, but we have a $\delta^{13}C$ amplitude smaller than 3‰ in northwestern Europe. The Nagelbeek horizon in Achenheim shows the lowest $\delta^{13}C$ value of the overall sequence, probably because of a specific degradation of the organic matter preserving lipids or de-carboxylated amino acids (O’Leary, 1981), due to drastic conditions encountered during the last glacial maximum. The Eemian BT horizons, developed on the older eolian deposit, show slower sediment accumulation, but rapid turnover of organic matter. Thus, a relatively thin section of sediment represents a long interval (1–1.5 m for about 30 k.y.) that integrates bioturbation and pedological processes reflecting mixing of loess previously deposited and interglacial organic matter. Furthermore, this soil (BT horizon of a brown leached soil) is “lessivé” as shown by the slow and regular decrease in carbon and carbonate contents. No interpretation of the $\delta^{13}C$ values can be proposed for this unit at the present.

Carbon isotope fractionation by plants depends also on the atmospheric CO$_2$ supply. When the CO$_2$ concentration ([CO$_2$]) is high, a large frac-
tionation is observed. But if \([\text{CO}_2]\) is low, growth is limited, and cells use all the available \(\text{CO}_2\) that they need, independently of its isotopic nature (O’Leary, 1981). Recent studies (e.g., Feng and Epstein, 1995) have predicted that \(\delta^{13}\text{C}\) of plants decreases by about 0.02‰ per 1 ppm increase in \([\text{CO}_2]\). As atmospheric \(\text{CO}_2\) changed by about 100 ppm between last glacial and interglacial periods, such oscillations have to be recorded by plants and the derived sedimentary organic matter \(\delta^{13}\text{C}\). To compare loess \(\delta^{13}\text{C}\) variations to Vostok ice \([\text{CO}_2]\) records (Lorius et al., 1985), we assume, as a first approximation, a constant loess accumulation rate between some of the mentioned chronological markers (Fig. 2): we did not take into account dates inducing apparent reversals and ages with minimum and maximum values, thus dates at 7.9 m, 11.3 m, 12 m, and 17.8 m for Achenheim and 13.2 m for Nußloch did not appear. Major trends recorded in the Vostok \([\text{CO}_2]\) are observed in the \(\delta^{13}\text{C}\) records, except in the lower part of the sequences, which is modified by pedogenesis (Fig. 2). Furthermore, the amplitude of the isotopic signals, 1.5‰–3‰, for a \([\text{CO}_2]\) variation of 100 ppm, is roughly in agreement with the results of Feng and Epstein (1995). Thus, it appears that the long-term trends of the \(\delta^{13}\text{C}\) of the organic matter in loess clearly matches the global \([\text{CO}_2]\) variations.

The rapid events recorded by loess \(\delta^{13}\text{C}\), however, must result from another forcing parameter with a high frequency superimposed on the \([\text{CO}_2]\)-induced variations. The isotopic composition of both C3 plants and derived loess organic matter indeed depend on the water supply as well. The plant physiological response to a decrease in moisture is a stomatal narrowing, limiting water loss by evapotranspiration. Thus, carbon isotope fractionation due to stomatal diffusion is reduced, leading to higher \(\delta^{13}\text{C}\) values. The same isotopic response is induced by an increase in soil strength (physical resistance to root penetration), such as occurs in dry soils (O’Leary, 1981). These possible isotopic effects lead us to interpret the measured \(\delta^{13}\text{C}\) variations as a function of the water availability: the highest

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**Figure 2.** Organic matter \(\delta^{13}\text{C}\) in Achenheim and Nußloch samples compared with \(\text{CO}_2\) level recorded in Vostok ice core. Time scale of loess sequences is calculated by assuming constant sedimentation rate between chronological marks (see text). Nonlinear depth scale is also shown. \(\text{CO}_2\) level is expressed in ppm (dotted line). \(\delta^{13}\text{C}\), given in per mil relative to PDB (Peedee belemnite) standard, is shown on an inverse scale (solid line). Bt horizon of both sequences is enhanced by gray zone.

**Figure 3.** Correlation between GISP2 \(\delta^{18}\text{O}\) and \(\delta^{13}\text{C}\) of organic matter in Achenheim and Nußloch samples. A: \(\delta^{13}\text{C}\) values of both sequences are plotted versus refined chronological scales, as is GISP2 \(\delta^{18}\text{O}\) record. \(\delta^{13}\text{C}\) is expressed in per mil relative to PDB standard and is shown on an inverse scale. \(\delta^{18}\text{O}\) is expressed in per mil relative to SMOW (standard mean ocean water) standard. Gray bars highlight some climatic points that can be correlated very easily. B and C: Accumulation-rate diagrams for both sequences. Dotted lines correspond to time scale obtained by constant accumulation rate between all chronological markers, and solid lines represent refined chronologies. Thermoluminescence and \(^{14}\text{C}\) ages are also plotted.
δ13C values reflect the driest episodes. During the late Pleistocene, the location of the polar front fluctuated largely latitudinally with associated changes in precipitation pattern in southwestern Europe (Rasmussen et al., 1996). The rapid warm episodes associated with the so-called Dansgaard-Oeschger events (Dansgaard et al., 1993; Bond et al., 1993; Bond and Lotti, 1995), recorded by δ18O in the GISP2 core (Grootes et al., 1993; Stuiver et al., 1995; Meese et al., 1994; Sowers et al., 1993), have been linked to such fluctuations. We assume that the Dansgaard-Oeschger events correspond to wet climatic episodes in Achenheim and Nußloch and thus are linked to events recorded by δ18O in the GISP2 core (Grootes et al., 1993; Stuiver et al., 1995; Meese et al., 1994; Sowers et al., 1993), which possibly records the cold events during the last glacial period (58–10 ka).

REFERENCES CITED

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