DEVELOPMENT OF ACCURATE AND RELIABLE ^{14}C CHRONOLOGIES FOR LOESS DEPOSITS: APPLICATION TO THE LOESS SEQUENCE OF NUSSLOCH (RHINE VALLEY, GERMANY)

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ABSTRACT. Due to very high accumulation rates, loess sequences are best suited archives for the continental paleoclimate of glacial periods. Accurate chronologies cannot be easily established by radiocarbon-dating, because of the lack of organic macrorests, the only material for reliable ^{14}C dating so far. A chemical protocol is reported to extract the organic matter of loess (organic carbon content lower than 0.1% by weight) for accelerator mass spectrometry (AMS) ^{14}C dating. Sediments were taken from the loess sequence of Nussloch, for which a large dataset of luminescence ages (TL, IRSL/OSL) is available. The ^{14}C chronology of the organic matter extracted from loess is in good agreement with the corresponding luminescence ages. It allows high resolution correlations with climatic proxy signals (magnetic susceptibility, malacological assemblages, $\delta^{13}C$ on organic matter, etc.) derived from the loess sequence and global environmental proxy records.

INTRODUCTION

Natural archives of paleoclimate information with long temporal coverage and high spatial resolution are usually ice cores and deep-sea records. However, it is continental records that yield information on human environment changes. The establishment of accurate and precise chronologies for continental sequences remains a major problem. Lake sediments can be dated using macrofossils (large organic remnants). Unfortunately, such material was not present sufficiently accumulated during glacial periods. In the glacial times, loess (eolian sediments) was accumulated with very high rate (up to 1 cm in 10 yr), and is a suitable archive for the glacial continental paleoclimate of regional relevance with very high temporal resolution (see for example, Kukla and An 1989; Porter and An 1995; Rousseau et al. 1998). Chronologies for loess sequences have been based on low precision luminescence ages and singular radiocarbon ages of few macrorests. Any reliable and high resolution loess chronology allows correlations between terrestrial glacial fluctuations and large scale climatic variations reflecting ocean circulation. Today, the accelerator mass spectrometry (AMS) technique provides a new way to establish reliable and high resolution continental chronologies by ^{14}C dating of organic matter within loess. This organic matter is ubiquitously available, although in very low concentrations. As a first application, an AMS ^{14}C chronology of organic matter is established for the loess deposits in Nussloch, Germany and compared with available TL and IRSL/OSL dates.

METHODS

Materials

The Nussloch sequence is located on the right bank of the Upper Rhine graben in southern Germany (49.3°N – 8.8°E) (Figure 1). A detailed description of the sedimentary succession and the paleosols is given in Antoine et al. (2001). The geomorphological setting is characterized by a wide alluvial plain and an abrupt increase in elevation to the east. During the Weichselian Pleniglacial, loess accumulated on the slope and the adjacent hill country, producing a series of large loess dunes. The stratigraphy of the sequence, divided in 11 units, is presented in Figure 2. The last interglacial/glacial climatic cycle is represented by the uppermost 20 m of loess. This sequence starts with a fossil

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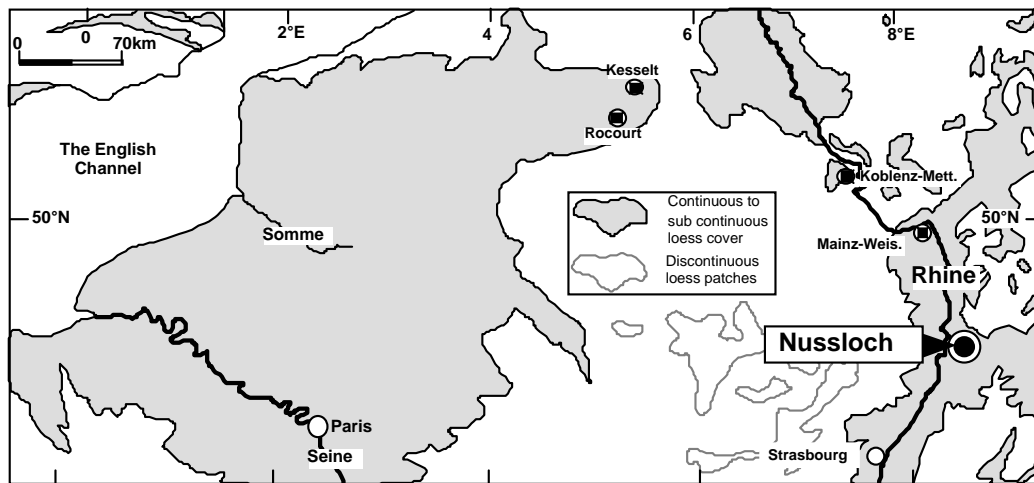[3]Geographische Institute der Universität Bonn. Meckenheimer Allee 166, D-53115 Bonn, Germany

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Figure 1 Location map for the Nussloch region with continuous and sub-continuous loess covers (in grey) (from Antoine et al. 2001)

Bt horizon (unit 11, below −17.5 m) from a truncated Eemian soil. From −17.5 to −16.8 m (units 10 to 8) three distinct horizons consisting of more or less clayey and humic material representing the Early Weichselian (Eo). The Lower Weichselian is represented by units 7 and 6. It consists of compacted sandy loess in which tundra gley soils are preserved. From −14 to −11.3 m, the sediments of the Middle Weichselian period consist of typical calcareous loess (unit 4) and are bordered by two brown clayey horizons of arctic-brown soils (units 5 and 3). A hiatus is present in the main loess section at 13.2 m depth. Above −11.3 m, more than 10 m of typical calcareous loess (unit 2) were deposited during the Late Weichselian. The uppermost unit, −0.7 m to the surface, is the truncated Holocene soil.

The carbonate content of the deposits ranges between 0% in the Eemian Bt and 30–40% in typical loess. The organic carbon contents is very low and near constant. It is less than 0.1%, except for the soils at around −12, −14, and −16 m, where the organic carbon content reaches 0.3%.

Treatment

All ^{14}C analyses were carried out at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE), using β-counting in the underground laboratory of Modane (samples referenced Gif/LSM-*) and the AMS facility (samples referenced GifA-*). The AMS ^{14}C measurements on graphite targets were performed at the Gif-sur-Yvette Tandetron (UMS 2004).

Treatment of Macrorests

Macrorests as gastropod shells as well as wood and bone objects were collected at 1.6 m and 13.2–13.4 m depth, respectively. Wood and bone samples were treated using common chemical techniques: acid/alkali/acid for the wood, and ninhydrine reaction (after Nelson 1991) for the bone. Gastropod shells were cleaned mechanically and separated into two aliquots: the first one as carbonate support for ^{14}C dating, and the second one to date the organic matter (conchioline) contained in mineral structure. The first aliquot was treated with HNO_3 0.1N for five minutes to remove possible surface recrystallizations. The second aliquot was treated with HCl 0.5N and 6N adjusting the pH to 3,
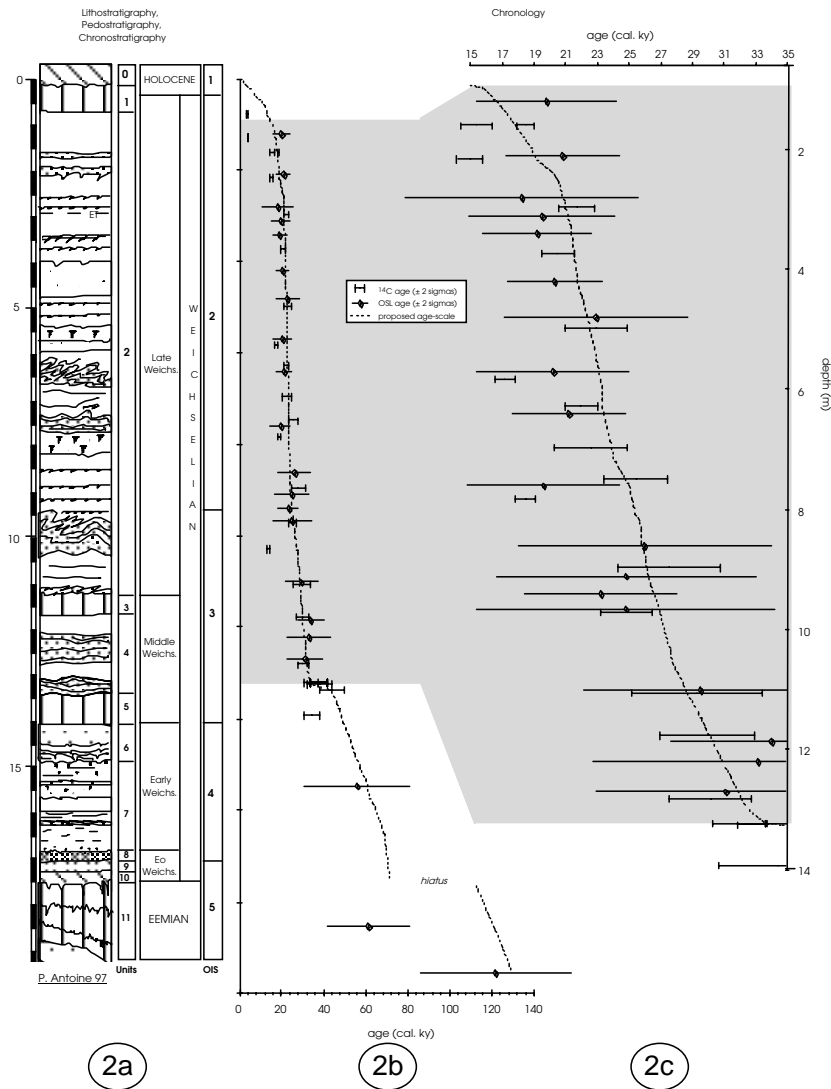
Figure 2 2A. Nussloch stratigraphy with a simplified description (after Antoine et al. 2001). 2B. Calibrated or temporary calibrated ^{14}C ages and OSL ages (with 2σ error margins) plotted versus depth of sampling. The proposed chronology is plotted as dotted line. 2C. Enlargement of 2B.

at room temperature, without agitation until total disappearance of the mineral structure. Conchioline, as colloids, was then recovered by filtration through a pre-treated GF/F quartz filter, and finally treated with NH_4OH 0.1N and HCl 1N. Samples were either combusted or treated with 100% H_3PO_4 to evolve CO_2 for β-counting (Gif/LSM-*) or for AMS analysis (GifA-*). In the latter case, the CO_2

obtained was reduced into graphite using an iron catalyst in a H_2 atmosphere at 600 °C. Graphite targets were stored in an Argon atmosphere until AMS ^{14}C analysis.

Treatment of Loess Organic Matter

Around 2 g of sediment was sampled from the cleaned outcrop. These were dried at 50 °C (no later than two days after collection), root remains were removed by hand-picking and sieved to <200 μm. The fine fraction was homogenized. The humin fraction was extracted according to the following protocol (based in Pessenda et al. 1996; modified): 1) acid digestion in 1N HCl at 60–70 °C in an ultrasonic bath and washing with ultra-pure water to pH 4–5, 2) treatment of the acid-insoluble residue with 0.1M $Na_4P_2O_7$ for about 3 hr and washing to pH 5–6, 3) hydrolysis of the solid residue with 1N HCl at 70–80 °C for 1 hour and washing to pH 5, 4) drying of the solid residue at 50 °C for 24–48 hr, 5) homogenizing of the samples and preservation under a nitrogen atmosphere. Samples were combusted to evolve CO_2 for reduction and graphite target preparation for AMS ^{14}C analysis.

Conventional ^{14}C ages are expressed in years Before Present (BP). Ages younger than 20 ka BP were calibrated using the Calib 4.18 program (Stuiver and Reimer 1993; cal BP) and older ages were "temporary calibrated" according to Kitagawa and van der Plicht study (1998) ("cor" BP).

RESULTS AND DISCUSSION

The ^{14}C dates are listed in Table 1 and shown in Figure 2. For comparison OSL (optically stimulated luminescence) ages from the same loess section (A Lang in Antoine et al. 2001) are included.

During cold and arid conditions of glacial period, steppe-like vegetation existed without trees and loess accumulated with very high rates. These conditions precluded strong pedogenesis. Organic matter found in the loess was buried quickly and important bioturbation did not occur. [14]C ages of this matter should thus closely reflect loess deposition ages just as the OSL ages. This conception was confirmed by the good agreement between the majority of the ^{14}C dates and the OSL dates.

Because the sediment samples were dried immediately after sampling, succeeding bacterial degradation of organic matter was avoided. Thus, solvent extraction to remove phospholipids and bacterial residue (Head et al. 1989) was not necessary, and contamination due to an eventual part evaporation of solvents was eliminated.

The ^{14}C dates obtained on wood and bones preleved at 13.2–13.4 m agree with the sedimentology and put the hiatus in the period 32–40 ka "cor." BP.

The ^{14}C chronology requires some explanation. The radiocarbon ages from organic matter of the two top samples collected at −0.8 m and −1.3 m should be treated with caution. They may be smaller than the actual ages due to contamination with humic acids from the Holocene topsoil that can be found down to 1.5 m. [14]C dates in this zone do not reflect the age of loess deposition that terminated in western Europe around 15 ka (Antoine et al. 1999). Likewise, the OSL age of 19.8 ± 2.2 ka for −1.2 m on the top of the typical loess should be considered as a maximum value, even if error margin is compatible with this value of 15 ka. The ^{14}C date obtained on carbonate gastropod shells from −1.6 m have also to be considered with care. It is well known that incorporation of fossil carbonate can be incorporated during the life-time of continental gastropods (e.g. Goodfriend and Hood 1983). Such may result in a reservoir correction of up to 2000 yr. Conchioline yields more reliable ^{14}C ages.

Further down the section, ^{14}C age-inversions occur. They represent soil horizons (gley-like soils) with iron concentrations higher than 2% (Antoine et al. 2001) and free iron occur as Fe^{2+} ions. Three

Table 1 Results from ^{14}C dating: depth, conventional age (1σ), calibrated or "temporary calibrated" age (2 sigma), material dating, sample code. For comparison OSL (Optically Stimulated Luminescence) ages from the same loess section (A. Lang in Antoine et al. 2001) are included.

| OSL age (± 2σ) | | | [14]C age | | | | | |
| | | | Conventional age (± 1σ) | | Calibrated age (± 2σ) | | | |
OSL age [a]	Error [a]	Depth (m)	Age conv. BP [a]	Error [a]	Interval min [a]	Interval max [a]	Material	Sample code
		0.8	3050	70	3061	3387	loess org. matter	GifA-99010
19,800	4400	1.2						
		1.3	3580	70	3688	4000	loess org. matter	GifA-99011
		1.6	12,880	110	14,777	15,777	shell org. matter	GifA-96244
		1.6	15,260	110	18,162	18,702	shell carbonate	GifA-96221
20,800	3600	2.1						
		2.2	12,670	100	14,497	15,316	loess org. matter	GifA-99012
18,200	7400	2.8						
		3.0	18,170	180	21,131	22,258	loess org. matter	GifA-99013
19,500	4600	3.1						
19,200	3400	3.4						
		3.8	17,250	140	19,944	20,996	loess org. matter	GifA -99014
20,300	3000	4.2						
22900	5800	4.8						
		5.0	19,590	220	21,950	23,900	loess org. matter	GifA -99015
20,200	4800	5.7						
		5.8	14,270	120	16,780	17,420	loess org. matter	GifA-98366
		6.3	18,350	160	21,404	22,433	loess org. matter	GifA -99016
21,200	3600	6.4						
		7.0	19,100	180	21,400	23,700	loess org. matter	GifA -99017
		7.5	22,100	220	24,400	26,400	loess org. matter	GifA -99018

Table 1 Results from ^{14}C dating: depth, conventional age (1σ), calibrated or "temporary calibrated" age (2 sigma), material dating, sample code. For comparison OSL (Optically Stimulated Luminescence) ages from the same loess section (A. Lang in Antoine et al. 2001) are included.

| OSL age (± 2σ) | | | [14]C age | | | | | |
| | | | Conventional age (± 1σ) | | Calibrated age (± 2σ) | | | |
OSL age [a]	Error [a]	Depth (m)	Age conv. BP [a]	Error [a]	Interval min [a]	Interval max [a]	Material	Sample code
19,600	4800	7.6						
		7.8	15,490	140	18,084	18,711	loess org. matter	GifA -99019
26,000	8000	8.6						
		9.0	24,020	250	25,900	29,100	loess org. matter	GifA-98367
24,800	8200	9.1						
23,200	4800	9.4						
24,800	9400	9.7						
		9.7	21,340	190	24,000	25,600	loess org. matter	GifA-99020
		10.3	11,700	120	13,340	13,989	loess org. matter	GifA-99021
29,500	7400	11.0						
		11.1	25,700	270	27,200	31,300	loess org. matter	GifA-99022
		11.8	26,000	310	28,400	31,400	loess org. matter	GifA-99023
34,000	6400	11.9						
33,100	10400	12.2						
31,100	8200	12.7						
		12.8	26,670	300	28,800	31,400	loess org. matter	GifA-99024
		13.2	31,800	400	32,025	35,575	wood	Gif/LSM-10442
		13.2	32,180	470	35,525	39,275	wood	GifA-97292
		13.2	32,800	510	35,475	39,325	wood	GifA-97294
		13.2	32,270	500	35,475	39,325	wood	GifA-97291
		13.3	35,800	1200	34,700	40,500	bone	GifA-97328
		13.4	42,100	1200	41,100	47,000	loess org. matter	GifA-99025
		13.9	31,400	440	32,500	36,200	loess org. matter	GifA-99026
55,700	25,200	15.5						
61,300	19,800	18.6						
122,000	35,600	19.6						

possible sources of contamination may be postulated: 1) post-sampling bacterial degradation in spite of the rapid samples drying after sampling? However, this would mean that paleosol organic matter would be more reactive to post-depositional or post-sampling bacterial degradation than loess organic matter, because apparent rejuvenation occur only for soil horizons, 2) contamination due to infiltration of humic acids from the top soil, even in large depth? But in that case, rejuvenation would existed in every level, or 3) possible contamination during laboratory treatments. In fact, during alkali treatment dissolved atmospheric CO_2 is incorporated in the sample structure as ferrous carbonate and cannot be removed by further acid treatment. An alternative is proposed in Hatté et al. (2001) but, due to the small amount of material, it was not applied to these samples. Because such apparent underestimations do not occur in every level showing high iron concentrations, for the present it is impossible to distinguish between internal and external sources of contamination. Refining of the chemical treatment for samples from gley horizons may improve results.

Nevertheless, the developed protocol permits to establish a reliable chronology of loess deposits. Our time-scale, based on ^{14}C and OSL dates and pedostratigraphical requirements (hiatus, sedimentation slowdown; Antoine et al. 2001), is shown in Figure 2. The last Interglacial soil developed on Saalian (Rissian) loess. A Bt horizon of around 1.5 m is still preserved. A large hiatus of around 40 ka follows. The Marine Isotope Stage 4 (ca 70–45 ka) is represented by some 4 m of loess, laid down with an accumulation rate of around 0.16 m/ka, and followed by a weak sediment accumulation of only 30 cm for the period of ca 45–32 ka (around 0.02 m/ka). Further loess deposition (around 13 to 2.5 m depth) followed between 32 and 20 ka with a sedimentation rate of around 0.8–0.9 m/ka. After the Last Glacial Maximum the sedimentation rate decreased (around 0.3 m/ka between 20 ka and 15 ka). At around 15 ka loess sedimentation terminated and pedogenesis commenced. The Nussloch loess sequence of almost 12 m thickness accumulated between 32 and 17 ka is well suited for studying the climate during the last glacial period at reasonable temporal resolution by means of ^{14}C dating.

CONCLUSIONS

The agreement between IR-OSL and ^{14}C dates demonstrates the usefulness of the ^{14}C method supporting studies of loess sequences like Nussloch. The new approach allows to set up chronologies for glacial continental sediment sequences to support terrestrial paleoclimatic studies for unravelling of continental response to climatic changes. Improvements in the knowledge of organic matter structure may once allow to jet even more accurate and high chronologies.

ACKNOWLEDGMENTS

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