CALIBRATION OF THE ^{14}C TIME SCALE BEYOND 22,000 BP

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ABSTRACT. The conventional ^{14}C time scale between 11,500 and 22,000 sidereal years has been calibrated by TIMS U/Th dates for corals. Only a few studies have been made for the time beyond this range. Obtaining samples suitable for numerical dating or estimating the reservoir correction of the ^{14}C dates has been difficult, but we do not have these problems with TIMS U/Th dating of interstadial and interglacial lignite, because reservoir corrections are unnecessary.

THE CALIBRATION OF THE ^{14}C TIME SCALE

The extension of the calibration of conventional ^{14}C ages beyond 22,000 cal BP (Bard *et al.* 1989, 1993; Stuiver and Reimer 1993; Edwards *et al.* 1993) is not only of interest to geochronologists. New insights into the global carbon balance during the climatically variable last 50,000 yr of the Pleistocene (late Pleistocene) can be expected. One group of scientists is convinced that the change in the ^{14}C value of atmospheric CO_2 with time is governed mainly by the ^{14}C production rate, which in turn is modulated by the geomagnetic field (*e.g.,* Mazaud *et al.* 1991; Sternberg and Damon 1992). Climatic effects should play a minor role. The deviation between the ^{14}C and the absolute time scale, which increases from 2000 to 3000 yr between 11,500 and 22,000 cal BP, can be modeled on the basis of the geomagnetic dipole moment during the late Pleistocene, which was 50–75% lower than that of the Holocene. For the period between 40,000 and 50,000 sidereal years, a ^{14}C level of about the present value or a disappearance of the deviation is expected due to the Laschamp geomagnetic event.

In contrast, another group of scientists assumes climatically and oceanographically controlled changes in the ^{14}C value and thus a distortion of the ^{14}C time scale due to variations in CO_2 concentration in the past (Siegenthaler *et al.* 1980; Keir 1983; Prentice and Fung 1990; Adams *et al.* 1990). A precise ^{14}C calibration curve of the late Pleistocene may help to answer this question.

The calibration of the Holocene and Late Glacial ^{14}C time scale is based on dendrochronological dating of wood that has a precision of 1 yr (Stuiver and Kra 1986). For 11,500 to 22,000 cal BP, TIMS U/Th dates of corals from a core in Barbados were used (Bard *et al.* 1989, 1993; Edwards *et al.* 1993). ^{14}C dates for modern corals yielded an estimate of –400 yr for the reservoir correction. There is still some reservation that this correction is also valid for the climatically variable late Pleistocene. Measurements on Greenland ice show that atmospheric CO_2 concentration was variable during this time (Barnola *et al.* 1987).

ATTEMPTS TO EXTEND THE ^{14}C CALIBRATION CURVE

The first attempt to extend the ^{14}C calibration curve into the Pleistocene was made by Vogel (1980). He determined ^{14}C ages of aragonite samples from marl of the Lake Lisan site in Israel, which had been dated by Kaufman (1971) using the $^{230}Th/^{234}U$ method. His results are compared in Table 1. A comprehensive study yielded corresponding ^{14}C and U/Th dates from an 8-m-long stalagmite from the Cango cave in South Africa (Table 1; Vogel 1983, 1997). A reservoir correction of –1500 yr was assumed, but according to other findings, it may be only −900 (Geyh 1970) or −3000 yr (Labeyrie *et al.* 1967). Bischoff *et al.* (1994) also dated coexisting travertine and charcoal from an archaeological site in Spain. They found corresponding ages of 43,000 BP for U/Th and 37,000 BP for ^{14}C.

Bell (1991) dated baked clay from aboriginal fireplaces at Lake Mungo (Australia) by the TL method and compared the results with ^{14}C dates. He estimated an age difference of 4000 yr between the two time scales. The most precise point of the Pleistocene ^{14}C calibration was determined with the ^{40}Ar/^{39}Ar laser method on a tuff sample from a site near Naples, Italy (Deino and Curtis 1994). Additional samples with a wide age range should be available that are suitable for dating with both methods.

TABLE 1. Absolute Numerical Dates (BP) Determined by Different Dating Methods (U/Th, TL, Ar/Ar) and Corresponding Conventional ^{14}C Ages (BP)

Site	Material	Method	Absolute age	^{14}C age (yr BP)	Difference	Reference
Lisan, Israel	Argonite	U/Th	30,500 ± 2500	29,300 ± 310	1200 ± 2520	Vogel (1980)
	fraction	U/Th	48,000 ± 4000	33,830 ± 370	14,170 ± 4020	
	from marl					
Cango Cave,	Stalagmite	U/Th	29,240 ± 1650	30,060 ± 990	−820 ± 1925	Vogel (1983)
South Africa		U/Th	35,075 ± 2000	29,700 ± 850	5375 ± 2175	
		U/Th	38,620 ± 2000	35,430 ± 920	3190 ± 2200	
Lake Mungo,	Quartz	TL	31,400 ± 2100	27,000 ± 500	4400 ± 2160	Bell (1991)
Australia	grains from	TL	36,400 ± 2500	31,700 ± 500	4700 ± 2550	
	fireplaces	TL	32,700 ± 2200	29,200 ± 400	3500 ± 2240	
		TL	33,500 ± 2300	28,400 ± 600	5100 ± 2380	
Barbados	Corals	U/Th	30,225 ± 160	25,430 ± 355	4795 ± 390	Bard *et al.* (1993)
Naples, Italy	Tuff	Ar/Ar	37,100 ± 400	34,500 ± 145	2600 ± 425	Deino and Curtis (1994)

During the 16th Radiocarbon Conference in Groningen, two papers were presented that dealt with the extension of the ^{14}C calibration beyond 22,000 BP. Kitagawa and van der Plicht (1998) determined more than 200 ^{14}C AMS dates of macrofossils taken from a 75-m-long varved sediment core of Lake Suigetsu, central Japan. Voelker *et al.* (1998) determined 50 ^{14}C AMS dates from a sediment core taken in the southwestern Icelandic Sea. Both sets of results show a ^{14}C maximum *ca.* 35,000 BP, corresponding to *ca.* 6000-yr deviation between the ^{14}C and the absolute time scale.

U/TH DATING OF LIGNITE

U/Th dating of lignite is possible when humic acids adsorb the uranium dissolved in the groundwater entering the organic deposits. The central parts of lignite beds, which are often 1–2 m thick, are frequently found to behave as a closed system in which uranium has been neither leached nor accumulated. These processes have occurred, however, in the top and bottom 10 cm, where the oxygen and uranium have been sorbed from the circulating groundwater. In the central part of the closed system, ^{230}Th has been produced by the decay of ^{234}U, just as the idealized U/Th model assumes. U/Th dating is possible until radioactive equilibrium between ^{230}Th and ^{234}U is established (Heijnis and van der Plicht 1992).

A complication exists in the form of detrital minerals, which may contain allochthonous ^{230}Th. The varying proportion of ^{230}Th activity due to allochthonous ^{230}Th can be determined and subtracted from the total ^{230}Th activity to obtain the autochthonous radiogenic activity, which is a function of the U/Th age. "Isochron" U/Th dating was developed to carry out the necessary detrital correction (Luo and Ku 1991). This correction requires three or usually more independent U/Th datings. A plot of ^{230}Th/^{232}Th *versus* ^{234}U/^{232}Th activity ratios yields an "isochron" (Fig. 1) that intersects the ordinate at the $^{230}Th/^{232}Th$ activity ratio used for the detrital correction. The distance of the points to the ordinate determine the fraction of detrital ^{230}Th.

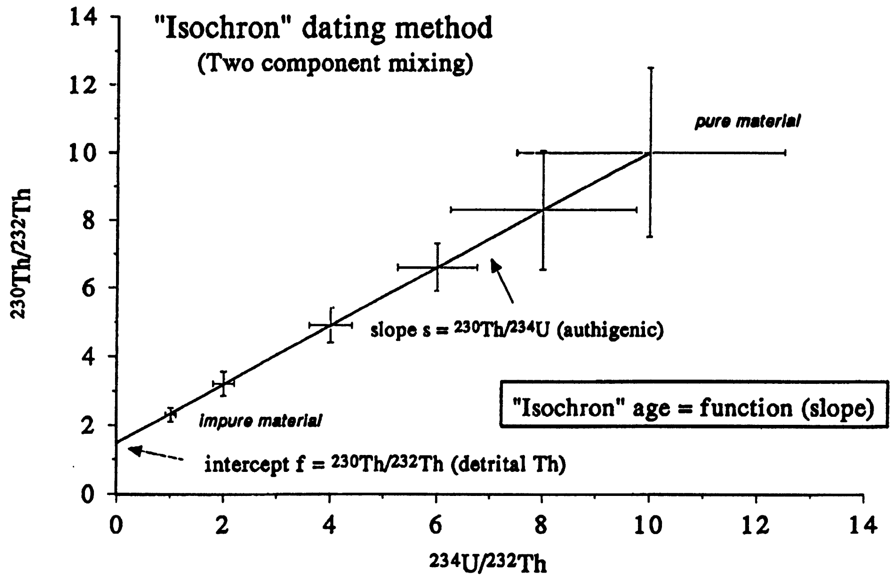

Fig. 1. Plot of $^{230}Th/^{232}Th$ *vs.* $^{234}U/^{232}Th$ activity ratios for estimating the detrital correction and the "isochron" U/Th age

When the lignite deposits are sampled, the top and bottom 10 cm of a lignite bed in the exposed sections and/or sediment core are excluded. That means that datable lignite beds have to be at least 25 cm thick. Samples contaminated with low, slightly higher and high proportions of detrital material are taken with a scalpel from the central part of the lignite bed. Twenty grams of dry matter are needed per analysis for the radiometric age determination. TIMS U/Th dating needs about a tenth of that amount.

Following Luo and Ku (1991), the total sample dissolution method (TSD) was found to be the most suitable one. The organic samples are burned at 600°C in a stream of oxygen and the ash is totally dissolved in hydrofluoric acid and nitric acid and a uranium/thorium spike is added. Uranium and thorium are then separated on ion-exchange columns and until now have been electrolytically plated on stainless steel discs for measurement with an alpha-spectrometer. In the future, the extracted uranium and thorium solutions will be evaporated on filaments for measurement on a TIMS mass spectrometer. This will increase the quality and reliability of the results. Since less material is needed, smaller areas can be sampled from lignite monoliths or cores that behave as closed systems. The precision of the TIMS U/Th dates is increased by one magnitude of order as well.

The suitability of the U/Th method for dating lignite was checked by dating Eemian material. For various European profiles a mean U/Th age of 111.5 ± 3.4 kyr was obtained, which corresponds to the end phase of the last interglacial period. This is plausible. Many glacial lakes must first have been filled with sediment before lignite and fen bog formation could begin.

The first published U/Th date for lignite related to the calibration of the Pleistocene ^{14}C time scale was obtained from a 28-cm-thick Pleistocene lignite seam in the Oberwasser canal in Rosegg, Austria. The base layers comprise silty clayey sediments and the top layers calcareous gravel (Fritz and

Ucik 1996). The conventional ^{14}C age was 34,700 ± 1350 BP (VRI-1222) and the "isochron" U/Th date was 40,670 ± 1080 BP (Table 2). Signs of ^{14}C contamination were not present, nor were indications of uranium leaching and/or accumulation.

An extended study was done on the Pleistocene lignite profile at Gossau in the Zurich Canton of Switzerland (Fig. 2; Schlüchter *et al.* 1985, 1987). It is better preserved than others in Switzerland and palynologically well investigated. The results can be correlated with global climate records. The profile reflects peat growth in a delta environment that was interrupted twice by deposition during flooding. There is 30 cm of sandy silty material between the top of the main lignite bed of 1 m and the basal lignite bed of 70 cm. This organic deposit is overlain by 2 m of reworked fluvial gravel and fine sand. The upper lignite bed, 25 cm thick, was formed in a swampy milieu. Nine samples from these organic deposits were dated using ^{14}C in the Zürich AMS laboratory (Schlüchter *et al.* 1987). Eight U/Th "isochron" dates were determined in the Hannover ^{14}C laboratory. The results are compiled in Table 2.

TABLE 2. Conventional ^{14}C and "Isochron" U/Th Ages for Lignite from the Section in Kärnten and from the Gossau Section in Switzerland (Schlüchter *et al.* 1987)

Stratigraphy	Layer	Depth (cm)	U/Th age (BP)	ETH no.	^{14}C age (yr BP)	Difference (yr)
Kärnten			40,670 ± 1080		34,700 ± 1350	5970 ± 1730
Upper lignite bed		528–532		2209	28,550 ± 310	
				2120	29,450 ± 1150	
				2210	28,250 ± 350	
			34,700 ± 4000	Mean	28,460 ± 225	6240 ± 4000
Main lignite bed	Upper	524–527		2211	33,410 ± 480	
				2121	33,000 ± 2500	
			37,600 ± 2300	Mean	33,400 ± 470	4200 ± 2350
	Base	579–582	47,800 ± 6000	2212	40,920 ± 1120	6880 ± 6100
Basal lignite bed	Upper	584–586		2213	45,000 ± 1200	
				2122	47,500 ± 1800	
				2214	54,000 ± 3000	
			49,100 ± 3700	Mean	46,840 ± 950	2260 ± 3820
Mean						5180 ± 960

The initial intention of the U/Th dating of the Gossau lignite section was to check the reliability of ^{14}C ages between 40,000 and 50,000 BP. A ^{14}C age of 49,100 BP was determined for the basal lignite bed. This date could represent a lignite formed during the Odderade interstadial at *ca.* 80,000 BP if it was contaminated by 20% humic acids or roots during the formation of the upper lignite at *ca.* 28,500 BP. This possibility is excluded by comparison of the ^{14}C ages with the U/Th ages (Table 2).

DISCUSSION

The conventional ^{14}C ages are plotted *versus* the absolute ages (Tables 1 and 2) in Figure 3. The large confidence intervals, especially for the radiometric U/Th ages, preclude the construction of a ^{14}C calibration curve. The maximum deviation between the ^{14}C and the absolute time scale may increase to 6000 yr *ca.* 35,000 BP (Fig. 4). The postulated disappearance of the deviation due to the Laschamp Event (Mazaud *et al.* 1991; Sternberg and Damon 1992) between 40,000 and 50,000 BP can be neither confirmed nor neglected. The modeled deviations appear to be generally too low.

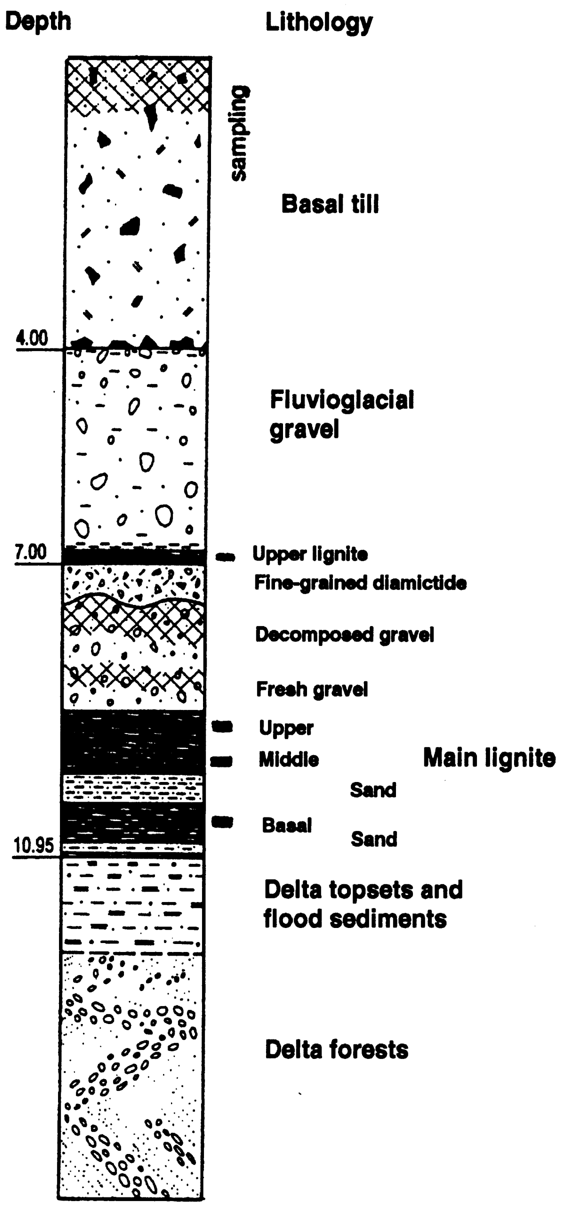

Fig. 2. Lithostratigraphy of the Gossau section in the Zürich Canton of Switzerland

The narrower confidence intervals of TIMS U/Th dates and precision ^{14}C ages of samples for the Gossau lignite section offer an additional opportunity to complement dates to the ^{14}C calibration curve up to 50,000 BP from the same terrestrial material. This may allow a check whether the sediment time scales are complete or shrunken due to erosion.

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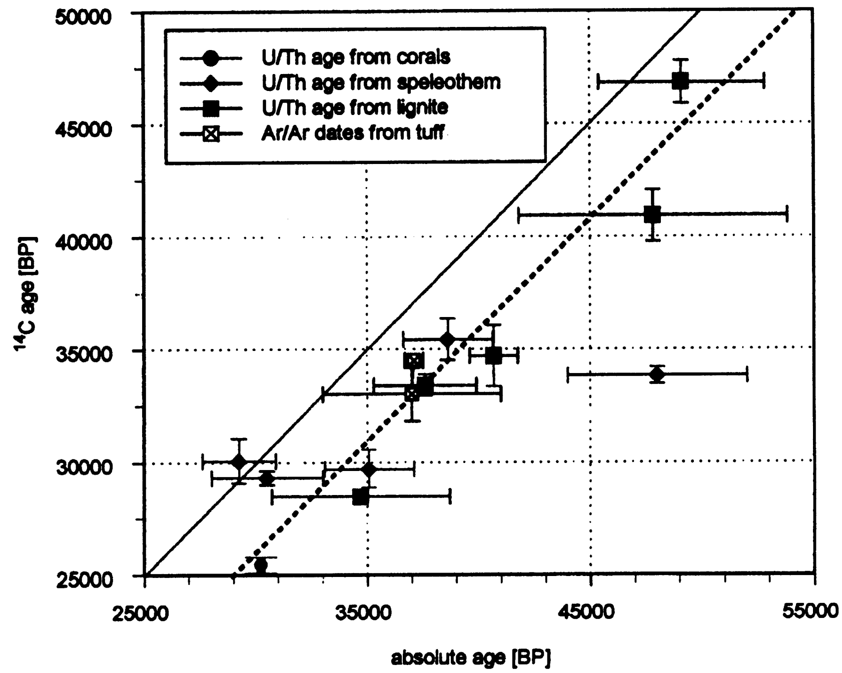

Fig. 3. Absolute numerical ages (U/Th, TL, Ar/Ar) and the corresponding conventional ^{14}C ages from the late Pleistocene (Table 1)

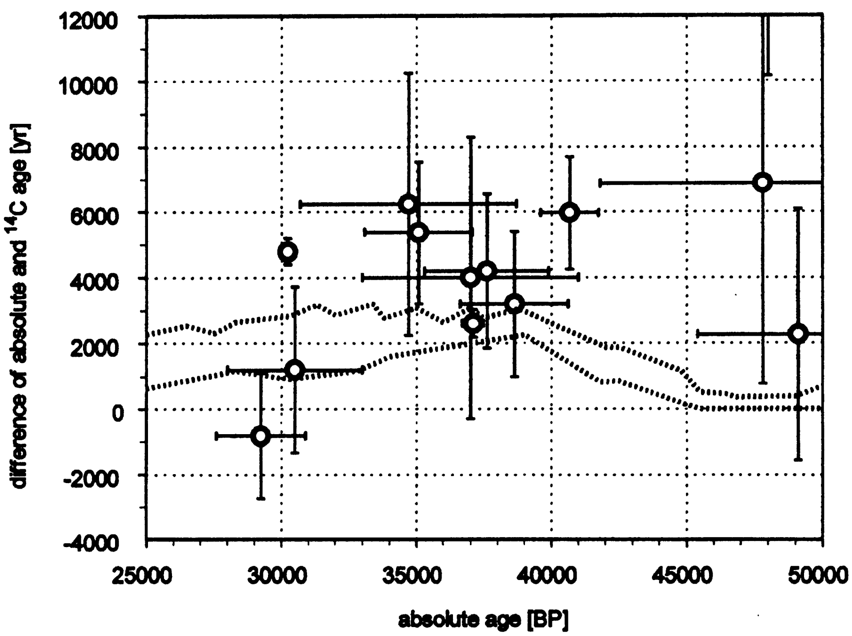

Fig. 4. Difference between absolute numerical ages and conventional ^{14}C ages. The dotted lines are the upper and lower limits of the geomagnetic modeling results by Mazaud *et al.* (1991).

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Conclusion

The difference between conventional AMS ^{14}C ages and radiometric "isochron" U/Th ages for lignite from the Gossau section in Switzerland, as well those for other suitable pairs of dates, suggest that the deviation between the ^{14}C and the absolute time scale is between 3000 and 6000 yr within the age range of 22,000 to 50,000 BP. On-going, more precise TIMS U/Th dating will permit a reliable, precise ^{14}C calibration curve to be constructed for the late Pleistocene. The precision will be high enough to differentiate between changes in the difference within the range of 3000 to 6000 yr.

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