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RADIOCARBON CALIBRATION BY MEANS OF MASS SPECTROMETRIC ^{230}TH/^{234}U AND ^{14}C AGES OF CORALS: AN UPDATED DATABASE INCLUDING SAMPLES FROM BARBADOS, MURUROA AND TAHITI

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ABSTRACT. As first shown by Bard *et al.* (1990a), high-precision ^{230}Th-^{234}U ages can be used successfully to calibrate the radiocarbon time scale beyond the high-precision tree-ring calibration that now reaches 11,900 cal BP (Kromer and Spurk 1998). Using mass spectrometric techniques, we measured ^{14}C and ^{230}Th ages on new samples collected from boreholes drilled off the islands of Tahiti and Mururoa (French Polynesia) in order to complement the database previously obtained on Barbados corals (Bard *et al.* 1990a, 1993).

METHODS

New ^{230}Th/^{234}U ages for Tahiti and Mururoa samples (Table 1) were measured with a VG-54-30 thermal ionization mass spectrometer (TIMS) fitted with an ion-counting Daly detector, at CEREGE (Aix-en-Provence). The chemical separations were similar to those previously described (Bard *et al.* 1990b). The 2σ precision of the ^{230}Th ages ranges from 30 to 60 yr, for ages between 8000 and 14,000 ^{230}Th yr BP.[4] This represents an improvement by a factor of 2 to 3 over the performance obtained on Barbados corals by single collection and analog Daly detector on an MM30 mass spectrometer (Table 1; Bard *et al.* 1990a,b). The precision of the ages was checked by measuring numerous replicates (Bard *et al.* 1996). In particular, we performed five analyses of different pieces of the same coral specimen (sample P7-7: 10,995 ± 40, 11,005 ± 30, 11,025 ± 30, 10,995 ±30 and 10,995 ± 30 ^{230}Th yr BP; ages are rounded to the nearest 5 yr). The five ^{230}Th/^{234}U ages agree with each other within the 2σ uncertainties, with an overall 2σ uncertainty on the mean of 12 yr and a maximum difference between replicates of *ca.* 30 yr.

Following Ludwig *et al.* (1992) and Stirling *et al.* (1995), the ^{229}Th/^{233}U ratio of our mixed spike was calibrated against the uraninite standard HU1 assumed to be at exact secular equilibrium. This calibration was shown to be accurate within 5‰ by means of gravimetric U and Th standards. This agreement is satisfactory if one takes into account the overall uncertainty on the half-lives of ^{234}U and ^{230}Th (2‰ and 8‰, respectively; see Ludwig *et al.* 1992).

Th samples are loaded with colloidal graphite on single-zone refined Re filaments and U samples on Re-Ta triple filaments. ^{234}U/^{238}U ratios are measured in dynamic multicollection mode: ^{233}U, ^{234}U and ^{235}U ion beams are measured with the Daly ion counting detector, whereas ^{235}U and ^{238}U ion currents are measured with Faraday cups. Correction for isotopic fractionation is performed by normalizing the measured ^{238}U/^{235}U atomic ratio to the natural value (137.88). Faraday/Daly gain is monitored with ^{235}U signals during each measurement block in order to correct for possible shifts of the gain.

The external precision on individual values of $\delta^{234}U_i$ (=[initial^{234}U/^{238}U – 1] × 1000) is on the order of 2‰ (at 2σ), as shown by repeated measurements of standards. The accuracy has been checked by

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[4] All radiometric ages expressed here as "BP" are relative to a fixed present of 1950.

TABLE 1. Comparison of Ages Obtained on Corals by AMS ^{14}C and TIMS ^{230}Th

Sample code	U/Th age (yr BP)	±2σ Th	^{14}C age (yr BP)	±2σ ^{14}C	Δ^{14}C	±2σ Δ
Barbados						
RGF B-56*†	773	10	960	90	−26	11
RGF 7-4-2	7460	80	6605	150	83	23
RGF 7-5-5	8450	50	7640	160	74	22
RGF 7-12-2*†	9265	60	8305	120	91	18
RGF 7-16-2	9730	50	8750	170	92	24
RGF 7-27-4	11090	70	9710	210	142	31
RGF 12-5-2†	11590	60	9980	170	173	26
RGF 12-6-7†	11530	70	10095	160	148	25
RGF 12-9-5†	12260	90	10220	130	235	24
RGF 12-16-5*†	13100	80	11270	100	199	19
RGF 12-21-6	13700	170	11710	200	221	39
RGF 12-21-10*	13730	100	11720	400	224	63
RGF 9-8-2	14235	100	12200	200	225	34
RGF 9-13-3*†	14690	85	12620	220	229	36
RGF 9-21-11	18240	140	15170	180	374	39
RGF 9-24-4	18890	250	16020	420	337	81
RGF 9-27-5*†	19000	70	16360	220	299	37
RGF 9-32-4	20610	120	17230	280	416	53
RGF 9-34-8*†	21980	130	18410	250	443	50
RGF 12-30-2*†	30230	160	25870	410	547	84
Tahiti						
Ta-P6-10*	9565	20	8410	140	116	20
Ta-P6-11*	9830	30	8790	120	99	17
Ta-P6-12	9920	40	8800	120	110	17
Ta-P6-13*	10205	30	8990	120	122	17
Ta-P6-14†	10120	50	9065	100	100	15
Ta-P7-1*	8520	25	7830	200	57	27
Ta-P7-2*	9255	30	8170	180	108	25
Ta-P7-4	10250	40	8970	140	131	20
Ta-P7-5	10575	50	9330	140	125	21
Ta-P7-6	10850	50	9550	140	132	21
Ta-P7-7*	11005	12	9580	140	149	20
Ta-P7-8	11280	30	9800	140	155	21
Ta-P7-9	11495	30	9980	140	160	21
Ta-P7-10	11930	50	10280	140	177	22
Ta-P7-11	12875	40	10830	140	233	22
Ta-P7-12	12800	30	10800	160	226	25
Ta-P7-13	12695	60	11010	160	179	25
Ta-P7-14	12710	50	11090	160	170	24
Ta-P7-15	12865	50	11030	160	201	25
Ta-P7-16	12905	50	11090	160	198	25
Ta-P7-17	13065	30	11430	200	171	29
Ta-P7-18*	13465	40	11630	220	198	33
Ta-P7-19*	13750	30	11790	220	216	34
Ta-P8-1‡	12905	30	11230	120	177	18
Ta-P8-2‡	13335	30	11690	110	171	17
Ta-P8-3‡	13665	35	12010	110	171	17

TABLE 1. Comparison of Ages Obtained on Corals by AMS ^{14}C and TIMS ^{230}Th *(Continued)*

Sample code	U/Th age (yr BP)	±2σ Th	^{14}C age (yr BP)	±2σ ^{14}C	Δ^{14}C	±2σ Δ
Ta-P8-4‡	13850	35	12260	110	161	17
Mururoa						
Mu 315*†	15585	50	13160	140	280	24
Mu 313*†	17595	70	14835	150	325	27
Mu 8-30-315‡	17170	40	14560	180	303	30
Mu 8-30-310.5‡	23510	70	20050	300	416	54
New Guinea						
KWA-I-1‡			*35770*	*1820*		
KWA-I-1‡			*35120*	*1660*		
KWA-I-1‡			*39600*	*2800*		
KWA-I-1‡			*34580*	*1620*		
KWA-I-1†‡	41100	500	35600	920	720	220

Note: All ages are expressed in yr before 1950 (BP) and statistical uncertainties are given at the 2σ level. ^{14}C ages are conventional ages with a reservoir correction of 400 yr for Barbados and New Guinea and 300 yr for Tahiti and Mururoa (see text). When several replicates were measured on different pieces of the same coral, the reported age and uncertainty are the weighted mean and error (except for sample KWA-I-1, for which individual ^{14}C ages are listed in italics). The U-Th ages of KWA-I-1 are from Dia *et al.* (1992). Sample Mu8-30-310.5 is composed of bothryoidal aragonite precipitated at shallow depth. All other samples are corals; species lists can be found in previous publications (Bard *et al.* 1990a, 1996). All samples were checked by XRD prior to dating to verify the absence of secondary low and/or high magnesium calcite (<1%).

*Reported ^{230}Th age is the weighted mean of 2 or more replicates (cf. Bard *et al.* 1993, 1996 for all individual ages).
†Reported ^{14}C age is the weighted mean of 2 or more replicates (cf. Bard *et al.* 1993, 1996 for all individual ages).
‡Age was not reported previously.

repeated measurements of NBS-010 (mean of −7.0 ± 0.7‰ $2\sigma_m$, 29 measurements) and NBS-SRM960-NIST4321B (mean = −35.6 ± 1.5‰ $2\sigma_m$, 6 meas.). The $\delta^{234}U_i$ values obtained on the Tahiti and Mururoa samples range between 140 and 150, with a mean value of 147 ± 2‰ (one standard deviation (SD) on 42 measurements). This average is very close to the values measured on present-day seawater (144 ± 4‰ SD on 9 meas., Chen, Edwards and Wasserburg (1986)) and on modern and recent corals (145 ± 5‰, SD on 25 meas., Bard *et al.* (1990a); 150 ± 1‰, SD on 20 meas., Edwards *et al.* (1993); 148 ± 2‰, SD on 3 meas., Szabo *et al.* (1994); 149 ± 1‰, SD on 3 meas., Stirling *et al.* (1995)). This further confirms that the samples used for this study are devoid of diagenetic alteration and remained closed systems for U-Th in the past. In addition, the absence of secondary calcite (<1%) was also checked in triplicate by x-ray diffraction (XRD) in the samples selected for dating.

^{14}C ages were measured by accelerator mass spectrometry (AMS) on the Tandetron facility installed at Gif-sur-Yvette (Arnold *et al.* 1987). 200–300 mg carbonate samples were first ground into millimeter-sized pieces preparatory to a strong acid leaching procedure (>40% weight loss) to remove surface contaminants (Bard *et al.* 1990b). Large carbonate subsamples (15–18 mg) were then converted to CO_2 and reduced to graphite in order to produce at least two accelerator targets for most samples and hence to increase the ^{14}C precision. Each carbonate subsample was composed of several grains selected randomly, which should help to minimize the influence of intra-annual changes of the ^{14}C reservoir ages, as shown by Brown *et al.* (1993). The ^{14}C ages for Mururoa and Tahiti samples were corrected for 300 yr, which is a mean ^{14}C reservoir age based on preanthropogenic data from the tropical South Pacific (Bard 1988). A reservoir age of 400 yr is used for corals from Barbados and New Guinea.

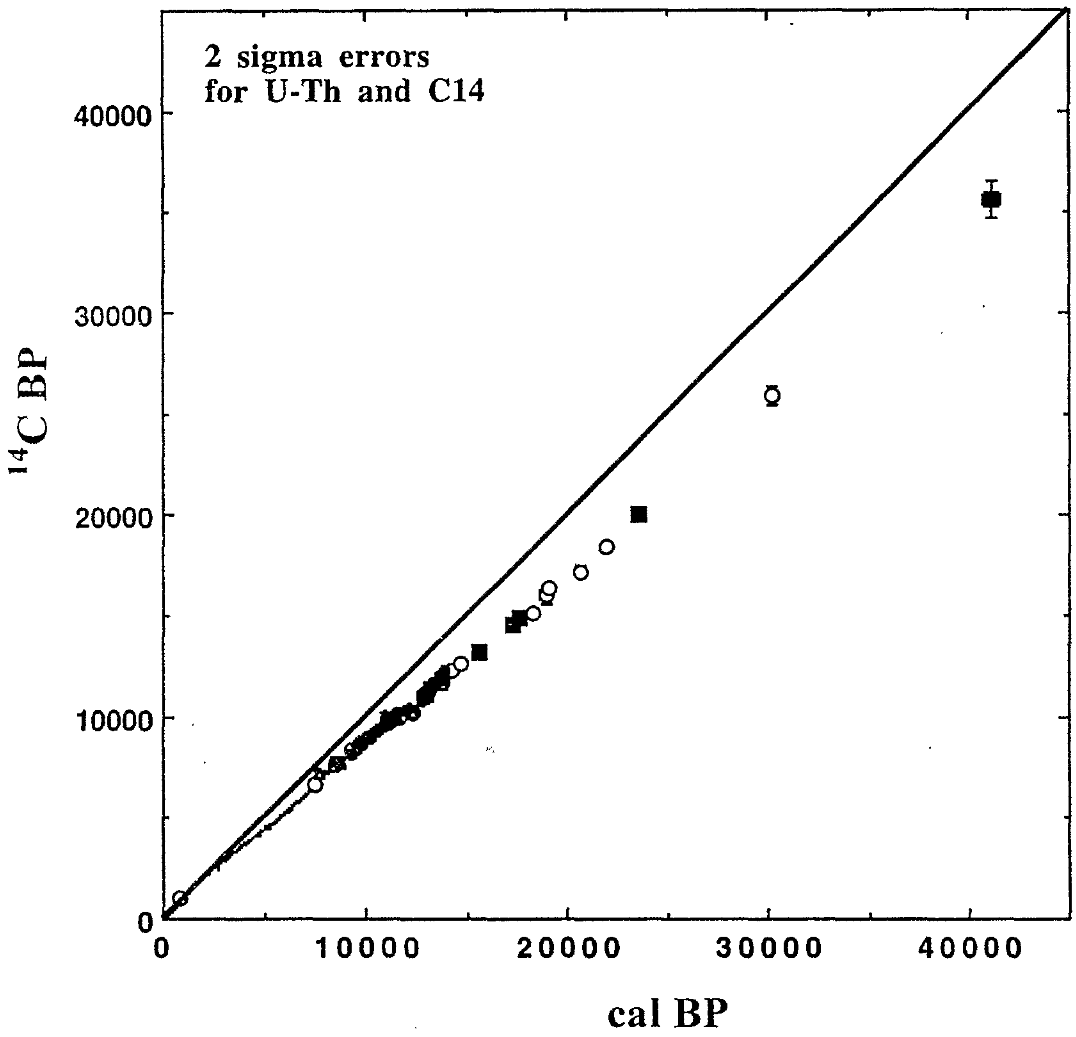

Fig. 1. AMS ^{14}C ages plotted *vs.* TIMS ^{230}Th ages obtained on corals. ^{14}C ages are conventional ages in yr BP with statistical errors given at the 2σ level. △ = the data from New-Guinea (Edwards *et al.* 1993), ○ = data from Barbados, ● = data from Tahiti and ■ = the data from Mururoa. The thin wiggly curve is the smoothed tree-ring calibration and the thick solid line is the 1:1 line. For ages beyond the Younger Dryas/Preboreal boundary (10,000 BP) the coral data can be approximated by a simple linear equation: [cal BP] = 1.168 × [^{14}C age BP], or even better by a second-order polynomial: [cal BP] = -3.0126×10^{-6} × [^{14}C age BP]^2 + 1.2896 × [^{14}C age BP] − 1005.

In addition to the samples collected by coring, we analyzed a very old *Porites lutea* sample collected in the lower uplifted terrace of Huon Peninsula, Papua New Guinea. This coral, sample KWA-I-1, was previously dated by TIMS U-Th at 41,100 ± 500 BP (Dia *et al.* 1992). Sample contamination and chemistry blank reproducibility are critical problems in dating such an old sample by ^{14}C (see Bard *et al.* 1993 for blank measurements obtained on calcite and aragonite). Four different pieces of KWA-I-1 were dated (*i.e.*, 8 C-Fe targets) and the individual ^{14}C ages are listed in Table 1 together with the weighted mean age based on these four values. The agreement among the four replicates is not optimal, which could be due to a small and residual contamination of this sample. The ^{14}C age of KWA-I-1 remains tentative and more samples should be dated in the same time range to confirm its surprisingly high Δ^{14}C (*ca.* 700 ‰).

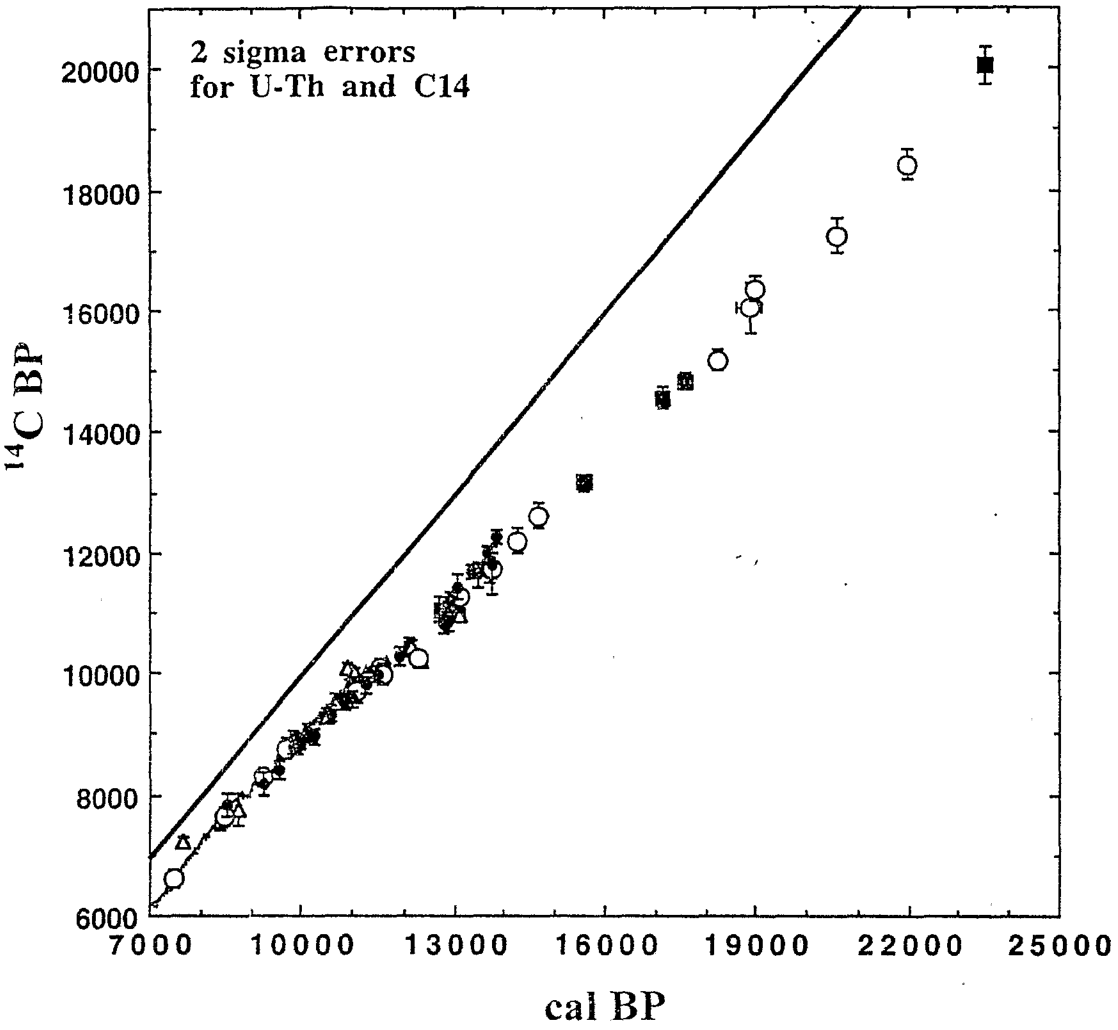

Fig. 2. Blowup of the Figure 1 diagram between 7000 and 25,000 cal BP. Symbols as in Fig. 1.

RESULTS AND COMPARISON WITH PREVIOUS CALIBRATIONS

As previously shown, there is a large difference between the ^{14}C and ^{230}Th ages (Bard *et al.* 1990a). The magnitude of the ^{14}C-^{230}Th age difference observed on the Tahiti and Mururoa samples (Figs. 1 and 2) agrees well with previous studies of corals (Bard *et al.* 1990a, 1993; Edwards *et al.* 1993). The accuracy of ^{230}Th ages is further demonstrated by the excellent agreement with the recently revised dendrocalibration by Kromer and Spurk (1998), in particular in the critical range of the German pine calibration (10,000–11,900 cal BP; see Fig. 3).

Altogether, these two different calibration methods lead to the reconstruction of significant variations of the atmospheric $^{14}C/^{12}C$ ratio through time (Fig. 4). In particular, the new data from Mururoa confirm clearly that the atmospheric $\Delta^{14}C$ was *ca.* 400–500‰ higher at *ca.* 20,000–30,000 cal BP and that it has essentially decreased during the period between 18,000 and 7000 cal BP. This long-term $\Delta^{14}C$ decrease has been attributed to a concomitant long-term increase of the intensity of the geomagnetic field (Bard *et al.* 1990a; Bard 1997; Stuiver *et al.* 1991).

In the critical range between 9500 and 12,000 cal BP, the coral results are in agreement with the data obtained from varved sediments from Lake Gościąż (Goslar *et al.* 1995), further confirming the new synchronization between the oak and the pine chronologies (Kromer and Spurk 1998). A new cali-

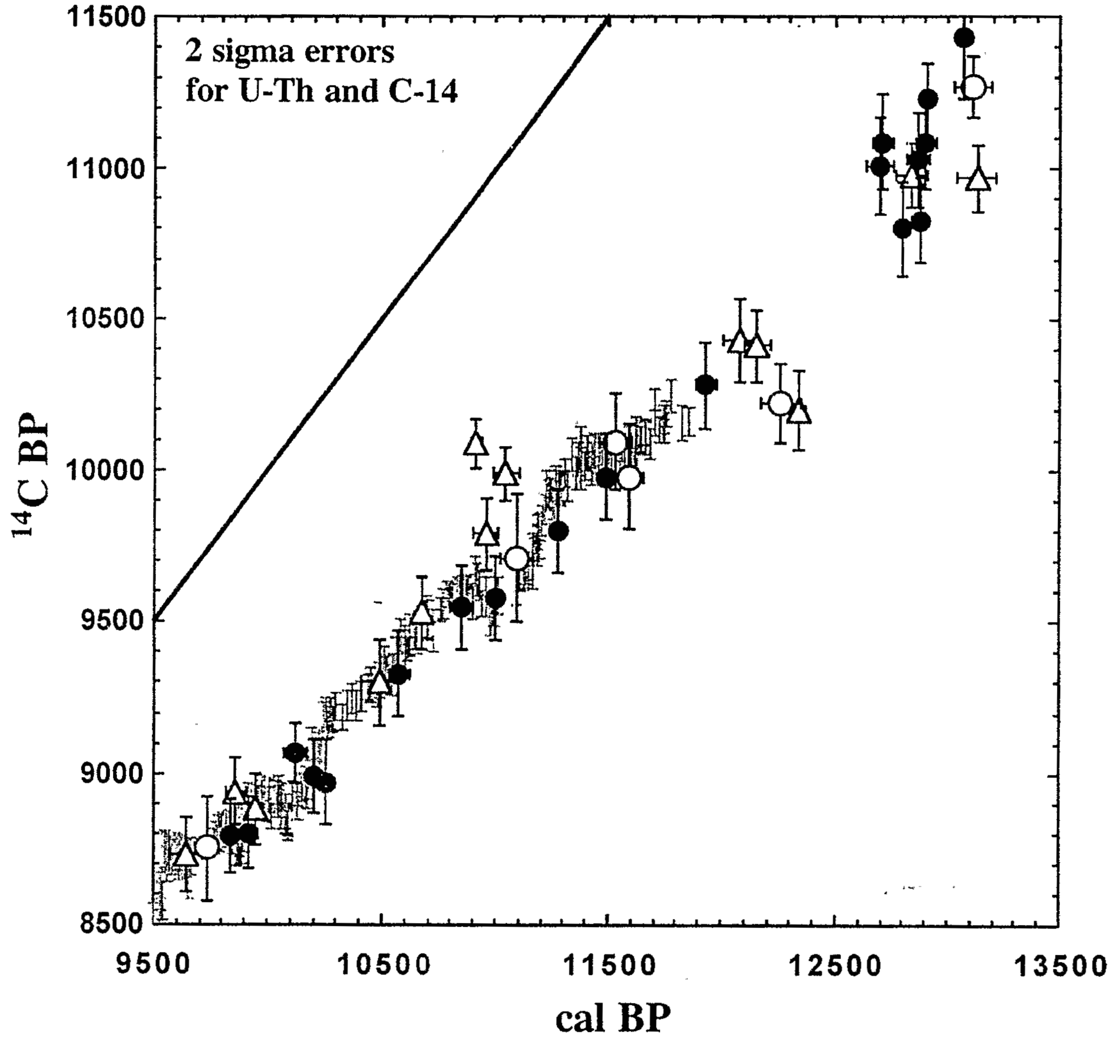

Fig. 3. Blowup of the Figure 2 diagram between 9500 and 13,500 cal BP. Symbols as in Fig. 1, except tree-ring calibration represented with gray error bars (from Kromer and Spurk 1998).

bration data set based on marine varves from the Cariaco Basin was recently proposed by Hughen *et al.* (1998). The Cariaco calibration curve goes back to 12,500 cal BP and is also in excellent agreement with our coral data (Hughen *et al.* 1998, especially Fig. 3b).

The coral ^{230}Th ages together with the Gościąż and Cariaco varve data finally confirm that the other calibrations based on varved sediments from Sweden (Wohlfarth 1996), Holzmaar in Germany (Hajdas *et al.* 1995), and Soppensee in Switzerland (Hajdas *et al.* 1993) are still in error even after the recent additions of so-called "missing varves" (~900 "missing varves" were added to the chronology from Holzmaar (Hajdas *et al.* 1995); ~550 "missing varves" were added to the chronology from Soppensee (Hajdas *et al.* 1993); ~500 "missing varves" were added to the Swedish chronology (Wohlfarth 1996)).

An independent check on the coral ^{14}C-^{230}Th calibration can be obtained by analyzing volcanic ash layers that can be recognized and dated by counting annual couplets in Greenland ice cores ("cryovarves"). Grönvold *et al.* (1995) have identified and characterized chemically the Saksunar and Vedde ash layers, which occurred respectively at 10,180 ± 120 and 11,980 ± 160 cal BP, according to the GRIP core chronology (2σ errors). These two ash layers have recently been redated by AMS

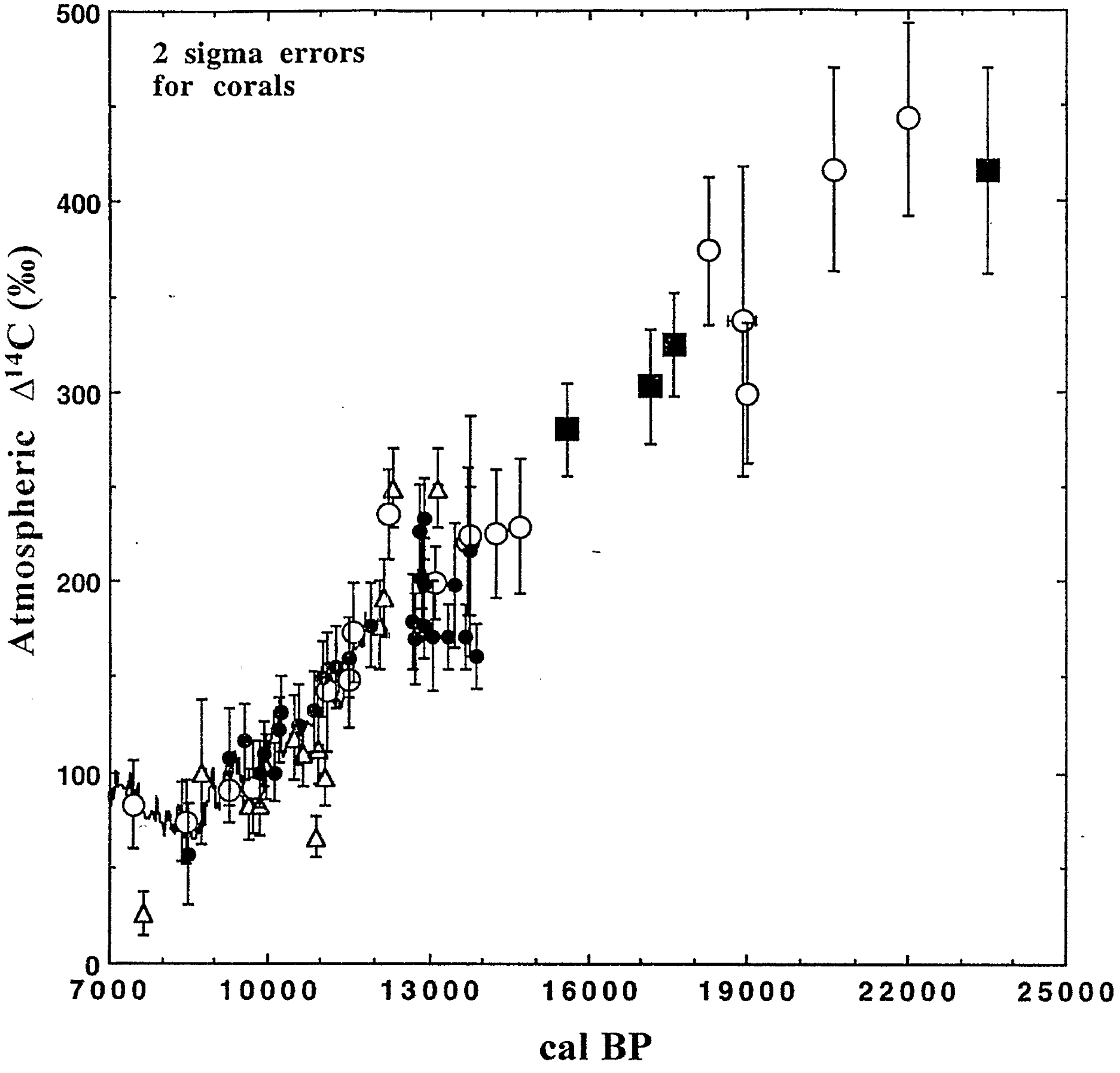

Fig. 4. Δ^{14}C *vs.* time as calculated by using the AMS ^{14}C ages *vs.* TIMS ^{230}Th comparison. Statistical errors for coral data are provided at the 2σ level. Symbols as in Fig. 1.

on terrestrial plant macrofossils at, respectively, 8960 ± 140 ^{14}C yr BP (2σ error based on 3 AMS ^{14}C ages from Birks *et al.* 1996) and 10,330 ± 60 ^{14}C yr BP (2σ error based on 11 AMS ^{14}C ages from Bard *et al.* 1994 and Birks *et al.* 1996). The data for these two volcanic events clearly demonstrate the compatibility of the German pine tree-ring chronology, ^{230}Th ages of corals, Gościąż varves and GRIP annual counts in the time range around the Younger Dryas/Preboreal boundary dated at *ca.* 11,500 cal BP.

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