

## ANOMALOUS RADIOCARBON AGES FOUND IN CAMPANIAN IGNIMBRITE DEPOSIT OF THE MEDITERRANEAN DEEP-SEA CORE CT85-5

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**ABSTRACT.** A detailed radiocarbon chronology has been established for the deep-sea core CT85-5 from the Tyrrhenian Sea. This chronology, which is based on the analysis of foraminifera shells, shows a set of reversed <sup>14</sup>C ages for sediments deposited during the eruption of the Campanian Ignimbrite (~40 ka cal BP). The anomalous young <sup>14</sup>C ages coincide with elevated concentrations of <sup>10</sup>Be measured in the same core. Although reversals in <sup>14</sup>C ages have been previously found in other records at 40 ka cal BP, such extreme changes have not been observed elsewhere. The enhancement in <sup>14</sup>C concentration in CT85-5 sediments associated with the Campanian Ignimbrite is equivalent to an apparent age ~15 ka younger than the age for the sediments deposited shortly before the eruption. Here, we present consistent results of repeated measurements showing no analytical problems that can explain the observed rapid changes in <sup>14</sup>C of this particular record.

### STUDY BACKGROUND

The detection of the “<sup>10</sup>Be peak” dated to 35 and 40 ka BP found in Antarctic ice cores (Raisbeck et al. 1987) and later in Greenland ice cores (Yiou et al. 1997) prompted studies of variable production rates of cosmogenic isotopes. The low geomagnetic field of the Laschamp event, which was first discovered in a lava flow of the Massif Central, France (Bonhommet and Zähringer 1969), and dated to ~40 ka cal BP (see Valet et al. 2007 for a review) and more recently to 40.65 ± 0.65 ka cal BP (Singer et al. 2009), has been discussed as the most likely cause of these changes. In the 1990s, measurements of <sup>10</sup>Be concentrations in deep-sea sediments became available showing enhanced <sup>10</sup>Be levels around 40 ka cal BP (McHargue et al. 1995, 2000; Robinson et al. 1995). Finally, reconstructions of geomagnetic field intensity in deep-sea sediments (Laj et al. 2000, 2002) and correlation with the ice-core record of cosmogenic isotopes <sup>10</sup>Be and <sup>36</sup>Cl has shown that the intervals of low geomagnetic field coincided with periods of increased flux of cosmogenic isotopes (Baumgartner et al. 1998; Wagner et al. 2000).

Castagnoli et al. (1995) published <sup>10</sup>Be measurements on sediment core CT85-5 recovered from the Tyrrhenian Sea. The detection of a clear <sup>10</sup>Be peak, which was coincident with the Campanian Ignimbrite (CI) ash layer, gave the background to our radiocarbon analysis across the sediment core and in particular the section corresponding to the <sup>10</sup>Be enhancement. The surprising results of our <sup>14</sup>C dating were first reported as a figure in Giaccio et al. (2006). In this study, we present the complete set of the results including all the tests carried out to assess the validity of the accelerator mass spectrometry (AMS) <sup>14</sup>C dating performed on the planktonic foraminifera shells of CT85-5 core. These results show that the high <sup>14</sup>C content coincides with the previously observed <sup>10</sup>Be enhancement (Castagnoli et al. 1995). The detailed <sup>14</sup>C-<sup>10</sup>Be comparison is allowed by using measurements of these 2 cosmogenic radioisotopes in the same core.

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## MATERIALS AND METHODS

The core CT85-5 was recovered from the Tyrrhenian Sea (40°19'02"N, 11°15'42"E) in 1985 at a water depth of 2833 m. This core had been the subject of various studies including measurements of  $^{10}\text{Be}$  (Castagnoli et al. 1995), carbonate content (Castagnoli et al. 1992), and magnetic properties (Castagnoli et al. 1998).

Samples were taken at the Turin Laboratory in 1992, 1993, and 1998 for our original study. More recently, in 2009, the second half of the core CT85-5 was sampled. For each  $^{14}\text{C}$  analysis, at least 2000 specimens of *Globigerina bulloides* or mixed planktonic foraminifera were handpicked and processed for AMS analysis. In addition, 1 sample was prepared from pteropods, i.e. shells of pelagic sea snails (Table 1). Prior to sieving, the sediment was soaked in 10% solution of  $\text{H}_2\text{O}_2$ . Shells were then picked and treated in an ultrasonic bath of  $\text{H}_2\text{O}$  to clean the surface and dissolved in concentrated (85%) phosphoric acid. The weight of all the picked samples was over 20 mg, sufficient for preparation of targets that contained 2 mg of pure carbon. Carbon dioxide was reduced to graphite (Hajdas et al. 2004b) and the  $^{14}\text{C}/^{12}\text{C}$  ratios were measured using the ETH 6MV tandem accelerator (Bonani et al. 1987) and the 200kV MICADAS, which is a dedicated  $^{14}\text{C}$  AMS instrument (Synal et al. 2007). Finite  $^{14}\text{C}$  ages were obtained down to the layer of tephra at a depth of 290–333 cm and then down to a depth of 359 cm, where the limit of the  $^{14}\text{C}$  dating method was reached for tandem measurements in the earlier stages of this study. The ages of the 6 deepest samples obtained in that set of data were indistinguishable from the background value (i.e. the measured  $^{14}\text{C}/^{12}\text{C}$  ratio of sample was smaller than double  $^{14}\text{C}/^{12}\text{C}$  ratio of the blank). For these samples, activity was not corrected for the blank and the calculated ages are referred to as “older than” and are considered to be minimum ages (Figure 1, Table 1).

Table 1 Measured concentrations of  $^{14}\text{C}$  ( $F^{14}\text{C}$  as defined by Reimer et al. 2004) and radiocarbon ages of mixed planktonic foraminifera shells (samples made up of only *Globigerina bulloides* are marked as *G. bull*) and 1 pteropod shell sample from the deep-sea core CT85-5.

Lab nr	Depth <sup>a</sup> (cm)	$F^{14}\text{C}$	$^{14}\text{C}$ age (BP)	Comments <sup>b</sup>
ETH-12683	95	0.30170 ± 0.00383	9625 ± 100	
ETH-12261	100	0.27640 ± 0.00272	10,330 ± 80	<i>G. bull</i>
ETH-19538	105	0.25800 ± 0.00344	10,880 ± 110	
ETH-12262	111	0.25200 ± 0.00320	11,070 ± 100	<i>G. bull</i>
ETH-12686	120	0.20918 ± 0.00315	12,570 ± 120	<i>G. bull</i>
ETH-12688	139	0.18121 ± 0.00257	13,720 ± 120	<i>G. bull</i>
ETH-12098	140	0.18214 ± 0.00218	13,680 ± 95	
ETH-12689	147	0.15935 ± 0.00226	14,750 ± 110	
ETH-12690	165	0.12564 ± 0.00191	16,660 ± 120	
ETH-14163	180	0.10188 ± 0.00162	18,350 ± 130	
ETH-14164	190	0.08093 ± 0.00145	20,200 ± 140	
ETH-12691	200	0.05675 ± 0.00138	23,050 ± 195	
ETH-13222	230	0.03738 ± 0.00111	26,400 ± 240	
ETH-13223	250	0.02756 ± 0.00111	28,850 ± 330	
ETH-13224	270	0.01732 ± 0.00096	32,580 ± 450	
ETH-14048	275	0.01843 ± 0.00085	32,080 ± 370	
ETH-37858	275	0.01590 ± 0.00054	33,265 ± 275	1, 2
ETH-14049	279	0.01794 ± 0.00082	32,300 ± 370	

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Lab nr	Depth <sup>a</sup> (cm)	$F^{14}\text{C}$	$^{14}\text{C}$ age (BP)	Comments <sup>b</sup>
ETH-12099	280	0.01642 ± 0.00065	33,010 ± 320	
ETH-13225.1	280	0.09058 ± 0.00170	19,290 ± 150	
ETH-13225.2	280	0.08206 ± 0.00143	20,090 ± 140	
ETH-19537.1	280	0.07071 ± 0.00172	21,280 ± 195	
ETH-19537.2	280	0.08202 ± 0.00128	20,090 ± 125	2
ETH-37859	280	0.09332 ± 0.00086	19,050 ± 75	1, 2
ETH-14050	282	0.03347 ± 0.00103	27,290 ± 250	
ETH-17306.1	282	0.04071 ± 0.00120	25,710 ± 240	Outside
ETH-17306.2	282	0.03885 ± 0.00114	26,090 ± 240	Inside, 35% leached away
ETH-17307.1	283	0.11660 ± 0.00177	17,260 ± 120	Outside
ETH-17307.2	283	0.11787 ± 0.00176	17,180 ± 120	Inside 50%
ETH-24997.1	283	0.04760 ± 0.00107	24,460 ± 180	
ETH-24997.2	283	0.05232 ± 0.00124	23,700 ± 190	
ETH-24997.3	283	0.04398 ± 0.00112	25,095 ± 205	2
ETH-24856.1	284	0.01677 ± 0.00075	32,840 ± 360	Outside
ETH-24856.2	284	0.01773 ± 0.00090	32,390 ± 410	Inside, 75% leached away
ETH-24856.3	284	0.02182 ± 0.00109	30,730 ± 400	Pteropods
ETH-24856.4	284	0.02241 ± 0.00078	30,510 ± 280	
ETH-37860	284	0.06021 ± 0.00079	22,570 ± 105	1, 2
ETH-12100.1	288	0.07324 ± 0.00143	21,000 ± 160	
ETH-12100.2	288	0.05177 ± 0.00207	23,790 ± 320	
ETH-12263	303	0.05395 ± 0.00106	23,760 ± 180	<i>G. bull</i>
ETH-12264	314	0.04032 ± 0.00122	25,975 ± 245	<i>G. bull</i>
ETH-38332	335	0.01126 ± 0.00111	36,040 ± 790	2
ETH-12693	337	0.01181 ± 0.00073	35,660 ± 500	<i>G. bull</i>
ETH-12694	344	0.01213 ± 0.00076	35,450 ± 510	<i>G. bull</i>
ETH-10629	346	0.00768 ± 0.00074	39,110 ± 770	
ETH-10630	352	0.00504 ± 0.00069	42,500 ± 1100	
ETH-38333	358	0.00543 ± 0.00106	41,900 ± 1570	2
ETH-10631	359	0.00588 ± 0.00069	41,260 ± 940	
ETH-10634	381	0.00631 ± 0.00044	>40,690	
ETH-10635	385	0.00709 ± 0.00048	>39,760	
ETH-11970	388	0.00879 ± 0.00039	>38,030	
ETH-10636	395	0.00769 ± 0.00049	>39,100	
ETH-38334	395	0.00270 ± 0.00026	>47,520	2
ETH-37865	414	0.00453 ± 0.00037	>43,350	2
ETH-37866	459	0.00337 ± 0.00036	>45,720	2

<sup>a</sup>Top of the 1-cm slice of sediment.<sup>b</sup>1= Additional samples 2009; 2 = AMS with MICADAS.

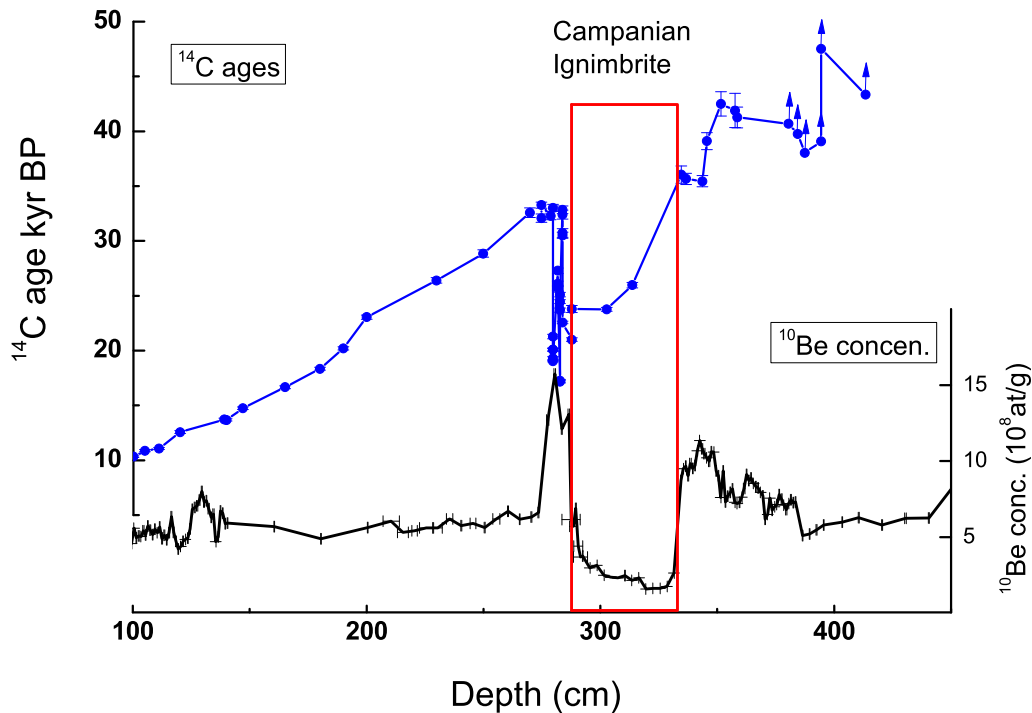


Figure 1  $^{14}\text{C}$  ages of planktonic foraminifera shells are plotted versus depth in core CT85-5: arrows show minimum ages (i.e. close to blank value, see Table 1). Lower panel shows concentration of  $^{10}\text{Be}$  in sediments of CT85-5 (Castagnoli et al. 1995); the Campanian Ignimbrite is marked as a box. Note that this sediment layer, which is 43 cm thick, was an instantaneous deposit (see text).

## RESULTS

The  $^{14}\text{C}$  chronology of the last 40 ka in the core CT85-5 shows regular features, but a reversal in  $^{14}\text{C}$  ages appears between 280 and 336 cm (Figure 1), which corresponds to a zone containing the deposit of the Campanian Ignimbrite tephra layer (290 to 333 cm) and just above the ash. Also, the interval partially overlaps with the layer where an enhanced  $^{10}\text{Be}$  concentration in sediment was found (Castagnoli et al. 1995). As shown in Figure 1, a twofold  $^{10}\text{Be}$  peak occurred: the  $^{10}\text{Be}$  concentration increased within the interval 273–384 cm and then the increase was interrupted at 290–339 cm depth by the CI eruption (dilution effect of  $^{10}\text{Be}$  atoms in the volcanic material). At 289 cm, where the glass shards disappear, the  $^{10}\text{Be}$  concentration increased as a spike, reaching its maximum value at 280 cm depth. We note that the highest  $^{14}\text{C}$  content were reached at about the same depth, i.e. at 280–283 cm. Because of the unusual magnitude of the age reversal, various tests have been performed to exclude any possible contamination as well as problems with measurements of very old samples.

Firstly, the possibility of contamination of the material is considered. The most probable source would be the deposition of secondary calcite on the surface of dated shells. We have performed leaching experiments of foraminifera in samples that had high  $^{14}\text{C}$  content and appeared “too young.” Our procedure involves on-line acidification of up to 50% of the sample material (surface) and subsequent separation of the produced  $\text{CO}_2$  from the remaining residue (inside) (Hajdas et al. 2004a). Both fractions of those samples were dated subsequently, showing no significant difference

in ages between fractions (282 cm, ETH-17306; 283 cm, ETH-17307; and 284 cm, ETH-24856) (Table 1).

A second potential reason for the younger ages is contamination with modern carbon and an underestimated blank correction. The blank values for IAEA marble C-1 for earlier measurements with the EN tandem were close to 0.005  $\text{F}^{14}\text{C}$  and samples stratigraphically older than those, showing enhanced  $^{14}\text{C}$ , i.e. below 333 cm, were successfully dated (Figure 1). Moreover, measurements with the MICADAS system ( $<0.003 \text{F}^{14}\text{C}$  on C-1, IAEA marble) confirmed our earlier results (Table 1).

Our leaching experiments and duplicate analyses provide evidence that the enhanced  $^{14}\text{C}$  levels in foraminifera shells deposited during or shortly after the volcanic eruption of Campanian Ignimbrite cannot be explained by limitations of the  $^{14}\text{C}$  measurements or by contamination by secondary carbonates.

There is no plausible explanation for the intrusion of younger sediments into this section of the core. The sediments showing the inversed ages are ~40 cm above the bottom of the core section; thus, contamination at the core break-off can be ruled out (Castagnoli et al. 1995). Additional measurements were obtained on samples from a nearby core CT85-6 (Table 2). The record of CT85-6 is shorter because the core was broken when penetrating the Campanian Ignimbrite. The  $^{14}\text{C}$  ages in this core also show an inversion, however, not to such an extent as the one observed in CT85-5 (Figure 2).

Table 2 Concentrations of  $^{14}\text{C}$  ( $\text{F}^{14}\text{C}$ ) and radiocarbon ages measured on material from the core CT85-6 (mixed planktonic foraminifera). Correlation between cores was based on the Campanian Ignimbrite (CI) layer and  $\text{CaCO}_3$  (Castagnoli et al. 1992). The top of the CI layer is at 290 cm depth.

Lab nr	Depth (cm)	$\text{F}^{14}\text{C}$	$^{14}\text{C}$ age (BP)
ETH-14165	270	$0.02656 \pm 0.00078$	$29,150 \pm 240$
ETH-14166	275	$0.02484 \pm 0.00079$	$29,680 \pm 260$
ETH-14167	280	$0.02417 \pm 0.00074$	$29,900 \pm 250$
ETH-14051	286	$0.01474 \pm 0.00078$	$33,880 \pm 430$
ETH-14597	287	$0.01438 \pm 0.00077$	$31,680 \pm 360$
ETH-14598	289	$0.01938 \pm 0.00087$	$29,710 \pm 350$
ETH-15197	290	$0.01709 \pm 0.00096$	$34,070 \pm 480$
ETH-15198	292	$0.01382 \pm 0.00083$	$35,180 \pm 515$
ETH-15051	293	$0.02475 \pm 0.00108$	$32,690 \pm 450$
ETH-14052	295	$0.01254 \pm 0.00080$	$34,070 \pm 430$
ETH-14599	296	$0.01438 \pm 0.00077$	$33,600 \pm 400$

The presence of the tephra layer found in the CT85-5 core at 290–333 cm depth is important for our results because we can use it as a time marker. This layer, which has previously been correlated with the Campanian Ignimbrite (marine tephra C-13 or Y-5) (Castagnoli et al. 1995), has a lower carbonate content than the surrounding sediment (reduced to ~25%). Nevertheless, we were able to obtain 2 samples from this interval. Correlation of nearby Mediterranean deep-sea cores to North Atlantic cores showed that this eruption preceded Heinrich event 4 (Paterne et al. 1999).

As described in Castagnoli et al. (1995), the thick layer of trachytic glass admixed with carbonate mud is found in the CT85-5 core at depths between 333 and 290 cm. The layer contains some grains of sanidine, plagioclase, biotite, and Na pyroxene. In the samples from this interval and sediment above it (280–290 cm), which had been washed for foraminifera, biotite and volcanic glass shards could be observed, confirming that inversed  $^{14}\text{C}$  ages are associated with the ash layer. The chemical

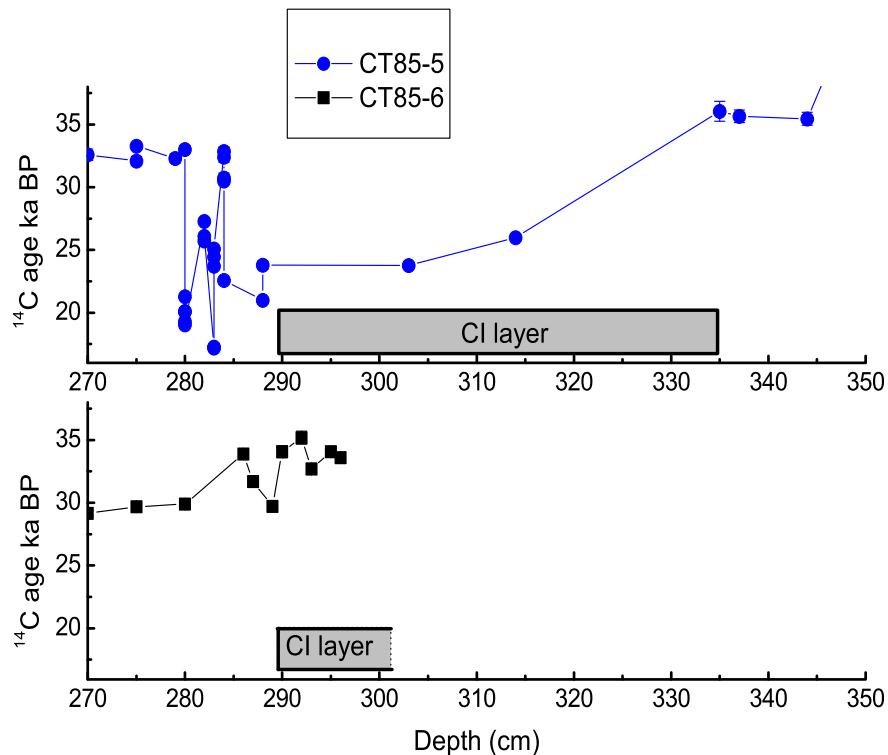


Figure 2 Reversed  $^{14}\text{C}$  ages of planktonic foraminifera shells from the section in core CT85-5 core shown together with  $^{14}\text{C}$  ages from a nearby core CT85-6. In both cores, the top of the CI tephra is at 290 cm.

composition of the glassy material (Castagnoli et al. 1995) points to the Campanian Ignimbrite eruption in the Phlegraean Fields, which is a well-known stratigraphic marker in the Mediterranean region. This powerful eruption left distinct deposits of ash both on land and in marine sediments in the region (Barberi et al. 1978) and most probably had a large impact on the environments in the region. The first  $^{14}\text{C}$  ages obtained on carbonized wood found in lava of the Campanian Ignimbrite had a large spread between 28 and 38 ka BP (Alessio et al. 1973, 1974). Other independent chronometers such as the  $^{40}\text{K}/^{40}\text{Ar}$  or  $^{40}\text{Ar}/^{39}\text{Ar}$  dating method provided ages for the lava that ranged from 34 to 38 ka cal BP (Wulf et al. 2004 and references cited therein). The most recent  $^{40}\text{Ar}/^{39}\text{Ar}$  dating of the Campanian Ignimbrite ash revealed an age of  $39.28 \pm 0.11$  ka cal BP (De Vivo et al. 2001) and  $41.1 \pm 2.1$  ka cal BP (Ton-That et al. 2001).

## DISCUSSION

The large change in  $^{14}\text{C}$  concentration observed in the CT85-5 core appears to be a rather short event. In spite of its thickness of 43 cm, the sediment layer in which the reversed ages were measured represents a very short event of volcanic eruption. Reversed ages are also found in the overlying 10 cm of sediments that have been described as turbidite deposits, probably associated with the CI event. Therefore, the short  $^{14}\text{C}$  event observed in this core might be unique and difficult to replicate in other records. Most of the published records of the last 50,000 yr show evidence of an increase in atmospheric  $^{14}\text{C}$  level that occurred around 40 ka cal BP due to the Laschamp excursion, but no reversal (Hughen et al. 2004; Reimer et al. 2009 and references therein). However, one of the first published indications of an age reversal at 40.3–41.7 ka cal BP is the record from core PS2644

in the Icelandic Sea (Voelker et al. 2000). This event precedes Heinrich event 4 and has been correlated with low values of paleomagnetic intensity in PS2644 and, via  $\delta^{18}\text{O}$ , with enhanced values of cosmogenic  $^{36}\text{Cl}$  and  $^{10}\text{Be}$  measured in ice cores (Wagner et al. 2000; Laj et al. 2002).

Other anomalously young  $^{14}\text{C}$  ages have been observed and reported in marine sediments corresponding to the interval close to the Laschamp event ( $\sim 40$  ka cal BP). For example, aberrant  $^{14}\text{C}$  ages have been reported for paleomagnetic reconstructions in the Arctic Ocean sediment cores (Nowaczyk et al. 2003). This raises the question of whether the observed  $^{14}\text{C}$  anomaly can be explained by the Laschamp event. However, model calculations show that switching off the geomagnetic dipole field increases the  $^{14}\text{C}$  production rate by only about a factor 2.5 compared to the present-day production rate. To quantify these effects, we used a box diffusion carbon cycle model (Oeschger et al. 1975), which showed that a doubling in the production rate for 3 ka leads to an increase of the atmospheric  $^{14}\text{C}/^{12}\text{C}$  ratio by about 40%, corresponding to an age reduction by 3200 yr, which is much less than the observed 15,000 yr. Reducing the thermohaline circulation is more effective. A complete shutdown, which is a rather unrealistic assumption, leads to an annual increase of the atmospheric  $^{14}\text{C}/^{12}\text{C}$  ratio by about 0.1%, assuming the present production rate. A more realistic reduction of the eddy diffusion constant from the present value of 4000 to 1000  $\text{m}^2 \text{yr}^{-1}$  causes an increase of about 0.01% per year. In conclusion, neither a change in the production rate nor a drastic reduction in the global thermohaline circulation seems feasible to explain the observed dramatic change in  $^{14}\text{C}$  measured in the CT85-5 record.

## CONCLUSIONS

The  $^{14}\text{C}$  chronology of the Mediterranean deep-sea core CT85-5 shows a period of reversed  $^{14}\text{C}$  ages coinciding with high levels of  $^{10}\text{Be}$  that were found in the sediments deposited before and after the eruption of the Campanian Ignimbrite (CI). Based on the radiometric ages of the CI eruption ( $^{40}\text{K}/^{40}\text{Ar}$  or  $^{40}\text{Ar}/^{39}\text{Ar}$ ) and on stable isotopic correlations obtained for Mediterranean deep-sea cores, this extreme  $^{14}\text{C}$  event can be dated to around 40 ka cal BP. We note that, despite several anomalously young ages in other records, the amplitude of the  $^{14}\text{C}$  changes measured in the foraminifera of the layer in the CT85-5 core is unique and has not yet been confirmed by any other data. We are convinced that these too-young  $^{14}\text{C}$  ages are not the result of any analytical problems. Although a plausible mechanism that could explain such extreme reversals in  $^{14}\text{C}$  age as observed in this core remains to be found, our results are presented here to stimulate discussion and comparison with other possibly unpublished studies.

## ACKNOWLEDGMENTS

Susan Ivy Ochs supported this study with discussions, investigation of ash layer sediment and review of this manuscript. We are grateful to all members of the AMS group at ETH, for their continuous support of  $^{14}\text{C}$  analysis. We dedicate this paper to the memory of Prof Giuliana Cini Castagnoli, who contributed significantly but could not complete this study.

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