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Evidence for enhanced ^{10}Be deposition in Mediterranean sediments 35 Kyr BP

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Abstract. In this letter, we report the profiles (~160 samples) of ^{10}Be, ^{9}Be, Zn in a Mediterranean sediment core spanning the last 60 kyr. We show the existence of a ^{10}Be peak, whose absolute age is estimated to be 34±3 kyr BP, based on its stratigraphic position between two tephra layers originating from two volcanic eruptions (Campanian Ignimbrite and Citara), dated by K-Ar, ^{40}Ar-^{39}Ar and ^{14}C methods. This peak is similar to the increase in the ^{10}Be concentration observed in Vostok and Dome C ice cores at the same age. The increase with approximately similar amplitude in both ice and sediment cores at different latitudes and hemispheres cannot be explained by changes in the archives. The present result supports the view of a well defined global enhancement of the ^{10}Be flux, related to an increase of the ^{10}Be production rate and not to a redistribution of the ^{10}Be fallout between different latitudes.

Introduction

The ^{10}Be concentration in Vostok and Dome C ice cores, Antartica, displays an increase by a factor of two at about 35 kyr BP which cannot be explained by changes in the accumulation rate [Yiou et al., 1985; Raisbeck et al., 1987]. Since its discovery in the south polar regions, the ^{10}Be peak has been confirmed in another Antarctic record: in the Byrd core [Beer et al., 1992]. In the northern hemisphere, the evidence for its existence was up to now confined to a limited number of data points in the Camp Century ice core. ^{10}Be anomalies in a sediment core of the Gulf of California were also found around this age [Mc Hargue et al., 1993]. Here we report on a successful search for this peak in a Mediterranean sediment core, at middle northern latitudes. These results from a different archive support the view of a well defined global enhancement of the ^{10}Be flux.

Experimental procedure

The Mediterranean sediment core CT85-5 considered here was taken in the Tyrrhenian Sea (40°19'02" N, 11°15'42" E) at a water depth of 2833 m by the Italian C.N.R. Vessel "Bannock" in 1985. The core has a diameter of 9 cm and a length of 616 cm. It consists mainly of deep sea clays and carbonates (25 to 50%). We performed ^{10}Be, ^{9}Be and Zn measurements in about 160 samples of 1 g each (taken from 1 cm intervals) at different depths. ^{9}Be and Zn were measured in order to estimate biogeochemical and sedimentological processes capable of influencing the ^{10}Be concentration.

The dating of the core CT 85-5 is based on tephrachronology [Cini Castagnoli et al., 1992a, 1993]. The procedure consists of two steps, namely: a) to recognize the different layers of volcanic origin interbedded in the sediment and b) to establish their terrestrial equivalents, which are more suitable for dating.

In the upper 20 cm of the core, historically dated eruptions of Vesuvius of the last 2 Millennia are recognized on the basis of the frequency distribution of volcanic pyroxene grains, characterized by skeletal morphology and sector zoning. The two major pyroxene peaks at 17 cm and 20 cm correspond to the volcanic events of Pollena (472 AD) and Pompei (79AD) leading to a sedimentation rate of ~10 cm/kyr. At greater depths in the lower half of the core two main tephra layers (vitric tuffs) can be used as time markers. The chemical composition of the glass shards was determined by SEM-EDS analysis. The terrestrial equivalents of the marine tephra were recognized [Cini Castagnoli et al., 1993], by comparison of the respective chemical analysis, according to the method of Paterne et al., 1986.

Evidence for an average constant sedimentation rate along the core and the absence of any significant postdepositional process comes also from the spectral analysis of the $CaCO_3$ content, which reveals very similar spectra in the upper and the lower part of the record [Cini Castagnoli et al., 1992a], and from the good agreement between the $\delta^{18}O$ curves of CT85-5 [Cini Castagnoli et al., 1992b] and KET 8003 [Paterne et al., 1986] cores for the uppermost 180 cm.

A thick tephra layer composed of trachytic glass (Table 1), admixed with carbonate mud and a few grains of phenocrysts of sanidine, plagioclase, biotite and Na-pyroxene is found between 334 and 290 cm. Extension and chemical analysis make the Campanian Ignimbrite the most probable candidate for the origin of this important marine tephra layer. It represents volcanic products from a major event in the Phlegrean Fields, which caused collaps of a 12 km wide caldera and a flow with an estimated volume of 80 km^3, covering the entire Campanian plane between Roccamonfina and Salerno [Rosi et al., 1987]. The chemical composition of the land products indicates features similar to those determined for the marine shards (Table 1). Both are trachytic in composition with a K_2O/Na_2O ratio of ~1.6 and similar Ca, Mg and Fe concentrations. The lower content of total alkalies in the marine glass shards is attributed to slight leaching effects in the marine environment. The thickness of the core section characterized by the Campanian volcanic debris, the sedimentological features and the existence of shallow water

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Table 1. Chemical analysis of the glassy matarial from the CT85_5 Thyrrhenian core section 290-333 and of the associated land products of the Campanian Ignimbrite (average of 27 samples [Rosi et al., 1987]).

Sample number depth(cm)	SiO_2	TiO_2	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	$\frac{K_2O}{Na_2O}$
290-291	62.3±0.6	0.3±0.2	18.7±0.3	3.5±0.3	0.6±0.2	2.4±0.3	4.4±0.4	7.7±0.7	1.75
333-334	63.0±0.6	0.4±0.2	19.2±0.6	3.2±0.2	0.4±0.2	1.8±0.2	4.7±0.3	7.3±0.3	1.55
Land 33.5±1.5 kyr	61.3±0.7	0.40±0.05	18.5±0.4	3.1±0.2	0.5±0.2	2.1±0.5	5.4±1.4	7.8±0.8	1.6

gastropodes (Niessen, personal communication) indicates that part of this section may be of turbiditic origin.

The Campanian Ignimbrite volcanic rocks have scattered ^{14}C ages (28-38 Kyr B.P.) [Alessio et al., 1973, 1974] and a K/Ar age of 33.5 ± 1.5 kyr [Cassignol et al., 1982]. Recent measurements by ^{14}C and ^{40}Ar/^{39}Ar methods give respectively (34.6±1) kyr and (37.1±0.4) kyr [Deino et al.,1994]. In the section 339-334 cm, adjacent to the vitric layer, we have found biotite and pyroxene grains, remnants of the starting phase of the eruption. We adopt for this section an age of 34 ± 3 kyr. Following the same procedure of chemical analysis as outlined for the Campanian Ignimbrite, we have identified the glass material of the section 426-402 cm as remnants of the Citara eruption on the island of Ischia 40±2 kyr ago [Gillot, 1984]. The chemical analysis of the Citara marine and land products [Vezzoli, 1988] (Tab.2) display a very similar trachytic composition.

The ^{10}Be peak, which according to the Vostok time scale was expected at ~ 35 kyr BP, is thus flanked in the Tyrrhenian core by the volcanic ash layers of the Citara eruption and interrupted by the Campanian Ignimbrite event.

Analytical methods and results

For the ^{10}Be, ^{9}Be and Zn analysis the samples were prepared using a 6M HCl leaching technique [Shen et al., 1992]. A set of samples were also prepared with 1M HCl attack; this test procedure showed that 1M HCl randomly leaches only 40 to 90% compared to 6M HCl; moreover it has been shown by Shen et al.,1992, that leaching with 6M HCl removes effectively all Be adsorbed to particle surfaces, which includes Be scavenged from ocean water (including cosmogenic ^{10}Be). ^{10}Be was measured using the AMS facility of ETH/PSI in Zürich. ^{9}Be and Zn were determined by ICP/AES at EAWAG. The results are displayed as a function of depth for ^{10}Be in Fig.1a, for ^{9}Be in Fig.1b and for Zn in Fig.1c. In these figures the shadowed areas correspond to tephra layers. We notice that: i) the ^{10}Be profile has a pronounced peak of ~2.5 times the average value, interrupted by the Campanian Ignimbrite tephra layer in which it is strongly diluted; ii) ^{9}Be concentration is highly enhanced in the tephra layers; iii) Zn is relatively constant at all depths.

In detail the profiles of ^{10}Be and ^{9}Be show three principal regimes, which are characterized by: (I) ordinary ^{10}Be and ^{9}Be concentrations: the average values in this section are respectively (6±1) 10^8 at/g and (0.9±0.2) ppm; (II) increasing ^{10}Be up to 15 10^8 at/g and ordinary ^{9}Be; (III) volcanic sections: high ^{9}Be (>2 ppm); low ^{10}Be (<4 10^8 at/g) in the thick Ignimbrite event (C.I. in Fig.1), while ordinary in the less pronounced eruptions (e.g. Citara, C. in Fig.1).

In section II, the ^{10}Be concentration slowly increases with respect to the ordinary background level in an interval spanning 46 cm (384-339 cm) and increases as a spike between 288-273 cm. The ^{10}Be peak is in fact interrupted by the Campanian Ignimbrite event. The maximum value of ^{10}Be (15.1 10^8 at/g) is reached at 280 cm near the top of the tephra.We note in the same section the ^{9}Be flatness. The different shapes of the Be isotope profiles are crucial to investigate the origin of the ^{10}Be peak.

In section III, ^{9}Be is clearly increased by the eruptions, showing a peak in correspondence to each volcanic event. In particular, ^{9}Be increases in the starting phase of the Campanian Ignimbrite eruption (thin double-shaded area in Fig.1) recorded between 339-334 cm by the presence of biotite and pyroxene grains. It extends with a stronger intensity into the vitric tuffs. Here the ^{10}Be concentration is low due to a dilution in the bulk of tephra matrix.

The Be built into silicate structures will not dissolve until these structures are broken, which requires a whole rock digestion procedure. For this reason, samples were also treated using an HF, HNO_3, $HClO_4$ bomb digestion [Albrecht et al., 1992]. The ^{9}Be results averaged over the 3 sections are displayed in Tab.3. We notice that in sections I and II, 6M HCl and total Be are similar, indicating no significant portion of silicate bound Be, while in section III, silicate bound Be increases significantly due to tephra input (here the difference between average leached (2.7 ppm) and whole rock Be (5 ppm) is most striking). At the boundary to the volcanic layer (339-334 cm), characterized by silicate bound Be, ^{10}Be is still elevated, indicating a partial overlap of the ^{10}Be peak with volcanic activity. In the same Tab.3, the results obtained for the 1M leachates show the low (and unreliable) efficiency of this attack. The volcanic influence of ^{9}Be concentration can be observed both in 6 and 1M leaches. These results clearly show that the volcanic influence on ^{9}Be can not be avoided regardless of leaching method chosen.

Table 2. Chemical analysis of the glassy material from the CT85_5 Thyrrhenian core 424-425 cm and of the land products of Citara [Vezzoli, 1988].

Sample number depth(cm)	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	$\frac{K_2O}{Na_2O}$
424-425	64±2	0.50	18.5±0.5	2.8±0.1	0.2±0.2	0.4±0.1	1.3±0.2	5.5±0.3	5.5±0.2	1.0
Land 40±2 kyr	63.0±1	0.5±0.1	18.8±0.4	2.5±0.1	0.1±0.1	0.5±0.1	1.1±0.2	6.2±0.4	6.7±0.1	1.1

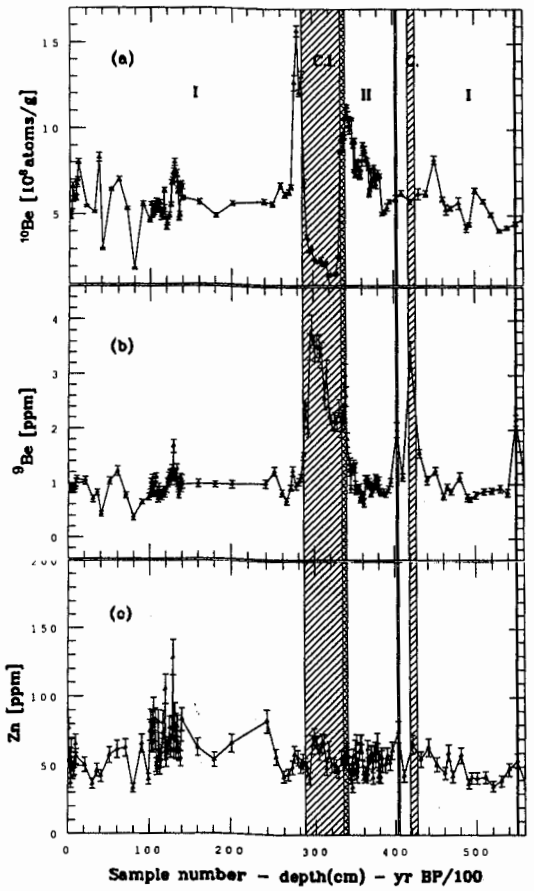

Figure 1. (a) ^{10}Be, (b) ^{9}Be and (c) Zn concentrations as a function of the core depth. Region (I) represents sections of ordinary ^{10}Be and ^{9}Be concentrations; region (II) contains the ^{10}Be peack. Shaded sections represent tephra. The double shaded area is the starting phase of the Campanian Ignimbrite (C.I.) eruption.

Another trace metal whose profile may through light on significant variations of metal transport mechanisms to the sediment is Zn. It may not have a similar biogeochemical behaviour compared to Be, but it is not influenced by volcanic ashes. In fact the Zn concentration values obtained with 6M HCl leaching, shows a rather constant concentration of ~60 ppm over the last 60 kyr (Fig.1c), with the only significant exception being the deglaciation event around 115 cm and the anthropogenically influenced last 100 yrs (top first cm).

Discussion

^{10}Be, like other metals in the ocean, is scavenged from the water column by sinking suspended particles [Turekian, 1977]. An increase in the metal concentration found in a sediment core can be explained by an increased atmospheric flux or by an enhanced particle flux and/or lateral transport of dissolved metals, known as sediment focusing or enhanced scavenging [Anderson et al., 1990], here called enhanced sediment pumping. If two metals have similar biogeochemical behaviour and a constant flux, the effect of enhanced sediment pumping should be alike and normalization should obliterate this effect. The most obvious choice to investigate this question is a comparison of ^{9}Be with ^{10}Be. Their sources are different, but transport and transfer pathways are to some extent similar, i.e. particulate dissolved riverine and particulate atmospheric. The most significant difference is the input of ^{9}Be by volcanic particles. The question regarding the similar biogeochemical behaviour of both Be isotopes can be rephrased as to whether a large portion of both was in solution a sufficient amount of time for equilibrium to be established.

Concentrations of Be in filtered and unfiltered ocean waters were essentially identical [Measures and Edmond, 1993], indicating that the most significant portion of Be in sea water is in solution. Even eolian dust is partially dissolved [Brown et al., 1992] and Be removed from the trophic zone in particulate form is returned to solution at depth [Peng et al., 1990]. Thus Be is mostly *in solution* and we can conclude that the isotopes ^{10}Be and ^{9}Be ought to be equilibrated. Any biogeochemical enrichment process that might have affected one should have affected the other as well. We therefore normalize ^{10}Be to ^{9}Be [following the suggestion by Bourles et al., 1989]. The results are displayed in Fig.2a. The position of the peak does not change. The distinct double peak caused by a dilution effect on ^{10}Be and an increasing ^{9}Be are both related to the high volcanic particle flux. The normalization of ^{10}Be to Zn, the other trace metal whose profile has been measured (Fig.1c), does not change the amplitude and the position of the peak, as shown in Fig.2b. The fact that the normalizations to ^{9}Be and Zn changes the ^{10}Be concentration peak only slightly is a strong argument against any significant change of the sediment pumping during this time.

The mean ^{10}Be concentration of (6±1) 10^8 atoms/g corresponds to a flux of (4.3±0.8) 10^6 atoms/cm^2/yr, based on a density of 0.8 g/cm^3 and a sedimentation rate of 0.01 cm/yr, which is comparable to that measured in Lake Zürich (5.10^6

Table 3. Average ^{9}Be concentrations in the CT85-5 Thyrrhenian core. Errors are 1 σ standard deviations.

leaching	units	section I	section II	sectionIII
6 M HCl	ppm	0.9±0.2	1.0±0.2	2.6±0.6
1 M HCl	ppm	0.6±0.1	0.7±0.3	1.7±0.7
tot digest	ppm	1.3±0.7	1.2±0.3	5±3

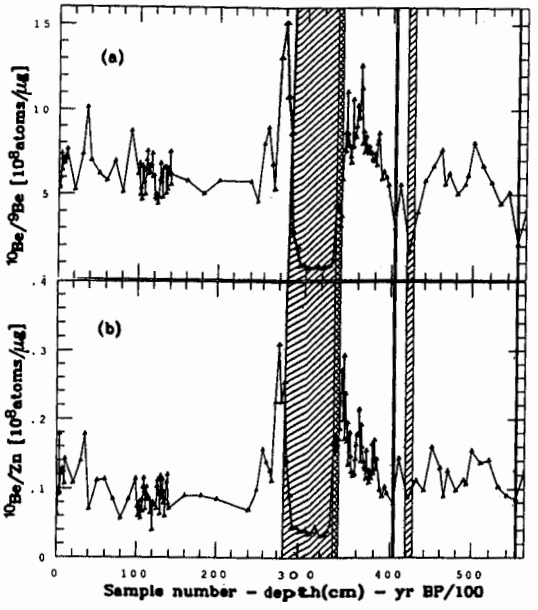

Figure 2.(a)^{10}Be normalized to ^{9}Be and (b) normalized to Zn.

at/cm^2/yr, [Schuler et al., 1991]) and to that of the precipitation in Berne (3.5 10^6 at/cm^2/yr, Luder and Beer, unpublished results). An additional source of ^{10}Be is related to the input of aeolian dust and riverine particles. Based on ^{10}Be determined by us in eolian dust samples ((4.4±1.3)10^8at/g) and suspended Rhone particles (2.5 10^8at/g) we estimate this additional flux to ~1.2 10^6 at/cm^2/yr. An increased flux of eolian or river borne particles would be reflected in both higher ^{10}Be and ^{9}Be fluxes, confirming in part the findings by Brown et al.,1992. The ^{10}Be/^{9}Be ratio would not change significantly. Our limited results on Saharan dust and Rhone samples give an indication that ^{10}Be/^{9}Be in dust and sediments are comparable.

Finally one might ask which geologic period recorded in our core would be the best candidate to show changes in the sediment pumping, which may alter ^{10}Be concentration. One candidate is certainly the end of the last glaciation 10 kyr ago (~100 cm in our core). In Fig.1a, 1b we can see that this period of significant climatic and hydrologic change caused only minor fluctuations in the ^{10}Be and in ^{9}Be concentration. The largest variation in the Zn profile appears indeed around this epoch (Fig.1c).

These are strong arguments in favour of the hypothesis that the increase in the ^{10}Be concentration up to a factor ~2.5, lasting a few kyr, is the consequence of an increased production rate and not of a change in physical processes with constant atmospheric ^{10}Be flux. Further evidence that the ^{10}Be peak is caused by an increase of the global atmospheric inventory derives from the fact that it has a similar amplitude in the sediment and in the ice cores.

Changes of the production rate can be related to changes of the cosmic ray flux due to helio- and geomagnetic modulation effects or due to fluctuations in the primary cosmic rays flux, e.g. a nearby supernova explosion [Sonett et al., 1987; Kocharov et al., 1992]. A contribution from cosmic dust can be excluded based on two ^{26}Al measurements performed on our core in the peak region. If the observed ^{10}Be peak is indeed the result of an increase of the production rate, then this has some important implications:

1. All cosmogenic radioisotopes with appropriate half-lives and production rates (e.g. ^{36}Cl and ^{14}C) should show a peak in the same region.
2. All archives recording with a sufficient time resolution the atmospheric fall-out should contain this signal. Therefore this ^{10}Be peak provides a unique relative time marker to synchronize ice cores and sedimentary archives; absolute dating of the peak in one specific archive allows to improve the time scales of all other archives.

The fact that the peak is stratigraphically situated between two dated tephra layers at 33.5 and 40 kyr BP allows to estimate its age to 34±3 kyr. The tephra layers offer the opportunity for additional dating leading possibly to a more accurate age of the ^{10}Be peak.

It will be the subject of future investigations to figure out the precise cause of the observed peak and the environmental implications of an increased cosmic ray flux to the Earth.

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