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Organic 14C activity in an abyssal marine sediment

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Figure 1 shows the data plotted as c against $1/r$ (where c = concentration and r = average radius of a size fraction). According to one model[16] a surface component is recognised from the slope of the line; the volume related component can be determined for particles of infinite radius from the intercept on the y axis. In this model the volume related component is assumed to be constant for all grain sizes. Such an assumption is invalid because lunar soils contain many, in fact sometimes a majority of, grains which are complex aggregates, either glassy agglutinates or microbreccias. The volume related component is due to the incorporation of a surface component into the interior of complex particles. There is no reason to suppose a volume component produced in this way would be constant for all grain sizes. On the contrary, it might be expected that fine agglutinates and breccias, which must be made up of constituent fragments with a smaller median grain size than their coarse counterparts, ought to have a larger volume related component due to the increased surface incorporated. A volume component which increases in fine fractions would be indistinguishable from a surface component on a plot of c against $1/r$. An alternative model[17] which considers $c \propto d^{-n}$ (where d is diameter) and recognises surface and volume related components from a plot of $\log c$ against $\log d$ is also incapable of distinguishing a surface from an increasing volume component.

We now contend that surface related components of $Fe(o)$ and C_{hyd} are minimal; c against $1/r$ or $\log c$ against $\log d$ plots recognise increasing volume related components, which are a result either of a greater abundance of aggregated particles or a greater complexity within such grains in fine fractions. Some support for the latter interpretation has come from detailed analysis of progressively more magnetic agglutinates from lunar soil 12023 (ref. 10). We have pointed out[2,12,18] that genuine surface components of $Fe(o) < 130 \text{ Å}$ in size would be unlikely to survive in the terrestrial atmosphere and that only metal incorporated into agglutinates would be protected from oxidation. Agglutinate metal behaving as an apparent surface related component because of increases in volume concentration does not conflict with such arguments.

If model predicted surface components of $Fe(o)$ and C_{hyd} are in fact volume components, what proportion of the apparent surface correlated solar wind hydrogen, rare gases, carbon and nitrogen can be accounted for by this effect? The answer to this question presumably will come from comparison of data from size fractions with measurements made by surface specific techniques such as ion microprobe[19,20] and nuclear reactions[21,22]. Calculations[23] and direct measurements[22] suggest maximum surface carbon concentrations are up to a factor of five less than estimates made on the basis of $1/r$ plots[24] and thus support arguments in favour of an increasing volume component.

We are not denying the existence of surface components, only questioning their magnitude; surface components must exist to be incorporated into complex grains to generate volume related components. We need better models to describe the accumulation of solar wind elements and solar wind derived species in lunar soil. Experiments using surface specific techniques to detect genuine surface components are highly desirable.

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Organic ^{14}C activity in an abyssal marine sediment

ONE measure of transport rates and residence times of organic carbon within the various organic carbon pools in the ocean is to follow perturbations from the 1952–58 and 1961–62 atmospheric thermonuclear bomb tests on the natural ^{14}C activities of living, detrital and dissolved organic matter. We report here our measurement of the ^{14}C activity of the total sedimentary organic carbon (SOC) in an abyssal red clay, as no such data were available for this organic carbon pool. Ultimately, these sedimentary organic ^{14}C activities may be compared with the ^{14}C activity of the source organic material in the water column and estimates made of the magnitude of organic carbon consumption at the seawater–sediment interface. What was found, unexpectedly, was evidence for the penetration of recent organic carbon from the 4 cm mixed layer at the sediment–seawater interface down to at least 12 cm in the sedimentary column. This suggests a different and more rapid mechanism for the sedimentation of some fraction of the SOC other than direct association with clay minerals.

Photosynthetic fixation of bomb-derived $^{14}CO_2$ in the euphotic zone and its subsequent incorporation into bathypelagic marine fish and crustacea and into deep-sea particulate and dissolved organic matter has been previously studied in the north Central and North-east Pacific Ocean[1–4]. This work (Table 1) showed that the dissolved (plus colloidal) organic carbon (DOC) had 'apparent ages' of 740 yr BP at the surface to 2,570–3,470 yr BP at 2,000 m, and that the ^{14}C activity of the particulate organic carbon (POC) at 2,000 m was 10% less than its activity at the surface. These observations are indicative of slow recycling of DOC between the surface and deep waters and rapid sinking of POC (or some fraction of it) in the water column. Thus, high ^{14}C activities of SOC in the upper mixed layer and at the seawater–sediment interface would reflect this rapid sinking of POC to the sea floor coupled with its relatively slow biochemical oxidation to CO_2 by benthic populations.

The 0–30 cm sediment sections (Table 2) were sub-sampled from two box cores[5] (0.25 m^2 in area) taken on 10 July 1970 (core 33) at 6,040 m in the central North Pacific Gyre (30°0.9′ N, 156°12.5′ W) and on 8 June 1977 (core 638) at 5,780 m in the same area (28°34.4′ N, 155°30.3′ W). This region is part of an extensive abyssal plain situated beneath low-productivity surface waters. The sediment–seawater slurry (equivalent to a

Table 1 Natural radiocarbon activities of various carbon pools in the central and eastern North Pacific Ocean

Pool	Depth (m)	Date	Location	$\Delta^{14}C$ (‰)	Age (yr BP)*
POC	10	1971[3]	30°00′ N 140°00′ W	+237 ± 24	—
POC	2,000	1971	,,	+182 ± 27	—
DOC	10	1971	,,	−88 ± 20	740 ± 170
DOC	500	1971	,, ,,	−176 ± 14	1,560 ± 140
DOC	2,000	1971	,,	−274 ± 13	2,570 ± 140
DOC	1,880	1968[1]	30°16′ N 119°49′ W	−351 ± 27	3,470 ± 330
DOC	1,920	1969[1]	30°16′ N 119°50′ W	−341 ± 23	3,350 ± 280
DIC	5,292	1973†	31°22′ N 150°01′ W	−219.5 ± 3.5	1,991 ± 46
SOC (this report) Core 33 (0–3 cm)	6,040	1970	30°01′ W 156°13′ W	−664 ± 22 (mean)	8,760 ± 510 (mean)
Core 638 (0–3 cm)	5,782	1977	28°34′ N 155°30′ W	−736 ± 20	10,700 ± 630

POC, particulate organic carbon; DOC, dissolved organic carbon; DIC, dissolved inorganic carbon; SOC, sedimentary organic carbon.
*Ages calculated relative to the NBS oxalic acid standard activity using the Libby half-life (5,568 yr). Since pre-nuclear bomb surface seawater carbonates were 4% lower in activity ($\Delta^{14}C = -40$‰), all the ages given in this report are about 340 yr younger using this correction.
†Pacific Geosecs, Leg 1, Station 204 (H. Östlund, personal communication).

2-mm vertical section) was sucked-up from the undisturbed centre (25 cm × 26 cm area) of core 33 and sieved through a 65-μm mesh stainless-steel screen. The solid upper 3 cm of this core was then scraped into five arbitrary sections. The upper 3 cm of core 638 was sliced into 1-cm sections only as the surface of this core was slightly disturbed. The remainder of each core was sampled in 2-cm increments down to 30 cm leaving about 5 cm of sediment on the bottom. The samples were then frozen at −20 °C for subsequent analysis. All feasible precautions were taken to prevent contamination of the samples with ^{14}C or dead carbon. The analytical results and a summary of experimental procedures for each analysis are given in Table 2. The $\delta^{13}C$ values are included to show that they fall within the range of marine organic-$\delta^{13}C$ analyses (−18 to −22‰ for subtropical waters).

Sedimentation rates below the mixed layer for the clay mineral fraction of cores 33 and 638, determined by $^{230}Th/^{232}Th$ activities, were 1.0 and 1.2 mm 10^{-3} yr^{-1}, respectively (Fig. 1a). It is clear from this plot that the depth of the mixed layer is 8.0 ± 1 cm (core 33) and 4.0 cm ± 0.5 cm (core 638), assuming uniform mixing within the layers. The 4 cm mixed layer thickness for core 638 is corroborated by the total SOC analyses (Fig. 1b). If SOC is laid down at the same rate as the clay minerals, then no measurable ^{14}C activity would be expected much below the mixed layer, however, significant ^{14}C activity was found down to at least 11–13 cm in core 638 (Table 2, Fig. 2).

The ^{14}C activity in the surface slurry (0–0.2 cm) from core 33 was not significantly higher than the ^{14}C activity found at 0.2–0.4 cm, and just significantly greater than the ^{14}C activity in the 2.7–3.0-cm section (Table 2). This implies rapid mixing and/or rapid utilisation in the mixed layer of POC reaching the seawater–sediment interface. The presence of bomb-^{14}C in the mixed layers in cores 33 and 638 can be seen by calculating a hypothetical mean age of the SOC in the mixed layer[9] assuming the $\Delta^{14}C$ value of the source organic carbon before the bomb tests was 0‰ (see Table 1). This calculation is based on the thickness of the mixed layers, M (8.0 and 4.0 cm), the $^{230}Th/^{232}Th$ sedimentation rates, S (1.0 and 1.2 mm 10^{-3} yr^{-1}) and the decay constant for ^{14}C, λ (1.2449 × 10^{-4} yr^{-1}) where the mean age = $1/\lambda \ln[1+(\lambda/S)M]$. For core 33 this calculated mean age is 19,200 yr and for core 638 it is 13,200 yr (vertical dashed line, Fig. 2). When these calculated ages are compared with the experimentally determined ages (Table 2, Fig. 2), it is apparent that more bomb ^{14}C has entered the mixed layer in core 33 than in core 638. This increased input of bomb ^{14}C in the

mixed layer of core 33 is also reflected by the 42% more $^{239+240}Pu$ that was found in the 0–3-cm section of core 33 than in the 0–3-cm section of core 638 (Table 2). The presence of $^{239+240}Pu$ activity in the mixed layer of both cores is evidence of the rapid sedimentation of high ^{14}C activity POC as the flux of $^{239+240}Pu$ is, in part, through association with sinking organic detritus[10].

The main feature of the organic ^{14}C activity in the sediments is the presence of measurable ^{14}C activity below the mixed layer in core 638 (Fig. 2). An 'apparent sedimentation rate' of recent SOC, calculated from the ^{14}C activities at 6, 8 and 12 cm is 1.15 cm 10^{-3} yr^{-1}, and 0.95 cm 10^{-3} yr^{-1} if calculated from the activities at 1.5, 6, 8, and 12 cm (Fig. 2). These rates are about 10 times those derived from $^{230}Th/^{232}Th$ ratios, but due to uncertainties in the ^{14}C activity determinations, the recent SOC rates could vary from 0.8 to 6 cm 10^{-3} yr^{-1}. Thus, the introduction of recent organic carbon below the mixed layer is
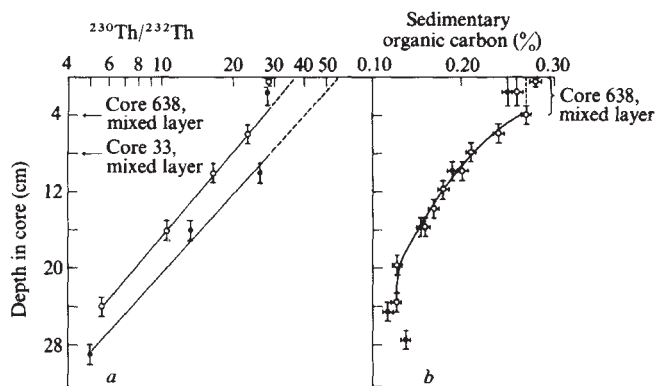

Fig. 1 a, $^{230}Th/^{232}Th$ ratios plotted as a function of core depth: ●, core 33; ○, core 638. Error bars denote one standard deviation. The lines are least squares fits and the depth of the mixed layers are indicated by arrows. The clay mineral sedimentation rates below the mixed layer are 1.0 mm 10^{-3} yr^{-1} for core 33 and 1.2 mm 10^{-3} yr^{-1} for core 638 where the half life of ^{230}Th is 7.52 × 10^4 yr. b, Total sedimentary organic carbon (SOC) expressed as per cent of dry weight and plotted as a function of core depth: ●, core 33; ○, core 638. Error bars denote one standard deviation. The dashed line from 0 to 4 cm is the mean of values at 0–1, 0–3 and 3–5 cm for core 638.

independent of the sedimentation rate of the clay minerals or SOC associated with them.

The mechanism or mechanisms responsible for this apparently anomalous injection of significant quantities (calculated to be 7–13% of the total SOC depending on whether the source carbon is pre-bomb, $\Delta^{14}C = 0‰$, or post-bomb, $\Delta^{14}C = +180‰$) of recent SOC into the sedimentary column below the mixed layer is not clear. One explanation is organic carbon transport by burrowing organisms such that the numbers and lengths of their excursions, and hence the organic carbon flux, decreases with depth. The long straight burrows, 10–30 cm in length, which have been observed in abyssal sediments[11] are due primarily to worms burrowing into the sediment. The worms pump in surface seawater, filter out organic matter and eventually retreat leaving organic tubules behind. This mechanism for organic carbon transport is questionable for two reasons: (1) the smooth distribution of thorium isotopes (Fig. 1a) do not reflect any large scale bioturbation, and (2) the number of burrows normally observed in deep sea sediments do not seem sufficiently dense[12,13] to maintain the necessary flux of recent organic carbon.

A second explanation for the injection of organic carbon into the sediments is diffusion of recent DOC into the sedimentary column from the mixed layer. This mechanism would require a negative gradient of DOC in the interstitial water and a high concentration of DOC to be continuously added to the mixed layer by relatively rapid biochemical processes (solubilisation of detrital POC, autolysis of organisms, and excretion of DOC by organisms). However, the opposite mechanism is indicated by an analysis of DOC in the interstitial water of a pelagic clay from the central equatorial Pacific[14] ($10°40'$ N, $147°40'$ W) where the DOC concentration increased from 2.5 mg C l^{-1} at the surface to 4.8 mg C l^{-1} at 30 cm in this core. Because the amount of DOC in the interstitial waters of red clays is only 0.1–0.4% of
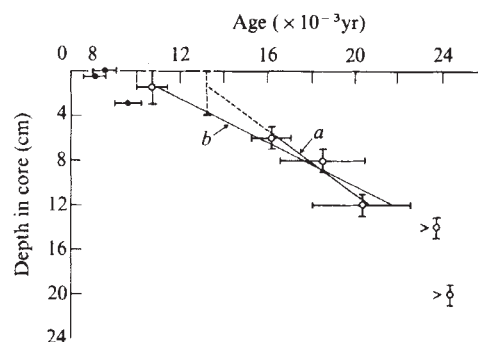

Fig. 2 The ^{14}C activity of the sedimentary organic carbon plotted as ages (yr BP) against core depth: ●, core 33; ○, core 638. Error bars denote one standard deviation (Table 2). The symbol (>) means that the ^{14}C-organic carbon activities at 13–15 and 19–21 cm were within 2σ of background and hence error bars were not applicable. The lines *a* and *b* are least squares fits for points at 1.5, 6, 8 and 12 cm; and at 6, 8 and 12 cm, respectively. The vertical dotted line from 0–4 cm represents the calculated age of the sedimentary organic carbon in the mixed layer for core 638 (see text).

the total SOC, unrealistically high diffusional fluxes of DOC would be required even with strong, negative DOC gradients. Thus, neither of the above mechanisms satisfactorily explains the presence of recent organic carbon 6–12 cm below the mixed layer in this pelagic red clay.

There is some corroborative information on possible bioturbation below the mixed layer from $^{239+240}Pu$ analyses of two box cores collected on the 1977 cruise. These two cores were taken 1.6 and 6.4 km from core 638. The $^{239+240}Pu$ analyses (V.

Table 2 Measurements made on the sediments and sedimentary organic matter from box cores 33 and 638

Sections (cm)	SOC (%)	H_2O (%)	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Age (yr BP)	$^{230}Th/^{232}Th$	$^{239+240}Pu$ (d.p.m. kg^{-1})
Core 33 (1970)							
Surface slurry (0–0.2)	0.20		−19.7	−655±22	8,500±500		
0.2–0.4	0.30		−19.7	−635±23	8,100±500		
2.7–3.0	0.27		−18.7	−703±22	9,700±600		
0–3		57				27.3±0.1	1.7±0.08
9–11	0.19	51				26.0±1.3	
15–17	0.16	50				13.2±0.4	
24–26	0.12	49					
28–30	0.14	49				4.9±0.2	
Core 638 (1977)							
0–1	0.28	53				27.8±2.2	
0–3	0.26	53	−20.1	−736±20	10,700±600		1.2±0.16
3–5	0.27	52				23.0±1.8	
5–7	0.24	51	−18.3	−866±15	16,200±900		
7–9	0.21	51	−20.3	−900±21	18,500±1,900		
9–11	0.20	50				17.6±0.7	
11–13	0.18	49	−21.0	−920±20	20,300±2,200		
13–15	0.17	50	−21.1	−948±0	>23,700		
15–17	0.16	49				10.2±0.2	
19–21	0.13	49	−21.3	−952±0	>24,300		
23–25	0.13	50				5.6±0.3	

The thawed sediment samples used for ^{14}C activity determinations were acidified to pH 3–4 with distilled 6 M HCl, and all samples were dried to constant weight at 80 °C. Thereafter, the dried sediment samples were burned at 800–900 °C for 2–3 h in a stream of prepurified oxygen. Conventional vacuum line techniques were used to obtain CO_2 of high purity necessary for gas-proportional counting. Each CO_2 sample was aged for 4 weeks before counting to ensure decay of any ^{222}Rn (3.8-d half life). The ^{14}C activity was measured using a 100 ml quartz gas counter filled to a pressure corresponding to 90 cm CO_2 at 25 °C. In these conditions, 95% of the activity of the NBS oxalic acid standard was 0.727 ± 0.015 c.p.m. above a background of 0.815 ± 0.012 c.p.m. A minimum of 10,000 counts was accumulated for each sample, normally over two separate counting periods. Two blanks were run; one using no sediment and the other using an oxidised portion of the original sample. No CO_2 was evolved by either procedure. The CO_2 recoveries were 70–90% based on the total SOC contents. The $\Delta^{14}C$ and $\delta^{13}C$ values and ages quoted in Table 2 have been calculated in the normal manner[6]. The $^{230}Th/^{232}Th$ (ref. 7) $^{239+240}Pu$ (ref. 8) methodologies were applied to the same non-acidified, dried sediment samples as used for the ^{14}C determinations, and the SOC contents were done using a Hewlett-Packard CHN Analyser. No differences were found in SOC between acidified and non-acidified sediment samples within the error of the method ($\pm 0.015\%$ C), indicating that the carbonate content of the sediment was <0.03%. This was confirmed by infrared analysis of the CO_3^{2-}–CO_2 in non-acidified sub-samples.

Bowen, personal communication) showed penetration of $^{239+240}$Pu down to 12 and 14 cm in these cores. Previous measurements[15] by Bowen for two box cores taken in 1974 in the same general area showed penetration of $^{239+240}$Pu from the surface down to 5 and 8 cm in the sedimentary column.

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Did emerging continents trigger metazoan evolution?

A DIVERSE fauna of trilobites, archaeocyathids, and other shelly invertebrates can be found in rocks of early Cambrian age, but in strata antedating the Cambrian such skeletonised remains are notably absent. This seemingly abrupt appearance of multicellular animals seemed illusory to Darwin[1], whose vision of evolution assumed the gradual transmutation of species over innumerable generations. His view of life necessitated a long Precambrian record of evolving Metazoa and he, therefore, attributed the apparent absence of Proterozoic fossils to the imperfection of the fossil record and the vagaries of sedimentary geology. Discoveries of the past two decades have shown the first metazoans to be less ancient than Darwin believed. It now seems that the Metazoa evolved only in the latest Precambrian (perhaps 750–650 Myr ago), and that 100–150 Myr of evolution was sufficient to delineate the various phyla in evidence at the base of the Cambrian. The question of whether emerging continents controlled the late appearance of multicellular animals on Earth is discussed here.

Hargraves' theory[2] of crustal evolution has inspired new hypotheses on metazoan origins. Hargraves believes that the primitive Earth had a thin, but continuous, sialic crust blanketed by a world ocean some 2.8 km in depth. As the Earth matured, mantle activity progressively built the sialic crust into continental masses. The thickness of these continents was controlled isostatically, the critical crustal depth being the 750 °C isotherm (the temperature at which granitic crust begins to melt). As long as the Earth's interior was hot and, consequently, the 750 °C isotherm was shallow, the continents could not become thick enough to rise above sea level. Only as the Earth cooled could continental blocks emerge from and dissect the world ocean. Hargraves sets wide limits on the timing of continental emergence. His geophysical model for terrestrial cooling predicts that continents should have appeared 1,400–900 Myr BP, while his estimate of sedimentary rock volumes through time suggests that the actual time of emergence was 900–600 Myr BP. Hargraves does, however, acknowledge that certain patterns of sedimentation are most consistent with the existence of emergent continents before 1,700 Myr BP.

Chamberlain and Marland[3] were the first to consider the biological implications of Hargraves' theory. If Hargraves is correct, they reasoned, then before the buildup of continents to within 200 m of sea level, the global sea would have been stratified. Nutrient recycling by upwelling would have been minimal, and consequently, organic productivity would have been low. Chamberlain and Marland link both increased algal productivity and metazoan evolution to the appearance of persistently emergent continents.

LaBarbera[4] has taken these arguments further and developed an explicitly hargravesian theory of metazoan origins. He argues that it was the emergence of continents in the late Precambrian that triggered the evolution of multicellular organisms. Before the end of the Proterozoic era, environments in which early invertebrate benthos could proliferate simply did not exist, except during a few transitory periods.

If we wish to accept the theories of metazoan evolution implied by Chamberlain and Marland and defined by LaBarbera, we must first examine the physical model on which they are based. Instead of judging the merits of the Hargraves' model in its entirety[5], I shall concentrate on the aspect that bears directly on the derivative biological arguments—the timing of the appearance of continental land masses. If sizeable continents with their associated implications for erosional runoff, shallow marine platform environments, and upwelling currents existed significantly before the end of the Precambrian, then it is difficult to attribute the evolution of Metazoa to their appearance. The appropriate data for the examination of this question are the preserved accumulations of Precambrian sedimentary rocks. From these strata, one can derive important information about the type, depth, and extent of depositional environments, as well as data relevant to the delineation of sediment source areas.

The Proterozoic sedimentary record of North America is relatively well known and illuminates the problem. The oldest Proterozoic sediments on this continent are those of the Huronian Supergroup exposed north of Lake Huron. This 2,300 Myr old sequence, which has an aggregate thickness of ~15,000 m near the southern limits of exposure, contains a variety of features suggestive of deposition on the margin of a large, emergent land mass: deposition on a pre-Huronian erosion surface, sedimentary structures indicative of fluvial deposition, other structures referable to tidal flat environments, clasts derived from a granitic source area to the north, and a set of characteristics (striated pavement and boulders, tillite, and dropstones) that record an episode of early Proterozoic glaciation[6-9]. Sediments of similar age and character are also known from other areas of North America: the Kaminak Basin, North-West Territories; the Chibougamau Basin, Quebec; and the Libby Creek Group of Wyoming[10].

Sedimentary rocks deposited between 2,200 and 1,800 Myr BP are common in North America, occurring in linear geosynclinal belts and as the remnants of broad platform sequences.