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Sedimentation rate as determined by ^{226}Ra activity in marine barite

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Abstract—In recently formed marine barite (BaSO_4) separated from two equatorial Pacific cores ^{226}Ra activity exceeds that of its parent ^{230}Th by at least an order of magnitude, indicating radium uptake during barite precipitation. The decay of ^{226}Ra with depth, in these samples, is exponential implying that no radium exchange with porewaters occurs after burial. Thus, barite behaves as a closed system below the sediment mixed layer. The absence of $^{226}\text{Ra}_{\text{exs}}$ activity in barite samples older than ~8000 years, the lack of any detectable ^{228}Th , ^{228}Ra , and ^{224}Ra in any of the barite samples analyzed, and the unaltered crystal size and habit with depth in the sediment, further support this conclusion. Hence, assuming that oceanic Ra/Ba ratio has not changed throughout the Holocene, the decay of unsupported ^{226}Ra permits dating of marine barite and estimating sedimentation rates. Holocene sedimentation rates calculated using the decay of $^{226}\text{Ra}_{\text{exs}}$ in barite are consistent with ^{14}C and $\delta^{18}\text{O}$ derived sedimentation rates of 2–3 cm/kyr for the same cores. The method could be extendible to carbonate-poor Holocene sediments.

1. INTRODUCTION

1.1. General Background

Barite in marine sediments records a variety of important oceanic processes and characteristics, i.e., paleoproductivity (Dymond et al., 1992; Schmitz, 1987; Shimmiel et al., 1988), organic carbon export from the euphotic zone (Bishop, 1988; Dehairs et al., 1990, 1991), and seawater strontium isotope composition (Paytan et al., 1993). Little information is available on the fate of barite after burial, especially during early diagenesis. To evaluate its potential for short- and long-range geochemical paleoceanographic studies, it is important to determine the diagenetic behavior of barite. Already in the seventies it was recognized that the U-series radionuclides systematics in marine barite and associated sediments could enhance our understanding of the formation and early diagenesis of this phase (Church and Bernat, 1972; Borole and Somayajulu, 1977) and possibly provide the geochronology of the associated sediments (Lal and Somayajulu, 1975; Koide et al., 1976).

Most seawater profiles are characterized by excess ^{226}Ra , ($t_{1/2} = 1600$ y) over ^{230}Th , due to the greater particle reactivity of thorium and the diffusion of radium into the water column from porewaters (Ivanovich and Harmon, 1992). In most marine sediments ^{230}Th activity decreases with depth while ^{226}Ra activity increases towards equilibrium with ^{230}Th (Cochran, 1979; Kadko, 1980; Piggot and Urry, 1941), resulting in a subsurface maximum of ^{226}Ra . The associated porewaters should have a similar ^{226}Ra activity profile due to desorption from mineral surfaces and dissolution of sedimentary components. Thus, if barite crystals exchange radium with porewaters, or grow below the bioturbated zone in the sediment, the $^{226}\text{Ra}/\text{Ba}$ ratio of sedimentary barite would also exhibit such a trend. Moreover, if barite continuously acquires barium and radium from porewaters, barite samples older than ~8,000 years would have excess ^{226}Ra activities, from porewaters that contain ^{226}Ra produced from ^{230}Th in the sediments. Exponential decay of ^{226}Ra in barite

and no detection of $^{226}\text{Ra}_{\text{exs}}$ activity in samples older than ~8000 years, however, would suggest that barite behaves as a closed system with respect to radium.

1.2. Previous Studies

Earlier studies of radium, lead, thorium, and uranium in marine barite samples implied rapid exchange and remobilization of these elements (Church and Bernat, 1972; Borole and Somayajulu, 1977). Church and Bernat (1972) measured thorium and uranium concentrations in barite samples, reported $^{228}\text{Th}/^{232}\text{Th}$ activity ratios (AR) of 2–21 (with most values in the range of 3–5) for barite from near core tops, and proposed that ^{226}Ra in the barite was in rapid exchange equilibrium with porewaters. These data suggest that radium, and by implication also barium, reside in the barite for only about one year before returning to the porewaters. Providing a mechanism for such rapid exchange was not forwarded and is problematic. Church and Bernat (1972) also reported $^{230}\text{Th}/^{232}\text{Th}$ AR in barite which are ten times lower than the AR of the bulk sediment from which the barite was extracted. To explain this surprising result it was assumed the bulk sediment scavenged thorium from surface seawater where they postulate the $^{230}\text{Th}/^{232}\text{Th}$ AR is high, while the barite acquired thorium from deep or porewater where, they postulated, the ratio is low. We now know that the surface Pacific Ocean $^{230}\text{Th}/^{232}\text{Th}$ AR is low and the deep water ratio is high, just the reverse of what was postulated. Accordingly, their data imply that barite must preserve a surface ocean $^{230}\text{Th}/^{232}\text{Th}$ AR and is not in rapid exchange equilibrium with porewaters.

Borole and Somayajulu (1977) measured ^{226}Ra and ^{210}Pb in barite samples separated from an eastern equatorial Pacific core with sedimentation rates of 3–5 cm/kyr from subsurface depth of 42–785 cm. Thus, all of the samples they analyzed were older than 8,000 years and should not contain any residual excess ^{226}Ra . They did, however, measure excess ^{226}Ra in the barite samples and observed no decrease

TABLE 1. ^{226}Ra and ^{230}Th activities in (a) marine barite from core MC69, 0.67°N, 139.43°W; 4307 m water depth; and core MC82, 2.03°N, 140.08°W; 4413 m water depth, collected in November, 1992. (b) Barite samples older than 8,000 years. (c) Bulk sediments from cores MC69 and MC82.

(a)

Depth (cm)	^{226}Ra in barite (dpm/g) $\pm 5\%$	^{230}Th in barite (dpm/g) $\pm 10\%$	$^{230}\text{Th}/^{232}\text{Th}$ (dpm/dpm)	$^{226}\text{Ra}_{\text{ex}}$ in barite (dpm/g)	* ^{14}C age (years)
Core 0.67°N 139.43°W, 4307 m water depth					
0.25	1405	117	61	1386	
0.75	1007				1,000
1.5	1096				
2.5	1004				1,250
3.5	1304	371	179	1126	1,500
4.5	1087				
5.5	968	169	105	873	2,500
6.5	1181				
7.5	1106	234	171	963	2,800
8.5	1041				
9.5	1017	270	88	828	3,275
11	893				3,750
13	640	117	70	556	4,500
15	604	264	105	378	5,250
17	472	120	189	365	6,400
19	382				
21	295	175	161	130	7,600
23	236	133	70	108	9,000
25	162				
27	113	198	90	0	10,500
Core 2.03°N 140.08°W, 4413 m water depth					
0.25	1290				
0.75	930	17	21	915	2,000
1.5	1092				3,700
2.5	929				
3.5	881	152	169	749	4,500
4.5	768				
5.5	728				5,000
6.5	693	414	114	315	
7.5	718	479	122	277	5,700
8.5	596	389	75	237	
9.5	436	240	89	220	
11	366	177	92	162	
13	280	192	71	93	7,500
15	207	130	45	78	
17	169	159	98	0	10,500
19	150				13,000
21	145	173	72	0	

(b)

Sample	** ^{226}Ra in barite (dpm/g)	^{230}Th in barite (dpm/g)	$^{230}\text{Th}/^{232}\text{Th}$ (dpm/dpm)	**** Age (kyr)
PC72- 37	67	120	89	12
PC72- 47	31	106	40	15
PC72- 157	233	2306	139	67
PC72- 315	33	56	168	163
PC72- 739	33	37	75	419
575B 13-2	*** nd	-		16300
574C 11-3	nd	-		20400
574C 20-2	nd	-		27000

in ^{226}Ra activity with depth in the core. Therefore, they concluded that the barite must be continuously growing in the sediment column. The Ra/Ba ratio in the porewaters and bottom waters in that area is, however, about a factor of 10 higher than the ratio in the barite and the distribution coefficient for radium in barite is close to 1 (Moore and Dymond, 1991); thus, the growth could not have been taking place in equilibrium with the porewater. Furthermore, no increase in barite crystal size nor change in crystal habit down-core were observed. They also recorded $^{210}\text{Pb}/^{226}\text{Ra}$ AR of only 0.04–0.15; therefore, ^{222}Rn escape from the barite crystals was speculated. Given the size of the crystals (1–5 μm), loss of

85–96% of the ^{222}Rn is puzzling; when precipitated in the laboratory, barite does not emanate much ^{222}Rn .

The new radium and thorium data from equatorial Pacific marine barite samples, presented below, differ from the above and provide insights on marine barite formation and preservation and on the use of ^{226}Ra decay in this phase as a dating tool of young marine sediments.

2. EXPERIMENTAL METHODS

Marine barite microcrystals from the upper 25 cm of two box cores from the central equatorial Pacific and from several older sediments were separated by sequential leaching with acetic acid,

TABLE 1. (Continued).

(c)

Depth (cm)	^{226}Ra (dpm/g) $\pm 5\%$	***** $^{230}\text{Th}_{\text{ex}}$ (dpm/g) $\pm 2\%$	$^{210}\text{Pb}_{\text{ex}}$ (dpm/g) $\pm 5\%$	* ^{14}C age (years)
Core MC69, 0.67°N 139.43°W, 4307 m water				
0.25	11.27		24.44	400
0.75	10.21		17.22	1,000
1.5	10.67	18.63	10.97	
2.5	11.10		10.58	1,250
3.5	11.54	18.01	5.91	1,500
4.5	10.87		3.20	
5.5	11.49	17.89	0.75	2,500
6.5	12.27			
7.5	11.26			2,800
8.5	11.74			
9.5	10.82	15.39		3,275
11	11.83			3,750
13	10.59	13.19		4,500
15	9.60	12.16		5,250
17	9.95			6,400
19	9.44			
21	8.68	9.40		7,600
23	8.88			9,000
25	9.80	9.54		
27				10,500
Core MC82, 2.03°N 140.08°W, 4413m water depth				
0.25	10.11			
0.75	10.57		27.29	2,000
1.5	8.68	27.24	13.79	3,700
2.5	8.37		4.07	
3.5	11.18	25.99		4,500
4.5	10.92	26.05		
5.5	11.03			5,000
6.5	11.34			
7.5	10.65	23.16		5,700
8.5	10.25			
9.5	9.91			
11	10.33	16.39		
13	9.76			7,500
15	9.85			
17	8.85	13.43		10,500
19	8.92			13,000
21	8.90			
23	9.37	13.09		
25	8.50			
27	7.79	13.16		

* Ages from DeMaster and Pope (1994).

** None of the barite samples in Table 1 (b) have any excess ^{226}Ra activity.

*** nd = not detected.

**** Ages for PC72 were determined using oxygen isotope age model (Murray et al., 1995) and for the ODP sites using biochronology (Barron et al., 1985).

***** ^{230}Th activities of the bulk sediment were measured and provided by R. Anderson at Lamont-Doherty Earth Observatory.

sodium hypochlorite, hydroxylamine hydrochloride, HNO_3 -HF mixture, and ashing, described in Paytan et al. (1993); all of the sediments are oxic. This procedure completely removes Fe-Mn oxyhydroxide coatings and preferentially removes radium relative to thorium from the barite surfaces, but does not affect the radium in the barite structure. The ^{226}Ra activities of these barites and ^{226}Ra and ^{210}Pb activities of the bulk sediment were measured by γ -ray spectrometry, using an intrinsic germanium detector with a 1 cm diameter well (Moore, 1984). The activities of other gamma emitters, specifically, ^{228}Th , ^{228}Ra , and ^{224}Ra , were monitored; no activities of these nuclides were detected above background level for any of the barite samples measured. The ^{230}Th , ^{232}Th , and uranium isotopes activities in barite samples were measured by dissolution in the presence of a ^{232}U - ^{228}Th isotope dilution spike and alpha spectrometry (Rubin, 1991). The errors reported in Table 1 are the 2σ counting variance.

To examine the possibility of adsorption of radium and thorium on barite surfaces from the bulk sediment during the separation procedure, ^{228}Ra and ^{229}Th spikes were added to each step of the barite separation treatment of selected samples. About 1% of the Th

and 0.5% of the radium spikes were adsorbed onto the cleaned barite surfaces. The activity of the adsorbed fraction of radium is insignificant relative to the total radium activity in barite crystals younger than 8,000 years, in the cores analyzed in this work. Therefore, corrections for these adsorbed activities were not made; they do not significantly change the results obtained in this work.

3. RESULTS AND DISCUSSION

3.1. ^{226}Ra Activity in Marine Barite and Associated Sediments

The ^{226}Ra and ^{230}Th activities of barite samples, the depth of the sediment from which they were extracted, and the ^{14}C ages of these sediments are given in Table 1a and b. The uranium concentrations in the samples were less than 0.5 ppm, negligible in comparison to thorium, indicating that essentially all the ^{230}Th in the barite crystals is unsupported.

$^{230}\text{Th}/^{232}\text{Th}$ AR ranged between 20 and 190, with a mean of about 100, which is consistent with the ratio in the bulk sediments in this area (R. F. Anderson, pers. commun.). Considering the high counting error associated with the very low ^{232}Th activities and small sample size the range of values is probably experimental. The ^{226}Ra activities versus depth of marine barite from the two equatorial Pacific cores are shown in Fig. 1. Bulk sediment ^{226}Ra activities were also measured and compared with bulk sediment $^{230}\text{Th}_{\text{exs}}$ and $^{210}\text{Pb}_{\text{exs}}$ activities (Table 1c; Fig. 2). The ^{226}Ra activity of barite is considerably higher than that of the bulk sediment (Fig. 1). Since barite comprises 0.25 wt% of these sediments, it accounts for up to 20% of the bulk sediment ^{226}Ra activity. The exponential decrease of ^{226}Ra in barite with depth in the upper 25 cm of the cores suggests that barite behaves as a closed system with respect to radium and is not affected by exchange or recrystallization (Fig. 1). It is unlikely that such a curve would be produced by precipitation of barite or exchange of barium and radium in the barite

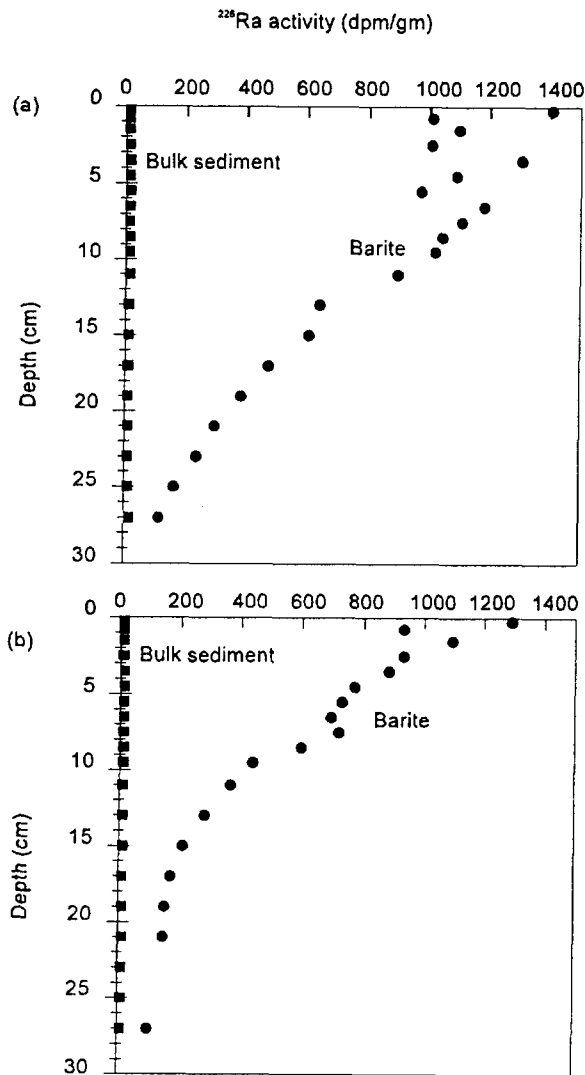


FIG. 1. ^{226}Ra activity in marine barite separated from (a) core MC69, 0.67°N 139.43°W and (b) core MC82, 2.03°N 140.08°W.

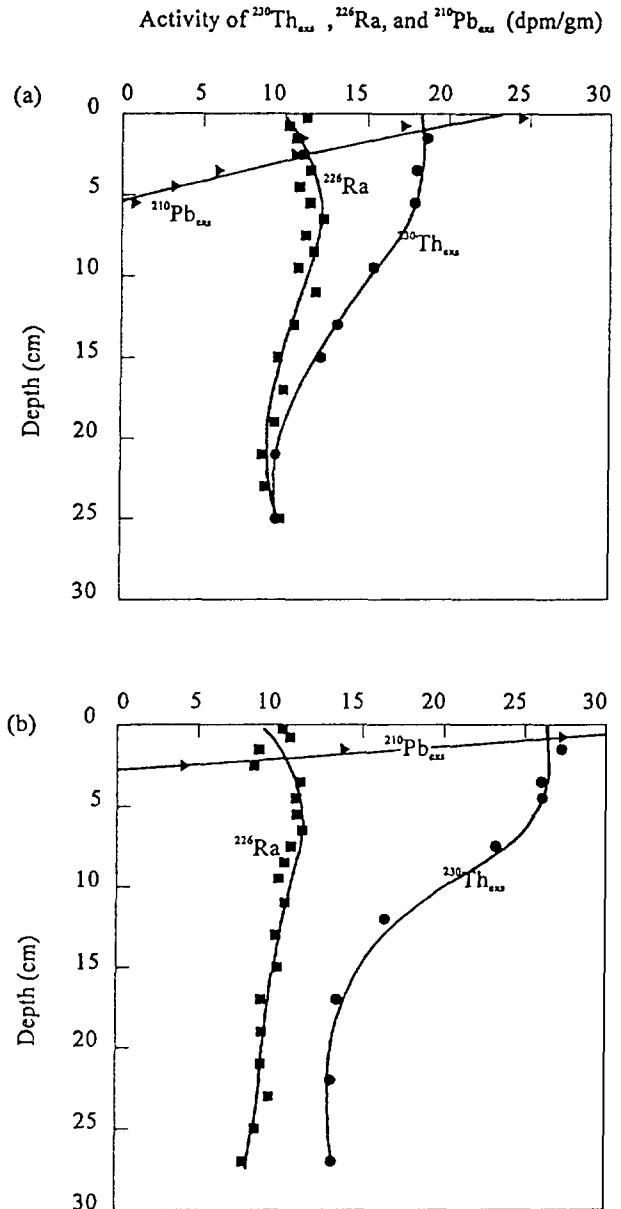


FIG. 2. Bulk sediment ^{226}Ra , $^{210}\text{Pb}_{\text{exs}}$ and $^{230}\text{Th}_{\text{exs}}$ activities: (a) core MC69, 0.67°N 139.43°W and (b) core MC82, 2.03°N 140.08°W. $^{230}\text{Th}_{\text{exs}}$ activities were measured and provided by R. Anderson at Lamont-Doherty Earth Observatory.

crystals with the porewater because the porewater barium concentrations in these cores remain relatively constant below a few centimeters depth (Paytan and Kastner, 1996). Lack of any detectable ^{228}Th , ^{228}Ra , and ^{224}Ra activities in any of the barite samples analyzed also suggest that no or insignificant barite growth is occurring in the sediment below the bioturbated zone. This conclusion is supported by the similar morphology of the crystals to those observed in the water column (Bishop, 1988; Dehairs et al., 1980) and the strontium isotope composition of previously analyzed barite samples (Paytan et al., 1993). The absence of any excess ^{226}Ra activity in barite from sediments older than ~8,000

years further reinforces this conclusion (PC72 and ODP samples, Table 1b). ^{222}Rn (decay product of ^{226}Ra) emanation from the barite crystals was also measured in order to verify the closed-system behavior. The emanation coefficient (radon emerging from mineral grains/radon generated in the mineral by decay of radium) was found to be 5%. This is equal to the emanation due to recoil of radon from a thin surficial layer of radium in grains which are $\sim 1 \mu\text{m}$ in size (Rama and Moore, 1990), and indicates no ^{222}Rn escape from the barite crystals, as expected from a closed-system behavior.

The $^{226}\text{Ra}/\text{Ba}$ ratio in barite separated from sediments in the mixed layer is about $0.3 \text{ dpm}/\mu\text{mol}$. This ratio is lower than the $^{226}\text{Ra}/\text{Ba}$ ratio of about $1.2 \text{ dpm}/\mu\text{mol}$ of particulate matter recovered from sediment traps in this area (Moore and Dymond, 1991). Assuming most of the barium and radium in the particulate matter resides in barite (Moore and Dymond, 1991), the lower ratio in the crystals is consistent with the decay of ^{226}Ra during the residence time of the sediment in the mixed-layer, which is $\sim 3,000$ years based on ^{14}C data by DeMaster and Pope (1994). These data suggest that barite is forming in the water column. But, assuming that the concentration in the upper centimeters of the pore-water radium is equal to that of the bottom water, the $^{226}\text{Ra}/\text{Ba}$ ratio of porewaters from the upper 0.5 cm of the sediment in this area would be $0.9 \text{ dpm}/\mu\text{mol}$ (Paytan, 1995) (which is clearly a minimum value); thus, an early-diagenetic barite formation, close to the sediment water interface where porewaters are supersaturated with respect to barite, cannot be ruled out. In either case the ^{226}Ra activity data indicate that barite once formed (in the water column and/or at the sediment water interface) remains a closed system with respect to radium. Hence, marine barite is a suitable phase for geochemical paleoceanographic studies and the decay of ^{226}Ra in these barite samples can be used for geochronology.

These results for radium and thorium in marine barite differ significantly from those of Church and Bernat (1972) and Borole and Somayajulu (1977) discussed above. We suspect that the milder sequential leaching procedure they used did not remove all detrital material and oxyhydroxide coatings from the barite; the X-ray analysis they used to confirm the sample purity is only semiquantitative. These impurities probably had a $^{230}\text{Th}/^{232}\text{Th}$ AR close to 1 and ^{228}Th , which would have lowered the apparent $^{230}\text{Th}/^{232}\text{Th}$ AR and produced an apparent high $^{228}\text{Th}/^{232}\text{Th}$ AR in the barite relative to the bulk sediment. The reported new data are from samples with considerably higher barite/detritus ratios, and a more extreme HF leach step was used to ensure the removal of detrital components. In addition, special precautions were taken to thoroughly leach the marine barite crystals surface coatings of Fe-Mn oxyhydroxides, which are known to adsorb radium and thorium, as described in Paytan (1995).

3.2. Sedimentation Rates Determined Using ^{226}Ra in Barite

Sedimentation rates of 3.6 cm/kyr at the equator and 2.7 cm/kyr at 2°N are derived from the slope of the logarithm of ^{226}Ra (dpm/gm) in barite versus depth below the bioturbation

zone (Fig. 3, empty symbols). These are maximum sedimentation rates because most likely a larger fraction of the measured radium in the older samples is produced by ^{230}Th in the barite (supported ^{226}Ra). It is unclear where the thorium resides in the barite crystals but it is most likely adsorbed onto the crystal surfaces from the surrounding porewater; the similar $^{230}\text{Th}/^{232}\text{Th}$ activity ratios determined in the bulk sediment support this conclusion. For comparison, the unsupported ^{226}Ra ($^{226}\text{Ra}_{\text{exs}}$) in the barite crystals was also calculated (Table 1a). This calculation assumes that all the barite is authigenic and that the ^{226}Ra in barite is incorporated

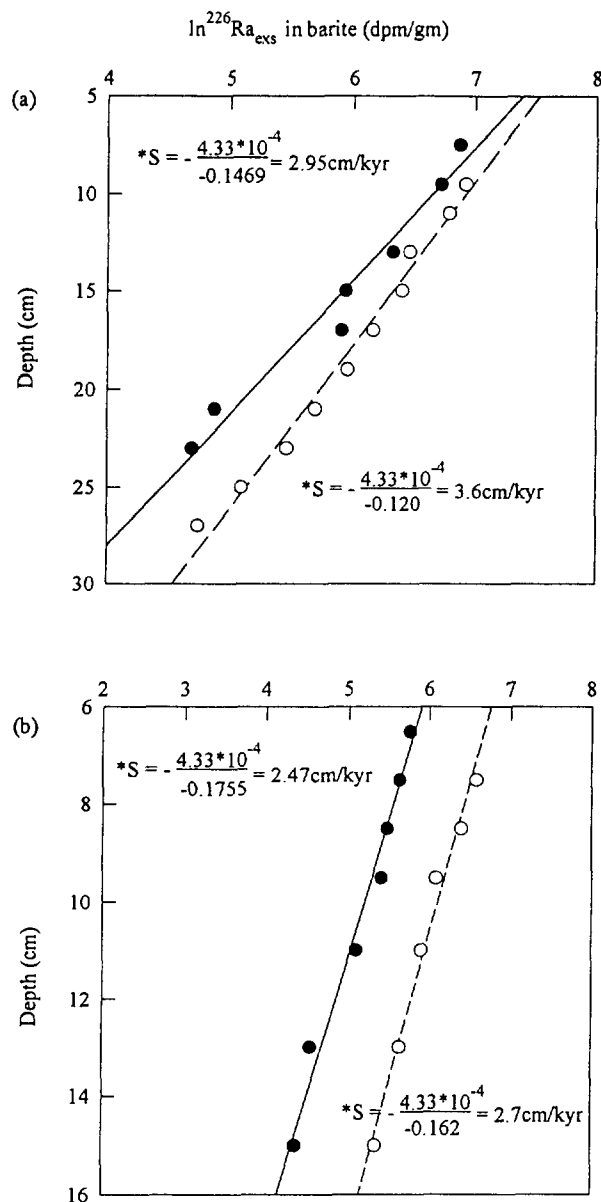


FIG. 3. Sedimentation rates in two equatorial Pacific cores. *S = Sedimentation rate, determined by dividing the decay constant (λ) of ^{226}Ra by the slope of the ^{226}Ra activity change with depth (empty circles) and $^{226}\text{Ra}_{\text{exs}}$ activity change with depth (full circles). (a) Core MC69, 0.67°N 139.43°W and (b) Core MC82, 2.03°N 140.08°W .

from the water column or at the sediment-water interface, while the thorium is adsorbed onto the barite surfaces from the porewater. With time ^{230}Th generates supported ^{226}Ra as the initial excess ^{226}Ra decays. The unsupported $^{226}\text{Ra}_{\text{exs}}$ is then given by $^{226}\text{Ra}_{\text{total}} - ^{226}\text{Ra}_{\text{sup.}} = ^{226}\text{Ra}_{\text{exs.}}$. Thus, the excess ^{226}Ra ($N_2^0 e^{-\lambda_2 t}$) was calculated using the following equation:

$$N_2 - \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) = N_2^0 e^{-\lambda_2 t}$$

in which the subscript 1 refers to the parent ^{230}Th and the subscript 2 refers to the daughter ^{226}Ra ; N stands for the total number of atoms of the isotope measured (dpm/ λ); λ is the decay constant of the isotope, t is the age of the sample, and N^0 is the initial number of atoms of the corresponding isotope, at zero age. ^{226}Ra has a half-life of 1600 years and ^{230}Th has a half-life of 75,200 years. The initial ^{230}Th activity is calculated from the measured ^{230}Th activity of each sample

and the age of the sample using: $N_1^0 = \frac{N_1}{e^{-\lambda_1 t}}$. The ^{230}Th -

produced ^{226}Ra was calculated from the ^{14}C age of the sample (DeMaster and Pope, 1994). This method of calculating the excess ^{226}Ra assumes that the ingrown radium is not lost to porewaters through alpha recoil and/or during the leaching. Also, because postdepositional thorium adsorption is a continuous process and the chemical treatment preferentially removes radium and does not completely remove thorium from surfaces, as indicated by the apparent Ra deficiency in the older samples (Table 1b), this method over-corrects for Th-supported radium and the $^{226}\text{Ra}_{\text{exs}}$ activities are minimum values. The calculated $^{226}\text{Ra}_{\text{exs}}$ in the barite crystals are given in Table 1a, and the calculated sedimentation rates derived from the logarithm of $^{226}\text{Ra}_{\text{exs}}$ (dpm/gm) in barite versus depth below the bioturbation zone (Fig. 3, full symbols) are 3.0 cm/kyr at the equator and 2.4 cm/kyr at 2°N . The sedimentation rates calculated with or without correction for supported radium are similar and only slightly higher than ^{14}C based estimates (2.3 and 2.1 cm/kyr, respectively, DeMaster and Pope, 1994), and of the same order as $\delta^{18}\text{O}$ derived sedimentation rates (~ 3.2 cm/kyr, Murray et al., 1995). Such sedimentation rates are quite typical for the equatorial Pacific Ocean and are much higher than those calculated from the slope of the logarithm of excess ^{230}Th in bulk sediment versus depth (0.26 and 0.23 cm/kyr, respectively), suggesting that ^{230}Th accumulation in these sediments is not constant with time and might be influenced by other processes such as carbonate dissolution (Marcantonio et al., 1995).

Sediments in the mixed layer are deficient in ^{226}Ra relative to ^{230}Th due to thorium scavenging from the water column and radium loss from the bioturbated zone, and the deficiency decreases with depth. Trap samples from 1°N , 139°W (MANOP site C) have a bulk $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio of >1 (W. S. Moore, unpubl. data). The $^{226}\text{Ra}/^{230}\text{Th}$ activity ratio in the sediment mixed layer is 0.6, in agreement with radium loss to the water column. The bioturbation coefficients (D_b), representing the intensity of sediment mixing, were calculated using the bulk sediment $^{210}\text{Pb}_{\text{exs}}$ data in the mixed layer and the relation $D_b = \lambda z^2 / [\ln(C_0/C_z)]^2$, where C_0 and C_z are the excess ^{210}Pb activities at depths of 0 and

z cm, and λ is the ^{210}Pb decay constant as described in Smith et al. (1993). Results yield coefficients of $0.1 \text{ cm}^2/\text{yr}$ for the equator and $0.06 \text{ cm}^2/\text{yr}$ at 2°N . Employing an equation that relates the $^{210}\text{Pb}_{\text{exs}}$ profile, bioturbation coefficient, and the sedimentation rate in a core (DeMaster and Cochran, 1982), a good fit to the data in the equator core was obtained using a sedimentation rate of 3 cm kyr^{-1} , which is consistent with the sedimentation rate calculated using ^{226}Ra decay in barite.

4. CONCLUSIONS

Marine barite in oxic pelagic sediments behaves as a closed system with respect to radium and thus is a suitable authigenic marine phase for chemical paleoceanographic studies. In Holocene sediments < 8000 years old the decay of excess ^{226}Ra in barite provides reliable sedimentation rates, and therefore can be utilized for dating carbonate poor sediments.

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