JOURNAL OF MARINE RESEARCH

The *Journal of Marine Research,* one of the oldest journals in American marine science, published important peer-reviewed original research on a broad array of topics in physical, biological, and chemical oceanography vital to the academic oceanographic community in the long and rich tradition of the Sears Foundation for Marine Research at Yale University.

An archive of all issues from 1937 to 2021 (Volume 1–79) are available through EliScholar, a digital platform for scholarly publishing provided by Yale University Library at https://elischolar.library.yale.edu/.

Requests for permission to clear rights for use of this content should be directed to the authors, their estates, or other representatives. The *Journal of Marine Research* has no contact information beyond the affiliations listed in the published articles. We ask that you provide attribution to the *Journal of Marine Research.*

Yale University provides access to these materials for educational and research purposes only. Copyright or other proprietary rights to content contained in this document may be held by individuals or entities other than, or in addition to, Yale University. You are solely responsible for determining the ownership of the copyright, and for obtaining permission for your intended use. Yale University makes no warranty that your distribution, reproduction, or other use of these materials will not infringe the rights of third parties.

Lead-210 and polonium-210 in pteropod and heteropod mollusc shells from the North Pacific: Evaluation of sample treatments and variation with shell size

by Victoria J. Fabry[1,2] and Margaret L. Delaney[3]

ABSTRACT

Lead-210 activities in carefully cleaned size groups of pteropod and heteropod shells from the eastern equatorial Pacific were typically 0.3 dpm/g shell, similar to those reported in other biogenic calcium carbonates. However, ^{210}Po activities were in excess of levels expected from the decay of shell-incorporated ^{210}Pb, with (^{210}Po/^{210}Pb) activity ratios ranging from 20 to 28 in size-fractionated samples. Sample treatment procedures were examined using pteropod shells collected from diverse locations of the North Pacific. Possible sources of ^{210}Po in excess of ^{210}Pb in shells include inclusion of ^{210}Po in the organic matrix during shell formation or adsorption of ^{210}Po from the ambient water or nuclide-rich animal tissues. We predict that other $CaCO_3$-precipitating organisms, including foraminifera, that have high surface/volume ratios and tissues in contact with carbonate surfaces, may also contain ^{210}Po in excess of that supported by the decay of ^{210}Pb.

Variation in ^{210}Pb activities measured in pteropod and heteropod shells suggests differences in the depth distributions for the species analyzed. Moreover, these results suggest ontogenetic migration in the pteropod *Cavolinia longirostris*. Pteropods and heteropods from regions in the equatorial Pacific were enriched 8–15 times with ^{210}Pb relative to calcium, based on reported ^{210}Pb activities in surface water and seawater calcium concentrations. Similarly, enrichment factors calculated for pteropod shells from the North Pacific transition zone and Subarctic Current were 13–20 times ^{210}Pb levels in surface waters. Skeletal enrichment of ^{210}Pb is higher in pteropods and heteropods than in corals by a factor of 3–10.

1. Introduction

Growth rates and life histories of euthecosomatous pteropods (Gastropoda: Opistho-branchia) and atlantid heteropods (Gastropoda: Prosobranchia) have been little studied. Since euthecosomatous pteropods and shelled heteropods are the major pelagic producers of aragonite (Milliman, 1974), oceanic aragonite production could

1. Department of Biological Sciences and Marine Science Institute, University of California, Santa Barbara, California, 93106, U.S.A.
2. Present address: Chemistry Department, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, 02543, U.S.A.
3. Institute of Marine Sciences, University of California, Santa Cruz, California, 95064, U.S.A.

be estimated if shell growth rates and population abundances were known. Our initial objective in this study was to measure shell growth rates and age in euthecosomatous pteropods and atlantid heteropods without maintaining animals in the laboratory or repeatedly sampling the same field population. Depth distributions of pteropods and heteropods are also of interest because the ecology of these animals is poorly known.

We attempted a radiometric method of determining growth rates, one of those using the disequilibrium of isotopes in the uranium or thorium decay series as natural chronometers (Goldberg and Bruland, 1974; Turekian and Cochran, 1978). These types of methods have been used previously with organisms that produce calcium carbonate hard parts, including corals (Moore and Krishnaswami, 1972), molluscs (Turekian *et al.*, 1975; Turekian *et al.*, 1979; Turekian and Cochran, 1981; Cochran *et al.*, 1981), and fish (Bennett *et al.*, 1982). We measured ^{210}Pb (half-life = 22.3 yr) and ^{210}Po (half-life = 138 d) in different size fractions of pteropod and heteropod shells. This nuclide pair, applicable for ages ranging from 0 to 2 years, was chosen for this study since estimates of pteropod and heteropod lifespans range from 1 to 2.5 years (Bé *et al.*, 1972; van der Spoel, 1973; Kobayashi, 1974; Wells, 1976; Fabry, 1988). In addition, since ^{210}Pb water column activities vary with depth, activities in shells could reflect the relative depth ranges of various species and age classes of these organisms.

As the animal grows, ^{210}Pb dissolved in seawater is incorporated into the crystal lattice of the aragonite shell, and subsequently decays to its granddaughter, ^{210}Po. Use of the disequilibrium of ^{210}Pb and ^{210}Po in age dating requires that ^{210}Po is not incorporated into the shell during calcification or is incorporated in known (^{210}Po/^{210}Pb) activity ratios. Unlike the divalent Pb cation which substitutes for Ca in aragonite, Po is incompatible with the aragonite crystal structure, largely because of its oxidation states in seawater. Low initial ^{210}Po activities ($\approx 0-0.1$ dpm/g CaCO$_3$) measured in the aragonite shells of other marine molluscs (Cochran *et al.*, 1981; Turekian and Cochran, 1981) support this premise. Hence the (^{210}Po/^{210}Pb) activity ratio in a shell should be a function of the radionuclide decay rates and the shell growth rate only. For example, the youngest pteropod or heteropod shell would be expected to have little or no ^{210}Po and the (^{210}Po/^{210}Pb) activity ratio would be close to zero. In contrast, the ^{210}Po and ^{210}Pb activities in the shell of an animal two years old would be close to equilibrium and the (^{210}Po/^{210}Pb) activity ratio would approach one.

While evidence suggests that the mineral phase of mollusc shells incorporates ^{210}Pb and excludes or discriminates against ^{210}Po, this may not be true of the organic component of shells, the organic matrix, which is the framework within which crystals are deposited. Additionally, the noncalcareous, organic tissues of zooplankton are enriched with ^{210}Po relative to ^{210}Pb by a factor ranging from 3 to 124 (Shannon *et al.*, 1970; Beasley *et al.*, 1973; Turekian *et al.*, 1974; Kharkar *et al.*, 1976). Thus, the goal of our study was to measure only the lattice-bound fraction of nuclides. Here we report ^{210}Po and ^{210}Pb activities measured in shells of euthecosomatous pteropods and atlantid heteropods in an attempt to determine species growth rates. Various sample treatment
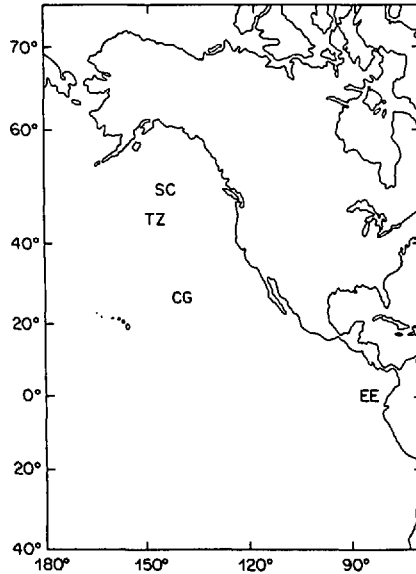
Figure 1. Location and collection date of samples. EE—Eastern equator (0°50'N, 86W); samples collected 3–19 March 1985. TZ—Northern transition zone (44N, 148W and 46N, 148W); samples collected on 12 July 1985. SC—Subarctic Current (50N, 145W); samples collected on 15 July 1985. CG—Central gyre (28N, 139W); samples collected from 17–19 July 1983. See Tables 1 and 2 for sample descriptions.

methods were also examined because of the potential contamination of shell surfaces from nuclides contained in soft animal tissues.

2. Materials and methods

a. Sample collections

Shell samples were collected with a RMT-4 trawl (1.5–2.0 mm mesh), towed obliquely from 250 m to the surface. Shelled pteropods and heteropods were immediately sorted from plankton collections and frozen.

Samples for the comparison of sample treatment methods were collected from several locations in the North Pacific including the eastern equatorial Pacific (March 1985), the central gyre (July 1983), the northern transition zone (July 1985), and the Subarctic Current (July 1985). Locations and sampling dates for collections are listed in Figure 1. Use of samples from different locations for this part of the study was necessary because the small individual mass of pteropod shells generally required sample sizes of more than 100 shells, and the total collection from any single station did not provide sufficient material for all the comparisons. When sample pairs were used to test a treatment, each sample of the pair was composed of shells of the same size and species that were collected at the same time.

Samples for the size class study undertaken to measure shell growth rates were collected in the eastern equatorial Pacific station from 3 March through 19 March 1985, as described above. Two pteropod species, *Cavolinia longirostris* and *Clio pyramidata,* and one heteropod species, *Atlanta plana,* were the most abundant molluscs captured, and thus were chosen for radiochemical analyses. All shells were individually weighed to the nearest 0.1 mg. For each species, shells were grouped into two to five weight classes based on the amount of material available. The number of shells in each size class averaged 381, and ranged from 63 to 1005 shells. The size-fractionated samples for these three species comprised a total of 4193 shells.

b. Comparison of sample treatments

Cleaning methods developed in this study were intended to rid samples of adsorbed ^{210}Pb and ^{210}Po not bound in the crystal lattice of the shell, because that is the portion which should exclude Po while it incorporates Pb. The retention of any nuclides associated with the organic matrix of the shell was unavoidable since there is no method which would selectively dissolve only the shell without leaching the matrix. Sample size limitations required that the least number of cleaning steps be used in order to minimize sample loss during cleaning. Therefore, because pteropod and heteropod samples were collected live from the water column and probably would not have the metal-rich surface coatings found in sediment samples, reductive cleaning methods used in trace elemental analyses of sedimentary foraminiferal shells and corals were not utilized (Boyle, 1981; Delaney and Boyle, 1983; Shen and Boyle, 1987, 1988; Shen *et al.,* 1987).

(i) Sample treatment A. A preliminary sample (sample A) of mixed pteropod and heteropod species collected from the equatorial Pacific station was analyzed using a two-stage process (Fig. 2). For the initial treatment, animals were placed in a low temperature plasma asher (International Plasma Corporation 1000 series) to oxidize the tissue within the shell. The temperature during ashing was approximately 175°C. Shells were then immersed for 12 hours in a solution of 30% H_2O_2 buffered with NaOH to pH 10, and were periodically agitated with ultrasound. This treatment eliminated any remaining ashes of organic tissues, yet did not dissolve shells or destroy their structural integrity by attacking the organic matrix. No organic tissue in shells was observed under microscopic magnification (500X). Shells were rinsed with buffered deionized water (pH = 10) and dried.

In the second phase of the cleaning process, the shell sample was gently crushed between two glass plates and transferred to a glass centrifuge tube. To ensure removal of organic coatings on shell surfaces, 30 mls of 0.1 N NaOH and 300 μl of 30% H_2O_2 were added to the sample, which was then heated in a 70°C water bath for 20–30 minutes and ultrasonically agitated at periodic intervals. After the supernatant in the sample tube was siphoned off, the sample was rinsed five times with glass distilled

SAMPLE TREATMENTS

```
PHASE I                          ┌─────────────────┐
    Step No.1                    │ Tissues in whole │
                                 │ shells oxidized  │
                                 │ via plasma asher │
                                 └─────────────────┘
                                 ┌─────────────────┐
         2                       │ H₂O₂ immersion   │
                                 │       +          │
                                 │ ultrasonic agitation │
                                 └─────────────────┘
                                 ┌─────────────────┐
         3                       │ Shells rinsed    │
                                 │ dried and weighed│
                                 └─────────────────┘
- - - - - - - - - - - - - - - - - - - - - - - - - - - - - -
PHASE II  4                      ┌─────────────────┐
                                 │  Shells crushed  │
                                 └─────────────────┘
                                 ┌─────────────────┐
         5                       │ NaOH/H₂O₂ immersion │
                                 │        +         │
                                 │ ultrasonic agitation │
                                 └─────────────────┘
                                 ┌─────────────────┐
         6                       │ Samples rinsed 5X│
                                 │        +         │
                                 │ ultrasonic agitation │
                                 └─────────────────┘
              A                                    B
     ┌─────────────────┐            ┌─────────────────┐
  7  │ Weak HCl immersion │          │ Brief HCl rinse │
     │        +          │          │ and filtration  │
     │ ultrasonic agitation │        └─────────────────┘
     └─────────────────┘
                       ┌─────────────────┐
         8             │ Samples rinsed 4X│
                       │ dried and weighed│
                       └─────────────────┘
```
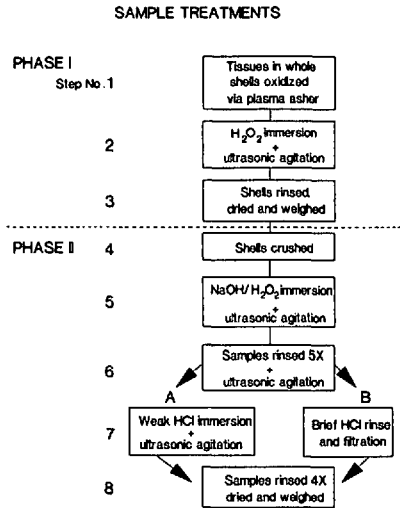
Figure 2. Flowchart of sample treatments. Pathway A was used for sample A and all size fractions of *Cavolinia longirostris*. Pathway B was used for sample B, all other samples in cleaning experiments and size-fractionated samples of *Clio pyramidata* and *Atlanta plana*. Treatment variations: sample C2—shells ground in step 4; D2*—omitted step 1; E2*— omitted step 1 and prolonged step 2.

water. Each rinse was followed by a brief burst of ultrasonic agitation. To remove any ^{210}Pb or ^{210}Po that may have adsorbed onto shell surfaces during the oxidation of organic tissues, 1.75 mls of redistilled 0.006 N HCl was added to the sample, which was subsequently mixed by intermittent ultrasonic agitation for 5 minutes. The volume and duration of the acid rinse were calculated to dissolve only a small fraction of the sample weight. The sample was then rinsed four times with glass distilled water, transferred to a clean, preweighed glass beaker, dried, and reweighed. Sample weight loss during the second stage of cleaning for sample A was 25%.

(ii) Sample treatment B. Sample B (mixed sizes of *Cavolinia longirostris* collected from the equatorial Pacific station) was cleaned as described above, except that the acid treatment was modified to maintain a constant, low pH to minimize readsorption of leached metals. Following the $NaOH/H_2O_2$ immersion described in the second stage of sample treatment A, sample B was transferred to a Millipore filter apparatus with a 0.45 μm filter. After dissolving a fraction of the sample with a brief rinse (30 sec) with 0.1 N HCl (40 ml), the acid solution was filtered off. The remaining sample was repeatedly rinsed with glass distilled water and filtered, for a total of four rinses. In all subsequent sample preparation, this modified acid treatment was used. Acid volume and duration of the rinse varied with sample weight. Sample weight loss during the second stage of cleaning with this method was typically 23%.

(iii) Effects of crushing vs. grinding. To determine if increased exposure of inner shell surfaces improved cleaning effectiveness, we investigated the possible effects of crushing shells into small chips compared to pulverizing samples into a coarse powder, a technique used for biogenic carbonates by several workers (Turekian *et al.,* 1979; Cochran *et al.,* 1981; Benninger and Dodge, 1986). Two samples (C1 and C2) of mixed size classes of *Clio pyramidata* collected from the equatorial Pacific were prepared using the methods described in sample treatment B. Samples C1 and C2 were treated identically, except that the shells of sample C1 were broken into small chips by crushing them between glass plates, while the shells of the other sample, C2, were ground with a mortar and pestle. In the acid rinse step for these samples, a 0.2 μm Millipore filter was used to prevent loss of finely ground particles. Sample weight loss during the second stage of cleaning was 27% for the crushed sample (C1) and 74% for the ground sample (C2).

(iv) Effects of plasma ashing. To determine if plasma ashing the samples introduced artifacts, such as the formation of metal oxides, we compared two samples (D1 and D2*) of mixed size classes of *Clio pyramidata* collected from the northern transition zone. These samples were treated identically except that sample D1 was plasma ashed before the 12-hour H_2O_2 treatment as described in the first stage of the cleaning process, and the other sample, D2*, was removed from the freezer and immediately treated with H_2O_2 for 12 hours, with no plasma ashing. No difference between the samples could be discerned by inspection with a dissecting microscope. The effects of plasma ashing coupled with a longer H_2O_2 treatment were tested with samples E1 and E2*, mixed size classes of *Clio pyramidata* collected from the Subarctic Current. Sample E1 was plasma ashed prior to being immersed in the buffered H_2O_2 solution for 24 hours, while sample E2* was removed from the freezer and immediately treated with H_2O_2 for 24 hours.

(v) "Old" sample as control. Sample F was composed of *Clio pyramidata* shells collected from the North Pacific gyre in 1983, about two years prior to the time of analyses. Shells were prepared for analyses using the methods of sample treatment B. Three weeks after capture, animal tissues in shells were removed by plasma ashing and the H_2O_2 treatment of the first stage of cleaning. Empty shells were then stored for twenty-three months, at which time the second cleaning stage was completed immediately prior to radiochemical analyses. Hence, if the assumptions of the $^{210}Po/^{210}Pb$ radiochemical method for the determination of growth rates were valid and the cleaning methods were adequate, the ^{210}Po activities in this sample would be expected to have reached transient equilibrium with respect to the ^{210}Pb.

c. Treatment of size-fractionated samples

   All four size fractions of *Cavolinia longirostris* were treated using the two-stage method of sample treatment A. In the acid cleaning step, typically 25 mls of redistilled

0.006 N HCl was added to each sample and mixed with ultrasonic agitation for 10 minutes prior to rinsing. Sample weight loss during the second phase of cleaning of these samples ranged from 2.2 to 3.1%.

All size classes of *Clio pyramidata* and *Atlanta plana* were prepared for analyses using the methods described in sample treatment B. Sample weight loss for these samples ranged from 16–49%.

d. Radiochemical analyses

Excluding Sample F, all samples were initially analyzed within 70–144 days of collection. Assuming that no ^{210}Po was deposited in the shell during calcification, this timespan exceeded the initial 30 days when the decay of ^{210}Bi (the intermediate daughter of ^{210}Pb with a half-life = 5 d) must be considered in calculations, yet was within the time period of steep ^{210}Po ingrowth which would permit the most precision in shell age determinations. Using standard radiochemical techniques (Flynn, 1968), ^{210}Po was plated onto silver planchets and counted with alpha spectrometers fitted with silicon surface barrier detectors. Samples were counted from 5 to 9 days. Background counts typically accounted for 1 to 6% of total counts measured in the ^{208}Po region, and 1 to 7% of total counts in the ^{210}Po region. Blanks processed through full sample treatments with each set were equal to or within the range of counting error of detector background counts. No further blank corrections were necessary.

After waiting six to seven months to allow for adequate ingrowth of ^{210}Po, samples were counted again for polonium, and the initial concentration of ^{210}Pb was calculated. Counting errors (1 σ) were propagated through calculations, and were typically 2% for ^{210}Po and 12% for ^{210}Pb. In order to characterize shells at their time of capture, all activities were corrected to the date of sample collection.

3. Results and discussion

Tables 1 and 2 and Figures 3–5 show the sample description and radiochemical data for shells treated with different procedures and for size-fractionated samples of pteropod and heteropod shells. Samples collected from the same station had similar ^{210}Pb activities and (^{210}Po/^{210}Pb) activity ratios, despite variation in the sample weight loss during cleaning treatments. In all samples, ^{210}Po values were an order of magnitude higher than the measured ^{210}Pb values, indicating that almost all of the ^{210}Po measured was unsupported by its parent nuclide, ^{210}Pb.

No differences in ^{210}Pb or ^{210}Po activities were detected within counting uncertainties between sample treatments A and B, which used different acid cleaning methods (Table 1). However, the physical means by which samples were prepared resulted in markedly different activities (Table 1). The sample that was ground with a mortar and pestle (C2) had five times more ^{210}Pb and ^{210}Po than the sample that was crushed between glass plates (C1). The fine particles of the ground sample provided increased surface area compared to the shell chips that resulted from crushing. Nuclides in the

Table 1. Sample description and radiochemical data for different samples treatments. Radioactivities are corrected to the time of sample collection and expressed as disintegrations per minute per gram $CaCO_3$. Errors reported are $\pm 1\sigma$ counting errors propagated through the calculations.

Sample I.D.	Species	Location #	Sample wt. (g)	No. of shells	Cleaning treatment	% Wt. loss in cleaning	^{210}Pb (dpm/g)	^{210}Po (dpm/g)	$^{210}Po/^{210}Pb$ activity ratio
A	Mixed	E	0.0660	N.D.	(see text)	−25	0.44 ± 0.16	5.9 ± 0.31	13 ± 5.0
B	*Cavolinia longirostris*	EE	0.1318	N.D.	modified acid cleaning	−44	0.21 ± 0.09	4.3 ± 0.26	21 ± 8.7
C1	*Clio pyramidata*	EE	0.1924	N.D.	crushed	−27	0.25 ± 0.05	5.1 ± 0.15	20 ± 4.1
C2	*Clio pyramidata*	EE	0.0667	N.D.	ground	−74	1.3 ± 0.23	24 ± 0.64	18 ± 3.2
D1	*Clio pyramidata*	TZ	0.4496	378	plasma ashed	−17	2.3 ± 0.08	20 ± 0.31	8.7 ± 0.3
D2*	*Clio pyramidata*	TZ	0.4617	385	not plasma ashed	−16	2.6 ± 0.11	24 ± 0.36	9.1 ± 0.4
E1	*Clio pyramidata*	SC	0.3151	160	plasma ashed H_2O_2 for 24 h	−19	2.0 ± 0.08	13 ± 0.21	6.4 ± 0.3
E2*	*Clio pyramidata*	SC	0.2903	166	not plasma ashed H_2O_2 for 24 h	−20	2.1 ± 0.09	11 ± 0.21	5.1 ± 0.2
F	*Clio pyramidata*	CG	0.1467	N.D.	(see text)	−18	0.99 ± 0.10	5.8 ± 0.13	5.8 ± 0.6

N.D. = not determined but >100.
*indicates sample was not plasma ashed during cleaning.
#Abbreviations are: EE = Eastern Equatorial; TZ = Transition Zone; SC = Subarctic Current; CG = Central Gyre. See Figure 1 for map of sample stations.

Table 2. Sample description and radiochemical data for pteropod and heteropod shells collected from the eastern equatorial Pacific. Radioactivities are corrected to the time of sample collection and expressed as disintegrations per minute per gram CaCO$_3$. Errors reported are ± 1σ counting errors propagated through the calculations.

| Sample no.	Sample wt. (g)	No. of shells	Mean shell wt. (mg)	Shell wt. range (mg)	% Wt. loss in cleaning	^{210}Pb (dpm/g)	^{210}Po (dpm/g)	^{210}Po/^{210}Pb activity ratio
Cavolinia longirostris								
CL 1	0.6862	1005	0.7	0.1–1.1	−3.1	0.45 ± 0.04	9.3 ± 0.18	21 ± 1.9
CL 2	0.8337	627	1.4	1.2–1.6	−2.5	0.32 ± 0.03	7.0 ± 0.15	22 ± 2.0
CL 3	0.8448	484	1.8	1.7–2.0	−2.2	0.30 ± 0.02	6.2 ± 0.12	21 ± 1.6
CL 4	0.5191	237	2.2	2.1–3.3	−2.2	0.24 ± 0.03	5.4 ± 0.13	22 ± 2.5
Clio pyramidata								
CP 1	0.1506	428	0.7	0.1–1.0	−49	0.25 ± 0.06	6.8 ± 0.22	27 ± 5.9
CP 2	0.3351	328	1.5	1.1–1.7	−30	0.29 ± 0.04	7.6 ± 0.15	26 ± 3.1
CP 3	0.5548	402	2.1	1.8–2.3	−33	0.35 ± 0.03	7.1 ± 0.12	20 ± 1.6
CP 4	0.2973	149	2.5	2.4–3.0	−21	0.19 ± 0.06	5.1 ± 0.12	27 ± 9.0
CP 5	0.2084	63	4.0	3.1–5.0	−16	0.18 ± 0.04	5.2 ± 0.17	28 ± 6.6
Atlanta plana								
AP 1	0.1284	331	0.5	0.1–0.5	−20	0.40 ± 0.08	7.8 ± 0.19	20 ± 3.7
AP 2	0.0667	140	0.7	0.6–1.1	−17	0.35 ± 0.16	6.9 ± 0.29	20 ± 9.0

Journal of Marine Research
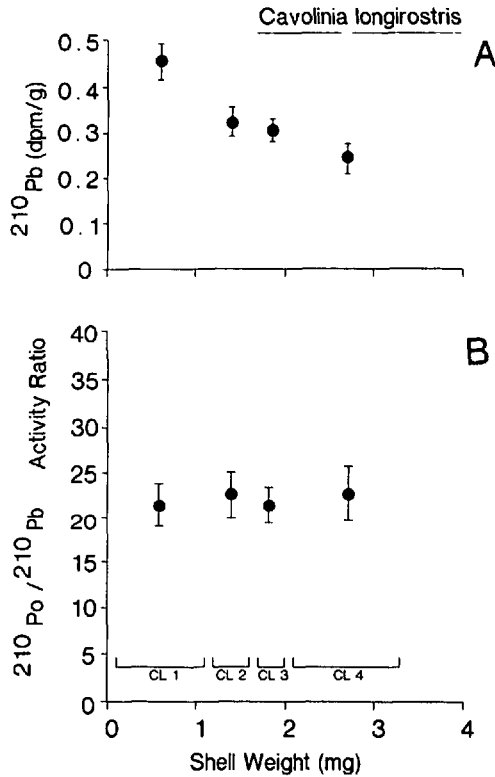
Figure 3. *Cavolinia longirostris*. Radioactivity in four size classes described in Table 2. Error bars represent ±1 standard deviation, estimated by propagating counting errors through the calculations. (A) ^{210}Pb activity (disintegrations per minute per gram $CaCO_3$) vs. shell weight (mg). (B) (^{210}Po/^{210}Pb) activity ratio vs. shell weight (mg). The shell weight range of each size class is shown above x axis.

ground sample either were not removed from surfaces as effectively, or if initially released, the nuclides then adsorbed to particle surfaces. These results suggest that ^{210}Pb and ^{210}Po are strongly reactive with shell surfaces. Crushing shells into small chips, the technique used for all other samples, is clearly preferable to pulverizing shell samples.

Plasma ashing shells to oxidize animal tissues within the shell had no consistent effect on measured nuclide concentrations. Although sample sets D and E were collected from different locations, the two-fold difference in ^{210}Po activities between these sample sets could indicate that the longer H_2O_2 treatment used in the preliminary cleaning stage for sample set E removed more of the excess ^{210}Po. However, no visible organic tissue remained in shells of any samples. For both sample sets, nearly all of the ^{210}Po measured was unsupported by the ^{210}Pb, suggesting that the duration of the H_2O_2 treatment was not a critical factor in the cleaning process. The difference between these sample sets may reflect variations in the hydrography of the locations where the samples were collected.
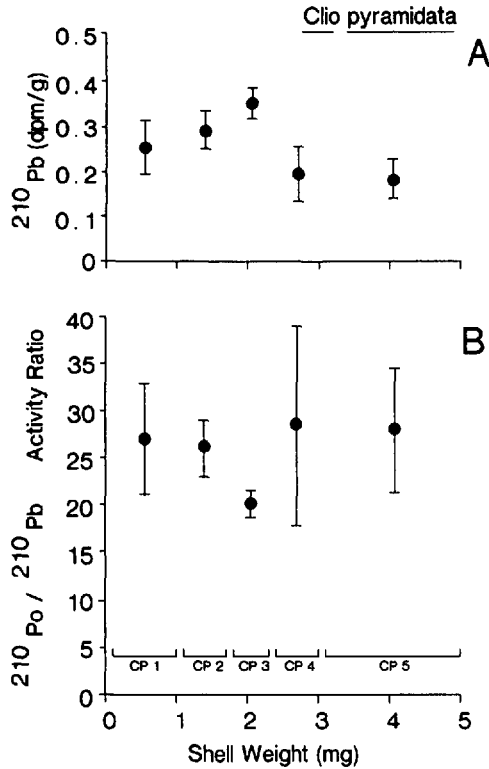
Figure 4. *Clio pyramidata*. Radioactivity in five size classes described in Table 2. Error bars represent ±1 standard deviation, estimated by propagating counting errors through the calculations. (A) ^{210}Pb activity (disintegrations per minute per gram $CaCO_3$) vs. shell weight (mg). (B) ($^{210}Po/^{210}Pb$) activity ratio vs. shell weight (mg). The shell weight range of each size class is shown above x axis.

The two-stage cleaning procedure developed in this study was more intensive than sample treatments used previously in radiochemical studies of growth rates of $CaCO_3$-precipitating organisms (Moore and Krishnaswami, 1972; Dodge and Thomson, 1974; Turekian *et al.,* 1975; Turekian *et al.,* 1979; Turekian and Cochran, 1981; Bennett *et al.,* 1982; Benavides and Druffel, 1986). Because contamination of $CaCO_3$ surfaces and inclusion of organic detrital matter in samples can lead to substantial overestimates of lattice-bound Pb (Benavides and Druffel, 1986; Shen and Boyle, 1988), the protocol we used for sample preparation was largely formulated for the accurate analyses of ^{210}Pb. While successful for the measurement of ^{210}Pb, these procedures did not eliminate all of the excess ^{210}Po associated with shells.

a. ^{210}Pb *activities*

^{210}Pb concentrations measured in pteropod and heteropod shell samples (Tables 1 and 2) were similar to previously reported ^{210}Pb activities in other biogenic $CaCO_3$
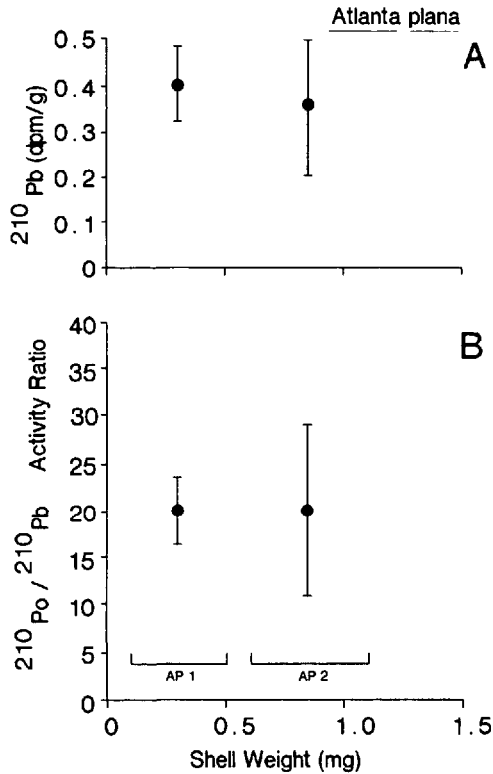
Figure 5. *Atlanta plana*. Radioactivity in two size classes described in Table 2. Error bars represent ±1 standard deviation, estimating by propagating counting errors through the calculations. (A) ^{210}Pb activity (disintegrations per minute per gram CaCO$_3$) vs. shell weight (mg). (B) (^{210}Po/^{210}Pb) activity ratio vs. shell weight (mg). The shell weight range of each size class is shown above x axis.

structures, which range from 0.1–0.5 dpm/g CaCO$_3$ (Moore and Krishnaswami, 1972; Dodge and Thomson, 1974; Turekian and Cochran, 1981; Cochran *et al.*, 1981). This consistency suggests that the cleaning procedures used here, more extensive than those of previous studies, were adequate for ^{210}Pb analyses. The ^{210}Pb measured in shells was most likely bound in the crystal lattice. No quantitative data on the concentration of stable Pb in pteropod or heteropod shells are available for comparison.

Except for a few bathypelagic species, most euthecosomatous pteropods live in the upper 600 m or less of the water column (Bé and Gilmer, 1977; Wormuth, 1981). In the open ocean, vertical profiles of ^{210}Pb in the upper 600 m typically show decreasing activity with depth (Broecker and Peng, 1982), although the decrease is not always monotonic (Nozaki and Tsunogai, 1976; Bacon *et al.*, 1976). The vertical variation in ^{210}Pb activity can be used as an indicator of the depth of shell calcification in pteropods and heteropods, if Pb uptake is always directly proportional to the seawater concentration of Pb.

Ideally, when using ^{210}Pb as an indicator of calcification depth, the vertical distribution of ^{210}Pb in seawater should be known for the sample collection site. In the absence of water column data at our collection station, we assume the simple case of decreasing ^{210}Pb activity with depth in the upper 600 m. The relative depth at which different size classes of shells were calcified can then be inferred from the ^{210}Pb activity in shells. For *Cavolinia longirostris,* ^{210}Pb activity in shells varied with the size of the animal (Fig. 3a). If the distribution of ^{210}Pb in seawater decreases with depth in the upper ocean, these results suggest that, in the eastern equatorial Pacific, *Cavolinia longirostris* calcifies its shell at progressively deeper depths as it grows. For *Clio pyramidata,* the ^{210}Pb data suggest that larger, and presumably older, animals probably calcify at deeper depths than smaller individuals (Fig. 4a). No difference in depth of calcification of the two size classes of the heteropod *Atlanta plana* can be detected from the ^{210}Pb activities (Fig. 5a).

Most depth distributions reported for pteropods and heteropods do not distinguish between different size classes of the same species. For *Clio pyramidata,* however, Meisenheimer (1905) reported that juveniles were found from 20 to 200 m, while adults occurred from 400 to 500 m. In contrast, Wormelle (1962) found that juveniles of *Clio pyramidata* and several other pteropod species were distributed at night from 50 to 200 m deeper than adults. The possible occurrence of ontogenetic changes in migration patterns in pteropods needs further investigation.

The ^{210}Pb results suggest that *Clio pyramidata* grows in deeper water than the heteropod *Atlanta plana* at the equatorial station (Figs. 4a, 5a). This conclusion is consistent with reported depth distributions determined by plankton tow studies (reviewed in Bé and Gilmer, 1977; Wormuth, 1981; Seapy, 1987, 1988). From δ^{18}O values of shells, Grossman *et al.* (1986) estimated that calcification of *Atlanta* spp. in the North Pacific occurred in the upper 125 m. However, no similar δ^{18}O data for *Clio pyramidata* and *Cavolinia longirostris* are available for comparison.

Enrichment factors of ^{210}Pb in shells relative to surface seawater were calculated from previously reported values of ^{210}Pb in surface waters. Shells collected from the equatorial Pacific station were 8–15 times enriched with ^{210}Pb relative to surface seawater activities of 2–4 dpm/kg, estimated from ^{210}Pb measurements in Galapagos corals (Delaney *et al.,* 1989). For samples collected from the northern transition zone and Subarctic Current, enrichment factors of ^{210}Pb in shells relative to surface water activities (Nozaki *et al.,* 1976; Broecker and Peng, 1982) ranged from 13–20. Comparatively, corals are enriched with Pb relative to surface seawater by a factor of two (Shen and Boyle, 1988), whereas sclerosponges have concentrations of Pb an order of magnitude higher than those in corals (Benavides and Druffel, 1986). These comparisons are made more difficult by the lack of concurrent collection of seawater samples with biogenic carbonates. The mechanisms responsible for the observed variation of ^{210}Pb enrichment in biogenic aragonites are unknown, but may involve differences in feeding methods, as suggested by Benavides and Druffel (1986), or other biological processes.

b. ^{210}Po activities

Use of ^{210}Po/^{210}Pb disequilibrium ratios in determining the shell growth rates of pteropods and heteropods assumes that ^{210}Po is not deposited in the shell during its formation, or .is incorporated in known ratios of (^{210}Po/^{210}Pb). Because all shell samples analyzed contained ^{210}Po levels which require an additional source other than the decay of ^{210}Pb, shell growth rates could not be determined from the ^{210}Po/^{210}Pb method (Figs. 3b, 4b, and 5b).

Vertical profiles typically indicate that the activity of ^{210}Po in seawater is close to equilibrium with ^{210}Pb except in the upper water column. In surface waters of the Pacific Ocean, (^{210}Po/^{210}Pb) activity ratios are less than one, ranging from 0.3–0.5 in the open ocean to 0.9 in upwelling or nearshore areas (Nozaki *et al.*, 1976). Hence, it is unlikely that mineralogical uptake could account for a significant part of the observed shell inventories which display (^{210}Po/^{210}Pb) activity ratios of 20–28 (Figs. 3b, 4b, 5b and Table 2).

To distinguish the source of excess ^{210}Po measured in shells, we considered two possibilities. First, we assumed that all ^{210}Po activity came from animal tissues. For *Clio pyramidata* samples D and E, we estimated the ^{210}Po activity of tissues contained in the original sample of pteropods (tissues + shells). Using the relationship between dry tissue weight and shell weight, determined for animals of similar size from the same stations (Fabry, unpublished data), we obtained an estimate of the dry tissue weight in each sample from the equation:

$$Y = 0.6385\,(X) + 0.1549 \qquad (r^2 = 0.92) \tag{1}$$

where Y is the dry tissue weight (in mg) and X is the shell weight (in mg). The mean individual shell weight for each sample was used to calculate the mean individual dry tissue weight. Multiplication of this value by the number of shells in the sample approximated the total dry tissue weight in the sample. If we assume that all the ^{210}Po measured in the shell samples came from tissues and that the entire tissue concentration was adsorbed to shell surfaces, sample sets D and E contained ^{210}Po activities equivalent to 15 to 31 dpm/g dry tissue weight. These estimates are within the range of ^{210}Po values reported for zooplankton tissues which vary from 2 to 197 dpm/g dry tissue weight (Turekian *et al.*, 1974).

An alternative source of ^{210}Po was also considered. We assumed that the source of unsupported ^{210}Po is not contamination from animal tissues, but that ^{210}Po is deposited in the organic matrix of the shell during shell secretion. The percent organic matrix in gastropod shells typically ranges from 2 to 7% (Milliman, 1974). If *Clio pyramidata* shells in sample E contain 5% organic matrix by weight and all excess ^{210}Po occurs in this organic matrix, the ^{210}Po activity would equal 223 dpm/g organic matrix. This estimated ^{210}Po value approximates ^{210}Po activities measured in particulate matter collected in deep sediment traps, which range from 327–980 dpm/g (Spencer *et al.*, 1978; Bacon *et al.*, 1985).

Although extensive sample treatments, including mechanical, oxidative, and acid dissolution methods, were used in this study, we cannot distinguish the source of unsupported ^{210}Po. Either excess ^{210}Po measured in pteropod and heteropod shells occurs because polonium is deposited during shell precipitation, probably in the organic matrix, or because our cleaning procedures failed to remove ^{210}Po adsorbed to shell surfaces from the water column or from the oxidation of animal tissues. The unique helical arrangement of the aragonitic rods in the shell microstructure of pteropod shells (Bé *et al.,* 1972) suggests that the organic matrix in these shells may be different than the organic matrix of other gastropods. It is possible that ^{210}Po is incorporated into the organic matrix during shell secretion in pteropods and hetero-pods. Alternatively, pteropod and heteropod shells are extremely thin compared to the shells of *Nautilus* or clams, and have higher ratios of surface area/volume. Reductive cleaning methods such as those developed for the measurement of cadmium (Boyle, 1981) and uranium and thorium (Delaney and Boyle, 1983) in sedimentary foramin-fera and the analyses of stable Pb and other trace elements in corals (Shen and Boyle, 1987, 1988; Shen *et al.,* 1987) may be necessary to remove excess ^{210}Po in pteropod and heteropod shells. However, because about 50% of the sample weight is lost in these additional cleaning steps, sample volumes two times greater than those available in the present work would be required.

The shells of pteropods and heteropods may not be unique in containing large amounts of unsupported ^{210}Po. We predict that other $CaCO_3$-precipitating organisms that have high surface/volume ratios and tissues in direct contact with surfaces (eg., foraminifera) may also have excess ^{210}Po in their carbonate skeletons. The affinity of ^{210}Po for surfaces and organic matter makes the disequilibrium of ^{210}Po and ^{210}Pb less useful as a natural chronometer of biogenic calcium carbonates.

REFERENCES

Bacon, M. P., C.-A. Huh, A. P. Fleer and W. G. Deuser. 1985. Seasonality in the flux of natural radionuclides and plutonium in the deep Sargasso Sea. Deep-Sea Res., *32,* 273–286.

Bacon, M. P., D. W. Spencer and P. G. Brewer. 1976. ^{210}Pb/^{226}Ra and ^{210}Po/^{210}Pb disequilibria in seawater and suspended particulate matter. Earth Planet. Sci. Lett., *32,* 277–296.

Bé, A. W. H. and R. W. Gilmer. 1977. A zoogeographic and taxonomic review of euthecosoma-tous pteropods, *in* Oceanic Micropaleontology, vol. 1, A. T. S. Ramsay, ed., Academic Press, London, 733–808.

Bé, A. W. H., C. MacClintock and D. C. Currie. 1972. Helical shell structure and growth of the pteropod *Cuvierina columnella* (Rang) (Mollusca, Gastropoda). Biomineral. Res. Rep., *4*, 47–79.

Beasley, T. M., R. J. Eagle and T. A. Jokela. 1973. Polonium-210, lead-210 and stable lead in marine organisms. Quarterly Summary Report Health Safety Laboratory, New York, (Fallout Program) HASL-273, 2–36.

Benavides, L. M. and E. R. M. Druffel. 1986. Sclerosponge growth rate as determined by ^{210}Pb and Δ^{14}C chronologies. Coral Reefs, *4*, 221–224.

Bennett, J. T., G. W. Boehlert and K. K. Turekian. 1982. Confirmation of longevity in *Sebastes diploproa* (Pisces: Scorpaenidae) from ^{210}Pb/^{226}Ra measurements in otoliths. Mar. Biol., *71*, 209–215.

Benninger, L. K. and R. E. Dodge. 1986. Fallout plutonium and natural radionuclides in annual bands of the coral *Montastrea annularis*, St. Croix, U. S. Virgin Islands. Geochim. et Cosmochim. Acta, *50*, 2785–2797.

Boyle, E. A. 1981. Cadmium, zinc, copper, and barium in foraminifera tests. Earth Planet. Sci. Letts., *53*, 11–35.

Broecker, W. S. and T.-H. Peng. 1982. Tracers in the Sea. Columbia University, NY, 690 pp.

Cochran, J. K., D. M. Rye and N. H. Landman. 1981. Growth rate and habitat of *Nautilus pompilius* inferred from radioactive and stable isotope studies. Paleobiology, *7*, 469–480.

Delaney, M. L. and E. A. Boyle. 1983. Uranium and thorium isotope concentrations in foraminiferal calcite. Earth Planet. Sci. Letts., *62*, 258–262.

Delaney, M. L., R. W. Williams and C. Low. 1989. Lead-210 and radium-226 in a massive coral (*Pavona clavus*) from the Galapagos. Geochim. et Cosmochim. Acta, *53*, 1633-1636.

Dodge, R. E. and J. Thomson. 1974. The natural radiochemical and growth records in contemporary hermatypic corals from the Atlantic and Caribbean. Earth Planet. Sci. Letts., *23*, 313–322.

Fabry, V. J. 1988. Aragonite production by pteropod molluscs: implications for the oceanic calcium carbonate cycle. Ph.D. dissertation, University of California, Santa Barbara, 166 pp.

Flynn, W. W. 1968. The determination of low levels of 210-polonium in environmental samples. Analytica Chimica Acta, *43*, 221–227.

Goldberg, E. D. and K. Bruland. 1974. Radioactive geochronologies, *in* The Sea, vol. 5, E. D. Goldberg, ed., John Wiley & Sons, NY, 451–489.

Grossman, E. L., P. R. Betzer, W. C. Dudley and R. B. Dunbar. 1986. Stable isotopic variation in pteropods and atlantids from North Pacific sediment traps. Mar. Micropaleont., *10*, 9–22.

Kharkar, D. P., J. Thomson and K. K. Turekian. 1976. Uranium and thorium decay series nuclides in plankton from the Caribbean. Limnol. Oceanogr., *21*, 294–299.

Kobayashi, H. A. 1974. Growth cycle and related vertical distribution of the thecosomatous pteropod *Spiratella* ("*Limacina*") *helicina* in the central Arctic Ocean. Mar. Biol., *26*, 295–301.

Meisenheimer, J. 1905. Pteropoda. Wiss. Ergebn. Tiefsee Exped. "Valdivia" *9*(1), 1–314.

Milliman, J. D. 1974. Marine Carbonates, Springer-Verlag, NY, 375 pp.

Moore, W. S. and S. Krishnaswami. 1972. Coral growth rates using ^{228}Ra and ^{210}Pb. Earth Planet. Sci. Letts., *15*, 187–190.

Nozaki, Y., J. Thomson and K. K. Turekian. 1976. The distribution of ^{210}Pb and ^{210}Po in the surface waters of the Pacific Ocean. Earth Planet. Sci. Letts., *32*, 304–312.

Nozaki, Y. and S. Tsunogai. 1976. ^{226}Ra, ^{210}Pb and ^{210}Po disequilibria in the western North Pacific. Earth Planet. Sci. Letts., *32*, 313–321.

Seapy, R. R. 1987. The heteropod fauna of oceanic waters off Hawaii. Western Society of Malacologists, Annual Report, *19*, 9–12.

—— 1988. Atlantid heteropods of Hawaiian waters. Western Society of Malacologists, Annual Report, *20*, 28–29.

Shen, G. T. and E. A. Boyle. 1987. Lead in corals: reconstruction of historical industrial fluxes to the surface ocean. Earth Planet. Sci. Letts., *82*, 289–304.

—— 1988. Determination of lead, cadmium and other trace metals in annually-banded corals. Chem. Geol. *67*, 47–62.

Shen, G. T., E. A. Boyle and D. W. Lea. 1987. Cadmium in corals as a tracer of historical upwelling and industrial fallout. Nature, *328*, 794–796.

Shannon, L. V., R. D. Cherry and M. J. Orren. 1970. Polonium-210 and lead-210 in the marine environment. Geochim. et Cosmochim. Acta, *34*, 701–711.

Spencer, D. W., P. G. Brewer, A. Fleer, S. Honjo, S. Krishnaswami and Y. Nozaki. 1978. Chemical fluxes from a sediment trap experiment in the deep Sargasso Sea. J. Mar. Res., *36*, 493–523.

Spoel, S. van der. 1973. Growth, reproduction and vertical migration in *Clio pyramidata* Linne, 1767 forma *lanceolata* (Lesueur, 1813) with notes on some other Cavoliniidae (Mollusca, Pteropoda). Beaufortia, *21*, 117–134.

Turekian, K. K. and J. K. Cochran. 1978. Determination of marine chronologies using natural radionuclides, *in* Chemical Oceanography, vol. 7, J. P. Riley and R. Chester, eds., Academic Press. NY, 313–360.

—— 1981. Growth rate of a vesicomyid clam from the Galapagos spreading center. Science, *214*, 909–911.

Turekian, K. K., J. K. Cochran, D. P. Kharkar, R. M. Cerrato, J. M. Vaisnys, H. L. Sanders, J. F. Grassle and J. A. Allen. 1975. Slow growth rate of a deep-sea clam determined by ^{228}Ra chronology. Proceed. Nat. Acad. Sci., *72*, 2829–2832.

Turekian, K. K., J. K. Cochran and Y. Nozaki. 1979. Growth rates of a clam from the Galapagos Rise hot spring field using natural radionuclide ratios. Nature, *280*, 385–387.

Turekian, K. K., D. P. Kharkar and J. Thomson. 1974. The fates of ^{210}Pb and ^{210}Po in the ocean surface. J. de Rech. Atmosphér., *8*, 639–646.

Wells, F. E. 1976. Growth rates of four species of euthecosomatous pteropods occurring off Barbados, West Indies. The Nautilus, *90*, 114–116.

Wormelle, R. L. 1962. A survey of the standing crop of plankton of the Florida Current. VI. A study of the distribution of the pteropods of the Florida Current. Bull. of Mar. Sci. Gulf Caribb., *12*(1), 95–136.

Wormuth, J. H. 1981. Vertical distribution and diel migrations of Euthecosomata in the northwest Sargasso Sea. Deep-Sea Res., *28*, 1493–1515.