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# Ichthyolith strontium isotope stratigraphy of a Neogene red clay sequence: calibrating eolian dust accumulation rates in the central North Pacific

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## Abstract

Cenozoic pelagic ('red') clays of predominantly eolian and hydrogenous origin blanket much of the central North Pacific ocean basin. The eolian component is a key indicator of past paleoclimatic conditions; thus, Cenozoic atmospheric circulation can potentially be reconstructed through provenance studies of Pacific red clays, provided there are precise age controls. Methods commonly employed in the past to date red clay cores have included cobalt accumulation rates, ichthyolith biostratigraphy, magnetostratigraphy, and ichthyolith strontium isotope stratigraphy. The first two dating methods yield ages with large uncertainties, while magnetostratigraphy is only relevant to cores with accumulation rates in excess of 1 mm/kyr. Ichthyolith strontium isotope stratigraphy has shown promise as a chronological tool in marine studies, but has been only sparingly employed in the dating of marine red clay sequences. In this study, we present a complete age–depth profile for a large diameter piston core from the central North Pacific Ocean (EW9709 PC-01, 32.5°N, 141.2°W), consisting of 11 m of primarily wind-deposited dust. To generate this age–depth profile, strontium isotopic compositions were determined on fish teeth ichthyoliths previously cleaned of contaminants using a newly modified reductive cleaning procedure. Ages were determined by reference to the recently refined Sr isotope curve for Neogene seawater. Comparison with nearby giant piston core LL44-GPC3 reinforces the accuracy of our methods. The data for EW9709 PC-01 indicate a fairly constant sediment accumulation rate of  $\sim 0.45$  mm/kyr over most of the 24 Myr time period represented by this core. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* ichthyoliths; Pisces; teeth; Sr-87/Sr-86; North Pacific; pelagic sedimentation; clay; dust

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## 1. Introduction

Fossil fish teeth are an important component of deep marine pelagic clays, frequently occurring in high concentrations where other microfossils are lacking [1–6]. This is especially characteristic of so-called red clay cores from the northern Pacific province, in which the terrigenous component is dominated by eolian dust derived from Asia [7–10]. It has long been known that these sites are characterized by very low average sedimentation rates ( $\ll 1$  mm/kyr), but precise age control is generally absent due to the lack of biostratigraphic constraints [1–6,9–11]. Earlier workers attempted to derive age information by taxonomic classification of fish skeletal remains (ichthyoliths) [4–6]. More recently, studies from several ODP sites (885, 886, 807A, and 786A) have demonstrated that, under ideal conditions, strontium isotopic compositions in fossil fish teeth can serve as a reliable proxy for seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  [1,2,12,13]. Dating of fish teeth (and enclosing pelagic clay) by reference to the Sr seawater curve should provide reliable ages, assuming: (a) they formed in isotopic equilibrium with seawater, (b) the isotopic composition was retained after burial, and (c) the original isotopic composition can be retrieved. Recent refinements in cleaning techniques [12–15] and a newly calibrated Cenozoic Sr seawater curve [16] have improved the potential of the method for delivering precise ages down to the  $\pm 1$  Myr level, particularly over the past 40 Myr.

Studies of modern fish and sharks have shown that isotopic equilibrium with seawater is generally attained in the phosphatic skeletal materials of the living organism [17]. However, problems in deriving a pristine marine  $^{87}\text{Sr}/^{86}\text{Sr}$  signature from ichthyoliths may arise from several factors. One possible complication is the failure to remove all contaminant Sr from authigenic coatings on ichthyoliths [1,2,12,13]). Another potential source of error (and more difficult to address) is the failure to account for diagenetically altered  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in some fish teeth [18–21]. Ingram [1,2] and Snoeckx et al. [12] used the Sr isotopic composition of ichthyoliths to establish ages and sedimentation rates in red clays dating back to the Late

Cretaceous at ODP sites 885 and 886. To the extent that their data could be calibrated with radiolarian and diatom biostratigraphy, they found that  $^{87}\text{Sr}/^{86}\text{Sr}$  was consistently high (radiogenic) for intervals where biostratigraphic age control was available, even after varied laboratory cleaning pretreatments that included: (a) acetic acid leaching to remove Fe–Mn coatings, (b) ultrasonic cleaning to remove clays in cavities, and (c) reductive cleaning to remove all Fe–Mn coatings, opal, organics and carbonate from the ichthyoliths. Some  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were shifted high by as much as 0.00008, resulting in an age discrepancy for a Late Cretaceous sample of about 30 Myr. They attributed these results to a combination of factors including: (a) incomplete cleaning of fish teeth before analysis, (b) burial diagenesis of the teeth, resulting in excess radiogenic Sr being incorporated into their partly recrystallized apatite structure from surrounding pore waters, (c) contamination (high blanks) from cleaning procedures, and (d) radiogenic ingrowth of  $^{87}\text{Sr}$  from  $^{87}\text{Rb}$ .

Martin and Haley [13] experimented with several cleaning methods to evaluate these problems, concluding that the method of cleaning had little effect on  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. Their results from ODP sites 807A and 786A showed discrepancies of up to 3 Myr when compared with known ichthyolith ages (based on stratigraphic interval), regardless of the cleaning method employed. Some fish teeth compositions were observed to be too radiogenic (or in some cases too unradiogenic) for their known age, although in general the fish teeth  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios plotted close to (or within) the uncertainty range defined by their Sr seawater curve. Citing Sr concentration data, they dismissed burial diagenesis as a cause of spurious Sr isotopic compositions, speculating instead that the biostratigraphic age assignments carried large uncertainties. Their analysis of pore water compositions and volcanogenic components in red clays indicated generally less radiogenic Sr compositions compared to contemporaneous seawater, which would not explain the more radiogenic compositions they observed in fish teeth. They estimated they could potentially achieve an age resolution of  $\pm 1.5$  Myr for parts of the cores

they studied. A more recent dataset by Scher and Martin [22] from ODP Site 1090 shows a consistent offset in  $^{87}\text{Sr}/^{86}\text{Sr}$  ( $\Delta = 0.000070$ ) between ichthyoliths and the  $^{87}\text{Sr}/^{86}\text{Sr}$  seawater curve (as determined by forams from the same core, with ages calibrated by magnetostratigraphy). In this case, ichthyolith  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios appear to be too low (unradiogenic), resulting in ages that are shifted high by 1–2 Myr. On the one hand, these data indicate that when teeth are properly cleaned, in situ decay of  $^{87}\text{Rb}$  to  $^{87}\text{Sr}$  is not a factor, even in older teeth (40–15 Ma). If the cause of the offset in this case is fish teeth diagenesis [22], it must not have affected associated forams.

In this paper, we present the ichthyolith Sr isotope stratigraphy of an 11 m large diameter piston core (EW9709 PC-01) collected in the central North Pacific ocean (32.5°N, 141.2°W) at 5 km depth (Fig. 1). The core is dominated by pelagic red clays [23,24], and is comparable to the upper portion of the classic ‘red clay’ in the giant piston core LL44-GPC3 (Fig. 1) studied by Corliss and Hollister [25,26], and many others. For this study, we focused on developing a rapid cleaning technique that would improve the potential of the method for dating pelagic clays. As previously mentioned, the use of ichthyoliths to date marine sediments is not a new method; however, problems (suspected and real) have been identified with this method in the past, including: (a) incomplete cleaning of Fe–Mn oxyhydroxides from tooth surfaces; (b) incomplete removal of carbonate, silica and clay material filling cavities; (c) contamination from cleaning reagents; (d) par-

tial diagenetic recrystallization of ichthyoliths and exchange of Sr with buried pore waters. To address some of these issues, we present below a low blank laboratory method that: (1) efficiently removes all carbonate, silica, organics, clays and oxyhydroxide coatings that could contribute Sr contamination to the analysis; and (2) provides a consistent, reproducible set of age estimates over the age interval of interest. We demonstrate that this approach is suitable for dating pelagic clays that are otherwise undatable by other methods. This approach, in combination with geochemical and isotopic analysis of the extracted eolian component in red clay cores, can potentially be used to reconstruct Cenozoic paleoclimate when applied at multiple sites (e.g., [11,27]).

## 2. Materials and methods

A rapid cleaning procedure for ichthyoliths is described here that is a modified version of the techniques more commonly used to remove calcium carbonate, iron and manganese oxyhydroxides, zeolites, biogenic silica and adhering clay particles from marine sediments [28,29]. We further adapted these methods to fish teeth using techniques described by Snoeckx et al. [12] and Boyle [30,31]. Scanning electron microscopy (SEM) imaging, EDS analysis and cathodoluminescence were performed on larger teeth to verify the effectiveness of the cleaning procedure, and to assess some of the compositional variations previously reported in fish teeth. Ca/P ratios and Sr concentrations were not obtained on the PC-01 samples, but are being analyzed in cleaned teeth from another core to assess possible diagenetic effects (e.g., [13,32]). For Sr isotopic analysis, we chose to analyze only triangular fish teeth ichthyoliths, thereby eliminating ichthyolith type as a variable [1,2]. Multiple teeth were analyzed from 14 different depth intervals of PC-01 to give maximum age resolution. The procedure is briefly outlined below.

After transferring ichthyoliths ( $\sim 50$ – $100 \mu\text{g}$  per sample) into pre-cleaned 1.5 ml centrifuge tubes (using binocular microscope and small camel hair brush), de-ionized water was added and

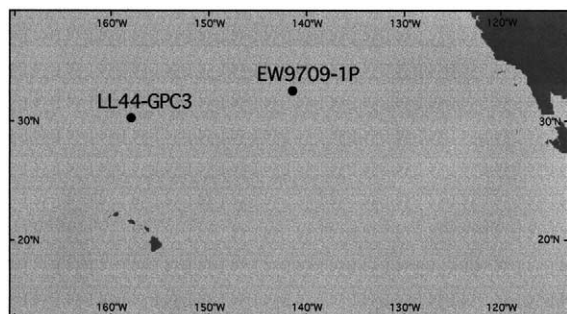


Fig. 1. Recovery locations of deep sea pelagic clay cores EW9709 PC-01 and LL44-GPC3.

care taken to ensure all teeth were at the bottom of the tube (the teeth are much denser than water, so once the air is worked out of the airpockets and surface tension reduced, they should sink rapidly). The tubes were placed in a small tube rack that fits into an ultrasonic bath preheated to  $\sim 65^{\circ}\text{C}$ . The teeth were then cleaned in the following sequence: (1) reductive cleaning (0.3 M sodium citrate, 1.0 M sodium bicarbonate, and pure sodium dithionite, aka sodium hydrosulfite) in hot ultrasonic bath for at least 20 min with periodic ultrasonic agitation to remove oxyhydroxide coatings; (2) oxidative cleaning ( $2 \times 10^{-5}$  M hydrogen peroxide in 0.1 M sodium hydroxide) for 10 min in hot ( $65^{\circ}\text{C}$ ) ultrasonic bath with

periodic agitation to remove organics and opal; (3) carbonate removal (2.5% acetic acid) in ultrasonic bath with periodic agitation for 2 min. Multiple ( $3 \times$ ) rinsings with de-ionized water followed by a few seconds of ultrasonic cleaning were necessary between each of these steps to remove reagents. The reductive cleaning step can be prolonged (or repeated) if the teeth are not visibly clean and transparent after Step 1. We note that excess agitation in a high frequency ultrasonic bath, especially during prolonged exposure to (hot) concentrated ( $> 25\%$ ) acetic acid, results in fragmented or destroyed fish teeth. The procedure outlined above is a rapid and efficient way to remove all adhering clay particles, organic material,

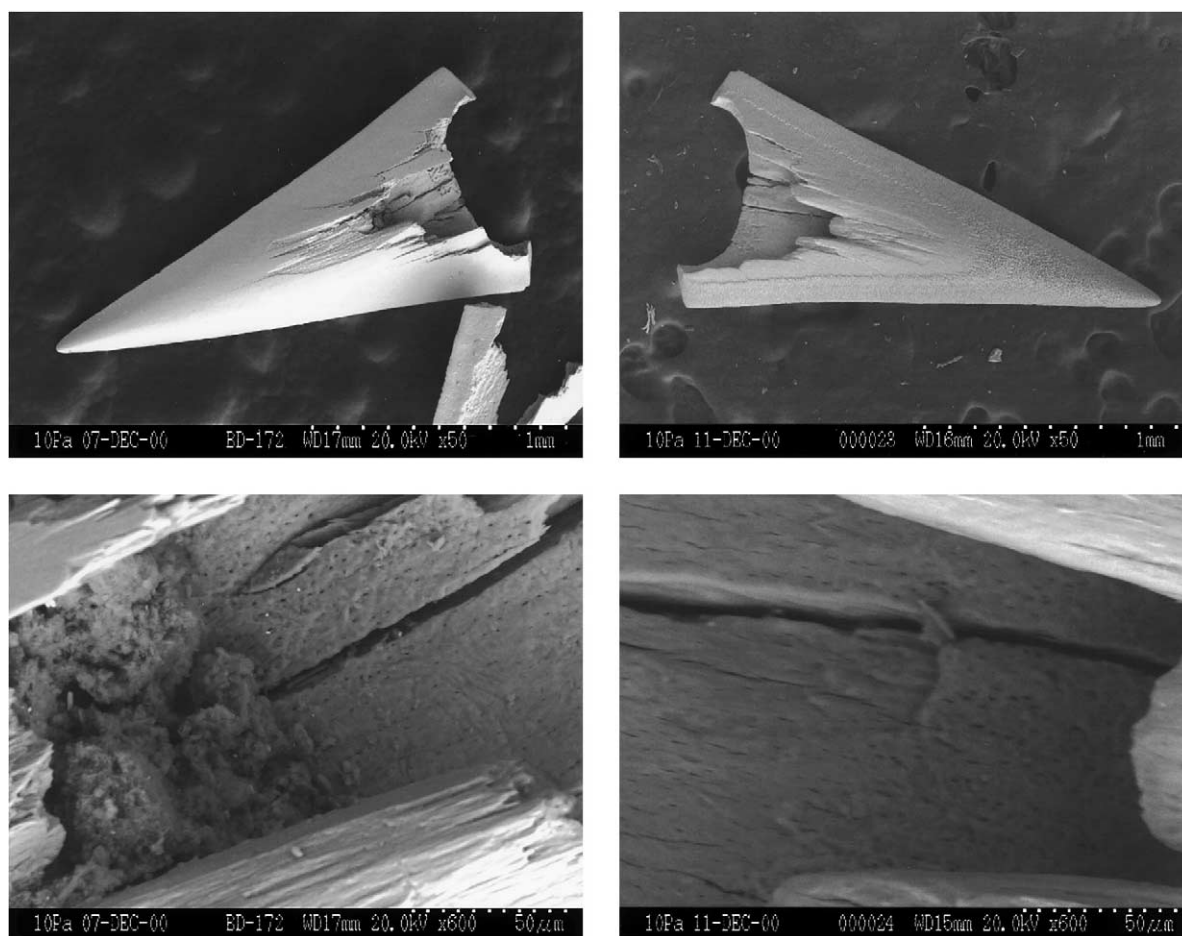


Fig. 2. (a) SEM images of fish teeth from core EW9709 PC-07 (depth 550 cm). Upper images are low magnification; lower images are high magnification of same areas before cleaning (left hand side) and after cleaning (right hand side).

authigenic Fe–Mn oxyhydroxide coatings, and carbonates from all surfaces and internal cavities of ichthyoliths. The effectiveness of the technique is confirmed by SEM imagery (Fig. 2).

For the final step in the procedure, the teeth were rinsed multiple times in dilute Seastar nitric acid, diluted to 0.001 N with ultrapure 3× water. This step is designed to remove any contaminants remaining from the cleaning procedure, especially those which might be adsorbed onto surfaces of the fish teeth. The teeth were then dissolved in Seastar 3 N nitric acid, and the centrifuged solution immediately transferred to a clean centrifuge tube to await column chemistry (the full cleaning procedure is available as a supplemental file from

EPSL or from the senior author). The total procedural blank has been determined to be approximately 100 pg, which we estimate is less than 1/1000 of the total Sr in the sample being analyzed. This blank is not enough to affect our results, but does limit the size teeth we can currently analyze. We are currently working to decrease the blank further, which should enable us to eventually analyze single teeth weighing less than 50 µg. Miniaturized SrSpec columns (and, earlier in the study, conventional Dowex AG 50W-X8 cation exchange columns) were used to separate Sr for isotopic analysis.

Approximately 50 ng of Sr was loaded on tungsten filaments with tantalum oxide activator and

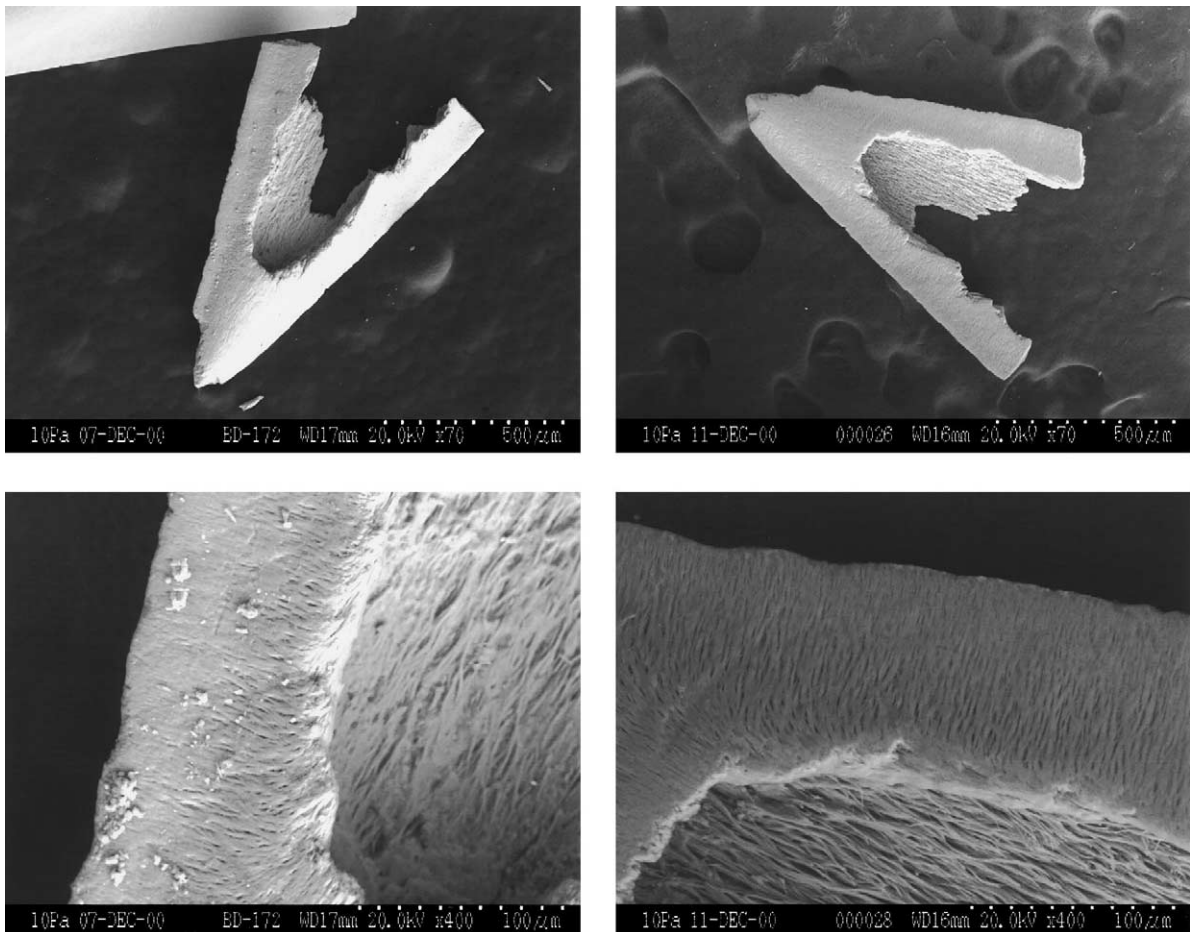


Fig. 2. (b) SEM images of fish teeth from core EW9709 PC-07 (depth 550 cm). Upper images are low magnification; lower images are high magnification of same areas before cleaning (left hand side) and after cleaning (right hand side).



analyzed in static mode on a Finnigan MAT 262 thermal ionization mass spectrometer equipped with eight Faraday collectors. Data were obtained on 150–200 ratios with an average signal of 1–2 V on mass 88. This resulted in average standard errors of typically 15–30 ppm on the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio, though smaller samples tended to yield higher errors. This level of internal precision is generally larger than the uncertainties inherent in the 0–40 Ma range of the Cenozoic Sr seawater curve [16], and we are now routinely achieving uncertainties of  $\pm 15$  ppm or better, though still limited in our precision for  $< 50$  ng loads. Nonetheless, the average uncertainty in age assignments using the recently refined marine Sr LOWESS fit of McArthur et al. [16] for this dataset varies from less than  $\pm 1$  Myr for the 15–40 Ma interval to  $\pm 1$ –3 Myr for the 0–15 Ma interval.

### 3. Results

Using these techniques, we were able to produce a fairly high resolution age–depth curve for the 11 m red clay core, concentrating on triangular ichthyoliths only (Table 1; Fig. 3). Our precision varies from  $\pm 3$  Myr (0–15 Ma) to  $< \pm 0.7$  Myr (15–24 Ma), resulting in a calculated (near linear) mean sedimentation rate of  $\sim 0.45$  mm/kyr over the 24 Myr represented by this core (Fig. 3b). A best-fit curve to selected data points (least error) suggests that sedimentation rates may have actually increased downcore from approximately 0.25 mm/kyr in the upper part to 0.6 mm/kyr at core base (Fig. 3b). Duplicate analyses of individual ichthyoliths from the same intervals indicate that good reproducibility can be obtained by this method. This level of reproducibility suggests that at least any strontium contamination from Fe–Mn oxyhydroxide coatings, opal, carbonate, organics and clay fillings in fish teeth cavities is being effectively removed by the reductive cleaning methods we have been employing in the laboratory. As mentioned, potential strontium contamination from the cleaning procedure has been minimized and monitored at levels of 100 pg or less (these blank levels represent less than 1/1000 of the Sr analyzed in our samples, assuming 50–

Table 1  
Strontium isotopic data for EW9709-PC01 ichthyoliths

Depth (cm)	$^{87}\text{Sr}/^{86}\text{Sr}^a$	Age <sup>b</sup> (Ma)	Error –Myr	Error +Myr
0–2	0.709221 $\pm$ 19	0	–	–
50–52	0.709095 $\pm$ 37	1.69	1.5	2.1
150–152	0.709035 $\pm$ 34	5.06	2.49	0.76
200–202	0.708977 $\pm$ 31	6.11	0.39	1.01
200–202	0.708976 $\pm$ 32	6.13	0.41	1.07
300–302	0.708930 $\pm$ 67	8.1	2.23	2.82
350–350	0.708952 $\pm$ 42	6.87	0.96	2.26
350–352	0.708890 $\pm$ 36	9.96	1.58	1.24
400–402	0.708896 $\pm$ 38	9.72	1.77	1.34
500–502	0.708825 $\pm$ 16	12.61	0.91	0.73
500–502	0.708793 $\pm$ 30	14.51	1.8	1.05
550–550	0.708812 $\pm$ 18	13.21	0.9	1.25
600–602	0.708725 $\pm$ 15	16.39	0.29	0.25
600–602	0.708694 $\pm$ 19	16.87	0.28	0.25
600–602	0.708719 $\pm$ 27	16.49	0.52	0.41
700–702	0.708548 $\pm$ 22	18.59	0.29	0.31
820–820	0.708343 $\pm$ 22	22.07	0.5	0.62
820–820	0.708392 $\pm$ 57	21.05	0.89	1.22
1010–1012	0.708307 $\pm$ 27	23.02	0.57	0.46
1070–1072	0.708260 $\pm$ 26	23.95	0.47	0.43

<sup>a</sup>  $^{87}\text{Sr}/^{86}\text{Sr}$  normalized to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ . 2-sigma errors represent in-run precision by TIMS on 150–200 ratios.

<sup>b</sup> Age determined from Sr seawater curve [16]

$^{87}\text{Sr}/^{86}\text{Sr}$  (2-sigma) = 0.710252  $\pm$  11 ( $n = 61$ ) for NBS987.

100  $\mu\text{g}$  of ichthyolith material per analysis at  $> 1000$  ppm concentration). It also suggests that any disturbance in ages resulting from sediment bioturbation is below the resolution of the data (assuming bioturbated layers of 10 cm or less, this represents  $< 250$  kyr of time for PC-01).

Potential diagenetic effects that might disturb the original  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the sample are more difficult to assess. If all teeth from a given interval were affected equally, then reproducibility among fish teeth fractions from a given interval would not be an effective indicator. Our SEM and cathodoluminescence work has demonstrated that ichthyoliths are being completely cleaned of any visible contamination, resulting in slightly etched surfaces that retain a mottled zonation that apparently corresponds to variations in carbonate–hydroxyapatite composition. Qualitative EDS analysis combined with cathodoluminescence indicates that this zonation represents compositions that vary between chlor- and fluor-apatite rich zones, a phenomenon we intend to investigate fur-

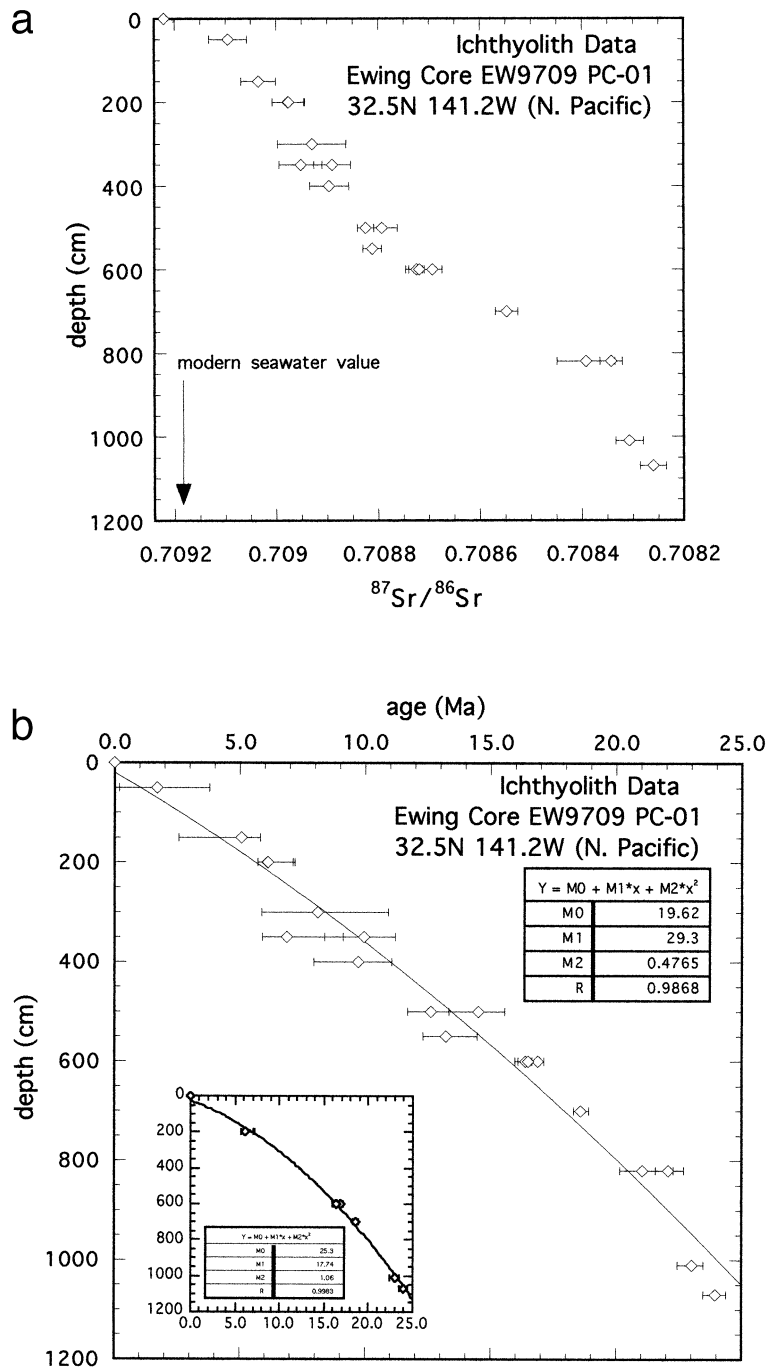


Fig. 3. (a) Strontium isotopic composition of ichthyoliths plotted against depth for EW9709 PC-01. Error bars represent analytical uncertainties as measured by TIMS. Note that a surface sample (at 0 m depth) plots close to modern seawater value of  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7092). (b) Age–depth curve for EW9709 PC-01 as determined from ichthyolith Sr isotopic compositions in (a). Ages were determined from a statistical fit to seawater Sr isotopic composition [16]. Error bars are larger during the first 15 Myr because of greater uncertainties in the Sr isotopic composition of seawater. A near-linear sedimentation rate of  $\sim 0.45$  mm/kyr is indicated.

ther. Infrared spectroscopy studies by Shemesh [18] suggested that the Sr concentration in marine biogenic phosphates decreases with increasing crystallinity as biogenic carbonate–hydroxyapatite partially converts to a fluor-apatite structure over time. ICP data we collected on fish teeth from another core indicate no obvious correspondence between Ca/P ratio (varying by up to 10% from pure apatite stoichiometry) and Sr concentrations. Sr concentrations (calculated using pure apatite stoichiometry) range from approximately 1500 to 4500 ppm, similar to concentrations reported in the literature by isotope dilution analysis [1,2,3,13]. We have found no solid evidence, however, that would enable precise correlation of any of our observations regarding ichthyolith type, size, zonation, Sr concentration, Ca/P ratio, or burial depth (age) in the samples we have studied thus far.

Despite the inherent complexities cited above, we believe we have eliminated many of the potential problems with the method, at least at the age-resolution we are aiming to achieve. As we continue to improve our method and analytical procedures, the chief limiting factor will be the age-resolution obtainable from the seawater Sr isotopic record. Between 15 and 40 Ma, this record is exceptional for our purposes, and from 0 to 15 Ma it is quite good [16]. For pelagic clays older than 40 Ma, the age-resolution degenerates considerably because of much smaller variation in seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  [16]. The ability to analyze multiple sub-50  $\mu\text{g}$  samples from a single stratigraphic interval, in combination with detailed chemical analysis of individual teeth, will be necessary to more fully evaluate the effects of diagenesis on fish teeth  $^{87}\text{Sr}/^{86}\text{Sr}$  compositions.

#### 4. Comparison with giant piston core LL44-GPC3

In order to check the reliability of our age–depth profile for PC-01, we compared it to the Cenozoic pelagic clay section in the nearby giant piston core LL44-GPC3. This core, recovered in the mid-1970s [25,26], has long served as an important record of Cenozoic sedimentation in the central North Pacific. Detailed geochemical anal-

ysis of pelagic clays in GPC-3 by Leinen [33] and Kyte et al. [9] identified multiple sediment source components, including eolian, volcanic, biogenous, hydrothermal and hydrogenous end-member components. Pegrum and Turekian attempted to derive a record for the Cenozoic Os isotopic composition of seawater through leaching experiments of GPC-3 clays [34]. Recently, Pettke et al. [11] determined the downcore Pb and Nd isotopic composition of eolian dust deposited at this site between 70 Ma and the present, with important implications for models of Cenozoic climate evolution. Magnetostratigraphic studies established a relatively precise stratigraphy for the uppermost 4.3 m of GPC3 [35]. Most studies have employed the age–depth curves based either on fish teeth biostratigraphy [4–6,10,36] or constant cobalt accumulation rates [9,11,33] for the remainder of the core. These studies, and one using a constant  $^{10}\text{Be}$  accumulation model [37], closely matched the magnetostratigraphy for the upper 4.3 m. However, the discrepancies between the biostratigraphic (ichthyolith) age–depth models, and those calculated from constant flux of hydrogenous components like Co, are particularly large during the late Eocene and early Oligocene, and in the Paleocene [9]. Various age estimates for the pre-Pliocene section in GPC3 differ by up to 8 Myr or more (Fig. 4).

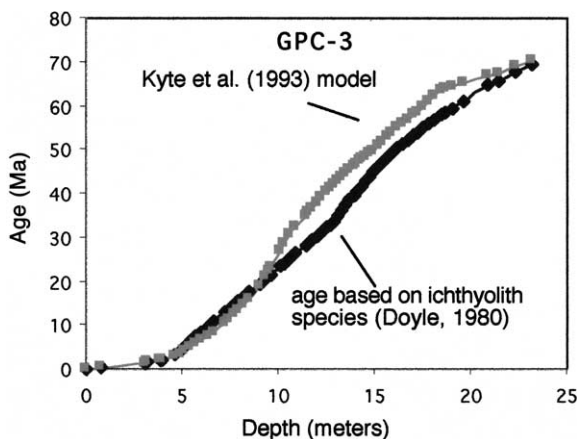


Fig. 4. Comparison of two age models for GPC3. Cobalt constant accumulation model is from Kyte et al. [9]. Fish teeth biostratigraphic ages are from Doyle [5], modified by Pettke et al. [11]. The greatest discrepancy between the models occurs between 20 and 40 Ma, below 10 m depth.



Despite these age uncertainties, ichthyolith biostratigraphy was thought to indicate the presence of no hiatuses > 5 Myr for most of the Cenozoic in GPC-3 [4,9]. Estimated sedimentation rates for

GPC3 based on these data range from as low as 0.2 mm/kyr during the mid-Cenozoic to as much as 2 mm/kyr in the Pleistocene [10]. The increase in accumulation rate during the Pleistocene was

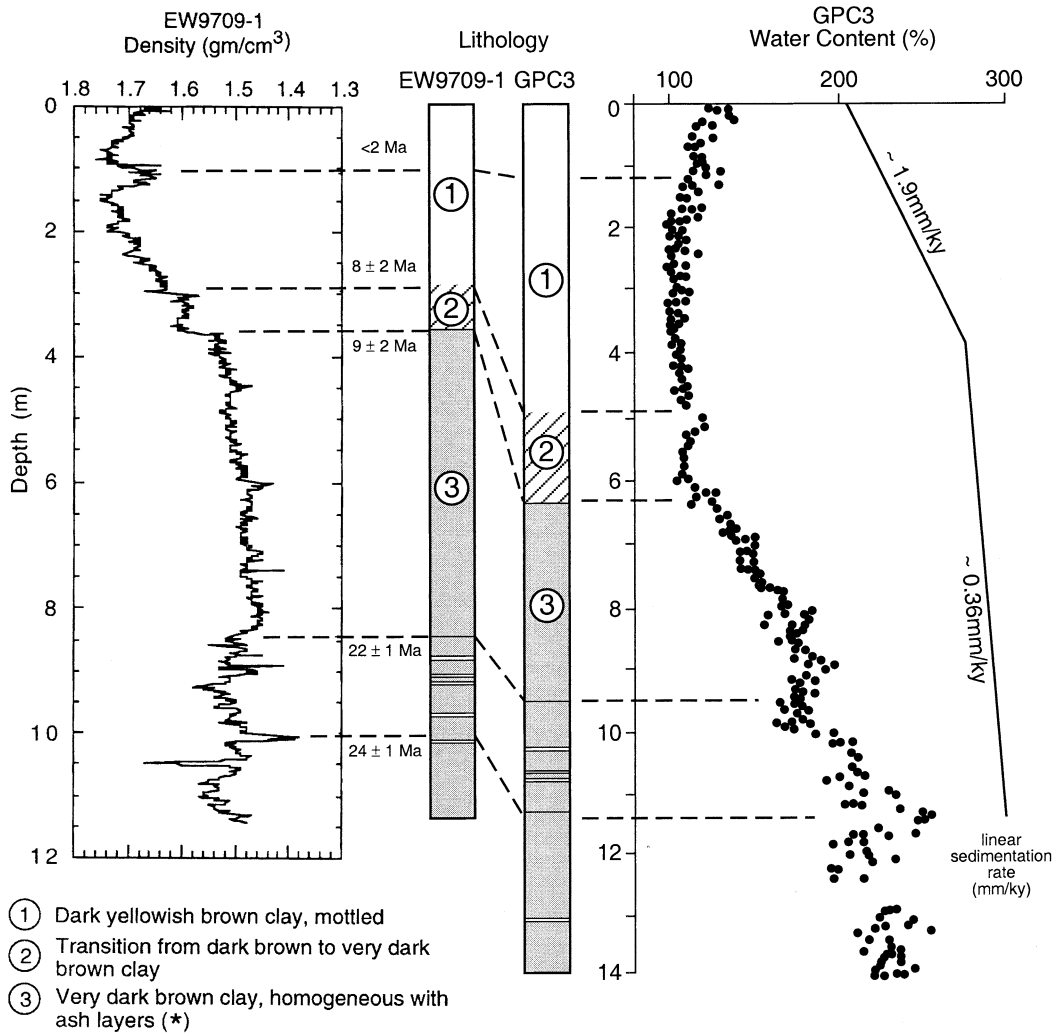


Fig. 5. Comparison of the lithologies of cores EW9709-1 and LL44-GPC3, based on core descriptions made at the Oregon State University Core Laboratory for EW9709 PC-01 and published in [26] for GPC-3. Bulk density measurements for EW9709 PC-01 derive from measurements on the whole core made using the Gamma Ray Attenuation Porosity Evaluator (GRAPE) on the multi-sensor track at the Oregon State Core Laboratory. The percent water content of GPC3 sediments was measured on discrete samples, corrected for 35% salt content, and reported in [39]. Although these two data sets measure two slightly different characteristics of the bulk sediments using different techniques, the two measured curves do show broad similarities that parallel correlations based solely on lithologic descriptions. For EW9709 PC-01, density measurements from both the trigger weight core and piston core were correlated and indicated that approximately 45 cm of the uppermost section was compressed or missed in the piston core (possibly resulting from a trip wire that was too long). Density records from the trigger weight and piston cores were merged and plotted here with the appropriate depth corrections applied to the composite record. Visual descriptions as well as the magnetic susceptibility and GRAPE records were used to identify ashes in PC-01; ash layers in GPC3 are reported in the appendix of [26].

Table 2

Estimated ages for Core EW9709 PC-01, compared with estimated ages for comparable depths in LL44-GPC3

PC-01 depth (cm)	Sr age <sup>a</sup> (Ma)	GPC3 depth (Ma)	Biostrat. age <sup>b</sup> (Ma)	Corrected age <sup>c</sup> (Ma)	Co age <sup>d</sup> (Ma)
33	0.77	117	0.56	0.70	0.53
235	6.70	492	4.57	5.02	3.69
297	8.40	631	9.57	7.62	7.50
773	19.68	953	21.39	22.02	22.68

<sup>a</sup> This paper.<sup>b</sup> Doyle and Riedel [4].<sup>c</sup> Berggren et al. [38].<sup>d</sup> Kyte et al. [9].

attributed to a dramatic increase in eolian dust production brought on by onset of northern hemisphere glaciation [10]. Staudigel et al. [3] analyzed fish teeth fractions from three intervals in GPC3 for their Sr isotopic ratio, obtaining compositions that in general matched these GPC3 age intervals; however, no further effort was made to produce a detailed age–depth curve for GPC3 by ichthyolith Sr stratigraphy (in that study, individual teeth were not analyzed, nor were the ichthyoliths cleaned beyond a preliminary acetic acid cleaning step to remove possible carbonate contamination).

In Fig. 5 we have attempted to correlate PC-01 with GPC3 based on distinctive lithologies and on similarities in sediment density and water content measurements. In Table 2, we compare the estimated ages of the four correlation points indicated in Fig. 5. Ages for PC-01 are taken from Table 1 and Fig. 3. Ages for GPC3 are those estimated by Doyle and Riedel [1] and Prince et al. [35], as reported by Corliss and Hollister [25]. These values have been corrected for recent revisions in the paleomagnetic and biostratigraphic timescales by Berggren et al. [38]. We used biostratigraphic datums employed by Doyle and Riedel [1] to map the old timescale onto the new one. For the lower Miocene through Oligocene part of GPC3, the ichthyolith stratigraphic zones reported by Doyle and Riedel [1] generally span 2–3 m in core depth and 7–8 Myr in time. This comparison suggests that our correlations and age estimates are in good agreement. We note that the large Pleistocene increase in dust production does not show up in our data set for PC-01, most likely because of poor sampling/age resolution in that

part of the core. In the future, we intend to generate a more detailed Sr ichthyolith stratigraphy and magnetostratigraphy for the upper part of PC-01, which we can use to compare with the ichthyolith Sr isotopic ages (not yet determined) and the magnetostratigraphic data for the upper part of GPC3.

## 5. Conclusions

Improvements to the techniques used to measure strontium isotope ratios in fish teeth enable more rapid and accurate dating of otherwise unfossiliferous marine pelagic clays. The core used in this study (EW9709 PC-01) is located in the same sedimentary province as the well-studied pelagic clay core LL44-GPC3, and has a comparable lithostratigraphy. Age estimates derived from this study compare well with stratigraphic studies of LL44-GPC3, and promise an improved chronostratigraphy for such cores. Red clay cores from this large oceanographic province are critical to the evaluation of flux rates of hydrogenous components and terrestrial eolian dust in global paleoclimate and paleoceanographic reconstructions.

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