Available online at www.sciencedirect.com

SCIENCE DIRECT

Palaeogeography, Palaeoclimatology, Palaeoecology 212 (2004) 355–366

PALAEO

www.elsevier.com/locate/palaeo

Age calibration of piston core EW9709-07 (equatorial central Pacific) using fish teeth Sr isotope stratigraphy

J.D. Gleason*, T.C. Moore Jr., T.M. Johnson[1], D.K. Rea, R.M. Owen, J.D. Blum, J. Pares, S.A. Hovan[2]

Department of Geological Sciences, University of Michigan, Ann Arbor, MI 48109, United States

Received 9 December 2003; accepted 5 July 2004

Abstract

A high-resolution age–depth profile is presented for a 16-m deep-sea piston core (EW9709-PC07) using three different methods: magnetostratigraphy, fish-teeth strontium isotope stratigraphy, and radiolarian biostratigraphy. Fish teeth are abundant throughout the core, allowing for precise age determinations by Sr isotope stratigraphy. Magnetostratigraphic ages, though not available for this core, were determined by correlation with the drill core record from adjacent ODP Site 1218. Biostratigraphic ages were independently assigned to the lower 12 m of the core, which contains abundant radiolaria. All three methods define an early Miocene age (~20 Ma) for the core base. A linear sedimentation rate of ~2.0 mm/ky was calculated for the lower 10 m of the core, which is dominated by siliceous clays and calcareous ooze. All three methods yield concordant ages over this interval (~20 to 15 Ma). Tectonic migration of the PC-07 site away from the equatorial high productivity zone produced a significant decrease in sedimentation rates after 15 Ma, diminishing to just ~0.30 mm/ky in the uppermost 3 m of the core. Correlated magnetic reversal and fish teeth ages are concordant within this upper red clay interval (~10 to 0.0 Ma), which is dominated by eolian dust accumulation; however, within the 15 to 10 Ma interval, fish teeth ages appear to show more scatter, departing from the magnetic ages by as much as 2–3 million years. Age discrepancies in this dominantly siliceous clay interval are most likely due to uncertainties in magnetostratigraphic age correlations. We conclude from this that the eolian dust component in red clay cores can be reliably dated by the fish teeth strontium technique. For otherwise undatable red clay cores from the vast northern Pacific pelagic clay province, this may prove to be the only available method for developing a regional Cenozoic chrono-stratigraphy.

Keywords: Ichthyolith stratigraphy; Strontium isotopes; Fish teeth; Pelagic clay; Neogene; Pacific

* Corresponding author.
E-mail address: jdgleaso@umich.edu (J.D. Gleason).
[1] Present address: Department of Geology and Geophysics, University of Wisconsin, Madison, WI 53706, USA.
[2] Present address: Geoscience Department, Indiana University of Pennsylvania, Indiana, PA 15705, USA.

0031-0182/$ - see front matter
doi:10.1016/j.palaeo.2004.07.005

1. Introduction

The North Pacific pelagic clay province spans some 40° of latitude and 80° of longitude, quantifying it as one of the largest sedimentary provinces on Earth (Leinen, 1989). Despite its vast extent, little is known about the geology of this province, owing in part to its remoteness (mostly 5 km below sea level, and much of it lying 1000s of km from the nearest shore). Prior studies have established that Pacific pelagic 'red' clay is mainly composed of Asian-derived wind blown (eolian) dust and hydrothermal (hydrogenous) components (e.g., Janecek and Rea, 1983; Leinen, 1989; Kyte et al., 1993; Nakai et al., 1993; Jones et al., 1994; Rea, 1994; Pettke et al., 2000, 2002). Cores from the central North Pacific pelagic clay province have mainly sampled Neogene or younger sediments, an important exception being the giant piston core LL44-GPC3, which penetrated the K–T boundary (Kyte and Wasson, 1986; Kyte et al., 1993). One of the greatest obstacles to studying Pacific pelagic clays has been the absence of good age control. With sedimentation rates averaging much less than 1 mm/ky, the resolution of the magneto-stratigraphic record is usually too poor to define reversals with much confidence. The upper (Pleistocene) part of LL44-GPC3 is an exception (Prince et al., 1980), as are several red clay cores recovered from the recent ODP Leg 199 (Pares and Lanci, 2002; Lanci et al., 2002). In most other cases, however, pelagic red clays appear to be undatable by conventional methods (Gleason et al., 2002). Datable ash layers are rare, and fossils (except for fish remains) are mostly absent. Deposition below the carbonate compensation depth (~4500 m) destroys most carbonate, while radiolaria are generally abundant only within a few degrees of the equator.

Despite these difficulties, improved techniques for dating red clays are being developed (e.g., Gleason et al., 2002). The goal is to better characterize Cenozoic dust sources and sinks for the north Pacific region through time, information which can potentially be used as a proxy for atmospheric paleo-circulation (e.g., Janecek and Rea, 1983; Rea, 1994; Hovan, 1995). Attempts have been made in the past to construct red clay stratigraphies from fish teeth (so-called ichthyolith stratigraphy) based on fish teeth taxonomy (Doyle and Riedel, 1979, 1985; Doyle, 1980; Gottfried et al., 1984). Other workers attempted to use Sr isotope stratigraphy of fish teeth for dating pelagic clays (Staudigel et al., 1985; Ingram, 1995a,b; Snoeckx et al., 1995), but encountered problems with the technique. Kyte et al. (1993) used a constant cobalt accumulation rate model to assign ages to LL44-GPC3, obtaining partial agreement with fish teeth biostratigraphy. More recent work has investigated the importance of cleaning techniques prior to analysis of fish teeth (Martin and Haley, 2000; Gleason et al., 2002). Martin and Scher (2004) have reported evidence for diagenetic disturbance of fish teeth $^{87}Sr/^{86}Sr$ in some cores with abundant carbonate, though red clay cores may not be as affected (Gleason et al., 2002). Comparison of ichthyolith $^{87}Sr/^{86}Sr$ isotopic ratios to the marine Sr isotope curve (McArthur et al., 2001) should theoretically permit age assignments down to a resolution of $\pm$0.5 my (or better) for the time period ~16 to ~38 Ma, and $\pm$1.0 my for ~16 Ma to the present. This improved age resolution using fish teeth Sr isotope stratigraphy is potentially sensitive enough to detect hiatuses of $\geq$2 My in red clay sections of late Eocene age or younger (Gleason et al., 2002). However, as age resolution has continued to improve, indications have been found for discordant data under certain circumstances (e.g., Martin and Scher, 2004). The reasons are poorly known, but have in some cases been linked to Sr exchange between marine phosphatic material and surrounding pore waters during burial diagenesis (e.g., Barrat et al., 2000; Martin and Scher, 2004). In this study, we demonstrate that the fish teeth dating method is generally reliable for red clay cores having low sedimentation rates, but that procedures need to be developed to screen out samples with potentially diagenetically altered Sr.

Piston Core EW9709-PC07 was recovered in 1997 by the R V Ewing as part of a site reconnaissance survey cruise in support of ODP Leg 199 (Fig. 1). One of the objectives of this cruise was to collect enough material to characterize the provenance of Cenozoic eolian dust deposits along a longitudinal transect between 0° and 40°N latitude of the North Pacific basin (Fig. 2). This database will ultimately help in reconstructing Cenozoic atmospheric circulation and the paleolatitude of the intertropical convergence zone (ITCZ), a key parameter for understanding Cenozoic climate change (Rea, 1994;

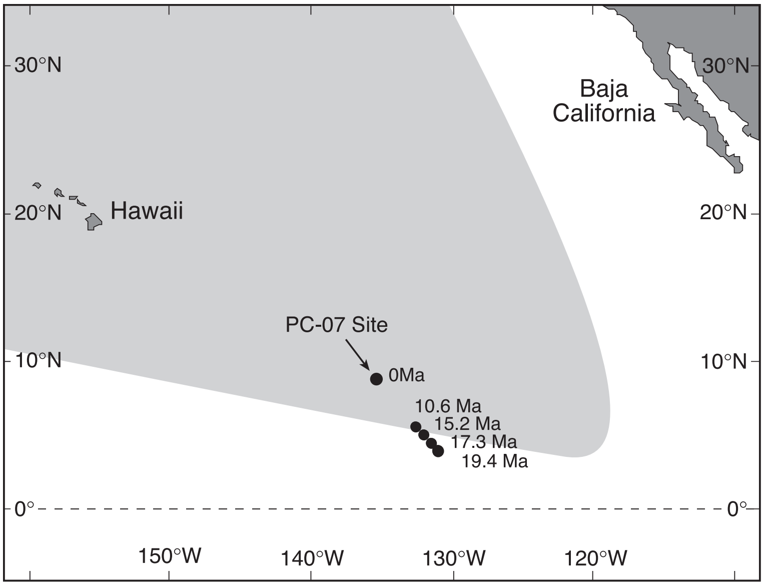

Fig. 1. Location of the EW9709-PC07 piston core (same as ODP Site 1218) within the central north Pacific pelagic clay province. Highlighted area (from Jones et al., 1994) receives dominantly eolian input from Asian sources. Pacific plate motion (tectonic backtrack) model for EW9709-PC07 piston core and ODP Site 1218 shows paleo-locations at 10.6, 15.2, 17.3, and 19.4 million years ago.

Hovan et al., 2000, 2002). PC-07 was retrieved at a depth of 4.8 km near latitude 8.8°N and longitude 135.4°W (Fig. 2). This 16-m core was chosen for this study specifically because of its fossiliferous lower section, with the potential to compare fish teeth ages with those obtained by conventional biostratigraphy. The upper 3.5 m of the core consists dominantly of red clay containing abundant fish teeth (Fig. 3).

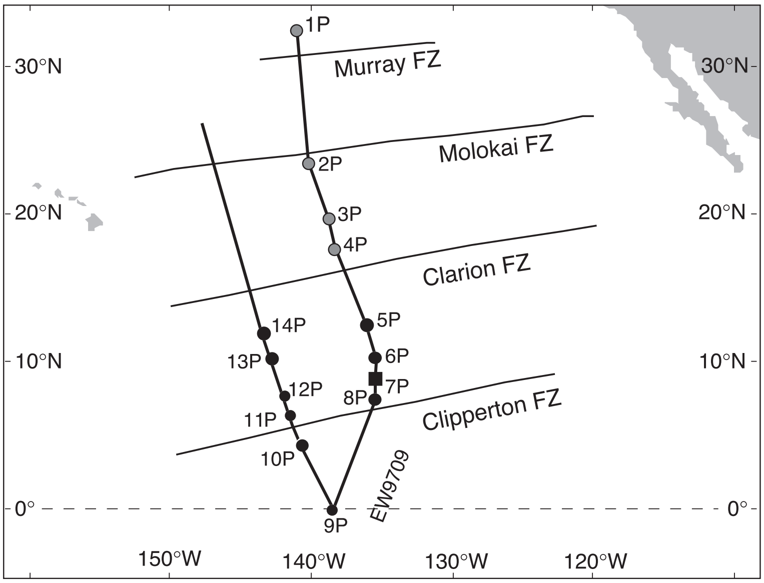

Fig. 2. Location of EW9709-PC07 piston core (7P), collected at 4777 m depth and 8.8°N latitude. Thirteen other piston cores from the 1997 EW9709 site survey are shown (black—abundant Neogene and upper Paleogene microfossils; grey—fish teeth dominant).

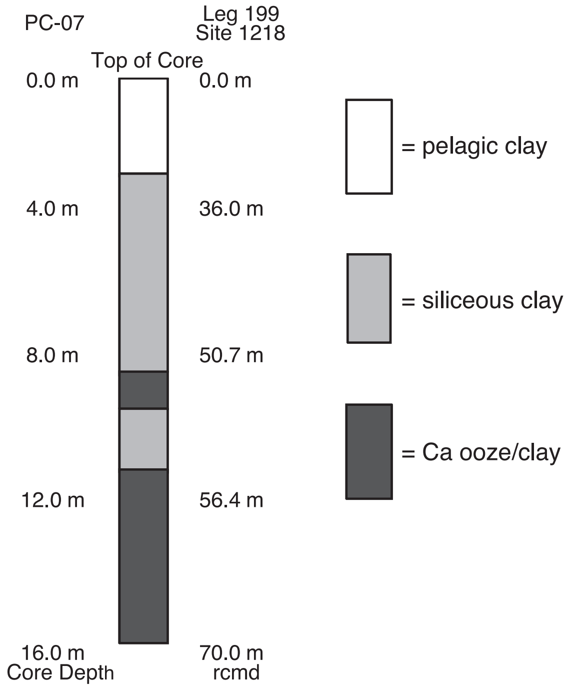

Fig. 3. Lithology of piston core EW9709-PC07 and correlated drill core from ODP Site 1218 (Leg 199). The upper ~3.5 m of PC-07 is dominantly red clay with abundant fish teeth ichthyoliths. Clay-rich radiolarian and nannofossil ooze dominates the rest of the 16 m core. Average sedimentation rates were much higher at Site 1218, resulting in a much thicker section relative to PC-07.

Siliceous clays and calcareous–siliceous clays characterize the remainder of the core. Foraminifera are very poorly preserved, but radiolarian-based stratigraphy for the lower 12 m of PC-07 (Fig. 3) places the base of the core at about 19–20 Ma (early Miocene). The youngest datable radiolaria occur at about 4.0 m. Radiolarian ages place this transition between 15 and 10 Ma as the site was crossing ~5°N latitude (Fig. 1), apparently migrating north of the equatorial high productivity zone.

2. Methods

Although magnetostratigraphic studies have yet to be conducted on PC07, we were able to correlate a recently obtained magnetostratigraphic record from drill core sections at ODP Site 1218, which sits adjacent to the PC-07 piston core site (Fig. 1). The drill core from ODP Site 1218 provides an unusually complete high-resolution record of magnetic reversals from middle Eocene to the present (Pares and Lanci, 2002; Lanci et al., 2002). Cores were correlated by detailed comparison of Multi-Sensor Track (MST) data, primarily bulk density and magnetic susceptibility (Fig. 4). Because core PC-O7 was taken on a topographic hill, whereas Site 1218 was drilled in a nearby seafloor valley, the section recovered at Site 1218 was about four times thicker than that recovered in PC-07. Correlation of both Gamma-ray attenuation porosity evaluator (GRAPE) bulk density and magnetic susceptibility data were checked for consistency against the radiolarian stratigraphy in samples from the two sites. Through the correlation of PC-07 with Site 1218, magnetic reversal data provide an independent time control on the PC-07 samples (Fig. 4).

The procedures used in the preparation and analysis of fish teeth closely followed those outlined by Gleason et al. (2002). All teeth were reductively cleaned, dissolved in 3 N nitric acid, and run through miniaturized SrSpec columns to separate Sr from the matrix. Analyses were performed at the University of Michigan on a Finnigan 262 thermal-ionization mass spectrometer operated in static mode. An ion beam of 2–3 V on Mass 88 was typically obtained for ~50 ng loads. All reported results are from on-line data reduction based on 150 ratios, normalized to $^{86}Sr/^{88}Sr=0.1194$. The NBS987 standard gave an average value of $^{87}Sr/^{86}Sr=0.710250\pm0.000014$ (n=74) during the course of this study, requiring no correction. Total procedural blanks, including cleaning blanks, are monitored at ~100 pg Sr or less per sample.

Sr isotope ages were assigned by direct comparison of $^{87}Sr/^{86}Sr$ ratios to the statistically smoothed marine Sr isotope curve (LOWESS) of McArthur et al. (2001). Uncertainties in ages thus obtained were assigned by evaluating both in-run precision and the stated uncertainties in the marine isotope record (McArthur et al., 2001). We report typically smaller errors (±0.5 my) for the 38 to 16 Ma time interval than for the 16 Ma to present interval, reflecting less rapid increase in marine $^{87}Sr/^{86}Sr$ ratios during this time. In most cases, multiple splits composed of several teeth each were run from the same depth interval in an effort to evaluate reproducibility. For this study, only triangular fish teeth ichthyoliths from the >63 μm size fraction were analyzed (analyzed teeth ranged from 0.1 to 1.7 mm in length). We

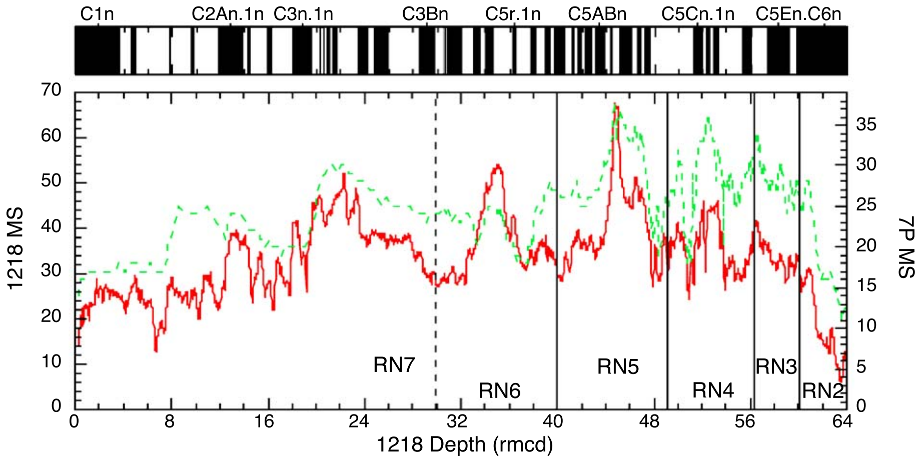

Fig. 4. Magnetic susceptibility (MS) in ODP Site 1218 (solid line) correlated to MS measured in nearby EW9709-7P (dashed line). Depth scale of EW9709-7P converted to revised meters composite depth (rmcd) in Site 1218 based on this correlation. The correlation of the MS data is checked by radiolarian stratigraphy in both EW9709-7P and Site 1218. Vertical solid lines mark the boundaries between radiolarian zones RN2-RN6 found in both EW9709-7P and Site 1218. The vertical dashed line marks the RN6/RN7 boundary found in Site 1218 only. Poor preservation of microfossils prevented identification of the zones in the upper parts of both sections. Plotted above the MS data is the paleomagnetic reversal stratigraphy (Cande and Kent, 1995) determined for Site 1218 (Lanci et al., 2002; Pares and Lanci, 2002). (For color see online version).

estimate each individual sample split contained between 50 and 100 μg of starting material before dissolution. A subset of these samples was also analyzed by ICP-MS to determine Sr concentrations and REE abundances.

3. Results and discussion

Forty strontium isotopic analyses representing separate fish teeth fractions from 18 different depth intervals were obtained for PC07 (Table 1; Fig. 5). For each $^{87}Sr/^{86}Sr$ value, an age and estimated error was assigned according to the McArthur et al. (2001) LOWESS age fit (Table 1). For most intervals, multiple splits of fish teeth were analyzed in order to characterize reproducibility. Nearly all splits for a given interval reproduced within the errors of in-run precision, lending confidence to the methods (Table 1; Fig. 5). Estimated errors in the assigned ages vary mainly according to in-run precision, as the marine Sr isotopic curve is extremely well defined for ~38 Ma to the present (McArthur et al., 2001). Uncertainties in the assigned ages increase slightly between 16 Ma and the present because of less rapid variation in $^{87}Sr/^{86}Sr$ of seawater with time, leading to poorer age resolution (Table 1).

Ages were also assigned for each interval in PC-07 based on magnetostratigraphic magnetic susceptibility (MS) correlation with ODP Site 1218 (Fig. 4; Table 1). A single fish tooth analysis from near the base of the core (1500 cm) defines an early Miocene age of 18.8±0.2 Ma, nearly concordant with the MS-correlated magnetostratigraphic age of 19.4 Ma from Site 1218 (Table 1). A single analysis from the top (surface) of the core gives a $^{87}Sr/^{86}Sr$ ratio of 0.709165±19, identical (within error) to that of modern seawater (McArthur et al., 2001).

In Figs. 6a,b, fish teeth Sr ages, magnetostratigraphic ages, and radiolarian ages were combined to produce age–depth profiles for PC07. Extrapolating these age–depth curves to 16.0 m yields concordant ages for the core base by all three methods (~19–20 Ma). All three methods also define concordant ages (at the±1 My level of resolution) for the lower 10 m of the core (16 to 6 m), for which we calculate a linear sedimentation rate (LSR) of ~2.0 mm/ky (20 Ma to 15 Ma; Fig. 6b). The sedimentation rate appears to decrease starting at about 15 Ma (Fig. 6b), diminishing to only ~0.30 mm/Ky for the upper 3.0 m (10 Ma to present). This represents nearly an order

Table 1
Strontium isotopic data for EW9709-PC07 fish teeth

Depth (m)	$^{87}Sr/^{86}Sr$[a]	Age[b] (Ma)	Error −my	Error +my	PC-07[c] age	1218[d] age	1218[e] rmcd
0.0	0.709165±19	0.00					
0.5	0.709122±30	0.80	0.98	0.98	1.34±0.67	0.826	5.760
0.5	0.709121±22	0.80	0.74	0.74			
0.5	0.709100±17	1.56	0.53	0.53			
0.5	0.709080±19	2.18	0.63	1.27			
1.0	0.709083±14	2.09	0.48	0.43	2.54±0.85	2.388	13.153
1.0	0.709085±24	2.02	1.50	1.50			
1.0	0.709061±37	3.52	1.92	1.83			
1.5	0.709019±17	5.49	0.46	0.31	5.34±0.21	4.242	19.260
1.5	0.709033±22	5.11	1.02	0.56			
1.5	0.709021±19	5.44	0.54	0.36			
2.0	0.708885±15	10.15	0.60	0.54	10.06±0.13	7.060	27.804
2.0	0.708890±18	9.96	0.75	0.66			
2.5	0.708891±18	9.92	0.67	0.75	9.78±0.21	9.760	34.237
2.5	0.708898±34	9.63	1.26	1.82			
3.0	0.708910±14	9.13	0.65	0.59	9.98±0.77	10.665	36.170
3.0	0.708884±14	10.19	0.56	0.50			
3.0	0.708872±16	10.62	0.58	0.51			
4.0	0.708842±12	11.66	0.51	0.71	11.56±0.15	11.930	39.154
4.0	0.708847±15	11.45	0.60	0.77			
4.5	0.708885±13	10.15	0.52	0.47	10.77±0.61	12.671	41.540
4.5	0.708867±12	10.80	0.43	0.37			
4.5	0.708849±12	11.37	0.39	0.47			
5.5	0.708833±14	12.10	0.65	0.79	12.15±0.14	14.394	45.650
5.5	0.708834±19	12.05	0.82	1.03			
5.5	0.708830±19	12.31	0.94	0.95			
6.5	0.708799±20	14.12	1.23	0.97	14.12	15.203	47.826
7.5	0.708806±26	13.52	1.35	1.53	14.32±0.77	15.236	49.910
7.5	0.708795±17	14.41	1.20	0.64			
7.5	0.708780±24	15.05	1.35	0.69			
9.0	0.708733±15	16.25	0.33	0.26	16.09±0.23	16.247	51.905
9.0	0.708748±18	15.92	0.44	0.38			
10.0	0.708752±17	15.83	0.43	0.38	16.29±0.59	16.784	53.507
10.0	0.708708±16	16.67	0.26	0.23			
11.0	0.708662±15	17.27	0.18	0.17	17.13±0.21	17.266	55.173
11.0	0.708686±14	16.98	0.19	0.17			
12.0	0.708667±16	17.21	0.19	0.19	17.21	17.821	56.388
13.5	0.708591±13	18.06	0.15	0.15	18.11±0.06	18.708	58.704
13.5	0.708583±13	18.15	0.15	0.15			
15.0	0.708532±15	18.82	0.22	0.21	18.82	19.387	61.987

$^{87}Sr/^{86}Sr$ NBS987 standard=0.710250±14 (n=74).

[a] $^{87}Sr/^{86}Sr$ normalized to $^{86}Sr/^{88}Sr$=0.1194 (2-sigma errors represent in-run precision by TIMS on 150 ratios).

[b] Age determined from Sr seawater curve (McArthur et al., 2001).

[c] Average age of interval calculated from individual ages.

[d] Correlated mag-strat age from ODP Site 1218 (see text).

[e] Correlated depth from ODP Site 1218 (see text).

of magnitude drop in the LSR over a ~5 million-year period, and can be attributed to motion of the PC07 site away from the equatorial high productivity zone (Fig. 1). Fish teeth ages and magnetostratigraphic ages (Fig. 6a) are also mostly concordant over the 10 Ma-to-present interval (upper 3.0 m); however, there are discrepancies between some fish teeth ages and the magnetostratigraphic ages over the 15 to 10 Ma interval (6.0 to 3.0 m). Three analyses at depth interval 550 cm yield a mean Sr age of 12.2±0.15

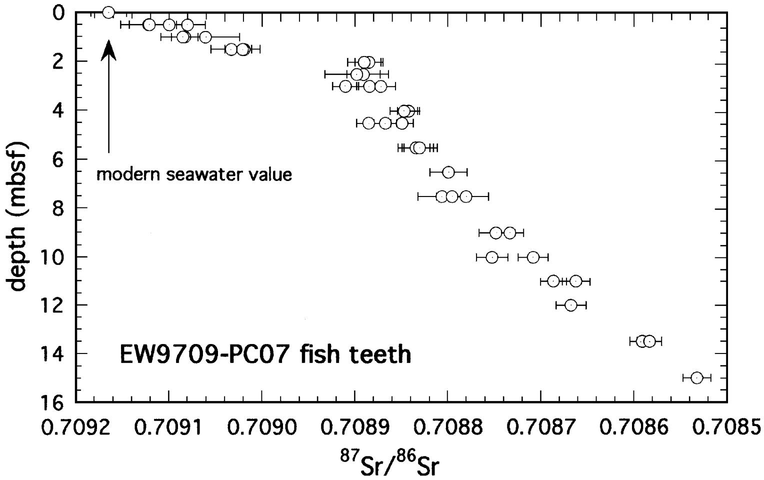

Fig. 5. Strontium isotope data for EW9709-PC07 fish teeth ichthyoliths (error bars represent in-run precision from Table 1).

Ma (Table 1), 1–2 million years younger than the corresponding magnetostratigraphic age and slightly younger than corresponding radiolarian ages (Fig. 6a,b). The fish teeth Sr ages for depth interval 450 cm are similarly too young (10.8±0.6 Ma; n=3), while ages for two concordant fish teeth analyses at depth interval 200 cm appear to be too old (Table 1; Fig. 6a) relative to the magnetostratigraphic age.

One factor which could account for this apparent scatter in the fish teeth data is diagenetic gain of Sr from pore waters (Martin and Haley, 2000; Martin and Scher, 2004). That seems unlikely in this case because: (a) multiple splits of fish teeth yield internally concordant ages for a given interval (but see Martin and Scher, 2004); (b) some intervals within the more poorly resolved section of the core appear to match the correlated magnetostratigraphic age; and (c) some of the ages appear too young, while others appear too old, requiring diagenetic gain of both *more* radiogenic, *and* less radiogenic Sr in this section. Unfortunately, pore water $^{87}Sr/^{86}Sr$ and Sr concentrations have not yet been obtained for PC-07, so we cannot evaluate this last possibility further. However, other factors also need to be considered. The chemical blank from the cleaning procedure is monitored at levels of <1/1000 of analyzed Sr (Gleason et al., 2002), thus it is judged to be insignificant. Failure to completely remove the natural contamination from the fish teeth seems to have been eliminated as a significant factor, based on extensive microscopic and backascattered electron (BSE) imaging of teeth surfaces (Gleason et al., 2002). Radiogenic in-growth from Rb has been shown to be insignificant over the time spans involved, based on the extremely low Rb abundances that we (and others) have measured in cleaned teeth (typically $^{87}Rb/^{86}Sr<0.01$). Finally, bioturbation and mixing of ichthyolith material across age horizons is likely insignificant at the 500 Ky time-resolution interval (Gleason et al., 2002). Even for red clay cores, bioturbated layers of 10 cm or less represent <300 Ky of sedimentation. Correlation errors from the MST analysis (Fig. 4) are also a possible source of apparent age discrepancies over the 10 to 15 Ma interval for PC-07, particularly if any hiatuses or substantial sediment reworking are present in either core. The MST records of the two cores are not particularly distinctive (particularly in density variations) over this interval, and an error of only a few tens of centimeters in PC-07 depth correlation would make a substantial difference in the estimated age of the samples.

Our work suggests that partial diagenetic conversion of some PC-07 ichthyoliths has taken place. Cathodoluminescence (CL) images (Fig. 7) of individual teeth reveal contrasting domains of both F-rich and Cl-rich phosphate, which may correspond to variable distributions of rare earth elements (REE) in the fish tooth structure. In an effort to further evaluate possible diagenetic influences on fish teeth chemistry, we determined Sr concentrations and REE patterns for a subset of PC-07 fish teeth by ICP-MS. Sr concentrations were calculated from Ca/P ratios by assuming

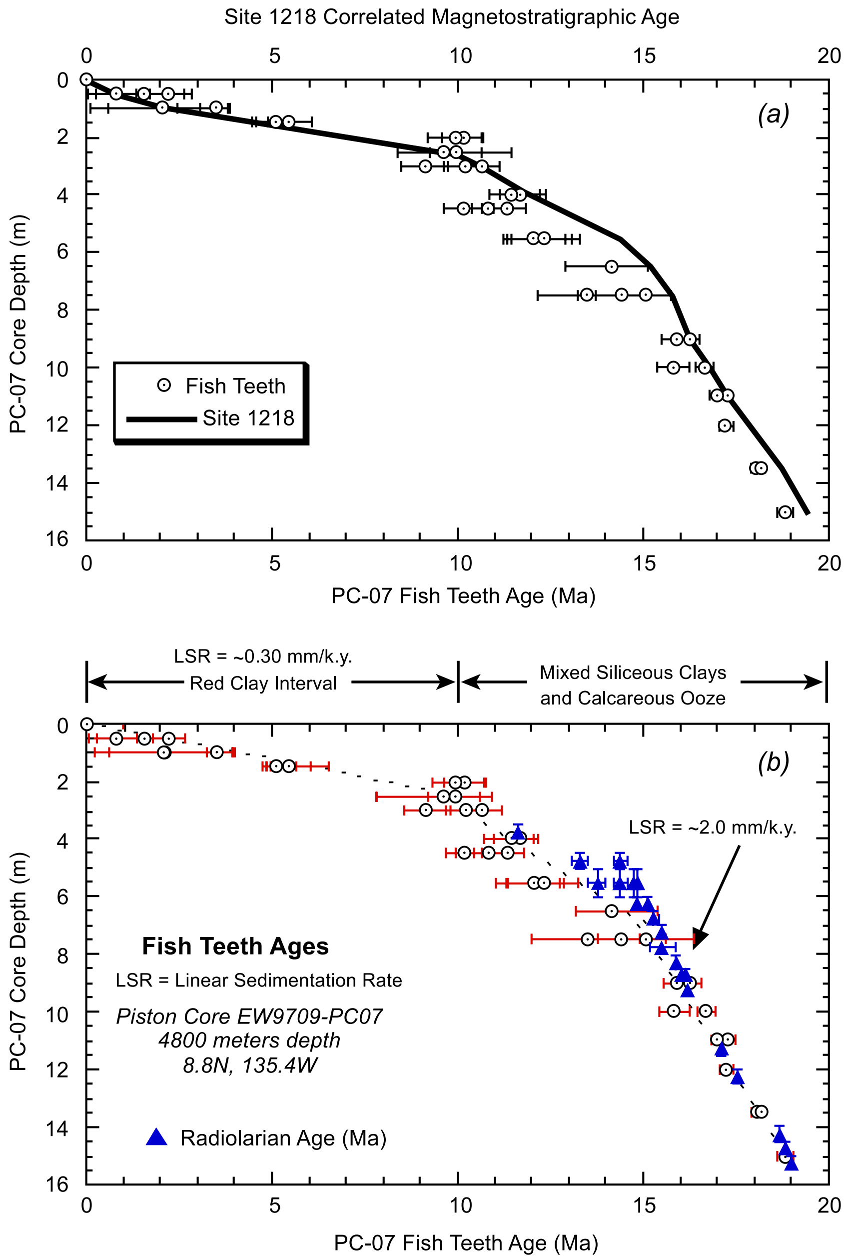

Fig. 6. (a,b) PC-07 age–depth curves. In (a) two datasets are superimposed: (1) PC-07 fish teeth $^{87}Sr/^{86}Sr$ ages (LOWESS), and (2) depth correlated magnetostratigraphic ages from Site 1218 drill core (ODP Leg 199). In (b) PC-07 radiolarian ages are combined with the fish teeth ages. Radiolarian ages were obtained by two linear regression equations through the data, one for the upper part and one for the lower part of the core (see **supplemental data** file). Radiolarian age error bars are based on calibration of datums to ODP Leg 199 paleomagnetic data (Lyle et al., 2002). Calculated sedimentation rates from PC-07 fish teeth and radiolarian stratigraphy vary between ~2 mm/ky (lower 10 m) and ~0.30 mm/ky (uppermost 3.0 m)(see text). All three dating methods give concordant ages for PC-07 except for a 5 my interval between 15 and 10 Ma (see text). (For color see online version).

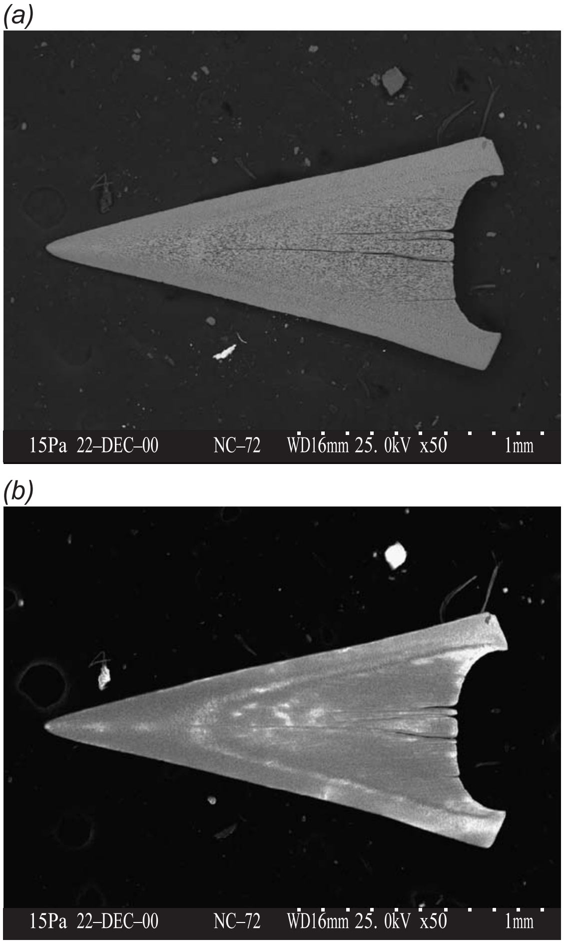

Fig. 7. (a) Backscattered electron (BSE) and (b) cathodoluminescence (CL) images of a cleaned fish tooth from PC-07 interval 450 cm (10.8±0.5 Ma). In (a) the slightly etched appearance and prominent outer rim (enamel) are typical of the larger triangular fish teeth ichthyoliths we have analyzed. In (b), CL imaging reveals contrasting fluorine-rich (brighter) and chlorine-rich regions of the tooth (the element being activated is likely a rare earth element that has substituted into a partly re-crystallized fluorapatite structure). A distinct compositional boundary between core and rim (enamel) is apparent, consistent with the in situ ion probe REE data of Grandjean and Albarede (1989).

ideal apatite stoichiometry, although this is known to vary in marine biogenic phosphates (e.g., Holmden et al., 1996). Because fish teeth ichthyoliths are not true apatite mineral structures (Shemesh, 1990), the conversion of organic carbonate-hydroxyapatite to carbonate-fluorapatite (francolite) or another structure could result in a range of Ca/P ratios that depart from the ideal (Schmitt et al., 2003). However, the Ca/P molar ratios that we measured do not depart significantly, at least within error of our measurements (deviations of <±10%), from the ideal $Ca_5(P0_4)_3$apatite structure (Ca/P_{molar}=1.667). Sr ppm concentrations in PC-07 fish teeth determined by this method are fairly uniform, ranging from ~1100 to 2200 ppm, but clustering around values of ~1600–1800 ppm (Table 2), comparable to what others have obtained by much more precise isotope dilution measurements (e.g., Martin and Haley, 2000; Ingram, 1995a,b; Schmitz et al., 1991; 1997; Koch et al., 1992) on both fossil and modern fish teeth. From these data, we can see no obvious indications of significant Sr gains or losses that might have disturbed the $^{87}Sr/^{86}Sr$ ratios over specific intervals of the PC-07 core, though the data do not rule out this possibility. REE patterns for the same samples are remarkably uniform, varying mainly in overall REE abundances (Fig. 8). The REE patterns are characterized by large negative Ce anomalies and small negative Eu anomalies, reflecting essentially 100% post-mortem diagenetic uptake of the REE's from seawater into the fish tooth structure (Staudigel et al., 1985; Shaw and Wasserburg, 1985; Elderfield and Pagett, 1986; Grandjean et al., 1987; Bertram et al., 1992; Reynard et al., 1999; Martin and

Table 2
EW9709-PC07 fish teeth chemistry

Depth (m)	Sr ppm calc.[a]
0.0	1700
0.5	1800
2.0	2000
2.0	1700
2.0	2200
3.0	1400
4.0	1600
4.0	1700
4.5	2100
4.5	1900
5.5	1100
5.5	1600
5.5	1600
7.5	1500
7.5	1800
10.0	2100
10.0	2000
10.0	1800
15.0	1300

[a] Estimated uncertainty in Sr concentrations ±5%.

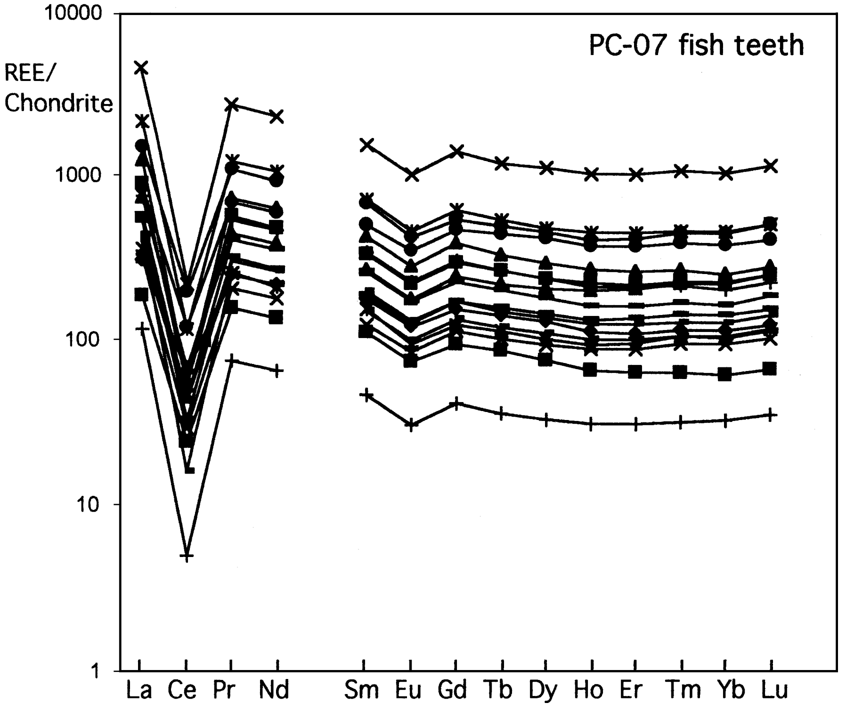

Fig. 8. Chondrite-normalized REE patterns for PC-07 fish teeth. Although overall abundances vary by more than an order of magnitude, the patterns are very similar to REE patterns of deep ocean waters and marine phosphates (e.g., Elderfield and Greaves, 1982; Grandjean et al., 1987; Banner, 2004).

Haley, 2000; Martin and Scher, 2004; Lecuyer et al., 2004).

Other studies (e.g., Martin and Scher, 2004) have indicated systematic offsets between fish teeth and foraminifera $^{87}Sr/^{86}Sr$ ratios from several precisely and independently dated deep-sea cores. Age offsets of up to 5 my have been attributed in part to high concentrations of pore water Sr having a large dissolved carbonate component (E. Martin, personal communication). In particular, older carbonate from deeper in the section may influence pore water $^{87}Sr/^{86}Sr$ values much higher in the section, producing systematically older ages in diagenetically altered fish teeth. The effect in red clay cores is likely to be different, as pore water compositions are generally depleted in Sr (Martin and Haley, 2000). Nonetheless, these studies emphasize the need for care to be taken in evaluating data sets used for dating red clay cores by the fish teeth Sr method. Our previous study of red clay core PC-01 (Gleason et al., 2002) demonstrated the advantages of improved techniques in the Sr dating method. The present study of PC-07 suggests that any age discrepancies, albeit small ones, in the fish teeth Sr ages with the calibrated age depth curve from Site 1218 are due mainly to uncertainties in depth correlations between the cores, and not to inherent problems with the fish teeth dating method.

4. Conclusions

The reliability of the fish teeth strontium isotopic method for dating red clay cores is reinforced by comparison with biostratigraphic ages and correlated magnetostratigraphic ages for piston core EW9709-PC07. All three methods define an early Miocene age (~20 Ma) for the base of the core. The top of the core yields fish teeth with $^{87}Sr/^{86}Sr$ ratios of 0.709165 ± 19, identical to modern seawater strontium. Sedimentation rates for the core vary from ~2.0 mm/ky for the lower 10 m (20–15 Ma) to ~0.30 mm/ky for the uppermost 3.0 m (10 Ma to present). This reflects tectonic migration of the site away from the equatorial high productivity zone, with eolian sources dominating the sediment flux after 10 Ma.

Despite some discordance between fish teeth and magnetic ages over a 5 million-year interval in this core, we conclude that dating red clay cores by the fish teeth strontium technique in general gives highly reliable results if a complete suite of downcore samples can be studied. For otherwise undatable red clay cores, this may prove to be the only tool available for determining precise age–depth profiles. More data are needed to fully evaluate the effects of structural and geochemical changes on $^{87}Sr/^{86}Sr$ ratios in fish teeth during burial diagenesis. The reliability of this method makes possible for the first time the precise down-core quantification of the Cenozoic dust flux as recorded in Pacific red clays.

Acknowledgements

Samples from the core were provided by the Oregon State University Marine Geology Repository, supported by NSF grant OCE 97-12024. The R/V Ewing piston cores were collected under the auspices of NSF grant OCE(ODP) 96-33802. NSF grant OCE-0136829 to Rea funded the analytical work. T. Huston (KECK Lab), M. Johnson, A. Klaue (RIGL Lab) and S. Morrison contributed essential lab support for this study. Dale Austin provided help with figure preparation. Thanks also to C. Jones, whose work and counsel in all things 'ichthyan' have benefited us in many ways. We appreciate the journal reviews by E. Martin and C. Lecuyer, who helped us to greatly improve the manuscript.

References

Banner, J.L., 2004. Radiogenic isotopes: systematics and applications to earth surface processes and chemical stratigraphy. Earth Sci. Rev. 65, 141–194.

Barrat, J.A., Taylor, R.N., Andre, J.P., Nesbitt, R.W., Lecuyer, Ch., 2000. Strontium isotopes in biogenic phosphates from a neogene marine formation: implications for paleoseawater studies. Chem. Geol. 168, 325–332.

Bertram, C.J., Elderfield, H., Aldridge, R.J., Morris, S.W., 1992. $^{87}Sr/^{86}Sr$, $^{143}Nd/^{144}Nd$ and REE's in Silurian phosphatic fossils. Earth Planet. Sci. Lett. 113, 239–249.

Cande, S.C., Kent, D.V., 1995. Revised calibration of the geomagnetic polarity timescale for the late Cretaceous and Cenozoic. J. Geophys. Res.—Solid Earth 100 (B4), 6093–6095.

Doyle, P.S., 1980. Seabed disposal program: improvement of ichthyolith stratigraphy for giant piston core 3. Prog. Rep.-Sandia Lab.

Doyle, P.S., Riedel, W.R., 1979. Cretaceous to Neogene ichthyoliths in a giant piston core from the central North Pacific. Micropaleontology 25, 337–364.

Doyle, P.S., Riedel, W.R., 1985. Ichthyolith biostratigraphy of western North Pacific pelagic clays, Deep Sea Drilling Project Leg 86. In: Heath, G.R., Burckle, L.H., et al. (Eds.), Initial Reports of the Deep Sea Drilling Project, vol. 86. U.S. Government Printing Office, Washington, DC, pp. 349–366.

Elderfield, H., Greaves, M.J., 1982. The rare earth elements in seawater. Nature 296, 214–219.

Elderfield, H., Pagett, R., 1986. REE in ichthyoliths: variations with redox conditions and depositional environment. Sci. Total Environ. 49, 175–197.

Gleason, J.D., Moore Jr., T.C., Rea, D.K., Johnson, T.M., Owen, R.M., Blum, J.D., Hovan, S.A., Jones, C.E., 2002. Ichthyolith strontium isotope stratigraphy of a Neogene red clay sequence: calibrating eolian dust accumulation rates in the central North Pacific. Earth Planet. Sci. Lett. 202, 625–636.

Gottfried, M.D., Doyle, P.S., Riedel, W.R., 1984. Advances in ichthyolith stratigraphy of the Pacific Neogene and Oligocene. Micropaleontology 30, 71–85.

Grandjean, P., Albarede, F., 1989. Ion probe measurement of rare earth elements in biogenic phosphates. Geochim. Cosmochim. Acta 53, 3179–3183.

Grandjean, P., Cappetta, H., Michard, A., Albarede, F., 1987. The assessment of REE patterns and $^{143}Nd/^{144}Nd$ ratios in fish remains. Earth Planet. Sci. Lett. 84, 181–196.

Holmden, C., Creaser, R.A., Muehlenbachs, K., Bergstrom, S.M., Leslie, S.A., 1996. Isotopic and elemental systematics of Sr and Nd in 454 Ma biogenic apatites: implications for paleoseawater studies. Earth Planet. Sci. Lett. 142, 425–437.

Hovan, S.A., 1995. Late Cenozoic atmospheric circulation intensity and climatic history recorded by eolian deposition in the Eastern Equatorial Pacific, Leg 138. In: Pisias, N.G., Mayer, L.A., et al. (Eds.), Proceedings of the Ocean Drilling Program, Texas A&M University, Scientific Results, vol. 138, pp. 615–625. College Station, TX.

Hovan, S.A., Branan, Y., Rea, D.K., Moore, T.C., Gleason, J.D., 2000. Latitudinal migration of the intertropical convergence zone (ITCZ) recorded by eolian sediments from the central and eastern Pacific. Eos. Trans.-AGU 81 (F734).

Hovan, S.A., Vanden Berg, M.D., Rea, D.K., Gleason, J.D., 2002. The Paleogene intertropical convergence zone. Eos. Trans.-AGU 83 (F946).

Ingram, B.L., 1995a. Ichthyolith strontium isotope stratigraphy of deep-sea clays: sites 885 and 886 (North Pacific Transect). In: Rea, D.K., Basov, I.A., et al. (Eds.), Proceedings of the Ocean Drilling Program, Texas A&M University, Scientific Results, vol. 145, pp. 399–412. College Station, TX.

Ingram, B.L., 1995b. High-resolution dating of deep-sea clays using Sr isotopes in fossil fish teeth. Earth Planet. Sci. Lett. 134, 545–555.

Janecek, T.R., Rea, D.K., 1983. Eolian deposition in the northeast Pacific Ocean: cenozoic history of atmospheric circulation. Geol. Soc. Amer. Bull. 94, 730–738.

Jones, C.E., Halliday, A.N., Rea, D.K., Owen, R.M., 1994. Neodymium isotopic variations in Noerth Pacific modern silicate sediment and the insignificance of detrital REE contributions to seawater. Earth Planet. Sci. Lett. 127, 55–66.

Koch, P.L., Halliday, A.N., Walter, L.M., Stearley, R.F., Huston, T.J., Smith, G.R., 1992. Sr isotopic composition of hydroxy-apatite from recent and fossil salmon: the record of lifetime migration and diagenesis. Earth Planet. Sci. Lett. 108, 277–287.

Kyte, F.T., Wasson, J.T., 1986. Accretion rate of extraterrestrial matter—iridium deposited 33 to 67 million years ago. Science 232, 1225–1229.

Kyte, F.T., Leinen, M., Heath, G.R., Zhou, L., 1993. Cenozoic sedimentation history of the central North Pacific: inferences from the elemental geochemistry of core LL44-GPC3. Geochim. Cosmochim. Acta 57, 1719–1740.

Lanci, L., Pares, J.M., Channell, J.E.T., 2002. Miocene–Oligocene magnetostratigraphy from equatorial Pacific sediments (ODP Site 1218, Leg 199). Eos. Trans.-AGU 83 (F946).

Lecuyer, Ch., Reynard, B., Grandjean, P., 2004. Rare earth element evolution of Phanerozoic seawater recorded in biogenic apatites. Chem. Geol. 204, 63–102.

Leinen, M., 1989. The pelagic clay province of the North Pacific Ocean. In: Winterer, E.L., Hussong, D.M., Drecker, R.W. (Eds.), The Eastern Pacific Ocean and Hawaii, vol. N. Geological Society of America, The Geology of North America, Boulder, CO, pp. 323–335.

Lyle, M., Wilson, P.A., Janecek, T.R., 2002. Proc. ODP Init. Repts, 199 [CD-ROM]. Available from: Ocean Drilling Program. Texas A&M University, College Station, TX 77845-9547, USA.

Martin, E.E., Haley, B.A., 2000. Fossil fish teeth as proxies for seawater Sr and Nd isotopes. Geochim. Cosmochim. Acta 64, 835–847.

Martin, E.E., Scher, H.D., 2004. Preservation of seawater Sr and Nd isotopes in fossil fish teeth: bad news and good news. Earth Planet. Sci. Lett. 220, 25–39.

McArthur, J.M., Howarth, R.J., Bailey, T.R., 2001. Strontium isotope stratigraphy: LOWESS Version 3: Best fit to the marine Sr-isotope curve for 0–509 Ma and accompanying look-up table for deriving numerical ages. J. Geol. 109, 155–170.

Nakai, S.A., Halliday, A.N., Rea, D.K., 1993. Provenance of dust in the Pacific Ocean. Earth Planet. Sci. Lett. 119, 143–157.

Pares, J.M., Lanci, L., 2002. Paleomagnetism of ODP Leg 199 sediments: implications for Paleogene and Neogene magnetic stratigraphy and paleolatitudes. Eos. Trans.-AGU 83 (F946).

Pettke, T., Halliday, A.N., Hall, C.M., Rea, D.K., 2000. Dust production and deposition in Asia and the north Pacific Ocean over the past 12 Myr. Earth Planet. Sci. Lett. 178, 397–413.

Pettke, T., Halliday, A.N., Rea, D.K., 2002. Cenozoic evolution of Asian climate and sources of Pacific seawater Pb and Nd derived from eolian dust of sediment core LL44-GPC3. Paleoceanography 17, pp. 3(1–13).

Prince, R.A., Heath, G.R., Kominz, M., 1980. Paleomagnetic stratigraphies of central North Pacific sediment cores: stratigraphy, sedimentation rates and the origin of magnetic instability. GSA Bull. 91, 1789–1835.

Rea, D.K., 1994. The paleoclimatic record provided by eolian deposition in the deep sea: the geologic history of wind. Rev. Geophys. 32, 159–195.

Reynard, B., Lecuyer, Ch., Grandjean, P., 1999. Chrystal–chemical controls on rare-earth element concentrations in fossil biogenic apatites and implications for paleoenvironmental reconstructions. Chem. Geol. 155, 233–241.

Schmitt, A.-D., Stille, P., Vennemann, T., 2003. Variation of the $^{44}Ca/^{40}Ca$ ratio in seawater during the past 24 million years: evidence from delta ^{44}Ca and delta ^{18}O values of Miocene phosphates. Geochim. Cosmochim. Acta 67, 2607–2614.

Schmitz, B., Aberg, G., Werdlin, L., Forey, P., Bendix-Almgreen, S.E., 1991. $^{87}Sr/^{86}Sr$, Na, F, Sr, and La in skeletal fish debris as a measure of the paleosalinity of fossil–fish habitats. GSA Bull. 103, 786–794.

Schmitz, B., Ingram, S.L., Dockery, D.T., Aberg, G., 1997. Testing $^{87}Sr/^{86}Sr$ as a paleosalinity indicator on mixed marine, brackish-water and terrestrial vertebrate skeletal apatite in late Paleocene–early Eocene near-coastal sediments, Mississippi. Chem. Geol. 140, 275–287.

Shaw, H.F., Wasserburg, G.J., 1985. Sm–Nd in marine carbonates and phosphates: Implications for Nd isotopes in seawater and crustal ages. Geochim. Cosmochim. Acta 49, 03–518.

Snoeckx, H., Rea, D.K., Jones, C.E., Ingram, B.L., 1995. Eolian and silica deposition in the central North Pacific: Results from Leg 145 sites 885/886. In: Rea, D.K., Basov, I.A., et al. (Eds.), Proceedings of the Ocean Drilling Program, Scientific Results, vol. 145, pp. 219–230.

Shemesh, A., 1990. Crystallinity and diagenesis of sedimentary apatites. Geochim. Cosmochim. Acta 54, 2433–2438.

Staudigel, H., Doyle, P., Zindler, A., 1985. Sr and Nd isotope systematics in fish teeth. Earth Planet. Sci. Lett. 76, 45–56.