Lead in corals: reconstruction of historical industrial fluxes to the surface ocean

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Twentieth century environmental lead chronologies for the western North Atlantic, Pacific, and Indian Oceans have been reconstructed from annually-banded scleractinian corals. Measurements of lattice-bound Pb in sequential coral bands reveal temporal changes in surface water Pb concentrations and Pb isotopic distributions. Perturbations are observable in all specimens studied, attesting to global augmentation of environmental Pb by industrialization.

In the western North Atlantic, Pb perturbations have occurred in direct response to the American industrial revolution and the subsequent introduction and phasing-out of alkyl Pb additives in gasoline. Surface ocean conditions near Bermuda may be reliably reconstructed from the coral data via a lead distribution coefficient of 2.3 for the species, Diploria strigosa. Based on $^{210}$Pb measurements, a similar distribution coefficient may be characteristic of corals in general. Surface Pb concentrations in the pre-industrial Sargasso Sea were about 15–20 pM. Concentrations rose to near 90 pM by 1923 as a result of metals manufacture and fossil fuel combustion. Beginning in the late 1940’s, increased utilization of leaded gasoline eventually led to a peak concentration of 240 pM in 1971, representing an approximate 15-fold increase over background. Surface ocean concentrations are presently declining rapidly (128 pM in 1984) as a result of curtailed alkyl Pb usage. Lead isotopic shifts parallel the concentration record indicating that characteristic industrial and alkyl Pb source signatures have not changed appreciably in time. Industrial releases recorded in the Florida Keys reflect a weaker source and evidence of recirculated Pb (5–6 years old) from the North Atlantic subtropical gyre. An inferred background concentration of 38 pM suggests influence of shelf and/or resuspended inputs of Pb to these coastal waters.

In remote areas of the South Pacific and Indian Oceans, industrial signals are fainter and the corals studied much younger than their Atlantic counterparts. Contemporary Pb concentrations implied by coral measurements (assuming $K_D = 2.3$) are 40–50 pM for surface waters near Tutuila and Galapagos in the South Pacific, and 25–29 pM near Mauritius in the Indian Ocean. A single coral band from Fiji (1920 ± 5 yr) implies a pre-industrial surface water concentration of 16–19 pM Pb for the South Pacific. In view of reported surface water measurements and the North Atlantic coral data, the Pacific coral extrapolations may be slightly high. This could be a result of small variations in $K_D$ among different coral genera, or incorporation of diageneric Pb by corals sampled in coastal environments.

1. Introduction

Over the past two decades, convincing evidence of global environmental contamination by industrial lead has accumulated. Murozumi et al. [1] documented historic increases of lead in snow strata cored in Greenland and Antarctica in 1969. More recent snow and ice core determinations from both hemispheres have confirmed their original findings (see review by Wolff and Peel [2]). Contamination continues to hamper measurement efforts in the most pristine locations, however, particularly in the case of ancient samples.

Extension of anthropogenic lead mapping to the oceans succeeded more recently when Schaule and Patterson [3] overcame sampling difficulties in 1976. Together with newer oceanic data by Flegal, Schaule, and Patterson [4–6] and Boyle et al. [7], and atmospheric flux measurements by Settle, Patterson and coworkers [8,9] and Jickells, Church and others [10,11], effects of industrial proximity and meteorology have been observed. Eolian delivery of stable lead parallels that of $^{210}$Pb [7,12,13], but the stable Pb source function differs from that of $^{210}$Pb and has evolved over time. The transient nature of this flux leads to the application of stable Pb as an oceanic chemical tracer to comple-
ment findings based on chlorofluorocarbons and bomb-produced radionuclides. As discussed by Boyle et al. [7], the success of such an application hinges on construction or recovery of accurate regional source deposition records. At present, the longest synoptic Pb measurement time series (now ending its third year) is that of Boyle and co-workers in the Sargasso Sea. Continued tracking of anthropogenic Pb in the ocean is needed, since the greatest changes in the upper ocean are expected over the next few years.

This paper describes the reconstruction of past surface ocean Pb concentrations and Pb isotopic distributions using the skeletal Pb content of annually-banded corals. Measurements on corals from the western North Atlantic, Florida Keys, Pacific, and Indian Oceans reconfirm the pervasive nature of industrial Pb aerosols and provide detailed chronologies of 20th century worldwide industrialization.

2. Sampling and analysis

The corals selected for this study were comprised of various scleractinian genera, all categorized as zooxanthellate, constructional, and hermatypic, according to the proposed terminology of Schuhmacher and Zibrowius [14]. Pertinent species, habitat, and sampling information are given in Table 1 and Fig. 1. Dating was accomplished by counting of annual bands on X-radiographs according to techniques outlined by Hudson [18] and Buddemeier et al. [17]. The Florida Keys and Bermuda chronologies are corroborated by 14C measurements by Druffel and Linick ([16,19], Bermuda data unpublished). In other cases, cross-checking was achieved by 210Pb dating.

A detailed description of trace metal analysis in corals will be given elsewhere [20]. Briefly, annual bands are mapped on transparent acetate film using X-radiographs of coral slabs (0.5–1.0 cm thickness), and these are then used as sectioning templates. Samples may be cut by any of several means, depending on band contours and thickness: i.e. low speed rock saw (Buehler – Isomet), band saw, or jeweler’s saw. Band intervals consisted of a high- and low-density band pair which comprised one year of growth in all cases. Sampling boundaries for corals from Bermuda and the Florida Keys spanned the bottom edge of a high-density band to the next lower high-density bottom edge. All other corals were sectioned along the top edges of the high-density bands. Dense band formation in corals has been shown to occur during the months of warmest water temperature [21,22]. Cut fragments were cleaned ultrasonically in acid and hydroxide/peroxide media to remove surface contamination associated with handling and organics. Coarse crushing in an agate mortar was followed by another preliminary cleaning sequence, before final crushing to a 280–700 μm particle size distribution. Where morphological considerations warranted (e.g. corals of genus Diploria), specific structural components were isolated to facilitate cleaning. These consisted of high-density, low-surface area, compound trabeculae which resemble spines radiating outward along the coral growth axis. The intervening network of secondary skeletal parts including loose trabeculae and synapticulae proved resistant to cleaning and usually demonstrated measurement offsets indicating contamination. For concentration determinations, triplicate samples weighing from 60 to 120 mg were cleaned intensely in both oxidizing and reducing media in the presence of ultrasonication and occasional heating. Isotope determinations often required additional sample to yield sufficient Pb for mass spectrometry. Cleaning and other subsequent preparation was carried out in 1.5 ml acid-leached polyethylene centrifuge vials.
Typical losses due to siphoning and dissolution were 30%. The cleaned samples were dissolved in 2.0N vycor-distilled HNO₃.

Lead concentration analysis was performed by graphite furnace atomic absorption spectrophotometry (GFAAS) using a Perkin-Elmer Model 5000 spectrophotometer, Model 400 furnace, and AS-40 autosampler. A L’vov platform was used to enhance sensitivity. Due to the trace Pb levels encountered in coral aragonite (8–150 ppb), separation of Pb from the calcium matrix was necessary for good reproducibility. This was accomplished by cobalt-APDC chelate co-precipitation [23,24]. Precision of the reported Pb concentration data varied both as a function of the coral species and coral band age. Generally, replicate analyses of older bands were more consistent than those of younger bands. Cleaning of very recent bands (< 10 years old) occasionally proved inadequate. Measurement precision variations were probably related to a variety of factors including skeletal morphology (susceptibility to detrital contamination and conversely, cleaning), turbidity of growth environment, prevalence of algal or other organic inclusions, and sample recovery/storage/handling. Since a general statement of precision is not useful, the reader is referred to error bars (1σ) supplied on all data plots. Blanks were typically less than 5% of measured signals in recent Atlantic corals and 10–30% in the most pristine coral bands. Blank contributions were almost always attributable to reagents, with procedural contamination only a minor infrequent component.

Lead isotopic measurements of samples purified by anion exchange chromatography [25] were run on 12" magnetic sector, solid source mass spectrometer (M.I.T., Department of Earth, Atmospheric and Planetary Sciences; S.R. Hart). Samples (typically 5–30 ng Pb) were loaded onto single rhenium filaments with H₃PO₄ and silica gel. Blank levels generally constituted less than 1% of the total lead deposited, consequently, corrections were not attempted. Measurement error (95% CFL) is conservatively estimated at ±0.0010 for the reported $^{206}\text{Pb}/^{207}\text{Pb}$ ratios to allow for variable mass fractionation.

$^{210}\text{Pb}$ determinations on corals were performed by alpha counting of $^{210}\text{Po}$ [26] on EG & G Ortec Model 576 alpha spectrometers fitted with 450 mm² low-background surface detectors. $^{210}\text{Po}$
(t_{1/2} = 138 days) was assumed to be in secular equilibrium with $^{210}$Pb in all samples since the youngest coral bands analyzed were 2 years old. $^{208}$Po was used as an autodeposition yield monitor. Errors due to counting statistics were generally less than 5%.

3. The coral lead record

3.1. Bermuda

Positioned in the southern portion of the North American Westerly flow path [27], Bermuda is a prime site for recording historic industrial lead fallout to the Sargasso Sea. Fig. 2a contains two such depositional records in corals. The lower record reflects the Pb transient in the open ocean (seaward side of North Rock, 14 km north of Bermuda), and the upper incorporates nearshore addition of diagenetic Pb (Southern Reef Preserve, 0.5 km south of Bermuda). The conspicuous gap (1955–1957) in the North Rock data is due to an attenuation of dense structural parts (compound trabeculae) which are isolated for analysis in this particular species of brain coral. Apparently, this coral suffered unidentified environmental stress during this three-year period while the more southerly coral did not. Analysis of the lower-density skeletal components in each of these affected bands resulted in variable elevated Pb concentrations (45–65 nmol Pb/mol Ca). The major features of the overall record are: (1) a gradual increase in skeletal Pb levels near the end of the 19th century; (2) a second more pronounced increase beginning in the 1950's, and (3) a dramatic decline initiated in the early 1970's. This progression of events very closely parallels the development of American industries tied to possible lead emissions, as can be seen in Fig. 3. The Pb source responsible for the turn of the century rise cannot be exactly specified, since early growth patterns for most large-scale industries are similar. Nevertheless, the early perturbation must be a direct consequence of the American industrial revolution. The striking resemblance between the subsequent portion of the coral record and U.S. alkyl lead consumption suggests that this source gained prominence with the rise of the automobile. Because competing sources appear to have levelled-off after 1940, the alkyl lead pattern is accurately superimposed on the earlier coral record. This is true to the extent that an extrapolated 1986 coral Pb concentration approaches the pre-alkyl Pb 1920-30's value. An approximate 1-year time lag between the peak coral Pb content in 1971 and the alkyl Pb consumption maximum in 1970 is consistent with estimates of $^{210}$Pb mixed layer residence times of 1.7–2.5 years [29,30].

The surface ocean Pb decline of 1.5-fold recorded by the Bermuda corals between 1979 and 1984 is in agreement with the earliest time series data available for dissolved Pb and $^{210}$Pb. The ratio of Schaule and Patterson's July 1979 surface water Pb measurement to our own in June 1984 is...
164 pM/103 pM or 1.6, however, extreme seasonality in surface ocean Pb places a high degree of uncertainty on this value [7]. Since Pb and 210Pb fluxes have exhibited a close coupling over Bermuda, one could also compare a 210Pb-normalized ratio over time: \((\text{Pb}/210\text{Pb})_{\text{july 1979}}/(\text{Pb}/210\text{Pb})_{\text{avg., (n=4)}} = 1.9\). A closer comparison might result if the coral Pb decrease from 1980 to 1985 were known. The absolute flux of Pb to the surface and deep ocean has been estimated by three independent rain and sediment trap measurements by Jickells et al. [10,31] and Church et al. [11] for the period 1981–1983. These results all fall within the range 0.88–1.18 mg/m² yr. Settle and Patterson’s [9] mean flux of 1.7 mg/m² yr is higher, but corresponds to surface water, rain, and dry deposition measurements from 1979 when the industrial flux was higher. Integrating an annual flux of 1.0 mg/m² yr over the western North Atlantic between 30° N and 50° N (latitudes over which U.S. westerlies prevail) gives a rough total Pb flux of \(10 \times 10^{10}\) g/yr for 1982. This represents about 20% of the total Pb consumed as alkyl Pb in the U.S. that year. However, it can be estimated (see Fig. 4) that alkyl Pb was responsible for only about 38% of the total industrial Pb flux in 1982 (based on the estimated contributions recorded by \(D. \text{strigosa}\) in 1983 which allows for a 1-year surface ocean lag time). Thus, a gasoline-derived Pb flux of approximately \(3.8 \times 10^{10}\) g (7% of the raw additive usage) was delivered to the western North Atlantic in 1982.

The coral-based Pb source breakdown of Fig. 4 is surprisingly consistent with Nriagu’s global Pb emission summary for 1975 [32]. His estimated contributions for anti-knock additives (58%), all other anthropogenic sources (37%), and background (5%) compare favorably to our own 1978 estimates (again allowing for a brief time lag) of 56%, 37%, and 7% for these same respective sources. As far as the relative roles of key industries and their Pb emissions, Nriagu’s contemporary analysis suggests that iron/steel production is about 1.5 times as important as lead production, twice as important as copper production, and 3 times as important as coal combustion or zinc production.

At the opposite end of the time scale, the question of pre-industrial environmental Pb levels arises. Before addressing this question, it would be useful to translate skeletal Pb concentrations to a more meaningful measure, namely, ambient Pb concentrations in seawater. This can be accomplished by means of a distribution coefficient \((K_D)\) for Pb in corals relative to surface water (see Appendix 1). Based on 1983-84 seasonally-averaged surface water dissolved Pb concentrations, the North Rock and Southern Reef Preserve coral records (both \(Diploria strigosa\)) extrapolate to \(K_D\)
$K_D = 2.1-2.3$ (Table 2). Thus, *D. strigosa* discriminates in favor of Pb over Ca during skeletogenesis.

Applying $K_D = 2.3$ to the coral record reveals that as of 1890, surface waters of the western North Atlantic contained 24 pM Pb. However, production of iron ore, coal, lead, and other primary metals had been steadily increasing the previous 20–30 years. If one carefully examines the relative growth rate of each possible source industry between 1890 and 1920, primary Pb production matches the coral record most closely (both experienced 3.5-fold increases versus 6-fold increases in the steel, copper and coal industries [26]). This comparison, however, leads to the expectation that surface water Pb fell to less than 1 pM by 1870. There are several reasons to believe this unrealistic: (1) the Pb decline implied by *D. strigosa* from 24 pM 1890 to the equivalent of 22 pM Pb in 1984 is too gradual to extrapolate to 1 pM by 1870; (2) Pb isotopes (section 3.5) show identical $^{206}/^{207}$Pb ratios in 1887 and 1895 which already fall within the background envelope; (3) a 1920 Fiji coral determination suggests a pre-industrial surface ocean Pb concentration of 16–19 pM in the South Pacific. Although the latter determination may contain an anomalous nearshore Pb component, it is probably not more than 50% of the total (see following section on island influences). Thus, it is unlikely that the North Atlantic, with its higher fluvial and aerosol inputs, could have supported a concentration much lower than 10 pM. If, on the other hand, control of the

### Table 2

<table>
<thead>
<tr>
<th>Lead distribution coefficients for two Bermuda corals</th>
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</thead>
<tbody>
<tr>
<td><strong>Bermuda Coral [Pb]/[Ca] (nmol/mol)</strong></td>
</tr>
<tr>
<td><strong>Southern Reef</strong></td>
</tr>
<tr>
<td><strong>Preserve</strong> (D. strigosa)</td>
</tr>
<tr>
<td>1983-84 est.</td>
</tr>
<tr>
<td>$42 \times 10^{-9}$</td>
</tr>
<tr>
<td><strong>North Rock</strong> (D. strigosa)</td>
</tr>
<tr>
<td><strong>Seawater [Pb] (pM)</strong></td>
</tr>
<tr>
<td>6/83</td>
</tr>
<tr>
<td>200 (filt.)</td>
</tr>
<tr>
<td>9/83</td>
</tr>
<tr>
<td>197 (filt.)</td>
</tr>
<tr>
<td>1/84</td>
</tr>
<tr>
<td>180 (filt.)</td>
</tr>
<tr>
<td>4/84</td>
</tr>
<tr>
<td>140</td>
</tr>
<tr>
<td>6/84</td>
</tr>
<tr>
<td>216 (filt.)</td>
</tr>
<tr>
<td>9/84</td>
</tr>
<tr>
<td>157</td>
</tr>
<tr>
<td>12/84</td>
</tr>
<tr>
<td>95</td>
</tr>
<tr>
<td>1983/84 avg.</td>
</tr>
<tr>
<td>$198 \pm 15$</td>
</tr>
<tr>
<td>$30 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

$K_D = 2.1$  
$K_D = 2.3$
early portion of the coral record was by one or a combination of the iron ore, copper, or coal industries, the projected pre-Industrial Revolution surface water value would be approximately 15 pM. Flegal and Patterson [5] suggest a comparable value in estimating that 1979 North Atlantic surface waters (160 pM) were enriched by 10-fold over pre-historic concentrations. Their estimate, however, was conceived to span over two centuries of anthropogenic activity as justified by the Greenland snow strata record of Murozumi et al. [1]. This poses the question of the importance of anthropogenic Pb prior to 1850. Simple scaling of our late 18th century surface water estimates to the snow record results in a prehistoric extrapolation of < 1 pM, which again appears unrealistic for the reasons cited earlier. Such an extrapolation is unwarranted, however, if one considers that (a) prehistoric aerosol fluxes to Camp Century, Greenland were very small relative to those reaching the Sargasso Sea; and (b) the Sargasso Sea may have received substantial fluvial inputs of Pb, whereas Greenland ice did not. Thus, an estimated Sargasso Sea surface water value of 15–20 pM Pb for the year 1850 is probably also a good prehistoric approximation.

If one accepts that the coral Pb record is equivalent to a record of dissolved Pb concentrations (differing only by the factor $K_D$), it is straightforward to interpret the coral data alternatively, as a flux history. The assumption must be made that the dissolved Pb concentration at a given location is at any time proportional to the incoming Pb flux. Conversion can then be accomplished simply by scaling the coral data to a suitable flux measurement (i.e. 1982 total Pb flux to Sargasso Sea $\approx 1.0 \text{ mg/m}^2 \text{ yr}$; resultant 1983 coral skeletal Pb level $\approx 30 \text{ nmol/mol Ca}$).

**Island influences at Bermuda.** Lead of local origin may influence coral-based reconstructions via habitat pollution or dissolved-particulate interactions in waters overlying reefs. Coastal Pb pollution resulting from urban effluents and mine tailings run-off has been documented by Patterson et al. [33], Stukas and Wong [34], and Bruland et al. [35] among others. A survey of Bermudian waterways (Fig. 5) reveals that neither large populations nor heavy industries are required to grossly contaminate inshore surface waters. The progression in dissolved Pb concentrations from well-flushed coastal zones to Hamilton Harbor yields values

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**Fig. 5.** Total and dissolved ($<0.4 \mu m$) lead in waterways and coastal areas around Bermuda (April 1984). Four samplings at point $A$ spanned 6/83–6/84 (see Table 2).
1.5 to 20 times open ocean concentrations. A similar situation has been documented for St. Croix, U.S. Virgin Islands from coral analyses of Dodge and Gilbert [36]. Particulate Pb in nearshore waters can also be observed in Fig. 5 to account for up to 85% (inner Hamilton Harbor) of the total measured Pb. This contrasts with levels of 10% or less encountered in the open ocean [5,29].

In the coastal zone of Bermuda, an interesting phenomenon is revealed by seasonal seawater measurements and comparison of the two Bermuda coral Pb records. Point A in Fig. 5 represents four separate water samplings accumulated over three different seasons from June 1983 to June 1984. The average dissolved Pb concentration here shows little seasonal variation and amounts to 198 ± 15 pM as compared to a seasonally-averaged oceanic value of 128 pM for 1984. The Southern Reef Preserve coral of Fig. 2a was collected only 2 km northeast of point A in similar waters. The constant skeletal Pb offset (approximately 10 nmol Pb/mol Ca) exhibited relative to the North Rock specimen suggests that an elevated dissolved Pb concentration is sustained by the sediment inventory or particulate Pb burden in nearshore waters. Additionally, absence of seasonality in the dissolved Pb measurements at point A suggests that these nearshore sources buffer the dissolved Pb concentration. The extent of this coastal effect was assessed in two transects heading away from Bermuda (Fig. 6). The first transect was directed toward North Rock, 9 miles north of the island. The second transect headed toward Station “S” (formerly known as the Panulirus Station), 20 miles away, where the bulk of our hydrographic work [7] is done. The results show convergence of total Pb concentrations to prevailing ocean values within 5 miles from shore. Dissolved Pb, the more relevant measure in terms of coral Pb uptake, appears to stabilize within 1.5 miles from the island. Given that Bermuda is well-populated by remote island standards, a 1.5 mile coral sampling boundary seems a reasonable rule for future collections targeted for trace elements. Seawater samples collected within 5 miles must be filtered before analysis in order to accurately assess ambient dissolved Pb concentrations.

3.2. Florida Keys

The general pattern of Pb increase in the Florida Keys over time (Fig. 7) is depressed relative to the Bermuda records. In addition, subtle distinctions suggest a modified source term from that affecting Bermuda. For example, the turn of the century rise is absent as levels appear to have remained

![Fig. 6. Local transect seawater Pb data heading from Bermuda toward: (a) North Rock (April 13, 1984); (b) Station “S” (Panulirus Station) (0–3 miles; June 12, 1984; 3–7 miles: December 11, 1984). Dashed lines depict dissolved Pb concentrations measured at Station “S” (20 miles southeast of Bermuda) during the same time periods.](image-url)
fixed at 10 nmol Pb/mol Ca back to the year 1698. Also, the post-World War II increase is moderated and the 1970's peak occurs several years later. Since Pb sources to the Florida Straits are borne by easterly winds and surface waters which have transited the Caribbean Sea, dissimilarities between records are expected. Episodic influence of Florida Bay discharges at this site has also been implicated by stress band studies of Hudson et al. [37]. Heavy industrial emissions originating in the northeastern U.S. should play a lesser role in the Florida Keys, with greater representation of Pb aerosols from the southern U.S. and perhaps nations encircling the Caribbean. Riverine inputs of Pb to the Florida Straits and Florida Bay, however, appear unimportant as dissolved Pb undergoes large-scale uptake onto suspended particles in the Mississippi River and estuary \( (K_D \geq 10^5); \) Lee and Boyle, personal communication.

The existence of a peak in the coral record at 1977 has important implications. This maximum identifies the presence of U.S. emissions in the area since use of octane-boosting alkyl leads in Latin America and Caribbean nations has not been curtailed to the extent legislated in the U.S. More importantly, though, the timing of this maximum is 6 years delayed relative to the signal at Bermuda. If horizontal transport of a North Atlantic source is responsible for this delay, this implies an average surface ocean recirculation velocity (assuming a 6000 km travel path from Bermuda, through the Antilles, and around the Caribbean) of 3.2 cm/s. This is comparable to surface Ekman transport estimates and wind drift speeds observed in the center of the subtropical gyre [38]. There are some qualifications to this interpretation, though. Since Pb is stripped from oligotrophic surface waters within 2–3 years, simple recirculation of a mixed layer source originating from northerly latitudes is unrealistic. Additionally, while subsurface waters \( (> 100 \text{ m}) \) complete an anti-cyclonic trajectory through the Caribbean, the northern branch of the North Equatorial Current hinders southward passage of North Atlantic surface waters. Thus, if the Florida Keys signal is derived from long-range horizontal transport, it must consist of Pb which has been mixed from deeper in the thermocline. The sill depths of the Anegada and Jungfern Passages separating the Caribbean from the North Atlantic are sufficiently deep \( (1500–2000 \text{ m}) \) to permit passage of thermocline waters containing longer-lived Pb. Re-enrichment of surface waters may occur by mixing in the Yucatan Channel and Florida Straits as sill depths shoal from 1600 to 800 m.

Additional insight can be drawn from data published by Dodge and Gilbert [36] for a coral (also \textit{M. annularis}) collected 1850 km southeast of Florida at St. Croix, U.S. Virgin Islands. Their 26-year record \( (1954–1980) \) at Buck Island shows a gradual rise from 10.3 nmol Pb/mol Ca in 1954 to a maximum of 24.5 nmol Pb/mol Ca in 1976. This maximum, which occurs between those recorded at Bermuda and the Florida Keys, appears to accord with a horizontally transported U.S. Pb source. The oldest concentration approaches the pre-industrial value measured in the Florida Keys. 1954, however, is relatively recent as far as industrial emissions are concerned, so an even lower pre-industrial value may be likely for this location.

3.3. South Pacific and Indian Ocean corals

In comparing the above data with coral measurements from the more remote locations of Galapagos, Tutuila, Fiji, and Mauritius (Fig. 8), the tremendous influence of the United States as an industrial source can be appreciated. Skeletal Pb levels here do not exceed 15 nmol Pb/mol Ca. As a consequence of these lower levels, it is more difficult to ascertain historic patterns. This problem is compounded by the scarcity of old sample cores in these outlying regions. The single
3.4. A survey of $^{210}$Pb in corals

Though a shortage of site-specific dissolved Pb measurements precludes additional estimates of stable Pb distribution coefficients for the corals described, $^{210}$Pb data are more plentiful. Citing open ocean values from the literature, a suite of $^{210}$Pb-based estimates of $K_D$ is reported in Table 3. It is immediately evident that these estimates are consistently higher than the value based on stable Pb in Bermuda ($K_D = 2.3$). This is true even for several specimens from North Rock, Bermuda (including the one analyzed in Fig. 2) for which an accurate dissolved $^{210}$Pb concentration can be deduced from seasonal measurements. Most of these inconsistencies are explainable.

In the case of the Bermuda corals where convergence with the stable Pb result is most expected, the discrepancy is likely due to two factors. First, $^{210}$Pb was determined from whole coral crushings while stable Pb analyses were performed only on the compound trabeculae of the Diploria corals. Attempts to determine stable Pb on fragments of $D$. labyrinthiformis which in-

usually high values, particularly among recent coral bands, are probably a result of a refractory contaminant Pb phase as discussed earlier.

### TABLE 3

<table>
<thead>
<tr>
<th>Location</th>
<th>Genus/species</th>
<th>Initial unsupported $^{210}$Pb (dpm/100 g coral)</th>
<th>Observed surface $^{210}$Pb (dpm/100 l)</th>
<th>Reference</th>
<th>Implied $K_D$</th>
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<td><strong>North Atlantic</strong></td>
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<td></td>
<td></td>
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<tr>
<td>Bermuda</td>
<td>$D$. strigosa</td>
<td>56</td>
<td></td>
<td>[7]</td>
<td>2.8</td>
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<tr>
<td>Bermuda</td>
<td>$D$. labyrinthiformis</td>
<td>63</td>
<td>19.7 ± 3.4 ($n = 5$)</td>
<td>[39]</td>
<td>3.2</td>
</tr>
<tr>
<td>Bermuda</td>
<td>$M$. annularis</td>
<td>65</td>
<td></td>
<td></td>
<td>3.3</td>
</tr>
<tr>
<td>Florida Keys</td>
<td>$M$. annularis</td>
<td>15</td>
<td></td>
<td></td>
<td>?</td>
</tr>
<tr>
<td><strong>North Pacific</strong></td>
<td></td>
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<td>Eniwetak</td>
<td>$F$. speciosa</td>
<td>75</td>
<td>13</td>
<td>[40]</td>
<td>5.8</td>
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<tr>
<td>Lisianski</td>
<td>$P$. lobata</td>
<td>69</td>
<td>20</td>
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<td><strong>Equatorial Pacific</strong></td>
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<td>Galapagos</td>
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<td>33</td>
<td>9</td>
<td></td>
<td>3.7</td>
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<td><strong>South Pacific</strong></td>
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<tr>
<td>Tutuila</td>
<td>$H$. microconos</td>
<td>30</td>
<td>10–11</td>
<td></td>
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</tr>
<tr>
<td>Heron Island</td>
<td>$P$. australiensis</td>
<td>18</td>
<td>7.6</td>
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<td>2.4</td>
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<td><strong>Indian</strong></td>
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<tr>
<td>Mauritius</td>
<td>$P$. rusticum</td>
<td>32</td>
<td>9–11</td>
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</tbody>
</table>
cluded septal trabeculae and synapticulae (low-density, high surface area structures), resulted in +10–20 nmol Pb/mol Ca offsets from the D. strigosa data and were marked by poor reproducibility [20]. This extraneous Pb amounts to approximately 30% of the true lattice-bound Pb pool. If $^{210}$Pb is distributed analogously to stable Pb as one might expect, this would effectively explain the difference in calculated distribution coefficients. The second factor is a less stringent cleaning protocol adopted for $^{210}$Pb assay compared with the stable Pb procedure (the initial assumption having been that in the absence of handling contamination for $^{210}$Pb, natural contaminants would constitute a small easily removed component). Coupled with a $^{210}$Pb sample bias toward very young bands (which are often difficult to clean), these natural contaminants are probably also responsible for part of the $K_D$ inconsistency. M. annularis would have been especially susceptible to a 2.5 and 6.5 years old. Additional evidence for a Pb distribution coefficient near 2 is suggested by Dodge and Thompson’s [43] determination of $^{210}$Pb in a specimen of D. labyrinthiformis from Castle Harbor, Bermuda. Refinement of their estimate depends, however, on actual measurement of dissolved $^{210}$Pb within this semi-enclosed basin.

As far as any of the Pacific and Indian Ocean $K_D$ estimates are concerned, it is first necessary to point out that the cited dissolved $^{210}$Pb measurements represent single season determinations of waters in the general vicinity of the sampled coral reefs. Sargasso Sea surface $^{210}$Pb concentrations have been observed to change by as much as 50% in three months, depending on rainfall and mixed layer integrity [7]. A small bias may actually be transmitted to the coral record through the interplay of seasonal surface water variation and skeletal mass accumulation. However, since coral growth is known to be continuous [44] and seasonal band width and density generally vary inversely [43,45], the effect of seasonally-dependent accretion is probably limited. Apart from the possibility of applying a non-representative surface water $^{210}$Pb concentration in calculating $K_D$, it should also be noted that neither of the two North Pacific corals in Table 3 produced useable stable Pb data. If this was a consequence of unfavorable morphology rather than poor sample storage (a strong possibility in the cases of Porites and Favia speciosa), the $^{210}$Pb results may also be suspect and should be considered as upper limits. In the Galapagos Islands case, the coral measurements are probably not so much at fault as the choice of a surface water $^{210}$Pb value. Eastern Equatorial Pacific waters are distinguished by variable upwelling and associated high- and low-productivity and scavenging regimes. The only surface water $^{210}$Pb measurements available in the area are from the Peru Basin at 11°S (9.1 dpm/100 kg) and 19°S (3.0 dpm/100 kg), non-upwelling and upwelling locations, respectively [40]. Although coral cadmium measurements indicate that the Galapagos site at San Cristobal Island is nutrient enriched by upwelling [46], a relatively high dissolved $^{210}$Pb concentration (> 11 dpm/100 kg) is required to yield $K_D < 3.0$. This condition would depart from the conclusion reached by Thomson and Turekian [40] that high-productivity zones exhibit depleted $^{210}$Pb relative to parent $^{226}$Ra, particularly in surface waters. With regard to the remaining cases, discrepancies between $^{210}$Pb and stable Pb $K_D$'s appear small or attributable to mechanisms previously discussed.

In view of the above discussion, the actual range of Pb distribution coefficients exhibited by eight species (seven genera) is probably very small, perhaps 2.3–3.0. This is a desirable outcome in that coral Pb measurements can be interpreted directly, without the need to normalize according to genus as in the case of $^{18}$O coral paleothermometers [47].

If one accepts, tentatively, that $K_D$ dependence on genus is negligible, plots such as those depicted in Fig. 9 can be constructed giving surface ocean Pb concentrations at any site, at any time in the past. The 1984 reconstructions (Fig. 9b) appear reasonable in light of SEAREX and WATOX atmospheric fluxes [8,9,11], but a pair of surface water measurements near American Samoa of 17 and 21 pM by Flegal and Patterson [5] suggests that the Tutuila coral may have been subject to island influences. On the “pre-industrial” plot (Fig. 9a), the 1920 ± 5 Fiji coral determination translates to a surface water dissolved Pb value of 16–19 pM (12–15 pM if $K_D = 3.0$), which may be slightly high if one accepts the South Pacific seawater data and a strong anthropogenic invasion to this region since 1920. Preliminary mass
spectrometric measurements of the same coral sample (acid leached to 40% of initial mass) have yielded a Pb concentration of 4.4 nmol/mol Ca, confirming our own results (J. Chen C.I.T., personal communication). If Flegal and Patterson are indeed correct in arguing a maximum pre-industrial Pacific surface water concentration of about 10 pM, then nearshore diagenetic Pb must be invoked as the source of the coral offset. By analogy to Bermuda, however, dissolved Pb anomalies 2.5 km away from Fiji are expected to be small. Therefore, the South Pacific prehistoric surface water Pb concentration was probably not much lower than 10 pM.

In contrast to the South Pacific, surface waters in the Florida Keys remained near 38 pM throughout the 18th and 19th centuries. Presumably, this is a reflection of the importance of shelf and/or resuspended Pb in waters overlying this coral reef.

3.5. The coral lead isotope record

Industrial leads are isotopically very heteroge-
Fig. 10. Preliminary Pb isotopic histories for other sample sites. Left margin: background ranges estimated from [51,52]. Right margin: industrial emission data are from [6,50] and Fig. 2b.

centrations are as yet unknown. For example, the waters around Mauritius are clearly industrially influenced, despite very low skeletal Pb levels in P. rustica. The magnitude of these perturbations cannot be assessed from Pb isotopes until historic source signatures have been better characterized. Point determinations in time of industrial emission signatures shown in the right margin of Fig. 10 only indicate that the measured departures from background are in the expected directions. The Tutuila record displays a curious trend away from Broken Hill-type Pb in recent years, which appears to be supported by a single surface water measurement ($^{206/207}$Pb = 1.176) by Flegal et al. at 15° 0′S, 150° 0′W in January, 1980 [6]. Introduction of unleaded fuels in Australia over the last several years, however, has been too recent to account for the isotopic shift. Also, the coral Pb concentration record from Tutuila (Fig. 5) shows no concomitant change. A large-scale conversion in ore usage either regionally or locally is probably responsible. The Florida Keys data suggest that as late as 1929, input of industrial lead to these waters was minimal. This was also the turning point in the concentration record after which levels began to increase. The subsequent isotopic shift as indicated by the lone measurement at 1974 resembles that which occurred at Bermuda.

4. Conclusions

(1) This survey of stable Pb and Pb isotopes in corals from four major ocean basins confirms (by independent means) the previously-inferred anthropogenic dominance of Pb found throughout the surface ocean today, and over the past century.

(2) Direct lattice substitution of lead in coralline aragonite is documented by (a) constancy of replicate measurements, (b) low background concentrations, and (c) consistency of the temporal and regional response to known industrial fluxes. A Bermuda-based coral:seawater Pb distribution coefficient of 2.3 is estimated for the species, Diploria strigosa. $K_D$ dependence on species and genus is estimated to be small (estimated range = 2.3–3.0) based on similarity of $^{210}$Pb $K_D$ estimates and plausibility of inferred seawater dissolved Pb concentrations.

(3) In view of the above conclusions, historic surface ocean conditions may be reconstructed as follows:

In Sargasso Sea surface waters, the pre-anthropogenic dissolved Pb concentration was probably between 15 and 20 pM ($^{206/207}$Pb = 1.215). This value rose to near 90 pM in the 1920′s as a result of the American industrial revolution ($^{206/207}$Pb = 1.184–1.190). Subsequent combustion of alkyl leads pushed the surface value to a maximum of 240 pM in 1971 ($^{206/207}$Pb = 1.202). A one-year time lag between this maximum and peak U.S. alkyl Pb combustion in 1970 reflects the brief mixed layer residence time of Pb. Since then, phasing-out of leaded gasoline has caused a precipitous return to levels near those of the 1920′s ($^{206/207}$Pb = 1.186)

The Florida Keys maintained a surface water concentration of 38 pM Pb until about 1930, which was probably supported by shelf/resuspended Pb inputs. Levels grew gradually to peak of 190 pM in 1977, followed by a decline to 142 pM in 1982. Relative to the Bermuda records, the Florida coral lacks a strong industrial revolution signal and exhibits a moderated post-World War II Pb increase and muted maximum. These patterns reflect dilution of U.S. Pb sources and delayed response due to long-range horizontal transport.

In the South Pacific, a single coral measurement from Fiji (1920 ± 5 yr) implies a pre-industrial surface water Pb concentration of 16–19 pM (12–15 pM if $K_D = 3.0$). Although coastal diagenetic Pb may have biased this result, such a
contribution is expected to be small. Therefore, South Pacific pre-industrial surface waters were probably not much lower than 10 pM Pb. Recent corals from Tutuila and Galapagos imply higher concentrations of 40–50 pM resulting from regional industrial influence and possible local effects.

The coral from Mauritius was too young to furnish historical perspective, but contemporary surface water Pb values are estimated at 25–29 pM. The Pb isotopic signature of this coral is clearly indicative of anthropogenic perturbation.

(4) A survey of near and inshore waters around Bermuda suggests the following general trace element sampling strategies for remotely situated islands. Unless local pollutant signals are the study object, enclosed and partially enclosed waterways must be avoided. Coastal sampling may also be prone to local outfall and addition of Pb from sediments and resuspension. The limits of these anomalies will vary from island to island, but the Bermuda results suggest that 2.5 km is probably a safe minimum sampling distance with respect to dissolved Pb concentrations.

(5) The paleo-chemical recording capability of corals offers a sensitive means of reconstructing historic Pb fluxes and isotopic labels to the temperate/tropical ocean. Future transport modeling of Pb in the ocean can be based on such reconstructions of regional Pb transients.

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Appendix 1 — The lead distribution coefficient in aragonite

The standard means of expressing an enrichment or depletion of a lattice-bound element relative to seawater is embodied in the distribution coefficient $K_D$:

$$K_D = \frac{([M]/[Ca])_{lattice}}{([M]/[Ca])_{seawater}} \quad (1)$$

Earlier, it was established by means of stable lead and 210Pb-based distribution coefficients that corals discriminate mildly in favor of Pb over Ca during skeletogenesis. A thermodynamic basis for this preference can be invoked if the solid solution behavior of PbCO$_3$ (cerrusite) and aragonite are examined. Both of these mineral phases generally occur in near end-member composition, but limited solid solution with Pb and Ca (up to 3 mol %) has been reported [53]. The equilibrium constant for Pb substitution in aragonite:

$$CaCO_3(s) + Pb^{2+} \rightarrow PbCO_3(s) + Ca^{2+} \quad (2)$$

is equivalent to equation (1) if the ratios of solid and aqueous phase total activity coefficients (including species complexing) are equal to unity. In this case, $K_D$ is given simply by the ratio of CaCO$_3$ (aragonite) and PbCO$_3$ solubility products in surface seawater. Since $K_{sp}$ (aragonite) in surface seawater (25°C) is reported by Morse et al. [54] as $10^{-31.5}$ mol$^2$/kg$^2$, and $K_{sp}$ (PbCO$_3$) ($10^{-13.1}$ mol$^2$/kg$^2$ @ 25°C—Smith and Martell [55]) can be corrected for seawater ionic strength by the Davies equation to give $10^{-31.8}$ mol$^2$/kg$^2$, a theoretical $K_D$ of $4 \times 10^5$ results. While $Ca^{2+}$ and $Pb^{2+}$ activity coefficients are expected to be similar ($\approx 0.23$), however, species complexing for the two elements are very different. Garrels and Thompson [56] calculated that 91% of dissolved Ca in seawater exists as the free $Ca^{2+}$ ion. In contrast, $CO_2$ and Cl$^-$ complexing of Pb reduces the free $Pb^{2+}$ concentration to only about 3% of the total Pb [57]. Thus, the effect of differential ion-association is to decrease $K_D$ to about $10^4$. This value, nearly 6000 times higher than the observed $K_D$ resulting from biogenic precipitation of aragonite, suggests that the activity coefficient of the solid solute, $f_{PbCO_3}$, must be very high—i.e. near 6000. A simple laboratory experiment demonstrated that inorganic precipitation of aragonite gives results similar to coral-mediated precipitation. Clean seawater was spiked to a Pb concentration of 8.2 nM, seeded with a few clean coral crystals, and allowed to precipitate at 60°C for one month. Two such solutions were then filtered and the precipitates immersed in 0.1 M HNO$_3$ to dissolve only the new crystal growth surrounding the coral seeds. Due to uncertainties stemming from adsorption of Pb onto container walls, the experimental $K_D$ ranged from 20 to 35; about an order of magnitude higher than the coral-based $K_D$. Part of the enhanced discrimination for Pb is likely due to increased precipitation rate induced by the higher temperature and presence of seed crystals, as described by Lorenz [58] for Sr precipitation in calcite. The experimental result, nonetheless, supports preferential uptake of Pb over Ca during aragonite precipitation.

Appendix 1— The lead distribution coefficient in aragonite
More generally, it has become increasingly apparent that lattice-compatible trace elements are incorporated into coral aragonite in the same ratios to calcium as exist in seawater, regardless of differences in chemical speciation. Distribution coefficients for Ra, Ba, Nd, Sr, Cd, Co, and Zn in corals are all surprisingly close to unity, despite varying degrees of ion association (see [20]). While this pattern bespeaks simplicity, a thermodynamic basis is not obvious. One possibility is that in the supersaturated, possibly reducing environment of the coral polyp, carbonate complexes prevail, and these are indiscriminately coprecipitated with CaCO₃ in a kinetically-controlled non-equilibrium process. The preference manifested toward Pb is a matter of speculation.

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