U-Th dating of deep-sea corals

Hai Cheng, Jess Adkins, R. Lawrence Edwards, and Edward A. Boyle

1 Minnesota Isotope Laboratory, Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455 USA
2 Geochemistry 62, Lamont-Doherty Earth Observatory, Rt. 9W, Palisades, NY 10964 USA
3 Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139-4307 USA

(Received February 24, 1999; accepted in revised form November 16, 1999)

Abstract—$^{230}$Th, $^{232}$Th, $^{234}$U and $^{238}$U compositions of several deep-sea solitary corals, mainly the species Desmophyllum cristagalli, were determined by thermal ionization mass spectrometry (TIMS). It is possible to obtain high precision ages on modern pristine corals that have low [$^{232}$Th] compared to surface corals, and the initial $^{230}$Th/$^{232}$Th ratio is uncertain, older deep-sea corals have larger age uncertainties ($\pm$ several hundred years for samples with a few thousand ppt $^{232}$Th). Therefore, the key hurdle for precise U-Th dating is to remove or account for contaminants which contain elevated $^{232}$Th and associated $^{230}$Th not due to closed system decay within the coral lattice. A modification of the trace metal cleaning methods used for foraminifera and surface corals can significantly reduce this contamination. By counting the visible growth bands and measuring the mean age of a single septum, the extension rate of $D$. cristagalli was estimated to be between 0.1 and 3.1 mm/year. In a mean sense, bands appear to be precipitated annually, but this estimate has a large uncertainty. If appropriate tracer calibrations can be established, these corals are therefore suitable to record decadal or sub-decadal oceanographic changes over the course of their lifetime. The $\delta^{234}$U values of all modern samples from different localities and different depths are similar (mean 145.5 $\pm$ 2.3‰) and indistinguishable from the data obtained from surface corals. At a precision of about $\pm$2‰, we find no structure in the oceanic profile of $\delta^{234}$U ratios over the top 2000 m of the water column.

1. INTRODUCTION

Uranium series dates from surface corals provide constraints on several late Quaternary climate processes. Past sea level estimates from $\alpha$-counted $^{230}$Th dates on raised coral terraces from Barbados supported the Milankovitch hypothesis on the relation between glacier ice volume and insolation (Broecker et al., 1968; Mesolella et al., 1969). Later, more precise and accurate thermal ionization mass spectrometry (TIMS) confirmed this result in a variety of locations (Edwards et al., 1987a,b; Gallup et al., 1994; Muhs et al., 1994; Stirling et al., 1995; Szabo et al., 1994). Drill cores of submerged corals that have been precisely dated by $^{230}$Th methods contain our most detailed and continuous record of sea-level since the last glacial maximum (Bard et al., 1993; Bard et al., 1996; Edwards et al., 1993). Coupled high precision radiocarbon and uranium series dates from surface corals constrain the history of atmospheric $^{14}$C beyond the tree ring calibration (Bard et al., 1993; Bard et al., 1990; Edwards et al., 1993). In addition, TIMS dates provide precise ages for coral tracer-based studies of past oceanographic conditions (Beck et al., 1997; Beck et al., 1992; Gagan et al., 1998; Guilderson et al., 1994; McCulloch et al., 1996).

Analogous studies of deep-sea corals promise to constrain a number of deep ocean processes (Adkins et al., 1998; Mangini et al., 1998; Smith et al., 1997). Several cosmopolitan genera of deep-sea scleractinia inhabit all major ocean basins. Coral has been dredged from the ocean floor since at least the days of the Challenger expedition, so the world’s collections contain thousands of samples. While reported depth habitats of deep-sea coral range from 60–6000 meters (Cairns and Stanley, 1981), most specimens are found between 500–2000 meters. This depth range makes deep-sea corals ideal for studies of intermediate and upper deep water masses. The great potential of this archive stems from the fact that the density banded coral skeletons are not subject to bioturbation and the fact that the skeletons are potentially datable by uranium-series techniques (Cheng et al., 1995; Goldstein et al., 1996; Smith et al., 1997).

Thus, deep-sea corals can provide absolute-dated records with temporal resolutions not generally attainable in deep-sea sediments and are a new archive of deep circulation rates by coupling U-series ages with $^{14}$C dates (Adkins and Boyle, 1998; Mangini et al., 1998). However, realization of this potential requires evaluating the U-Th dating systematics (Lomitschka and Mangini, 1999) and growth rates of deep-sea corals. This study focuses on the ubiquitous pseudo-colonial species, Desmophyllum cristagalli, using both a modern and a fossil sample set.

Several previous studies have examined deep-sea coral growth rate and its relationship to species specific density banding. Duncan (1877) and Pratje (1924) reported extension rates of 6.8 and 7.5 mm/year for specimens of the genus Lophelia that were attached to underwater transatlantic cables. Teichert (1958) also estimated growth rates of 7.5–15 mm/year for Lophelia. Grigg (1974) determined a value of about 20 mm/year vertically and 3 mm/year horizontally for two gorgonians by tagging colonies of Muricea californica and Muricea furticosa from a relatively shallow depth of 14–20 m. He suggested that the periodicity of growth ring formation was annual based on matching the estimated ages to the number of growth bands. Using the $^{210}$Pb dating method, Druffel et al.
Sea corals may incorporate a significant amount of unsupported initial $^{230}$Th. Our results are specifically applicable to the calcitic deep-sea gorgonian *Corallium niobe*, which grew at 600 m depth. In that study, the periodicity of growth systematics in several deep-sea corals. The behavior of $^{234}$U, $^{230}$Th, and $^{232}$Th in reef-building corals and the suitability of reef-building corals for $^{230}$Th dating is the subject of an extensive literature starting with Barnes et al. (1956) and continuing up to the present, see Ivanovich and Harmon (1992) and references therein. The behavior of uranium-series nuclides in surface-dwelling solitary corals has also received attention (Ku and Kern, 1974; Muhs et al., 1994; Stein et al., 1991; Szabo, 1985). However, similar studies on deep-sea corals are generally lacking (Adkins et al., 1994; Stein et al., 1998; Cheng et al., 1995; Goldstein et al., 1996; Smith et al., 1998). In many respects, one would expect the U-Th dating systematics of deep-sea corals to be similar to those of their surface-dwelling counterparts. However, deep-sea coral systematics should differ in at least two key respects. First, deep ocean waters have much higher $^{230}$Th concentrations than surface waters. Thus, deep-sea corals may incorporate a significant amount of unsupported $^{230}$Th during growth. If so, a correction for initial $^{230}$Th must be made, and the precision and accuracy of the $^{230}$Th age will depend on the precision and accuracy of the correction. Second, the environments in which deep-sea corals are quite different from those in which surface corals age. Thus, diagenetic processes may affect corals in the two settings in different ways.

In this study, we investigate the U-Th dating systematics of several species of aragonitic deep-sea corals, focusing on *Dendrophyllum Cristagalli*, which is the most abundant coral in our collection of dredged specimens. We establish growth rates and initial chemical and isotopic characteristics by analyzing $^{238}$U, $^{234}$U, $^{230}$Th, and $^{232}$Th concentrations in modern samples. We constrain diagenetic shifts in the pertinent nuclides by comparing the isotopic characteristics of the modern specimens to those of fossil samples, and by analyzing coatings on the specimens. By analyzing different sub-samples of the same coral, we show that deep-sea corals generally have significant amounts of initial and/or added thorium. We investigate sources of this thorium, as well as methods to remove or correct for initial $^{230}$Th. Our results are specifically applicable to the study of Adkins et al. (1998), which established that deep-ocean circulation changed dramatically in less than several decades at 15.4 ka. The time and the duration of the circulation change is established with uranium-series data and interpretations presented here. Beyond this specific application, we envision that our results will be more generally applicable to further studies in the emerging field of deep-sea coral paleoceanography.

## 2. SAMPLES AND METHODS

### 2.1. Samples

Deep-sea coral samples were provided by the Smithsonian Institution and the Woods Hole Oceanographic Institution dredge collection. Five modern samples of *D. cristagalli* were collected by dredging programs in the Pacific, the Atlantic, and the Southern Oceans over the past 30 years (Table 1 and Fig. 1). Sample depths range from 420 to 2200 m. Samples were judged to be modern either because of intact organic matter, noted upon recovery, or very fresh looking preservation of the septa in the dredge collections. Prior to cleaning, the modern samples were covered with a yellowish organic coating. Six fossil samples were dredged from the Atlantic between depths of 1700 to 2000 m (Table 1). All specimens are *D. cristagalli* except for one *Solenosmilia sp.* specimen and one unidentified sample. As opposed to the modern samples, the fossil samples are almost always covered with a black crust. Energy-dispersive electron microprobe analysis indicates that this crust is composed of iron and manganese oxides mixed with detrital aluminosilicates (Fig. 2a). It is also possible to find discrete metal sulfide deposits in the crust’s matrix (Figure 2b).

### 2.2. Sample Cutting

Samples were cut into small slabs parallel to the radially symmetric septa, which are connected around the outer rim by a thick-walled theca (Fig. 3). Septa in individual deep-sea corals are classified on the basis of their relative cross-sectional areas in a radial plane, where the S1 septa have the largest cross-sectional areas (Fig. 3, refer to (Cairns, 1981) for classification of septa). Each slab generally consists of one whole S1 septum associated with either one or two smaller septa on both sides of the S1. S1 septa typically have tens of density bands sub-parallel to their upper surfaces (Fig. 4). The thickness of individual septa are about 0.1–0.7 mm, with the S1 being the thickest. Each septum’s thickness decreases vertically from a bulge near the top and increases from the interior towards the theca. After cutting, the slabs were set aside for one of two cleaning procedures described below. Slabs of the five modern *D. cristagalli* samples were further sampled into smaller pieces roughly parallel to their growth bands using a small blade (Fig. 3). Final weights of these modern coral sub-samples ranged from 28.9 to 143.3 mg.

### Table 1. Deep sea coral samples used in this study.

<table>
<thead>
<tr>
<th>Sample set</th>
<th>Sample number</th>
<th>Analysis number</th>
<th>Collection time</th>
<th>Depth (m)</th>
<th>Locality</th>
<th>Coral species</th>
<th>Solitary or colonial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>47413</td>
<td>DC-2 a, b</td>
<td>Jan. 21, 1964</td>
<td>421</td>
<td>50°38’S</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td></td>
<td>84820</td>
<td>DC-4 a, b</td>
<td>Nov. 23, 1986</td>
<td>806</td>
<td>0°14’N</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td></td>
<td>85080</td>
<td>DC-3 a, b</td>
<td>Feb. 25, 1990</td>
<td>990–1150</td>
<td>43°47’S</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td></td>
<td>84740</td>
<td>DC-5</td>
<td>Oct. 28, 1973</td>
<td>1420–1470</td>
<td>48°40’N</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td></td>
<td>78459</td>
<td>DC-1</td>
<td>Apr. 16, 1987</td>
<td>2110–2180</td>
<td>38°45’N</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td>Paleo</td>
<td>JFA-2</td>
<td>2</td>
<td>1684–1829</td>
<td>42°N</td>
<td>29°W</td>
<td>Solenosmilia sp.</td>
<td>Colonial</td>
</tr>
<tr>
<td></td>
<td>JFA-17</td>
<td>17</td>
<td>1684–1829</td>
<td>42°N</td>
<td>29°W</td>
<td>Solenosmilia sp.</td>
<td>Colonial</td>
</tr>
<tr>
<td></td>
<td>JFA-24C</td>
<td>24</td>
<td>1784</td>
<td>38°N</td>
<td>60°W</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td></td>
<td>JFA-20A</td>
<td>20A</td>
<td>1954</td>
<td>38°N</td>
<td>62°W</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td></td>
<td>JFA-20B</td>
<td>20B</td>
<td>1954</td>
<td>38°N</td>
<td>62°W</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
<tr>
<td></td>
<td>JFA-20C</td>
<td>20C</td>
<td>1954</td>
<td>38°N</td>
<td>62°W</td>
<td>Desmophyllum cristagalli</td>
<td>Solitary</td>
</tr>
</tbody>
</table>

(90) calculated a mean value of 0.11 ± 0.02 mm/year in width for the calcitic deep-sea gorgonian *Corallium niobe*, which grew at 600 m depth. In that study, the periodicity of growth band formation did not appear to be annual. Our approach is to use U-series disequilibria to constrain dating and growth systematics in several deep-sea corals.
2.3. Ultrasonic Cleaning

All sub-samples of the five modern samples (Table 2) and some sub-samples of the six fossil corals (labeled “N” in Table 3) were cleaned with the following ultrasonic cleaning technique. Under a binocular microscope, samples were checked for organic coatings or iron-manganese oxide crusts, which were scrubbed with small dental tools. Samples were put in a plastic bottle, ultrasonically cleaned in deionized water for 10 min. and then completely rinsed. This process was repeated several times until the coral looked clean (free of crusts) under the microscope. The above procedure was then repeated three times in a Teflon beaker with 5 min. of ultrasonic cleaning each time. Finally, the sample was dried in an oven at about 70°C and set aside for isotopic analysis. Some of the yellowish organic material from modern samples 85080 and 78459 (labeled “D” in Table 2) and some of the iron-manganese crust from fossil samples JFA 2 and JFA 24C (also labeled “D” in Table 3) were also saved for isotopic analysis.

2.4. Chemical Cleaning

Early in this project it became clear that one of the major limiting factors in U-Th dating of deep-sea corals would be the ability to accurately and precisely account for initial and added thorium. Removal of thorium on or near coral surfaces can help solve this problem. We therefore modified chemical and physical cleaning techniques developed some years ago at M.I.T. for trace metal analysis (Boyle, 1981; Boyle and Keigwin, 1985/6; Shen and Boyle, 1988) and applied them to the remaining modern and fossil sub-samples. As has been demonstrated previously for surface corals and foraminifera, these techniques can remove exterior contaminants from fossil samples and improve accuracy and reproducibility. We followed the procedure of Shen and Boyle (1988) except that the pre-cleaning step was altered to better remove the black crusts. After scrubbing with a brush and deionized water, samples were placed in plastic tubes with clean distilled H₂O and ultrasonicated for 15 min. Corals were then submerged in a 50/50 mixture of 30% H₂O₂ and 1M NaOH for 15 min. with ultrasonication. This step was repeated several times until there was little crust left. Occasionally samples were scrubbed with a brush between oxidative leaches to remove loose material. The last step was a brief (30 sec. to 2 min.) rinse in a 50/50 mixture of 30% peroxide and 1% HClO₄. This step effectively removes all organic stains left on the coral but also removes about 5–10% of the skeleton. The cleaning solution in this last step always had a pH, which was monitored throughout. Samples were then thoroughly rinsed with clean distilled water and left to dry in a HEPA filtered laminar flow bench. The visible iron-magnesium oxide crusts are easily removed with these oxidizing steps, flaking off in small sheets. This suggests that the crust is bound by an organic “glue”, possibly remnant polyp organic matter. Subsequent cleaning followed the method of Shen and Boyle (1988) and used clean reagents throughout.
2.5. Thermal Ionization Mass Spectrometry

Procedures for chemical separation and instrumental analysis of uranium and thorium are modifications of those previously described for surface corals (Chen et al., 1986; Edwards et al., 1993; Edwards, 1988; Edwards et al., 1987b). Ultrasonically or chemically cleaned samples were slowly dissolved in nitric acid. This was sufficient to dissolve all samples completely, except for a residue in the iron-manganese oxide crust samples. The residue, presumably detrital aluminosilicate contained in the crust, dissolved readily in hydrofluoric acid. The solutions were spiked with $^{233}$U-$^{236}$U ($^{233}$U/$^{236}$U $= 1.010527$) and $^{229}$Th solutions of known concentration. Following the chemical separation of thorium and uranium, the thorium fraction was loaded on a graphite-coated single Re filament, which had been previously checked for its thorium blank. The filament blank for $^{232}$Th is generally 100–150 counts per second at around 1700°C and increases with increasing temperature. This is a significant fraction of the total $^{232}$Th beam in typical sample runs, particularly for the runs on small samples with relatively low $^{232}$Th concentrations. We corrected for this blank assuming an uncertainty of ±75% in the value of the filament blank. In order to minimize the filament blank, we measured $^{232}$Th at temperatures under 1700°C; nevertheless, as has been shown previously (Edwards et al., 1987b), the uncertainty in the filament blank correction is the main source of error in the $^{232}$Th measurements. The uranium fraction was loaded on a Re filament without graphite and run with the double-filament technique. Uranium and thorium were measured on the Minnesota Isotope Laboratory’s Finnigan-MAT 262-RPQ mass spectrometer on the first stage electron multiplier prior to the static quadrupole second stage. Tails were accounted for by measuring count rates at half masses.

3. RESULTS AND DISCUSSION

3.1. Reproducibility

Uranium and thorium isotope compositions of modern and fossil samples are presented in Tables 2 and 3 respectively. We measured a number of samples in replicate. In one case we analyzed separate aliquots of the same solution (Table 2: DC-1 T(I) and DC-1 T(II)). These analyses agreed within error for the $^{230}$Th age and all uranium and thorium concentrations and isotope ratios. In four cases (Table 3), we analyzed two separate septa from the same fossil coral that were cleaned using the same method. Three pairs were treated using the ultrasonic cleaning method; JFA 2 (N) I and II, JFA 24C (N) I and II, and JFA 20C (N) I and II, and one pair was treated using the chemical cleaning method; JFA 24C I and II. In all four cases, the $^{238}$U and $^{232}$Th concentrations did not replicate within analytical errors, indicating that concentrations of these nuclides differ in separate sub-samples of the same coral. In three of the cases the $^{230}$Th ages, uncorrected for initial $^{230}$Th, agreed within analytical errors. In the fourth case (the JFA 24C (N) pair), the uncorrected $^{230}$Th ages differed significantly. In this case, the $^{232}$Th concentrations differed by more than a factor of two and the $^{230}$Th ages quite likely differed because of differing initial $^{230}$Th contents (see discussion below). In all four cases the measured $\delta^{234}$U values (defined as $(^{234}$U/$^{238}$U)$_{\text{sample}}$/$^{234}$U/$^{238}$U$_{\text{standard}}$ – 1) × 1000) replicated within errors. In sum,
replicate analyses agreed within analytical error in all cases where one would expect agreement.

3.2. Modern Samples

3.2.1. Uranium concentrations and isotopic ratios

Ku et al. (1977) and Chen et al. (1986) demonstrated that within several percent uranium is conservative in seawater. Our measured uranium concentrations in modern D. cristagalli, on the other hand, vary from 2963 to 5531 ppb (Table 2). These uranium values are higher than those of most hermatypic corals (e.g., 2–4 ppm, Burnett and Veeh, 1992) and are similar to those of other ahermatypic corals (Stein et al., 1991; Thompson and Livingston, 1970; Lomitschka and Mangini, 1999). In surface corals, uranium variations are correlated to changes in sea surface temperature (Min et al., 1995; Shen and Dunbar, 1995). However, for a single septum of D. cristagalli, the measured range of uranium concentration is larger than the surface coral data, while the deep water temperature variations are much smaller. Clearly there is a combination of other environmental parameters, such as temperature, pH, carbonate ion concentration, growth rate, and/or a biologically induced “vital effect” affecting the D. cristagalli uranium concentration (Gvirtzman et al., 1973). In general, the primary uranium concentrations in deep-sea corals are higher than those of most other biogenic deep-sea carbonates. For example, foraminifera shells have primary uranium concentrations about 200 times lower than deep-sea corals (Delaney and Boyle, 1983; Henderson and O’Nions, 1995; Ku, 1965; Russell et al., 1994). These high uranium contents make deep-sea corals ideal candidates for uranium-series dating.

The $\delta^{234}$U value for modern hermatypic corals measured in the Minnesota lab is $145.8 \pm 1.9^\circ$ (Cheng et al., 1999; Edwards et al., 1993). This ratio is about 3‰ lower than earlier reports because we have used the new $\lambda_{234}$ value determined by Cheng et al. (1999). Each modern initial $\delta^{234}$U value for our deep-sea corals is within error of the surface coral value (Fig. 5, Table 2). The mean and two sigma error of all 20 values is $145.3 \pm 2.3^\circ$. As the deep-sea samples were collected from nine different depths across the Pacific, Atlantic, Indian and Southern Oceans, these data indicate that the sea water $\delta^{234}$U value is conservative in the upper 2000 meters of the world’s oceans within about $\pm 2^\circ$. In addition, surface coral data indicate that since the last glacial maximum (Bard et al., 1993; Edwards et al., 1993) and for sea level high stands over the past 200,000 years (Gallup et al., 1994; Gallup and Edwards, 1997) the $\delta^{234}$U of surface seawater has been the same as the modern value within several per mil (Henderson et al., 1993). Since seawater $\delta^{234}$U appears to be temporally and spatially constant, the $\delta^{234}$U values in fossil deep-sea corals may be used as a check of diagenetic alteration.

Fig. 4. Transmitted light image of the side view of modern D. cristagalli sample number 47413. This single septum was placed in a standard photographic enlarger to expose the density banding structure. X-rays were not required to see the bands. Alternating light and dark density bands are visible sub-parallel to the top edge of the septum. The white area on the bottom is the thickened portion where the septum connects to the rest of the skeleton around the outer edge of the coral. White flecks are from dust on the sample. Bands can be seen with the naked eye but are more clear in transmitted light.
3.2.2. Initial \(^{230}\)Th

As opposed to uranium, thorium is not conservative in seawater. Since both \(^{230}\)Th and \(^{232}\)Th concentrations increase with depth (Anderson et al., 1983; Bacon and Anderson, 1982; Cochran; 1992; Guo et al., 1995; Huh and Beasley, 1987; Huh et al., 1989; Moran et al., 1995; Nozaki and Horihe, 1983; Nozaki et al., 1987; Roy-Barman et al., 1996), we expect much higher initial \(^{230}\)Th concentrations in deep sea corals than in surface corals. Therefore, we need to estimate the initial \(^{230}\)Th/\(^{238}\)U ratio for deep-sea corals in order to calculate their \(^{230}\)Th ages. We can write the \(^{230}\)Th age equation, including the term for initial \(^{230}\)Th/\(^{238}\)U:

\[
\frac{^{230}Th}{^{238}U} = 1 + \left( \frac{^{230}Th}{^{238}U} \right)_{0} e^{-\lambda_{230}t} + \frac{^{234}U(0) - \lambda_{234}}{1000 \lambda_{230} - \lambda_{234}} \left( 1 - e^{(\lambda_{234} - \lambda_{230})t} \right)
\]

where all isotope ratios are activity ratios, the \(\lambda\)'s are decay constants, \(t\) is the \(^{230}\)Th age, \(\left(\frac{^{230}Th}{^{238}U}\right)_{0}\) is the term for initial \(^{230}\)Th/\(^{238}\)U, and \(^{234}U(0)\) is as defined previously (Edwards et al., 1987b). We can substitute \(\left(\frac{^{230}Th}{^{238}U}\right)\) (\(^{230}Th\)/\(^{238}\)U) for \(^{230}\)Th/\(^{238}\)U:

\[
^{230}Th/^{238}U = 1 + \left( \frac{^{230}Th}{^{238}U} \right)_{0} e^{-\lambda_{230}t} + \frac{^{234}U(0) - \lambda_{234}}{1000 \lambda_{230} - \lambda_{234}} \left( 1 - e^{(\lambda_{234} - \lambda_{230})t} \right)
\]

As \(^{232}\)Th/\(^{238}\)U can be measured, our problem reduces to one of estimating the initial \(^{230}\)Th/\(^{232}\)Th ratio, an issue that we will discuss at length below. Because \(^{230}\)Th/\(^{232}\)Th cannot be determined exactly, the error in its estimation introduces error in \(t\), the \(^{230}\)Th age. We will show that this uncertainty is the main source of error in the \(^{230}\)Th age for most deep-sea corals.

In general one might expect two possible sources of initial thorium: one from the water column, similar to the "hydrogenous" component of Lin et al. (1996), and one from continentally derived detrital particles. Both dissolved and particulate sea water \(^{230}\)Th/\(^{232}\)Th generally increase with depth and water mass age. Surface waters are as low as about 5–10 \times 10^{-6} (atomic ratio) (Cochran et al., 1987; Guo et al., 1995; Nozaki et al., 1987), while maximum values in the deep Pacific are \(>700 \times 10^{-6}\) (Moore, 1981). On the other hand, the thorium isotopic composition of detrital clays is expected to be close to the bulk earth value of \(4 \times 10^{-6}\), which is based on a \(^{232}\)Th/\(^{238}\)U value of 3.8 and the assumption of secular equilibrium.
Table 3. U and Th isotopic composition and $^{230}$Th ages of old deep sea corals.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Analysis number</th>
<th>$^{238}$U (ppb)</th>
<th>$^{232}$Th (ppb)</th>
<th>$^{230}$Th/$^{232}$Th (atomic x 10$^{-6}$)</th>
<th>$\delta^{234}$U (measured)</th>
<th>$^{230}$Th/$^{232}$U (activity)</th>
<th>Age (BP year$^{-1}$)</th>
<th>Cor. age (BP year$^{-1}$)</th>
<th>Cor. $\delta^{234}$U (initial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFA 2</td>
<td>2</td>
<td>3752 ± 2</td>
<td>1723 ± 26</td>
<td>4936 ± 78</td>
<td>141.3 ± 1.5</td>
<td>0.13731 ± 0.00068</td>
<td>13962 ± 75</td>
<td>147.0 ± 1.6</td>
<td>13736 ± 223</td>
</tr>
<tr>
<td></td>
<td>2 (N) (I)</td>
<td>4059 ± 2</td>
<td>4217 ± 49</td>
<td>2195 ± 28</td>
<td>142.5 ± 1.3</td>
<td>0.13842 ± 0.00076</td>
<td>14065 ± 1.3</td>
<td>148.3 ± 1.3</td>
<td>13556 ± 488</td>
</tr>
<tr>
<td></td>
<td>2 (N) (II)</td>
<td>4196 ± 2</td>
<td>6749 ± 43</td>
<td>1421 ± 16</td>
<td>141.5 ± 1.4</td>
<td>0.13814 ± 0.00124</td>
<td>14046 ± 1.5</td>
<td>147.2 ± 1.5</td>
<td>13258 ± 760</td>
</tr>
<tr>
<td></td>
<td>2 (N) (D)</td>
<td>4114 ± 4</td>
<td>757300 ± 9350</td>
<td>102 ± 2</td>
<td>143.2 ± 3.0</td>
<td>1.1357 ± 0.0172</td>
<td>13063 ± 63</td>
<td>149.0 ± 1.3</td>
<td>12951 ± 120</td>
</tr>
<tr>
<td>JFA 17</td>
<td>17</td>
<td>3851 ± 1</td>
<td>877 ± 22</td>
<td>9372 ± 232</td>
<td>143.6 ± 1.3</td>
<td>0.12923 ± 0.00057</td>
<td>13063 ± 63</td>
<td>149.0 ± 1.3</td>
<td>12951 ± 120</td>
</tr>
<tr>
<td>JFA 24C</td>
<td>24 (I)</td>
<td>3740 ± 3</td>
<td>2901 ± 26</td>
<td>3317 ± 31</td>
<td>144.5 ± 2.8</td>
<td>0.15581 ± 0.00058</td>
<td>15932 ± 73</td>
<td>151.2 ± 2.9</td>
<td>15552 ± 363</td>
</tr>
<tr>
<td></td>
<td>24 (II)</td>
<td>3858 ± 1</td>
<td>3255 ± 36</td>
<td>3202 ± 35</td>
<td>141.3 ± 1.3</td>
<td>0.15453 ± 0.00059</td>
<td>15820 ± 68</td>
<td>147.8 ± 1.4</td>
<td>15406 ± 396</td>
</tr>
<tr>
<td></td>
<td>24 (N) (I)</td>
<td>3293 ± 2</td>
<td>7960 ± 53</td>
<td>1084 ± 9</td>
<td>144.8 ± 2.1</td>
<td>0.15870 ± 0.00064</td>
<td>16245 ± 77</td>
<td>151.6 ± 2.2</td>
<td>15058 ± 1131</td>
</tr>
<tr>
<td></td>
<td>24 (N) (II)</td>
<td>3521 ± 5</td>
<td>19231 ± 176</td>
<td>502 ± 5</td>
<td>145.2 ± 4.1</td>
<td>0.16612 ± 0.00092</td>
<td>17058 ± 121</td>
<td>152.4 ± 4.4</td>
<td>14359 ± 2607</td>
</tr>
<tr>
<td></td>
<td>24 (N) (D)</td>
<td>2941 ± 40</td>
<td>4511000 ± 37800</td>
<td>48 ± 1</td>
<td>206.3 ± 79</td>
<td>4.4194 ± 0.0667</td>
<td>192370 ± 121</td>
<td>151.2 ± 4.4</td>
<td>151.2 ± 4.4</td>
</tr>
<tr>
<td>JFA 20A</td>
<td>20 A</td>
<td>4524 ± 2</td>
<td>1623 ± 24</td>
<td>23470 ± 343</td>
<td>116.6 ± 1.2</td>
<td>0.50999 ± 0.00133</td>
<td>65787 ± 254</td>
<td>140.4 ± 1.5</td>
<td>65610 ± 239</td>
</tr>
<tr>
<td></td>
<td>20 A (N)</td>
<td>4935 ± 3</td>
<td>8472 ± 48</td>
<td>4943 ± 37</td>
<td>119.7 ± 1.3</td>
<td>0.51388 ± 0.00248</td>
<td>66200 ± 445</td>
<td>144.4 ± 1.6</td>
<td>65353 ± 863</td>
</tr>
<tr>
<td>JFA 20B</td>
<td>20 B</td>
<td>4507 ± 1</td>
<td>4809 ± 43</td>
<td>6834 ± 64</td>
<td>119.7 ± 1.2</td>
<td>0.44160 ± 0.00151</td>
<td>54209 ± 248</td>
<td>139.5 ± 1.4</td>
<td>53682 ± 532</td>
</tr>
<tr>
<td></td>
<td>20 B (N)</td>
<td>4473 ± 2</td>
<td>6555 ± 35</td>
<td>5045 ± 29</td>
<td>120.9 ± 1.4</td>
<td>0.44978 ± 0.00135</td>
<td>55109 ± 229</td>
<td>141.3 ± 1.5</td>
<td>54386 ± 706</td>
</tr>
<tr>
<td>JFA 20C</td>
<td>20 C</td>
<td>3114 ± 2</td>
<td>856 ± 17</td>
<td>30920 ± 612</td>
<td>128.8 ± 1.0</td>
<td>0.51485 ± 0.00166</td>
<td>65589 ± 296</td>
<td>155.0 ± 1.3</td>
<td>65455 ± 246</td>
</tr>
<tr>
<td></td>
<td>20 C (N) (I)</td>
<td>3109 ± 1</td>
<td>2108 ± 36</td>
<td>12501 ± 213</td>
<td>142.7 ± 1.4</td>
<td>0.51334 ± 0.00144</td>
<td>64180 ± 266</td>
<td>171.1 ± 1.7</td>
<td>63854 ± 356</td>
</tr>
<tr>
<td></td>
<td>20 C (N) (II)</td>
<td>3319 ± 25</td>
<td>3043 ± 69</td>
<td>9086 ± 212</td>
<td>140.3 ± 8.7</td>
<td>0.50461 ± 0.00462</td>
<td>62914 ± 1025</td>
<td>167.6 ± 10.2</td>
<td>62471 ± 708</td>
</tr>
</tbody>
</table>

Uranium series data of fossil corals analyzed in this study. Samples labeled with an (N) were ultrasonically cleaned. All other samples were chemically cleaned as described in the text. (I) and (II) are separate pieces of the same sample. (D)—detrimental material scrubbed off the surface of the coral. All errors are 2σ. † Age before 1950. ‡ Corrected using an initial $^{230}$Th/$^{232}$Th ratio of 85 ± 80 x 10$^{-6}$. Errors are due only to the uncertainty in the initial ratio. See text.
Determination of initial $^{230}\text{Th}^{232}\text{Th}$ is not as straightforward as making an accurate measurement on a “modern sample”. If the coral was alive at the time of collection, we know the age of the youngest portion of the skeleton. However, each sub-sample has a finite mass and therefore contains material that grew over some interval of time potentially ranging from the time of collection back to the initiation of growth. A priori, the amount of radiogenic $^{230}\text{Th}$ that formed during the sample interval is not known. To calculate an initial $^{230}\text{Th}^{232}\text{Th}$ ratio from Eqn. 2 one needs to know the age (or more exactly, the mean age weighted by mass) of the sample. So, for each sub-sample, we have one equation (Eqn. 2) and two unknowns (initial $^{230}\text{Th}^{232}\text{Th}$ and age).

The classic approach to solving this type of problem is through isochron methods, in which the sub-samples have different parent-daughter ratios, but the same age and initial daughter isotope composition. We use a variation of this approach because our assumptions do not always fit those used in the isochron method and the stratigraphy of samples from the same septum are an added constraint on the age. Instead, we use development diagrams (Fig. 6, see Faure, 1986 or DePaolo, 1981 for analogous examples with other isotope systems), in which we plot ($^{230}\text{Th}^{232}\text{Th}$)$^0$ versus age for each sub-sample. Assuming closed system behavior, each sub-sample is represented by a curve (in age vs. ($^{230}\text{Th}^{232}\text{Th}$)$^0$ space) which is the solution to Eqn. 2. For modern samples, this curve closely approximates a straight line over the time scale of interest. This can be demonstrated by taking the zero and first order terms of a MacLaurin Expansion of Eqn. 2 (about $t$, assuming that decay of initial $^{230}\text{Th}$ and the ingrowth of $^{234}\text{U}$ are insignificant, and simplifying:

$$
\left( \frac{^{230}\text{Th}}{^{232}\text{Th}} \right)^d = \left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)^m \lambda_d t + \left( \frac{^{230}\text{Th}}{^{232}\text{Th}} \right)^0
$$

(3)

Here all isotope ratios are atomic ratios, the subscript “m” refers to the measured value, and the superscript “°” refers to an initial value. Because the measured $^{230}\text{Th}^{232}\text{Th}$ value is fixed, older ages correspond to smaller initial $^{230}\text{Th}^{232}\text{Th}$ ratios, and vice-versa. Pairs of ages and initial ratios lie along a line for which we know the slope and a single point. We can transform the abcissa of this line such that the zero time reference point is the measurement date rather than the initiation of growth. In this case, we are extrapolating back from measured $^{230}\text{Th}^{232}\text{Th}$ ratios instead of extrapolating forward from initial $^{230}\text{Th}^{232}\text{Th}$ ratios. Here the variable $t$, the new x-axis, is equal to $-(t + \text{sample age})$. Eqn. 3 then becomes:

$$
\left( \frac{^{230}\text{Th}}{^{232}\text{Th}} \right)^0 = \left( \frac{^{234}\text{U}}{^{238}\text{U}} \right)^m \lambda_d t + \left( \frac{^{230}\text{Th}}{^{232}\text{Th}} \right)^0
$$

(4)

By assuming that the initial $^{230}\text{Th}^{232}\text{Th}$ ratios in all sub-samples of the same coral have the same value, we can use this equation to constrain the initial $^{230}\text{Th}^{232}\text{Th}$ value (Fig. 6). If the sub-samples have the same stratigraphic position, the age and initial $^{230}\text{Th}^{232}\text{Th}$ value are represented by the intersection of the lines of the sub-samples. If the stratigraphic sequence of ages is known, the initial $^{230}\text{Th}^{232}\text{Th}$ value must fall within a range that gives a sequence of ages which agrees with the known stratigraphic order. No values of initial $^{230}\text{Th}^{232}\text{Th}$ that give ages younger than the time of collection are possible.

The development diagram for septum 47413a is shown in Figure 6. Data, including the $\sigma t$ error bars, for the bottom sub-sample of 47413a describes the dark gray wedge. Only values of initial $^{230}\text{Th}^{232}\text{Th}$ that lie within the wedge and to the right of the time of collection are possible. Similarly, the light gray area describes the range of acceptable pairs of ages and initial $^{230}\text{Th}^{232}\text{Th}$ ratios for the top of 47413a. The sides of the light gray area are curved because of measurement error propagation through the various isotopic ratios in Eqn. 4. Due to the stratigraphic order of the top and bottom pieces, the point marked “A” is the first stratigraphically acceptable initial ratio. Values higher than this intersection (younger ages) make the dark gray wedge younger than the light gray area. However, because point “A” is younger than the time of collection, the
largest stratigraphically acceptable atomic \( ^{230}\text{Th}/^{232}\text{Th} \) value is really \( 147 \times 10^{-6} \). All values between 0 and \( 147 \times 10^{-6} \) give ages for 47413a sub-samples that agree with stratigraphic constraints and do not give negative ages for the septum. One of the two middle pieces from this septum is shown for completeness (black lines), but does not further constrain the system. In this manner, each coral septum in Table 2 can be analyzed for both the minimum and maximum allowable initial \( ^{230}\text{Th}/^{232}\text{Th} \) ratios.

Due to lack of space, we do not show all data in graphical form. Instead, we summarize the results of this analysis in Table 4 and Figure 7. Outside of one coral, all samples have initial isotopic compositions that fall between 0 and \( 160 \times 10^{-6} \) (the black dashed line in Fig. 7). Sample 84820 gives a very large range of possible initial \( ^{230}\text{Th}/^{232}\text{Th} \) values and correspondingly old ages. This sample was probably already dead when dredged from the ocean bottom and the large isotopic ratio is due to radiogenic \( ^{230}\text{Th} \) rather than a high initial ratio (see below).

### 3.3. Growth Rate and Band Periodicity from Measurements on Modern Samples

In order to use individual \textit{D. cristagalli} specimens as archives of oceanographic time series, we need to constrain their growth rate and band periodicity. Given the constraints on initial \( ^{230}\text{Th}/^{232}\text{Th} \) deduced in the previous section, we can use the age equation and the mass weighted mean of our isotope data to calculate the mean septal age for each sample (Table 4). Ages for all sub-samples are less than 150 yr., and, for the most part, in the range of tens of years or even less. Furthermore, the age differences between stratigraphically older and younger sub-samples of the same septa (Table 2) are generally less than 20 yr. For four of the five specimens, the youngest sub-sample of each septum has an uncorrected age within error of 0 to 20 yr., and a whole septum mean age less than 80 yr. However, for both septa analyzed from sample number 84820, the ages of the youngest sub-samples are much greater than 20 yr. (150 ± 7 and 158 ± 9 yr., uncorrected for initial \( ^{230}\text{Th} \)). Either this coral grew more slowly than the others, or it had a very high \( ^{230}\text{Th}/^{232}\text{Th} \) initial ratio, or it died prior to collection. Because the difference in age between the top and bottom portions is similar to the same difference in the other 4 specimens, we conclude that coral 84820 died long before it was collected. In this case we can not constrain the \( ^{230}\text{Th}/^{232}\text{Th} \) or the mean age of the sample so we do not discuss the calculated growth rate for 84820.

For the other samples, we calculate growth rates from mean
Given these assumptions, twice the mean age divided by the constant with time and that the coral died when it was collected. 232 Th ratios is between 0 and 160. Nearby water column values (open squares) and measured detrital values. The overall range of possible initial 230 Th/232 Th values is consistent with these sample 85080 are much lower than our estimated range, lending sup-
port to the argument that this sample died before collection. In general, sample 84820 and 78459’s range of initial 230 Th/232 Th values is consistent with these sample 84820. Water values from the area around the anomalous sample 84820 are much lower than our estimated range, lending support to the argument that this sample died before collection. In general, where data to make such comparisons exist, the initial thorium isotope ratios of the aragonitic portion of the specimen are consistent with sea water and detrital values. The overall range of possible initial 230 Th/232 Th ratios is between 0 and 160 × 10⁻⁶.

Table 4. Summary of evolution isochron data, growth rates and band periodicity.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Analysis number</th>
<th>230/232</th>
<th>Mean septal Age</th>
<th>Growth Rate</th>
<th>Periodicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>max</td>
<td>Error</td>
<td>Length</td>
<td>Error</td>
</tr>
<tr>
<td>47413</td>
<td>DC-2a</td>
<td>0</td>
<td>147</td>
<td>7.5</td>
<td>6</td>
</tr>
<tr>
<td>85080</td>
<td>DC-2b</td>
<td>0</td>
<td>994</td>
<td>6.6</td>
<td>39</td>
</tr>
<tr>
<td>84820</td>
<td>DC-3a</td>
<td>0</td>
<td>155</td>
<td>2.5</td>
<td>10</td>
</tr>
<tr>
<td>478459</td>
<td>DC-1</td>
<td>50</td>
<td>130</td>
<td>72</td>
<td>9</td>
</tr>
</tbody>
</table>

Summary of initial 230 Th/232 Th ratio results from the development diagrams (see Fig. 6). Mean septal ages are calculated using a weighted average of all U-series data from a single septum. Growth rates/periodicities are calculated by dividing the length/bands by twice the mean septal age. ² Ages use an initial atomic 230 Th/232 Th ratio of 80 ± 80 × 10⁻⁶ except for 47840 and 78459 where the ratio is better constrained by the development diagram data. Ages are also corrected for time since collection. ³ Includes data from only the top piece. Length and bands are adjusted accordingly.
depths of coral growth, banding cannot be controlled by seasonal variations in sunlight, temperature or other climate variables. The banding pattern may be governed by endogenous physiological rhythms (Emilianii et al., 1978) or by the raining food supply from above (Deuser et al., 1981).

3.4. Fossil Samples

3.4.1. Sources of \(^{232}\text{Th}\) and diageneric Uranium

Ultimately we would like to use data from modern samples to correct fossil coral ages for initial and added thorium. Fossil samples are clearly enriched in \(^{232}\text{Th}\) relative to modern samples (compare Tables 2 and 3). Largely this enrichment is due to the black crusts that coat older corals and are elevated in \(^{232}\text{Th}\) by about 10\(^6\) times over modern samples (labeled “D” in Table 3). As these crusts also contain \(^{230}\text{Th}\) associated with the concentrations ranging from 856 to 4809 ppt, about 30 – 80% lower than (Edwards, 1988; Gallup and Edwards, 1997; Richter and Turekian, 1993), nor is it likely to have shifted significantly over time scales of several thousand years or less. Thus, the range in \(\delta^{234}\text{U}\), the fact that most of the values are distinguishable from the modern value, and the differing \(\delta^{234}\text{U}\) within specimen JFA 20C all suggest diageneric exchange of uranium. The degree of exchange is more extensive in the older corals than in the younger samples. Although the source of the diageneric uranium is unknown, sea water and pore fluid uranium could plausibly provide uranium of the appropriate isotopic composition to cause these effects. In the following sections, we investigate and compare two calculation methods that correct for these potential problems to U-series dating in fossil deep-sea corals.

3.4.2. Correcting fossil coral ages: Equation 2

In section 3.2.2 we established that all samples in our modern data set have an initial atomic \(^{230}\text{Th}^{232}\text{Th}\) ratio lower than 160 \(\times\) 10\(^{-6}\) (Table 4, Fig. 7). Using Eqn. 2 and a value of 80 \(\pm\) 80 \(\times\) 10\(^{-6}\) for \(^{230}\text{Th}^{232}\text{Th}\), we can calculate a conservative estimate for the age range of a fossil sample. However, as discussed above, initial thorium is not the only component of non-radiogenic thorium in our fossil corals. If we assume that the added thorium has the same isotopic composition as the initial thorium, within the broad bounds that we have set, and that the thorium was added soon after coral growth, then Eqn. 2 is a solution to the age equation. The actual timing of thorium addition, whether episodic or continuous, early or late is not critical for corals significantly younger than the half-life of \(^{236}\text{Th}\) (75 ky), but becomes an issue for samples older than a good fraction of a \(^{236}\text{Th}\) half-life.

Given the measured modern initial Th isotopic range, we can evaluate the sensitivity of calculated age errors to the amount of measured \(^{232}\text{Th}\). Figure 8 is a plot of error in age versus age for a \(^{230}\text{Th}^{232}\text{Th}\) value equal to 80 \(\pm\) 80 \(\times\) 10\(^{-6}\) and a uranium concentration of 4 ppm. The thick black line represents typical analytical errors as a function of age. The solid circles are the age and 2\(\sigma\) error in age for all sub-samples, uncorrected for non-radiogenic thorium. The open circles represent the same analyses corrected for non-radiogenic \(^{230}\text{Th}\) using Eqn. 2 and the 80 \(\pm\) 80 value. For these, uncertainties are a combination of analytical error and the assumed range in the \(^{230}\text{Th}^{232}\text{Th}\) value. As the open circles plot above the solid circles, in some cases by more than an order of magnitude, the dominant source of error is clearly not analytical but the range in initial thorium isotopic composition. Thin black lines are the calculated total error in age as a function of age, contoured in \(^{232}\text{Th}\) concentration. Where these lines are horizontal, age errors are dominated by the \(^{230}\text{Th}^{232}\text{Th}\) ratio. The thick dashed line marks the region where analytical errors begin to contribute to the age error as the influence of the error on the \(^{230}\text{Th}^{232}\text{Th}\) ratio falls away. These contours illustrate quantitatively the point made above, that all other factors being equal, the lower the \(^{232}\text{Th}\) concentration, the lower the error in age. For paired \(^{230}\text{Th}^{14}\text{C}\) studies aimed at determining the ventilation age of past water masses, one would like to determine \(^{230}\text{Th}\) age to \(\pm\) 10\(^3\) years or better (Adkins et al., 1998; Mangini et al., 1998). Figure 8 shows that to achieve this, one must clean deglacial age corals to the level of about 1000 ppt. Table 3 indicates that our cleaning procedure has achieved these levels in some cases.
Fig. 8. Age plotted versus its 2σ error. Solid points are the uncorrected deep-sea coral data and are close to the typical analytical uncertainty (solid black line). After correction (open circles) using Eqn. 2, points are shifted to younger ages and larger errors. Each row in Tables 2 and 3 represents one pair of points, one corrected (open) and one uncorrected (solid). The relation between measured \([^{232}\text{Th}]\) and the error in age for an assumed initial \(\frac{^{230}\text{Th}}{^{232}\text{Th}}\) ratio of \(80 \pm 80 \times 10^{-6}\) is given by the thin lines. Higher \(^{232}\text{Th}\) results in a larger absolute age uncertainty. For young ages, the error is dominated by uncertainty in the initial Th correction. The older the age and the smaller the measured \([^{232}\text{Th}]\) the lower the relative age error. In the region between the dashed and thick black lines, age uncertainty is jointly determined by analytical and initial Th errors. It is clear that further cleaning of \(^{232}\text{Th}\) from older corals can significantly lower age uncertainties.

3.4.3. Correcting fossil coral ages: Isochrons

In addition to the method of correcting for initial \(^{230}\text{Th}\) using Eqn. 2 and our estimate of initial \(\frac{^{230}\text{Th}}{^{232}\text{Th}}\), we have also calculated ages by applying isochron methods to different fragments of the same coral. Isochrons, in essence, allow one to calculate a radiogenic end member isotopic composition from a set of two or more materials that lie on a two-component mixing line between radiogenic and non-radiogenic components. Given the isotopic composition of the radiogenic component, one can calculate an age. Inherent in the calculation is the assumption that there are only two end members, an assumption that deep sea corals potentially violate. For example, each coral is deposited over a finite interval of time so that the radiogenic component of the oldest part of the coral may have a different isotopic composition than the radiogenic component of the youngest part of the coral. Because the lifetime of the coral (typically tens to 200 yr based on our growth rate determinations) is similar to our analytical error in age (for corals older than about 10 ka), this is not a significant problem for corals older than about 10 ka. Also, non-radiogenic components are added at different times (as evidenced by fossil corals with generally higher \(^{232}\text{Th}\) concentrations than modern corals). Earlier generations of non-radiogenic component may have changed isotopic composition by radioactive decay and ingrowth by the time subsequent generations of non-radiogenic component are added, again violating the two-component assumption. Isochron methods do not require that the non-radiogenic component be present initially, but do require that the non-radiogenic component is introduced at one instant in time. For samples significantly younger than the half-life of \(^{230}\text{Th}\), the addition of a radiogenic component over a period of time should not introduce significant inaccuracy. Therefore the timing of addition should not be an issue for our 10 to 20 ka old samples. A third potential problem is the fact that there are at least two possible non-radiogenic thorium components, the hydrogenous and detrital components discussed above. A fourth potential problem relates to the issue of the cleaning of some of our samples by chemical (as opposed to physical) techniques. This set of procedures could potentially shift U/Th ratios either by preferential leaching from the solid or by preferential adsorption onto the solid. To a certain degree, we can test for all of these potential problems with isochrons. If there are three components present in different proportions in different sub-samples, the isotopic composition of the sub-samples would likely deviate from a line in an isochron plot. If cleaning techniques shift U/Th ratios, chemically treated samples should also deviate from a line defined by untreated samples.

Results of isochron calculations (Ludwig, 1993; Ludwig and Titterington, 1994) are shown in Table 5 and Figure 9. For all three corals with enough data points, the MSWD statistic exceeds one. As a measure of the linear fit of each isochron, this result implies that one or more of the assumptions outlined above is not valid. However, this statistic is sensitive to the errors assigned to each measurement. Doubling the \(^{232}\text{Th}\) uncertainties reduces the MSWD to near or below one for each sample. As \(^{232}\text{Th}\) errors are difficult to evaluate due to the uncertainty in the filament blank, underestimating this value is the likely reason for elevated MSWDs on our regressions. Alternately, the slightly elevated MSWDs may reflect slight deviations from linearity due to natural processes or chemical treatment. If so, these deviations are on the order of analytical error, suggesting that the isochron approach is valid at about the level of our analytical precision. Additionally, chemically treated and untreated sub-samples are co-linear at about the level of our analytical precision, suggesting that chemical cleaning has not shifted U/Th ratios significantly.

Corals in Table 3 fall into two age ranges, 10–20 ka and 50–70 ka. Assuming that the non-radiogenic component was added early for the younger samples JFA-2 and JFA 24C, we can calculate initial \(\frac{^{230}\text{Th}}{^{232}\text{Th}}\) ratios for both corals from the intercepts in Figure 9. For each sample these values (\(19 \times 10^{-6}\) for JFA-2 and \(37 \times 10^{-6}\) for JFA-24) fall within the \(80 \pm 80 \times 10^{-6}\) range that we established with modern corals. Thus, for these younger samples, both the isochron and initial \(\frac{^{230}\text{Th}}{^{232}\text{Th}}\) methods appear to be valid. In each case, it is important that at least one sub-sample have low \(^{232}\text{Th}\) concentration to get a reasonable age estimate. In practice, this requires the use of some sort of chemical cleaning technique to remove surficial contaminants.

For the three samples (JFA-20A, JFA-20B, and JFA-20C)
between 50 and 70 ka old, we have also calculated ages using both correction schemes (Tables 3 and 5). Corrected and uncorrected ages for each sample differ by no more than a few thousand years, suggesting that the ages are accurate to about this level. However, there are some consistencies and some inconsistencies in the details. Sample JFA 20A gives consistent corrected ages (Table 3). Sample JFA 20B yields an isochron age that is slightly younger than the ages corrected using the initial value, while sample JFA 20C gives an isochron age that is older. However, the initial $^{230}$Th/$^{232}$Th ratio calculated for this sample, assuming that the non-radiogenic component was added early, is negative (Fig. 9). This observation is consistent with a non-radiogenic component that had a $^{230}$Th/$^{238}$U ratio significantly less than that of the primary coralline aragonite at the time of addition; and that was added significantly after original precipitation of the primary coralline aragonite. Thus, it appears that both uranium and thorium could have been added to this sample. The uranium isotopic composition of the sub-samples supports this idea. The sub-samples with the highest $^{232}$Th concentrations have initial $\delta^{234}$U(T) values that are furthest from the marine value. The correction for initial $^{230}$Th using the value is not designed to correct for uranium addition and therefore yields an inaccurate age in this case. The isochron method, on the other hand, may well yield an accurate age. In addition to co-linearity of the sub-sample points, the initial $\delta^{234}$U value calculated using the

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Data points</th>
<th>Corrected ($^{230}$Th/$^{238}$U)</th>
<th>Corrected ($^{234}$U/$^{238}$U)</th>
<th>Corrected age (year)</th>
<th>95% Conf. error (yr)*</th>
<th>Corrected $\delta^{234}$U(T)</th>
<th>MSWD value*</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFA-2</td>
<td>4</td>
<td>0.13322 ± 0.00048</td>
<td>1.1418 ± 0.00084</td>
<td>13510 ± 50</td>
<td>±280</td>
<td>147.3 ± 1.0</td>
<td>15.1</td>
</tr>
<tr>
<td>JFA-24C</td>
<td>5</td>
<td>0.15241 ± 0.00033</td>
<td>1.1428 ± 0.00103</td>
<td>15580 ± 40</td>
<td>±130</td>
<td>149.2 ± 1.1</td>
<td>7.39</td>
</tr>
<tr>
<td>JFA-20A</td>
<td>2</td>
<td>0.50889 ± 0.00178</td>
<td>1.1158 ± 0.00159</td>
<td>66880 ± 340</td>
<td>139.4 ± 1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JFA-20B</td>
<td>2</td>
<td>0.42499 ± 0.00647</td>
<td>1.1163 ± 0.00549</td>
<td>51830 ± 1100</td>
<td>134.6 ± 6.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JFA-20C</td>
<td>3</td>
<td>0.51718 ± 0.00270</td>
<td>1.1195 ± 0.00212</td>
<td>66800 ± 500</td>
<td>±2200</td>
<td>144.3 ± 2.6</td>
<td>4.39</td>
</tr>
</tbody>
</table>

Results of the isochron calculations for fossil deep-sea corals. Calculations are based on “Rosholt Type-II diagrams” (Ludwig and Titterington, 1994) and were performed using the UISO program (Ludwig, 1993). * Age before 1950. * Mean Square of Weighted Deviates of data from the regression line.

Fig. 9. Isochrons for three fossil deep-sea corals. These plots are half of a traditional Rosholt “Type II” isochron diagram. Calculation of isochrons and error ellipses follow the method of (Ludwig and Titterington, 1994) using the program of (Ludwig, 1993). Normally isochron plots use activity ratios, however we use atomic ratios to emphasize the implied initial $^{230}$Th/$^{232}$Th represented by the $y$-intercepts. The lowest points in JFA 2 and JFA 24C are from detrital pieces scraped from the coral exterior. Gray scale points at the high end of each plot were chemically cleaned.
Isochron method is indistinguishable from the marine value. It also appears that our chemical cleaning method removed most of the added uranium as well as most of the added thorium. The two sub-samples cleaned only by ultrasonic methods, have high \(^{232}\text{U}\) (and high \(^{232}\text{Th}\)), whereas the sub-sample that was also chemically cleaned, has a \(^{234}\text{U}\) much closer to the modern value (and low \(^{232}\text{Th}\)).

In sum, both isochron methods and methods that use modern \(^{230}\text{Th}/^{232}\text{Th}\) values to correct for initial \(^{230}\text{Th}\) give consistent results for samples in the 10 to 20 ka age range. Samples in the 50 to 70 ka age range give consistent results within a few thousand years, but in at least one case show clear evidence for diagenetic addition of both uranium and thorium. In this case, the isochron method appears to have corrected for this diagenetic component. For all fossil samples, chemical cleaning methods removed added thorium and uranium. This cleaning step is important in reducing errors in U-Th dating of fossil corals. Further improvements in cleaning techniques would further reduce dating errors.

4. CONCLUSIONS

Uranium rich deep-sea corals are suitable for precise dating by the \(^{238}\text{U}/^{234}\text{U}:^{230}\text{Th}\) decay scheme. Measurements on a suite of modern \textit{D. cristagalli} constrain the growth rate of this pseudo-colonial species to be between 0.1 and 3.1 mm/yr. Because of uncertainties in the amount of initial \(^{230}\text{Th}\), relative errors on growth rates appear large. However, maximum ages, and minimum growth rates, are well constrained because of the relatively low amounts of measured \(^{230}\text{Th}\). Combining age determinations with counts of density bands provides an estimate of assumed initial \(^{230}\text{Th}/^{232}\text{Th}\) ratios, \(80 \times 10^{-6}\). Data from modern deep-sea corals indicate that this species is conservative in the upper 2000 meters of the water column. Because this sample set comes from a variety of open ocean settings, \(^{234}\text{U}\) initial measurements in fossil corals can be an indicator of diagenetic alteration. Age errors on fossil samples exceed the analytical uncertainty because of the range of assumed initial \(^{230}\text{Th}/^{232}\text{Th}\) ratios, \(80 \pm 80 \times 10^{-6}\). Reducing the amount of measured \(^{232}\text{Th}\), by using more rigorous cleaning techniques, is the most promising way to improve the precision of fossil ages. Isochron ages for samples of deglacial age agree with our \(^{232}\text{Th}\) corrected ages indicating that the proposed method properly accounts for all initial \(^{230}\text{Th}\). Older specimens with more diagenetic alteration, may require better cleaning and/or isochron measurements to obtain accurate and precise ages.

Acknowledgments—D. Richards and J. Doral provided stimulating discussions about many of the issues raised in this work. S. Cairns helped identify the coral samples. T. Kleindinst of WHOI produced the photograph in Figure 4. We would like to thank G. Henderson and D. Muhs for helpful reviews of the manuscript. JFA thanks the UCAR Post-Doctoral Fellowship Program and LDEO for support during the writing of this paper.

REFERENCES


Druffel E. R. M., King L. L., Belastock R. A., and Buesseler K. O.


