

Uranium-series Dating of Marine and Lacustrine Carbonates

R.L. Edwards¹, C.D. Gallup², and H. Cheng¹

¹*Department of Geology and Geophysics
University of Minnesota, Twin Cities
Minneapolis, Minnesota, 55455, U.S.A.*

²*Department of Geological Sciences
University of Minnesota, Duluth
Duluth, Minnesota, 55812, U.S.A.*

1. HISTORICAL CONSIDERATIONS

Of the possible uranium-series dating schemes, the most important and most widely applied to marine carbonates is ^{230}Th dating, with ^{231}Pa dating playing an increasingly important role. For this reason, this review will focus on these two methods. ^{230}Th dating, also referred to as U/Th dating or ^{238}U - ^{234}U - ^{230}Th dating, involves calculating ages from radioactive decay and ingrowth relationships among ^{238}U , ^{234}U , and ^{230}Th . ^{232}Th is also typically measured as a long-lived, essentially stable index isotope (over the time scales relevant to ^{230}Th dating). At present ^{230}Th dating can, in principle, be used to date materials as young as 3 years and in excess of 600,000 years (Edwards et al. 1987a, 1993; Edwards 1988; see Stirling et al. 2001 for an example of dating corals in excess of 600,000 years old). ^{231}Pa dating, also referred to as U/Pa dating, involves calculating ages from the ingrowth of ^{231}Pa from its grandparent ^{235}U . At present ^{231}Pa dating can be used to date materials as young as 10 years and as old 250,000 years (Edwards et al. 1997). ^{230}Th dating covers all of the ^{231}Pa time range and more, with somewhat higher precision, and is therefore the method of choice if a single method is applied. However, the combination of ^{231}Pa and ^{230}Th dating is of great importance in assessing possible diagenetic mobilization of the pertinent nuclides, and thereby, the accuracy of the ages (Allegre 1964; Ku 1968). Even if the primary age exceeds the 250,000 year limit of ^{231}Pa dating, the combined methods can be used to assess the degree to which the samples have remained closed over the past 250,000 years (e.g., Edwards et al. 1997). Thus ^{231}Pa analysis can play an important role in assessing age accuracy. Taken together, ^{230}Th and ^{231}Pa dating cover a critical time period in earth history, which often cannot be accessed with other radiometric dating techniques. Other reviews that may be of interest to the reader include a review of dating of marine sediments by Ku (1976), a review of disequilibrium dating methods (Ivanovich and Harmon 1992), and portions of the lead author's doctoral thesis (Edwards 1988), which includes a review of ^{230}Th dating from the discovery of radioactivity (Becquerel 1896) until 1988, a detailed discussion of mass spectrometric techniques for measurement of ^{230}Th and ^{234}U , and the first in depth discussion of models of marine uranium isotopic composition.

Marine and lacustrine carbonates that have been particularly amenable to ^{230}Th dating (and in some cases ^{231}Pa dating) include coralline aragonite (Barnes et al. 1956), aragonitic oolites (Veeh 1966), aragonitic carbonate bank sediments (Slowey et al. 1996), and lacustrine tufas (Kaufmann and Broecker 1965) and other lacustrine precipitates (e.g., Ku et al. 1998; Schramm et al. 2000). Because of the large amount of work that has been done with coralline aragonite, this review will focus on dating of corals that live in shallow waters. We will then discuss dating of some of the other materials with regard to the surface coral discussion.

Historically, the most important applications of uranium-series dating techniques of marine and lacustrine carbonates have followed soon after important technical breakthroughs. Two factors have generated this close link. First, such dating methods are important because they can elucidate a broad range of processes including the timing, nature, and causes of climate change, oceanographic processes, and tectonic and seismic processes. ^{230}Th dating has also played a central role in calibration of the radiocarbon time scale and in elucidating atmospheric radiocarbon history. In some cases, ^{230}Th or ^{231}Pa dating has been the only way to characterize some aspect of these processes. Second, for most of the last century the field has been limited by measurement capabilities, which have, in turn limited the degree to which we can characterize these important processes. Thus, technical advances have generally been followed, soon thereafter by uranium-series dating applications.

The reasons for the technical limitations are the vanishingly small concentrations of the key intermediate daughter nuclides. For example, a relatively high concentration material (a 50,000 year old coral) typically has a ^{230}Th concentration of about 100 femtomoles/gram (60 billion atoms/g) and a ^{231}Pa concentration of about 3 femtomoles/gram (2 billion atoms/g). An intermediate concentration material (a 100 year old coral) has a ^{230}Th concentration of about 200 attomoles/gram (100 million atoms/g) and a ^{231}Pa concentration of about 8 attomoles/gram (5 million atoms/gram). At the extreme low end of the concentration range, surface seawater contains about 4 yoctomoles (yocto = 10^{-21}) of $^{230}\text{Th}/\text{g}$ (3000 atoms of $^{230}\text{Th}/\text{g}$) and about 80 zeptomoles (zepto = 10^{-24}) of $^{231}\text{Pa}/\text{g}$ (50 ^{231}Pa atoms/g). Although we are still limited by analytical capabilities for some applications and are actively pursuing analytical improvements, measurements of ^{230}Th and ^{231}Pa in all of the above materials can now be made with relatively small samples and relatively high precision, despite these low concentrations.

Historically this was not always the case. ^{230}Th was first identified by Boltwood (1907), prior to the discovery of isotopes and was initially called "ionium." However, direct measurements of ^{230}Th concentrations in natural materials were not made until half a century later when Isaac and Picciotto (1953) applied nuclear track techniques to deep-sea sediments. The first demonstration that ^{230}Th could be used to date carbonates (corals) was by Barnes et al. (1956), using alpha-counting techniques to measure the pertinent nuclides. This work spawned a whole field that depended upon alpha-counting uranium-series measurements of natural materials. The field flourished in the 1960's and 1970's. A large portion of this effort focused on ^{230}Th dating of marine carbonates, principally corals (e.g., Veeh 1966; Broecker et al. 1968; Mesolella et al. 1969; Bloom et al. 1974; Chappell 1974; Ku et al. 1974). The field ultimately languished because of the technical limitations of alpha-counting techniques, in terms of sample size and precision (see Edwards 1988, 2000; Wasserburg 2000). The basic problem was a limit on the fraction of atoms that can be detected by decay counting techniques given the large difference between the half-lives of the pertinent nuclides (on the order of 10^5 years or more) and reasonable laboratory counting times (weeks). This problem was solved with the development of mass spectrometric methods for the measurement of ^{234}U (Chen et al. 1986) and ^{230}Th (Edwards et al. 1987a) in natural materials. Mass spectrometric measurements obviate the need to wait for the nuclides of interest to decay as mass spectrometers detect the ions/atoms of interest directly. In this regard, the development of mass spectrometric techniques for ^{230}Th and ^{234}U measurement is analogous to the development of accelerator mass spectrometer techniques for ^{14}C measurement, which improved upon traditional beta-counting techniques. Mass spectrometric methods for measuring ^{230}Th and ^{234}U greatly reduced sample size requirements and improved analytical precision. These technical improvements reinvigorated uranium-series studies and spawned a new era of in the full range of fields discussed in this book. With regard to

dating of carbonates, the technique improved the precision of ^{230}Th ages, extended the range of ^{230}Th dating to both older and younger age, improved our ability to detect diagenetic alteration of nuclides used in ^{230}Th dating, and generated substantial activity (see below) in ^{230}Th dating applications to paleoclimatology, paleoceanography, ^{14}C calibration and atmospheric ^{14}C history, and tectonics. Today, the original mass spectrometric technique (Edwards et al. 1987a) is still the preferred method for analyzing ^{238}U , ^{235}U , ^{234}U , ^{230}Th , and ^{232}Th , with a number of modifications applied by different laboratories.

^{231}Pa measurements and their relationship to carbonate dating follow a similar history. Protactinium was discovered by Fajans and Gohring in 1913 in studies of ^{234}Pa . Protactinium was initially called “brevium” reflecting ^{234}Pa 's short half-life (6.7 hours). Meitner and Hahn identified ^{231}Pa in 1918 and renamed the element protoactinium, as ^{231}Pa (the longest-lived isotope of protactinium) is the parent of ^{227}Ac , the longest-lived isotope of actinium. The team of Soddy, Cranson, and Fleck and independently, Fajans, also isolated ^{231}Pa at about the same time as Meitner and Hahn. “Protoactinium” was later shortened to “protactinium.” Early decay-counting methods for direct measurement of ^{231}Pa in natural materials were presented by Potratz and Bonner (1958) and Sackett (1960). Rosholt (1957), Koczy et al. (1957), and Sackett et al. (1958) present early decay-counting methods for indirect determination of natural levels of ^{231}Pa via measurement of ^{227}Th as a proxy for its grandparent ^{231}Pa . Early applications of ^{231}Pa to the dating of marine carbonates include contributions by Rosholt and Antal (1962), Sakanoue et al. (1967), and Ku (1968). The method was applied in conjunction with ^{230}Th dating to make key tests of open system behavior in marine carbonates (e.g., Ku 1968; Rosholt 1967; Szabo and Rosholt 1969; Kaufmann et al. 1971). Analogous to the development of mass spectrometric techniques for ^{230}Th and ^{234}U , similar techniques were developed for the measurement of ^{231}Pa (Pickett et al. 1994). This method has already begun to fuel activity in the full range of fields discussed in this book. The first application of the Pickett et al. (1994) mass spectrometric techniques to the dating of carbonates was performed by Edwards et al. (1997). As with ^{230}Th , the use of mass spectrometric ^{231}Pa measurement techniques (as opposed to traditional decay counting techniques) improves the precision of ages, reduces sample size requirements, and extends the range of ^{231}Pa dating to both older and younger times. As discussed below, ^{231}Pa dating has and will play a critical role in combination with ^{230}Th dating in testing for diagenesis and age accuracy.

2. THEORY

2.1. Decay chains

^{238}U decay chain. ^{230}Th dating is based on the initial portion of the ^{238}U decay chain (see Bourdon and Turner 2003). ^{238}U decays by alpha emission with a half-life of $4.4683 \pm 0.0048 \times 10^9$ years (Jaffey et al. 1971) to ^{234}Th , which in turn decays (half-life = 24.1 days) by beta emission to ^{234}Pa , which decays (half-life = 6.7 hours) by beta emission to ^{234}U , which decays (half-life = $245,250 \pm 490$ years, Cheng et al. 2000b) by alpha emission to ^{230}Th (half-life = $75,690 \pm 230$, Cheng et al. 2000b), which decays through a series of intermediate daughters ultimately to stable ^{206}Pb . Because of their short half-lives compared to the timescales in question, ^{234}Th and ^{234}Pa can be ignored in carbonate dating applications, and from a mathematical standpoint, we can view ^{238}U as decaying directly to ^{234}U . (Despite our slight herein, ^{234}Th does have the important distinction of being one the radionuclides that was originally used to determine the decay law $dN/dt = -\lambda N$ or $N = N^0 e^{-\lambda t}$, where N is the present number of a parent atom, N^0 is the initial number of parent atoms, t is time and λ is the decay constant. Rutherford and Soddy 1902). For carbonate dating, the pertinent nuclides are: ^{238}U , ^{234}U , and ^{230}Th .

^{235}U decay chain. ^{231}Pa dating is based on the initial portion of the ^{235}U decay chain. ^{235}U decays by alpha emission (half-life = $7.0381 \pm 0.0096 \times 10^8$ years; Jaffey et al. 1971) to ^{231}Th , which decays (half-life = 1.06 days) to ^{231}Pa , which decays (half-life = 32760 ± 220 y, Robert et al. 1969) through a set of intermediate daughters ultimately to ^{207}Pb . Because of its short half-life, ^{231}Th can be ignored for ^{231}Pa dating applications. Thus, the pertinent nuclides for ^{231}Pa dating are ^{235}U and ^{231}Pa .

2.2. Secular equilibrium and uranium-series dating

In decay chains like the ^{238}U and ^{235}U chains, if a system remains closed to chemical exchange for time scales that are long compared to the half-lives of the intermediate daughters, the system reaches a state of secular equilibrium (see Bourdon and Turner 2003) in which the activities of all of the nuclides in a particular decay chain are equal. All U-series dating methods depend on some natural process that fractionates nuclides in the decay chain and thereby disrupts this secular equilibrium state. In the case of ^{230}Th and ^{231}Pa dating of marine and lacustrine carbonates, this event is the extreme fractionation of the parent (uranium, which is generally soluble in natural waters) from the daughter (thorium or protactinium, which generally have low solubilities in natural waters) during weathering and the hydrologic cycle. If one knows isotope ratios immediately after the fractionation event, the subsequent approach to secular equilibrium is a function of time, which can be calculated from the equations of radioactive decay and ingrowth (Bateman 1910).

2.3. ^{230}Th , ^{231}Pa , and $^{230}\text{Th}/^{231}\text{Pa}$ age equations

Initial daughter isotope abundances. A fundamental issue in many radiometric dating systems is the ability to quantify the initial amount of daughter isotope, permitting a determination of the relative fractions of radiogenic and initial daughter. The age is then calculated from the amount of radiogenic daughter. Ideally the initial amount of radiogenic daughter is negligible and correction for initial daughter is not necessary. If the initial amount of daughter is small but significant, it may be possible to make the correction by estimating the initial ratio of the daughter isotope to a stable isotope of the same element as the daughter. This ratio is then multiplied by the present abundance of the stable isotope as an estimate of the initial daughter abundance. If the initial amount of daughter is yet higher, then isochron techniques may be required in order to resolve the initial and radiogenic components (see below and Ludwig 2003).

Fractionation of Th and Pa daughter isotopes from U parent isotopes. One of the great advantages of ^{230}Th and ^{231}Pa dating of corals is that initial daughter concentrations are extremely low, in most cases negligible. This results from the extreme fractionation of uranium from both thorium and protactinium during the weathering process. All are actinides, but have different valences under oxidizing conditions. Uranium is typically +6 under oxidizing conditions, protactinium, +5, and thorium, +4. Uranium is soluble as uranyl ion and in various uranyl carbonate forms. Thorium has extremely low solubility in virtually all natural waters (extremely alkaline waters being the exception). Protactinium also has low solubility in natural waters, although its solubility is generally slightly higher than for thorium. A striking illustration of the extreme solubility difference between uranium and the other two elements is the fact that surface sea water has $^{230}\text{Th}/^{238}\text{U}$ values 10^5 times lower than secular equilibrium values (Moore 1981), and $^{231}\text{Pa}/^{235}\text{U}$ values 10^4 times lower than secular equilibrium (Nozaki and Nakanishi 1985). The initial fractionation of uranium from thorium and protactinium takes place during weathering and soil formation (see Chabaux et al. 2003) where a significant proportion of the uranium tends to dissolve in the aqueous phase and both thorium and protactinium tend to remain associated with solid phases. This process is initially responsible for the

relatively high surface water concentrations of uranium and low concentrations of thorium and protactinium (see Porcelli and Swarzenski 2003).

Uranium in solution decays to produce both ^{230}Th and ^{231}Pa . Nevertheless, the aqueous concentrations of ^{230}Th and ^{231}Pa in surface seawater do not build up because of they are continuously removed by adsorption onto solid particles and complexation with organic molecules associated with solid particles (see Cochran and Masque 2003). Most of this ^{230}Th and ^{231}Pa is removed from the water column as the particles with which they are associated settle to the seafloor. However, as the particles settle through the water column, the adsorbed/complexed thorium and protactinium continuously re-equilibrate with seawater (see the reversible exchange model of Bacon and Anderson, 1982). The process is analogous to an ion exchange column (particles equivalent to the solution passing through an exchange column and sea water equivalent to the ion exchange resin). As a result, both ^{230}Th and ^{231}Pa generally increase with depth in the ocean. Thus, with regard to dating of marine carbonates, surface carbonates are less likely to have significant initial ^{230}Th and ^{231}Pa than deep water carbonates. This is the main difference between the dating of surface corals and dating of deep-sea corals (see below).

When coralline aragonite forms from surface seawater, there is potential to fractionate uranium, thorium, and protactinium yet again. As it turns out, however, these elements do not fractionate by large amounts during this process, incorporating the three elements in approximately their proportions in seawater. Molar uranium/calcium ratios of surface corals are within about 30% (Fig. 1, see Shen and Dunbar 1995; Min et al. 1995; see discussion below on primary uranium concentrations in corals and other marine carbonates) of the seawater value of 1.3×10^{-6} (see Broecker and Peng 1982). Molar $^{232}\text{Th}/^{238}\text{U}$ values of young surface corals (Fig. 2, Edwards et al. 1987a) are typically somewhat lower than typical seawater values of 3×10^{-5} (Fig. 2, Chen et al. 1986), but within a factor of 3 of this value. ^{231}Pa values for modern corals have not been measured directly because of their extremely low concentrations; however, a measurement on one coral has placed an upper limit on initial $^{231}\text{Pa}/^{235}\text{U}$ of 5×10^{-10} (Edwards et al. 1997). This upper limit agrees with the very limited number of surface seawater $^{231}\text{Pa}/^{235}\text{U}$ seawater measurements (see Edmonds et al. 1998 and references therein). Thus, existing data suggests that surface corals initially have $^{231}\text{Pa}/^{235}\text{U}$ ratios that are similar to or lower than seawater values. Taken together, this data indicates that the main fractionation (several orders of magnitude) leading to low initial $^{231}\text{Pa}/^{235}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ in corals is that between solids and natural waters prior to the precipitation of coralline aragonite. Fractionation during precipitation of aragonite is small (less than a factor of a few).

The ^{230}Th age equation. Because of extremely low initial $^{230}\text{Th}/^{238}\text{U}$ ratios in surface corals, we first present the version of the ^{230}Th age equation calculated assuming an initial condition of $^{230}\text{Th}/^{238}\text{U} = 0$. Below, we present tests that indicate that this assumption holds for most surface corals. We then present a variant of this equation, which relaxes the criterion that initial $^{230}\text{Th}/^{238}\text{U} = 0$, but requires some knowledge of initial $^{230}\text{Th}/^{232}\text{Th}$ values. It may be necessary to employ this second equation in unusual cases involving surface corals, with deep-sea corals, and in some other marine and lacustrine carbonates. The ^{230}Th age equation, calculated assuming (1) initial $^{230}\text{Th}/^{238}\text{U} = 0$, (2) all changes in isotope ratios are the result of radioactive decay and ingrowth (no chemical/diagenetic shifts in isotope ratios), and (3) ^{238}U (half life of several billion years) has not decayed appreciably over the timescales (several hundred thousand years or less) of interest is:

$$\left[\frac{^{230}\text{Th}}{^{238}\text{U}} \right] - 1 = -e^{-\lambda_{230}t} + \left(\frac{\delta^{234}\text{U}_m}{1000} \right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) \left(1 - e^{-(\lambda_{230} - \lambda_{234})t} \right) \quad (1)$$

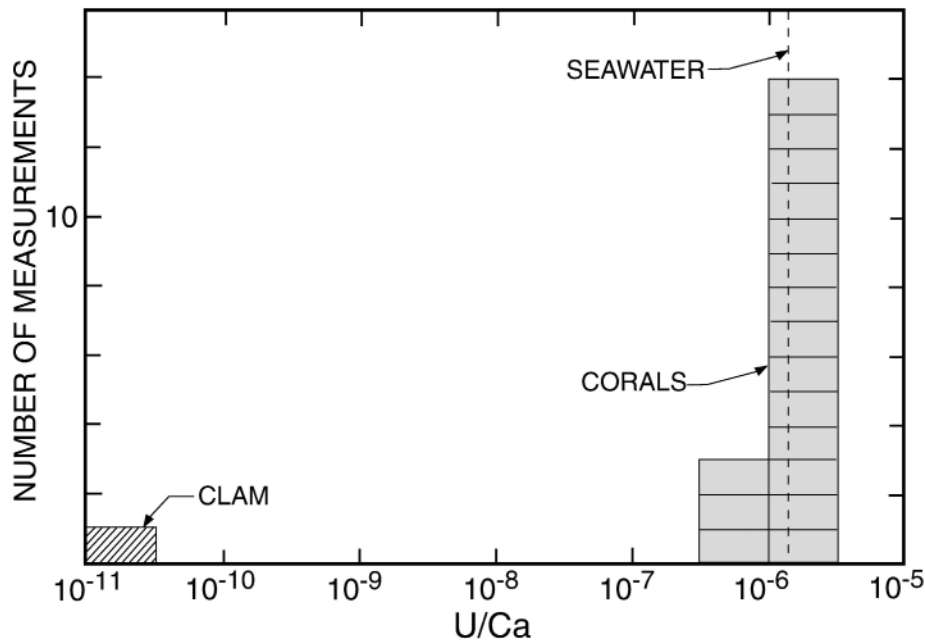


Figure 1. Histogram of measurements of molar U/Ca ratio in a number of samples of reef-building corals and one giant clam sample (after Edwards 1988). Also indicated is the U/Ca ratio of seawater. This illustrates the point that corals do not fractionate U from Ca by large amounts when they make their skeletons. U/Ca ratios of corals are similar to values from inorganically precipitated marine aragonite. Mollusks along with most other biogenic minerals exclude uranium. Note that the horizontal axis is on a log scale and that the U/Ca ratio of the clam is almost 5 orders of magnitude lower than that of the corals. This difference is the fundamental reason why there are difficulties with uranium-series dating of mollusks.

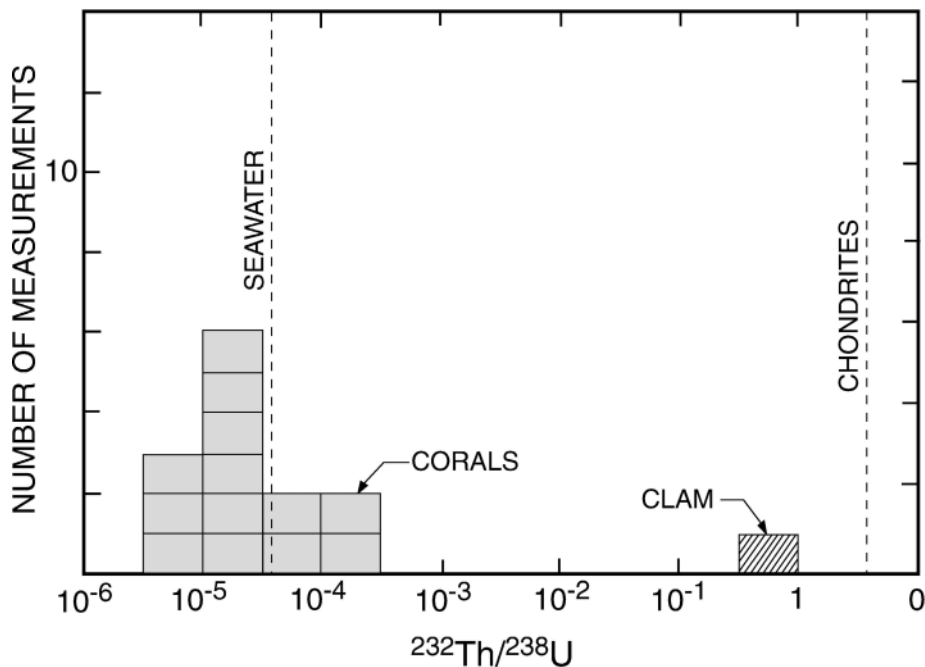


Figure 2. Histogram of measurements of molar $^{232}\text{Th}/^{238}\text{U}$ for a number of corals and a giant clam sample (after Edwards 1988). Also indicated are the $^{232}\text{Th}/^{238}\text{U}$ value of sea water and of chondrites. This illustrates the fact that corals do not fractionate thorium from uranium by large amounts during growth. The chondritic value is approximately that of the bulk earth and similar to the crustal value. Thus the large fractionation of uranium from thorium, which makes ^{230}Th dating possible, takes place during the weathering process and hydrologic cycle. Note the log scale of the horizontal axis and the 5 order of magnitude difference between chondrites and sea water. The giant clam has a much higher $^{232}\text{Th}/^{238}\text{U}$ ratio than corals because clams exclude uranium during growth (see Fig. 1).

The brackets around $^{230}\text{Th}/^{238}\text{U}$ indicate that this is an activity ratio. λ 's are decay constants; t is age; and $\delta^{234}\text{U}_m$ is the present deviation in parts per thousand (per mil) of the $^{234}\text{U}/^{238}\text{U}$ ratio from secular equilibrium: $\delta^{234}\text{U} = ([^{234}\text{U}/^{238}\text{U}] - 1) \times 1000$. Given measured $^{230}\text{Th}/^{238}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$, the only unknown is age, which can be calculated from Equation (1). Because age appears twice, the equation must be solved graphically (Fig. 3) or by iteration (by substituting $\delta^{234}\text{U}_m$ and then different values of “ t ” until the measured $^{230}\text{Th}/^{238}\text{U}$ is calculated). The general form of this equation was first solved by Bateman (1910).

A specific form of this equation was solved by Barnes et al. (1956) when he presented the first decay counting ^{230}Th data for corals. The equation of Barnes et al. (1956) did not include the second term on the right side $\{(\delta^{234}\text{U}_m/1000)(\lambda_{230}/(\lambda_{230} - \lambda_{234}))(1 - e^{-(\lambda_{230} - \lambda_{234})t})\}$ of Equation (1). This term accounts for initial $^{234}\text{U}/^{238}\text{U}$ values different from equilibrium. At the time of the Barnes et al. (1956) work, it was not known that seawater is out of equilibrium with respect to $^{234}\text{U}/^{238}\text{U}$, and the discovery that $^{234}\text{U}/^{238}\text{U}$ can be out of equilibrium in natural waters was only made one year earlier (Cherdyntsev 1955; by analysis of river water). This actually came as a surprise since there is no obvious chemical mechanism for this. ^{234}U is linked to its great-grandparent, ^{238}U by two very short-lived intermediate daughters, and isotopes of the same element, ^{234}U and ^{238}U should not fractionate appreciably from each other. The discovery that natural waters generally have higher $^{234}\text{U}/^{238}\text{U}$ values than secular equilibrium (and soils generally have lower $^{234}\text{U}/^{238}\text{U}$ values than secular equilibrium), led to the conclusion that a higher proportion of ^{234}U atoms than ^{238}U atoms

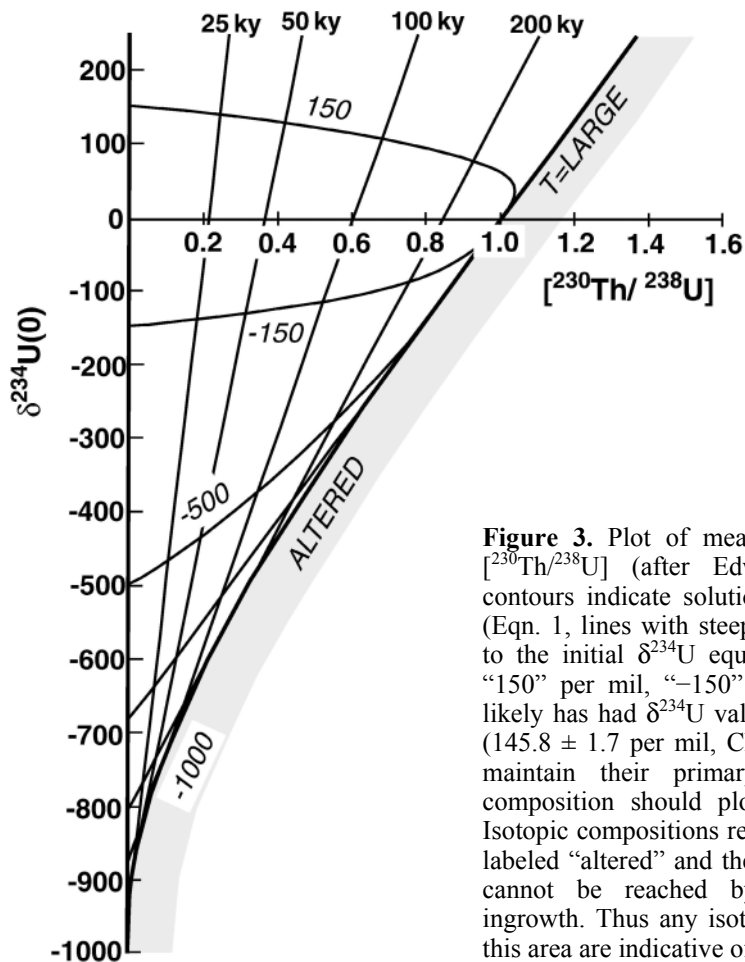


Figure 3. Plot of measured $\delta^{234}\text{U}$ versus measured $[^{230}\text{Th}/^{238}\text{U}]$ (after Edwards 1988). Two sets of contours indicate solutions to the ^{230}Th age equation (Eqn. 1, lines with steep positive slope) and solutions to the initial $\delta^{234}\text{U}$ equation (Eqn. 2, curves labeled “150” per mil, “-150” per mil, etc.). As sea water likely has had $\delta^{234}\text{U}$ values close to the modern value (145.8 ± 1.7 per mil, Cheng et al. 2000b), corals that maintain their primary marine uranium isotopic composition should plot close to the “150” curve. Isotopic compositions represented by the stippled band labeled “altered” and the area to the right of this band cannot be reached by closed-system decay and ingrowth. Thus any isotopic compositions that plot in this area are indicative of open-system behavior.

are available for leaching from minerals undergoing weathering. The rationale was that ^{234}U atoms are produced from decay of ^{238}U , a process that involves alpha emission. Recoil from alpha-emission can damage chemical bonds that hold the nuclide in a particular site, thereby causing ^{234}U to be more susceptible to leaching into the aqueous phase than ^{238}U . Thurber (1962) first showed that the $^{234}\text{U}/^{238}\text{U}$ ratio of seawater was out of secular equilibrium (about 15% higher than secular equilibrium). Immediately thereafter, Broecker (1963) presented the specific equation (Eqn. 1) that includes the term for disequilibrium in initial $^{234}\text{U}/^{238}\text{U}$. Derivations of Equation (1) that include numerous intermediate steps can be found in Edwards (1988) and Ivanovich and Harmon (1992).

Disequilibrium initial $^{234}\text{U}/^{238}\text{U}$ ratio is a happy complication. As is clear from Equation (1), this phenomenon requires measurements of both $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ to solve for age. However, given both measured values, we can solve for age uniquely given the assumptions presented above. Furthermore, a second equation that relates measured and initial $^{234}\text{U}/^{238}\text{U}$ can be calculated from the equations of radioactive production and decay, subject only to the assumption that chemical reactions (diagenesis) involving uranium have not occurred since precipitation of the aragonite:

$$\delta^{234}\text{U}_m = (\delta^{234}\text{U}_i) e^{-\lambda_{234}t} \quad (2)$$

where the subscript “i” refers to the initial value and the decay constant is that of ^{234}U . Thus, Equations (1) and (2) constitute two equations that can be solved for two unknowns (age and initial $\delta^{234}\text{U}$). As it turns out, for marine samples, knowledge of initial $\delta^{234}\text{U}$ is of great importance in assessing dating accuracy. A number of arguments and supporting data suggest that marine $\delta^{234}\text{U}$ has been constant within fairly tight bounds (see below and Henderson and Anderson 2003). If so, deviations from marine values would indicate diagenetic shifts in uranium and potential inaccuracy in the ^{230}Th age.

Figure 3 shows a graphical solution to both the ^{230}Th age equation (Eqn. 1) and the initial $\delta^{234}\text{U}$ equation (Eqn. 2). Plotted on the ordinate and abscissa are the two measured quantities $\delta^{234}\text{U}_m$ and $[^{230}\text{Th}/^{238}\text{U}]$. Contoured with sub-vertical lines is one of the calculated unknowns, age; the ordinate is coincident with the age = zero contour. Emanating from the ordinate are a set of curves (sub-horizontal near the ordinate), which contour the other unknown, $\delta^{234}\text{U}_i$. Secular equilibrium is represented by the point (0,1). The age contours get closer together with increasing age and increasing $[^{230}\text{Th}/^{238}\text{U}]$, reflecting the exponential approach of $[^{230}\text{Th}/^{238}\text{U}]$ to secular equilibrium. Beyond about 50 ky analytical errors in $[^{230}\text{Th}/^{238}\text{U}]$ are more or less constant. Thus, as age increases beyond 50 ky, error in age increases because of the compression of age contours. Eventually the age contours become so close that, for a given analytical error, one can no longer distinguish between the isotopic composition of a particular age sample and the isotopic composition of an infinite age sample. This is the upper limit of the ^{230}Th age range, which given current analytical errors is about 700,000 years (Edwards et al. 1987; Edwards et al. 1993; Stirling et al. 2001). Note that there are no age or initial $\delta^{234}\text{U}$ contours in the right portion of the diagram (“altered region”). Isotopic compositions in this region of the diagram cannot be reached through closed-system decay and ingrowth of materials that initially have zero $^{230}\text{Th}/^{238}\text{U}$. Thus, samples that plot in this region have undergone diagenetic alteration.

Modifications of the ^{230}Th age equation. We show below that surface corals generally satisfy the $^{230}\text{Th}/^{238}\text{U} = 0$ assumption used in calculating Equation (1). However, in unusual cases involving surface corals, most deep-sea corals, and other marine and lacustrine dating applications, correction for non-zero $^{230}\text{Th}/^{238}\text{U}$ may be necessary. With some knowledge of the initial $^{230}\text{Th}/^{232}\text{Th}$ ratio, age can be calculated with the following equation:

$$\left\{ \left[\frac{{}^{230}\text{Th}}{{}^{238}\text{U}} \right] - \left[\frac{{}^{232}\text{Th}}{{}^{238}\text{U}} \right] \left[\frac{{}^{230}\text{Th}}{{}^{232}\text{Th}} \right]_i (e^{-\lambda_{230}t}) \right\} - 1 = -e^{-\lambda_{230}t} + \left(\frac{\delta^{234}\text{U}_m}{1000} \right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) (1 - e^{-(\lambda_{230} - \lambda_{234})t}) \quad (3)$$

The second term on the left side ($[\frac{{}^{232}\text{Th}}{238}\text{U}] [\frac{{}^{230}\text{Th}}{232}\text{Th}]_i (e^{-\lambda_{230}t})$) corrects for initial ${}^{230}\text{Th}$. If this term is negligible compared to measured $[\frac{{}^{230}\text{Th}}{238}\text{U}]$, Equation (1) can be used. Included in this term is initial ${}^{230}\text{Th}/{}^{232}\text{Th}$, which must be known independently in order to calculate age. For this reason, Equation (3) is typically used when the magnitude of the second term on the left is small but significant. In this case, even if ${}^{230}\text{Th}/{}^{232}\text{Th}$ is not known precisely, the contribution to error in age is small. Low ${}^{232}\text{Th}/{}^{238}\text{U}$, low initial ${}^{230}\text{Th}/{}^{232}\text{Th}$, or large “t” will contribute to small values for this term. For surface corals there is a limited range of ${}^{238}\text{U}$ concentrations and initial ${}^{230}\text{Th}/{}^{232}\text{Th}$ values. Thus, this term is only significant if the sample is young (< a few thousand years) and the sample has unusually high ${}^{232}\text{Th}$ concentrations. For deep sea corals, the same parameters are important; however the term is generally larger and increases with depth as ${}^{230}\text{Th}/{}^{232}\text{Th}$ generally increases with depth in the ocean. For most other materials discussed here, this term should be evaluated on a case by case basis.

To estimate the magnitude of this term, several strategies have been employed. Zero-order estimates have been made by calculating an initial ${}^{230}\text{Th}/{}^{232}\text{Th}$ value (4.4×10^{-6} by atom) assuming a bulk earth ${}^{232}\text{Th}/{}^{238}\text{U}$ value (3.8 by atom) and presuming secular equilibrium. Estimates of initial ${}^{230}\text{Th}/{}^{232}\text{Th}$ can also be made by analyzing modern analogues to the samples in question, analyzing samples with ages that are known independently, or by applying development diagrams (see Cheng et al. 2000a) or isochron techniques (see below, Ludwig 2003).

Isochrons. In cases where the initial ${}^{230}\text{Th}$ term in Equation (3) is large enough that ${}^{230}\text{Th}/{}^{232}\text{Th}$ must be established precisely, isochron methods can be used. Such methods consider the sample to be composed of a mixture of two components. By analyzing sub-samples of the same age with different proportions of the components, one can extrapolate to an endmember that includes only radiogenic daughter and establish an age on the basis of that endmember. The extrapolation also establishes an initial ${}^{230}\text{Th}/{}^{232}\text{Th}$ ratio, assumed to be the same in both components, and the initial ${}^{234}\text{U}/{}^{238}\text{U}$ value for the radiogenic endmember. Isochron methods generally require that the sample only contain two components, although methods that deconvolve more than two components have been developed (see Henderson et al. 2001).

As an example, imagine a carbonate-rich sediment that contains a small but significant fraction of detrital silicate. The sediment might be a lake sediment, a surface coral, a deep-sea coral, a carbonate-rich bank sediment, or a speleothem (see for example, Richards and Dorale 2003). The carbonate has a very high ${}^{238}\text{U}/{}^{232}\text{Th}$ ratio (on the order of 10^4 by atom) and the detrital material has a lower ${}^{238}\text{U}/{}^{232}\text{Th}$ ratio of about 10^0 . The carbonate and detrital materials each have specific $\delta^{234}\text{U}$ values that differ from each other. Both have the same initial ${}^{230}\text{Th}/{}^{232}\text{Th}$ ratio. Through time, the mixture evolves following the laws of radioactive ingrowth and decay. Sub-samples of the sediment with different proportions of carbonate and detrital material, and therefore different ${}^{238}\text{U}/{}^{232}\text{Th}$, ${}^{234}\text{U}/{}^{238}\text{U}$, and present day ${}^{230}\text{Th}/{}^{232}\text{Th}$ ratios, are measured. If the sub-samples started with the same initial ${}^{230}\text{Th}/{}^{232}\text{Th}$, their isotopic compositions will evolve so that they lie on a line in three-dimensional isotope ratio space. If the points do not lie on a line, there must be an additional thorium or uranium component represented in the mixture or the

sediment has been altered. Different choices for the three axes can be made (see Ludwig and Titterton 1994); however, a convenient set for illustrative purposes is $^{230}\text{Th}/^{232}\text{Th}$, $^{238}\text{U}/^{232}\text{Th}$, and $^{234}\text{U}/^{232}\text{Th}$ [see Hall and Henderson (2001) for a recent example of use of these types of axes]. Regardless of the choice of axes, the resultant line is termed an isochron. The equation of the line can be used to extrapolate to a hypothetical uranium-free end member, from which initial $^{230}\text{Th}/^{232}\text{Th}$ can be calculated, and to a ^{232}Th -free (radiogenic) end member, from which age and initial $^{234}\text{U}/^{238}\text{U}$ of the end member can be calculated, essentially from Equations (1) and (2).

The isochron approach is powerful, but ultimately limited by the degree to which the constant initial $^{230}\text{Th}/^{232}\text{Th}$ assumption holds in a particular sample. There are indications from different settings (e.g., Lin et al. 1996; Cheng et al. 2000a; Slowey et al. 1996; Henderson et al. 2001) for two distinct sources of initial thorium, a “hydrogenous” source (from solution or colloids) and a “detrital source.” The co-linearity (or lack thereof) of data points is an important test of this phenomenon. Even in cases where there are two initial sources of thorium, there may be methods to correct for this additional source (Henderson et al. 2001). Ideally one would physically separate the carbonate-rich fraction from the thorium-rich fraction, but often this cannot be done because of cementation or small grain size. Methods of chemical separation of these components have been attempted (e.g., acid dissolution of the carbonate component leaving the detrital silicate component behind); however, differential adsorption of uranium and thorium onto the solid residue and/or differential leaching of uranium and thorium from the residue have proven to cause problems (Bischoff and Fitzpatrick 1991; Luo and Ku 1991). Thus, in cases where physical separation is not possible, isochron techniques with total sample dissolution are recommended. Further discussion of isochron approaches can be found in Bischoff and Fitzpatrick (1991), Luo and Ku (1991), Ludwig and Titterton (1994) and Ludwig (2003).

The ^{231}Pa age equation. The ^{231}Pa age equation, calculated assuming no chemical shifts in protactinium or uranium and an initial $^{231}\text{Pa}/^{235}\text{U} = 0$, is analogous to the ^{230}Th age equation (Eqn. 1), but simpler. There is no term analogous to the $\delta^{234}\text{U}$ term because there is no long-lived intermediate daughter isotope between ^{235}U and ^{231}Pa :

$$\left[\frac{^{231}\text{Pa}}{^{235}\text{U}} \right] - 1 = -e^{-\lambda_{231}t} \quad (4)$$

We will show below that the initial $^{231}\text{Pa}/^{235}\text{U} = \text{zero}$ assumption holds for a number of corals that have typical low ^{232}Th concentrations. Initial $^{231}\text{Pa}/^{235}\text{U}$ values for most other carbonates have not been studied in detail. Furthermore, in contrast to thorium, there is no long-lived isotope of protactinium that can be used as an index isotope although some work has employed corrections for initial ^{231}Pa . Such corrections essentially assume that ^{232}Th is an isotope of protactinium and assume a bulk earth $^{232}\text{Th}/^{238}\text{U}$ ratio and secular equilibrium between ^{231}Pa and ^{235}U . The term for applying this correction is analogous to the initial ^{230}Th term in Equation (3).

The $^{231}\text{Pa}/^{230}\text{Th}$ age equation. Equation (4) can be divided by Equation (1) to give the following $^{231}\text{Pa}/^{230}\text{Th}$ age equation:

$$\left[\frac{^{231}\text{Pa}}{^{230}\text{Th}} \right] = \frac{(1 - e^{-\lambda_{231}t})}{\left[\frac{^{238}\text{U}}{^{235}\text{U}} \right] \left\{ 1 - e^{-\lambda_{230}t} + \left(\frac{\delta^{234}\text{U}_m}{1000} \right) \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \right) (1 - e^{-(\lambda_{230} - \lambda_{234})t}) \right\}} \quad (5)$$

$[^{238}\text{U}/^{235}\text{U}]$ is not a variable because it is constant in nature; our present best estimate of

its value is: $(^{238}\text{U}/^{235}\text{U})(\lambda_{238}/\lambda_{235}) = 137.88 (1.5513 \times 10^{-10} \text{ y}^{-1}/9.8485 \times 10^{-10} \text{ y}^{-1}) = 21.718$. As opposed to Equations (1) and (4), Equation (5) does not depend explicitly on ^{238}U or ^{235}U abundance. $^{231}\text{Pa}/^{230}\text{Th}$ ages are analogous to $^{207}\text{Pb}/^{206}\text{Pb}$ ages in this respect and many others. $^{231}\text{Pa}/^{230}\text{Th}$ ages are not sensitive to very recent uranium loss; nor are they sensitive to very recent uranium gain if the added uranium has the same $\delta^{234}\text{U}_m$ as the sample. This is clear from Equation (5). On the other hand $^{231}\text{Pa}/^{230}\text{Th}$ ages are sensitive to uranium gain or loss at earlier times, as these processes affect the subsequent ingrowth and decay of ^{231}Pa and ^{230}Th . Nevertheless, $^{231}\text{Pa}/^{230}\text{Th}$ can be used in conjunction with ^{230}Th and ^{231}Pa ages to characterize, and potentially “see through” certain types of diagenesis.

2.4. Tests for ^{231}Pa - ^{230}Th age concordancy

Perhaps the greatest strength of $^{231}\text{Pa}/^{235}\text{U}$ data is its use in concert with ^{230}Th - ^{234}U - ^{238}U data in testing age accuracy (see Cheng et al. 1998). A good method for interpreting this data is through a $^{231}\text{Pa}/^{235}\text{U}$ vs. $^{230}\text{Th}/^{234}\text{U}$ concordia diagram (Fig. 4; Allegre 1964; Ku 1968; see Cheng et al. 1998). The ordinate is the key isotopic ratio for ^{231}Pa dating and the abscissa is the key isotopic ratio for ^{230}Th dating. Plotted parametrically is age along the locus of isotopic compositions for which ^{231}Pa and ^{230}Th age are identical: concordia. This plot is analogous the U-Pb concordia plot (Wetherill 1956a; 1956b) except that the $^{231}\text{Pa}/^{235}\text{U}$ vs. $^{230}\text{Th}/^{234}\text{U}$ diagram has different concordia for different initial $\delta^{234}\text{U}$ values. If a data point plots off of concordia, the sample must have been

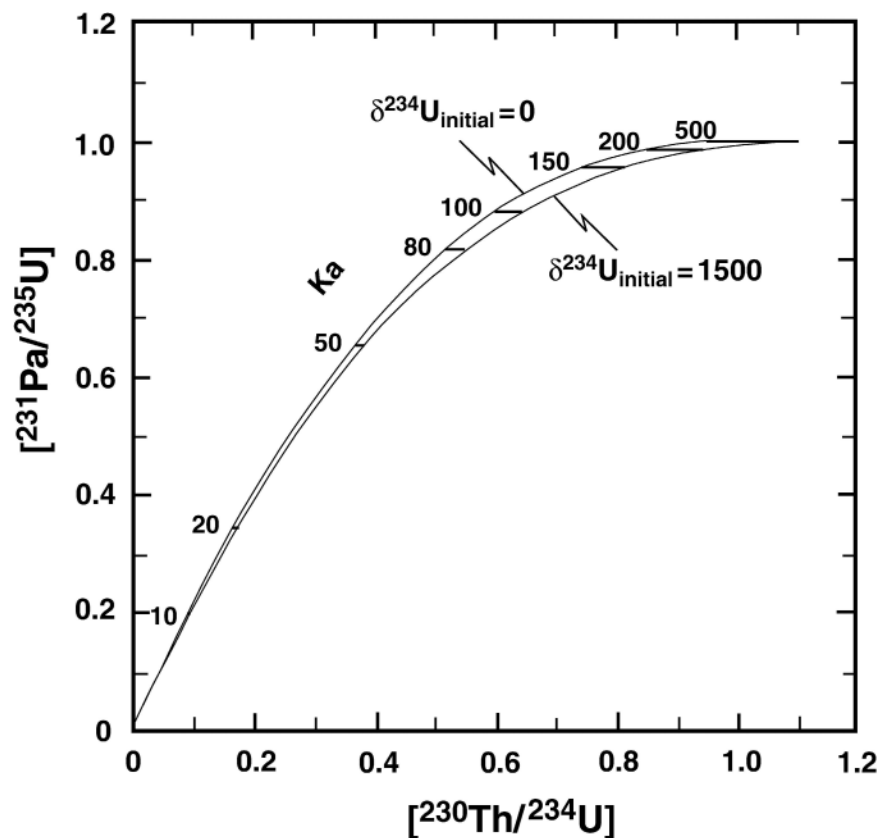


Figure 4. $^{231}\text{Pa}/^{235}\text{U}$ vs. $^{230}\text{Th}/^{234}\text{U}$ concordia diagram (after Cheng et al. 1998). Concordia represent the locus of isotopic compositions for which the ^{231}Pa age (see Eqn. 4) and the ^{230}Th age (see Eqn. 1) are equal. Two concordia curves are indicated, one for an initial $\delta^{234}\text{U} = 0$ and one for an initial $\delta^{234}\text{U} = 1500$. Age is depicted parametrically along the concordia curves (horizontal line segments). The concordia curves are analogous to U/Pb concordia curves used in zircon dating.

altered chemically and one or both of the ages are not accurate. If a data point plots on concordia, then the sample's isotopic composition is consistent with closed-system behavior of the pertinent nuclides. This constitutes a robust test for age accuracy.

Furthermore, should a data point lie off of concordia, it may still be possible to constrain the true age of the sample. Interpretations of points that lie off of concordia are model-dependent. However, there are commonalities among models of a number of likely diagenetic processes (Cheng et al. 1998). Figure 5 shows isotopic compositions generated by one such model. Two separate calculations are illustrated, one for a set of co-genetic materials with a primary age of 80 ky (dashed curve), another for a set of materials with a primary age of 150 ky (thin solid curve). Considering the 80 ky materials first, the intersection of the dashed line with concordia represents a material that has behaved as a closed system and records primary ^{230}Th and ^{231}Pa ages. All other isotopic compositions on the line represent materials that have undergone different degrees of the same type of diagenesis: continuous addition or loss of uranium. The portion of the dashed curve between concordia and the origin represents the isotopic composition of materials that have gained uranium (with a $\delta^{234}\text{U}$ identical to that of the sample) continuously. The portion immediately below concordia represents material that has gained uranium at a low rate; progressively closer to the origin, the rate of uranium gain increases. The origin represents material that has gained uranium at an infinite rate. Similarly, the portion of the curve above concordia represents the isotopic composition of material that has lost uranium. The portion above and immediately adjacent to the

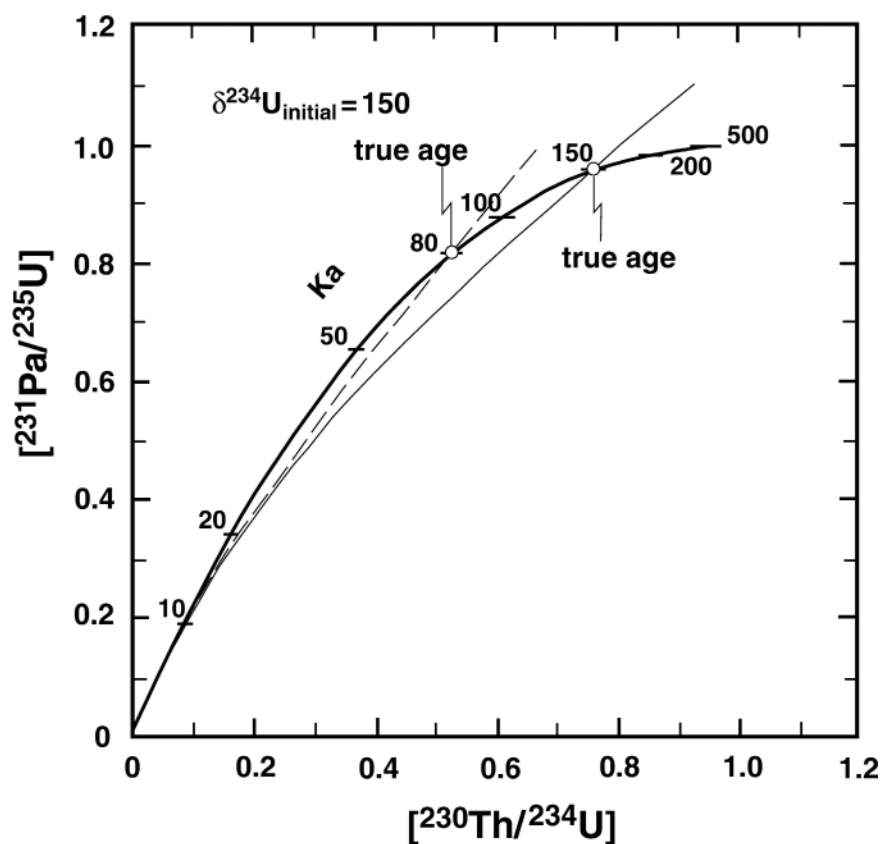


Figure 5. Concordia diagram similar to Figure 4 illustrating the concordia curve for initial $\delta^{234}\text{U} = 150$ (appropriate for marine samples), with age in ka depicted parametrically along concordia. Also illustrated are continuous uranium gain/loss model curves for samples with primary ages of 80 ka (dashed) and 150 ka (thin solid curve). See text for discussion of this model and related models (after Cheng et al. 1998).

concordia represents the isotopic composition of material that has lost uranium at a low rate. Points progressively higher on the curve represent progressively higher rates of uranium loss. The thin solid curve is analogous to the dashed curve, but pertains instead to a set of materials with a primary age of 150 ky.

Both of these curves approximate a line in the vicinity of concordia. This is one of the commonalities between this continuous uranium gain/loss model and a number of other open system models (e.g., instantaneous uranium gain/loss models, continuous daughter (thorium and protactinium) gain/loss models, or instantaneous daughter gain/loss models; see Cheng et al. 1998). This has led to the idea that if one can identify a set of equal-age materials affected by the same diagenetic process, but to different extents, the isotopic compositions of this set of materials should approximate a line. By extrapolating or interpolating this line to concordia, one may be able to establish the primary age of the material (see Fig. 6). This possibility exists even if the specific diagenetic process is not known, as long as the diagenetic process includes one of the modeled processes discussed above.

In the model that we illustrate (Fig. 5), points above concordia indicate continuous uranium loss and points below concordia indicate uranium gain. Models of instantaneous uranium loss/gain plot in the same sense relative to concordia. Similarly, models of instantaneous or continuous daughter loss generally (but not always depending on the ratio of lost ^{231}Pa to lost ^{230}Th) yield isotopic compositions below concordia, whereas models of daughter gain generally (but not always) give isotopic compositions above

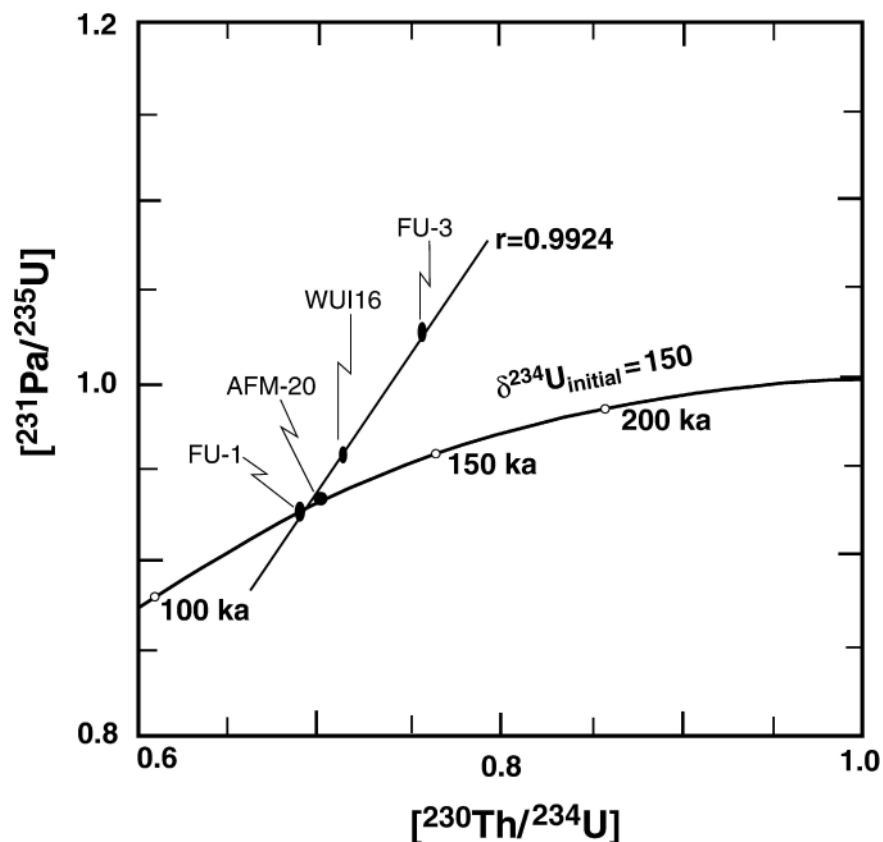


Figure 6. A portion of the concordia curve for initial $\delta^{234}\text{U} = 150$ and four data points (Edwards et al. 1997) for coral samples from the last interglacial terrace in Barbados. The points lie along a line, and illustrate the possibility of using best-fit lines through discordant points to extrapolate to concordia and possibly the true age of a set of samples (after Cheng et al. 1998).

concordia. Thus, isotopic compositions above concordia are consistent with uranium loss or daughter gain, whereas those below concordia are consistent with uranium gain or daughter loss. If so, isotopic compositions above concordia yield ^{231}Pa and ^{230}Th ages that are maximum ages, whereas those below concordia yield minimum ages. In sum, isotopic compositions that yield discordant ages place constraints on both diagenetic mechanisms and age. Isotopic compositions that yield concordant ages provide some confidence that the ages are accurate. These two statements, in a nutshell embody the power of combined ^{230}Th - ^{231}Pa dating.

3. TESTS OF DATING ASSUMPTIONS

3.1. Are initial $^{230}\text{Th}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ values equal to zero?

One of the keys in ^{230}Th and ^{231}Pa dating is establishing initial $^{230}\text{Th}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ values. Upper limits were originally placed on these ratios in surface corals by analyzing modern corals by alpha-counting techniques (Barnes et al. 1956; Broecker 1963 for $^{230}\text{Th}/^{238}\text{U}$ and Ku 1968 for $^{231}\text{Pa}/^{235}\text{U}$). With the advent of mass spectrometric techniques, tighter bounds on initial values were needed. In this regard, the first data that suggested that initial $^{230}\text{Th}/^{238}\text{U}$ values of surface corals were extremely low were the $^{232}\text{Th}/^{238}\text{U}$ values measured by mass spectrometric techniques (Edwards et al. 1987a). The values were three orders of magnitude lower than the upper limits from the earlier alpha-counting measurements. When multiplied by typical $^{230}\text{Th}/^{232}\text{Th}$ ratios of surface sea water, these measurements yielded initial $^{230}\text{Th}/^{238}\text{U}$ values equivalent to about 1 year's worth of radiogenic ingrowth (negligible compared to analytical errors of >2 years).

This calculation was further tested by dating portions of a coral with ages known a priori from the counting of annual density bands (Fig. 7). A plot of ^{230}Th age calculated

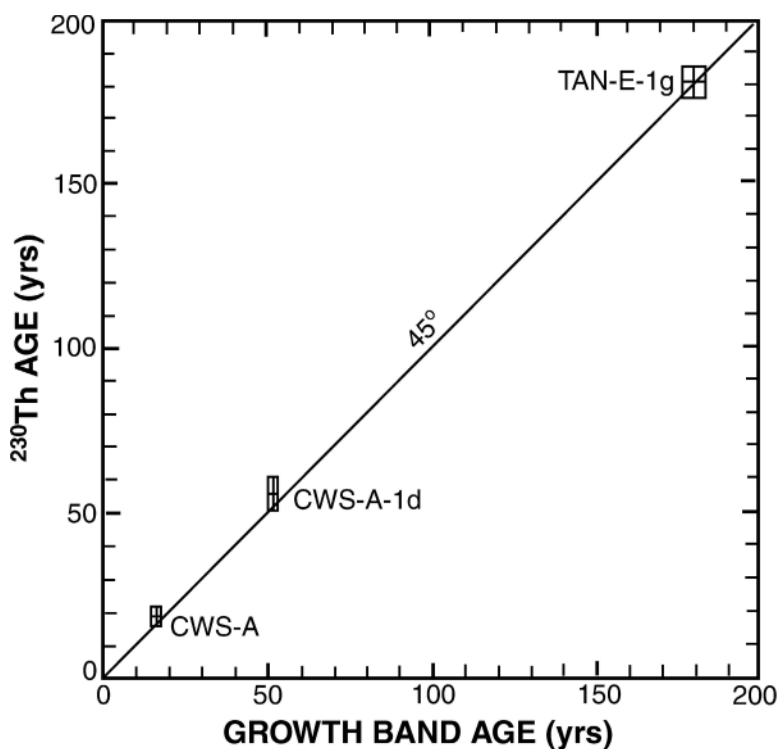


Figure 7. ^{230}Th age vs. growth band age for three coral sub-samples, all younger than 200 years old (after Edwards 1988 and Edwards et al. 1988). All three points lie on a 1:1 line indicating that the ^{230}Th ages are accurate and that initial $^{230}\text{Th}/^{238}\text{U}$ is negligible, justifying the use of Equation (1) to determine ^{230}Th age.

with Equation (1) vs. band counting age (Edwards 1988; Edwards et al. 1988) for three such coral sub-samples is shown in Figure 7. Errors are indicated by boxes, with the vertical dimension equivalent to analytical error in ^{230}Th age and the horizontal dimension equivalent to the number of annual bands encompassed by the sub-sample. Equation (1) has no term for correcting for initial ^{230}Th . Thus, if there were significant initial ^{230}Th , the ^{230}Th age would be older than the band counting age. This is not the case as all three points plot within error of a 45° line, indicating that initial ^{230}Th is not significant within errors of about 3 years. All three Figure 7 samples have ^{232}Th concentrations less than 100 pg/g. Thus, this study suggested that initial ^{230}Th levels were negligible in surface corals with ^{232}Th levels below about 100 pg/g. Subsequent work has demonstrated that most surface corals have ^{232}Th levels of about 100 pg/g or less, leading to the conclusion that initial $^{230}\text{Th}/^{238}\text{U}$ is negligible for typical surface corals.

However, subsequent work has also shown that a small fraction of surface corals can have elevated ^{232}Th values. ^{232}Th levels of several hundred to 1000 pg/g have been reported from the central Pacific (Cobb et al. in review) and in extreme cases levels of several thousands of pg/g (Zachariassen 1998; Zachariassen et al. 1999) for a small subset of corals from Sumatra. For coralline samples older than several thousand years, even levels of ^{232}Th as high as a few thousand pg/g are not likely to be associated with levels of initial ^{230}Th that are significant compared to analytical error. However, for samples less than several thousand years old, such samples are best avoided, as initial ^{230}Th is likely to be significant. In the very highest ^{232}Th samples from Sumatra, the corals were visibly discolored with a brown stain, and thus could easily be identified. The stain could be partially removed in an ultrasonic bath, a procedure that also lowered ^{232}Th levels. Thus, the thorium is associated with the discoloration, quite likely organic matter. In both the Cobb et al. (in review) and Zachariassen et al. (1999) studies, samples with the highest ^{232}Th levels could be avoided. However, in both studies, it was important to obtain ages on coralline material with somewhat elevated ^{232}Th levels (hundreds of pg/g). In both studies, this was accomplished using Equation (3) with $^{230}\text{Th}/^{232}\text{Th}$ determined by analyzing local corals of known age or for which there were constraints on age. In the Sumatra study, initial atomic $^{230}\text{Th}/^{232}\text{Th}$ values between 0 and 1.3×10^{-5} were determined and in the central Pacific values covered a similar range from 0 to 2.0×10^{-5} , broadly consistent with values for surface seawater. In each of these studies, corrections for initial ^{230}Th using these isotopic values were on the order of 20 years or less, even for samples with several hundred pg/g of ^{232}Th .

In sum, for surface corals, the assumption that initial $^{230}\text{Th}/^{238}\text{U}$ values are negligible holds in most cases, satisfying one of the assumptions used in deriving Equation (1). However, in unusual cases corals younger than several thousand years may have significant initial $^{230}\text{Th}/^{238}\text{U}$ compared to analytical errors. In those cases, corrections for initial $^{230}\text{Th}/^{238}\text{U}$ can be made accurately with some knowledge of the range of possible $^{230}\text{Th}/^{232}\text{Th}$ values.

Initial $^{231}\text{Pa}/^{235}\text{U}$ levels are more difficult to assess, primarily because there is no long-lived or stable isotope of protactinium that can be used as an index isotope. Edwards et al. (1997) analyzed a set of surface coral sub-samples younger than 1000 years by both ^{230}Th and ^{231}Pa techniques. For all samples, ^{232}Th concentrations were less than 100 pg/g so that initial $^{230}\text{Th}/^{238}\text{U}$ values were negligible. Each sub-sample yielded ^{230}Th and ^{231}Pa ages identical within analytical errors (Fig. 8), indicating that initial $^{231}\text{Pa}/^{235}\text{U}$ was negligible. This suggests that surface corals with typical ^{232}Th values do not require corrections for initial ^{231}Pa . Whether or not corals with elevated ^{232}Th require such corrections is an open question.

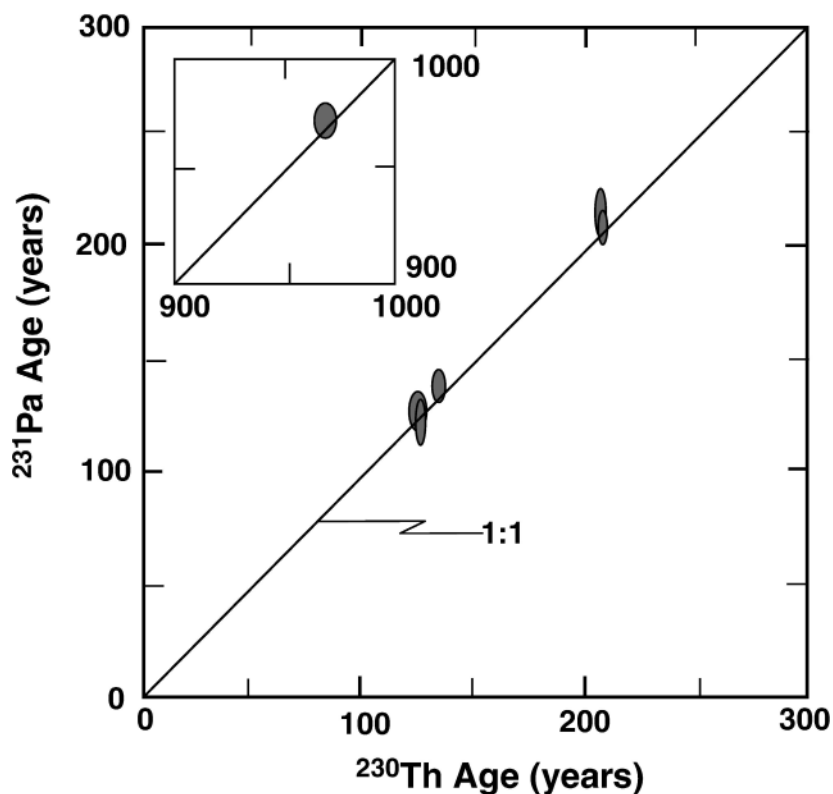


Figure 8. ^{231}Pa age vs. ^{230}Th age for a set of corals all younger than 1000 years old (after Edwards et al. 1997). All points lie along a 1:1 line indicating that the corals record identical ^{230}Th and ^{231}Pa ages, suggesting that the ^{231}Pa ages are accurate and that initial $^{231}\text{Pa}/^{235}\text{U}$ is negligible, justifying the use of Equation (4) to determine ^{231}Pa age.

3.2. Tests of the closed-system assumption

The second assumption, used in deriving Equations (1) through (4) is that the system has remained closed to chemical exchange. Testing this assumption is more difficult. A number of different approaches have been used to assess this assumption. Perhaps the most powerful of these is combined ^{231}Pa and ^{230}Th dating, but most of the methods discussed below play a role.

Concerns that diagenetic alteration could affect measured ^{230}Th ages of corals have existed since the early applications using alpha-counting methods. Thurber et al. (1965) offered the following list for reliable coral ^{230}Th ages: a) no evidence of recrystallization, b) uranium concentration of ~ 3 ppm, c) $[\text{}^{230}\text{Th}/\text{}^{232}\text{Th}]$ of > 20 , d) $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$ of 1.15 ± 0.02 , and e) stratigraphically consistent ages. These phenomena are still applied today, but numerical limits have changed drastically, reflecting higher precision measurement techniques and better understanding of the processes that result in primary and diagenetic values for these parameters.

Initial mineralogy, petrology, and associated elemental concentrations. Corals create an aragonitic skeleton in a seawater environment. Because sea levels are low during glacial and interstadial periods, most fossil corals have been exposed to meteoric waters for a significant portion of their post-depositional history. This exposure creates the potential for these corals to be recrystallized to the more stable calcium carbonate, calcite, by dissolution/reprecipitation reactions associated with percolating waters (Matthews 1968). X-ray diffraction is commonly used to screen for calcite, where the heights of aragonite and

calcite peaks of a sample are compared to the peak heights of a series of standards, from 100% calcite and 0% aragonite down to the detection limits of the instrument, usually 1-2% calcite. As Thurber et al. (1965) suggested, a measurable calcite peak indicates that the sample has been recrystallized to some degree, which suggests that the ^{230}Th age is not reliable. However, where samples with and without detectable calcite have been measured that are from the same terrace, and presumably are the same age, there is no clear systematic effect on the ^{230}Th age (e.g., Bloom et al. 1974).

Matthews (1968) documented that the frequency of exposed coral recrystallization generally increases with coral age on Barbados. Chappell and Polach (1972) had similar results for corals from the Huon Peninsula in Papua New Guinea, but with thin section work showed that the microscopic bundles of aragonite that make up the coral skeleton become fused or thickened as recrystallization proceeds (see Figs. 9 and 10). Bar-Matthews et al. (1993) attempted to correlate such petrologic changes (where the thickening is due to secondary aragonite) with shifts in uranium-series isotopes in last interglacial corals from the Bahamas, but could find no clear correlation with the presence of secondary precipitation features and $\delta^{234}\text{U}$ value or ^{230}Th age. In addition, thin section work can detect precipitation of aragonite cements in pores within the coral skeleton. As aragonite cements initially have similar isotopic characteristics to coralline aragonite, the presence of aragonite cement does not necessarily pose a problem. However, if the cement has a different age than the coral skeleton, the apparent age of the coral-cement mixture will differ from the true age of the coral.

Bloom et al. (1974) measured Sr and Mg concentrations as a possible measure of recrystallization of coral skeletons. Sr concentrations in calcite are less than in aragonite and high-Mg calcite has higher Mg concentrations than aragonite (e.g., Edwards 1988 for Sr and Mg measurements of cements in fossil corals). Consistent with this difference, Bloom et al. (1974) found that samples with detectable calcite had slightly lower Sr concentrations and those with high-Mg calcite had Mg concentrations ~5 times higher than aragonitic corals. Bar-Matthews et al. (1993) did not find a correlation between Sr and Mg concentrations in corals with secondary aragonite and initial $\delta^{234}\text{U}$ value. However, they did find a distinguishable negative correlation between Na and SO_3 concentrations and initial $\delta^{234}\text{U}$ value, which they interpreted as suggesting diagenetic alteration in a marine environment (many of the samples were within a few meters of sea level). This correlation has not been explored in uplifted corals that have spent most of their history many meters above sea level. Primary coralline aragonite generally has extremely low ^{232}Th concentrations (tens of parts per trillion, Edwards et al. 1987a). Thus, ^{232}Th values significantly higher than this indicate contamination from detrital sources, organic-thorium complexes, or unusual growth settings (e.g., Zachariasen et al. 1999; Cobb et al., in review). In some cases, limiting sample to denser portions of the coral, with little pore space and low macroscopic surface to volume ratio has proven to improve the sample in terms of a number of the measures of diagenesis (Stirling et al. 1995) discussed above and below (e.g., $\delta^{234}\text{U}$, ^{232}Th content).

Initial $^{234}\text{U}/^{238}\text{U}$. Corals incorporate marine uranium into their skeleton without isotopic fractionation. The modern marine $\delta^{234}\text{U}$ value as measured in marine waters is 140-150 (Chen et al. 1986) and in modern corals is $145.8 \pm 1.7\%$ (using updated half-lives; Cheng et al. 2000b). The marine $\delta^{234}\text{U}$ value does not vary more than the analytical error with depth or geographic location (Chen et al. 1986; Cheng et al. 2000a), consistent with the long marine residence time of uranium (200,000 to 400,000 years; Ku et al. 1977) and the long half-life of ^{234}U , compared to the mixing time of the ocean (about 10^3 y). If the uranium isotopic composition of the ocean also remained constant with time, the $\delta^{234}\text{U}$ value would add a second chronometer in the ^{238}U decay chain for corals

FIGURE 10

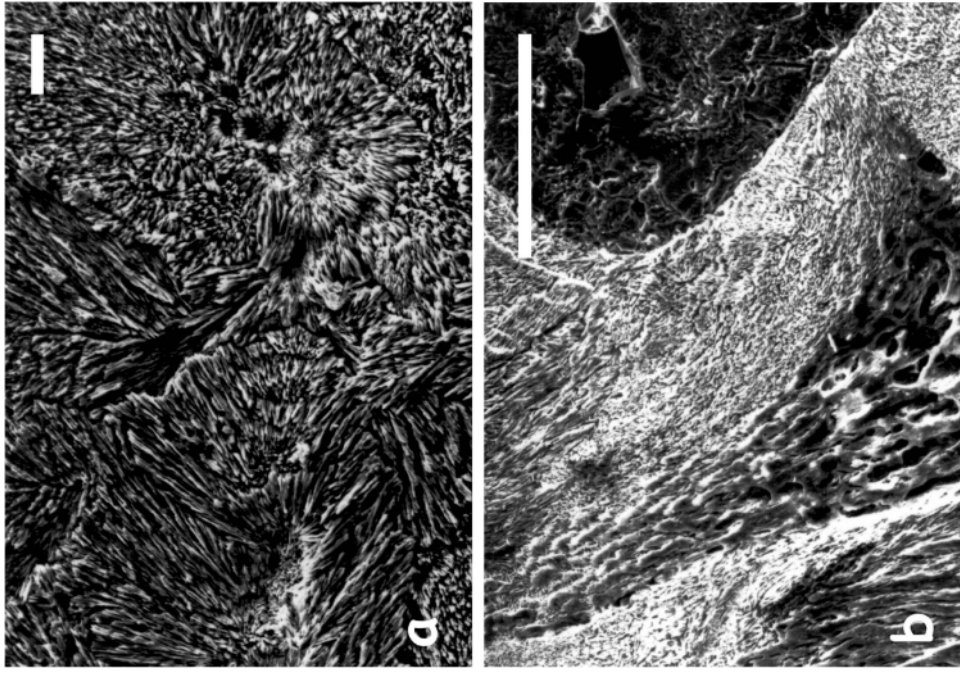
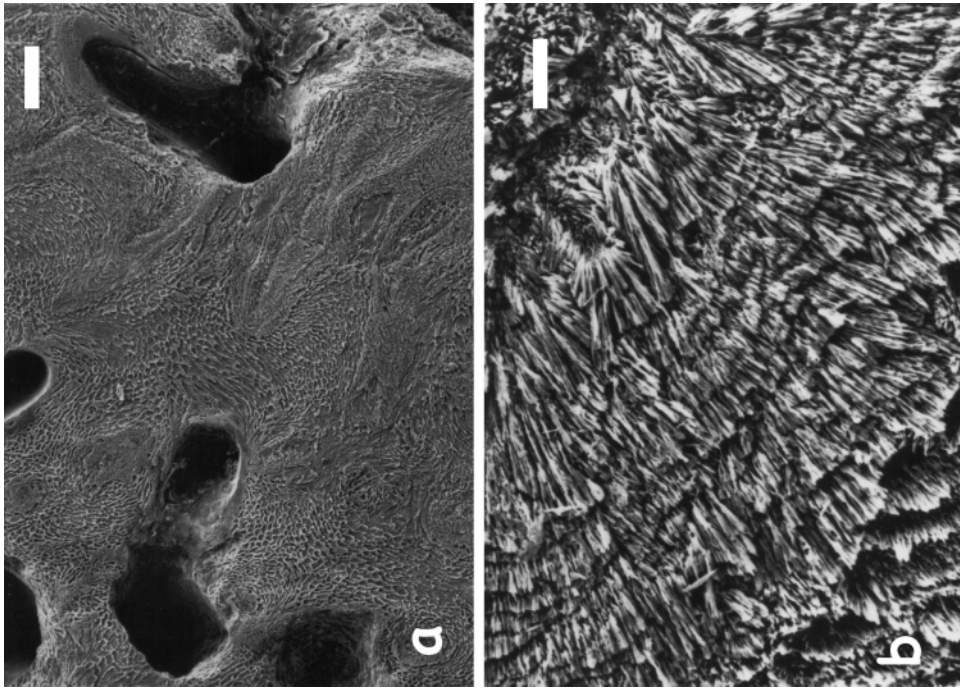


Figure 9. SEM photographs of polished, etched thin sections of modern *Acropora palmata* coral (after Edwards 1988). The scale bar in "a" is 100 microns. Visible in "a" are large macroscopic pores in the skeleton and well as the texture of the very fine aragonite crystals. "b" is the same section as "a" but at higher magnification. The scale bar is 10 microns. Individual aragonite crystal fibers are visible in "b."

Figure 10. SEM photographs of polished, etched thin sections of fossil *Acropora palmata* coral (after Edwards 1988). The scale bar in "a" is 10 microns. "a" depicts sample AFS-12, a last interglacial coral from Barbados. The crystal morphology in this well-preserved sample is indistinguishable from that of a modern sample (see Fig. 9b). The scale bar in "b" is 100 microns. "b" depicts sample PB-5B, a fossil coral collected from North Point Shelf on Barbados. The crystal morphology of this sample shows clear evidence of alteration, including a large calcite crystal filling in a macroscopic pore (dark area in upper right portion of photograph).

FIGURE 9



(Ku 1965). However, the wide range in riverine $\delta^{234}\text{U}$ values (0 to 2000; Cochran 1982) suggests that the elevation of the marine $\delta^{234}\text{U}$ value above secular equilibrium results from a complex combination of weathering and alpha-recoil processes (see above). Thus, it is possible that the marine $\delta^{234}\text{U}$ value has changed by small amounts with time. In practice, the main impediment to a $\delta^{234}\text{U}$ chronometer is the sensitivity of $\delta^{234}\text{U}$ to diagenesis (see below).

When dating corals, there are two results when Equations (1) and (2) are solved: the ^{230}Th age and the initial $\delta^{234}\text{U}$ value. If all corals remained closed to diagenetic alteration, the initial $\delta^{234}\text{U}$ value would reflect changes in the marine $\delta^{234}\text{U}$ value with time. Early studies indicated that there is substantial variation in the initial $\delta^{234}\text{U}$ value and that, in general, higher initial $\delta^{234}\text{U}$ value corresponds with higher ^{230}Th ages (Bender et al. 1979). The question was, did these variations reflect changes in the marine uranium isotopic composition or represent the effects of diagenesis?

Given that the long residence time of uranium should place limits on how much the marine $\delta^{234}\text{U}$ value could change over Late Quaternary time scales, several workers have used models to determine what these limits should be (see Henderson and Anderson 2003). Chen et al. (1986) and Edwards (1988) used a simple one-box model and assumed steady state conditions. They showed that:

$$\delta^{234}\text{U}_{\text{ss}} = \frac{\delta^{234}\text{U}_{\text{r}}}{1 + (\tau_{\text{U}}/\tau_{234})} \quad (6)$$

where $\delta^{234}\text{U}_{\text{ss}}$ is the steady state marine $\delta^{234}\text{U}$ value, $\delta^{234}\text{U}_{\text{r}}$ is the average $\delta^{234}\text{U}$ value of the input to the ocean, assumed to be rivers, τ_{U} is the residence time of uranium in the ocean, and τ_{234} is the mean-life for ^{234}U . To a first approximation, the $\delta^{234}\text{U}_{\text{ss}}$ is $\sim 1/2$ of the $\delta^{234}\text{U}_{\text{r}}$, as the residence time of the ocean is roughly equal to the mean-life of ^{234}U , which makes $\tau_{\text{U}}/\tau_{234} \sim 1$. The modern ocean satisfies this equation, as the average riverine $\delta^{234}\text{U}$ value is $\sim 300\text{‰}$ and the modern $\delta^{234}\text{U}$ value is $\sim 150\text{‰}$. To evaluate how much the marine $\delta^{234}\text{U}$ value could change, Edwards (1988) assumed that the input would have an instantaneous jump to a new value and showed that the transition to a new steady state marine $\delta^{234}\text{U}$ value would be an exponential function (Henderson, 2002, has recently presented a similar equation):

$$\delta^{234}\text{U}_{\text{marine}} = \delta^{234}\text{U}_{\text{ss2}} + (\delta^{234}\text{U}_{\text{ss1}} - \delta^{234}\text{U}_{\text{ss2}}) e^{-[(1/\tau_{\text{U}}) + (1/\tau_{234})]t} \quad (7)$$

where the subscripts “1” and “2” refer to steady state marine values before and after the shift in riverine $\delta^{234}\text{U}$ (calculated from Eqn. 6). However, for timescales short compared to $1/(1/\tau_{\text{U}} + 1/\tau_{234})$ ($\sim 160,000$ years) the shift in the marine $\delta^{234}\text{U}$ value can be approximated by:

$$\Delta\delta^{234}\text{U}_{\text{marine}} \approx \Delta\delta^{234}\text{U}_{\text{r}} (t/\tau_{\text{U}}) \quad (8)$$

where the $\Delta\delta^{234}\text{U}_{\text{marine}}$ and the $\Delta\delta^{234}\text{U}_{\text{r}}$ are the shifts from their initial (steady state in the marine case) values. Thus, for a shift of a quarter of the modern-day range of $\delta^{234}\text{U}$ for most rivers (a range of about 400‰, $\Delta\delta^{234}\text{U}_{\text{r}} = 80\text{‰}$) for 50,000 years, the shift in the $\delta^{234}\text{U}_{\text{marine}}$ would be $\sim 13\text{‰}$. If a 50% shift lasted 20,000 years, the shift in the $\delta^{234}\text{U}_{\text{marine}}$ would be $\sim 10\text{‰}$. Thus, Edwards (1988) concluded that the $\delta^{234}\text{U}_{\text{marine}}$ should have remained within 10-20‰ of its modern value during the last several hundred thousand years.

Hamelin et al. (1991) came to similar conclusions regarding the magnitude of shifts in the $\delta^{234}\text{U}_{\text{marine}}$ value caused by instantaneous shifts in the $\delta^{234}\text{U}_{\text{r}}$, using computer

simulation as opposed to solving the specific differential equations. They also investigated periodic changes in $\delta^{234}\text{U}_r$ and found that with a 30% shift in the value (100‰) with a 100,000 year period the change in the $\delta^{234}\text{U}_{\text{marine}}$ value was only ~1% (or 10‰ if the modern $\delta^{234}\text{U}_{\text{marine}}$ is used) and was out of phase with the forcing.

Richter and Turekian (1993) also assumed a simple one-box model for the ocean. They derived a set of equations with the assumption that 1) the volume of the ocean does not change, 2) mass is conserved, i.e., the change in the marine U concentration with time equals the flux in from rivers minus the flux out, and 3) that the marine U concentration does not change with time, which implies that the flux in equals the flux out. This results in the equation:

$$\frac{d\delta A_o}{dt'} + (1 + \tau_U \lambda_{234}) \delta A_o = \delta A_r \quad (9)$$

where δ here represents small changes in A_o , the marine uranium activity, and A_r , the average riverine uranium activity and $t' = t/\tau_U$. At steady state ($d\delta A_o/dt'=0$), this reduces to Edwards' first equation (Eqn. 6). To test the simple system's response to periodic forcing, Richter and Turekian let A_r vary according to:

$$A_{r(t')} = A_{r(0)} + \sum_n a_n \sin\left(\frac{2\pi t'}{P_n}\right) \quad (10)$$

where $A_{r(0)}$ is the initial riverine uranium activity, a_n is the amplitude of the change in A_r , and P_n is the period. The results of solving Equation (9) for δA_o for various a_n (using the most simple case, where $n = 1$) are shown in Figure 11 (similar to Richter and Turekian's Fig. 3). As Richter and Turekian concluded, a change of ± 0.1 in A_r (equivalent to a change in $\delta^{234}\text{U}_r$ of 100‰, ~30% of the modern value) would produce barely detectable changes (~5‰) in the marine uranium isotopic composition for a period of 100,000 years (similar to the Hamelin et al. results) and undetectable changes at shorter periods. They point out that 1) a change of 0.1 in A_r is equivalent to a ~25% change in the flux of uranium into the ocean, given its current isotopic composition and 2) one could include changes in the flux of uranium into the ocean in the equations as well, but, as the flux and the isotopic composition of uranium in modern rivers is generally inversely correlated, the addition would not significantly change the results. Figure 11 shows that to get clearly detectable changes (~10‰) in the marine uranium isotopic composition would require a change in A_r of 0.2 (or 200‰, ~66% of the modern value) with a period of 100,000 years or longer; to get marine changes from forcing at periods of less than 100,000 years would require even greater changes in A_r . These results are consistent with Edwards' estimate of an outside envelope of a 10-20‰ change in the marine uranium isotopic composition on a 10^5 -year time scale.

Within the 10-20‰ envelope, it was less clear if samples at the higher end of this range had been altered or reflected small changes in the marine $\delta^{234}\text{U}$ value. Hamelin et al. (1991) made a histogram of initial $\delta^{234}\text{U}$ values of apparently well-preserved last interglacial corals and showed that the mean was 160 (157 with new half-lives), ~11‰ above the modern value. However, an extensive data set of corals that grew during the last deglaciation show no deviation from the modern value at a 2σ precision of $\pm 1\%$ (Fig. 12; Edwards et al. 1993), suggesting that glacial/interglacial changes do not affect the marine $\delta^{234}\text{U}$ value on a 10^4 -year time scale. What was missing was a constraint on how the diagenetic effects that lead to elevated initial $\delta^{234}\text{U}$ values in corals affect their ^{230}Th age.

While many models have been proposed for changes in uranium-series isotopic composition with diagenetic alteration (e.g., Hamelin et al. 1991), documentation of a

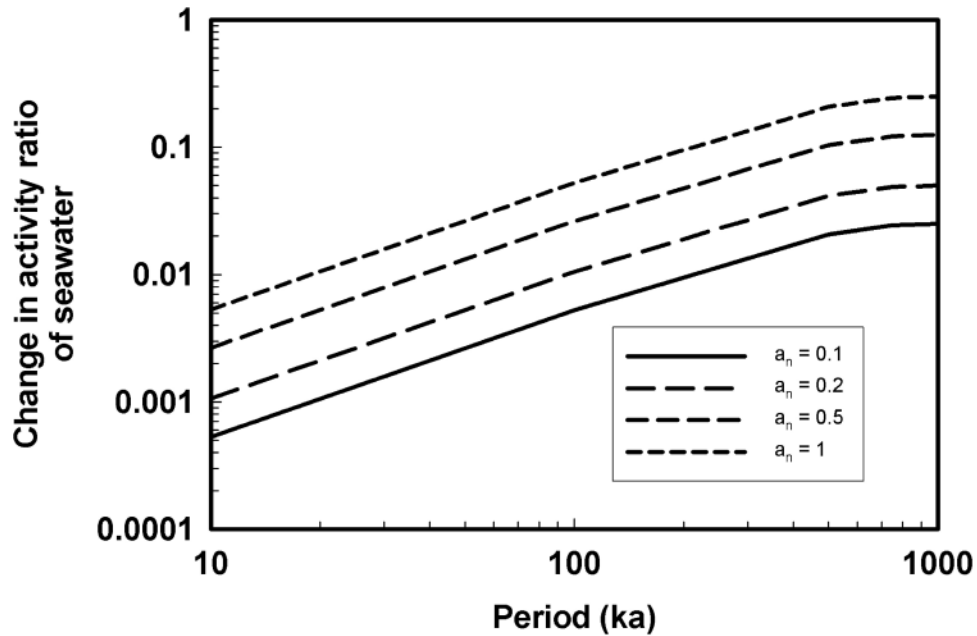


Figure 11. Results from Richter and Turekian (1993) model (Eqns. 9 and 10) for the simplest case, where $n = 1$. Similar to Figure 3 in Richter and Turekian (1993), but with multiple values for a_n .

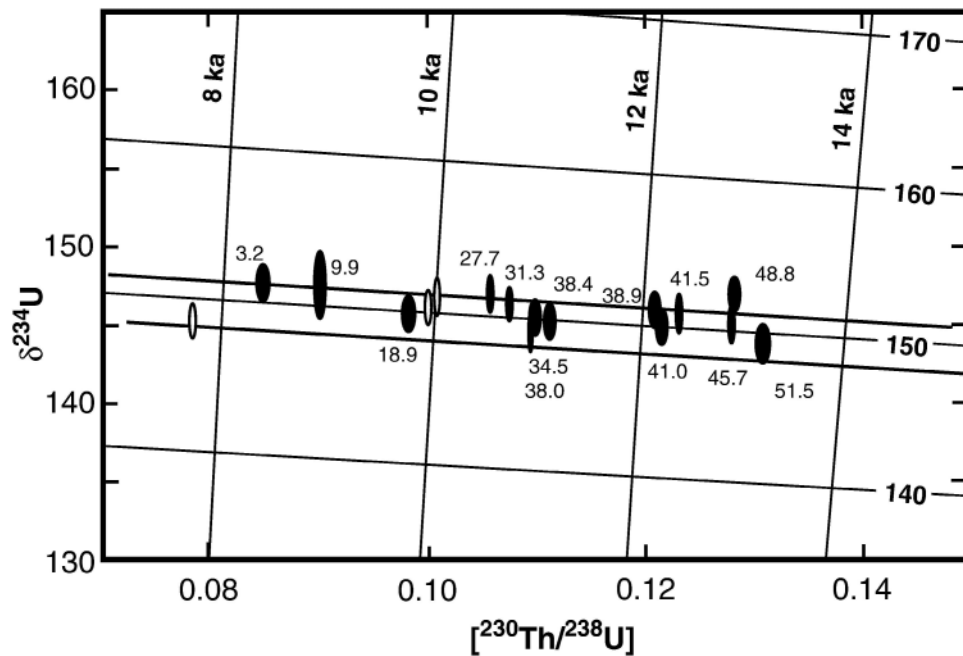


Figure 12. Plot of measured $\delta^{234}\text{U}$ vs. measured $[^{230}\text{Th}/^{238}\text{U}]$ for a set of samples collected from the Huon Peninsula, Papua New Guinea (after Edwards et al. 1993). Open ellipses are data for samples collected from outcrop; closed ellipses are data for samples collected from drill core. All points plot along the initial $\delta^{234}\text{U} = 150$ contour, indicating that all samples have maintained a primary marine uranium isotopic composition, consistent with closed-system behavior. Relatively young samples such as these are more likely to satisfy the closed-system assumption whereas older corals such as those depicted in Figure 13 are not as likely to satisfy this assumption.

correlation between initial $\delta^{234}\text{U}$ values and ^{230}Th ages was made possible by the extensive dating that has been done on Barbados corals. Gallup et al. (1994) demonstrated that for corals from the same terrace, and presumably the same age, $\delta^{234}\text{U}$ values and ^{230}Th ages co-vary. This can best be observed in a plot of measured $\delta^{234}\text{U}$ vs. [$^{230}\text{Th}/^{238}\text{U}$] (similar to Fig. 3). Figure 13 shows TIMS data for Barbados corals available in 1994, coded by terrace. For each terrace, there is a range of initial $\delta^{234}\text{U}$ values, where the lowest value is within error of the modern marine $\delta^{234}\text{U}$ value or above it. The data for each terrace are not randomly scattered but form a rough line that goes to higher ^{230}Th age with higher initial $\delta^{234}\text{U}$ value. Gallup et al. modeled this process assuming continuous addition of ^{230}Th and ^{234}U . In their model, the rate of addition was allowed to vary, but the ratio of ^{230}Th to ^{234}U addition was fixed. The value of this ratio ($^{230}\text{Th}/^{234}\text{U} = 0.71$) was chosen so that the model would reproduce the isotopic composition of VA-1 (Fig. 13) an altered coral of known age (from U/He dating, Bender et al. 1979). They integrated the differential form of the age equation, modified to include ^{230}Th and ^{234}U addition terms in the calculated ratio. This yielded an equation that describes the isotopic composition resulting from adding ^{234}U and ^{230}Th in a fixed ratio and to varying degrees to samples of a given true age (dashed lines on Fig. 13). These “addition lines” follow the trends in the data from each terrace, suggesting that addition is broadly continuous and that it involves both ^{234}U and ^{230}Th in a ratio of about 0.71. This ratio of addition corresponds to an increase of ^{230}Th age of 1 ka for every 4‰ rise in initial $\delta^{234}\text{U}$ value. This provided a semi-quantitative criterion for reliable ^{230}Th ages for corals that have similar trends in isotopic composition. It has been used for corals from many areas, including the Western Atlantic (e.g., Blanchon et al. 2001), the Western Pacific (e.g., Stirling et al. 1995, 1998; Esat et al. 1999), and the Eastern Pacific (e.g., Szabo et al. 1994; Stirling et al. 2001). However, it is often difficult to demonstrate that corals have a similar diagenetic trend where there are a limited number of terraces to sample, or in some cases, such as in Papua New Guinea, corals do not seem to show the same diagenetic trend. Thus, the criterion should be used in conjunction with other measures of diagenesis.

Thompson et al. (in review) have followed up on the Gallup et al. (1994) work with additional analyses and more in depth modeling. The new coral analyses, from the same Barbados terraces, confirm the original Gallup et al. diagenetic trends. Thompson et al. surmised that ^{230}Th and ^{234}U addition could have taken place as ^{230}Th and ^{234}Th adsorption from ground water, prior to decay of ^{234}Th (half-life = 24.1 days to ^{234}U). Although they consider a number of possible sources for aqueous ^{230}Th and ^{234}Th , a likely possibility is recoil ejection from solids into solution during decay of ^{238}U and ^{234}U . This follows a similar idea proposed by Henderson and Slowey (2000) in the context of dating of carbonate bank sediments. Thompson et al. model ^{230}Th and ^{234}U addition on this basis. The model results are a set of calculated addition lines that are numerically similar to the Gallup et al. lines. Their model confirms the Gallup et al. suggestion of broadly continuous addition of both ^{234}U and ^{230}Th . Furthermore, the Thompson et al. model suggests a genetic tie to recoil phenomena. In addition, Thompson et al. suggest that their model can be used to correct ages of samples with non-marine $\delta^{234}\text{U}$, and term these “open-system ages.” These ages (perhaps better be termed “model ages” as they are model-dependent) essentially use a refined version of the Gallup et al. (1994) addition lines to correct for age as a function of $\delta^{234}\text{U}$. This approach may prove useful for certain applications. For example, the empirical trends at Barbados and elsewhere do generally increase in apparent age, with progressive increase in $\delta^{234}\text{U}$. Thus, (1) in localities where trends can be demonstrated to be particularly robust and (2) for scientific problems that allow significant error in age, the addition lines may provide the basis for an age correction. However, the trends observed at different localities

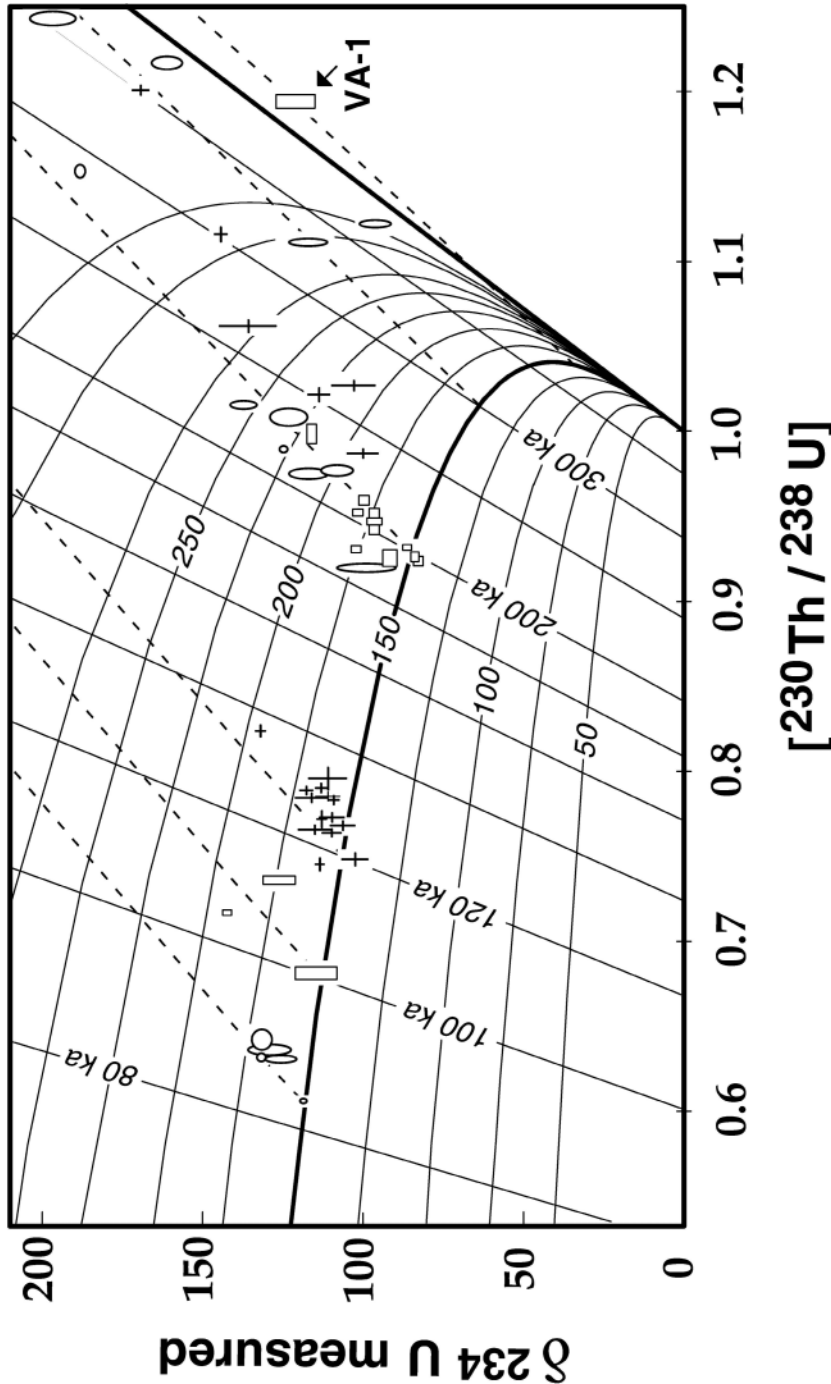


Figure 13. Plot of measured $\delta^{234}\text{U}$ versus $^{230}\text{Th}/^{238}\text{U}$ activity ratio (from Gallup et al. 1994) of all TIMS Barbados data published through 1994 (see Gallup et al. 1994 for references). Data are grouped by terrace, where age and elevation increase from left to right; note symbols are reused for increasingly older terraces. The size of the symbols roughly represents the 2σ error ellipse. The curved lines are contours of initial $\delta^{234}\text{U}$ value (the heavy contour is for an initial equal to the modern marine value) and lines with steep positive slope are contours of ^{230}Th age. The area without contours represents isotopic compositions that are inaccessible through closed-system decay. Dashed lines are ^{234}U - ^{230}Th addition lines, as discussed in the text, calculated with ages of 83, 100, 120, 200, 300, and 520 ka. With additional data from Barbados, Thompson et al. (in review) have confirmed the linear trends originally established by Gallup et al. (1994). Stirling et al. (1998, 2001) have observed similar trends elsewhere.

worldwide are not the same, and in general, the data points from a given terrace are not all co-linear within analytical error (Fig. 13), as required for an exact correction using either the Gallup et al. or Thompson et al. models. Thus, some diagenetic process in addition to the modeled process must affect certain samples. Recent combined ^{231}Pa and ^{230}Th measurements on Barbados corals bear this out (Gallup et al. 2001; Cutler et al. 2003). For example, of 14 corals all with $\delta^{234}\text{U}$ values within 8 per mil of the marine value, 6 had discordant ^{231}Pa and ^{230}Th ages, demonstrating without ambiguity, diagenetic processes that have affected Pa, Th, and/or U, but not $\delta^{234}\text{U}$.

In sum, initial $\delta^{234}\text{U}$ values place important constraints on diagenesis. We are beginning to understand some of the most important processes whereby diagenesis affects $\delta^{234}\text{U}$ and ^{230}Th age. However, we still do not understand a number of important aspects of this process and $\delta^{234}\text{U}$ does not appear to respond to all diagenetic processes. This suggests that, in addition to initial $\delta^{234}\text{U}$ considerations, we need to apply the full range of diagenetic tests.

The above analysis of Barbados corals also places constraints on the history of the marine $\delta^{234}\text{U}$ value. Empirical evidence suggests that diagenesis generally acts to raise the $\delta^{234}\text{U}$ value of Barbados fossil corals, which makes the lowest initial $\delta^{234}\text{U}$ value for each terrace the best estimate of the marine value at the time the terrace was formed. This makes it possible to extend evidence for a stable marine $\delta^{234}\text{U}$ value beyond the last deglaciation (Fig. 12; Edwards et al. 1993) to Marine Oxygen Isotope Sub-stage 5a (Fig. 13, Gallup et al. 1994), the last interglacial (Henderson et al. 1993) and the penultimate interglacial, 200,000 years ago (Fig. 13; Gallup et al. 1994). Similar arguments can be applied to coral data from East Pacific corals (Stirling et al. 2001) and aragonitic carbonate bank sediments from the Bahamas (Henderson 2002), extending evidence that the marine $\delta^{234}\text{U}$ value has remained within error of its present value for interglacial periods in the last ~325 ka and ~360 ka, respectively.

Initial U concentration. If uranium concentration has changed as a result of diagenetic reactions, one may, in principle detect this by comparison between uranium concentrations in modern corals and their fossil counterparts. Early work documenting and studying uranium concentrations in corals is extensive (e.g., Barnes et al. 1956; Tatsumoto and Goldberg 1959; Veeh and Turekian 1968; Schroeder et al. 1970; Thompson and Livingston 1970; Gvirtzman et al. 1973; Amiel et al. 1973; Swart 1980; Swart and Hubbard 1982; Cross and Cross 1983). This broad body of data shows that primary surface coral uranium concentrations lie between 1.5 and 4 ppm (see Fig. 1). Concentrations appear to be species dependent (Cross and Cross 1983). Furthermore, uranium concentrations vary within individual coral skeletons (Schroeder et al. 1970; Shen and Dunbar 1995; Min et al. 1995).

Shen and Dunbar (1995) and Min et al. (1995) showed that uranium concentrations in individual skeletons and between colonies anti-correlate with sea surface temperature, with a shift in U/Ca ratio of about 4.7% per degree Celsius for *Porites lobata*. At the higher latitudes of the tropics and in the sub-tropics, this may result in variation in uranium concentration in excess of 20% within a single skeleton (Shen and Dunbar (1995); Min et al. (1995)). Even in localities with seasonal amplitudes in temperature of one or two degrees, U/Ca varies by several percent seasonally. Thus, primary uranium concentrations in *Porites lobata* vary seasonally by large amounts compared to analytical errors. Because of this temperature-related variation, it is difficult to compare fossil uranium concentrations to primary uranium concentrations in detail, as the true primary concentrations are not known. On the other hand, the Shen and Dunbar (1995) and Min et al. (1995) works suggest that seasonal variation in U/Ca is a general feature of reef-building coral skeletons. Thus, a possible test for diagenetic shifts in uranium is whether

a fossil coral maintains its primary annual variation in U/Ca ratio. Although this test has been suggested (Shen and Dunbar 1995; Min et al. 1995), it has yet to be applied, but may well become an important tool in future dating and diagenesis studies.

Concordancy tests. Combined ^{231}Pa and ^{230}Th dating of corals provides perhaps the most rigorous test for closed-system behavior. Because mass spectrometric ^{231}Pa techniques are still fairly new and because the measurements themselves are not easy, there is still limited data of this sort. In coming years, ^{231}Pa measurements will play a major role in assessing the accuracy of ^{230}Th -based chronologies, such as the late Quaternary sea level curve. The few such data sets on reef-building corals include data reported by Edwards et al. (1997), Gallup et al. (2002), and Cutler et al. (2003), and Koetsier et al. (1999).

These data sets have helped in establishing with high probability the accuracy of the ages of key corals that record important aspects of climate change (Gallup et al. 2002; Cutler et al. 2003). They have also demonstrated that coral samples that might otherwise be considered pristine are, in fact, altered. Data from these samples, which plot off of concordia include those that plot above concordia and those that plot below concordia. Shown in Figure 14 (Edwards et al. 1997) are a set of samples from the Huon Peninsula, Papua New Guinea (left graph) and from Barbados (right graph). The younger (around 10 ka old) Huon Peninsula samples are all on or very close to concordia suggesting that these ages are affected little by diagenetic processes. Older Huon Peninsula samples (10's to more than 100 ka old) from the Huon Peninsula generally plot on, below, and above concordia (Cutler et al. 2003). This indicates a variety of diagenetic conditions on the Huon Peninsula can result in daughter loss/parent gain as well as daughter gain/parent loss. In general this contrasts with Barbados samples of about the same age, which have isotopic compositions that generally plot on or above concordia (Fig. 14). Thus, Barbados diagenetic processes tend to be characterized by parent loss/daughter gain.

Combined ^{231}Pa - ^{230}Th studies will be important in understanding diagenetic processes, and perhaps using this knowledge to constrain age even in cases where the data are discordant (e.g., Fig. 6). However, given our present state of knowledge regarding these issues, the most immediate benefit of these measurements is the identification, along with other tests, of material that has remained a closed to chemical exchange and therefore records accurate ^{230}Th and ^{231}Pa ages. The relatively small number of analyses that have been made so far indicate that concordant material can be identified and can be used to establish solid chronologies.

4. SOURCES OF ERROR IN AGE

A quick glance at Equations (1) through (5) shows sources of error that contribute to error in age, presuming that the assumptions used in calculating the equations hold (initial condition assumptions and the closed-system assumption). These include errors in the decay constants/half-lives, errors in the measurement of the pertinent isotope ratios, and in the case of Equation (3), the error in our estimate of initial $^{230}\text{Th}/^{232}\text{Th}$. Relationships among error in half-lives, laboratory standardization procedures, and ^{230}Th age are discussed in detail by Cheng et al. (2000b).

4.1. Errors in half-lives and decay constants

Half-lives have typically been determined by measuring the activity (rate of decay) of a sample containing a known number of atoms of the nuclide in question and calculating the decay constant via the equation: $N\lambda = a$, where "a" is the measured activity. The half-lives of all of the nuclides pertinent to ^{230}Th and ^{231}Pa dating have been determined in this fashion. Among those that are known most precisely are those of ^{238}U

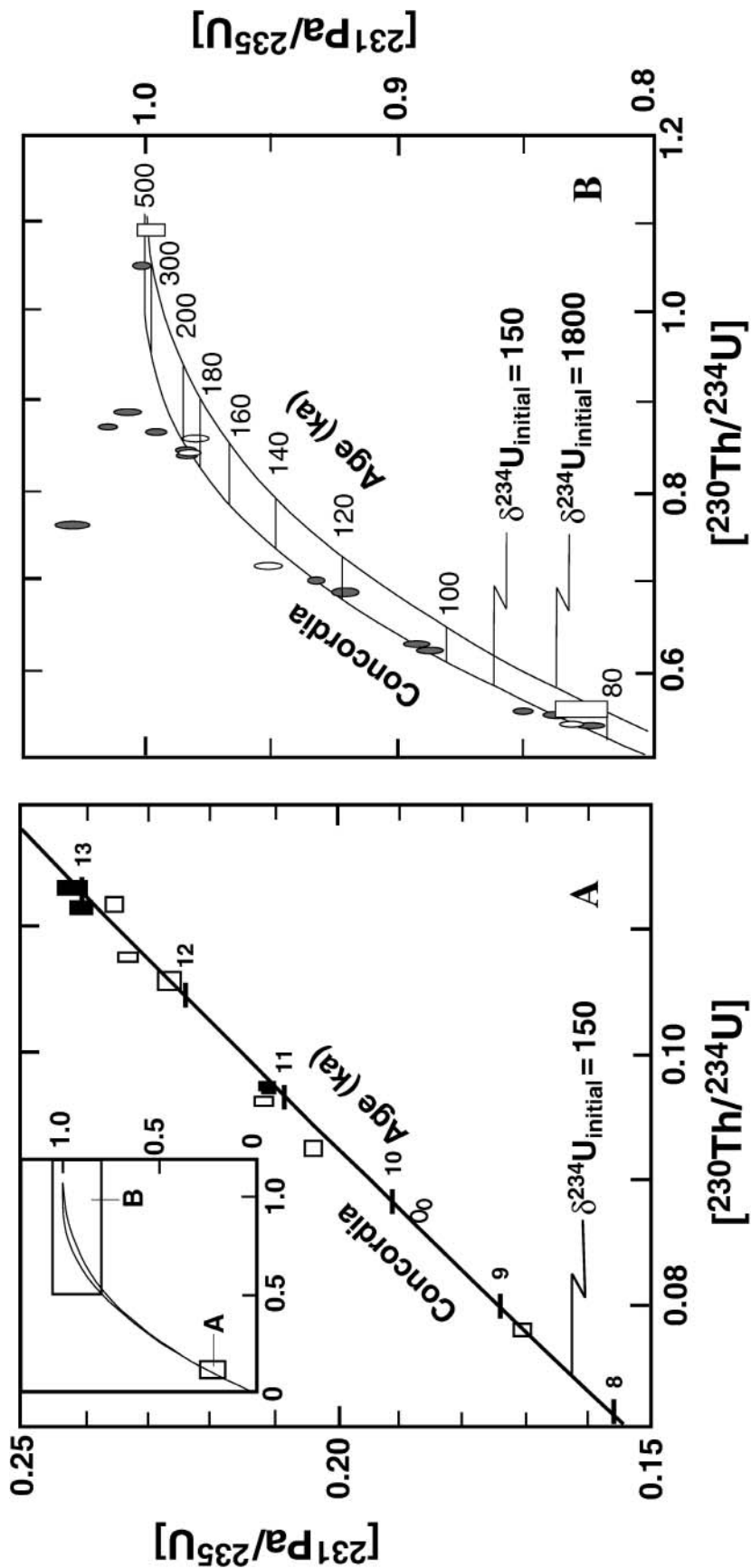


Figure 14. Coral isotopic data from the Huon Peninsula, Papua New Guinea (left diagram) and Barbados (right diagram) plotted in concordia diagrams (after Edwards et al. 1997). The younger Papua New Guinea data all plots close to concordia, suggesting that these samples have behaved as closed-systems. The right diagram includes two concordia curves. The upper curve (initial $\delta^{234}\text{U} = 150$) is appropriate for the coral samples (ellipses), whereas the lower curve ($\delta^{234}\text{U} = 1800$) is appropriate for Devils Hole samples (Ludwig et al. 1992; depicted by open rectangles). Many of the Barbados corals have concordant isotopic compositions, suggesting closed-system behavior. Those that are discordant plot above concordia, consistent with uranium loss and/or daughter gain. Older samples from Papua New Guinea (not illustrated here) plot on concordia, above concordia, and below concordia (Cutler et al. 2003). Thus diagenetic reactions affecting the Papua New Guinea samples appear to be more complex than those affecting the Barbados samples.

and ^{235}U , with errors close to $\pm 0.1\%$ at the 2σ level. For this reason an alternate method for determining half-lives of geologically important radio-nuclides has emerged (Renne et al. 1998). This method starts by establishing the age of a material very precisely using U-Pb dating. As the half-lives of ^{238}U and ^{235}U are known very well, they contribute little error to the age. The known-age material can then be “dated” by another method. As the age is known a priori, one can choose the decay constant as an unknown, and in some cases determine its value more precisely than in a pure laboratory study.

Ludwig et al. (1992) and Cheng et al. (2000b) have applied a similar approach to re-determination of the half-lives of some uranium-series nuclides. This method involves identifying materials that have behaved as closed systems for times long compared to the half-lives of uranium-series intermediate daughters. As such materials are in secular equilibrium, $\lambda_{230} = (\lambda_{238})^{238}\text{U}/^{230}\text{Th}$ and $\lambda_{234} = (\lambda_{238})^{238}\text{U}/^{234}\text{U}$, where the isotope ratios are atomic ratios. In these two cases the only sources of error in the calculated λ_{230} and λ_{234} values are the error in λ_{238} and the error in the appropriate measured isotope ratio of the secular equilibrium material. As the error in λ_{238} is small, the errors in the calculated decay constants are dominated by errors in the measured isotope ratios, which in turn are dominated by uncertainty in our knowledge of isotope ratios in uranium and thorium isotopic standards. Nevertheless, errors in λ_{234} and λ_{230} , determined in this fashion (Cheng et al. 2000b) are small compared to existing determinations in pure laboratory studies, and are therefore the recommended decay constant (half-life) values given in this volume (Table 1, Bourdon and Turner 2003).

Of note are the values for ^{230}Th and ^{234}U as the revised values postdate the development of mass spectrometric techniques for measurement of ^{234}U and ^{230}Th in natural materials. Data published prior to Cheng et al. (2000b) does not use the revised values whereas data published subsequently may or may not use the new values. The revised half-lives do have a small, but significant effect on calculated ^{230}Th ages, particularly ages older than about 100 ka. Furthermore, the new value for the ^{234}U half-life changes $\delta^{234}\text{U}$ values as these are calculated from measured $^{234}\text{U}/^{238}\text{U}$ atomic ratios using the secular equilibrium $^{234}\text{U}/^{238}\text{U}$ value: $\lambda_{238}/\lambda_{234}$. $\delta^{234}\text{U}$ values calculated with the new λ_{234} are about 3 per mil lower than those calculated with commonly used λ_{234} values, hence the revised modern sea water $\delta^{234}\text{U}$ of 145.8 ± 1.7 per mil (Cheng et al. 2000b), compared to earlier values about 3 per mil higher. In general half-lives are now known precisely enough so that their contribution to error in age is comparable to or smaller than typical errors in isotope ratios (determined with mass spectrometric techniques).

Table 1. Preferred half life values.

<i>Isotope</i>	<i>Half Life (years)</i>	<i>Decay Constant (year⁻¹)</i>	<i>Reference</i>
^{238}U	$4.4683 \pm 0.0048 \times 10^9$	$1.5513 \pm 0.0017 \times 10^{-10}$	Jaffey et al. (1971)
^{235}U	$7.0381 \pm 0.0096 \times 10^8$	$9.8485 \pm 0.0134 \times 10^{-10}$	Jaffey et al. (1971)
^{234}U	$245,250 \pm 490$	$2.8263 \pm 0.0057 \times 10^{-6}$	Cheng et al. (2000b)
^{230}Th	$75,690 \pm 230$	$9.1577 \pm 0.0278 \times 10^{-6}$	Cheng et al. (2000b)
^{231}Pa	32760 ± 220	$2.1158 \pm 0.0014 \times 10^{-5}$	Robert et al. (1969)

4.2. Errors in measurement of isotope ratios

As discussed above, mass spectrometric techniques are the methods of choice for measurement of nuclides pertinent to this study. They supercede earlier decay-counting techniques because of their ability to detect a much larger fraction of the nuclides of

interest, thereby reducing sample size and counting statistics error by large amounts. Historical aspects of this transition are discussed by Wasserburg (2000) and Edwards (2000). In terms of precision, the capabilities of mass spectrometric measurements were clear from the very first measurements of the sort (Chen et al. 1986 for ^{234}U ; Edwards et al. 1987a for ^{230}Th). Then, as now, the measurements were limited by counting statistics. From a practical standpoint, given typical sample sizes, natural abundances, and ionization efficiencies, measurements of ^{230}Th and ^{234}U are limited to 2σ precisions of about 1 per mil. For this reason, ^{230}Th precisions have not improved by large amounts since the original mass spectrometric measurements. Precisions in ^{234}U have improved modestly from about ± 5 per mil in the original measurements (Chen et al. 1986; Edwards et al. 1987a) to about ± 1 per mil (Edwards et al. 1993). This latter improvement resulted from modest changes to the original procedures, including removal of reflected peaks from the spectrum, changing from the single-filament graphite loading technique to the double-filament technique to stabilize the ion beam, and a modest increase in sample size to increase the number of ions counted.

Mass spectrometric measurements on corals typically result in errors in ^{238}U , ^{234}U , ^{235}U , and ^{230}Th of ± 2 per mil or better (2σ), with the exception that fractional error in ^{230}Th typically increases progressively from this value for samples progressively younger than several ka. This results from the low concentrations of ^{230}Th in very young corals. Errors in ^{231}Pa are typically somewhat larger than those of the other isotopes, with errors of \pm several per mil, except for corals younger than a few ka.

Errors age resulting from analytical errors are given in Figure 15. Considering ^{230}Th ages, samples a few hundred years old have errors in age of about ± 3 years, 10,000 year-old samples have errors in age of about ± 30 years, and 100,000 year-old samples

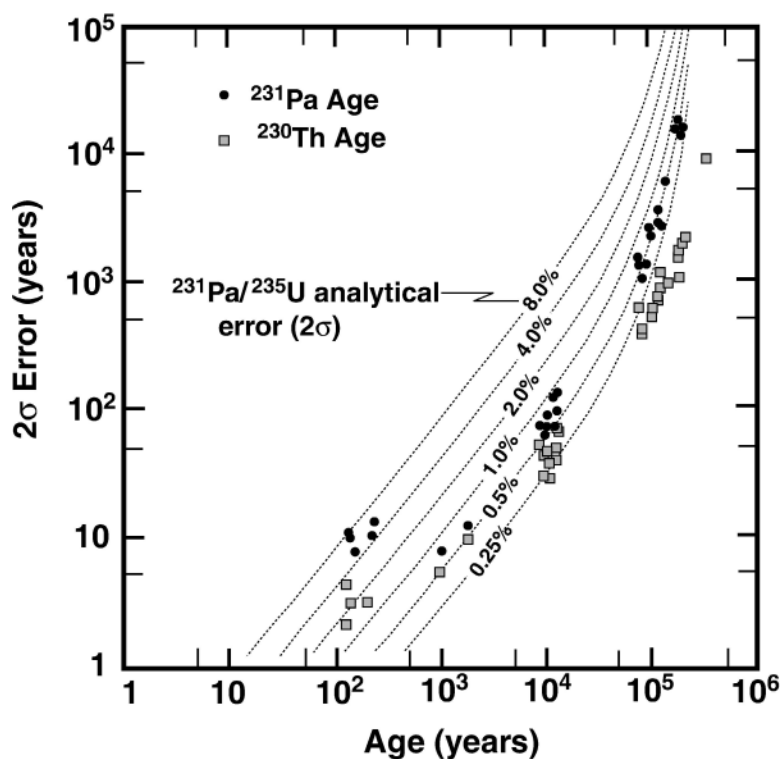


Figure 15. Error in age vs. age, both on log scales (after Edwards et al. 1997). Each data point represents data from a particular sample analyzed by thermal ionization mass spectrometric techniques. Solid circles represent ^{231}Pa ages. Contours of analytical error in $^{231}\text{Pa}/^{235}\text{U}$ pertain to the ^{231}Pa data points. Shaded squares represent ^{230}Th ages. See text for discussion.

have errors in age of ± 1 ka. Samples as young as 3 years have ages distinguishable from zero and samples as old as 700 ka have ages distinguishable from infinity. Considering ^{231}Pa ages, samples younger than 1000 years have errors in age of several to 10 years, 10,000 year-old samples have errors in age of several tens to 100 years, and 100,000 year-old samples have errors in age of a few ka. Samples as young as 7 years have ages distinguishable from zero and samples as old as 250 ka have ages distinguishable from infinity. In sum, ^{230}Th ages can be measured precisely for materials younger than about 600,000 years, and ^{231}Pa analyses can be used to test the closed system assumption and age accuracy over the past 250,000 years.

4.3. Error in initial $^{230}\text{Th}/^{232}\text{Th}$

Errors in $^{230}\text{Th}/^{232}\text{Th}$ only contribute to error in ^{230}Th if the initial ^{230}Th term in Equation (3) ($[\frac{^{232}\text{Th}}{^{238}\text{U}}] [\frac{^{230}\text{Th}}{^{232}\text{Th}}]_i e^{-\lambda_{230}t}$) is significant compared to measured $[\frac{^{230}\text{Th}}{^{238}\text{U}}]$. As discussed above, this term is insignificant for most surface corals and can be ignored, along with any error in this term. However, for some of the unusual samples from the central Pacific (Cobb et al. in review) and Sumatra (Zachariassen et al. 1999) this term is significant and errors in age are limited not by analytical error, but instead by the ability to constrain the $^{230}\text{Th}/^{232}\text{Th}$ values to a specific range. Although not generally a source of error for surface corals, error in initial $^{230}\text{Th}/^{232}\text{Th}$ is more likely to contribute error in ^{230}Th ages of some of the other marine or lacustrine materials discussed below.

5. LATE QUATERNARY SEA LEVELS FROM CORAL DATING

One of the real successes of ^{230}Th dating (and to a lesser degree ^{231}Pa dating) has been its application to the study of sea level change and the causes of the Quaternary glacial cycles. Early work in this area suggested that sea level followed Milankovitch cycles (Broecker et al. 1968; Mesolella et al. 1969). The degree to which this relationship holds and the details of this relationship have been the subject of intense research ever since. The development of mass spectrometric techniques for determining ^{230}Th ages promised to resolve some of these issues. Some of that promise has been realized and more will be forthcoming. Some of the delay has resulted from our incomplete knowledge of diagenetic processes and the fairly recent development of high precision ^{231}Pa techniques. Nevertheless a picture is beginning to emerge from coral dating efforts, in which glacial cycles are partly forced by changes in orbital and rotational geometry, but also respond to other factors, including those responsible for millennial-scale change and perhaps atmospheric CO_2 values. In addition, the timing and rates of sea level change during both glaciation and melting have been established for certain times, and bear on the causes of glaciation and melting. A more extensive review of late Quaternary sea level studies can be found in Edwards et al. (2003).

5.1. Deglacial sea level

One of the major successes of high-precision ^{230}Th dating has been the establishment of a detailed deglacial sea level history (Fig. 16). This has been accomplished directly and indirectly through ^{230}Th dating of corals. One of the main impediments has been the difficulty in recovering sequences of corals that formed during times of low sea level. Fairbanks (1989) first overcame this problem by drilling offshore near Barbados, recovering the full deglacial sequence back to the Last Glacial Maximum (LGM), and dated the corals with ^{14}C techniques. Because the ^{14}C timescale was not yet calibrated in the deglacial time range, the curve was not yet on an absolute timescale. Bard et al. (1990a) dated the same sequence using ^{230}Th techniques. Combined with the ^{14}C data, this yielded an absolute deglacial sea level curve and a ^{14}C calibration. Chappell and Polach (1991) and

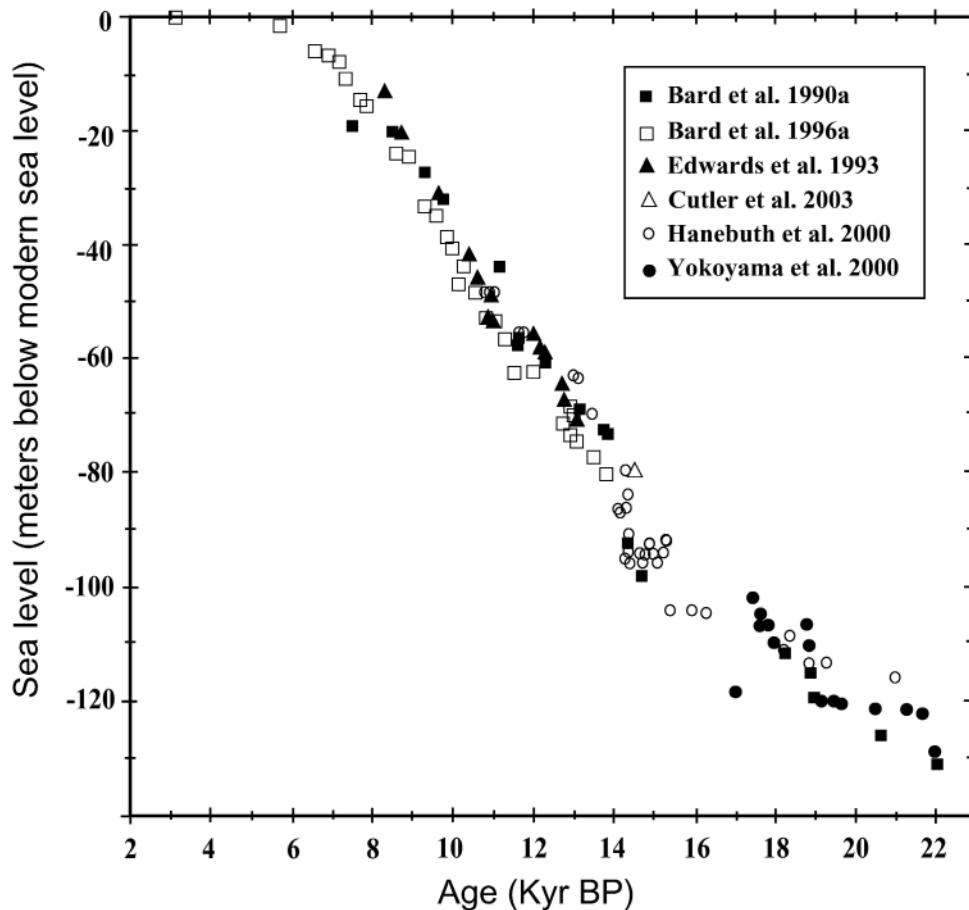


Figure 16. Direct sea level data (23 ky to present) from the indicated references. The data from different sites generally agree, suggesting that different far-field sites have not been affected differentially by isostatic effects. Note also the apparent rapid rises (melt water pulses) in sea level at about 19 ky, 14.6 ky, and 11 ky. The latter two correspond to times of abrupt rise in Greenland temperature (Dansgaard et al. 1993) and East Asian Monsoon intensity (Wang et al. 2001), supporting the idea that sea level can be affected by millennial-scale events. The general rise in sea level observed in this figure corresponds in time to an interval of relatively high insolation at high northern latitudes during summer (see Fig. 17), relatively low insolation at low northern latitudes during winter, and relatively low northern latitudinal gradients during winter. Thus, this curve demonstrates correlations between orbital geometry and sea level, as well as millennial-scale climate change and sea level.

Edwards et al. (1993) obtained a similar sequence of corals by drilling on land into the uplifted deglacial sequence on the Huon Peninsula, Papua New Guinea. Corals were recovered from the portion of deglacial sequence subsequent to 14 ky B.P. ^{230}Th and ^{14}C dating confirmed and increased the resolution of the Barbados results, both in terms of sea level and ^{14}C calibration (Edwards et al. 1993). Similar studies from Tahiti (Bard et al. 1996a) and additional work from the Huon Peninsula (Cutler et al. 2003) have largely confirmed the earlier work. In addition, based in large part upon the ^{14}C calibration work in the ^{230}Th -based coral studies, additional ^{14}C -based sea level studies have contributed further sea level information (Hanebuth et al. 2000; Yokoyama et al. 2000).

The combined data (Fig. 16) show that sea level reached a minimum during the LGM between 20 and 22 ky ago. The rate of subsequent sea level rise was not constant, with relatively rapid rise (melt water pulses) at about 19 ky, between 15 and 14 ky and at about 11 ky, with intervals of little or no rise in sea level immediately before each of these pulses. The latter two of these low sea level rise-melt water pulse pairs correspond

to distinct climate events recorded as temperature change in Greenland ice (Dansgaard et al. 1993) and as change in the intensity of the East Asian Monsoon in Chinese Caves (Wang et al. 2001). The most recent pair corresponds to the Younger Dryas and the warming at the end of the Younger Dryas whereas the earlier of the two pairs corresponds to the interval prior to the Bolling-Allerod and the transition into the Bolling-Allerod. Most the most recent deglaciation took place during a time of increasing summer insolation in the high northern latitudes. Thus, the detailed deglacial sea level curve demonstrates sea level response to both insolation and to millennial-scale climate change (e.g., Younger Dryas, Bolling-Allerod).

5.2. Sea level during the last interglacial/glacial cycle and earlier

Figure 17 summarizes coral sea level data since the last interglacial period and illustrates the current state of sea level reconstructions over the timescale of a full glacial-interglacial cycle. The inset in part b shows all available ^{230}Th data coded so that solid points have initial $\delta^{234}\text{U}$ values within 8 per mil of the marine value and open points have non-marine $\delta^{234}\text{U}$. There are clear inconsistencies for the complete dataset, as well as some inconsistencies for the subset of data with marine $\delta^{234}\text{U}$ values, likely caused by diagenesis. If the dataset is screened further, largely on the basis of ^{231}Pa - ^{230}Th concordancy (see Cutler et al. 2003 for details), one obtains a self-consistent dataset, albeit with a limited number of points (Fig. 17b, main portion). The curve shows a clear correlation with high northern latitude summer insolation, supporting the idea that a significant portion of sea level variability results from changes in orbital geometry. The curve also constrains the rate of sea level drop for specific times during the last glacial cycle. The largest and most rapid drop took place between 76 and 71 ky, when sea level dropped 60 m at a rate in excess of 10 m/ky. This and other times of sea level fall correspond to times of low summer insolation at the high northern latitudes, supporting the conventional view of the Milankovitch Theory. However, these intervals also correspond to times of high winter insolation at low northern latitudes and high winter insolation gradients between low and high northern latitudes. These relationships suggest that glacial growth may have been facilitated by high water vapor pressures in the atmospheric source areas for glacial ice, coupled with efficient moisture transport. Thus, insolation clearly has played a role in controlling sea level, from a number of different perspectives.

Further support for insolation control of sea level comes from a large number of studies employing mass spectrometric ^{230}Th dating of corals, carbonate bank sediments, and speleothems, including dating of Marine Oxygen Isotope Stage 5a (e.g., Edwards et al. 1987b, Li et al. 1991; Gallup et al. 1994; Richards et al. 1994; Ludwig et al. 1996; Edwards et al. 1997; Toscano and Lundberg 1999; Cutler et al. 2003), the Last Interglacial high stand (e.g., Edwards et al. 1987a,b, 1997; Li et al. 1989; Bard et al. 1990b, Chen et al. 1991; Henderson et al. 1993; Zhu et al. 1993; Collins et al. 1993a,b; Stein et al. 1993; Muhs et al. 1994, 2002; Szabo et al. 1994; Gallup et al. 1994; Stirling et al. 1995, 1998; Slowey et al. 1996; Eisenhauer et al. 1996; Esat et al. 1999; McCulloch et al. 2000; Cutler et al. 2003), the Penultimate Interglacial high stands (e.g., Li et al. 1989, Bard et al. 1991; Gallup et al. 1994; Lundberg and Ford 1994; Richards 1995; Slowey et al. 1996; Bard et al. 1996b; Edwards et al. 1997; Robinson et al. 2002; Bard et al. 2002), and earlier interglacial periods (Richards 1995; Stirling et al. 2001). However, there is mounting evidence for sea level change that cannot be caused directly by insolation forcing. In addition to the deglacial evidence for millennial-scale changes in sea level, Chappell (2002) has demonstrated millennial-scale variation in sea level, with an amplitude of about 40 m, during Marine Isotope Stages 3 and 4. The frequency of these changes is much higher than orbital frequencies and cannot result directly from insolation changes. Furthermore, there is now mounting evidence that Termination II sea level rise

preceded high northern latitude summer insolation rise (Stein et al. 1993; Broecker and Henderson 1998; Henderson and Slowey 2000; Gallup et al. 2002). The cause of this apparent early rise is not clear; however, possibilities include insolation changes other than high northern latitude changes, indirect insolation forcing modulated by glacio-isostatic factors, a response to atmospheric CO₂ rise, or a tie to millennial-scale changes. In sum, uranium-series dating of corals and other marine carbonates have demonstrated that sea level responds directly to changes in insolation resulting from changes in orbital geometry. There is also strong evidence that sea level responds to other processes, such as those responsible for millennial-scale climate change, changes in atmospheric CO₂ levels, and/or insolation forcing modulated in some fashion.

6. DATING OF OTHER MARINE AND LACUSTRINE MATERIALS

6.1. Deep sea corals

Deep sea corals are known to live at depths ranging from 60 to 6000 m. Deep sea corals with aragonitic skeletons have uranium concentrations similar to surface corals. Although the literature on uranium-series dating of deep-sea corals is very limited compared to that on surface corals, both mass spectrometric ²³⁰Th ages (Smith et al. 1997; Adkins et al. 1998; Mangini et al. 1998; Lomitschka and Mangini 1999; Cheng et al. 2000a; and Goldstein et al. 2001) and ²³¹Pa ages (Goldstein et al. 2001) have been determined on deep-sea corals. Deep sea corals are of great importance because they are

Figure 17 (on facing page). Coral sea-level record (after Cutler et al. 2003) compared to insolation (Berger 1978) and benthic $\delta^{18}\text{O}$ records (Shackleton et al. 1983). **a.)** 65°N summer half-year insolation curve. Gray bars delineate periods of rapid sea-level fall. (*left inset*) Winter half-year insolation gradients: top curve is 35-50°N, middle is 50-65°N, and bottom is 20-35°N. (*right inset*) 15°N winter half-year insolation curve. **b.)** Coral sea-level record. Circles in inset are data from Edwards 1988; Bard et al. 1990a,b; 1996a; Chen et al. 1991; Edwards et al. 1993; 1997; Stein et al. 1993; Collins et al. 1993; Szabo et al. 1994; Gallup et al. 1994; Stirling et al. 1995; 1998; Ludwig et al. 1996; Chappell et al. 1996; Esat et al. 1999; Toscano and Lundberg 1999; Cabioch and Ayliffe 2001; Yokoyama et al. 2001; and Cutler et al. 2003. Data presented in main portion of (b) are a subset of the samples from the inset, which show no evidence of diagenesis (see Cutler et al. 2003). Triangles are from Cutler et al. 2003; circles from earlier publications. Papua New Guinea samples are upright and Barbados samples inverted. Light gray symbols are data that satisfy both concordancy and $\delta^{234}\text{U}$ criteria (see Cutler et al. 2003). Solid black symbols are a subset of the data that satisfy one of the two criteria (see Cutler et al. 2003). Replicate samples were combined using a weighted average and error bars are 2σ (if not visible, they are smaller than the symbol). Boxes enclose samples older than 15 ky of the genus *Acropora*, known to track sea level closely. Black bars give the duration of MIS 5e sea-level high according to the $\delta^{234}\text{U}$ -screened, coral data sets of Stirling et al. (1995, 1998; upper) and Chen et al. (1991; lower). The dark gray curve provides Cutler et al.'s best estimate of past sea-level change. The portion of the curve immediately before the Last Interglacial (no data shown) is based on data from Gallup et al. (2002). Numbers give average rates of sea-level fall for each of 4 sea level drops. The inset shows all coral sea-level data presently available for times subsequent to the Last Interglacial period, measured with high-precision ²³⁰Th dating methods. Solid symbols represent samples having $\delta^{234}\text{U}$ values that match the modern marine value, open symbols represent samples that do not. **c.)** Benthic $\delta^{18}\text{O}$ record for Carnegie Ridge core V19-30 (Shackleton et al. 1983). Numbers are marine oxygen isotope sub-stages. Dotted tie lines match similar features in the coral and $\delta^{18}\text{O}$ records. Note that sea-level broadly correlates with 65°N summer insolation and broadly anti-correlates both with winter insolation at low latitudes (15°N) of the northern hemisphere and with latitudinal insolation gradient during northern hemisphere winters. This observation supports the idea that a number of aspects of orbitally-controlled insolation change affect sea level. Not shown are high-resolution, high-frequency sea level changes during Marine Isotope Stage 3 and 4 (Chappell 2002), indicating response of sea level to millennial-scale events. Note also high sea level at about 135 ky, preceding the rise in insolation during Termination II (see Henderson and Slowey 2000 and Gallup et al. 2002). This suggests that the beginning of Termination II was not forced directly by insolation changes.

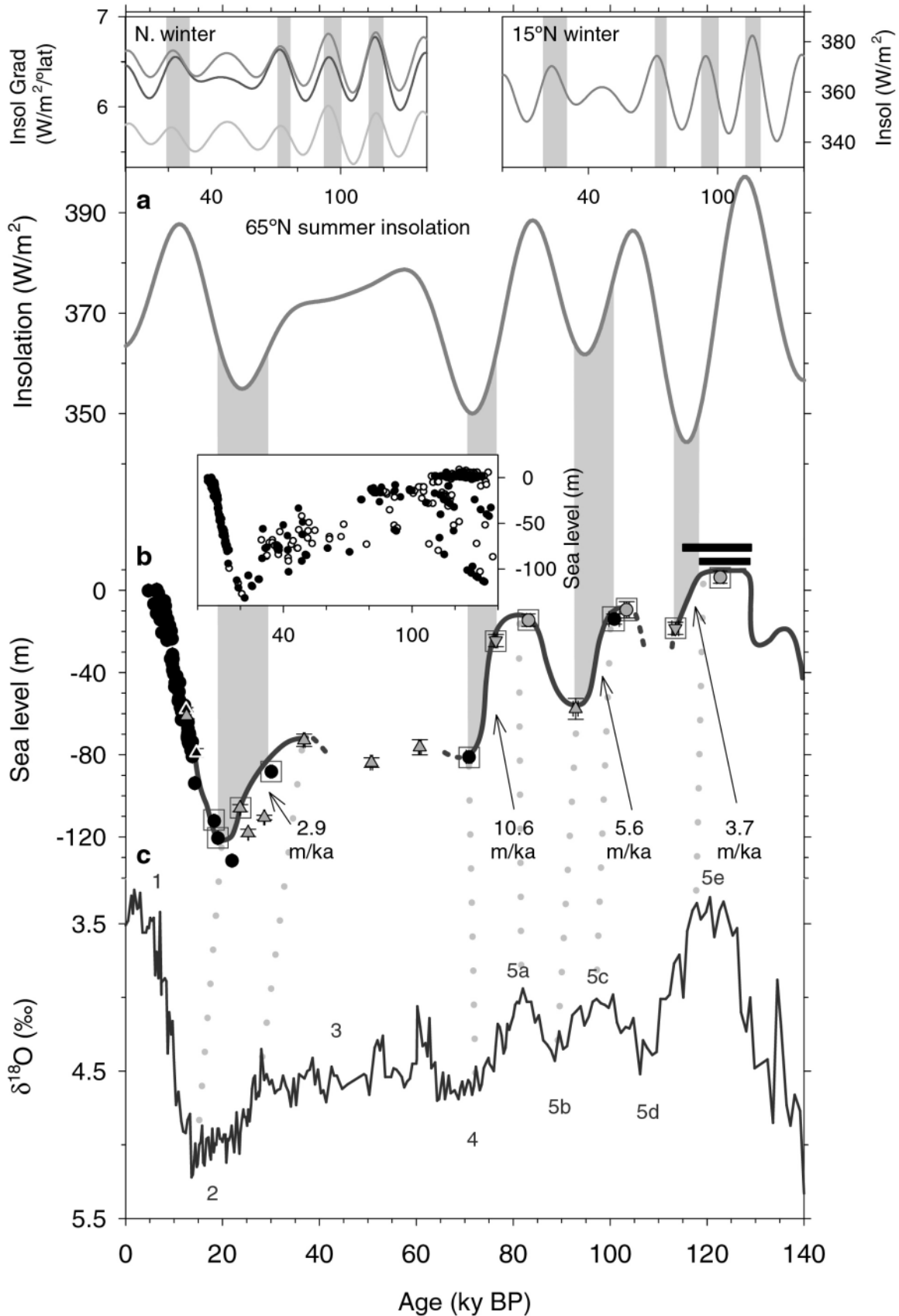


Figure 17. (caption on facing page)

one of a very limited number of archives that record deep-sea conditions at very high resolution. For example, individuals of the deep sea coral species, *Desmophyllum cristagalli* live for on the order of a century or two (Cheng et al. 2000a) and can be sampled at sub-decadal resolution for many proxies. One of the goals of all of the deep-sea coral studies referenced above has been to characterize some aspect of deep ocean circulation and the timing of changes in deep ocean circulation.

The principles of ^{230}Th and ^{231}Pa dating of deep-sea corals are the same as those of surface corals. However, the correction for initial $^{230}\text{Th}/^{238}\text{U}$ and $^{231}\text{Pa}/^{235}\text{U}$ is generally significant for deep sea corals and the error in the age is generally limited by our ability to quantify initial values for these isotope ratios. This stems from the fact that (1) $^{230}\text{Th}/^{232}\text{Th}$ values, ^{230}Th concentrations, and ^{231}Pa concentrations generally increase with depth in the oceans and (2) deep sea corals generally age in the presence of sediments with high ^{230}Th and ^{231}Pa contents, having scavenged these nuclides from the water column. Often the surfaces of deep sea coral skeletons are covered with Mn oxide-rich crusts mixed with detrital sediments. Chemical cleaning techniques (modifications of those used by Shen and Boyle 1988) can remove almost all of this material (Cheng et al. 2000a). Nevertheless, typically fossil deep sea corals have ^{232}Th concentrations (several hundred to thousands of pg/g) significantly higher than their surface counterparts. As the $^{230}\text{Th}/^{232}\text{Th}$ ratio of this thorium is also significantly higher than that for surface corals, the initial ^{230}Th term ($[\frac{^{232}\text{Th}}{^{238}\text{U}}] [\frac{^{230}\text{Th}}{^{232}\text{Th}}]_i (e^{-\lambda_{230}t})$) in Equation (3) is generally significant. Thus, all of the principles and issues discussed for surface corals apply to deep-sea corals, with the added requirement that initial levels of ^{230}Th and ^{231}Pa must be carefully quantified.

The following strategies for minimizing the error in the $\{[\frac{^{232}\text{Th}}{^{238}\text{U}}] [\frac{^{230}\text{Th}}{^{232}\text{Th}}]_i (e^{-\lambda_{230}t})\}$ -term have been applied. Chemical cleaning techniques can remove much of the thorium and protactinium on surfaces, lowering $^{232}\text{Th}/^{238}\text{U}$ dramatically. Potentially, modifications of cleaning procedures can further reduce ^{232}Th levels. $^{230}\text{Th}/^{232}\text{Th}$ values have been determined with isochron techniques and by analyzing young samples. Cheng et al. (2000a) determined a $^{230}\text{Th}/^{232}\text{Th}$ value of $(85 \pm 80) \times 10^{-6}$ for a suite of corals, largely from the Atlantic. Using isochron techniques, Goldstein et al. (2001) determined a $^{230}\text{Th}/^{232}\text{Th}$ value within the Cheng et al. range for a Southern Ocean sample. Goldstein et al. (2001) also applied a two component mixing model to correct for initial $^{231}\text{Pa}/^{235}\text{U}$, in essence using ^{232}Th as an index isotope of protactinium and isochron techniques. After correcting for initial $^{231}\text{Pa}/^{235}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$, they were able to obtain a concordant age on a 16 ka sample from the Southern Ocean. In sum, by using cleaning techniques and carefully characterizing initial isotope ratios, ages with errors approaching those of surface corals can be obtained for some deep sea coral samples (e.g., \pm several to 10 years for samples that are few hundred years old and \pm 100 to 400 years for samples that are between 10 and 20 ka old).

6.2. Carbonate bank sediments

Given the high uranium and generally low Th concentrations of aragonite precipitated biogenically from shallow seawater, carbonate bank sediments, which are dominated by fine aragonite needles formed by *Halimeda* algae, are good targets for U-series dating. *Halimeda* lives on shallow banks and breaks into fine aragonite needles after death, which then accumulate on the shallow banks and are also transported to nearby basins (Glaser and Droxler 1991). Early efforts to date such sediments were mixed (Slowey et al. 1995; Gallup et al. 1995). Attempts to date sediment from the Nicaragua Rise in the Walton Basin were unsuccessful (Gallup 1997) because the sediments were deposited in 900 to 1100 m of water (Droxler et al. 1991), resulting in a long settling path that resulted in high Th concentrations (^{232}Th from 0.2 to 0.6 ppm) due

to adsorption of Th in the water column. Washing and leaching techniques were unable to remove this adsorbed thorium and it did not appear to be of a uniform composition that would allow a correction to be made (Gallup 1997).

However, the Slowey et al. (1995) work on shallower carbonate bank sediments (off of the Bahamas) was successful and led to the dating of a number of important events in the marine oxygen isotope record (including the timing of the Last Interglacial (Slowey et al. 1996), Termination II (Henderson and Slowey 2000) and portions of the Penultimate Interglacial (Slowey et al. 1996, Robinson et al. 2002). The shallower depths obviate the most serious of the initial thorium problems encountered in the Nicaragua Rise work.

However, the quantification of initial ^{230}Th values was still the most important hurdle in establishing precise and accurate ages. Carbonate deposition rates are much higher during interglacial periods as compared to glacial periods. Thus, the fraction of detrital material (along with the ^{230}Th contained in the detrital component) is higher during glacial periods and lower during interglacial periods. Because of the relatively low initial ^{230}Th concentrations in interglacial sediments, bulk sediment dating is possible (Slowey et al. 1996; Robinson et al. 2002). In this case initial ^{230}Th is quantified using a variant of Equation (3), using two initial ^{230}Th terms, one for ^{230}Th in the detrital fraction, one for ^{230}Th in the marine (also referred to as “hydrogeneous” or “adsorbed”) fraction. The fraction of ^{232}Th associated with the detrital component is determined from the aluminum concentration and reasonable estimates of the $\text{Al}/^{232}\text{Th}$ ratio in the detrital component. The detrital ^{230}Th is then determined using estimates of the $^{230}\text{Th}/^{232}\text{Th}$ ratio in the detrital component. The ^{232}Th in the marine component is determined from the difference between measured bulk ^{232}Th and calculated detrital ^{232}Th . The marine or hydrogenous ^{230}Th is then calculated using an estimate of the marine $^{230}\text{Th}/^{232}\text{Th}$ ratio. Using this method, fractional errors in initial ^{230}Th are large. However, for interglacial sediments with low initial ^{230}Th , the contribution to error in age is small. Therefore, this bulk sediment approach has been successful in dating Last Interglacial (Slowey et al. 1996) and Penultimate Interglacial (Slowey et al. 1996; Robinson et al. 2002) bank sediments.

Because of higher initial ^{230}Th contents, different techniques were necessary to date Termination II carbonate bank sediments (Henderson and Slowey 2000). In this case, the detrital fraction was quantitatively removed with washing techniques. Aragonite and calcite fractions were then separated with heavy liquid techniques. The carbonate fractions were then used to obtain ages using isochron techniques. However, patterns in the uranium-isotopic composition of the sediments made it clear that an additional correction was necessary. While the bulk sediment gave a $\delta^{234}\text{U}$ value consistent with the isochron age, subsamples upon which the isochron were based did not. This suggested mobility of uranium-series isotopes within the sediment column, which the authors attributed to recoil processes. A model of this process made it possible to correct for this mobilization by assuming that the subsample should have a $\delta^{234}\text{U}$ value consistent with the isochron age. The resulting corrected isochron ages have a precision of ~ 3 ka and agree with ages for the penultimate deglaciation determined by combined ^{231}Pa and ^{230}Th methods on Barbados corals (Gallup et al. 2002).

6.3. Mollusks and foraminifera

Whereas surface corals, deep sea corals, inorganically precipitated marine aragonite, and algal-precipitated aragonite all have U/Ca ratios within a factor of a few of sea water (e.g., Fig. 1 for surface corals), and consequently uranium concentrations in the ppm range, most biologically precipitated minerals have much lower U/Ca ratios. Mollusks and foraminifera are good examples of the latter. Low U/Ca ratios in and of themselves do not preclude ^{230}Th or ^{231}Pa dating. Present analytical techniques have sufficient sensitivity to

date low U/Ca materials precisely. However, it has been demonstrated that both mollusks and forams pick up and exchange uranium diagenetically, precluding their use for ^{230}Th or ^{231}Pa dating, unless the history of uranium uptake and exchange can be determined.

Broecker (1963) first documented low uranium concentrations in modern mollusks, reporting values in the range of 10 ng/g. Edwards et al. (1987b) published a value about a hundred times lower (75 pg/g) from the aragonitic portion of a giant clam shell (see Fig. 1). The Broecker (1963) values and the Edwards et al. (1987b) value are all well below uranium concentrations of fossil mollusks, which typically lie in the 100's of ng/g to $\mu\text{g/g}$ range. Thus, uranium in fossil mollusks is virtually all diagenetic, violating one of the main assumptions used in solving the ^{230}Th and ^{231}Pa age equations. Two key early studies (Szabo and Rosholt 1969; Kaufman et al. 1971) evaluated ^{230}Th and ^{231}Pa dating of mollusks. Both documented a diagenetic origin for uranium. Szabo and Rosholt (1969) proposed an open system model for determining molluscan ages using combined ^{230}Th - ^{231}Pa analyses. Kaufman showed that even with combined ^{230}Th - ^{231}Pa analyses, general models for uranium uptake could not be used to accurately determine the true age. Given these studies, there is little possibility that even combined ^{230}Th - ^{231}Pa analyses will yield ages similar in precision and accuracy to ages of most of the other materials discussed here. However, there may be a glimmer of hope for using combined ^{230}Th - ^{231}Pa analyses to at least constrain ages in some fashion. The sensitivity of mass spectrometric methods may allow focused ^{230}Th - ^{231}Pa studies that constrain local diagenetic processes and age. Such studies might require numerous analyses of groups of shells from the same stratigraphic horizon or multiple analyses of the same shell, and would only be worthwhile if broad age constraints on the particular deposit would be of importance.

Dating of forams is perhaps even less viable than dating of mollusks. Forams are similar to mollusks in that primary uranium concentrations are low. Ku (1965) showed that calcitic forams have uranium concentrations of about 20 ng/g, about 100 times lower than corals. Delaney and Boyle (1983), Henderson and O'Nions (1995), and Russell et al. (1996) obtained more extensive data, all broadly within this range of tens of ng/g. In addition to their low uranium concentrations, forams have the disadvantage of being associated with deep sea sediments that have high ^{230}Th concentrations scavenged from the water column above. Delaney and Boyle (1983) showed that even after chemical cleaning techniques were applied, foram samples had [$^{230}\text{Th}/^{234}\text{U}$] values in excess of 1 (plot in the "altered" portion of Fig. 3), and therefore had undergone diagenetic addition of ^{230}Th , violating the closed system assumption. Henderson and O'Nions (1995) showed that chemically cleaned foram samples had both elevated uranium concentrations and elevated $\delta^{234}\text{U}$ values, indicating diagenetic addition and likely exchange of uranium, again violating the closed system assumption. Thus, direct ^{230}Th dating of forams is not presently possible.

6.4. Lacustrine carbonates

Lacustrine carbonates with relatively high uranium concentrations include tufas and inorganically precipitated calcite and aragonite sediments, sometimes rich in organic matter. As with deep sea corals and aragonite bank sediments, the basic dating principles are the same as for surface corals. As with deep sea corals and aragonite bank sediments the initial ^{230}Th term ($[\frac{^{232}\text{Th}}{^{238}\text{U}}] [\frac{^{230}\text{Th}}{^{232}\text{Th}}]_i (e^{-\lambda_{230}t})$ term in Eqn. 3) is generally significant. This results from the general association of the carbonates with detrital sediments containing significant levels of thorium. As a consequence isochron techniques are often necessary when dating lacustrine carbonates. Because uranium residence times in lakes are much shorter than in the ocean, lacustrine uranium concentrations and uranium isotopic compositions vary from lake to lake and temporally. Thus, neither initial $\delta^{234}\text{U}$ values nor uranium concentrations yield information about possible

diagenetic reactions, as they would in the marine realm. Because these tools are not available for testing the closed system assumption, future work may well move toward combined ^{230}Th - ^{231}Pa dating for tests of the sort. At present only ^{230}Th dating, typically using isochron techniques, has been applied to this sort of sediment. Early work on lacustrine tufas was done by Kaufman and Broecker (1965). This work characterized times of relatively moist climate in the western U.S., and is also one of the first papers to place constraints on Pleistocene atmospheric ^{14}C levels. Lin et al. (1996) followed up on this work using modern techniques and carefully characterizing two different initial thorium components, detrital thorium with low $^{230}\text{Th}/^{232}\text{Th}$ values and hydrogenous thorium with higher $^{230}\text{Th}/^{232}\text{Th}$ values. Israelson et al. (1997) dated Holocene bulk lake sediment, which was composed of organic-rich carbonate. They were able to obtain ^{230}Th ages without large initial ^{230}Th corrections because of extremely high uranium concentrations in their samples (up to 76 ppm). Schramm et al. (2000) analyzed an extensive sequence of aragonitic lacustrine sediments deposited from Lake Lisan, the last glacial analogue of the Dead Sea. This study is one of a very limited number of studies that constrains atmospheric ^{14}C levels over the first half of the radiocarbon time range. Hall and Henderson (2001) dated early Holocene carbonate lake sediments from Antarctica using detailed isochron techniques. They showed that ^{14}C dating in these lakes was not viable because of large reservoir effects. In addition to dating of lacustrine carbonates, some recent studies have applied ^{230}Th techniques to the dating of lacustrine salts, using the same principles discussed above. As with lacustrine carbonates, isochron approaches are necessary. One such study elucidates the timing of climate change over the last two glacial cycles from Death Valley sediments (Ku et al. 1998), whereas another study characterizes climate change in northern Chile over the last glacial cycle (Bobst et al. 2001). Additional studies such as these are needed in order to characterize and understand climate change on glacial-interglacial time scales at continental sites.

7. CONCLUSIONS

As ^{230}Th and ^{231}Pa dating are among few methods available for dating natural materials that formed in the past 600,000 years, these methods play an important role in the Earth Sciences. In addition to the ongoing efforts to characterize sea level, these methods have been important in, calibrating the ^{14}C time scale, characterizing recent tectonic movement, characterizing ocean circulation changes, and characterizing climate change. The ^{14}C calibration literature can be accessed through references cited in Beck et al. (2001). Although the ^{230}Th and ^{231}Pa dating literature is extensive and this field has made major contributions to the Earth Sciences, major questions remain. For example, there are still major questions regarding the Late Quaternary sea level curve that may require combined ^{230}Th - ^{231}Pa techniques to resolve (see Cutler et al. 2003). There are major questions regarding ^{14}C calibration, which again will likely require combined ^{230}Th - ^{231}Pa techniques to resolve (see Beck et al. 2001). These and other important problems will likely be tackled using combined ^{230}Th - ^{231}Pa dating, and to some degree relying on new inductively-coupled plasma mass spectrometric techniques for increasing throughput and in some instances modestly enhancing precision (see Stirling et al. 2001; Shen et al. 2002; Stirling and Goldstein 2003).

ACKNOWLEDGMENTS

We thank G. Henderson and C. Stirling for careful reviews of an earlier version of this manuscript. This work was supported in part by National Science Foundation Grant ESH 9809459.

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