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An open-system model for U-series age determinations of fossil corals

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Abstract

The source of excess ^{234}U in fossil corals and its relationship to U-series age determinations has been an outstanding problem in geochronology for more than 20 years. With increasing numbers of U-series isotope measurements in corals, and significant improvements in analytical precision through mass spectrometry, it is increasingly apparent that a substantial fraction of observed isotope ratios cannot be reasonably explained by closed-system decay. Moreover, observations of a positive correlation between $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios in corals from the same terrace are difficult to explain. However, the decay of dissolved uranium and α -recoil mobilization of uranium daughters produce particle-reactive ^{234}Th and ^{230}Th , and the coupled addition of these Th isotopes could simultaneously increase coral $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$. Here we present a quantitative model, based on decay-dependent redistribution of ^{234}Th and ^{230}Th , permitting calculation of open-system coral ages. These equations provide a general solution to the α -recoil redistribution problem, applicable to any alpha decay series. While measured isotope ratios of corals from the three youngest stratigraphically defined Barbados terraces are inconsistent with closed-system decay, they fall in broadly linear arrays agreeing with model predictions. Isotopic arrays of older Barbados corals, and corals from terraces around the world, are also consistent with model predictions suggesting the open-system model is generally applicable. Corals with extreme isotopic compositions that are impossible to produce by closed-system decay are consistent with the limited range of isotopic compositions predicted by the model at ages older than 600 ka. For corals from a single terrace, ^{234}Th and ^{230}Th redistribution appears to be a source of systematic conventional age error, even for corals with slightly elevated ^{234}U . However, open-system ages are consistent, even for corals with extremely elevated ^{234}U . For the youngest three Barbados terraces, mean open-system terrace ages are consistent with mean conventional terrace ages calculated from pristine samples. If the most accurate conventional ages are from corals with an initial $^{234}\text{U}/^{238}\text{U}$ identical to modern seawater, then the open-system model will improve the accuracy of coral U-series age determinations and dramatically increase the number of reliable ages.

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1. Introduction

1.1. U-series age determinations and excess ^{234}U

The elevations and U–Th ages of fossil coral reefs provide important constraints on Quaternary sea-level history. However, it has long been known that $^{234}\text{U}/^{238}\text{U}$ ratios of many fossil corals are incompatible with closed-system decay from a modern seawater $^{234}\text{U}/^{238}\text{U}$ ratio, and corals with elevated ^{234}U have excess ^{230}Th and older apparent ages [1]. This positive correlation, often observed in corals from the same terrace [1–5], is inconsistent with the contrasting behavior of U and Th in natural waters. Here we review the evidence for open-system behavior of U-series isotopes in fossil corals, and the outstanding questions posed by these isotopic anomalies. We suggest the redistribution of U-series daughters during decay could provide a qualitative and quantitative explanation for previously puzzling observations. Furthermore, we demonstrate that open-system age equations offer an attractive alternative to conventional equations for the determination of U–Th ages.

1.2. The problem of elevated initial $^{234}\text{U}/^{238}\text{U}$ in corals

The fundamental premise of U–Th dating is that corals incorporate substantial seawater uranium and negligible thorium into their aragonite skeletons during growth, and remain subsequently closed to uranium and thorium loss or gain [6]. The accuracy of U–Th ages currently depends on this assumption. Mass balance considerations suggest secular variation in seawater $\delta^{234}\text{U}$ is limited [7] and constrained to 10‰/100 kyr [8] (small variations in $^{234}\text{U}/^{238}\text{U}$ activity are expressed in delta notation [9], where $\delta^{234}\text{U}$ is the deviation, in per mil, of $^{234}\text{U}/^{238}\text{U}$ activity from its secular equilibrium value of 1.000). Data from fossil corals suggest interglacial seawater $\delta^{234}\text{U}$ was within error ($\pm 2\%$) of the modern value up to 330 ka [3–5,10]. There is little information from glacial

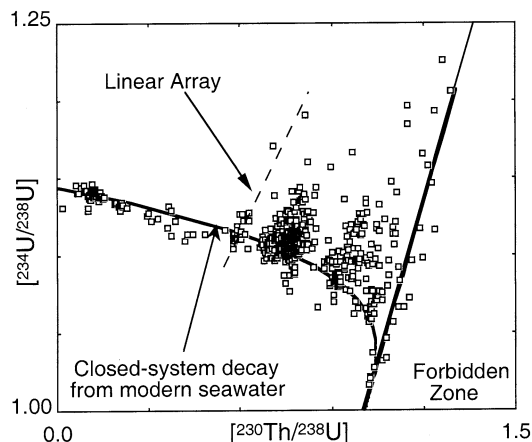


Fig. 1. A compilation of U-series isotope measurements on a $^{234}\text{U}/^{238}\text{U}$ – $^{230}\text{Th}/^{238}\text{U}$ activity ratio diagram. If the uranium isotopic composition of the ocean has not changed with time, all coral isotope measurements should plot on the indicated closed-system decay curve. The heavy straight line represents closed-system evolution from an ‘infinite’ $^{234}\text{U}/^{238}\text{U}$ activity ratio at an ‘infinite’ age. Points that plot to the right of this line have isotopic compositions that are impossible to achieve through closed-system decay. The dashed line indicates a linear compositional array representative of those observed for corals from the same fossil reef. Data from Table 1¹ and [1,3–5,8,10,11,13,14,17–21,34,47–54].

periods, but some data suggest seawater $\delta^{234}\text{U}$ as low as 136‰ [11] during the most recent glacial. Marine sediment measurements suggest that seawater $\delta^{234}\text{U}$ was within $\pm 15\%$ of modern during the last 360 kyr, and there is no indication of a secular $\delta^{234}\text{U}$ trend to 780 ka, although the data scatter is large [12].

While modern corals faithfully record seawater $^{234}\text{U}/^{238}\text{U}$ [13], fossil coral $^{234}\text{U}/^{238}\text{U}$ often does not reflect closed-system evolution from a modern seawater $^{234}\text{U}/^{238}\text{U}$ ratio (Fig. 1). The magnitude of these anomalies increases systematically with age to at least 550 ka [14]. Uranium exchange with ^{234}U -enriched waters has been suggested as a plausible mechanism to elevate coral $^{234}\text{U}/^{238}\text{U}$

¹ See Table 1 in the online version of this paper.

[13–15]. However, in Barbados and the Bahamas, where there is abundant evidence of high $^{234}\text{U}/^{238}\text{U}$ in fossil corals [3,13,14,16–20], $^{234}\text{U}/^{238}\text{U}$ of groundwater is quite low; close to secular equilibrium [21,22].

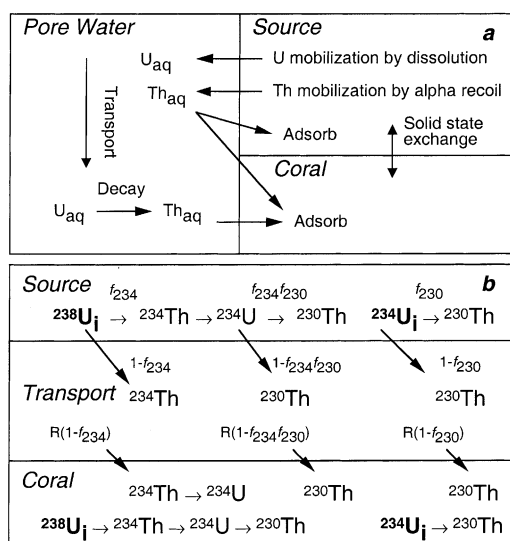


Fig. 2. (a) Schematic diagram of three possible pathways of ^{234}Th and ^{230}Th transport between the source and the measured coral. The dissolved U pathway requires water, while the α -recoil pathway can either be aqueously mediated or occur in the solid state. All three processes include a rate-limiting step that depends on radioactive decay. (b) Schematic diagram of the two-box model for decay-dependent transfer of ^{234}Th and ^{230}Th . In contrast to Henderson [26,27], f_{234} and f_{230} are defined only for the source and are always less than 1. At the source, f_{234} is the retained fraction of the ^{234}Th production. The retained fraction of the ^{230}Th from ^{238}U -produced ^{234}U is f_{230} , but this ^{234}U has already been reduced by a factor of f_{234} , and the final retained fraction of ^{230}Th from an initial amount of ^{238}U ($^{238}\text{U}_i$) is $f_{234}f_{230}$. The retained fraction of the ^{230}Th production from an initial amount of ^{234}U ($^{234}\text{U}_i$) is f_{230} . The escaping fractions are $1-f_{234}$, $1-f_{234}f_{230}$, and $1-f_{230}$. For example, if 10% of all decays escape, 90% of the ^{234}U production remains, 81% (90% of 90%), of the ^{230}Th produced from ^{238}U remains, and 90% of the ^{230}Th production from ^{234}U remains. The escaping fractions are 10%, 19%, and 10%, respectively. More of the ^{230}Th produced from ^{238}U escapes because there are two α -decays involved in its production. Some fraction of the escaping nuclides arrives at the coral, and is added to its closed-system production. R (Appendix 1², Eq. 19) is a scaling factor that accounts for the fraction arriving and the relative amounts of uranium in the boxes.

The observed range of positively correlated $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ anomalies in corals from the same terrace is difficult to explain by uranium mobility, and the mobility of thorium is low in natural waters [23]. Addition or exchange of ^{234}U -enriched uranium would increase $^{234}\text{U}/^{238}\text{U}$ but decrease $^{230}\text{Th}/^{238}\text{U}$, and addition may measurably increase uranium concentration. A correlation between uranium concentration and $^{234}\text{U}/^{238}\text{U}$ has not been observed [1,8]. Conversely, increasing $^{230}\text{Th}/^{238}\text{U}$ by uranium loss should not change $^{234}\text{U}/^{238}\text{U}$. Addition of ^{230}Th by detrital contamination would dramatically increase ^{232}Th , and ^{232}Th concentrations in fossil corals are uniformly quite low. These anomalies have been extensively investigated, but the difference between the closed-system evolution and observed isotope ratios has yet to be satisfactorily explained [1–3,8,13–15,24]. Furthermore, in a recent study, more than half of the corals passing a stringent initial $\delta^{234}\text{U}$ ($\delta^{234}\text{U}_i$, calculated from a samples age and measured $\delta^{234}\text{U}$) criterion had discordant $^{231}\text{Pa}/^{235}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ ages, and 3 of 7 corals with concordant $^{231}\text{Pa}/^{235}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ failed the $\delta^{234}\text{U}_i$ criteria [19]. These U-series isotopic anomalies suggest corals are generally open systems, and it has long been clear that the accuracy of U/Th ages is not limited as much by analytical precision as by our understanding of isotopic anomalies in fossil coral [2].

1.3. The effects of coupled ^{234}Th and ^{230}Th addition

The positive correlation of $^{234}\text{U}/^{238}\text{U}$ with $^{230}\text{Th}/^{238}\text{U}$ in corals of approximately the same true age suggests there is a common mechanism causing the enrichment of ^{234}U and ^{230}Th . The initial decay product of ^{238}U is ^{234}Th , which has a 24.1-day half-life. Any process operating during or shortly following decay would affect ^{234}Th and ^{230}Th equally while potentially fractionating these daughters from their uranium parents. It has recently been proposed that a small fraction of radiogenic ^{230}Th and ^{234}Th (which rapidly decays to

² See Appendices 1 and 2 in the online version of this paper.

^{234}U) is locally redistributed within the fossil reef [24]. Although thorium mobility is low, uranium decay provides two mechanisms for thorium redistribution, and this could occur via three pathways (Fig. 2a). In the first mechanism, any dissolved uranium in pore water would produce aqueous ^{234}Th and ^{230}Th by decay. In the second mechanism, ^{234}Th and ^{230}Th are ejected from the crystal lattice by α -recoil during decay [25–27] and could be redistributed directly by recoil or through an aqueous intermediary with brief advective transport. In either case, the geochemical fate of ^{234}Th and ^{230}Th produced by decay is controlled by rapid adsorption. If this is the case, excess ^{234}U in corals is an index for added ^{230}Th , and open-system addition can be quantitatively modeled [26–29]. It is worth noting that the behavior of ^{231}Pa is somewhat similar and a positive correlation of $^{231}\text{Pa}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ is reported [30], suggesting parallel implications for the ^{231}Pa – ^{235}U chronometer. This hypothesis is consistent with three previously unexplained observations regarding ^{234}U enrichments in corals. First, the identical aqueous geochemistry of ^{234}Th and ^{230}Th is consistent with the observed correlation between $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$. Second, small amounts of ^{234}Th addition could produce the observed elevations of $^{234}\text{U}/^{238}\text{U}$ without measurably increasing uranium concentration. Finally, the continuous process of radioactive decay implicated in ^{230}Th and ^{234}Th redistribution is consistent with the systematically increasing magnitude of coupled ^{234}U and ^{230}Th anomalies with age.

1.4. Previous diagenetic models

Gallup et al. [3] were the first to include diagenetic addition terms in the U-series differential equations and derive an age equation with these terms included. The equations describe the addition of ^{234}U and ^{230}Th at constant rates. Addition rates were estimated using the U/He age and U/Th isotopic composition of a coral with $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios that could not be explained by closed-system evolution. Henderson et al. [26,27] showed that α -recoil had significant effects on the isotopic composition of marine carbonate

sediments, and made the first attempt to account for α -recoil in U-series decay equations. Combining these two ideas, we derive equations to account for the coupled addition of ^{234}U and ^{230}Th to fossil corals. Our model uses the systematics of U-series decay with appropriate physical and geochemical constraints, not the empirical assessment of model parameters from selected data, distinguishing our approach from that of Gallup [3]. Moreover, working from the same differential equations, we derive an analytical solution that is significantly different from that of Henderson [26,27].

2. Analytical methods

Isotopic ratios of corals were determined using a double focusing magnetic sector multiple collector Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) (FISONS Plasma-54) at the Lamont–Doherty Earth Observatory, using a ^{233}U – ^{229}Th mixed spike. Measurements used a multi-static mode procedure modified from Luo [31], where both mass discrimination and Daly/Faraday gain are corrected during the sample run by measuring the natural $^{235}\text{U}/^{238}\text{U}$ ratio. Seven measurements of New Brunswick Laboratory standard CRM-U010, interspersed with sample analyses over the course of a year, had a mean $^{234}\text{U}/^{238}\text{U}$ atom ratio of 5.43×10^{-5} (0.03, 2 σ), within error of the certified value of 5.466 ± 0.051 , and previously reported measurements of 5.44 ± 0.015 , 5.42 ± 0.04 , 5.425 ± 0.005 [32], 5.43 ± 0.02 [33], and 5.445 ± 0.004 [34]. Reported errors (Table 1¹) are propagated from in-run counting statistics, and are the 2- σ error of the mean.

3. The model

3.1. A two-box model

A two-box model was constructed for decay-dependent ^{234}Th and ^{230}Th addition. Some fraction of the daughters produced by ^{238}U and ^{234}U are transferred from the source to the measured coral during decay. While the uranium source

may reside in the dissolved and/or solid phase (Fig. 2a), the model assumes that the isotopic composition of dissolved uranium reflects the surrounding carbonate and treats all source uranium as one box (Fig. 2b). We derive general solutions for the time-dependent evolution of the $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ activity ratios of the source, the nuclides lost, and the measured coral (Appendix 1²). The resulting open-system age equation is:

$$\begin{aligned} \left[\frac{^{230}\text{Th}}{^{238}\text{U}} \right]_{\text{measured}} &= (1 - e^{-\lambda_{230}t}) + \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \\ &\left(\left[\frac{^{234}\text{U}}{^{238}\text{U}} \right]_{\text{coral}}^{\text{coral}} - 1 \right) (e^{-\lambda_{234}t} - e^{-\lambda_{230}t}) + \\ &\frac{1}{m} \left(\left[\frac{^{234}\text{U}}{^{238}\text{U}} \right]_{\text{measured}} - \right. \\ &\left. \left(\left(\left[\frac{^{234}\text{U}}{^{238}\text{U}} \right]_{\text{initial}}^{\text{coral}} - 1 \right) e^{-\lambda_{234}t} + 1 \right) \right) \end{aligned} \quad (1)$$

Where:

$$m = \frac{(1 - f_{234})(1 - e^{-\lambda_{234}t})}{\left((1 - f_{234}f_{230}) \left(1 - \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} e^{-\lambda_{234}t} + \frac{\lambda_{234}}{\lambda_{230} - \lambda_{234}} e^{-\lambda_{230}t} \right) \right) + (1 - f_{230}) \frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}} \left[\frac{^{234}\text{U}}{^{238}\text{U}} \right]_{\text{initial}} (e^{-\lambda_{234}t} - e^{-\lambda_{230}t})} \quad (2)$$

Eq. 1 is significantly different from previous α -recoil equations [26,27] that were adapted from simplified [6] U-series equations, yielding an incorrect solution (see Appendix 1²). However, at ages younger than 150 ka, the difference between Eq. 1 and those of Henderson [26,27] is small. A full analytical solution of the original differential equations shows that measured $^{230}\text{Th}/^{238}\text{U}$ is that expected from closed-system evolution plus a correction based on the difference between measured and expected closed-system $^{234}\text{U}/^{238}\text{U}$ ratios. This correction, the net $^{230}\text{Th}/^{234}\text{U}$ activity added, depends on the systematics of U-series decay, the fraction of decays retained (f_{234} and f_{230}), and $\delta^{234}\text{U}_i$. For corals that have lost ^{234}Th and ^{230}Th , the parameters in Eq. 2 refer to the measured coral. For most corals, which have gained ^{234}Th and ^{230}Th , the parameters in Eq. 2 refer to the source, and f_{234} and f_{230} of the source cannot be calculated from the isotope ratios of the mea-

sured coral (Appendix 1²). At any instant, the atom ratio of $^{230}\text{Th}/^{234}\text{Th}$ escaping is approximately equal to the $^{234}\text{U}/^{238}\text{U}$ activity ratio of the source, so the addition ratio decreases with time and is not constant as in Gallup's model [3]. Any difference between f_{234} and f_{230} arising from differing α -decay energies introduces a small and constant offset between $^{234}\text{U}/^{238}\text{U}$ activity and $^{230}\text{Th}/^{234}\text{Th}$ atom ratios. $^{234}\text{U}/^{238}\text{U}$ at secular equilibrium is determined by f_{234} ; if 5% of ^{238}U decays are lost the secular equilibrium activity ratio will be 0.95. Therefore, at ages < 150 ka, the primary control on the addition ratio is $\delta^{234}\text{U}_i$, because source evolution has not yet departed significantly from a closed system. At ages > 500 ka, the primary control is f_{234} , because $\delta^{234}\text{U}$ is closer to secular equilibrium than $\delta^{234}\text{U}_i$. With a set of estimated parameters, these equations can be used to determine an open-system age from $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ measurements (Appendix 2²). While this model is applied here to the U-series dating of corals, the equations provide a general solution to the problem of α -recoil redistribution, and are applicable to any α -decay chain.

3.2. The estimation of model parameters

While f_{234} and f_{230} can be calculated for corals that have lost ^{234}U , gaining corals require these parameters be independently estimated (Appendix 1²). The $\delta^{234}\text{U}_i$ of the source and/or coral must also be estimated. A best estimate, likely range, and extreme limit are provided for each parameter, based on physical and geochemical constraints. This approach results in an independent theoretical model with potential errors that can be directly assessed. The model results can subsequently be compared with the data without the risk of circular reasoning.

3.2.1. Initial $^{234}\text{U}/^{238}\text{U}$

It seems reasonable to assume that the $\delta^{234}\text{U}_i$ of the source and the measured coral are identical, since all carbonate in a reef is likely to have precipitated from seawater at approximately the same time, and any dissolved uranium should reflect the isotope ratio of the surrounding carbon-

ate. Isotope measurements of modern corals [5], with the new decay constants for ^{234}U and ^{230}Th [35] (used in all calculations), yield an estimate of 1.145 for the initial $^{234}\text{U}/^{238}\text{U}$ activity ratio ($\delta^{234}\text{U}_i = 145\text{‰}$), in close agreement with a recently determined mean of 145.8‰ for a compilation of modern corals [36]. The likely range of coral $\delta^{234}\text{U}_i$ appears to be small, about $\pm 3\text{‰}$ for interglacial periods. Although the extreme values of seawater $^{234}\text{U}/^{238}\text{U}$ over the range of U/Th dating are not yet completely constrained, it seems unlikely that it has been more than 20‰ below and 5‰ above the modern value during this period.

If the source of daughter addition is the surrounding carbonate, the likely difference between coral and source $\delta^{234}\text{U}_i$ is small. While it is possible that a reef contains some fraction of material eroded from a previous reef, the $^{234}\text{U}/^{238}\text{U}$ of an older reef is unlikely to be different enough to shift the bulk isotopic composition of the new reef significantly. For example, the incorporation of 25% 100 000-year-old carbonate would lower the bulk $\delta^{234}\text{U}$ of a modern reef by only 9‰. The two-box model assumes that the $^{234}\text{U}/^{238}\text{U}$ of the dissolved and solid phase U are identical. Although continental waters frequently have $^{234}\text{U}/^{238}\text{U}$ that is greater than the rocks through which they flow, this has been attributed to preferential leaching of ^{234}U from recoil-damaged crystal lattice sites [37] and to direct recoil from dissolution-resistant high-uranium mineral phases [25]. Direct recoil of ^{230}Th and ^{234}Th from the solid phase is accounted for explicitly in our model. When elevated $^{234}\text{U}/^{238}\text{U}$ has been observed in water flowing through older carbonates, experiments have implicated the leaching of incorporated U-rich detrital minerals [38]. In fresh, young carbonates within the range of U/Th dating, dissolution is likely to proceed more rapidly than leaching of recoil-damaged sites, resulting in a dissolved $^{234}\text{U}/^{238}\text{U}$ that is very close to that of the carbonate. If the dissolved U source is not the reef carbonate, more extreme values of uranium activity ratios must be considered. While surface waters are probably limited between 1 and 2, groundwaters can range from 0.75 to > 30 [39].

3.2.2. f_{234}

During α -recoil, the probability of escape from a mineral grain depends on the grain's size and shape and the recoil distance [25]. Kigoshi [25] measured a 0.055- μm recoil distance in zircons and suggested that the recoil distance should be inversely proportional to density. This implies a 0.087- μm recoil distance for aragonite. Therefore, the theoretical production loss of ^{234}U by α -recoil [25], given the observed size range (1–5 μm) and roughly cylindrical shape of coral aragonite needles, is about 3% ($f_{234} = 0.97$). Any loss of uranium from the crystal surface, where recoil loss is greatest, will tend to keep the effective f_{234} near 1. Corals having $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios lying below the closed-system evolution line (Fig. 1) have a restricted range of ^{234}U depletions, indicating any α -recoil loss that may be occurring does not exceed 5%, agreeing reasonably well with theoretical predictions. However, the primary source of ^{234}Th and ^{230}Th may be carbonate sediment. In a reef setting, the dominant source of such sediment is the bioerosion of corals, and it is estimated that 95% of sediment retained on reefs is sand-sized ($> 63 \mu\text{m}$) [40]. Therefore, the dominant control on f_{234} is still the size of the aragonite crystals. In the case of dissolved uranium, all its decays are lost to adsorption, which might suggest the fraction remaining (f_{234}) is 0. However, the decay rate is likely to be much slower than the rate of uranium replenishment from dissolution, so the effective f_{234} is controlled by the surrounding carbonate. During dissolution, there should be no change in the $^{234}\text{U}/^{238}\text{U}$ ratio of the remaining solid in the absence of α -recoil, so the fraction of ^{234}U production remaining in the solid should be 1. Therefore, the best estimate of f_{234} lies between 0.97 and 1; the model uses $f_{234} = 0.975$. An $f_{234} < 0.9$ requires a mean crystal size $< 1 \mu\text{m}$, or a significant mass fraction ($> 20\%$) of particles $< 1 \mu\text{m}$, both of which seem unlikely. This constrains the likely range of f_{234} between 0.9 and 1; the extreme limits are 0 and 1, by definition.

3.2.3. f_{230}

Corals that have lost ^{234}U are assumed to have done so by α -recoil. Therefore, for an f_{234} of

0.975, f_{230} is 0.971 (Eq. 26, Appendix 1²), and the f_{230}/f_{234} ratio is 0.996. For corals that have gained ^{234}U , dissolved uranium decay must be considered. If the timescale for thorium adsorption is significantly shorter than the 24.1-day half-life of ^{234}Th , there should be no fractionation of ^{234}Th from ^{230}Th , and $f_{230}/f_{234} = 1$. The final value of f_{230} depends on f_{recoil} (the fraction of excess daughters contributed by α -recoil), which is not known. An f_{recoil} of 0.5 minimizes the potential error. Fortunately, f_{230}/f_{234} for the α -recoil and dissolved-uranium-decay cases is nearly identical. This yields best estimates of $f_{\text{recoil}} = 0.5$, $f_{230} = 0.973$, and $f_{230}/f_{234} = 0.998$. By definition, the extreme limits of f_{recoil} are 0 and 1. Given $0.9 \leq f_{234} \leq 1$ and $0 \leq f_{\text{recoil}} \leq 1$, the likely range of f_{230} is 0.88–1 and f_{230}/f_{234} 0.983–1.

4. Results

4.1. Correlation of $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios of coeval corals

In order to examine the relationship between true age and isotopic composition of corals, we measured a suite of 64 samples (Table 1¹) from the three lowest terraces of Barbados, West Indies (13°10'N, 59°33'W). These terraces, Barbados I, II and III, have been previously mapped, correlated, and dated by U–Th [1,3,8,15,17,19,20,41]. Corals from a particular terrace should be broadly coeval, with an age range not exceeding several thousand years. Thus, terraces defined as geomorphic units provide an age constraint independent of the U–Th system. In addition, we also analyzed samples from some of the higher terraces, where geomorphic correlation is less well constrained.

A closed-system model is inconsistent with measured $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios (Fig. 3). Coral isotopic compositions from each terrace should fall on a closed-system evolution line, given their limited age range and the negligible variation of seawater $^{234}\text{U}/^{238}\text{U}$ possible on that time-scale. Instead, corals from each terrace form a broadly linear array of isotopic anomalies intersecting the closed-system evolution line for mod-

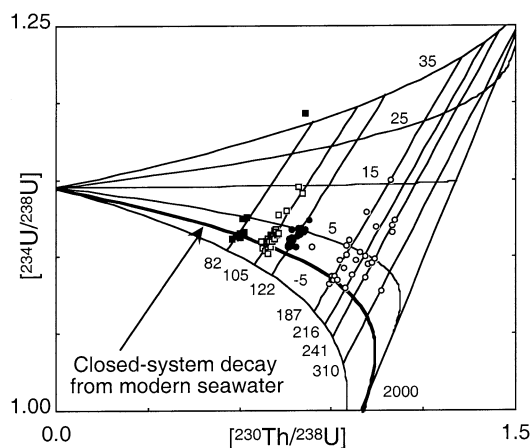


Fig. 3. U-series isotope measurements from Table 1¹, on an open-system diagram. The error bars are smaller than the plot symbols. Sub-horizontal curves are open-system evolution curves, representing the indicated percentages of apparent ^{234}U -production gain and loss. The sub-vertical lines are lines of equal age calculated from the indicated ages (ka). The open-system diagram is uniquely determined by Eqs. 15, 16, 20, and 21 (Appendix 1²), with the appropriate parameters for gain or loss as described in the text and Appendix 1². Closed-system decay from an initial $^{234}\text{U}/^{238}\text{U}$ ratio of modern seawater (1.145) is shown. Solid squares, open squares and solid circles are corals from the Barbados I, II and III terraces, respectively. The open circles are corals from older Barbados terraces.

ern seawater. However, our open-system model is consistent with these measurements (Fig. 3). The observed range of isotopic compositions evolves from an initial $^{234}\text{U}/^{238}\text{U}$ of modern seawater, and almost 90% of the data can be explained with an apparent excess ^{234}U production of 5% or less. Lines of equal age, with slopes which are uniquely determined by Eq. 2 and independent of the data, fall along the isotopic arrays from the Barbados I, II, and III terraces. Isotopic arrays of older corals also fall along model-predicted slopes.

Nine samples from an exposed section through the Barbados II terrace provide stratigraphic context. Measured isotope ratios exhibit a wide range of values, a strong positive correlation ($R^2 = 0.93$), and a systematic increase with depth (Fig. 4). While increasing $^{230}\text{Th}/^{238}\text{U}$ might be explained as increasing true age with depth, $^{234}\text{U}/^{238}\text{U}$ is expected to decrease with depth in this case. The opposite trend is observed. These observations are

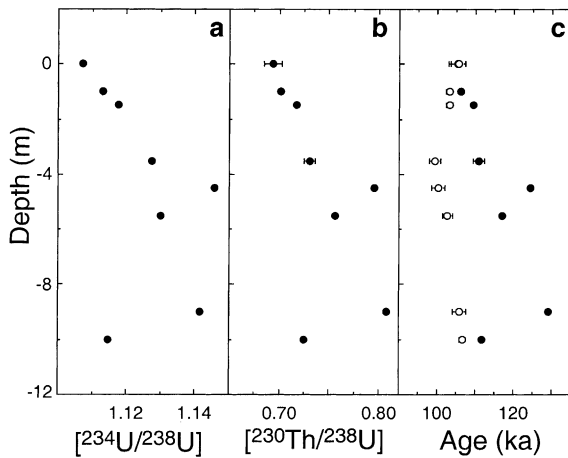


Fig. 4. U-series isotope data from a section through the Barbados II terrace. Data are from Table 1¹, samples NU1501, NU1502, NU1503, NU1504, NU1505, NU1506, NU1442B (mean of two measurements) and NU1478. (a) Measured $^{234}\text{U}/^{238}\text{U}$ activity ratios. (b) Measured $^{230}\text{Th}/^{238}\text{U}$ activity ratios. (c) Ages: filled circles are closed-system ages and open circles are open-system ages. Except where visible, error bars are smaller than plot symbols.

consistent with the concept of aqueously mediated thorium isotope redistribution, which predicts an isotopic gradient along the direction of transport.

4.2. Model comparison with previously published isotope measurements

Corals occasionally have isotopic compositions that are impossible to attain through closed-system evolution (Fig. 1). A compilation of the most extreme of these ‘forbidden’ compositions agrees reasonably well with a narrow range of isotope ratios predicted by the open-system model for corals older than 616 ka (Fig. 5a). It is very encouraging that the model results are consistent with the data at this extreme upper limit, where changes in isotopic composition due to variations in true age are minimal, and cumulative errors from model failure are potentially large. Our model is also consistent with the anomaly patterns in other data sets from Barbados, Australia, the Bahamas, New Guinea, and the East Pacific, suggesting that the good agreement of the model with our Barbados data is not a special case (Fig. 5a,b).

4.3. Open-system age determinations

The recovery of consistent ages from broadly coeval corals is a fundamental and practical model test. The most accurate conventional U–Th age estimates should be obtainable from corals showing no evidence of open-system behavior. Closed-system corals should be 100% aragonite, have a

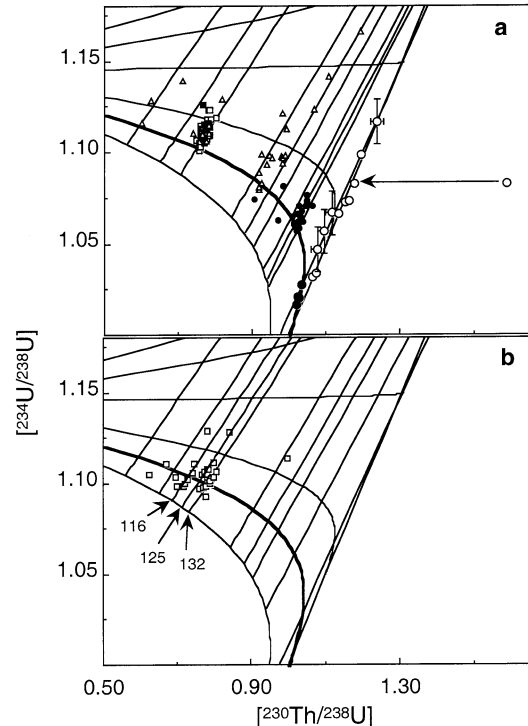


Fig. 5. U-series isotope measurements of previous workers plotted on an open-system diagram. Errors for mass spectrometry measurements are smaller than the plot symbols; typical errors for α -counting measurements are shown. (a) Open squares, triangles, solid squares and solid circles are data from the Bahamas [13], Barbados [3], Western Australia [5], and the southeast Pacific [4], respectively. Open circles are corals with the most extreme ‘forbidden’ closed-system compositions from [1,4,10,20,21,50]. Only a single measurement significantly exceeds isotope ratios predicted by the open system. This coral, JH-15-1 [10], has approximately 25% less uranium than others of the same species from this study do. When the $^{230}\text{Th}/^{238}\text{U}$ is corrected by restoring the missing uranium (indicated by arrow), the resulting isotopic composition agrees well with the rest of the data. The sub-horizontal and sub-vertical lines are the same as Fig. 3, except for added model lines for 288, 330 and 616 ka. (b) Data from New Guinea [49,53]. Three linear arrays are evident at 116, 125, and 132 ka.

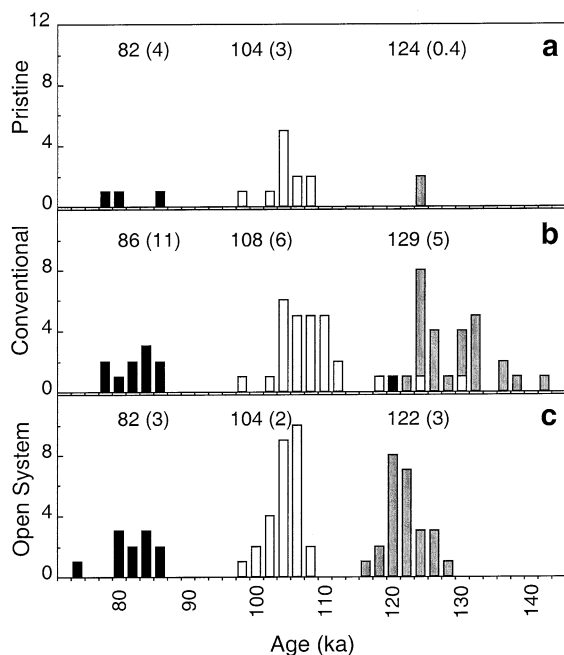


Fig. 6. Histogram of age determinations from the corals of the Barbados I, II and III terraces. (a) Conventional ages of the best available samples, using selection criteria described in the text and Table 1¹ notes. (b) Conventional ages of all corals. (c) Open-system ages of all corals. In all panels, the black bars are corals from the Barbados I terrace, white bars are corals from the Barbados II terrace, and gray bars are corals from the Barbados III terrace. The mean and standard deviation of ages from each terrace are shown.

$\delta^{234}\text{U}_i$ near modern seawater, and have uranium concentrations [42,43] of modern corals. We will refer to corals that meet these three criteria as pristine. Pristine corals from the Barbados I, II, and III terraces represent samples drawn from the population of all measured corals from each terrace. In the absence of systematic error, the mean ages of pristine and all measured corals should be similar. However, the mean conventional ages of all samples from each terrace are older and show greater scatter than conventional ages of pristine samples (Fig. 6). In contrast, the mean open-system ages of these corals agree very well with pristine coral ages (Fig. 6). These results suggest that the open-system age model effectively eliminates apparent systematic error in conventional ages and that open-system ages are as accurate as conventional ages calculated from pristine corals.

Ages from the Barbados II terrace section (Fig. 4) again provide stratigraphic context. While the section is bounded by closed-system ages of 105 and 112 ka at the top and bottom, respectively, the intervening ages range from 106 to 129 ka over a vertical distance of 8 m, with two significant inversions of 7 and 17 kyr (Fig. 4c). Open-system ages cluster around a mean of 103 ± 3 ka, agreeing well with the mean conventional ages of pristine corals. Major age inversions are eliminated. The recovery of consistent ages from a single outcrop where coral $\delta^{234}\text{U}_i$ ranges from modern seawater at the surface to a 14% gain at depth provides strong support for the accuracy of open-system ages.

The variation of mean age with $\delta^{234}\text{U}_i$ (Fig. 7) provides a test for systematic error. Any collection of corals from one terrace represents a population with a single (unknown) mean true age, and samples drawn from this population should have reasonably consistent mean ages approximating the population mean. The mean conventional age clearly depends on $\delta^{234}\text{U}_i$, demonstrating the ubiquitous and consistent systematic error associated with elevated ^{234}U . Mean open-system ages are generally within error of the grand open-system mean, which agrees extremely well with the mean conventional age where $\delta^{234}\text{U}_i$ is equal to modern seawater (Fig. 7), and with the mean conventional age of pristine corals (Fig. 6). Scatter in mean ages (Fig. 7a–c) is very likely due to small sample sizes; with a larger data set (Fig. 7d) scatter is greatly reduced. While systematic error in conventional ages predicted by the open-system model is clearly evident, even at small deviations of $\delta^{234}\text{U}_i$, open-system ages are consistent, even at extreme $\delta^{234}\text{U}_i$. If the conventional age of corals with a $\delta^{234}\text{U}_i$ identical to modern seawater provides the best estimate of true age, then the open-system age model will improve the accuracy of coral age determinations.

5. Discussion

5.1. Error in open-system and conventional ages

The reproducibility of mean open-system ages

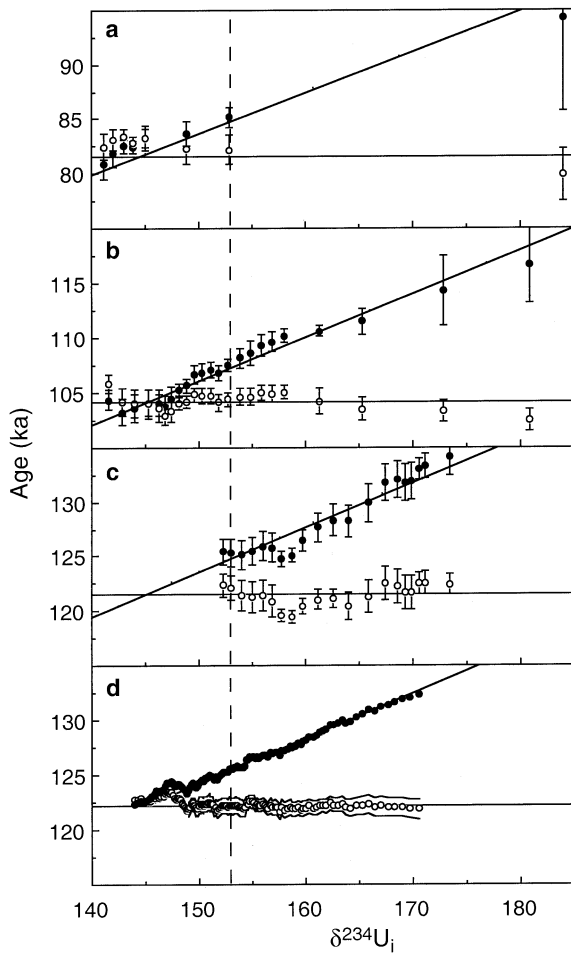


Fig. 7. Test for systematic error associated with elevated ^{234}U . The mean ages and $\delta^{234}\text{U}_i$ of corals from the same terrace are plotted. The vertical dashed line is a typical upper limit for conventional ages currently considered acceptable, using a $\delta^{234}\text{U}_i$ criterion of modern seawater $\pm 8\%$ [3]. The horizontal and sub-horizontal lines are model-predicted ages based on the mean of all open-system ages. Filled circles are conventional ages and open circles are open-system ages, and error bars are $1\text{-}\sigma$ error of the mean. (a) Corals from the Barbados I terrace (Table 1¹), each point is the mean of 4 measurements ($n=4$). (b,c) Corals from the Barbados II and III terraces, respectively (Table 1¹), ($n=6$). (d) A compilation of corals from the Last Interglacial terrace [5,13,18,51–53] and (Table 1¹), ($n=40$). For clarity, an error envelope is shown for open-system ages with $\delta^{234}\text{U}_i > 147\%$ only. The other errors are similar. Samples with $>10\%$ calcite, >2 ppm Th, and conventional ages >150 ka were excluded. Model ages are from mean of open-system ages with $\delta^{234}\text{U}_i > 147\%$.

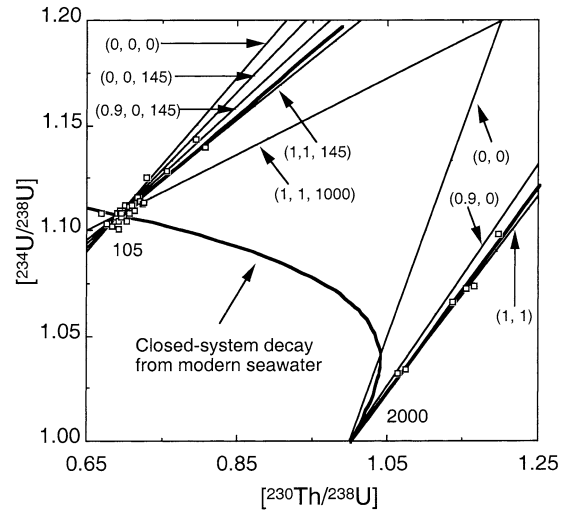


Fig. 8. Limits on model slopes. Heavy straight lines are model lines of equal age calculated with the indicated ages (ka) and our chosen model parameters. Lines around each model slope are slope limits from extreme values of f_{234} , f_{recoil} , and source $\delta^{234}\text{U}_i$. Labels on each line indicate the parameters used to generate it, either $(f_{234}, f_{\text{recoil}}, \delta^{234}\text{U}_i)$ or $(f_{234}, f_{\text{recoil}})$. The two closest limits to the 105-ka model line are the limits of f_{recoil} given the likely range of f_{234} : (1, 1, 145), and (0.90, 0, 145). The intermediate limit to the left is the lower limit of f_{234} and f_{recoil} : (0, 0, 145). Extreme limits for $\delta^{234}\text{U}_i$ shown are (0, 0, 0) and (1, 1, 1000). For the 2000-ka isochron, $\delta^{234}\text{U}_i$ does not affect the slope. The extreme limits of f_{234} and f_{recoil} are (0, 0) and (1, 1). The intermediate limit to the left is the likely lower bound of f_{234} and f_{recoil} (0.90, 0). Coral isotopic compositions are from the Barbados II terrace (Table 1¹), and ‘forbidden’ coral compositions measured by mass spectrometry compiled from the literature [4,10,21,50]. Typical error bars are the size of plot symbols.

for corals from the same terrace (Fig. 7) suggests that uncertainty in calculated ages is small, particularly when compared to the systematic bias in conventional ages associated with elevated $\delta^{234}\text{U}_i$. An analysis of error in both age models shows the reason for this. Error in the estimation of f_{234} , f_{recoil} , and the $\delta^{234}\text{U}_i$ of the source would affect the slope of equal age lines (Fig. 8). At ages <150 ka, the primary control on model slope is $\delta^{234}\text{U}_i$. However, even large changes have a limited impact on slope. Data scatter along the closed-system decay curve cannot be explained by varying model parameters (Fig. 8) and is likely due to variation in true age. Patterns of isotopic variation are not consistent with variation in

slope parameters (Fig. 8), which would produce increased scatter at greater degrees of Th addition. Furthermore, the scatter of isotopic compositions around equal age lines decreases with age (Fig. 3). While this pattern is not consistent with model error because small deviations from modeled behavior would accumulate with time, it is consistent with compositional variation due to variation in true age. If the constraint of $\delta^{234}\text{U}_i = 145$ is accepted, the range of slopes between the extreme limits of f_{234} and f_{recoil} is quite small (Fig. 8). At ages < 150 ka, uncertainty in f_{234} and f_{recoil} has little effect on calculated ages, except for the most extreme isotopic compositions. If the lower limit of $f_{234} \geq 0.90$ is accepted, the slope uncertainty is smaller still. At ages > 1500 ka, $\delta^{234}\text{U}_i$ has no effect on the model slope, and the impact of f_{234} is maximum. The most extreme isotopic compositions of corals ‘forbidden’ via closed-system decay can only be explained by an f_{234} very close to 1, and no composition plots below $f_{234} = 0.90$ (Fig. 8). While the number of data points is small, this supports our independent estimate of the value and likely range of f_{234} . Variation in slope from the limits of f_{recoil} is within the analytical precision of most data. Given likely parameter ranges, model slopes are well constrained and potential errors from slope uncertainty are less than typical analytical errors (Fig. 9a).

The assumption that isotope addition is a continuous process is implicit in the derivation of open-system equations. While radioactive decay is certainly continuous, the transport efficiency of isotopes from source to sink may vary, introducing an age error that increases at higher degrees of addition. The sensitivity of calculated ages to a catastrophic failure of the continuous addition assumption was tested. For each age plotted in Fig. 9a, ^{234}Th and ^{230}Th addition was modeled at a 5% rate for half the total time and then the system was allowed to evolve as a closed system. In this worst-case scenario, the age error introduced is always comparable to typical measurement error (Fig. 9a). The apparent initial $^{234}\text{U}/^{238}\text{U}$ of fossil corals increases with time to at least 550 ka [14], suggesting that the addition of ^{234}U is broadly continuous until that time.

Therefore, the effects of possible variations in transport efficiency on the calculated ages should be negligible.

Two potential sources of error are relatively constant with the degree of addition: true coral $\delta^{234}\text{U}_i$ and measurement uncertainty. The $\delta^{234}\text{U}$ of paleo-seawater is a potential source of systematic error that may be significant at ages < 250 ka (Fig. 9a). The $^{234}\text{U}/^{238}\text{U}$ measurement is the dominant source of analytical error, contributing approximately two-thirds of the total. For the same absolute analytical errors, the total analytical uncertainty in open-system and conventional ages is similar, with open-system ages having a slight advantage at ages older than 400 ka (Fig. 9a). Gain or loss of uranium or thorium, other than accounted for by the model, will produce similar errors in both open-system and conventional ages. Fortunately, standard screening criteria for uranium concentration, ^{232}Th , and mineralogy should eliminate most unsuitable samples.

For conventional ages, increasing age with measured $\delta^{234}\text{U}_i$ (Fig. 7) is a source of systematic error that has not been explicitly included in previous estimates. The current practice is to accept only those ages that fall within a limited range of measured $\delta^{234}\text{U}_i$ close to the modern seawater value (e.g. $\pm 8\%$ [3]). This approach eliminates highly inaccurate ages, but does not remove the bias from the remaining ages (Fig. 7). This systematic error is about 400 years for every 1% deviation from the modern seawater value at 125 ka. In the case where measured $\delta^{234}\text{U}_i$ is identical to modern seawater, analytical uncertainty in the calculated coral $\delta^{234}\text{U}_i$ represents a significant age uncertainty. For example, a 2% uncertainty in $\delta^{234}\text{U}_i$ is equivalent to an 800-year age error at 125 ka that should be included in total age uncertainty.

In assessing the utility of open-system ages, it is useful to compare the combined uncertainties of open-system and conventional ages. Systematic error from the uncertainty in the $\delta^{234}\text{U}$ of paleo-seawater affects both ages equally and can be neglected in a comparison. Combined potential age error arising from uncertainty in slope parameters increases with age (Fig. 9b) and degree of addition (Fig. 9c), and can be treated as two end-

member cases. If errors are random, due to natural variation of true parameter values about the estimated value, the propagated errors can be combined in the same fashion as analytical errors. In this case, the uncertainty from potential slope parameter error adds a small additional uncertainty to the measurement error, and the total uncertainty is comparable to the analytical uncertainty of conventional ages (Fig. 9b,c). If the estimated slope parameters are systematically different from their true values, they are a source of systematic error and must be added. In the unlikely case that all estimated parameters contribute a systematic error of the same sign, the combined analytical uncertainty and parameter error could be large (Fig. 9b,c). However, the possibility of open-system age bias can be explicitly tested

(Fig. 7). Although small degrees of bias may escape detection, the impact of such biases will be small. Furthermore, the error of the mean (Fig. 7) is expected to increase with $\delta^{234}\text{U}_i$ if there are errors in the open-system ages due to random parameter variation. There is little in the data to suggest either systematic or random error in the open-system ages (Fig. 7), consistent with our independent error estimates based on likely parameter ranges (Fig. 9).

5.2. A mass balance for dissolved uranium

While the decay of dissolved uranium is an attractive mechanism for transporting daughters for a substantial distance between source and sink, the uranium mass balance is problematic. Certainly leaching and dissolution of carbonate

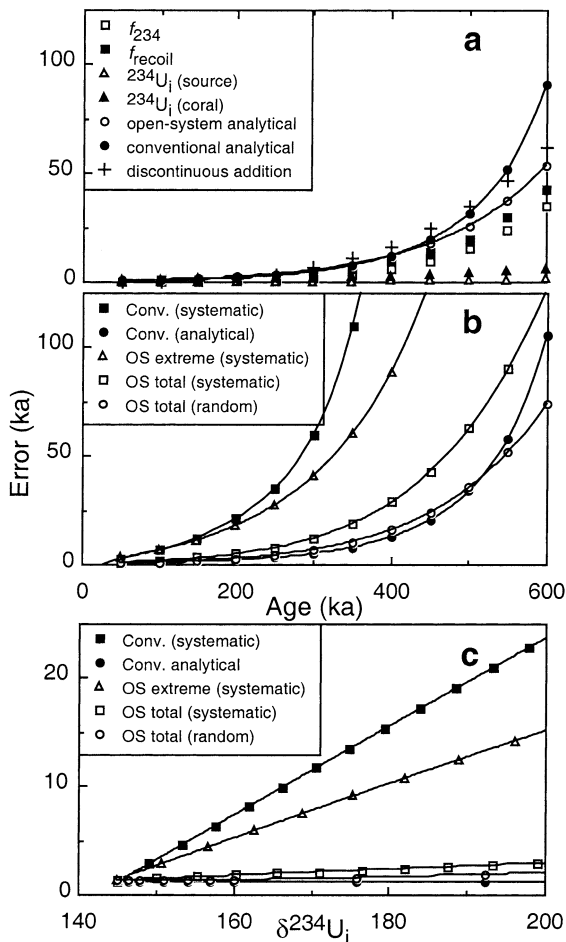


Fig. 9. (a) Open-system age error from incorrect parameter estimates. Isotopic compositions were calculated from Eqs. 20 and 21 (Appendix 1²) with incorrect parameter values: $f_{234} = 0.90$, $f_{\text{recoil}} = 0$, source $\delta^{234}\text{U}_i = 135$, coral $\delta^{234}\text{U}_i = 148$. Ages were calculated from these compositions with Eq. 1 using a value of 1.145 for the initial $^{234}\text{U}/^{238}\text{U}$ ratios, a value of 0.975 for f_{234} , and a value of 0.973 for f_{230} . Conventional and open-system age errors are propagated from 0.0015 and 0.0025 absolute analytical errors in the measured $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{238}\text{U}$ ratios, respectively. For errors that depend on the degree of addition, the results for an apparent excess ^{234}U production of 5% are given. Sensitivity test results for catastrophic failure of continuous addition are also shown. For each age plotted, ^{234}Th and ^{230}Th addition was modeled at a 5% rate for half the total time and then the system was allowed to evolve as a closed system. (b) Combined error estimates for conventional and open-system ages. Systematic conventional age errors reflect the result of a 5% ^{234}Th and ^{230}Th addition, and conventional analytical errors include age uncertainty from calculated $\delta^{234}\text{U}_i$ as discussed in the text. Combined errors for open-system ages include the contributions from f_{234} , f_{recoil} , source $\delta^{234}\text{U}_i$, and measurement uncertainties. Both systematic and random uncertainties from parameter estimation are shown. The extreme systematic error was calculated with $f_{234} = 1$, $f_{\text{recoil}} = 1$, and source $\delta^{234}\text{U}_i = 1000\%$. Potential systematic error in coral $\delta^{234}\text{U}_i$ was not included in either conventional or open-system estimates. (c) Combined error estimates as a function of measured $\delta^{234}\text{U}_i$ at 122 ka. Systematic conventional error is calculated from modeled effects of Th addition. Conventional analytical error and open-system errors are calculated as in (b).

should be a source of dissolved uranium. The conversion of aragonite to calcite during diagenesis may also provide a source of uranium-enriched water because uranium is more easily accommodated in the aragonite lattice [44]. However, dissolved uranium concentrations required to produce observed isotopic anomalies are, in most cases, up to 5% of the coral uranium concentration. For every cm^3 of water moving through the system 0.05 cm^3 of carbonate must be dissolved or completely stripped of its uranium to maintain the required concentration. Assuming that dissolved uranium moves through the reef system at the same rate as percolating water, impossibly large volumes of carbonate are required to maintain this concentration over hundreds of thousands of years. However, a portion of the water moves by overland flow during heavy rainfall events, and a substantial fraction of meteoric water flows quickly through fractures, while a much smaller fraction flows slowly by seepage allowing significant interaction with the carbonate [45]. Still, maintenance of the required U concentration appears to require the dissolution of tens of meters of carbonate. If dissolved uranium decay is to be a significant contributor to ^{234}Th and ^{230}Th addition, uranium must move more slowly through the reef than meteoric water. Retention of uranium in the reef system on cation exchange sites, and repeated precipitation and dissolution events may slow the movement of uranium through the system.

5.3. Isotopic mass balance and composition of source areas

The physics of α -recoil predict that approximately 2.5% of the ^{234}Th and ^{230}Th production will escape coral aragonite needles in the source region, and enriched corals (Table 1¹) show a mean gain of 4%. If the source region is composed of corals, or coral-derived sediment, then the initial U concentrations of source and sink are equal, and the mass ratio of source to enriched coral must be about 1.6. Intact corals make up about 40% of the total reef mass [40]. If 3/4 of these are enriched, the mass ratio of source to enriched coral is approximately 2 and the isotopic

mass balance is potentially reasonable. Of 68 measured corals (Table 1¹) 26% show insignificant ^{234}U enrichment, and 67% of unenriched corals came from terrace surfaces.

While the isotopic enrichment of many measured corals is clear, depletion in source regions has yet to be positively identified. Potential source regions are original surfaces of terraces, and preferential paths of surface and subsurface water flow, such as creek beds, fractures, dissolution features, unconformity surfaces, and zones of loosely consolidated sediments. Alpha recoil should result in source regions with younger U/Th ages and lower $\delta^{234}\text{U}_i$. However, U loss by either leaching or dissolution will leave ^{230}Th behind, producing older U/Th ages and elevated $\delta^{234}\text{U}_i$. Source regions may have lower U concentrations if U leaching is important. Alpha-recoil depletion is greatest at the crystal surface, where depleted uranium is most likely to be removed. Very slow rates of crystal dissolution ($0.1 \mu\text{m}/100 \text{ kyr}$) could remove significant amounts of depleted uranium, pushing $^{234}\text{U}/^{238}\text{U}$ towards closed-system values while the ^{230}Th left behind increases the apparent age, further increasing $\delta^{234}\text{U}_i$. In the data (Table 1¹), there is no clear indication of systematically younger ages and only a few corals approach a 2.5% recoil loss. However, a small but significant increase in mean coral ages at low $\delta^{234}\text{U}_i$ (Fig. 7d) is consistent with the combined effects of α -recoil and uranium loss. This shift in age can be produced if these corals have lost 2.5% of their ^{234}U and ^{230}Th by recoil, and 3–4% of their uranium by leaching. The calculated isotopic composition of the lost uranium is that expected at the surface of the crystal, where 50% of the decays are lost by recoil. Furthermore, the observed mean uranium concentration of measured *A. palmata* corals with $\delta^{234}\text{U}_i \leq 147$ (Table 1¹) is about 5% lower than the rest. If these corals have lost small amounts of U from recoil-depleted crystal surfaces, these corals might be recoil sources, even though some $\delta^{234}\text{U}_i$ is higher than modern seawater. In such a scenario, dissolved uranium slowly removed from the system over time will have a lower $^{234}\text{U}/^{238}\text{U}$ than the carbonate it was removed from. The uranium isotope ratios of Barbados and Bahamas

groundwater [21,22], which are near secular equilibrium, are consistent with this explanation.

5.4. Alpha-recoil and thorium transport

The aqueously mediated α -recoil pathway solves the elemental uranium mass balance problem because only ^{234}Th and ^{230}Th are mobilized, while $>99\%$ of the initial ^{238}U stays in place because of its long half-life. However, transport distances of aqueous thorium are likely to be small. It is possible that early diagenesis creates a gradient of increasing uranium concentration with depth similar to observed Sr profiles [46]. In this case, ^{234}Th and ^{230}Th addition would increase with depth while transport distances remain small. Direct recoil exchange in the solid phase seems unlikely because of the very short distance of α -recoil in mineral grains [25], although the recoil distance in carbonates has never been measured. However, potential for ^{234}Th and ^{230}Th gain may still exist if the source material has relatively high U concentrations, is finely divided, and is in close contact with or intermingled with coral aragonite. The growth of secondary minerals and cements, and the aqueous transport of fine carbonate particles, may provide such material.

5.5. ^{234}Th adsorption

The details of ^{234}Th adsorption and retention remain unclear. Why is the adsorbed ^{234}Th not remobilized on decay to ^{234}U ? If the proposed mechanisms are to explain elevated ^{234}U , the adsorption process must be irreversible. It may be that some corals are protected from uranium loss because the water that reaches them has already equilibrated with carbonate. However, cleaning experiments indicate that while freshly adsorbed Th is readily removed from calcite, Th in natural marine aragonite is not, suggesting these isotopes are not simply adhering passively to the surface [27]. Moreover, a clear example of U loss (Fig. 5a) does not appear to restore the ^{234}U to closed-system levels, suggesting the added ^{234}U is not preferentially removed. Physically removing the pore walls or outer surfaces of corals does not seem to change their $^{234}\text{U}/^{238}\text{U}$ significantly [10]. This sug-

gests the added ^{234}U is finely dispersed in the coral. It is possible that Th is not simply adsorbed to the surfaces of the coral itself, but to the surfaces of the 1–5- μm diameter aragonite needles that comprise the coral structure. Perhaps Th initially adsorbs to coral surfaces and subsequently migrates by diffusion along crystal boundaries into the coral. In this case, physical or chemical cleaning of corals might well prove ineffective, and loss of ^{234}Th after decay to ^{234}U negligible.

In summary, although each of the proposed mechanisms has its drawbacks when examined in detail, the potential exists for all three to contribute excess ^{234}U and ^{230}Th to measured corals. There is no question that dissolved uranium and α -recoil provide a source of ^{234}Th and ^{230}Th . Where one process alone may not explain the observations, several in conjunction may suffice. Taken together, these processes offer a self-consistent qualitative and quantitative explanation for observed U-series anomalies in corals.

6. Conclusions

The processes of dissolved uranium decay and α -recoil provide a source of ^{234}Th and ^{230}Th , and the coupled addition of these Th isotopes offers a self-consistent explanation for observed U-series anomalies in corals. Equations, based on a two-box model of decay-related ^{234}Th and ^{230}Th redistribution, permit calculation of open-system ages. The U-series isotope ratios of corals from stratigraphically defined terraces produce distinct, broadly linear arrays on a $^{234}\text{U}/^{238}\text{U} - ^{230}\text{Th}/^{238}\text{U}$ isotope ratio diagram, and open-system model slopes are consistent with array trends. Model slopes are also consistent with measurements of older Barbados corals, and other coral measurements around the world, out to the extreme limits of possible open-system isotopic compositions. The consistent agreement of model-determined slopes with linear data arrays over a wide range of apparent excess ^{234}U production and ages suggests the aggregate error in estimated parameters is not significant. The good agreement of open-system ages with conventional ages of pristine corals suggests the accuracy of open-system ages

is comparable to conventional ages of the best available samples. While the systematic error in conventional ages is evident even at small deviations of $\delta^{234}\text{U}_i$, the open-system model yields consistent ages, even at extreme $\delta^{234}\text{U}_i$. There is little evidence of random or systematic errors to open-system ages due to errors in parameter estimation. If the conventional age of corals with a $\delta^{234}\text{U}_i$ identical to modern seawater provides the best estimate of true age, then the open-system model will improve the accuracy of coral age determinations. While sea-level reconstructions using U-series coral ages are severely hampered by the scarcity of samples that appear to have remained closed systems, the use of open-system ages offers the possibility to increase the database of reliable ages dramatically.

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