

Caribbean chronostratigraphy refined with U-Pb dating of a Miocene coral

Rhawn F. Denniston*

Department of Geology, Cornell College, 600 1st Street West, Mount Vernon, Iowa 52314, USA

Yemane Asmerom

Victor Y. Polyak

Department of Earth and Planetary Science, Northrop Hall, University of New Mexico, Albuquerque, New Mexico 87131, USA

Donald F. McNeill

James S. Klaus

Division of Marine Geology and Geophysics, Rosenstiel School, University of Miami,

4600 Rickenbacker Causeway, Miami, Florida 33149, USA

Peter Cole

Department of Geology, Cornell College, 600 1st Street West, Mount Vernon, Iowa 52314, USA

Ann F. Budd

Department of Geoscience, Trowbridge Hall, University of Iowa, Iowa City, Iowa 52242, USA

ABSTRACT

An exceptionally well-preserved aragonitic coral of the extinct species *Goniopora hilli* was collected from late Cenozoic sedimentary deposits in the Dominican Republic and dated using U-Pb techniques. Nine coralline subsamples yielded a $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ three-dimensional (3-D) inverse linear concordia age of 5.52 ± 0.15 (2σ) Ma, which, when coupled with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained from the same coral, allows for tighter constraints on temporal variability of marine species diversity prior to closure of the Central American Seaway. The recognition that pre-Quaternary aragonitic corals can be suitable for U-Pb dating creates new possibilities for refining the chronologies of late Cenozoic marine sedimentary sequences.

Keywords: coral, U-Pb, Dominican Republic, Miocene, Central American Seaway, Sr chemostratigraphy.

INTRODUCTION

Closure of the Central American Seaway in the Pliocene isolated the Caribbean and Pacific Basins and contributed to a pulse of extinction and origination of species of shallow-marine fauna on both sides of Central America (Jackson et al., 1996). Studies aimed at calculating evolutionary rates associated with this event require not only detailed paleontological assessment, but also robust chronologies of sedimentary units deposited prior to, during, and after the closure. One limitation to such studies has been insufficient age control on some fossil-bearing lithologies that has introduced significant uncertainty into the rates of change of marine communities (Budd et al., 1996; McNeill et al., 2000). The Cibao Valley of the Dominican Republic (Fig. 1) contains an ~3-m.y.-long record of well-preserved fossil taxa that existed in the Caribbean prior to final closure of the Central American Seaway. One thoroughly studied unit in this area is the Gurabo Formation, which was deposited prior to final closure of the Central American Seaway, but the precise age of the Gurabo Formation remains the subject of debate. In fact, over the past 90 yr, 19 studies have reported various and disparate ages for Cibao Valley units; these ages have ranged from the middle Miocene (ca. 10 Ma) (Ramirez, 1956) to the middle Pliocene (ca. 3 Ma) (van den Bold, 1975) (Fig. 2). The work of Saunders et al. (1986) (which places the middle Gurabo in the late Miocene) has been the most robust and commonly applied chronology.

Shallow-marine sequences can be difficult to categorize chronostratigraphically given highly variable deposition rates, reworking of sediments, lack of age-diagnostic fossils, and diagenetic alteration (Getty et al., 2001). Direct radiometric dating of marine units such as the Gurabo Formation

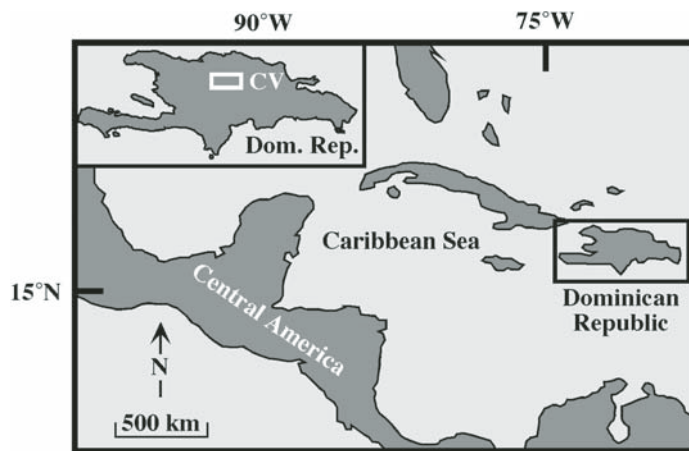


Figure 1. Map of Caribbean region with inset of Dominican Republic. White box denotes location of Cibao Valley (CV).

is typically quite complex owing to the likelihood that biogenic materials have been diagenetically altered. However, portions of the middle Gurabo Formation are composed of low-permeability muds and silts, and, as a result, some corals remain largely pristine. We identified an extremely well-preserved coral head from this interval and dated it using $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ techniques in order to provide new age constraints for the Gurabo Formation. A tighter chronology will allow future calculations of rates of species origination and extinction associated with closure of the Central American Seaway to be performed with increased precision.

*E-mail: RDenniston@CornellCollege.edu.

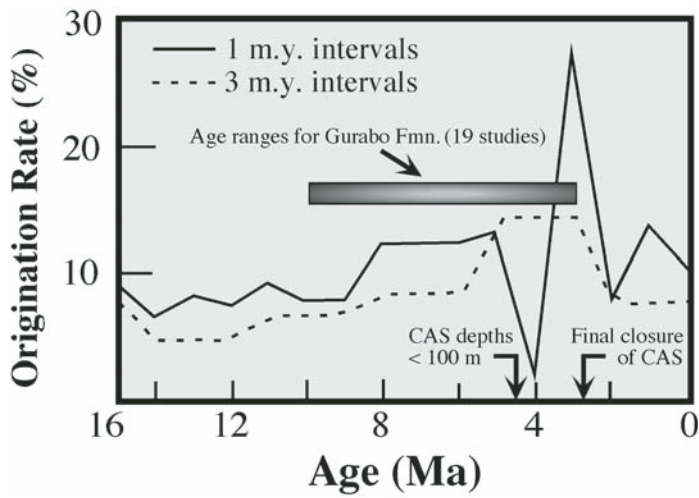


Figure 2. Rate of coral species originations in Caribbean since 16 Ma calculated using 3 m.y. and 1 m.y. time slices (from Budd et al., 1996). Note increase in origination rates during final closure of Central American Seaway (CAS) and differential origination rates at 4 Ma due to different sampling methodologies. Gray horizontal bar denotes range of ages assigned to Gurabo Formation by 19 studies over past 90 yr. See text for references.

GEOLOGIC SETTING

The Cercado, Gurabo, and Mao Formations make up the key Neogene deposits of the Yaque Group within the Cibao Valley of the northern Dominican Republic (Fig. 1). The Gurabo Formation, exposed within the Rio Gurabo, is composed of a >400-m-thick package of fine-grained, weakly indurated shelf deposits with intervals rich in corals and coralline debris. Corals from the middle Gurabo were not buried in situ but were transported downslope with slump deposits and then rapidly entombed in densely packed, fine-grained clayey calcareous sediments that limited groundwater flow (Evans, 1986; Saunders et al., 1986). We identified an extremely well-preserved coral head of the extinct species *Goniopora hilli*

at locality NMB15855 of Saunders et al. (1986), which lies at 275 m in the section, ~115 m above the Cercado-Gurabo Formation contact and ~305 m below the contact with the overlying Mao Formation.

U-Th-Pb ISOTOPE SYSTEMATICS IN CORALS

In some aspects, corals are well suited for U-Pb dating. U is abundant in the oceans (Ku et al., 1977; Chester, 1990) and partitions readily into aragonite, so that U abundances in modern corals average >1 ppm (Edwards et al., 1987; Delanghe et al., 2002). Both Th and Pb, on the other hand, are particle reactive and thus have low concentrations in seawater (~0.003 ppb for Pb) and in corals (Edwards et al., 1987; Shen and Boyle, 1987; Chester, 1990). In addition, because the ocean water $^{234}\text{U}/^{238}\text{U}$ ratio (hereafter referred to as $\delta^{234}\text{U}$) (Table 1) has remained essentially constant ($\delta^{234}\text{U} = \sim 145\text{‰}$) over the past 360 k.y., and no temporal trend is apparent over the last 800 k.y. (Henderson, 2002), it is not unreasonable to assume that ocean water $\delta^{234}\text{U}$ values during the late Miocene–early Pliocene (the age of the coral dated here) were similar to modern values.

The overwhelming limitation to U-Pb dating of corals is the susceptibility of their porous and metastable aragonite skeletons to diagenetic alteration. Secondary cementation and/or dissolution may occur in both marine and vadose environments and is common to some degree in the vast majority of fossil corals (McGregor and Gagan, 2003). Precipitation of secondary cements or loss of U, Pb, or intermediate U-series daughter products can impact calculated ages. Studies have documented pre-Quaternary aragonitic corals that have preserved their original stable isotopic and/or minor-element (e.g., Sr, Mg) signatures at 3 Ma (Roulier and Quinn, 1995), 10 Ma (Brachert et al., 2006), 30 Ma (Ivany et al., 2002), and ca. 40 Ma (Mackenzie et al., 1997), but none of these samples was tested for the fidelity of its U-series systematics. Diagenetic calcite in a Devonian coral was dated by U-Pb techniques (Smith and Farquhar, 1989), but the only study involving U-Pb dating of primary coral aragonite is that of Getty et al. (2001), who dated 1.0–1.3 Ma samples from the eastern Caribbean.

SCREENING FOR SIGNS OF DIAGENETIC ALTERATION

Coral subsamples were carefully screened for signs of diagenetic alteration. Scanning electron microscopy (SEM), performed on both acid-leached and unleached samples, shows a well-preserved fibrous aragonite

TABLE 1. *GONIOPORA HILLI* U, Th, Pb ISOTOPE DATA

Sample	Mass (mg)	U* (ppm)	Pb (ppb)	$(^{230}\text{Th})/(^{238}\text{U})^\dagger$	$\delta^{234}\text{U}^\S$ (‰)	$^{238}\text{U}/^{208}\text{Pb}$ (meas)	$^{206}\text{U}/^{208}\text{Pb}$ (meas)	$^{207}\text{Pb}/^{206}\text{Pb}$ (meas)	$^{206}\text{U}/^{208}\text{Pb}$ (corr)	$^{207}\text{Pb}/^{206}\text{Pb}$ (corr)	$^{204}\text{Pb}/^{206}\text{Pb}$ (corr)
GH1	98.6	1.53 (0.2)	10.72 (0.5)	1.00 (0.5)	-2.3 (1.0)	264.46 (3.3)	0.7069 (0.3)	0.5859 (0.3)	0.7092 (0.4)	0.5841 (0.3)	0.0365 (0.2)
GH2	114.3	1.55 (0.1)	11.74 (0.6)	1.01 (0.7)	-0.7 (1.9)	241.37 (3.5)	0.6826 (0.4)	0.6055 (0.3)	0.6847 (0.5)	0.6038 (0.3)	0.0376 (0.2)
GH3	63.3	1.54 (0.1)	13.94 (0.7)	1.00 (0.6)	-1.8 (1.2)	199.95 (3.9)	0.6567 (0.6)	0.6289 (0.5)	0.6585 (0.8)	0.6273 (0.5)	0.0398 (0.3)
GH6A**	453.1	1.53 (0.2)	23.33 (4.4)	1.00 (1.0)	-0.6 (2.5)	114.25 (10.3)	0.5850 (1.0)	0.7007 (1.2)	0.5860 (1.2)	0.6996 (1.2)	0.0441 (0.9)
GH7A**	369.3	1.50 (0.2)	37.20 (2.4)	1.02 (1.0)	-2.2 (2.5)	68.91 (3.4)	0.5459 (0.4)	0.7538 (0.5)	0.5465 (0.4)	0.7530 (0.5)	0.0482 (0.3)
GH8	181.7	1.55 (0.1)	17.17 (0.3)	1.00 (0.7)	-1.4 (0.9)	160.54 (1.4)	0.6217 (0.3)	0.6634 (0.2)	0.6231 (0.3)	0.6620 (0.2)	0.0420 (0.2)
GH9	148.3	1.57 (0.1)	9.29 (0.4)	1.01 (0.6)	-2.5 (1.5)	319.79 (3.4)	0.7522 (0.3)	0.5538 (0.3)	0.7550 (0.5)	0.5519 (0.3)	0.0346 (0.2)
GH10	202.6	1.54 (0.1)	11.33 (0.3)	1.00 (0.6)	-1.5 (0.8)	251.53 (1.9)	0.6973 (0.2)	0.5927 (0.2)	0.6995 (0.3)	0.5909 (0.2)	0.0369 (0.1)
GH11	119.3	1.55 (0.2)	11.77 (0.4)	1.01 (0.5)	-2.9 (2.2)	241.26 (2.5)	0.6857 (0.3)	0.6038 (0.2)	0.6878 (0.4)	0.6020 (0.2)	0.0377 (0.2)

*Values in parentheses are 2σ absolute errors in last significant figure. Errors on $\delta^{234}\text{U}$ are an exception, however, and are in per mil (‰).

† Ratio obtained from splits of U-Pb subsamples.

§ The $^{238}\text{U}/^{234}\text{U}$ is given as $\delta^{234}\text{U}$ value, where $\delta^{234}\text{U} = [(^{234}\text{U}/^{238}\text{U})/(^{234}\text{U}/^{238}\text{U})_{\text{eq}} - 1] \times 1000\text{‰}$ and $(^{234}\text{U}/^{238}\text{U})_{\text{eq}}$ is the secular equilibrium atomic ratio of decay constants: $\lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$.

*Values were corrected for in-growth of ^{206}Pb from ^{234}U in excess of secular equilibrium values and deficit of ^{230}Th from the secular equilibrium value by: $^{206}\text{Pb}/^{208}\text{Pb}_{\text{corr}} = ^{206}\text{Pb}/^{208}\text{Pb}_{\text{meas}} + ^{238}\text{U}/^{208}\text{Pb}[\lambda_{238}/\lambda_{230} - (0.150 \times \lambda_{238}/\lambda_{234})]$, where $\lambda_{238}/\lambda_{230} = 1.6939 \times 10^{-5}$ and $\lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$.

^{232}Th abundances were 1–2 ppb. The ^{207}Pb values were corrected similarly for the deficit of ^{231}Pa from the secular equilibrium value as follows: $^{207}\text{Pb}/^{206}\text{Pb}_{\text{corr}} = ^{207}\text{Pb}/^{206}\text{Pb}_{\text{meas}} + ^{235}\text{U}/^{208}\text{Pb}(\lambda_{235}/\lambda_{231})$, where $(\lambda_{235}/\lambda_{231}) = 4.6547 \times 10^{-5}$.

**All isotopic ratios in these samples were measured by thermal ionization mass spectrometry (TIMS).

skeleton with original porosity and delicate, fine-scale structures such as calcification centers (Figs. 3A and 3B). Thin-section petrography also reveals calcification centers, radiating fibers, fine-scale growth layers, and primary porosity (Figs. 3C and 3D), although some pores are partially lined with aragonite cements and/or modestly infilled by carbonate detritus and muds. X-ray diffraction analysis of multiple ~1-g-sized coral powders revealed only well-defined aragonite peaks; no calcite peaks were detected. Stable isotopic analyses were conducted on powders micromilled parallel to growth banding at 150- μm -wide traverses over 5 consecutive years of growth. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values average -3.2‰ and -0.2‰ Vienna Pee Dee belemnite (VPDB), respectively, and form sinusoids with ranges of 0.4‰ and 0.9‰ , respectively (see supplemental data in the GSA Data Repository¹), similar to Holocene corals from the Dominican Republic (Greer and Swart, 2006). Finally, U and Th isotopic ratios were measured by thermal ionization mass spectrometry (TIMS) at the University of New Mexico (see the GSA Data Repository for methods). The $^{230}\text{Th}/^{238}\text{U}$ activity ratios and $\delta^{234}\text{U}$ values fell within error of their respective secular equilibrium values (1.0 and 0.0) (Table 1). Given initial $^{230}\text{Th}/^{238}\text{U}$ ratios and $\delta^{234}\text{U}$ values in late Pleistocene corals (Edwards et al., 1987), these ratios should fall to within 1% of secular equilibrium at 0.6 and 1.6 Ma, respectively. Thus, secular equilibrium values suggest undisturbed U-Pb systematics over at least the past 1.6 m.y.

$^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ DATING AND $^{87}\text{Sr}/^{86}\text{Sr}$ ANALYSIS

Nine splits of the samples that passed these screening tests were dissolved, spiked with a mixed ^{236}U - ^{233}U - ^{205}Pb tracer, and processed using standard column-chemistry techniques (Manhes et al., 1978). All Pb iso-

¹GSA Data Repository item 2008036, results of tests for diagenetic alteration, and marine Sr isotopic curves for the late Miocene to present, is available online at www.geosociety.org/pubs/ft2008.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

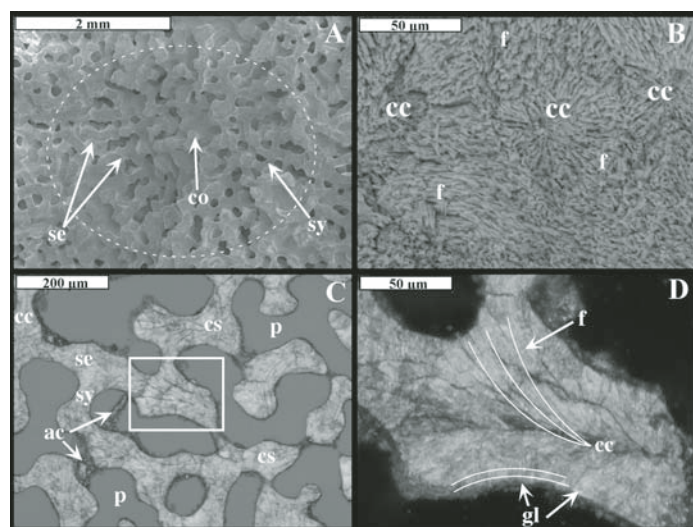


Figure 3. A: Low-magnification, scanning electron microscope (SEM) photograph of a corallite (dashed oval) in *Goniopora hilli* (without acid leaching) showing columella (co), septa (se), and synapticula (sy); note high degree of primary porosity. B: High-magnification SEM photograph of acid-leached *G. hilli* illustrating calcification centers (cc) with radiating fibers (f). C: Plane light photomicrograph showing coral skeleton (cs) with septa (se), synapticulae (sy), pores (p), and a calcification center (cc). Note aragonite cements (ac) coating interior of some pores. White rectangle is enlarged in part D. D: Polarized light photomicrograph showing growth layering (gl) and fibers (f) radiating from a calcification center (cc).

topic ratios were measured by TIMS, and U isotopic ratios were measured using multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) or TIMS. Isotopic ratios were reduced with PBDAT (Ludwig, 1993) using corrections made for deviations of $^{234}\text{U}/^{238}\text{U}$, $^{231}\text{Pa}/^{235}\text{U}$, and $^{230}\text{Th}/^{238}\text{U}$ ratios from secular equilibrium at the time of deposition (Table 1). A $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ three-dimensional (3-D) inverse linear concordia age of 5.52 ± 0.15 Ma (2σ) and a $^{238}\text{U}/^{208}\text{Pb}$ - $^{206}\text{Pb}/^{208}\text{Pb}$ isochron age of 5.34 ± 0.15 Ma (2σ) (GSA Data Repository) were then calculated using Isoplot (Ludwig, 1999) (Fig. 4). In addition, Sr isotopic ratios measured on four subsamples of the coral yielded an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.708993 ± 0.000029 (2σ) (GSA Data Repository).

U-Pb AGE CONSTRAINTS AND UNCERTAINTIES

U-Pb dating of any fossil coral is subject to several sources of uncertainty, including preservation of original U-series ratios. The $\delta^{234}\text{U}$ values measured by MC-ICP-MS fall within the combined internal analytical error (and well within external errors) and minimum uncertainty of 1% associated with the half-life of ^{234}U (Cheng et al., 2000). Secondly, small amounts of marine cement and detritus not removed by ultrasonication introduce noncoralline Sr, U, Th, and Pb isotopic signatures. However, several observations argue for a minimal contaminant influence on the calculated U-Pb age: (1) the relative abundances of these contaminants are quite low, as evidenced by the high degree of primary porosity remaining in the corals (Fig. 3), (2) they would have formed at or near the same time as the coral and likely from the same seawater, and (3) the linearity of points along the $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ 3-D concordia (Fig. 4) is high. Finally, departures of late Miocene seawater $\delta^{234}\text{U}$ values from the modern value of 145‰ would change the impact of the $^{234}\text{U}_{\text{excess}}$ - ^{206}Pb correction. However, any deviation from the modern value would likely be small relative to the general $\delta^{234}\text{U}$ excess in modern seawater (Table 1), and the correction for $^{234}\text{U}_{\text{excess}}$ changed the concordia age by only 0.04 m.y.

The U-Pb age of 5.52 ± 0.15 Ma is also corroborated by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios obtained from four subsamples of *G. hilli* (Table 1), the average value of which intersects the global marine Sr curve at ca. 5.3 Ma using the data set of Farrell et al. (1995) and at ca. 5.5 Ma using the data set of McArthur et al. (2001) (GSA Data Repository). The concurrence of these two distinct geochemical clocks provides strong support for the accuracy of the U-Pb date.

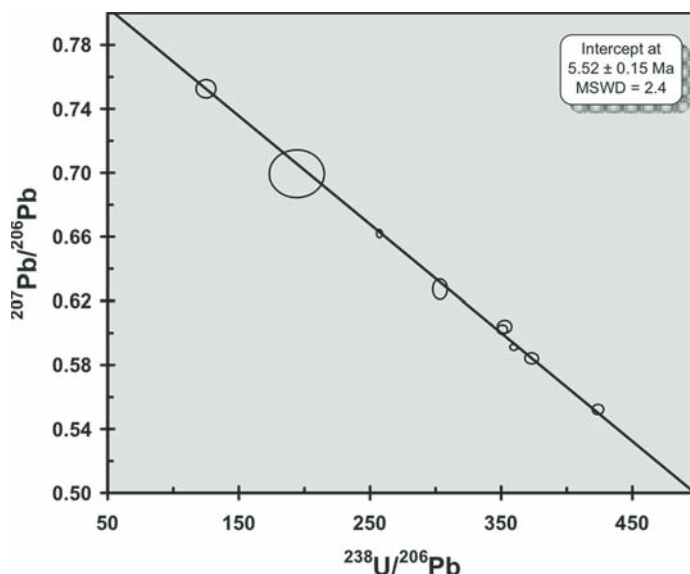


Figure 4. $^{238}\text{U}/^{206}\text{Pb}$ - $^{207}\text{Pb}/^{206}\text{Pb}$ three-dimensional (3-D) inverse linear concordia for *Goniopora hilli*. The same data plotted as a $^{238}\text{U}/^{208}\text{Pb}$ - $^{206}\text{Pb}/^{208}\text{Pb}$ isochron yield an age of 5.34 ± 0.15 Ma with a mean square of weighted deviates (MSWD) = 0.69 (GSA Data Repository [see text footnote 1]).

IMPLICATIONS FOR CARIBBEAN CHRONOSTRATIGRAPHY AND MARINE TAXA SPECIATION RATES

Closure of the Central American Seaway occurred gradually from ca. 13 to 2 Ma, with depths reaching 100 m by 4.6 Ma (Haug et al., 2001). At this point, exchange between Pacific and Caribbean waters became limited, and shallow-marine environmental conditions in the Caribbean changed significantly, including increases in average surface-water temperatures, clarity, and calcium carbonate saturation (Romine, 1982; Vermeij and Petuch, 1986). In response, many shallow-marine taxa underwent a series of pulses of speciation (Budd et al., 1996). Quantification of the nature and timing of these changes is critical to understanding temporal trends in faunal diversity and their environmental controls. Of the 19 age models ascribed to the Gurabo Formation, we establish that the age model of Saunders et al. (1986), who assigned the Gurabo to the latest Miocene–early Pliocene, is the most consistent with our U-Pb date.

One implication of such limited chronological control is that researchers were forced to consider longer-than-desired study intervals. For example, Budd et al. (1996) found that origination rates of coral species at 4 Ma calculated using 1 m.y. intervals were only ~2%, while 3 m.y. intervals produced origination rates of ~15% (Fig. 2). Thus, this U-Pb coral chronology opens the door for more direct absolute age determinations in this sequence and tighter constraints on rates of species origination prior to closure of the Central American Seaway. Given the paucity of such well-preserved corals, Sr and paleomagnetic studies should eventually refine the ages of the remainder of the Cibao Valley section, but the recognition that pre-Quaternary aragonitic corals can be suitable for U-Pb dating creates new possibilities for refining the chronologies of late Cenozoic marine sedimentary sequences.

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