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## Rigorous quality control criteria for screening coral samples and radiocarbon calibration data based on $^{14}C$, $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ dated corals—A reply to the comment by Yusuke Yokoyama and Tezer M. Esat on "Extending the radiocarbon calibration beyond 26,000 years before present using fossil corals" by T.-C. Chiu, R.G. Fairbanks, R.A. Mortlock, A.L. Bloom (Quaternary Science Reviews 24 (2005) 1797–1808)

We have read the comments of Yokoyama and Esat (2006) and provide the following reply.

Fairbanks et al. (2005), Chiu et al. (2005, 2006) and Mortlock et al. (2005) provide rigorous quality control criteria for screening coral samples and radiocarbon calibration data based on $^{14}C$, $^{230}Th/^{234}U/^{238}U$, and $^{231}Pa/^{235}U$ dated coral samples. Some of the criteria are well established in the uranium-series dating community while others are newly defined. The following is a list of sample and data quality control criteria summarized in Fairbanks et al. (2005), Chiu et al. (2005, 2006) and Mortlock et al. (2005) for the construction of our radiocarbon calibration program (http://radiocarbon.LDEO.columbia.edu/).

- X-ray diffraction (XRD) measurements on each sample must indicate no detectable calcite based on a documented 0.2% calcite or better detection limit. Calibration standards of varying percentages of calcite in a coral aragonite sample are run with each batch of samples.
- The [U] of corals must be within the range of living/modern samples taking into consideration the species and the correlation of [U] and calcification temperature (Min et al., 1995).
- The $\delta^{234}U_{initial}$ of coral samples must be between 138 and 150 per mil.
- After ultrasonic cleaning, samples are examined microscopically for any evidence of foreign particles or cements. Samples with visible contamination that cannot be ultrasonically removed are rejected.
- U-series and radiocarbon samples are taken from two concentric cores drilled into 4 mm thick slabs of the coral samples, with the radiocarbon sample taken from the inner core. This assures systematic sampling and cleaning procedures and the proximal location of the two age determinations. XRD samples are taken from the outer "donut" sampled for the U-series and the remainder of the subsample is archived.
- Radiocarbon measurements will be measured with a precision better than or equal to $\pm 4.0$ per mil ($1\sigma$) for samples less than 30,000 years BP.
- $^{230}Th/^{234}U/^{238}U$ age determinations will be measured with a precision of better than $\pm 3.0$ per mil ($1\sigma$) over the entire calibration 0–50,000 years BP.
- A representative sampling of corals older than 30,000 years BP, which have been exposed to the vadose fresh water environment during the Last Glacial Maximum lower sea level, are analyzed for $^{231}Pa/^{235}U$ ages in addition to $^{230}Th/^{234}U/^{238}U$ ages and $^{14}C$ ages in order to validate the $^{230}Th/^{234}U/^{238}U$ age determinations (Mortlock et al., 2005; Chiu et al., 2006).
- Coral samples are ranked according to the following scale and our calibration curve only uses the highest Category samples available for a given interval. Our ultimate goal is to construct a calibration curve that utilizes as many Category I and II samples as possible. Category III samples are used only where sea-level variations limit the possibility of collecting Category I and II samples.

  *Category I*: This category is reserved for samples that have resided in the marine environment exclusively and have replicate radiocarbon and replicate $^{230}Th/^{234}U/^{238}U$ age measurements that fall within $2\sigma$ analytical error, respectively. Sample $^{230}Th/^{234}U/^{238}U$ ages are in stratigraphic order with respect to their relative depth in core.

  *Category II*: Samples that have resided in the marine environment exclusively and are either not replicated or not replicated to within $2\sigma$. Sample $^{230}Th/^{234}U/^{238}U$ ages are in stratigraphic order with respect to their relative depth in core.

  *Category III*: Samples that have been exposed to vadose (rainwater percolating zone) fresh water and have $^{231}Pa/^{235}U$ and $^{230}Th/^{234}U/^{238}U$ ages that agree within $2\sigma$ analytical error.

  *Category IV*: Samples that have been exposed to vadose fresh water and dated by the $^{230}Th/^{234}U/^{238}U$ method only.

  *Category V*: Samples that have been exposed to the fresh water table (phreatic lens) and have $^{231}Pa/^{235}U$ and $^{230}Th/^{234}U/^{238}U$ ages that agree

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within $2\sigma$ error. Category V samples are not used in the Fairbanks et al. (2005) calibration and samples that have been exposed to the phreatic lens are automatically rejected from future calibration curve updates.

*Category VI*: Samples that have been exposed to the phreatic lens (fresh water table) and are not validated by concordant $^{230}Th/^{234}U/^{238}U$ and $^{231}Pa/^{235}U$ dates. Category VI samples are not used in the Fairbanks et al. (2005) calibration and samples that have been exposed to the phreatic lens are automatically rejected from future calibration curve updates.

Yokoyama and Esat (2006) as well as Reimer et al. (2006) primarily challenge our "no detectable calcite" quality control criterion. Reimer et al. (2006) state that "Fairbanks et al. (2005) and Chiu et al. (2005) insist that a protocol of "no detectable calcite" be adopted as the new standard. This may well be good advice, but doing so would exclude nearly all of the (published) coral data presently available". The potential consequence of not using our stringent quality control criteria is perhaps, best demonstrated in Fig. 1. The radiocarbon calibration data presented in Yokoyama et al. (2000) are widely scattered compared with the data presented in Fairbanks et al. (2005) and other studies (Voelker et al., 2000; Hughen et al., 2004a; Hughen et al., 2004b). When the quality control criteria listed above are applied to the radiocarbon calibration data of Yokoyama et al. (2000), nearly all of the Yokoyama et al. (2000) data fail at one or more levels (Fig. 1).

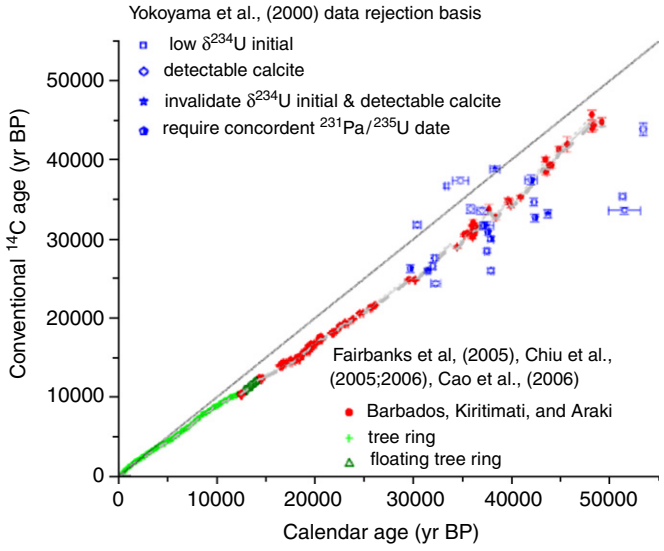


Fig. 1. Our 0–50,000 yr BP calibration curve data set (Chiu et al., 2005; Fairbanks et al., 2005, 2006; Cao et al., 2006) plotted in red along with the tree ring and floating tree ring data sets. Yokoyama et al. (2000) data are plotted in blue symbols. Most of the Yokoyama et al. (2000) samples or data fail one or more of our quality control criteria (Fairbanks et al., 2005; Mortlock et al., 2005; Chiu et al., 2005, 2006), which we believe are the primary reasons for the wide scatter in the Yokoyama et al. (2000) data set. The Yokoyama data symbols correspond to the quality control criteria basis for exclusion.

Yokoyama and Esat (2006) and Reimer et al. (2006) also attempt to challenge our observation that trace amounts of calcite are enriched in coral samples during the etching step prior to conversion to graphite. Chiu et al. (2005) observe and model the effect of the contaminant calcite produced in the vadose zone on the radiocarbon age and conclude that digenetic calcite generally causes the contaminated radiocarbon ages to be biased toward younger ages, i.e. the diagenetic calcite produced in the vados environment is generally younger than the coral sample. Yokoyama and Esat (2006) and Reimer et al. (2006) cite examples from their data sets that indicate just the opposite effect of etching; namely that radiocarbon ages shift to older ages with enhanced etching or reach a plateau after approximately 50% volume loss (Fig. 2a, b). More careful examination of the Yokoyama et al. (2000) data set and an example from Bard et al. (1998) cited in Reimer et al. (2006) in fact shows that some samples become older with enhanced etching (Fig. 2a, b) and some become younger with enhanced etching similar to Chiu et al. (2005)'s findings (Fig. 2c, d). The reason for this discrepancy is that Fairbanks et al. (2005) and Chiu et al. (2005) *do not include* samples that have been exposed to the phreatic zone (fresh water table), where calcite is precipitated from groundwater that may contain dissolved carbonate from fossil reefs. The widely cited partially recrystallized coral sample from Tahiti where the $^{14}C$ age of the calcite is $15{,}940 \pm 100$ years BP and the aragonite coral is $13{,}160 \pm 140$ years BP (Bard et al., 1998; Reimer et al., 2006) is a direct result of the local fresh water aquifer discharging offshore through the Tahiti fossil coral reefs (Deneufbourg, 1971; Ribaud-Laurenti et al., 2001; Reimer et al., 2006).

Our offshore coring sites and surface samples are strategically located or sampled in order to avoid samples that were once bathed in the phreatic lens, a diagenetic environment that is highly disruptive to $^{230}Th/^{234}U/^{238}U$ ages (Mey et al., 2005) and radiocarbon contamination by fossil carbon. The phreatic lens exposed samples reported in Yokoyama et al. (2000), in Bard et al. (1998) and in Reimer et al. (2006) correspond to our Category V and VI samples that are not used in our radiocarbon calibration.

There remains considerable confusion or ambiguity in the radiocarbon calibration literature concerning the exposure history of coral samples to seawater, versus vadose and phreatic fresh water environments back through time. Typically authors do not distinguish between the two very different freshwater diagenetic environments and lump them as meteoric waters (Reimer et al., 2006). For example, Reimer et al. (2006) state that "It should be noted that virtually all corals that grew before the last glacial maximum (LGM) have been exposed to some level of meteoric alteration. The only exception to this rule are corals from subsiding islands where subsidence rates are sufficient to compensate for the sea-level fall that took place right before the LGM (i.e. between 26,000 and 35,000 yr BP)." This statement does not take into account those coral samples that were growing in relatively deep water in the forereef

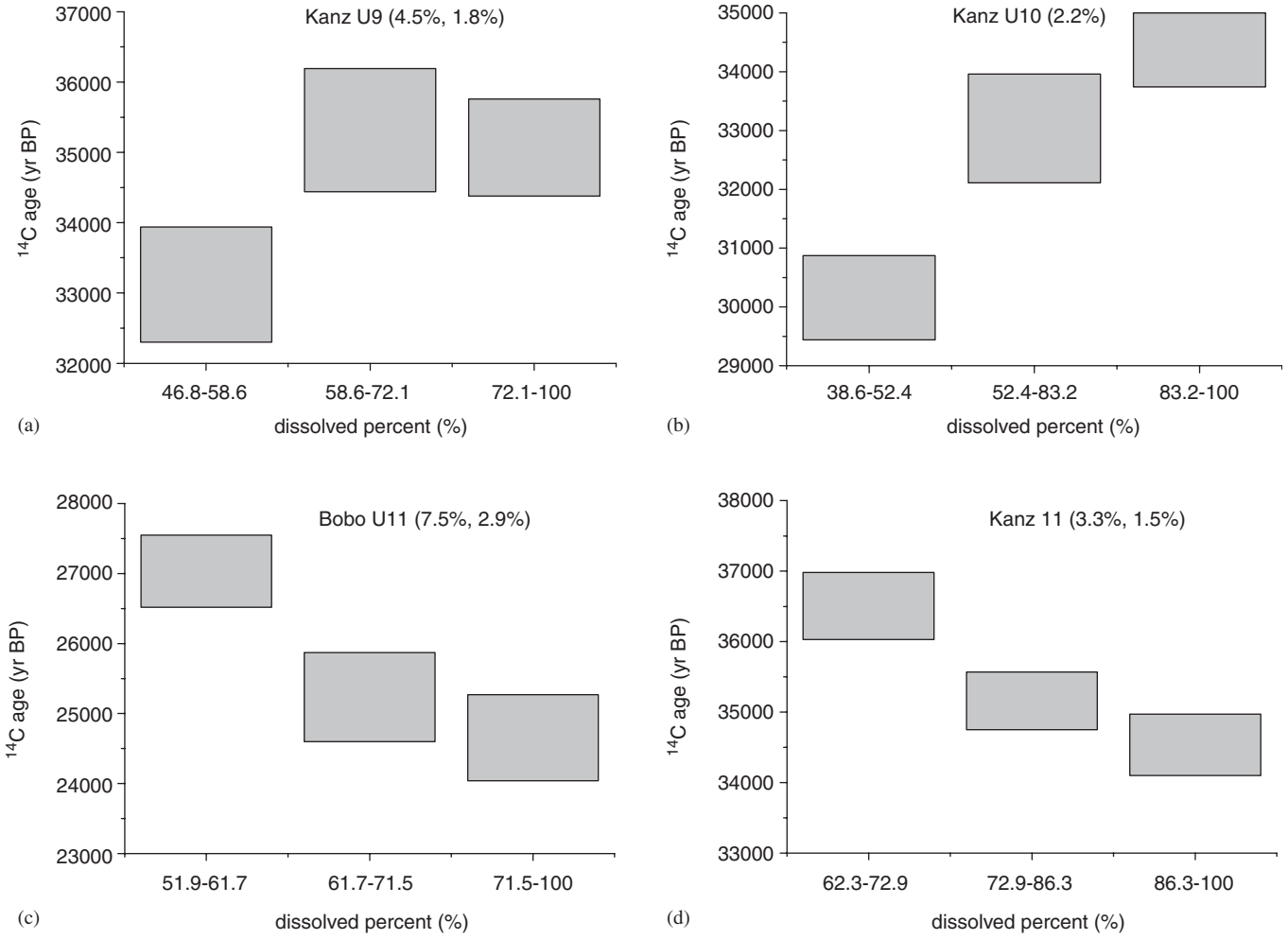


Fig. 2. Yokoyama et al. (2000) coral etch experiment of corals containing calcite and illustrate examples that increase in age with increasing percentage of etch (a, b) and examples that decrease in age with increasing percentage of etch (c, d). The samples that decrease in age with increasing percentage of etch (c, d) are consistent with diagenetic calcite that is formed in the vados environment, whereas the samples that increase in age with increasing percentage of etch may be partially recrystallized in the phreatic zone (fresh water lens) (Bard et al., 1998; Reimer et al., 2006). Our radiocarbon calibration criteria exclude samples exposed to the phreatic zone primarily because this environment rapidly alters the uranium-series ages (Mey et al., 2005) as well as the radiocarbon ages (Bard et al., 1998; Reimer et al., 2006). Much of the confusion concerning comparisons of our data with those of others (e.g., Reimer et al., 2006; Yokoyama and Esat, 2006) stems from the fact that we do not use samples exposed to the phreatic zone while others report and interpret uranium-series data sets that include some samples exposed to the phreatic zone (Bard et al., 1998; Reimer et al., 2006; Yokoyama et al., 2000).

environment during Marine Isotope Stage 3 that were not subsequently exposed to freshwater during the LGM lowstand. In fact, samples that have always remained submerged in seawater are specifically targeted in our offshore drilling programs (Fairbanks et al., 2005).

Of course, all carbonate samples have adsorbed surface $^{14}$C contamination that is routinely removed by a 50% etch and this is well illustrated by Burr et al. (1992) and Yokoyama et al. (2000) among others.

Technical questions regarding Plasma 54 mass spectrometry raised by Yokoyama and Esat (2006) can be answered by a more careful reading of the methods sections in our recent papers (Fairbanks et al., 2005; Mortlock et al., 2005). For example, our Plasma 54 mass spectrometer is fitted with an ion counting Daly detector, so references in Yokayama and Esat (2006) referring to the capabilities and corrections applied to secondary electron multiplier systems such as they use are not specifically relevant to our instrument or data.

In conclusion, the radiocarbon calibration data reported by Yokoyama et al. (2000) were not adopted by the community for radiocarbon calibration because the data did not meet accepted quality control criteria. Reimer et al. (2006) state this explicitly when they write that "the data reported by Yokoyama et al. (2000) did not meet quality criteria set by the IntCal group (Reimer et al., 2002, 2004; Hughen et al., 2004a; Hughen et al., 2004b) and were thus not selected for inclusion in the IntCal compilation (Hughen et al., 2004a; Hughen et al., 2004b; Reimer et al., 2004)". Conclusions drawn from these same Yokoyama et al. (2000) radiocarbon and $^{230}$Th/$^{234}$U dates used in sea level (Yokoyama et al., 2001a; Lambeck et al., 2002) and rapid climate change reconstructions (Yokoyama et al., 2001b) must be re-evaluated. Lastly, sample quality and not mass

spectrometer type nor analytical technique is all too frequently the limitation in uranium-series dating. As Reimer et al. (2006) conclude: "Time will tell whether reducing the XRD calcite limit to "no detectable calcite" will improve the coherency observed in the coral database".

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