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Uranium uptake history, open-system behaviour and uranium-series ages of fossil *Tridacna gigas* from Huon Peninsula, Papua New Guinea

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Abstract

Molluscs incorporate negligible uranium into their skeleton while they are living, with any uranium uptake occurring post-mortem. As such, closed-system U-series dating of molluscs is unlikely to provide reliable age constraints for marine deposits. Even the application of open-system U-series modelling is challenging, because uranium uptake and loss histories can affect time-integrated uranium distributions and are difficult to constrain. We investigate the chemical and isotopic distribution of uranium in fossil *Tridacna gigas* (giant clams) from Marine Isotope Stage (MIS) 5e (128 – 116 ka) and MIS 11 (424 – 374 ka) reefs at Huon Peninsula in Papua New Guinea. The large size of the clams enables detailed chemical and isotopic mapping of uranium using LA-ICPMS and LA-MC-ICPMS techniques. Within each fossil *Tridacna* specimen, marked differences in uranium concentrations are observed across the three *Tridacna* growth zones (outer, inner, hinge), with the outer and hinge zones being relatively enriched. In MIS 5e and MIS 11 *Tridacna*, the outer and hinge zones contain approximately 1 ppm and 5 ppm uranium respectively. In addition to uptake of uranium, loss of uranium appears prevalent, especially in the MIS 11 specimens. The effect of uranium loss is to elevate measured [²³⁰Th/²³⁸U] values with little effect on [²³⁴U/²³⁸U] values. Closed-system age estimates are on average 50% too young for the MIS 5e *Tridacna*, and 25% too young for the MIS 11 *Tridacna*. A complex, multi-stage uptake and loss history is interpreted for the fossil *Tridacna* and we demonstrate that they cannot provide independent, reliable geochronological controls on the timing of past reef growth at Huon Peninsula.

1. Introduction

U-series dating of corals has been a key tool for constraining the history of climate and sea level change during the Late Quaternary (Bloom et al., 1974; Chappell, 1974; Edwards et al., 1987; Stein et al., 1993;

Stirling et al., 1998; Esat et al., 1999; Potter et al., 2004). While reliable closed-system U-series ages often can be obtained from well preserved corals, few corals actually satisfy established criteria for closed-system U-series dating. In particular, fossil corals often contain excess initial ^{234}U relative to generally accepted seawater values (i.e. initial $\delta^{234}\text{U}$ values significantly greater than the nominal range of $146 \pm 6\text{‰}$) indicating isotopic enrichment in ^{234}U (or possibly depletion in ^{238}U) after their initial equilibration with seawater (Banner et al., 1991; Bard et al., 1991). Several open-system U-series dating models have been proposed that correct for uranium-series isotope mobilisation in fossil corals as a result of α -recoil processes (Thompson et al., 2003; Villemant and Feuillet, 2003). These models sometimes produce ages that are consistent with reliable closed-system ages from the same reef unit, but in other instances, produce inconsistent ages from one another, and also for measurements taken on sub-samples of the same coral, indicating their failure to adequately correct for open-system behaviour in many fossil reef localities (Scholz and Mangini, 2007; Andersen et al., 2008; Stirling and Andersen, 2009; Andersen et al., 2010). In addition, these models cannot account for post-depositional uranium uptake or loss. An alternative method for U-series dating of fossil corals displaying evidence of open-system behaviour was presented by Scholz et al. (2004), known as coral isochron dating. The assumption for this approach is that all parts of a fossil specimen simultaneously gain different amounts of uranium at a fixed $^{234}\text{U}/^{238}\text{U}$ composition, followed by possible simultaneous loss in all sub-samples that is proportional to the uranium gain. If these conditions are met, a linear correlation between coral $[\text{}^{234}\text{U}/^{238}\text{U}]$ and $[\text{}^{230}\text{Th}/^{238}\text{U}]$ is observed, and the slope of the 'addition line' (isochron) reflects the specific diagenetic history for the fossil coral. True age of the specimen is extracted by intersecting the isochron with the seawater $\delta^{234}\text{U}$ evolution curve (Scholz et al., 2004; Scholz and Mangini, 2006). However this model cannot account for recrystallization of primary aragonite, variation in isotopic composition of the uranium source, uranium uptake or loss in the sample that is not simultaneous throughout, or uranium loss that is not proportional to the uranium uptake. In summary, no single open-system model presented thus far appears to be universally applicable to correct for open-system behaviour of uranium in fossil corals (Scholz and Mangini, 2007).

Approaches to open-system U-series dating for other materials have been developed based on uranium uptake by diffusion-adsorption and reaction between aqueous uranium bearing fluids and permeable samples (Pike et al., 2002; Kohn, 2008; Sambridge et al., 2012). For simple U-uptake by isotropic materials such as fossil bones and teeth, these models produce characteristic U-shaped U concentration profiles, U-series isotope and apparent closed-system age profiles, the exact form of which depends on the uptake history and age (Millard and Hedges, 1996; Pike and Hedges, 2001). This approach has been explored and further developed by Grün and co-workers (Grün et al., 2008; Sambridge et al., 2012), with apparent success for some molluscs (Eggins et al., 2005).

Giant clams (*Tridacna gigas*) are often present in fossil coral reef tracts, and owing to their dense crystalline structure are often better preserved than fossil corals in terms of retention of primary aragonite and primary geochemical signatures (e.g. Ayling et al., 2015). However, unlike corals, molluscs do not incorporate appreciable uranium into their skeleton during growth and modern specimens commonly contain less than 100 parts-per-billion (ppb) (e.g. Kaufman et al., 1971; Kaufman et al., 1996). Nonetheless fossil molluscs often exhibit uranium concentrations that are many orders of magnitude greater than in living shells, indicating uptake of uranium after death and hence open-system behaviour. Previous studies have shown that U-series ages obtained from molluscs generally differ from deposit ages constrained by other methods (e.g. U-series ages of fossil corals), and U-series ages for fossil molluscs from the same deposit are also often inconsistent with one another (Kaufman et al., 1971; Hearty and Aharon, 1986; McClaren and Rowe, 1996). Early attempts to date fossil *Tridacna* by U-series methods are notable for having produced closed-system U-series age estimates that are significantly less than corals recovered from the same reef tract (Veeh and Chappell, 1970).

Despite the evidence for post-mortem open-system behaviour of uranium in mollusc shells, fossil molluscs preserved in shoreline and other marine deposits continue to attract U-series dating efforts, particularly in the absence of other datable materials (e.g. corals) and where deposit ages lie beyond the range of ^{14}C dating (Ivanovich et al., 1983; Hillaire-Marcel et al., 1995; Hillaire-Marcel et al., 1996; Giresse et al., 2000; Belluomini et al., 2002; Jedoui et al., 2003). These efforts have been justified by the suggestion that reliable U-series may be obtained in circumstances where uranium mobility has ceased shortly after deposition, due to loss of permeability to groundwater, hyper-aridity, or the onset of reducing conditions (Hillaire-Marcel et al., 1995). Other studies have investigated the spatial distribution of U-series isotopes in fossil molluscs in south-eastern USA, and in Chile, to further evaluate the uranium uptake history and reliability for U-series geochronology (e.g. Kaufman et al., 1996; Labonne and Hillaire Marcel, 2000). Based on transects across the fossil shells and measured geochemical and isotopic gradients, both studies report uptake of marine uranium and subsequent closure of shell interiors to uranium uptake within a few thousand years of burial. In contrast, the outer parts of the same shells were subject to more extended periods of open-system uranium uptake (Kaufman et al., 1996; Labonne and Hillaire Marcel, 2000).

In this study, we document the spatial, chemical and isotopic variability of uranium in fossil *Tridacna gigas* (the giant clam) from Huon Peninsula (HP), Papua New Guinea, and compare these data to two modern shells: one from HP, and the other from Palm Island in the Great Barrier Reef, Australia. The fossil *Tridacna* samples analysed here were collected from reef tracts that correlate to the interglacial intervals of Marine Isotope Stage (MIS) 5e (128 – 116 ka) and MIS 11 (424 – 374 ka) (ka = thousand years before present). We evaluate possible U-uptake histories and open-system behaviour to assess whether the fossil *Tridacna* can provide independent, reliable, geochronological control on the timing of reef growth at HP.

We use a combination of LA-ICPMS to measure trace element profiles, and solution MC-ICPMS and LA-MC-ICPMS to examine the uranium isotopic composition in different parts of these fossil shells. The combination of highly-sensitive multi-collector inductively-coupled plasma mass spectrometry (MC-ICPMS) with laser ablation (LA) micro-sampling now makes *in situ* analysis of ^{238}U - ^{235}U - ^{234}U - ^{230}Th isotopes feasible and relatively straightforward for uranium concentrations as low as only a few hundred ppb (Eggins et al., 2005). This technique makes it possible to investigate the distribution of uranium and its decay products within shells over length scales ranging from hundreds of microns to centimetres, with tens to hundreds of U-series analyses able to be collected during a 10-12 hour analytical session. Although lacking the accuracy and precision of isotope measurements by solution MC-ICPMS, achievable analytical precision is similar to alpha counting techniques where uranium concentrations exceed 1 ppm. *Tridacna* clams are ideal candidates for using LA-MC-ICPMS to examine U-series open system behaviour given their large size: the distances over which uranium-series isotopes must migrate are one to two orders of magnitude greater than in other molluscs and thereby provide enhanced potential for preserving isotopic and concentration variations along uranium uptake/migration pathways.

2. Field Methods

2.1 *Tridacna* sampling and geochronology

Fossil *Tridacna* were sampled in March 2004 from the uplifted off-lapping coral reef terraces of HP, Papua New Guinea, where fluctuations in global glacio-eustatic sea level are superimposed on the tectonically-rising coastline (Chappell, 1974; Chappell et al., 1996). These terraces have been the subject of many studies that have used ^{14}C and closed-system U-series dating of fossil corals to constrain global sea level changes and climate during previous glacial/interglacial cycles (e.g. Bloom et al., 1974; Chappell, 1974; Aharon et al., 1980; Esat et al., 1999; McCulloch et al., 1999). In this study, samples were collected from reef tract VII, which is further subdivided into VIIa (fringing reef on the landward side of the lagoon) and VIIb (barrier reef), and corresponds to the Last Interglacial as established by U-series dating of corals (Veeh and Chappell, 1970; Stein et al., 1993). The top of reef terrace VIIa is estimated to correspond to MIS 5e (129 -118 ka) in age (Esat et al., 1999), coincident with the start of interglacial high sea-level at well dated sites in Western Australia (128 ka) (Stirling et al., 1998). Two *T. gigas* specimens were selected for geochemical analysis and dating (samples SL-11 and SL-12) from the fringing reef VIIa (Fig. 1). Both specimens were sampled *in-situ* from beneath a thin soil layer on the ancient reef surface, where they occurred as articulated valves that were cemented to the surrounding reef matrix.

Several fossil *Tridacna* were collected from an older, higher reef terrace near Ririwe village at elevations ranging between 1170 and 1205 m above sea level (Fig. 1). This paleoreef forms a broad and extensive terrace that suggests formation during a major interglacial interval. Unlike Huon Reef VII, the fossil reef at Ririwe has poor chronological control and the best age constraints available are based on tectonic uplift rate. Mean

uplift rates for the Holocene and since the Last Interglacial for this part of the Huon coastline are 2.7-3.0 m/ka (Ota et al., 1993). Applying these uplift rates to *Tridacna* sample site elevations produces age estimates ranging from 446 to 390 ka, which overlap with the age-range of MIS 11 of 424 - 374 ka (Lisiecki and Raymo, 2005).

2.2 *Tridacna* structure and preservation

The valves of *Tridacna* spp. clams have three distinct growth zones: the hinge area (umbo), inner zone and outer zone (Fig. 2a), which display differing, non-porous aragonite ultra-structures. The hinge and outer zones display a complex cross-lamellar ultrastructure, penetrated by V-shaped clusters of crystallites (Fig. 2g,h), whereas the inner layer comprises finely laminated, distinct growth increments of a prismatic form (Fig. 2b,c,e,f) (Pätzold et al., 1991).

The six fossil *Tridacna* analysed in this study are all very well preserved for samples of MIS 5e and MIS 11 age, with primary aragonite fibres and crystal ultrastructure preserved with only subtle changes to the aragonite fibres (i.e. rounding of the crystal facets) and minor, localised areas of calcite recrystallization usually restricted to exterior surfaces. Rarely, localised zones of calcite recrystallization occur within the inner zone of the fossil *Tridacna* and are constrained to individual growth bands (e.g. MIS 11 specimens RW-1-1 and RW-3-2: refer to Fig. S1b). The compositional variation of stable isotopes and trace elements (Mg, Sr, B and Ba) across growth bands in these fossil specimens supports our interpretation of excellent preservation of the primary aragonite (Ayling, 2006; Ayling et al., 2015).

2.3 Groundwater sampling

To constrain the U-series isotopic signatures of local groundwater at HP, groundwater samples were collected from four different locations where natural spring waters are discharging at HP: at Paradise Springs, Sialum, Sambe and Tunge (Fig. 1). The samples were collected in 500 ml-volume Nalgene bottles to which two drops of concentrated ultrapure nitric acid were added, before the lids were capped and taped to prevent any evaporation. The samples were not filtered prior to acidification, thus any suspended particles that were present in the water could have dissolved and affected the measured $\delta^{234}\text{U}$ composition of the water: if suspended particles were at or below secular equilibrium, $\delta^{234}\text{U}$ might be expected to be lower than the marine value.

3. Analytical methods

3.1 LA-ICPMS

The spatial distribution of uranium and other trace elements (Ba, Mg, Sr and B) in modern and fossil *Tridacna* valves were analysed by LA- ICPMS as continuous transects both along and across the different growth bands in sections cut through the modern and fossil specimens. Trace element analysis of *Tridacna* was performed following the methods developed at the Australian National University (ANU) by Sinclair et al. (1998) and

Fallon et al. (1999). Briefly, this involved cutting segments from the *Tridacna* valves that were up to 90 mm long, 20 mm wide and 8 mm thick. The segments were then cleaned thoroughly in ultra-pure (Milli-Q) water with an ultrasonic probe to remove surface contaminants, before being dried overnight in an oven at 40°C prior to analysis.

LA-ICPMS analyses were conducted using an ArF excimer laser (193 nm wavelength) coupled to a modified VG Elemental PQ2 STE quadrupole inductively coupled plasma-mass spectrometer (ICP-MS) via ANU designed HelEx laser ablation sample cell (Eggins et al., 1998). Laser ablation was performed in a helium atmosphere and the ablated material subsequently entrained with an argon gas stream for analysis by ICP-MS. Multiple isotopes were measured including ^{11}B , ^{25}Mg , ^{43}Ca , ^{46}Ca , ^{86}Sr , ^{138}Ba , ^{238}U . The laser was operated at a 10 Hz pulse rate with an applied energy density of 4 J/cm² to the sample surface, using simple aperture imaging optics to produce a 67 µm diameter ablation spot which was translated across the sample surface at a rate of 2.4 mm min⁻¹. The measured isotope sensitivities were calibrated using a matrix-matched in-house pressed coral powder standard (Davies Reef) with known composition for each of the analyte elements (Sinclair et al., 1998; Fallon et al., 1999).

Prior to LA-ICPMS analysis, the predefined analysis track was cleaned by conducting a laser cleaning run at a laser pulse rate of 15Hz and large diameter spot (180 µm) to remove any residual surface contamination and to expose a fresh surface of *Tridacna* for analysis. Data acquisition intervals were 0.56 seconds, corresponding to a distance of approximately 0.022 mm. The data were smoothed to minimise analytical noise, by calculating a running mean over 9 data points which corresponds to ~200 µm spatial resolution. Data reduction involved subtracting interpolated background values between background measurements made before and after each sample analysis. All analyte data were subsequently normalised to ^{43}Ca count rates measured in the same mass spectrometer cycle to correct for variation in ablation yield, before being drift corrected and standardised using bracketing analyses of the Davies coral standard.

3.2 U-series analysis by solution MC-ICPMS

3.2.1 Sample selection

The LA-ICPMS scans were used to select regions within the *Tridacna* valves that were suitable for U-series isotopic analysis: regions with sufficiently high uranium concentrations were targeted. In the inner zone of the fossil *Tridacna*, low U concentrations (<100 ppb) were measured and thus diagenetic calcite layers that contained more uranium were targeted for sampling (see Fig. S1 for photos of fossil specimens and sub-sample locations in each specimen). Samples not exceeding 1 g in weight were drilled from the fossil *Tridacna* using a high speed dental drill with a circular blade attached. The solid pieces of *Tridacna* were then ultrasonically cleaned in Milli-Q water with multiple rinses until the water was clear, and dried in a 40°C oven overnight prior to the laboratory U and Th extraction.

3.2.2 Solution MC-ICPMS

The protocol for extracting U and Th from fossil *Tridacna* and measuring the U-series isotopes by solution MC-ICPMS follows that developed at the Research School of Earth Sciences, ANU, for U-Th dating of modern and fossil corals (McCulloch and Mortimer, 2008). The Th and U fractions were measured in separate analytical runs using a Neptune MC-ICPMS following the procedure detailed by McCulloch and Mortimer (2008). This method exploits the enhanced sensitivity of MC-ICPMS for U-series measurements, and is capable of precisely determining the age of modern corals by using an energy discriminator (RPQ) to attain high sensitivity for ^{230}Th measurements by minimizing tailing contributions from ^{238}U , ^{235}U and ^{233}U to the small ^{230}Th signal. The ANU Neptune MC-ICPMS used in this study was equipped with 9 Faraday cups and a single ion counter (SEM) on the central channel. The Th and U isotopes are measured separately with the same cup configuration but with different measurement protocols. Samples were introduced to the MC-ICPMS using an APEX desolvating nebuliser system fitted with a Teflon PFA flow path and a low-flow Teflon PFA nebuliser. At the beginning of each analysis session, instrumental gains and baselines were measured, and the instrument was tuned for optimum sensitivity and peak shape by introducing a solution containing ~1 ppb U and Th.

Sample uranium concentrations sufficient to create a 5-10 V signal of ^{238}U were used, and sample analyses were bracketed with the SRM 960 standard. The RPQ was not used for the U measurements, to stabilise the SEM gain and thus obtain the best precision for the ^{234}U measurements. An aliquot from the U fraction was added to the Th fraction and diluted to 2 ml to yield ~30 ppb U, which is needed to obtain 3 Volts ^{238}U , and enables use of the $^{235}\text{U}/^{238}\text{U}$ ratio for mass bias correction. Relative to the total uranium extracted from the sample, this amount of U added to the Th fraction is small and still enables the maximum ^{230}Th signal to be measured without interferences from a large ^{238}U tail or collector saturation with ^{238}U . Th measurements were performed in four steps, and used the RPQ.

A rigorous multi-sequence washout was performed between sample analyses to minimise cross-sample contamination. The initial washout incorporated a 0.05% HF - 2% HNO_3 mixture, to scavenge the Th, followed by a TRITON (surfactant) wash to wet and rinse the inside of the spray chamber, and then a final 2% HNO_3 rinse.

3.2.3 Data reduction

Data reduction involved background and blank corrections (procedural blanks), the calculation of the SEM yield based on bracketing SRM 960 standards, and correction of mass fractionation using an exponential mass bias law based on normalisation to the measured $^{238}\text{U}/^{235}\text{U}$ ratio assuming a true $^{238}\text{U}/^{235}\text{U}$ ratio value of 137.88. Although recent studies have determined greater variability in $^{238}\text{U}/^{235}\text{U}$ ratios of natural samples

(Condon et al., 2010), the variability is only within the epsilon range and is thus within the uncertainty of the measurements we report.

Results are reported as activity ratios (Equation 1) and delta notation (Equation 2):

$$\left[\frac{{}^{230}\text{Th}}{{}^{238}\text{U}} \right]_{act} = \frac{\left(\frac{{}^{230}\text{Th}}{{}^{238}\text{U}} \right)}{\left(\frac{\lambda_{238}}{\lambda_{230}} \right)} \quad \text{EQ. 1}$$

λ_{230} = decay constant for ${}^{230}\text{Th} = 9.158 \times 10^{-6} \text{ yr}^{-1}$ (Cheng et al., 2000)

λ_{238} = decay constant for ${}^{238}\text{U} = 1.551 \times 10^{-10} \text{ yr}^{-1}$ (Jaffey et al., 1971)

$$\delta^{234}\text{U} = \left\{ \left[\frac{\left(\frac{{}^{234}\text{U}}{{}^{238}\text{U}} \right)}{\left(\frac{{}^{234}\text{U}}{{}^{238}\text{U}} \right)_{eq}} \right] - 1 \right\} \times 10^3 \quad \text{EQ.2}$$

Where $({}^{234}\text{U}/{}^{238}\text{U})_{eq}$ is the atomic ratio at secular equilibrium and is equal to $\lambda_{238}/\lambda_{234} = 5.472 \times 10^{-5}$

3.3 Laser Ablation-MC-ICPMS

U-series isotopes were measured in-situ by LA-MC-ICPMS using the ANU's custom built HelEx ($\lambda=193 \text{ nm}$) laser ablation systems and the more recently acquired Thermo-Finnigan Neptune-Plus MC-ICPMS configured with a higher sensitivity interface (high capacity interface pump and use of a Jet sample cone) and multiple ion counters. The analysis procedure is modified from that previously reported by Eggins et al. (2005; and in section 3.2.2) to take advantage of newer multiple ion counting capabilities. Specifically, a CDD (compact dynode device) located on the low mass side of Faraday cup L3 and the central SEM (electron multiplier) have been used for simultaneous measurement of ${}^{230}\text{Th}$ and ${}^{234}\text{U}$. At the same time the more abundant U-series isotopes ${}^{232}\text{Th}$ - ${}^{235}\text{U}$ - ${}^{238}\text{U}$ are collected using the movable Faraday cup array, which is arranged according to the detector configuration given in Table S1. This particular configuration permits simultaneous analysis of ${}^{230}\text{Th}$ - ${}^{232}\text{Th}$ - ${}^{234}\text{U}$ - ${}^{235}\text{U}$ - ${}^{238}\text{U}$, as well as characterisation of tailing contributions to ${}^{230}\text{Th}$ and ${}^{234}\text{U}$ in the presence of large ${}^{232}\text{Th}$ and ${}^{238}\text{U}$ ion beams.

Laser sampling was conducted by ablating large diameter spots ($180 \mu\text{m}$) for a period of 60-90 seconds at a laser pulse rate of 10 Hz and laser fluence of $\sim 5 \text{ J/cm}^2$. These conditions produce an ablation rate between 1 and 2 microns/second, and yield an ablated sample volume of $\sim 2.5 \times 10^6 \mu\text{m}^3$, or about $5 \mu\text{g}$ of CaCO_3 for each analysis. Unknown analyses were made at consistent spacing (typically 2 or 3 mm) along computer-programmed transects across cut sections of *Tridacna* valves. Typically, between 10 and 20 laser spot analyses were made along each transect and were bracketed between standard reference material analyses in order to calibrate and correct for instrument drift during the course of each transect.

Instrument calibration involved determination of U-series isotope intensities when ablating two aluminosilicate glass standards: SRM NIST610 and ANU UG1 (an in-house secular equilibrium glass standard which contains ~500 ppm U and has been synthesised from in-house ANU uraninite standard; Bernal et al., 2006). UG1 was employed as the primary instrument calibration standard and also for determination of tailing contributions to the ^{230}Th and ^{234}U isotopes from abundant neighbouring isotopes (^{238}U or ^{232}Th). A secondary in-house CaCO_3 standard with a relatively high natural uranium content (~18 ppm) has been prepared from a *Persisistrombus latus* shell, by milling to a fine powder and pelletizing a 20:1 powder:PVA mix at approximately 100 MPa. The resulting pellet can be re-sectioned and polished as required. The $^{230}\text{Th}/^{238}\text{U}$ values for this material measured by solution MC-ICPMS is used to apply a CaCO_3 matrix correction to the measured *Tridacna* shell $^{230}\text{Th}/^{238}\text{U}$ values, to account for the matrix dependent difference in Th and U yields that occurs between the silicate glass standards and the mollusc shell matrix.

4 Results

4.1 Crystallography and *Tridacna* ultrastructure

SEM and petrographic observations of each growth zone in *Tridacna* specimens indicate distinct differences in structural arrangement of aragonite crystals in the hinge and outer zones compared to the inner zone. The inner zone is nacreous and composed of horizontal lamellae, which are aggregates of aragonite crystals oriented with their c axis perpendicular to the shell surface (Watabe, 1965). In contrast, the outer and hinge zones display a complex, fine, cross-lamellar structure (Fig. 2g,h; Fig. 3f-h). Petrographic observations from the inner zone of a modern *Tridacna* specimen illustrate darker material associated with the growth bands (Fig. 2b): this is interpreted to be organic material in the aragonite matrix that is deposited with the aragonite during skeleton growth.

The preservation of the *Tridacna* specimens was examined using a petrographic microscope. The oldest fossil specimens (MIS 11) demonstrate excellent preservation overall, with only subtle thickening of the aragonite fibres, minor etching of the primary aragonite crystals, and some localised zones of sparry calcite alteration that are distinctive and easy to identify. The zones of calcite alteration are largely confined to specific growth bands within shells (e.g. Fig. 3e), but alteration is also observed to extend beyond individual daily growth bands via an advancing front of neomorphism from aragonite to sparry calcite (Fig. 3b). The inner zone of fossil specimens exhibit darker bands parallel to the growth bands (Fig. 3a,b) which, by comparison with the modern *Tridacna*, are interpreted to reflect relict organic material in the skeletal matrix. The MIS 5e specimens appear to be very well preserved with no obvious calcite alteration.

4.2 LA-ICPMS uranium and trace metal (Mg/Ca) transects

The uranium concentration in the modern *Tridacna* shells from Palm Island and HP is very low throughout all growth zones (<10-20 ppb) (Figs. 4, 5, 6; Fig. S2), apart from a slight increase near the exterior surface of the shell in the modern specimen from Palm Island, and some anomalous spikes in both specimens. Uranium concentration shows no correlation with either Mg/Ca or Ba/Ca trace element ratios in any growth zone in the modern specimens (Fig. 5). In the fossil *Tridacna* from MIS 5e and MIS 11, uranium concentrations reach up to 1 and 6 ppm respectively (Fig. 4, 6; Fig. S3, S4), with a strong association between uranium concentration and growth zone. The hinge zone and outer layers are enriched in uranium (e.g. ~5-6 ppm for MIS 11 *Tridacna*), whereas the inner shell layers typically contain less than 0.1 ppm (Fig. 4, 5, Fig. S3, S4). The hinge and outer growth zones of clams of the same age have similar uranium concentrations (~1 ppm for MIS 5e clams, ~5-6 ppm for MIS 11 clams). Uranium concentrations are also notable for being relatively homogeneous within the growth zones of fossil *Tridacna*, with only subtle concentration gradients occurring toward the exterior surfaces in some shells (Fig. 4, 6). The Mg/Ca ratio in both modern and fossil specimens is elevated in the inner zone, compared to the outer and hinge zones (Fig. 5, Fig. S3, S4): this pattern has been interpreted to reflect biological partitioning of magnesium during shell formation (e.g. Elliot et al., 2009).

4.3 Solution U-series results

Measured uranium concentrations obtained from the solution method are generally consistent with the LA-ICPMS results, in that the inner zones contain negligible amounts of uranium compared to the hinge and outer zones, in both the MIS 5e and MIS 11 *Tridacna*. Samples that were collected from localised zones of calcite alteration are generally more enriched in uranium compared to adjacent samples collected from primary aragonite (Table 1).

The isotopic data indicate that the fossil *Tridacna* of MIS 5e and MIS 11 age have distinct [$^{230}\text{Th}/^{238}\text{U}$] values. The highest [$^{230}\text{Th}/^{238}\text{U}$] values lie between 0.8 and 1.4 and are associated with the MIS 11 *Tridacna*, whereas values between 0.4 and 0.6 are associated with the MIS 5e *Tridacna* (Table 1, Fig. 7). [$^{230}\text{Th}/^{238}\text{U}$] is variable within each fossil clam and does not show any trend associated with different shell zones. The corresponding closed-system apparent ages range from 49 to 85 ka for the MIS 5e *Tridacna* (averaging ~50% too young), and between 227 and 384 ka for the MIS 11 *Tridacna* (averaging 25% too young). The spread of ages within the MIS 5e and MIS 11 *Tridacna* data reflects differences in isotopic compositions between clams, and also within individual clams. Measured $\delta^{234}\text{U}$ values in the fossil *Tridacna* range between -25.9‰ and 110 (Table 1).

Four calcite layers sampled from a MIS 11 *Tridacna* shell, and a sample of Miocene limestone from HP, display [$^{230}\text{Th}/^{238}\text{U}$] values in excess of secular equilibrium (Table 1, Fig. 7). The four groundwater samples

collected from HP had low measured $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ values, and measured $\delta^{234}\text{U}$ compositions ranging between 70‰ and -30‰ (Table 1).

4.4 Laser Ablation-MC-ICPMS results

Two fossil *Tridacna* from MIS 5e and two from MIS 11 were selected for detailed LA-MC-ICPMS analysis, which involved making transects along and across growth layers in different growth zones (Fig. S5).

4.4.1 MIS 5e *Tridacna*

The laser ablation results for the two MIS 5e *Tridacna* are consistent with the solution MC-ICPMS data. Results from fossil specimen SL-12 show greater dispersion and include occasional anomalously high $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ values (0.8 – 0.9), whereas SL-11 data plot in a tight cluster (Fig. 8). All data from SL-11 and most from SL-12 plot below the seawater $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$ evolution curve, consistent with the solution MC-ICPMS results for these specimens.

Spatially, we observe subtle gradients in uranium concentration from the exterior to interior of the *Tridacna*: highest uranium concentrations are observed towards the surface of the *Tridacna*, which decrease with distance from the surface (Fig. 9; Fig. S6,S7). Associated with this, there is weak correspondence between uranium concentration, $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ and $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$ values; when uranium concentration increases, $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ and $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$ also increase (excluding the data from the inner zone, where the low uranium concentration prevents reliable isotopic determinations) (Fig. 9). This trend contrasts with the MIS 11 results, where increases in uranium concentration are typically associated with stable $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ and $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$ values (see 4.4.2).

Statistical analysis of these data reveals a weak positive correlation between $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ and $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$ in the aragonitic samples ($r^2 = 0.31$, $p < 0.0001$), and no significant correlation between uranium concentration and $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$. A weak, positive correlation is observed between uranium concentration and $\delta^{234}\text{U}$ (Fig. 10), which differs to the MIS 11 data. For the calcite specimens, no significant correlation is observed between the isotopes and with uranium concentration, and the isotopic data are more scattered when compared to the MIS 11 calcite analyses (Fig. 10). The calcite specimens do have relatively enriched $\delta^{234}\text{U}$ values compared to the aragonite samples, as well as the highest $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ values for the MIS 5e *Tridacna*.

4.4.2 MIS 11 *Tridacna*

The LA-ICPMS U-series data produce closed-system age estimates consistent with the solution data for the MIS 11 samples, albeit with larger uncertainties (Fig. 8). The results obtained from each fossil specimen are also notable for being clustered and tending to be distinct. The results from MIS 11 *Tridacna* RW-3-2 are characterised by higher $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$ ratios (~1.10 – 1.17) than the other MIS 11 *Tridacna* Eddie. Almost all

values from RW-3-2 fall above the seawater [$^{234}\text{U}/^{238}\text{U}$] evolution curve, although the solution data also include several values that fall between 0.99 and 1.1 (Table 1). The [$^{234}\text{U}/^{238}\text{U}$] values obtained for Eddie range between 1.0 – 1.1 and are consistent with solution data from two other fossil MIS 11 *Tridacna* (RW-1-1 and RW-1-2: refer to Table 1). The results obtained from the outer zone in Eddie typically fall above the seawater [$^{234}\text{U}/^{238}\text{U}$] evolution curve value, whereas results from the inner and hinge zone in Eddie typically fall below it (Table 2).

The data reveal few consistent spatial trends. Transects across the hinge and outer growth zones show subtle, variable gradients in uranium, $\delta^{234}\text{U}$, and closed-system age estimates. For example, in the hinge zone of Eddie, closed system ages generally increase away from the exterior of the fossil *Tridacna* along growth bands, whereas $\delta^{234}\text{U}$ gradually decreases (Fig. 11). However, transect 3 that is sub-parallel to the exterior of the hinge exhibits variable uranium concentrations, and much higher closed-system ages (average ~478 ka). In the outer zones of Eddie (Fig. S8) and RW-3-2 (Fig. S9), closed system ages and $\delta^{234}\text{U}$ are relatively stable or slightly increase away from the outer surface, while uranium decreases.

Statistical examination of the uranium isotopic and chemical data that the aragonitic parts of the two MIS 11 specimens analysed by LA-MC-ICPMS (excluding the analyses made in the inner zone where the uranium concentrations are much lower and thus error bars are considerable), exhibit a significant positive correlation between [$^{230}\text{Th}/^{238}\text{U}$] and [$^{234}\text{U}/^{238}\text{U}$] ($r^2 = 0.73$, $p < 0.0001$), but no correlation of either with uranium concentration. In the areas with calcite recrystallization, isotopic compositions are more tightly clustered (Fig. 12), with a narrower range in both [$^{230}\text{Th}/^{238}\text{U}$] and [$^{234}\text{U}/^{238}\text{U}$]. Additionally, the $\delta^{234}\text{U}$ values are generally below the seawater evolution curve (average value of $55\text{‰} \pm 9\text{‰}$ (1SD)). Similar to the aragonite samples, there is no significant correlation between uranium concentration and isotopic composition (Fig. 12).

5. Discussion

5.1 Controls on uranium uptake

In all fossil *Tridacna*, higher uranium concentrations are measured in both the hinge and outer zones than in the inner zone (Fig. 4,5,8,9; Fig. S4-S7). Similar differences have been observed previously in other molluscs, for example *Mercenaria* clams (Kaufman et al., 1996). U-uptake in molluscs is thought to occur via a diffusion-adsorption process governed by diffusion of uranyl ions (UO_2^{2+}) into the mollusc skeleton, followed by adsorption of the uranyl ion. With this mechanism of uranium uptake, uranium profiles that are homogeneous indicate that equilibrium has been reached, whereas gradients in uranium concentration indicate non-equilibrium conditions (e.g. Pike et al., 2002). Sorption of uranyl ions by minerals is known to depend on several factors, including pH, availability of surface binding sites, solution composition and aqueous complexation (Savenko, 2001; Elzinga et al., 2004). We believe it is reasonable to assume that at any given

point in time, all growth zones of an individual fossil *Tridacna* would be simultaneously exposed to pore fluids of similar uranium concentrations, pH and aqueous complexation, given that parts of every growth zone is in direct contact with the external environment. Thus the differences in the availability of surface binding sites may be responsible for the measured differences in uranium concentrations between *Tridacna* growth zones. Differences in binding-site availability may result from crystallographic and/or structural differences between the hinge and outer zone, and the inner zone, for example crystal orientation, crystal specific surface area (SSA), growth band orientation and/or organic content of the skeleton (Kaufman et al., 1996; Millard and Hedges, 1996; Labonne and Hillaire-Marcel, 2000). Our SEM observations confirm distinct differences in structural arrangement of aragonite crystals in the hinge and outer zones versus the inner zone of *Tridacna*. The inner zone is nacreous and composed of horizontal lamellae (Watabe, 1965), whereas the outer and hinge zones display a complex, fine, cross-lamellar structure (Fig. 2b). These ultra-structural differences may result in differences in crystal SSA and/or organic content. This is consistent with other studies where cross-lamellar molluscs were found to have greater surface areas than lamellar, nacreous molluscs, and molluscs with cross-lamellar ultrastructure have higher uranium contents than the nacreous molluscs (Anderson et al., 1973). Thus we infer that differences in SSA control the concentrations of uranium in different growth zones in *Tridacna*.

There are also distinct differences between the absolute concentrations of uranium in the MIS 5e and MIS 11 *Tridacna*. In the MIS 5e clams, uranium concentrations of ~1 ppm are observed in the hinge and outer zones. In the MIS 11 clams, concentrations are ~4 – 8 ppm in these same growth zones. Our observations of groundwater uranium concentration at HP show a decrease with increasing altitude: two samples from elevations of 700-800 m contained approximately 0.4 ppb uranium, while two samples from low-altitude springs (<100 m) contained 1.6 and 0.8 ppb uranium, possibly reflecting greater residence times of the lower-altitude spring-water in the Quaternary reef complex (Table 1). This trend of decreasing uranium concentration with increasing elevation is the reverse of that observed in the fossil *Tridacna*.

Due to tectonic uplift over the last ~400 kyrs (thousand years) the MIS 11 clams are now 1200 m above modern sea level. If uranium adsorption by the clams is only controlled by contemporaneous groundwater uranium concentration, we could expect to see evidence of uranium loss from the MIS 11 clams in response to the lower groundwater uranium concentrations found at higher elevation (assuming that we have adequately characterised the local groundwater conditions). Although evidence exists for loss of uranium from the MIS 11 clams (discussed in section 5.3), they appear to have maintained uranium concentrations taken-up at lower elevations and/or have continued to take up uranium despite exposure to lower groundwater uranium concentrations with time and increasing elevation. This suggests that, in addition to uptake history, diagenetic changes may be responsible for determining the amount of uranium adsorbed over time for different growth zones within shells. The ultrastructural differences may lead to preferential acceleration of diagenesis in the outer and hinge zones of the *Tridacna* compared to the inner zone. The degradation of the organic matrix in the aragonite skeleton of *Tridacna* may be a supporting mechanism to increase SSA with time. The organic

matrix is secreted by the mantle during skeletal precipitation by living *Tridacna* to initiate and control crystallisation (Chalker, 1983). In the inner nacreous layers for example, the organic matrix is interposed between the lamellae as thin horizontal sheets, and between the crystals as walls (Watabe, 1965). Different organic contents and compounds may result in varying rates of degradation and/or protection of aragonite crystals from diagenesis in each zone as this matrix break down (Glover and Kidwell, 1993) which, in turn, may determine the surface area available for uranium adsorption. A negative exponential relationship was observed previously between amino acid content and uranium concentration in modern and fossil specimens of the gastropod *Concholepas concholepas* in Chile: specimens from the Last Interglacial contained $\sim 1/6^{\text{th}}$ of the amino acid content and up to 8 times more uranium than modern specimens (Labonne and Hillaire-Marcel, 2000). It was suggested that the decay of organic matrix of the shell increases micro-porosity and may favour increased uranium uptake (Labonne and Hillaire-Marcel, 2000). In modern and fossil *Tridacna* from HP (including Holocene, MIS 3, MIS 5 and older specimens), total amino acid contents measured in the inner zones showed little degeneration with age (Hearty and Aharon, 1986), and overall, were much lower than for other bivalve genera (total amino acid content of ~ 50 pmol/mg vs 3000-8000 pmol/mg for *C. concholepas*) (Hearty and Aharon, 1988; Labonne and Hillaire-Marcel, 2000).

Whether related to low organic content in the first place, preservation of the primary organic matter and associated organic ‘protection’ of the primary aragonite crystals, and/or primary crystallographic ultrastructure associated with low crystal SSA, the inner zones of all fossil *Tridacna* analysed at HP contain negligible uranium and appear least affected by diagenesis. The properties of the organic matrix in the outer and hinge growth zones in *Tridacna* are unknown. However, we speculate that these zones are more susceptible to diagenesis relative to the inner zone as a result of their primary cross-lamellar ultrastructure (with organic matter potentially playing a role), and infer that increasing crystal SSA with progressive diagenesis is responsible for the measured differences in absolute uranium concentrations between the MIS 5e and MIS 11 *Tridacna*.

5.2 Uranium sources at HP

Transport of uranium in the reef complex at HP is likely to occur via groundwater and local-scale pore water. The fossil *Tridacna* samples with a measured $\delta^{234}\text{U}$ of less than 80‰ are compatible with a groundwater uranium source (either recent or early uptake), based on the groundwater isotopic composition measured at HP (Fig. 7). All results above 80‰ require a different source of uranium to account for the enriched $\delta^{234}\text{U}$ values. Focusing on the MIS 11 data, we observe an array with $\delta^{234}\text{U}$ values both above and below the seawater $\delta^{234}\text{U}$ evolution curve (Fig. 7,8). Examining the data from MIS 11 specimen RW-3-2 that was analysed via solution MC-ICPMS and LA-MC-ICPMS, in the hinge and outer zones we observe values above the seawater evolution curve, with enriched $\delta^{234}\text{U}$ values and elevated $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ (Fig. 7,8, Table 1). These data appear compatible with a proximal coral source that is leaching uranium (presumably enriched in ^{234}U

due to α -recoil processes in the coral aragonite skeletons (Thompson et al., 2003)). Coral U-series data from HP indicate that many fossil corals from MIS 5e are enriched in ^{234}U (Fig. 7).

In contrast, the solution data indicate that the inner zone of RW-3-2 is characterised by low $\delta^{234}\text{U}$ values (ranging between -8 to 52‰), which are more compatible with the groundwater composition at HP. In the other MIS 11 fossil *Tridacna* analysed by solution MC-ICPMS (RW-1-1, RW-1-2; Table 1), we also observe that the most depleted ^{234}U values are associated with measurements taken in the inner zone (although the $\delta^{234}\text{U}$ for all samples from these two specimens is low (< 55‰)). LA-MC-ICPMS data from sample Eddie are both above and below the seawater $\delta^{234}\text{U}$ evolution curve (Fig. 8).

Focusing now on the MIS 5e results, where we have both coral and mollusc data at HP, we observe a clustering of *Tridacna* results in between the coral and groundwater values (Fig. 7). This suggests that similar to the MIS 11 *Tridacna*, the MIS 5e *Tridacna* have received uranium from both uranium sources. The MIS 5e *Tridacna* do not exhibit the same trends in $\delta^{234}\text{U}$ in inner vs hinge/outer zone, however we do observe a weak positive correlation between uranium concentration and $\delta^{234}\text{U}$ in the hinge and outer aragonite samples for the MIS 5e *Tridacna* (Fig. 10). This may indicate a proportionally-greater contribution of the coral-sourced uranium to the overall uranium uptake for these samples.

In comparison to other mollusc U-series results obtained from other site locations (e.g., Italy, Mauritania, Chile and Mallorca), our *Tridacna* data exhibit lower $[^{234}\text{U}/^{238}\text{U}]$ ratios, and generally fall below the seawater $[^{234}\text{U}/^{238}\text{U}]$ evolution curve whereas other mollusc data fall above the seawater $[^{234}\text{U}/^{238}\text{U}]$ evolution curve (Fig. S10). These differences likely reflect the primary isotopic composition of uranium sources at these sites that are more enriched in ^{234}U . Additionally, other studies that have conducted uranium transects across fossil molluscs concluded that uptake of marine uranium and subsequent closure of shell interiors to uranium uptake occurred within a few thousand years of burial, given the reasonable agreement of closed-system U-series ages with known deposit ages (Kaufman et al., 1996; Labonne and Hillaire Marcel, 2000). The closed-system U-series ages for the HP *Tridacna* are 25-50% too young given known deposit ages, and isotopic and uranium profiles do not support early uptake of marine uranium at HP and subsequent closure of the system. This may reflect differences in the mollusc taxa studied (*Tridacna* vs. *Mercenaria* clams and *C. Concholepas* gastropods) and/or differences in geological/geographic setting. HP is located in an actively-uplifting, tropical environment that receives up to 2000 mm/year rainfall, in contrast to the stable south-eastern coastal plain in the USA (Kaufman et al., 1996) and hyper-arid conditions in northern Chile (Labonne and Hillaire Marcel, 2000). Such differences may affect both the mobility and potential sources (and thus isotopic composition) of uranium available for uptake in the fossil molluscs.

5.3 Indicators and mechanisms of uranium loss

Closed-system age estimates could not be calculated in several instances because measured isotopic compositions are greater than secular equilibrium. These samples include the Miocene limestone sample from HP, and several samples from MIS 11 fossil *Tridacna* (Fig. 7a; 8a, Table 1). We interpret these results as reflecting loss of uranium from the samples, which elevates [$^{230}\text{Th}/^{238}\text{U}$] values due to the relative immobility of thorium. Subtle indicators of uranium loss are also present in the MIS 11 *Tridacna* where closed-system ages greater than 400 ka have been calculated, as in the specimen Eddie (Fig. 11; Fig. S8). The LA-MC-ICPMS data also indicate uranium loss in some MIS 5e fossil *Tridacna*, such as specimen SL-12 where some samples fall to the right of the central array, and produce apparent closed-system ages above 150 ka (Fig. 8b). Given the robust chronological control of these specimens to the MIS 5e reef tract based on reliable closed-system U-series ages from adjacent fossil corals and paleoreef morphology (Stein et al., 1993; Esat et al., 1999), loss of uranium is required to explain these anomalous ages in parts of these MIS 5e *Tridacna*.

The occurrence of uranium loss is associated with both secondary calcite and primary aragonite mineralogy in *Tridacna* at HP. The four MIS 11 samples measured by solution MC-ICPMS that have [$^{230}\text{Th}/^{238}\text{U}$] values in excess of secular equilibrium are calcite (Table 1). The much larger LA-MC-ICPMS dataset reveals that both aragonite and calcite samples appeared to have experienced uranium loss. Shell areas replaced with calcite are often associated with increased [$^{230}\text{Th}/^{238}\text{U}$] values, older closed-system ages and higher uranium concentrations relative to adjacent aragonite zones, particularly for the MIS 11 *Tridacna* (e.g. Fig. 9, 10, 12; Fig. S6, S8). Evidence of uranium loss also occurs in aragonite mineralogy, for example, in a hinge transect in a MIS 11 fossil *Tridacna* in aragonite (transect 3 in specimen Eddie), where multiple analyses indicate values exceeding secular equilibrium (Fig. 11). Counter-intuitively, MIS 11 samples that exhibit evidence for this uranium loss are the most enriched in uranium (>5 ppm uranium). It may be that uranium mobility (both uptake and loss) is greater in parts of the fossil *Tridacna* that are most affected by diagenetic changes (i.e. the hinge and outer zones, and calcite zones), and enables ongoing uranium loss and uptake. Alternatively, our observations lend support to the model that uranium uptake and loss in fossil *Tridacna* occurs via adsorption and desorption processes, vs ‘primary’ incorporation into the aragonite lattice during precipitation or recrystallization and loss of uranium from the skeleton via leaching processes (which would be associated with dissolution of aragonite or calcite, and decreased uranium concentration). Diffusion/adsorption-desorption processes may more readily-permit isotopic exchange of uranium while preserving bulk uranium concentrations.

Our observation of uranium enrichment in *Tridacna* calcite zones contrasts to some other studies examining calcite recrystallisation in aragonite speleothems and fossil carbonate reefs, where uranium concentrations are typically lower in recrystallised calcite, due to interpreted preferential exclusion of uranium in the calcite lattice (e.g. Jones et al., 1995; Ortega et al., 2005; Lachniet et al., 2012). However, other studies also observe

no uranium loss during aragonite to calcite transformation in an aragonite speleothem, suggesting the recrystallisation happened in a closed system and uranium was preserved (Spötl et al., 2002). For the fossil *Tridacna*, we speculate that our results reflect differences in the mode of initial uranium incorporation in the aragonite skeleton (adsorption vs. precipitation during primary crystallization as is the case for speleothem and coral aragonite). This may translate to different uranium incorporation in the subsequently-recrystallised calcite.

5.4 Potential for open-system modelling and U-uptake history

Open-system U-series uptake models that are centred on diffusion-adsorption processes have been used effectively to provide more reliable and accurate age estimates in materials such as bone and teeth (e.g. Pike et al., 2002). Such models rely on distinctive spatial gradients in uranium concentration and isotopic composition across the bone or tooth. A modern *Tridacna* specimen from Palm Island exhibits a uranium concentration profile that decreases from ~40 ppb at the surface to <10 ppb in the interior (Fig. 4), consistent with U uptake occurring through diffusion-adsorption processes that begin post-mortem while the clam is in the marine environment. In the fossil *Tridacna* however, although there are some subtle gradients in uranium concentration in some transects (e.g. Fig. 8; Fig. S5,S6), the uranium concentrations are usually relatively uniform within each growth zone. This suggests that the uranium concentrations have reached equilibrium within these respective growth zones. Similarly, isotopic profiles exhibit small-scale variability but no systematic spatial trends. In combination with the complex, non-symmetrical growth zone geometry and associated multiple potential uptake pathways (in contrast to the symmetry and isotropy of bone), our observations suggest that simple diffusion-adsorption modelling approaches are not suited for application to fossil *Tridacna*. Coral-based open-system models are also not applicable to the *Tridacna* dataset: the α -recoil open-system models (Thompson et al., 2003; Villemant and Feuillet, 2003) cannot be applied to the fossil *Tridacna* given that uranium uptake (and loss) universally applies to the clams. Similarly, the coral-isochron approach (Scholz et al., 2004) also cannot be applied, as in addition to the various assumptions mentioned in the introduction that are unlikely to apply to the uranium uptake at HP, it requires the ‘addition’ isochron be intersected with the seawater $\delta^{234}\text{U}$ evolution curve to extract the true age of the sample. The initial composition of *Tridacna* $\delta^{234}\text{U}$ is unconstrained and not fixed at the seawater value, and completely dependent on the isotopic composition of any uranium that enters the *Tridacna* shell post-mortem.

To evaluate possible uptake models for the HP fossil *Tridacna*, we calculated several simple scenarios to compare with our measured dataset:

1. Early U uptake (within 1 kyr)
2. Mid U uptake (after 50 kyrs; 70 kyrs)
3. Late U uptake (after 100 kyrs)
4. Later U uptake (after 150 kyrs; 200 kyrs) (for the MIS 11 *Tridacna* only)

5. Linear U uptake

6. U uptake after 50 kyrs, with subsequent U loss: (a) 5% loss, (b) 10% loss, (c) 20% loss, (d) 40% loss

7. U uptake after 100 kyrs, with subsequent U loss: (a) 5% loss, (b) 10% loss, (c) 20% loss, (d) 40% loss

For these calculations, several assumptions were made: (1) only uranium is added to or lost from the sample: mobility of ^{230}Th was not considered; (2) ^{234}U and ^{238}U are not fractionated during loss of uranium events; (3) For linear uptake, uranium uptake did not occur from an evolving uranium source; (4) only one uptake event is considered for each scenario (although multiple uptake events are possible); and (5) other than linear uptake, a single uptake event is considered to occur over 1000 yrs. Given the range in measured uranium isotopic compositions at HP (i.e. groundwater $\delta^{234}\text{U}$ composition, and possible marine uranium sources), five uranium sources were simulated with $\delta^{234}\text{U}$ values of -20, 40, 80, 145, and 180. Although not directly measured in this study, the higher value of 180 is intended to simulate a possible enriched ^{234}U source that is speculated to exist in fossil marine carbonates due to ^{234}U mobilization and α -recoil processes.

Fig. 13 presents the measured solution and LA-MC-ICPMS data for the MIS 5e specimens, with the results of the various simulated uptake scenarios superimposed. The very early (<1 kyr) and very late uptake (>100 kyrs) scenarios show poor agreement with the measured data for both specimens. Samples from the SL/11 dataset appear compatible with more than one of the simulated scenarios: linear uptake, a single uptake event after 70 kyrs, and/or uptake after 70 kyrs followed by loss of up to 20% uranium. Additionally, some samples indicate even later uptake, (i.e. some results fall to the left of the 70 kyr uptake scenario). Parts of the SL/12 specimen are also compatible with linear uptake, however there is greater spread in both $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ and $\delta^{234}\text{U}$ composition, which necessitates a more complex uptake history. Some sub-samples from this specimen are compatible with uptake after 50 kyrs followed by loss of 40% uranium, other sub-samples are compatible with earlier uptake (occurring after ~50 kyrs or earlier) that may have been derived from marine uranium (or ^{234}U -enriched fluids), and other sub-samples are compatible with later uptake (~70 kyrs) from a lower ^{234}U groundwater source. The key message is none of these simple uptake models can adequately explain the entire dataset for an individual specimen. Different samples within each *Tridacna* have different apparent uptake histories. Examining the MIS 11 results (Fig. 14), we observe similar variability in apparent uptake histories. For specimen Eddie, the measured data are compatible with uptake occurring immediately-post-mortem through to as late as 200 kyrs post mortem. Additionally, many samples have $[\text{}^{230}\text{Th}/\text{}^{238}\text{U}]$ values in excess of secular equilibrium and are compatible with uranium uptake occurring after 50 to 70 kyrs, followed by 5-10% uranium loss. In contrast, RW-3-2 has a wide range of uranium $\delta^{234}\text{U}$ compositions (ranging from -8‰ to over 160‰), and is relatively enriched in ^{234}U compared to the known groundwater and marine uranium sources: a possible source might be preferential loss of ^{234}U from fossil corals via α -recoil processes. Regardless of source, this specimen has samples compatible with uptake occurring immediately-post-mortem through to uptake after 200 kyrs. No sub-samples from the MIS 11 *Tridacna* are compatible with the linear uptake

model, which provides closed-system age estimates that are too young (Fig. 14), and similar to the MIS 5e specimens, no single uptake/loss scenario is universally applicable to all sub-samples from an individual MIS 11 fossil *Tridacna* (Fig. 14).

Given these simple model comparisons, we infer that the HP *Tridacna* have experienced multi-stage uptake with varying uranium sources with one or more loss events that do not allow the application of existing open-system models (e.g. Thompson et al., 2003; Villemant and Feuillet, 2003; Scholz et al., 2004), or simple uptake scenarios as simulated in this study, to obtain reliable geochronological estimates. Moreover, the observed variability in uranium isotopic composition and isotopic signatures of uranium loss are somewhat challenging to reconcile with the observed ~homogeneous uranium concentrations for specimens of similar ages. As discussed in Section 5.1, bulk uranium uptake and loss in *Tridacna* is thought to happen via adsorption and desorption mechanisms, thus the mode of uranium incorporation differs to that in fossil coral and speleothems. We hypothesise that the amount of uranium adsorbed by the *Tridacna* at any given point in time is a function of the SSA available for sorption (section 5.1), and that the SSA is always increasing with time (i.e. diagenetic changes through time do not decrease SSA). Therefore, we speculate that diagenetic changes in SSA may be the primary factor controlling/limiting uranium uptake in terms of timing and amount, while secondary factors affect the isotopic characteristics of the uranium available for uptake and/or exchange, such as variation in uranium sources (e.g. tectonic uplift at HP continuously repositions paleoreefs relative to groundwater (c.f. the permanent water table)) and variation in other meteoric conditions that regulate U mobility and uptake from groundwater and proximal coral sources. The uranium uptake process is likely to have involved multiple uptake and/or desorption events or phases, which isotopically overprint and disturb earlier uptake while maintaining bulk uranium concentrations. The simple uptake models presented in Fig. 14 also suggest that uranium uptake in the MIS 11 *Tridacna* occurred during the first 200 kyrs after shell death: if our hypothesis of diagenetic-induced increases in SSA and associated uranium adsorption is correct, this would suggest that increases in uranium adsorption capacity occurred within the first 200 kyrs, after which time there was limited additional increase in SSA to permit further uptake of uranium.

6 Summary

This study documents the complex nature of uranium uptake and loss in fossil *Tridacna gigas* from Huon Peninsula, Papua New Guinea. Significant variations in uranium concentration and isotopic composition are present within individual specimens and between specimens from both the MIS 5e and MIS 11 reef tracts. Specific growth zones within the *Tridacna* display distinct patterns of uranium uptake. The outer and hinge growth zones are significantly enriched compared to the inner zone, with U concentration averaging 1 ppm in MIS 5e specimens, and 5 ppm in MIS 11 specimens. The inner zone in all specimens contains negligible uranium (<0.01 ppm). These zonal differences in U concentration are attributed to crystallographic differences between the growth zones, which are likely to affect the specific surface area of the aragonite crystal lattice

and thus the availability of surface binding sites for uranium adsorption. The systematic enrichment in uranium with time is inferred to reflect the effects of minor diagenesis and/or the gradual decay of the organic matrix in the mollusc skeleton, which contribute to increasing crystal specific surface area with time (and thus sorption capacity). In the fossil *Tridacna* all growth zones display relatively homogenous profiles of uranium enrichment, indicating that equilibrium between the groundwater and *Tridacna* uranium occurs rapidly.

U-series data exhibit [$^{234}\text{U}/^{238}\text{U}$] values that fall both above and below the seawater evolution curve. Huon Peninsula groundwater samples exhibit low [$^{234}\text{U}/^{238}\text{U}$] values, ranging between 0.975 and 1.07, and the *Tridacna* data are compatible with uranium uptake from local groundwater sources, in addition to contributions from proximal fossil corals that may be losing ^{234}U -enriched uranium via α -recoil processes. MIS 5e *Tridacna* have closed-system age estimates at ~60 ka, therefore being ~50 % too young. In contrast, three *Tridacna* from the MIS 11 reef have closed-system age estimates averaging ~300 ka that are only ~25 % too young. Detailed LA-MC-ICPMS transects provide isotopic evidence for uranium loss in MIS 11 *Tridacna* (in addition to the apparent, extensive loss of 5-10% uranium that has resulted in [$^{230}\text{Th}/^{238}\text{U}$] values beyond secular equilibrium) as well as subtle loss indications in the MIS 5e specimens. Our results are not consistent with a single, early-uptake event followed by system closure as has been found in previous mollusc studies, and simple modelled uptake scenarios indicate that no single scenario is consistent with all data from an individual specimen. Instead, sub-samples within individual *Tridacna* are compatible with multiple possible uptake scenarios in terms of timing of uptake, isotopic composition of uranium sources, and extent of uranium loss. It is thus challenging to apply or develop a universally applicable open-system model for these fossil specimens. Despite high-resolution analysis of fossil *Tridacna* at HP using state-of-the-art analytical techniques (LA-ICPMS, LA-MC-ICPMS and solution MC-ICPMS), we conclude that fossil *Tridacna* from HP cannot provide independent geochronological control using either closed or open-system U-series dating techniques, and such limitations likely to apply to fossil molluscs in other tectonically-active, tropical settings.

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Table and Figure Captions

Table 1. Solution MC-ICPMS data for the Huon Peninsula fossil *Tridacna*. Errors are reported as 2SE and do not incorporate decay constant uncertainties. See supporting supplementary material for photos of the fossil specimens and sample locations.

Table 2: Average closed-system age estimates and $\delta^{234}\text{U}$ compositions from the MIS 5e and MIS 11 *Tridacna* specimens (LA-MC-ICPMS data).

Figure 1: Location of Huon Peninsula and sampling locations of fossil *Tridacna* (a) Sampling locations of the fossil *Tridacna* at Huon Peninsula: MIS 5e specimens were collected on the interglacial reef above Sialum village; MIS 11 specimens were collected at approximately 1000 m elevation near Tunge village. Blue circles represent the spring water sampling sites (four in total) (b,c) Geomorphology of the glacial-interglacial fossil reef succession near Sialum. Reef VII is associated with MIS 5e: the two fossil specimens collected were from reef VIIa (back lagoon location, indicated by red dots).

Figure 2: *Tridacna* skeletal observations in a modern *T. gigas* from Palm Island. (a) Photograph of a transverse slice through a fossil *Tridacna gigas* specimen, illustrating the three major growth zones (hinge, inner and outer) and positions of the pallial lines, which represent the lines of attachment of the mantle lobes. (b) Photomicrograph taken under plane-polarised light, illustrating the daily growth bands and fanning aragonite crystal bundles in the inner zone. Darker zones are interpreted to represent increased concentration of organic material in the skeletal matrix. (c) Photomicrograph of the inner zone under cross-polarised light, which highlights the daily growth bands, and fanning aragonite bundle ultra-structure over-lying this. (d) Photomicrograph illustrating the boundary between the inner and outer zones, separated by the pallial line.

(e,f) SEM images of the inner zone, illustrating the daily growth bands and boundary between each daily growth band, and parallel, laminar arrangement of the aragonite fibres. (g,h) SEM images of the outer zone, illustrating the cross-laminar ultra-structure of this zone.

Figure 3: *Tridacna* skeletal observations in MIS 11 fossil *T. gigas* from Huon Peninsula, illustrating good preservation of primary aragonite and indications of subtle and/or localized diagenetic alteration. (a) Photomicrograph of the inner zone under cross-polarised light, illustrating the preservation of daily growth bands and larger fanning, aragonite bundles. (b) Photo-micrograph (cross-polarised light) illustrating a localized zone of calcite neomorphism adjacent to primary aragonite. Note the remnant ‘skeletons’ of daily growth bands in the calcite zone, perhaps reflecting the original organic components of the skeleton. (c,d) SEM images of the inner zone, illustrating subtle etching of the primary aragonite (i.e. crystal edges are smoother and pitted appearance of the aragonite fibres). (e) SEM image illustrating localized replacement of a growth band with calcite in the inner zone. (f) SEM image of the outer zone, with excellent preservation of primary aragonite. (g,h) SEM images of the hinge zone, illustrating excellent preservation of the primary aragonite and subtle etching of the crystals.

Figure 4: Profiles of uranium concentrations in modern, MIS 5e and MIS 11 *T. gigas*, acquired across the outer and inner zones using LA-ICPMS.

Figure 5: Scatter plots illustrating the relationship between uranium concentration and Mg/Ca and Ba/Ca ratios in modern *Tridacna* specimens from Palm Island, and Huon Peninsula (data acquired using LA-ICPMS). The plots illustrate there is no correlation between uranium and these trace elements in any growth zone.

Figure 6: Profiles of uranium concentrations in modern and MIS 11 *T. gigas* specimens, spanning the hinge, inner and outer zones (data acquired using LA-ICPMS).

Figure 7. Solution U-series data from Huon Peninsula groundwater and fossil *Tridacna*, plotted on an isochron plot with isotopic evolution curves. Thick blue line represents expected closed-system evolution for a sample incorporating marine uranium (e.g. corals) where initial $[^{234}\text{U}/^{238}\text{U}]$ is 1.145 (equivalent to a $\delta^{234}\text{U}$ of 145‰). Isochron intervals are 50 ka. Existing coral U-series data from Huon Peninsula are also plotted for comparison. Error bars represent 2 SE.

Figure 8. LA-MC-ICPMS data (excluding inner zone analyses for clarity- these analyses have large uncertainties as a result of low concentrations of uranium) and solution MC-ICPMS data presented for comparison on isochron plots, with isotopic evolution curves. The seawater evolution curve is indicated by the

blue line (based on an initial $\delta^{234}\text{U}$ of 145‰). (a) Analyses from the two MIS 11 fossil *Tridacna*. (b) Analyses from the two MIS 5e fossil *Tridacna*. Error bars represent 2SE.

Figure 9: LA-MC-ICPMS transects through the hinge zone of fossil specimen SL-12 from MIS 5e. Green bands indicate analyses conducted in calcite. Grey shaded band indicates inner zone of *Tridacna*. Error bars represent 2SE.

Figure 10: Scatter plots illustrating the statistical relationships between uranium isotopes and uranium concentrations in the aragonite and calcite parts of MIS 5e fossil *Tridacna*. Data collected using LA-MC-ICPMS. Analyses from the inner zone are not plotted or included in the statistical analyses due to their higher uncertainties as a consequence of low uranium concentrations. Error bars represent 2SE; p-values less than 0.05 are considered to be significant.

Figure 11: LA-MC-ICPMS transects through the hinge zone of fossil specimen ‘Eddie’ from MIS 11. Grey shaded band indicate inner zone of *Tridacna*. Where no closed-system age estimates are plotted (lower plot), isotopic values in excess of secular equilibrium prevented an age estimate. Error bars represent 2SE.

Figure 12: Scatter plots illustrating the statistical relationships between uranium isotopes and uranium concentrations in the aragonite and calcite parts of MIS 11 fossil *Tridacna*. Data collected using LA-MC-ICPMS. Analyses from the inner zone are not plotted or included in the statistical analyses due to their higher uncertainties as a consequence of low uranium concentrations. Error bars represent 2SE; p-values less than 0.05 are considered to be significant.

Figure 13: Results of simple modelled uptake scenarios for MIS 5e *Tridacna* presented on an isochron plot, overlain on measured LA-MC-ICPMS (excluding inner zone analyses for clarity- these analyses have large uncertainties as a result of low concentrations of uranium) and solution MC-ICPMS data (error bars represent 2SE). The seawater evolution curve is indicated by the blue line (based on an initial $\delta^{234}\text{U}$ of 145‰). 5 uranium sources with different $\delta^{234}\text{U}$ composition are modelled for each uptake scenario, labelled as follows: (A) 180‰, (B) 145‰, (C) 80‰, (D) 40‰, (E) -20‰. See text for further description of the various uptake scenarios.

Figure 14: Results of simple modelled uptake scenarios for MIS 11 *Tridacna* presented on an isochron plot, overlain on measured LA-MC-ICPMS (excluding inner zone analyses for clarity- these analyses have large uncertainties as a result of low concentrations of uranium) and solution MC-ICPMS data (error bars represent 2SE). The seawater evolution curve is indicated by the blue line (based on an initial $\delta^{234}\text{U}$ of 145‰). 5 uranium sources with different $\delta^{234}\text{U}$ composition are modelled for each uptake scenario, labelled as follows:

(A) 180%, (B) 145%, (C) 80%, (D) 40%, (E) -20%. See text for further description of the various uptake scenarios.

ACCEPTED MANUSCRIPT

● SL/12: LA-MC-ICPMS	● Uptake after 50 kyr
● SL/11: LA-MC-ICPMS	○ Uptake after 50 kyr + subsequent U loss
■ SL/12: solution data	● Uptake after 70 kyr
■ SL/11: solution data	○ Uptake after 70 kyr + subsequent U loss
■ Linear uptake	△ Uptake after 100 kyr
▲ Uptake within 1 kyr	

• RW-3-2: LA-MC-ICPMS	• Uptake after 50 kyrs
• Eddie: LA-MC-ICPMS	○ Uptake after 50 kyrs + subsequent U loss
□ RW-1-2 solution data	• Uptake after 100 kyrs
• RW-1-1 solution data	○ Uptake after 100 kyrs + subsequent U loss
• RW-3-2 solution data	△ Uptake after 150 kyrs
■ Linear uptake	• Uptake after 200 kyrs
▲ Uptake within <1 kyr	

Sample No.	Sample Name ¹	U (ppm) ± 2SE	²³⁰ Th (ppt) ± 2SE	δ ²³⁴ U (‰) ² ± 2SE	[²³⁰ Th/ ²³⁸ U] ³ ± 2SE	[²³⁰ Th/ ²³² Th] ± 2SE	Age (ka) ⁴ ± 2SE
1	RW-1-2 inner	0.1799 ± 0.0003	2.81 ± 0.04	-7.8 ± 3.5	0.960 ± 0.012	1278 ± 18	384 ± 53
2	RW-1-2 inner	0.0725 ± 0.0001	1.059 ± 0.005	-25.6 ± 2.6	0.900 ± 0.004	24745 ± 579	292 ± 9
3	RW-1-2 outer	3.95 ± 0.02	63.76 ± 0.43	38.3 ± 1.3	0.994 ± 0.008	51068 ± 2517	320 ± 15
4	RW-1-2 hinge	3.67 ± 0.004	56.54 ± 1.1	17.7 ± 2.2	0.949 ± 0.018	58052 ± 5450	286 ± 25
5	RW-1-1 inner (rind)	18.23 ± 0.02	321.7 ± 11.7	54.8 ± 1.8	1.086 ± 0.040	297716 ± 41062	Undefined
6	RW-1-1 inner (calcite)	0.531 ± 0.001	8.87 ± 0.11	13.4 ± 2.7	1.029 ± 0.013	63236 ± 3362	Undefined
7	RW-1-1 inner (calcite)	0.2451 ± 0.0004	5.16 ± 0.03	41.2 ± 2.1	1.296 ± 0.007	8460 ± 42	Undefined
8	RW-1-1 inner (calcite)	0.3801 ± 0.0003	5.60 ± 0.06	-25.1 ± 1.7	0.904 ± 0.009	18362 ± 458	300 ± 16
9	RW-1-1 inner	0.0611 ± 0.0001	0.840 ± 0.003	-25.9 ± 2.9	0.846 ± 0.003	45472 ± 4636	227 ± 4
10	RW-1-1 hinge	5.321 ± 0.005	84.36 ± 2.34	24.5 ± 1.1	0.976 ± 0.027	16258 ± 235	317 ± 55
11	RW-3-2 inner (rind)	8.98 ± 0.07	145.45 ± 1.24	52.8 ± 8.0	0.997 ± 0.012	103788 ± 4886	292 ± 20
12	RW-3-2 inner (calcite)	1.691 ± 0.003	29.00 ± 0.43	13.6 ± 2.7	1.055 ± 0.016	66314 ± 4149	Undefined
13	RW-3-2 inner (calcite)	1.138 ± 0.001	17.14 ± 0.09	-8.1 ± 2.0	0.926 ± 0.005	39068 ± 507	300 ± 10
14	RW-3-2 inner	0.2123 ± 0.0001	3.23 ± 0.01	21.1 ± 1.1	0.937 ± 0.003	113246 ± 4441	266 ± 4
15	RW-3-2 hinge	3.287 ± 0.004	57.37 ± 0.96	100.1 ± 1.2	1.074 ± 0.018	146310 ± 11350	323 ± 31
16	RW-3-2 outer (surface)	2.990 ± 0.002	51.46 ± 0.13	111.7 ± 1.5	1.054 ± 0.003	360615 ± 53146	277 ± 3
17	RW-3-2 outer	3.521 ± 0.001	55.99 ± 0.12	46.4 ± 0.9	0.979 ± 0.002	1540582 ± 3119379	280 ± 3
18	SL-12 hinge	0.3110 ± 0.0002	2.23 ± 0.01	49.9 ± 2.1	0.441 ± 0.002	48129 ± 2214	59.2 ± 0.4
19	SL-12 hinge	0.796 ± 0.001	7.84 ± 0.02	110.7 ± 1.7	0.606 ± 0.001	241574 ± 8087	84.7 ± 0.4
20	SL-12 hinge (surface)	0.4417 ± 0.0003	4.05 ± 0.01	101.2 ± 1.7	0.565 ± 0.002	315263 ± 74932	77.5 ± 0.4
21	SL-12 hinge	0.1303 ± 0.0001	0.87 ± 0.01	26.9 ± 2.0	0.410 ± 0.006	60809 ± 12139	55.4 ± 1.0
22	SL-12 inner	0.0057 ± 0.0001	0.039 ± 0.001	25.1 ± 13.1	0.413 ± 0.012	3179 ± 366	56.2 ± 2.3
23	SL-12 outer (surface)	1.0117 ± 0.0008	9.06 ± 0.02	95 ± 1	0.551 ± 0.002	647142 ± 168121	75.5 ± 0.3
24	SL-12 outer	0.2889 ± 0.0003	2.09 ± 0.01	38.8 ± 1.6	0.446 ± 0.002	55039 ± 4719	61.0 ± 0.4
25	SL-12 outer	0.1653 ± 0.0001	1.17 ± 0.01	34.0 ± 2.9	0.436 ± 0.004	103903 ± 7947	59.7 ± 0.7
26	SL-11 inner	0.1397 ± 0.0002	0.982 ± 0.004	82.9 ± 2.1	0.432 ± 0.002	8244 ± 191	55.2 ± 0.3
27	SL-11 outer	1.050 ± 0.001	7.73 ± 0.03	82.4 ± 1.1	0.453 ± 0.002	95844 ± 5139	58.7 ± 0.3
28	SL-11 hinge (surface)	0.948 ± 0.001	7.39 ± 0.02	96.0 ± 0.7	0.479 ± 0.001	111347 ± 3915	62.2 ± 0.2
29	SL-11 hinge	1.149 ± 0.001	8.07 ± 0.02	78.5 ± 1.2	0.433 ± 0.001	476662 ± 146089	55.6 ± 0.2
30	SL-11 hinge	0.708 ± 0.001	4.42 ± 0.01	55.2 ± 1.3	0.384 ± 0.001	122693 ± 3316	49.3 ± 0.2
31	Sambe Springwater	0.00034 ± 4 E-7	0.00011 ± 1 E-5	66.9 ± 4.2	0.020 ± 0.001	12.9 ± 1	2.05 ± 0.14
32	Tunge Springwater	0.00036 ± 4 E-7	0.00006 ± 2 E-6	73.5 ± 2.0	0.0105 ± 0.0003	14.2 ± 0.5	1.07 ± 0.04
33	Sialum Springwater	0.00162 ± 15 E-7	0.0003 ± 6 E-7	41.3 ± 1.3	0.0124 ± 0.0002	4.7 ± 0.1	1.31 ± 0.02
34	Paradise Springs	0.00077 ± 2 E-6	2.1E-6 ± 9 E-7	-27.6 ± 1.4	0.0002 ± 0.0001	4.6 ± 1.4	0.02 ± 0.01
35	Miocene Limestone	1.034 ± 0.002	19.87 ± 0.03	12.4 ± 1.1	1.182 ± 0.003	1132 ± 2	Undefined

¹Analysis date: March - June 2005²Measured δ²³⁴U³Decay constants used for activity ratios and age calculation: ²³⁸U: 1.55125 × 10⁻¹⁰ (Jaffey et al., 1971), ²³²Th: 4.95 × 10⁻¹¹.²³⁴U: 2.8262 × 10⁻⁶, ²³⁰Th: 9.158 × 10⁻⁶ (Cheng et al., 2000),⁴Age calculations do not include decay-constant uncertainties

Average Age (ka)	Tridacna	Eddie	RW-3-2	SL-11	SL-12
Zone (calcite + aragonite)	Hinge	370	-	56.3	95.7
	Inner	289	-	54.7	126.6 [^]
	Outer	443.4	301.4	-	65.9
[^] only 4 analyses: high uncertainties					
Average Age (ka)	Tridacna	Eddie	RW-3-2	SL-11	SL-12
Zone (aragonite only)	Hinge	370	-	56.3	76.1
	Inner	285	-	52.5	126.6 [^]
	Outer	401	301.4	-	65.9
[^] only 4 analyses: high uncertainties					
Average Age (ka)	Tridacna	Eddie	RW-3-2	SL-11	SL-12
Zone (calcite only)	Hinge	-	-	-	188
	Inner	377.7	-	74.7	-
	Outer	519.7	-	-	-
$\delta^{234}\text{U}$ (‰)	Tridacna	Eddie	RW-3-2	SL-11	SL-12
Zone (calcite + aragonite)	Hinge	40.1	-	79.6	103.2
	Inner	25.6*	-	115.8	93.5
	Outer	80.8	150.4	-	62.8
* excluding anomalous values over 1000					
$\delta^{234}\text{U}$ (‰)	Tridacna	Eddie	RW-3-2	SL-11	SL-12
Zone (aragonite only)	Hinge	40.1	-	79.6	100.9
	Inner	23.5 *	-	117.6	93.5
	Outer	103.5	150.4	-	62.8
* excluding anomalous values over 1000					
$\delta^{234}\text{U}$ (‰)	Tridacna	Eddie	RW-3-2	SL-11	SL-12
Zone (calcite only)	Hinge	-	-	-	117.3
	Inner	84.6	-	98.7	-
	Outer	54.7	-	-	-