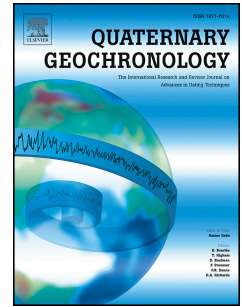


# Accepted Manuscript

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# Uranium-thorium dating potential of the marine bivalve *Lithophaga lithophaga*

Rowe, P. J.<sup>a\*</sup>, Turner, J. A.<sup>a</sup>, Andrews, J. E.<sup>a</sup>, Leeder, M. R.<sup>a</sup>, van Calsteren, P.<sup>b</sup>, Thomas, L.<sup>b</sup>

<sup>a</sup> School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK.

\* corresponding author. E-mail address: [p.rowe@uea.ac.uk](mailto:p.rowe@uea.ac.uk) Tel. +44 (0)1603592529

<sup>b</sup> OU-NERC U-Series Facility, Department of Earth Sciences, Faculty of Science, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK

**Key words:** Uranium-thorium dating; *Lithophaga lithophaga*; mollusc shells; Mediterranean; raised shorelines; uplift rates; isotope migration.

**Abstract:** Poor chronological control hampers efforts to constrain uplift event frequency in the Eastern Mediterranean Basin and develop regional tectonic models. Borings of the colonial marine mollusc *Lithophaga lithophaga* are commonly associated with uplifted Mediterranean shorelines and the suitability of its fossil shell for uranium-series dating is investigated to assess its potential for refining uplift chronologies. Living specimens contain very little uranium but Holocene fossils suggest rapid *post-mortem* uptake from a marine source. However, in common with many other mollusc species, Pleistocene samples show clear evidence of subsequent exchange with uranium from groundwater and although two out of eight samples returned ages compatible with their stratigraphic locations, these may be chance results given the compelling evidence for general open system behaviour. Detrital contamination appears not to be a significant problem in pre-Holocene samples. Open system modelling, using techniques developed to correct for alpha recoil effects in reef corals, shows that the recoil mechanism is inadequate to explain the magnitude of the isotopic alterations observed. Our results show that whilst uranium-series dating of Holocene *L. lithophaga* shells may be possible, Pleistocene specimens suffer from significant geochemical alteration and cannot be used to refine crustal uplift chronologies over longer timescales.

## 1. Introduction

The rate of Pleistocene crustal displacement in the Eastern Mediterranean–Aegean region remains poorly resolved because the timing of uplift events is uncertain due to a paucity of suitable dating material. This

32 lack of reliable chronologies has hindered construction of robust models that capture the tectonic  
33 complexities of the region and which might furnish insights into future seismic events. Uplifted palaeo-  
34 shorelines are excellent recorders of relative crustal displacement and here we investigate the uranium-  
35 thorium (U/Th) dating potential of *Lithophaga lithophaga*, a rock-boring marine bivalve that chemically  
36 excavates sub-horizontal boreholes in lithified carbonate substrates into which the shell is recessed  
37 (Morton and Scott, 1980). This species is indigenous to Mediterranean, Red Sea and Atlantic coasts (El-  
38 Menif et al., 2007), and its preferred habitat lies in a zone up to ~6 metres below contemporary sea level  
39 (Galinou-Mitsoudi and Sinis, 1997). Along uplifted coastlines the linear upper limit of a colony often  
40 coincides with marine notches (Fig 1a), defining palaeo-sea level to within about 0.5 m, the approximate  
41 tidal range in the Mediterranean. Bored holes sometimes contain preserved shells where degradation by  
42 encrusters and bioeroders in the littoral zone has been minimised by abrupt or rapid relative sea-level fall  
43 associated with co-seismic uplift. *L. lithophaga* shells have been radiocarbon dated (Evelpidou et al.,  
44 2012; Morhange et al., 2006; Pirazzoli et al., 1994; Stewart and VitaFinzi, 1996), but incorporation of old,  
45 radioactively dead, carbon into the shells from the limestone substrate significantly increases apparent  
46 ages (Shaw et al., 2010), and the ~40 ka upper limit of the method effectively restricts its use to the  
47 Holocene highstand. Dating these shells by U-series methods would significantly increase this time  
48 horizon and allow chronostratigraphic separation of many mid-late Pleistocene interglacial  
49 palaeoshorelines. This in turn would help resolve many tectonic, stratigraphic and palaeoclimatic  
50 ambiguities, allow uplift rates to be more accurately calculated and constrain tectonic models in those  
51 regions where datable material is available.



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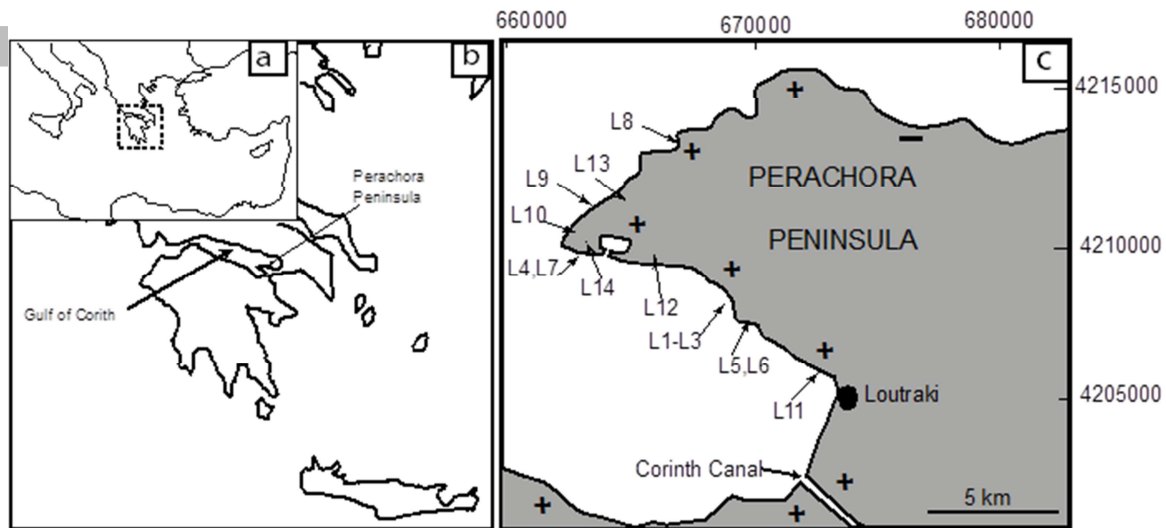
53

54

55 Fig 1(a). *L. Lithophaga* boreholes in limestone bedrock at the base of raised wave-cut notch 1.5 m  
 56 above modern sea level, Agriliou Bay (Fig. 2) from which samples L5 and L 6 (Table 1) were collected.  
 57 Notch is about 0.5 m in height (b) *L. lithophaga* borehole entrances in Holocene fossiliferous calcarenitic  
 58 sands which drape limestone bedrock (solid circles), and in the limestone bedrock (dashed circles).  
 59 Preserved shells L4 and L7 (Table 1) in boreholes at Cape Heraion (Fig. 2) are arrowed. Coin for scale.

60  
61 However, U-series dates from mollusc shells are widely regarded as unreliable since there is abundant  
62 evidence that they behave as geochemically open systems (Kaufman et al., 1971; Kaufman et al., 1996;  
63 McLaren and Rowe, 1996). *Post-mortem* burial in unconsolidated sediments, followed by sub-aerial  
64 exposure, encourages groundwater infiltration and consequent diffusion of uranium and its daughter  
65 radionuclides through the shells, possibly via organic pathways within the shell structure. Where shells  
66 are preserved under anhydrous conditions, (in arid climates, or within impermeable substrates), uranium  
67 mobility may be minimal and it might be possible to recover reliable ages (Causse et al., 1989; Causse et  
68 al., 2003; HillaireMarcel et al., 1996; Ivanovich et al., 1983). The highly unusual habitat occupied by *L.*  
69 *lithophaga* (i.e. recessed tightly in a confined space within a practically impermeable limestone substrate)  
70 might isolate fossil shells from later groundwater infiltration sufficiently to reduce isotopic mobilisation  
71 within the shells to negligible levels. Here we report and appraise U-series isotopic data from three  
72 modern (live-collected) and eleven fossil *L. lithophaga* shells that have been recovered from the rapidly  
73 uplifting shorelines of the Perachora Peninsular at the eastern end of the Gulf of Corinth, Greece (Fig. 2),  
74 the geology and stratigraphy of which have been previously described and discussed in detail (Andrews et  
75 al., 2007; Dia et al., 1997; Leeder et al., 2003; Leeder et al., 2005; Pirazzoli et al., 1994; Roberts et al.,  
76 2009; Turner et al., 2010). Uplift of  $\sim 0.2\text{-}0.3\text{ mm a}^{-1}$  since at least 240 ka has preserved evidence of  
77 Holocene and Pleistocene high sea level stands in the form of fossiliferous marine sediments forming  
78 constructional terraces, and of wave-cut notches which, when cut in limestone, are frequently bored by *L.*  
79 *lithophaga*. Four of the fossil *L. Lithophaga* samples are of Holocene age based on stratigraphy and  
80 radiocarbon dating of similar shells from the same localities (see below). The remaining seven are  
81 Pleistocene, with four inferred to be of MIS 5a or 5c age, two MIS 5e and one MIS 7 based on detailed  
82 stratigraphic mapping and U/Th dating of associated *Cladocora* coral stems. The locations from which  
83 the shells were recovered are detailed in Table 1 and shown on Figure 2. (Andrews et al., 2007; Dia et al.,  
84 1997; Leeder et al., 2003; Leeder et al., 2005; Pirazzoli et al., 1994; Roberts et al., 2009; Turner et al.,  
85 2010).



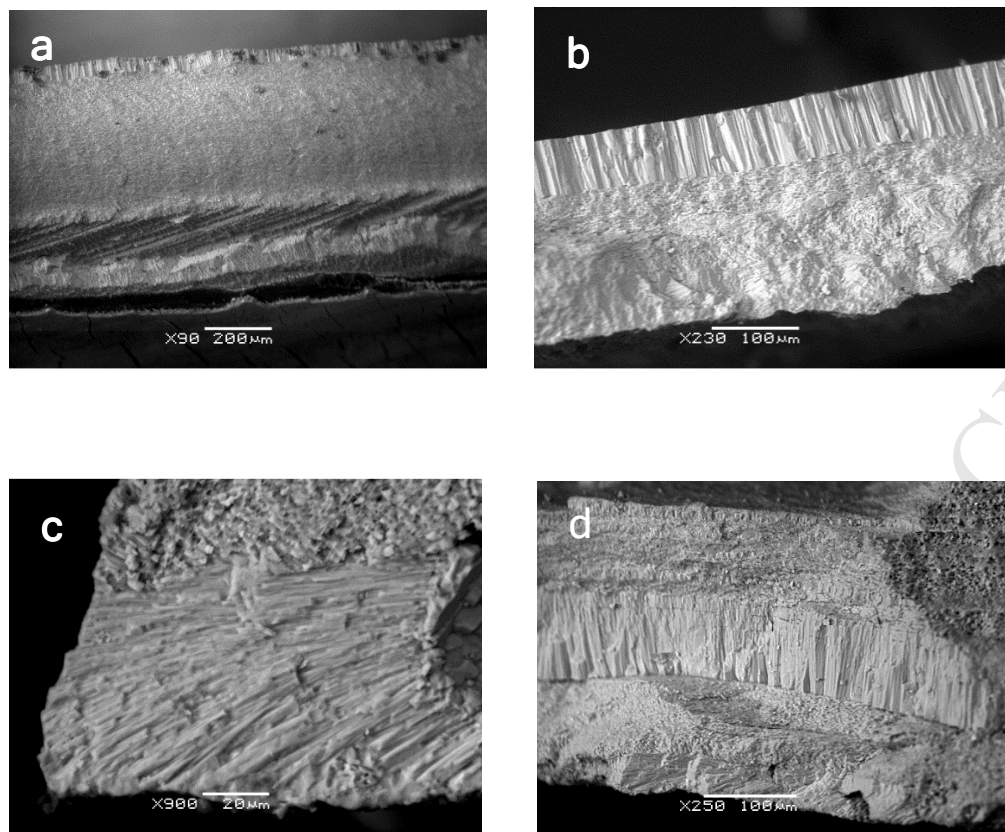


87  
 88 Fig 2. Location maps of (a) central Greece, (b) Gulf of Corinth and Perachora Peninsula, (c) *L. lithophaga*  
 89 shell samples from raised marine shorelines (+) around the coast of the Perachora Peninsula. Grid  
 90 reference is UTM zone 34S. See Table 1 for precise sample locations.

91  
 92 **2. Materials and methods**

93 Shells were removed from their boreholes using tweezers, penknives or chisels and were usually  
 94 recovered as fragments. Each was cleaned by gentle scraping followed by etching through brief  
 95 immersion in dilute hydrochloric acid then in a sonic bath of distilled water. *L. lithophaga* shells are  
 96 typically 300-800  $\mu\text{m}$  thick and in modern specimens the periostracum is underlain by a distinct layer of  
 97 calcite  $\sim 100 \mu\text{m}$  thick, beneath which the inner part of the shell is composed of aragonite with nacreous  
 98 texture (Fig. 3a), a bimineralic microstructure typical of Mytilids. In Holocene and older specimens the  
 99 periostracum is not preserved due to oxidation. X-ray diffraction (XRD) and scanning electron  
 100 microscopy (SEM) were carried out on representative shell fractions from the entire chronostratigraphic  
 101 range of our samples, although not every dated shell could be analysed. These showed that the  
 102 mineralogy of all our *L. lithophaga* shells, both modern and fossil, is  $\sim 85\text{-}90\%$  aragonite and  $\sim 15\text{-}10\%$   
 103 calcite, arranged in distinctive microstructural layers (Figs. 3a-d). These microstructural units, and the  
 104 crystal ultrastructure within them, are well preserved in Holocene, MIS 5 and MIS 7 samples (Figs. 3a-d)  
 105 demonstrating preservation of primary shell carbonate. SEM analysis showed no ultrastructural evidence  
 106 for alteration and although the fossil skeletal aragonite has lost its nacreous lustre, it still comprises  
 107 around 85-90% of the shell mineralogy. Alteration from lustrous nacre to a progressively flaky or chalky

108 texture is a well-known phenomenon that does not necessarily alter mineralogy (Hallam and O'Hara,  
 109 1962; Hudson, 1968).



110  
 111  
 112  
 113  
 114  
 115  
 116 Fig. 3. SEM images of *L. lithophaga* shells taken on uncoated fracture surfaces under low vacuum on a  
 117 JEOL JSM-5900. (a) modern shell (sample JT 051108-11a). The outer part of the shell is at the bottom of of  
 118 the image where the dark layers are part of the periostracum. A calcite layer with foliate structure, about  
 119 100 µm thick, overlies the periostracum, followed by aragonite nacre forming the bulk of the shell and  
 120 finally a distinctive 50 µm wide prismatic aragonite layer on the inner margin; (b) fossil shell from MIS  
 121 5a/c sediments (JEA 11907-2). The outer part of the shell is at the bottom of the image. This image  
 122 illustrates preservation of the distinctive 50 µm wide prismatic aragonite layer on the inner margin,  
 123 identical to that in the modern sample. (c) fossil shell from MIS 5a/c sediments (JEA 11907-2). The outer  
 124 part of the shell is at the bottom of the image. This image illustrates preservation of the foliate structured  
 125 calcite layer, overlain by aragonite nacre. (d) fossil shell from MIS 7 sediments (JS 091106-2, not dated);  
 126 despite its antiquity this shell contains well-preserved ultrastructure, including the foliate structured  
 127 calcite layer (bottom centre of image) and a prominent prismatic aragonite layer (centre of image), itself  
 128 overlain by more nacreous aragonite layers in this specimen.

U/Th dating followed standard methods which are described in detail elsewhere (Van Calsteren and Thomas, 2012). 300-500 mg samples were totally dissolved following spiking with a mixed  $^{229}\text{Th}/^{236}\text{U}$  spike which was calibrated against gravimetric standards prepared from CRM112a for U and CRM3159 for Th. U and Th fractions were separated on 2 ml 1-X8 Biorad© anion exchange columns. U was loaded onto graphite coated Re filaments and analysed using a Finnigan MAT262 mass spectrometer with a retarding potential quadrupole and secondary electron multiplier. A dynamic peak switching routine was employed measuring  $^{234}\text{U}/^{236}\text{U}$  and  $^{235}\text{U}/^{236}\text{U}$ . Th was measured using a standard bracketing approach on a Nu Plasma Multi-Collector ICPMS. Instrumental drift and mass-dependent fractionation were corrected for using TIMS calibrated laboratory standards which are close to the analytical characteristics of the samples. A well-characterised internal calcite powder standard, prepared from pure Iceland spar with an age of >1 Ma and in secular radioactive equilibrium, was analysed with the *L. lithophaga* samples to monitor the accuracy of the results. Since the shells are <1 mm thick, analysing different parts to assess isotopic variability was not generally possible, although replicate measurements were made on one shell.

### 3. Sample Stratigraphy and Age Control

Three modern (live) *L. lithophaga* were removed for analysis from a single large limestone block in Agriliou Bay on the southern Perachora peninsula from 0.5 m below mean sea level (samples L1-L3, Fig. 2, Table 1). Four Holocene shells were collected from limestone substrate at +1.5-3.0 m, two from Agriliou Bay and two from Cape Heraion, at the south-west tip of the peninsular (samples L4-L7, Figs. 1 and 2, Table 1). Radiocarbon dated *L. lithophaga* shells from the Holocene colonies at these localities gave calibrated ages of 6300 – 6415 yrs BP at +1.9 m in Agriliou Bay (Leeder, 2007), and 6320-6440 and 4440-4260 yrs BP at +3.1 m and +2.2 m respectively at Heraion (Pirazzoli et al., 1994). Age ranges incorporate 2 sigma errors and are corrected for global marine reservoir age (400 yrs) but not local reservoir age ( $53\pm 85$  yrs (Reimer and McCormac, 2002)). These ages are likely to be maxima since there is evidence that *L. lithophaga* shells contain a significant, but variable, amount of dead carbon derived from the substrate. Radiocarbon dates on museum specimens of *L. lithophaga* of known age are 900-



156 1400 years too old, and measured ages on Holocene uplifted fossil shells from western Crete exceed  
157 estimated age by 350-2800 years (Shaw et al., 2010). The precise contribution of dead carbon in the  
158 Cretan samples could not be determined accurately as some of the lithophagids may have expired long  
159 before uplift occurred.

160  
161 The Pleistocene samples collected from uplifted shorelines are assigned to MIS 5a/5c, MIS 5e and MIS 7  
162 highstands on the basis of U-series dating of corals and/or stratigraphic associations (Dia et al., 1997;  
163 Leeder et al., 2003; Leeder et al., 2005; Turner et al., 2010). One of the two MIS 5e shells (L12) is from a  
164 23 m palaeoshoreline on Makrugoaz Ridge, comprising coraliferous sands and serpulid reefs. The MIS 5e  
165 age attribution is based on U-Th dates from associated coral stems (Leeder et al., 2005). The second MIS  
166 5e sample (L13) is from +19 m within a shallow limestone cave on the north of the peninsular and it is  
167 correlated with shorelines dated to MIS 5e (elsewhere) and mapped along the north coast of the  
168 peninsular to the sample location (Leeder et al., 2003; Leeder et al., 2005). The single MIS 7 shell (L14)  
169 is from limestone bedrock on Cape Heraion at an elevation of 43 m which correlates with a MIS 7a  
170 terrace ~0.25km to the east, where corals have been U-Th dated to ~190 ka (Dia et al., 1997).

171  
172 Whilst MIS 5e and 7 palaeoshorelines are well documented at altitudes of ~25 m and ~40 m respectively,  
173 the age of a well-defined shoreline at 8-12 m is more ambiguous. Since it is on an uplifting coastline and  
174 at a lower altitude than the MIS 5e palaeoshoreline it must be younger than that feature and the only pre-  
175 Holocene relative high sea-level stands during the intervening period occurred during MIS 5a and 5c.  
176 Direct dating evidence is lacking and the uncertainty on calculated uplift rates is too large to discriminate  
177 between the two possibilities and consequently it cannot be confidently attributed to either. The four  
178 lithophagid samples (L8-L11) associated with this shoreline are therefore assigned a generic age of MIS  
179 5a/c.

.Sample code	UEA reference	Sample location (see Fig 2c), and elevation	Sample substrate	Control Age Reference	Confidence in Age
<b>Shells live when collected</b>					
L1	JT 03/05/08-2	Agriliou Bay -0.5 m asl 34S 669089 m E 4208440 m	Basement limestone boulder	N/A	Strong
L2	JT 05/11/08-11a	Agriliou Bay -0.5 m asl 34S 669089 m E 4208440 m	Basement limestone boulder	N/A	Strong
L3	JT 05/11/08-12a	Agriliou Bay -0.5 m 34S 669089 m E 4208440 m	Basement limestone boulder	N/A	Strong
<b>Holocene shells</b>					
L4	JS 21/4/07-3	Heraion 3.0 m asl 34S 662464 m E 4210550 m	Basement limestone	Adjacent to shells <sup>14</sup> C dated to 6.3 ka (Pirazzoli <i>et al</i> 1994)	Strong
L5	JS 12/11/05-5	Agriliou Bay 1.5 m asl 34S 669220 m E 4207994 m	Basement limestone	Adjacent to shells <sup>14</sup> C dated to 6.4 ka (Leeder <i>et al</i> 2007)	Strong
L6	JT 03/05/08-4	Agriliou Bay 1.5 m asl 34S 669220 m E 4207994 m	Basement limestone	Adjacent to shells <sup>14</sup> C dated to 6.4 ka (Leeder <i>et al</i> 2007)	Strong
L7	JS 21 /04/07-4	Heraion 3.0 m asl 34S 662464 E 4210550 m	Basement limestone	Adjacent to shells <sup>14</sup> C dated to 6.3 ka (Pirazzoli <i>et al</i> 1994)	Strong
<b>MIS 5a/c shells</b>					
L8	JEA 11907-2	Laka-Zeza Bay 15 m asl 34S 668032 m E 4214389 m	Lithified calcarenitic, fossiliferous sands	Association with raised shoreline dated by extrapolation of average local uplift rates in (Leeder <i>et al</i> 2003, 2005)	Weak
L9	JS 05/11/06-2	Gorge Point 4 m asl 34S 663711 m E 4211564 m	Lithified red algae marine drape	Stratigraphic association with raised shoreline dated by U/Th on corals to MIS 5e (Leeder <i>et al</i> 2003)	Moderate-strong
L10	JS 08/11/06-12	N side Cape Heraion 5 m asl 34S 662578 m E 4210708 m	Lithified calcarenitic, fossiliferous sands	Stratigraphic association with raised shoreline dated by U/Th on corals to MIS 5e (Leeder <i>et al</i> 2003)	Strong
L11	JS 10/11/06-2	West Loutraki bay 3.0 m asl 34S 672035 m E 4206040 m	Lithified calcarenitic, fossiliferous sands	Extrapolation of average local uplift rates in (Leeder <i>et al</i> 2003, 2005)	weak
<b>MIS 5e shells</b>					
L12 L12a	JEA 11907-3 JEA 11907-3b	Makrugoaz Ridge 23 m asl 34S 665141 m E 4209990 m	Lithified coraliferous sands	Adjacent to corals U/Th dated to MIS 5e (Leeder <i>et al</i> 2003)	Strong
L13	JS 08/11/06-9	Funnel Cave 19 m asl 34S 665411 m E 4212684 m	Cave in limestone	Stratigraphic association with raised shoreline dated by U/Th on corals to MIS 5e (Leeder <i>et al</i> 2003, 2005)	Strong
<b>MIS 7 shells</b>					
L14	JS 09/11/06-3	Cape Heraion 43 m asl 34S 662581 m E 4210611 m	Limestone	Stratigraphic association with raised shoreline dated by U/Th on corals to MIS 7 (Leeder <i>et al</i> 2005)	Strong

181 **Table 1.** *L. lithophaga* shell sample collection data: sample codes and location grid reference (UTM and  
182 local site name), elevation above mean sea level (asl), substrate type, and reference for the geological age  
183 allocations with degree of confidence in each.

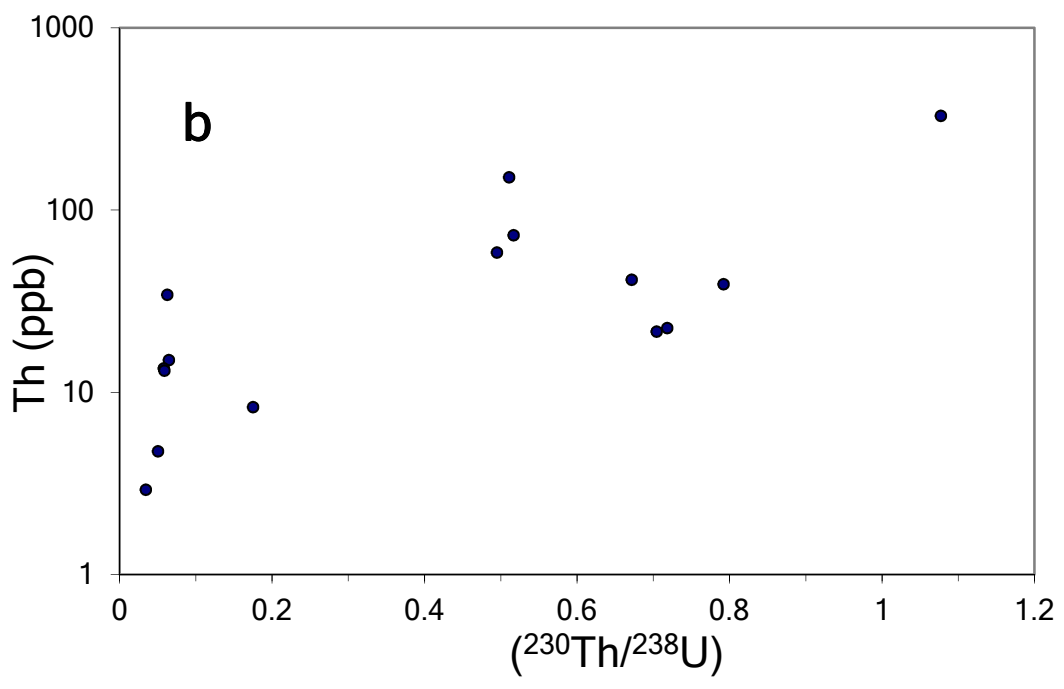
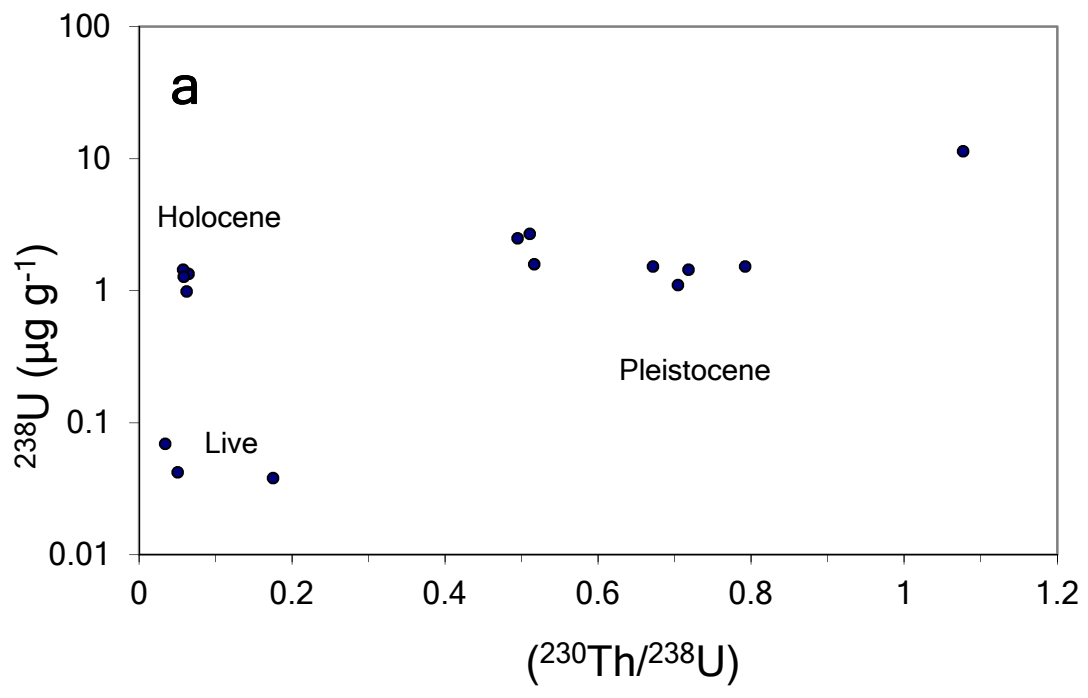
#### 185 **4. Results:**

186 The U-series data for the *L. lithophaga* shells are shown in Table 2. Modern shells all have very low U  
187 and Th contents (0.04-0.07 ppm and 2.5-8.5 ppb respectively). In contrast, the Holocene and Pleistocene  
188 shells contain significantly higher U and Th concentrations, generally in the range 1-2  $\mu\text{g g}^{-1}$  and 10-80  
189 ppb respectively, although one sample, L8 (5a/c), records 11.3  $\mu\text{g g}^{-1}$  and 328 ppb. The U and Th  
190 concentrations are both much higher than usually found in fossil molluscs, U levels being more typical of  
191 corals and Th an order of magnitude higher than most of the values reported in the literature. It is  
192 therefore clear that virtually all the uranium and thorium uptake has occurred *post mortem*. A plot of U  
193 concentration vs ( $^{230}\text{Th}/^{238}\text{U}$ ) (Fig. 4a) shows that five of the seven Pleistocene shells have U  
194 concentrations similar to Holocene specimens, (averages 1.76 and 1.26 ppm respectively). This suggests  
195 that U uptake may occur relatively early rather than as a late event or continuous process, as has been  
196 previously suggested (Ivanovich et al., 1983; Kaufman et al., 1996), although the possibility that these  
197 five shells once possessed higher levels of U, some of which has subsequently been lost, cannot be  
198 excluded. The difference between Pleistocene and Holocene Th concentrations is more marked (Fig. 4b)  
199 with averages of 58 ( $\pm 45$ ) ppb (excluding L8) and 19 ppb respectively. However, there is almost a factor  
200 of three difference between Th concentrations in the two sub-samples of L12 so distribution of Th within  
201 the samples is probably very heterogeneous. A plot of U vs Th concentrations in the fossil samples (Fig.  
202 4c) show a strong correlation ( $R^2 = 0.91$ ,  $p < 0.05$ ), but this is strongly influenced by two samples with  
203 particularly high Th content (L8 and L12a). If L8 is omitted  $R^2 = 0.64$  ( $p < 0.01$ ) and if both L8 and L12a  
204 are omitted  $R^2 = 0.32$  ( $p < 0.01$ ). The lower correlations may suggest differing uptake patterns for U and  
205 Th in most of the samples, or later differential geochemical modification, or both.

Shell No.	Sample i.d.	$^{238}\text{U}$ ( $\mu\text{g g}^{-1}$ )	$^{232}\text{Th}$ (ppb)	$(^{230}\text{Th}/^{232}\text{Th})$	$(^{230}\text{Th}/^{238}\text{U})$	$(^{234}\text{U}/^{238}\text{U})$	Calculated Age (ka)	Model Age (ka)	Allocated Age
<i>Live Shells</i>									
L1	JT 03/05/08 -2	0.042	4.7±0.9	1.50±0.08	0.0508(9)	1.1428(53)	4.96 ± 0.22	6.08	Modern
L2	JT 05/11/08 -11a	0.038	8.3±1.5	2.59±0.12	0.1754(23)	1.1482(50)	18.04 ± 0.60	15.36	Modern
L3	JT 05/11/08-12a	0.069	2.9±0.5	2.91±0.19	0.0348(10)	1.1395(57)	3.38 ± 0.22	8.33	Modern
<i>Holocene Shells</i>									
L4	JS 21/4/07-3	1.338(04)	15.0±2.7	19.02±0.81	0.0651(6)	1.1481(57)	6.36 ± 0.13	5.45	Holocene
L5	JS12/11/05 -5	0.983(02)	34.3±6.2	5.73±0.24	0.0628(5)	1.1363(46)	6.21 ± 0.11	9.50	Holocene
L6	JS 21 /4/07-4	1.436(05)	13.5±2.4	19.94±0.83	0.0582(5)	1.1481(49)	5.67 ± 0.11	4.85	Holocene
L7	JT03/05/08-4	1.266(05)	13.1±2.4	17.48±0.73	0.0589(5)	1.1428(55)	5.77 ± 0.10	6.77	Holocene
<i>Pleistocene Shells</i>									
									<b>MIS</b>
L8	JEA 11907 -2	11.306(46)	328.7±59.4	113.44±4.75	1.0775(85)	1.1684(62)	238.73 ± 12.50	158.97	5a/c
L9	JS 05/11/06-2	1.518(06)	39.1±7.1	94.24±3.94	0.7925(65)	1.1148(66)	131.05 ± 4.03	123.54	5a/c
L10	JS 08/11/06-12	1.520(06)	41.4±7.5	75.42±3.13	0.6719(53)	1.1181(59)	98.12 ± 2.56	95.07	5a/c
L11	JS10/11/06-2	1.101(04)	21.5±3.9	110.49±4.66	0.7046(59)	1.1307(66)	103.80 ± 2.96	93.28	5a/c
L12	JEA 11907-3	2.487(12)	58.3±10.5	64.69±2.71	0.4951(41)	1.1072(80)	64.00 ± 1.49	71.74	5e
L12a	JEA 11907-3b	2.678(13)	150.7±27.2	27.80±1.14	0.5111(39)	1.1021(75)	67.26 ± 1.44	77.08	5e
L13	JS 08/11/06-9	1.436(06)	22.5±4.1	140.62±5.85	0.7187(57)	1.1332(72)	106.83 ± 2.87	94.39	5e
L14	JS 09/11/06-3	1.580(07)	72.6±13.1	34.49±1.46	0.5170(45)	1.1128(64)	67.36 ± 1.68	71.95	7

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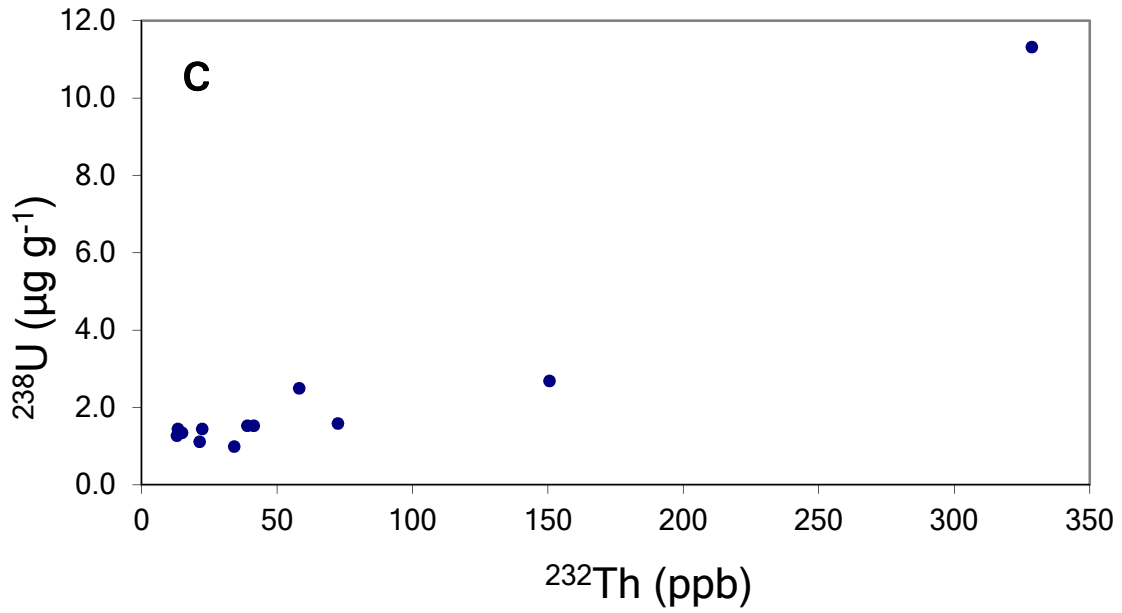
208 **Table 2.** U-series data for *L. lithophaga* shells. Figures in parenthesis are uncertainties in the last digit(s) of the relevant parameters. All errors are  $2\sigma$ . U  
209 concentration errors for modern shells are  $<0.001$ . Model ages are calculated using the algorithms of (Thompson et al., 2003). See text for discussion of  
210 allocated ages. Isotope ratios are activity ratios.



211

212



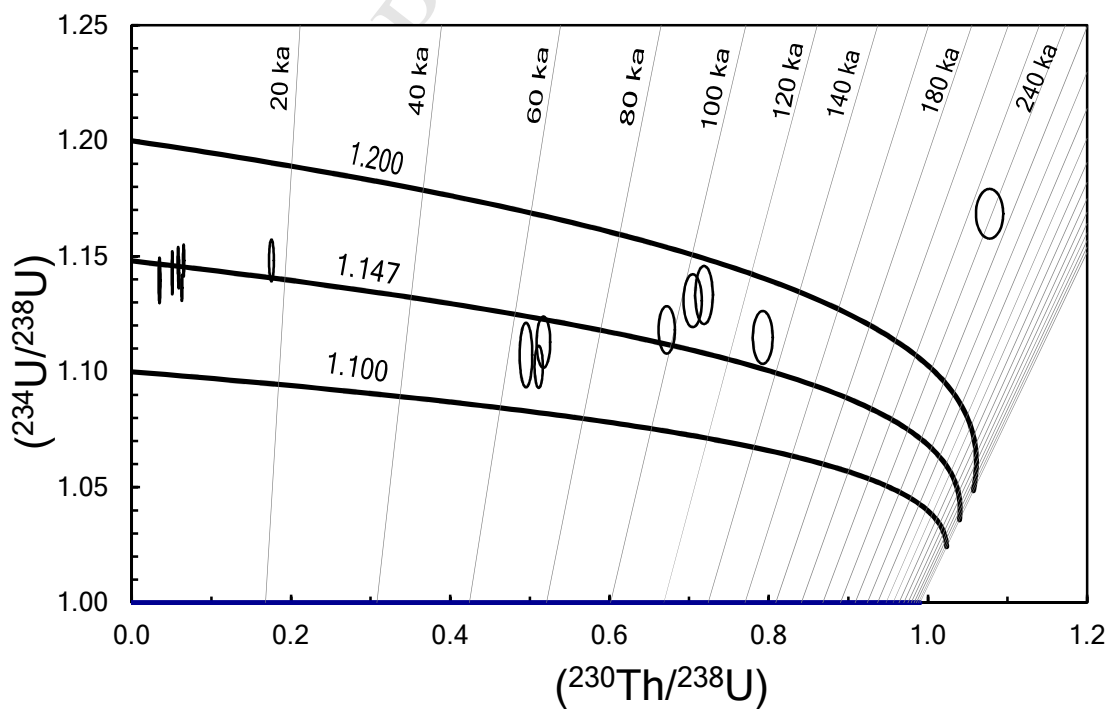


213

214 Fig. 4. (a) U concentration and (b) Th concentration plotted vs.  $(^{230}\text{Th}/^{238}\text{U})$ . Note log scales on vertical  
 215 axes. (c) U vs. Th concentrations for fossil samples. Excluding the two outliers  $R^2 = 0.32$  (see text).

216

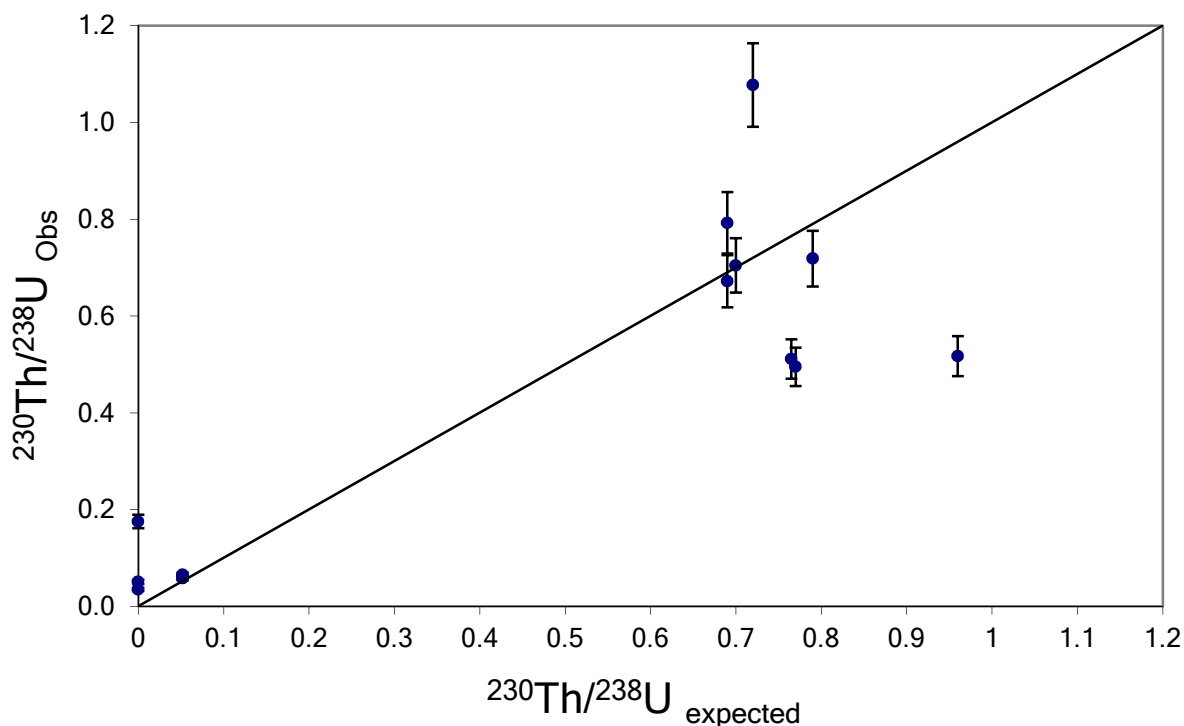
217 Six of the of seven  $(^{234}\text{U}/^{238}\text{U})$  ratios in modern and Holocene shells lie between 1.136 and 1.149, close to  
 218 the modern seawater value of  $\sim 1.147$  (Stirling and Andersen, 2009), and on or near the seawater evolution  
 219 curve when plotted vs.  $(^{230}\text{Th}/^{238}\text{U})$  (Fig. 5). Pleistocene fossils by contrast show considerable scatter and  
 220 do not follow the seawater  $(^{234}\text{U}/^{238}\text{U})$  trajectory.



221

222 Fig. 5. Plot of all *L. lithophaga* data in ( $^{234}\text{U}/^{238}\text{U}$ ) vs. ( $^{230}\text{Th}/^{238}\text{U}$ ) space. Pleistocene samples do not lie  
 223 along the marine ( $^{234}\text{U}/^{238}\text{U}$ ) evolution line (1.147).

224  
 225 Figure 6 shows measured ( $^{230}\text{Th}/^{238}\text{U}$ ) ratios plotted against expected values derived from estimated shell  
 226 ages determined from radiocarbon analyses (Holocene shells) or stratigraphic mapping (Pleistocene  
 227 shells). The modern lithophagid shells yield Holocene or Late Pleistocene ages (3.3-18.0 ka) rather than  
 228 zero ages due to slight but measurable thorium contamination (~2-10 ppb, Table 2). Despite their  
 229 boreholes being in close proximity, they also have differing ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios (1.5-2.9). Holocene  
 230 specimens yield ages that cluster between 5.67 and 6.36 ka, very similar to their radiocarbon dates (4260-  
 231 6890 yrs BP). However, the low ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios indicate significant thorium contamination, (three  
 232 ratios between 17 and 20 and one of 5.7), and therefore the calculated ages are likely to be overestimates.  
 233 The likely range of corrected ages calculated using the ( $^{230}\text{Th}/^{232}\text{Th}$ ) detrital ratios from the modern  
 234 samples (1.5-2.9) are shown in Table 3. True ages probably lie around 5.0 ka, although the shells are  
 235 unlikely to all be exactly the same age.



236

237 Fig. 6. Observed ( $^{230}\text{Th}/^{238}\text{U}$ ) ratios vs ( $^{230}\text{Th}/^{238}\text{U}$ ) ratios expected, based on U-series coral dates and  
 238 stratigraphic evidence. Samples attributed to MIS 5a/c are assumed to be ~100 ka. Two of these lie within  
 239 error of the 1:1 line.

240  
 241 Apparent ages of Pleistocene specimens range from ~64 ka to ~239 ka. Only two shells (L10 and L11 of  
 242 MIS 5a/c age) yield dates compatible with their expected ages (98.1 and 103.8 ka respectively) assuming  
 243 their true age is ~100 ka (MIS 5c). Two further MIS 5a/c shells (L8 and L9) produced ages that are much  
 244 too old, 238.7 ka and 131.0 ka respectively. Although their ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios are sub-optimal (~100),  
 245 they are sufficiently high that age corrections for any feasible ( $^{230}\text{Th}/^{232}\text{Th}$ ) detrital ratio would not exceed  
 246 the  $2\sigma$  age error limits and cannot explain the discrepancies between the measured and geological ages of  
 247 these two samples. The older shells (L12 and L13, MIS 5e; L14, MIS 7) have apparent ages that are  
 248 significantly too young (63.99 and 67.3 ka, 106.8 ka, and 67.4 ka respectively). The period 60-70 ka  
 249 coincides with low global sea level, clearly demonstrating the unreliability of the dates.

250  
 251 Since the four 5a/c samples (L8-L11) can be considered to be approximately coeval in age, isochrons  
 252 were constructed in ( $^{230}\text{Th}/^{232}\text{Th}$ ) vs. ( $^{238}\text{U}/^{232}\text{Th}$ ) and ( $^{234}\text{U}/^{232}\text{Th}$ ) vs. ( $^{238}\text{U}/^{232}\text{Th}$ ) space (not shown) to  
 253 establish whether a common age could be derived. However, there was no significant correlation between  
 254 ( $^{230}\text{Th}/^{232}\text{Th}$ ) and ( $^{238}\text{U}/^{232}\text{Th}$ ) and no meaningful ( $^{230}\text{Th}/^{238}\text{U}$ ) value could be calculated, although there  
 255 was a strong linear relationship between ( $^{234}\text{U}/^{232}\text{Th}$ ) and ( $^{238}\text{U}/^{232}\text{Th}$ ), with a regression line slope of  
 256 1.1075.

## 257 5. Discussion

259 *Live Samples:* Low U and Th concentrations (typically 50 ppb and 5 ppb respectively) in the modern  
 260 shells relative to fossil samples ( $>1 \mu\text{g g}^{-1}$  and 10-350 ppb) demonstrate that these elements are only  
 261 sparingly absorbed during life. The ( $^{234}\text{U}/^{238}\text{U}$ ) ratios lie within error of the modern seawater value  
 262 suggesting that uranium is absorbed from seawater during feeding rather than from the host limestone  
 263 during boring. The presence of trace amounts of detrital thorium in the (zero age) modern shells is  
 264 responsible for their calculated apparent ages of 4.96, 18.04 and 3.38 ka. Detrital thorium is a common

265 and serious problem when dating sub-aerial deposits by U-series methods although if the initial  
266 ( $^{230}\text{Th}/^{232}\text{Th}$ ) activity ratio is known, as here, it is possible to correct for the excess thorium and calculate  
267 a true age. Usually, however, this ratio is unknown and a value of  $\sim 0.8$  is often adopted, being the value  
268 derived from a contaminant having the average upper crustal  $^{232}\text{Th}/^{238}\text{U}$  atomic ratio of  $\sim 4$ , (Wedepohl,  
269 1995), and  $^{230}\text{Th}$  in secular equilibrium with  $^{238}\text{U}$ . However, the ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios of 1.5-2.9 observed  
270 here correspond to Th/U atomic ratios in the contaminant of 1.1–2.1 rather than  $\sim 4$ , probably because the  
271 thorium derives from carbonate sediments which are rich in uranium (and consequently  $^{230}\text{Th}$ ) and  
272 relatively poor in  $^{232}\text{Th}$ . Clearly it is inappropriate to use average crustal U/Th values to correct  
273 contaminated dates in this type of carbonate environment. The variation in initial ( $^{230}\text{Th}/^{232}\text{Th}$ ) occurs  
274 despite the three live samples having been collected in close proximity from the same limestone block.  
275 Interestingly, the values encompass the empirical ratio of  $1.7 \pm 0.7$  reported by (Kaufman, 1993) from a  
276 range of carbonate materials around the globe. The lack of a single well constrained detrital ratio in our  
277 samples presumably reflects a diversity of local detrital sources.

278  
279 *Holocene samples:* The four Holocene samples were recovered from limestone bedrock. They all have U  
280 levels more than an order of magnitude higher than modern shells (typically  $\sim 1 \mu\text{g g}^{-1}$ ) and similar to  
281 Pleistocene samples (see below), suggesting that uptake occurs fairly rapidly (within a few thousand  
282 years) of the death of the organism. *Post-mortem* U uptake would not materially affect age estimates for  
283 uplifted shorelines provided it occurs shortly before or after relative sea level fall whilst the shells are  
284 either still submerged or remain in the swash zone, since the shells will remain close to contemporary sea  
285 level during uptake. Three of the four samples have ( $^{234}\text{U}/^{238}\text{U}$ ) ratios that lie within error of seawater  
286 values (1.147) with one only outside the range at  $1.136 \pm 0.005$ . These data suggest that significant  
287 uranium is indeed taken up from seawater whilst the shells remain in the swash zone following shoreline  
288 uplift, or following death and prior to emergence. Th concentrations are 2-10 times higher than modern  
289 samples but typically two to five times lower than Pleistocene samples. These relative values might mean  
290 that U uptake is a rapid event whereas Th uptake is a slower, more continuous, process. Alternatively, U  
291 uptake may be a semi-continuous process that eventually reverses following long exposure to sub-aerial

Pleistocene weathering, resulting in some uranium loss (such that concentrations fall towards Holocene values) but Th remains immobile within the shell.

Sample	$(^{230}\text{Th}/^{232}\text{Th})$	Calculated Age (ka)	Corrected Age Range (ka)
L4	19.02±0.81	6.36±0.13	5.35-5.85
L5	5.73±0.24	6.21±0.11	3.00-4.60
L6	19.94±0.83	5.67±0.11	4.80-5.20
L7	17.48±0.73	5.77±0.10	4.80-5.25

Table 3. Detritally corrected ages for Holocene shells. Values for authigenic ( $^{230}\text{Th}/^{238}\text{U}$ ) activity ratios

are calculated using the equation:  $(^{230}\text{Th}/^{238}\text{U})_{\text{auth}} = (^{230}\text{Th}/^{238}\text{U})_{\text{meas}} - (^{232}\text{Th}/^{238}\text{U})_{\text{meas}} \times R_0 \cdot e^{-\lambda_{230}t}$

where  $R_0$  is the initial ( $^{230}\text{Th}/^{232}\text{Th}$ ) activity ratio, in this case the range of observed ( $^{230}\text{Th}/^{232}\text{Th}$ ) values in the live-collected specimens.

The true ages of the Holocene lithophagids are broadly constrained by radiocarbon dates on shells from the same colony (4260-6890 calendar years BP, (Leeder, 2007; Pirazzoli et al., 1994)). However, if the radiocarbon dates were dead-carbon corrected, they would probably be significantly younger, possibly by 1000 years or so (Shaw et al., 2010), and a range of 3300 – 5900 years BP is likely to be more realistic. U/Th ages using measured ( $^{230}\text{Th}/^{232}\text{Th}$ ) values from the modern samples to correct for detrital contamination lie in the range 3.0 – 5.9 ka (Table 3), compatible with that estimate. This level of agreement supports the inferred timing of the uplift event, bearing in mind that the shells may differ in age by many hundreds of years and possibly a few thousand years. U/Th dating may therefore be a useful dating tool for Holocene samples, particularly if future better understanding of initial ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios in modern lithophagids were to allow more accurate correction of detritally contaminated samples. In this regard the method may be preferable to  $^{14}\text{C}$  dating where a similar problem, that of dead carbon contamination, may be more difficult to characterise.

*Pleistocene Samples:* U concentrations in five of the seven Pleistocene samples lie between 1.10 and 1.58  $\mu\text{g g}^{-1}$ , similar to Holocene values, whilst two are significantly higher. L12 and 12a have 2.48 and 2.68  $\mu\text{g g}^{-1}$ ,



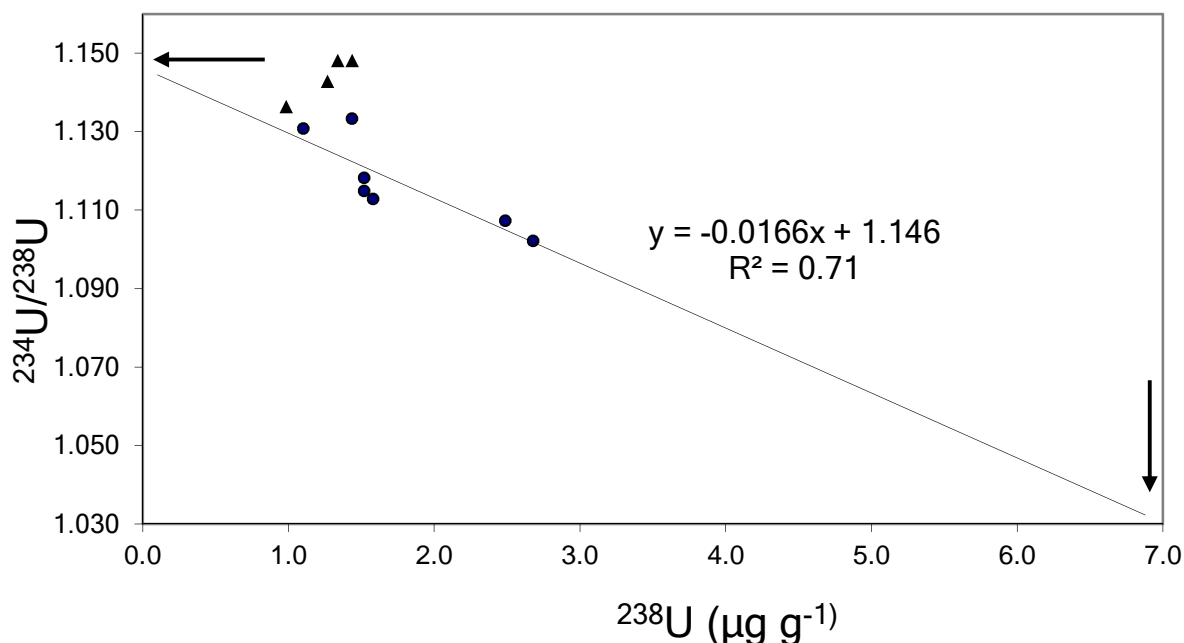
317  $\text{g}^{-1}$  respectively and L8 has uranium levels almost an order of magnitude higher at  $11.3 \mu\text{g g}^{-1}$ . Th  
318 concentrations are generally  $>20 < 100$  ppb except for L12a (151 ppb) and L8 (329 ppb). L8 also has the  
319 highest ( $^{230}\text{Th}/^{238}\text{U}$ ) ratio (1.0775), but overall there is no correlation between U or Th content and  
320 ( $^{230}\text{Th}/^{238}\text{U}$ ) (Fig. 4a, b). The absence of a positive relationship between U concentration and apparent age  
321 might be construed as support for a geochemical model of early uranium uptake from seawater with  
322 negligible subsequent migration (i.e. closed system behaviour). However, the ( $^{234}\text{U}/^{238}\text{U}$ ) ratios do not lie  
323 along the seawater evolution line (Fig. 5), implying that either the U in these shells has a non-marine  
324 source, or the samples have not remained closed systems, or both. Since the evidence from modern and  
325 Holocene samples strongly indicates an initial marine origin for the uranium, the most likely explanation  
326 for the observed deviations is open system behaviour. Five ( $^{234}\text{U}/^{238}\text{U}$ ) ratios lie above the marine  
327 evolution line and two below. Those below (L12 and L14) have not simply experienced preferential  $^{234}\text{U}$   
328 removal from damaged lattice sites during sub-aerial leaching of marine uranium from the shells as this  
329 would cause apparent ages to be overestimated rather than underestimated as observed here. Both have  
330 apparent ages between 60 ka and 70 ka (a global marine lowstand) whereas one sample is actually of MIS  
331 5e age and the other MIS 7. Probably uranium has been derived, at least partly, from meteoric water with  
332 ( $^{234}\text{U}/^{238}\text{U}$ ) ratios lower than marine, and taken up either quasi-continuously or late in the shells' history  
333 to achieve the observed ages and ( $^{234}\text{U}/^{238}\text{U}$ ) ratios.

334  
335 The actual ages derived for the Pleistocene shells will of course depend on the timing of U uptake  
336 (whether from marine or meteoric sources) and its subsequent geochemical behaviour. Early uptake  
337 followed by closed system conditions will produce accurate ages, continuous or late uptake,  
338 underestimated ages, and early U uptake followed by later loss, overestimated ages. Here three ages are  
339 too young (L12, L13, L14), two are compatible with the probable true (MIS 5c) age (L10, L11) and two  
340 are too old (L8, L9). The two samples that yield plausible (MIS 5c) ages have calculated ( $^{234}\text{U}/^{238}\text{U}$ )<sub>init</sub>  
341 ratios of  $1.1566 \pm 0.0059$  and  $1.1763 \pm 0.0066$  respectively. Whilst 1.1566 is quite close to a marine  
342 signature, 1.1763 is compatible only with meteoric water values and it is likely that one or both of these  
343 shells have experienced geochemical disturbance. So although it is possible that the apparent accuracy of

344 the L10 age is real and the shell has only suffered minor isotopic alteration, probably it has experienced  
345 significant alteration and yields a plausible age only by chance. Two samples (L8 and L9) are older than  
346 their geological ages, the former by an entire glacial-interglacial cycle. This sample has by far the highest  
347 U and Th content ( $11 \mu\text{g g}^{-1}$  and 329 ppb respectively) which may reflect high early uptake of uranium  
348 and thorium followed by relatively recent uranium loss. This would account for the high ( $^{230}\text{Th}/^{232}\text{Th}$ )  
349 ratio of 113. L9 may also have suffered recent uranium loss since detrital thorium levels are insufficient  
350 ( $^{230}\text{Th}/^{232}\text{Th} = 94$ ) to account for the upward age displacement of 30-50 ka to  $\sim 131$  ka. It may be  
351 significant that the MIS 5e and MIS 7 sample ages are much younger than expected whilst two of the MIS  
352 5a/c ages are much older, although this pattern is difficult to interpret.

353  
354 There is a strong inverse correlation ( $R^2 = 0.71$ ,  $p < 0.05$ ) between uranium concentrations and ( $^{234}\text{U}/^{238}\text{U}$ )  
355 for six of the seven shells (Fig. 7) and the y-axis intercept of 1.146 is very close to the uranium isotope  
356 composition of seawater. The negative slope indicates that any non-marine uranium taken up by the shells  
357 must have a ( $^{234}\text{U}/^{238}\text{U}$ ) ratio below that of seawater. We currently have no uranium isotope data from  
358 local groundwaters, but alpha spectrometric analysis of a local vadose flowstone, formed on limestone  
359 bedrock and dated to  $27.7 \pm 1.3$  ka ( $1\sigma$ ), showed ( $^{234}\text{U}/^{238}\text{U}$ )<sub>init</sub> to be  $1.032 \pm 0.024$ ; how representative  
360 this might be of local groundwaters over a glacial-interglacial timescale is unknown. The intersection of  
361 the regression line with the ( $^{234}\text{U}/^{238}\text{U}$ )<sub>init</sub> value of the dated flowstone occurs at a uranium content of  $\sim 7$   
362  $\mu\text{g g}^{-1}$  (Fig. 7). If 1.032 is broadly representative of ( $^{234}\text{U}/^{238}\text{U}$ ) ratios in groundwaters on the Perachora  
363 Peninsula through the mid-late Pleistocene, then the regression line approximates a mixing line between  
364 two uranium end members, seawater and groundwater. The local geology is very complex and highly  
365 tectonised and is dominated by Mesozoic and Neogene limestones and flysch deposits, with basic rocks  
366 and sandstones and phyllites occurring along the southwest coastal margin (IGME 1984). The whole-rock  
367 ( $^{234}\text{U}/^{238}\text{U}$ ) is likely to be close to 1.00 and thus a groundwater ( $^{234}\text{U}/^{238}\text{U}$ ) value of 1.032 would be  
368 compatible with a derivation from rocks that have been heavily leached over a prolonged period. One  
369 sample (L8) does not fit this pattern, having a ( $^{234}\text{U}/^{238}\text{U}$ ) value of  $1.168 \pm 0.006$  and U concentration of  
370  $11.3 \mu\text{g g}^{-1}$ . These values might reflect a different geological origin for the U, or uptake might have

371 occurred at a time when higher U concentrations (enriched in  $^{234}\text{U}$  due to recoil effects) had accumulated  
 372 in the surface rocks due to enhanced weathering and limited removal by leaching.



373

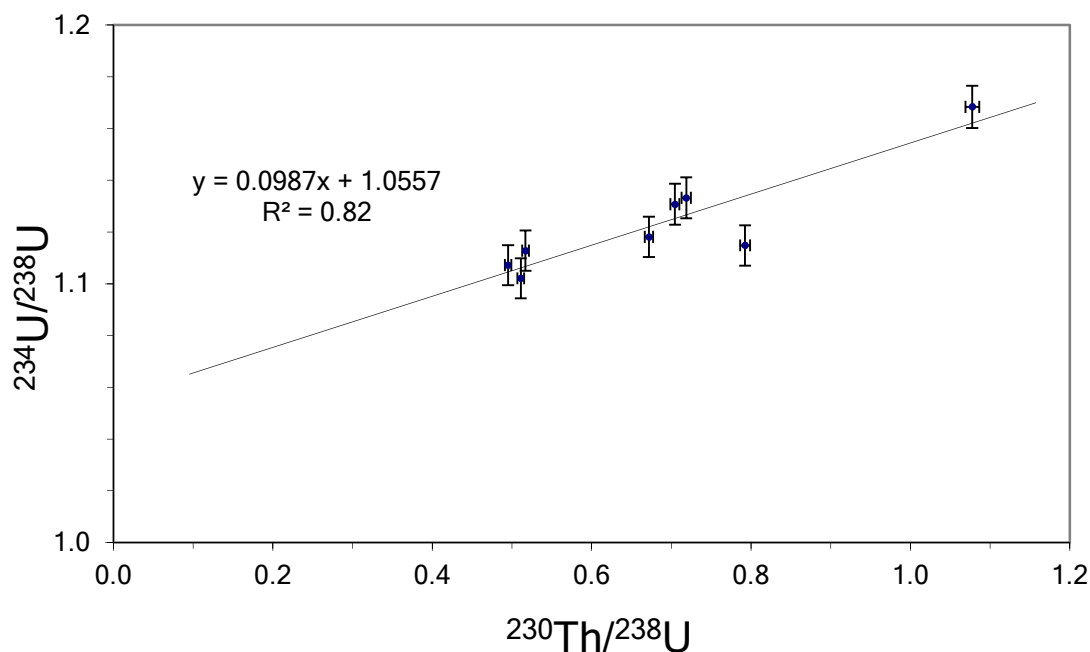
374 Fig. 7. ( $^{234}\text{U}/^{238}\text{U}$ ) vs. U concentration for Pleistocene *L. lithophaga* shells (filled circles), excluding  
 375 sample L8. These data may lie along a uranium mixing line between seawater (upper left arrow) and  
 376 meteoric water (lower right arrow) end-members characterised by differing ( $^{234}\text{U}/^{238}\text{U}$ ) signatures (see  
 377 text). Solid triangles are Holocene shells which have uranium isotopic ratios close to the seawater value.

378

### 379 6. Open System Modelling

380 There is a strong positive correlation ( $R^2 = 0.82$ ,  $p < 0.01$ ) between measured ( $^{234}\text{U}/^{238}\text{U}$ ) and ( $^{230}\text{Th}/^{238}\text{U}$ )  
 381 in the Pleistocene *L. lithophaga* shells (Fig. 8). This relationship is often seen in diagenetically altered  
 382 reef corals, although the slopes in those cases are usually much steeper. U-series analyses of Pleistocene  
 383 corals have shown that they frequently experience *post-mortem* isotopic disturbance and despite careful  
 384 sample screening and selection, ( $^{234}\text{U}/^{238}\text{U}$ ) ratios often lie significantly above (occasionally below) the  
 385 marine evolution curve, the discrepancy increasing with age (Gallup et al., 1994; Stirling et al., 1995).  
 386 Marine uranium isotope values have changed little during the Mid-Late Pleistocene (Henderson, 2002)  
 387 and alpha-recoil processes, which are predictable and allow micro-scale redistribution of daughter  
 388 isotopes from recoil-damaged lattice sites, have been suggested as a probable causal mechanism

389 (Henderson and Slowey, 2000; Henderson et al., 2001). Such isotopic redistributions lead to positive  
390 correlations between ( $^{230}\text{Th}/^{238}\text{U}$ ) and ( $^{234}\text{U}/^{238}\text{U}$ ) and cause divergence between calculated and true ages  
391 that increase with time (Stirling et al., 2001). Data from coeval samples often form quasi-linear arrays  
392 above the ( $^{234}\text{U}/^{238}\text{U}$ ) evolution curve and numerical models have been developed to correct for recoil  
393 effects and retrieve true ages from affected samples (Thompson et al., 2003; Villemant and Feuillet,  
394 2003). An empirical approach was adopted by (Scholz and Mangini, 2006; Scholz et al., 2004) which also  
395 allows for U uptake and loss, and they assumed that coeval subsamples of individual corals gain different  
396 amounts of uranium but with similar ( $^{234}\text{U}/^{238}\text{U}$ ) ratios. ( $^{230}\text{Th}/^{238}\text{U}$ ) and ( $^{234}\text{U}/^{238}\text{U}$ ) are then positively  
397 correlated and a fitted regression (mixing) line through the data intersects the ( $^{234}\text{U}/^{238}\text{U}$ ) marine  
398 evolution curve at the true ( $^{230}\text{Th}/^{238}\text{U}$ ) ratio, thus providing a corrected age for the suite of samples.  
399 (Frank et al., 2006) reviewed these methods and found that both numerical models gave almost identical  
400 corrected ages for samples that had experienced only slight diagenetic alteration, although the Thompson  
401 et al. (2003) model performed rather better for older samples that were significantly altered. However,  
402 they were unable to test the approach of (Scholz et al., 2004) since their data lacked significant correlation  
403 between ( $^{230}\text{Th}/^{238}\text{U}$ ) and ( $^{234}\text{U}/^{238}\text{U}$ ).



405  
406

407 Fig. 8. ( $^{234}\text{U}/^{238}\text{U}$ ) vs. ( $^{230}\text{Th}/^{238}\text{U}$ ) for Pleistocene *L. lithophaga* shells. The strong correlation is

408 indicative of *post-mortem* isotopic disturbance. A similar relationship is frequently observed in MIS 5e  
409 reef corals.

410  
411 Unlike the coral samples, the lithophagid shells are neither precisely coeval nor spatially compact.

412 However, to assess whether alpha recoil processes might have played a significant role in disturbing the

413 shell ages we applied one of the models (Thompson et al., 2003) to our data. Recalculated ages are shown

414 in Table 2. It is clear that these “corrected” ages do not correspond with the stratigraphic ages, although

415 some are shifted in the right direction, and that, as expected, alpha recoil does not fully account for the

416 observed isotopic disturbance. The four lithophagid samples of MIS 5a/c age are likely to be of similar

417 age (i.e. broadly coeval), and their ( $^{230}\text{Th}/^{238}\text{U}$ ) and ( $^{234}\text{U}/^{238}\text{U}$ ) ratios are positively correlated ( $R^2 = 0.79$ ).

418 Following the approach of (Scholz et al., 2004), a regression line through these data intersects the marine

419 curve at 90.3 ka (Fig. 9), which lies within the correct interglacial complex (MIS 5); however it

420 corresponds to marine lowstand MIS 5b and is therefore implausible. The two MIS 5e samples plot far

421 apart (Fig. 5) and could not form part of a linear array intercepting the marine curve near 120 ka. It

422 therefore appears that the Pleistocene shells have experienced diagenetic processes more complex than

423 alpha recoil or simple U uptake and subsequent loss, and that existing models are unable to retrieve

424 meaningful ages from the current data.



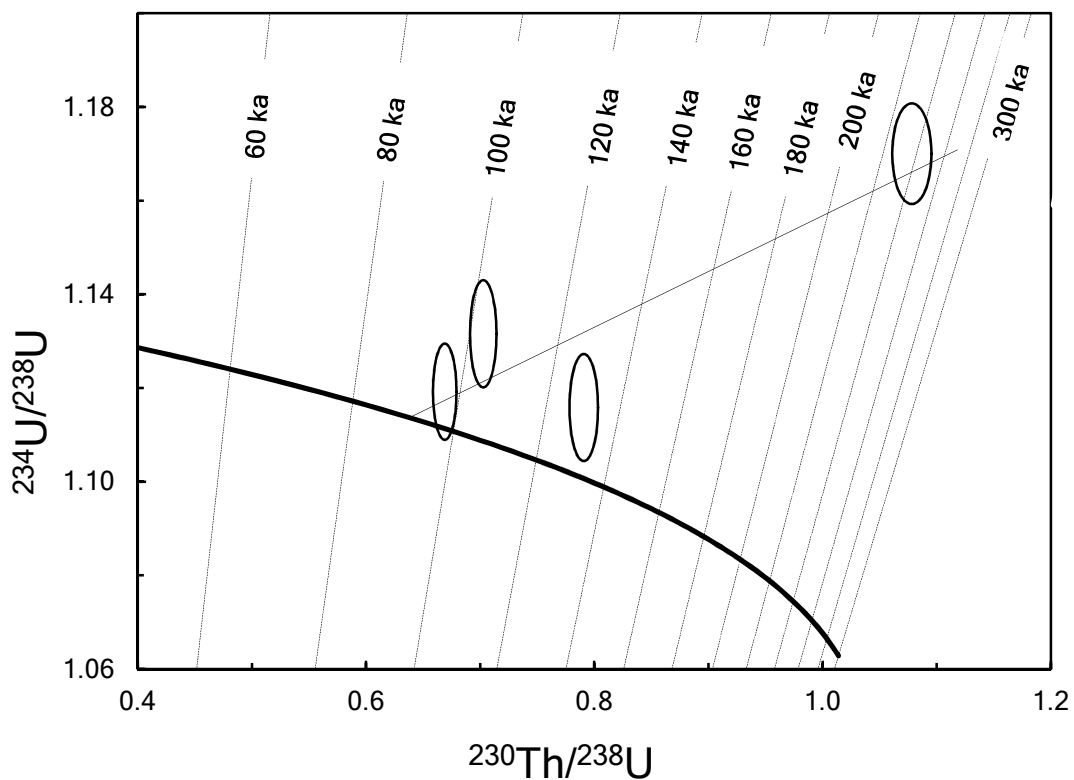


Fig. 9. Plot of MIS 5a/c *L. lithophaga* data in ( $^{234}\text{U}/^{238}\text{U}$ ) vs. ( $^{230}\text{Th}/^{238}\text{U}$ ) space. The regression line intercepts the ( $^{234}\text{U}/^{238}\text{U}$ ) marine evolution curve at 90.3 ka (MIS 5b).

## 7. Conclusions

*L. lithophaga* shells show remarkably good mineralogical preservation over glacial-interglacial timescales with little or no petrographic or XRD evidence of alteration in specimens as old as ~200 ka. U-series data suggest that it may be possible to date emergent Holocene shells by the U/Th method, although significant age correction is necessary because of detrital contamination. Successful correction depends upon using realistic estimates of U/Th ratios in the contaminants rather than average crustal values which are inappropriate for carbonate-dominated environments. U-series dating may, therefore, prove to be a useful tool for constraining the age of uplifted Holocene shorelines in the Mediterranean. Despite their almost pristine appearance, the evidence from our field area suggests that Pleistocene shells cannot be reliably dated. They show unequivocal evidence of open system behaviour, there is little consistency in isotope patterns between samples and in the absence of detailed understanding of the diagenetic processes involved, correcting for the effects of isotopic disturbance is not currently possible. Such disturbance is probably subject to many process controls, perhaps, *inter alia*, decay of intra-shell organic matter or

443 availability of transport pathways along mineralogical boundaries. The rate and extent of such isotopic  
444 turnover may be at least partially controlled by micro-environmental factors related to substrate  
445 weathering, aspect, slope angles and rainfall runoff. The evidence presented here shows that *L. lithophaga*  
446 boreholes apparently provide insufficient protection from meteoric waters for the shells to maintain  
447 closed-system conditions over prolonged periods of time ( $10^4$ - $10^5$  years). It remains possible that  
448 particularly sheltered borehole sites might contain geochemically closed-system shells but this has yet to  
449 be demonstrated. Since regular winter rainfall is part of the Mediterranean climatic regime, it seems likely  
450 that similar results could be expected from other parts of the basin. *L. lithophaga* shells, like most other  
451 mollusc shells and some *Cladacora* sp. corals in the Eastern Mediterranean, exhibit complex open system  
452 behaviour with respect to U-series isotopes, which precludes their use in constructing reliable  
453 chronologies for Mid-Late Quaternary tectonic and climatic events.

454  
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**Highlights**

- Uranium-thorium methods are used for the first time to date the boring marine mollusc *Lithophaga lithophaga*
- Uranium is taken up by the shells early *post mortem* from a marine source
- Later uranium isotope mobility interferes with accurate age determination
- Holocene specimens of *L. lithophaga* can probably be successfully dated
- Pleistocene specimens cannot be successfully dated