U–Th dating of speleothems to investigate the evolution of limestone caves in the Gunung Mulu National Park, Sarawak, Malaysia.

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Abstract: The Gunung Mulu National Park, Sarawak, Malaysia has been a focus of scientific research and exploration for several decades. Previous work investigated the relationship between fluvial incision into the limestone massif and the chronological evolution of the 500m-deep network of cave passages. This study involved analyses of newly available speleothem material using state-of-the-art U–Th dating methods and assessment of the potential for extension of the chronological record using U–Pb dating techniques.

Introduction

Caves are useful in landscape evolution studies because they commonly mark the level of previous water tables and, when dated, yield estimates of the rates of fluvial incision and tectonic uplift. Entrenchment of the Melinau and Melinau Paku rivers within the Gunung Mulu National Park, Sarawak, Malaysia (Fig.1) has created a base level for cave development. Thus, as incision has proceeded during the Quaternary, a vertically stacked sequence of cave passages has formed (Fig.2), extending up to 500m above the present Clearwater resurgence level.

During wet interglacial periods, increased frequency of landslips and sediment production resulted in aggradation of the Melinau and Melinau Paku rivers and the development of large alluvial fans, which are now represented by terrace remnants (Rose, 1982). Large volumes of coarse gravel derived from the adjacent sandstone uplands were also transported into the caves and deposited at resurgence level, preventing incision and focusing erosion laterally on the cave walls to create morphologically distinctive notches (Smart *et al.,* 1985). If the alluvial fan extended so far as to block the resurgence, ponding occurred within the passages and finely laminated sediments were deposited. During drier glacial climates, incision of the Melinau and Melinau Paku rivers dominated processes and the local water table dropped. If the base level fell faster than the rate of incision, upper cave passages were abandoned and groundwaters were diverted to new, lower, phreatic routes. Once abandoned, the passages became suitable for the formation of speleothems; thus, cave deposits typically comprise coarse gravels overlain by finely laminated sediments and a capping layer of speleothem (Fig.3) (Smart *et al.,* 1985).

A chronology for the development of the lower 120m of cave passages, lying between 20–140 m above sea level (m asl), was obtained by Farrant *et al.* (1995) using alpha spectrometric (α-spec) dating of speleothems, a technique that has an upper age limit of c.350 thousand years (ka). Above 140 m asl, the speleothems were too old to be dated using the methods available at the time. Thus, Farrant *et al*. (1995) used the record of palaeomagnetic reversals preserved within cave sediments to develop a chronology extending back to 850 ka. However, above 206 m asl the record was too sparse for reliable interpretation. The upper c.300 m of cave development from the late Pliocene–early Pleistocene therefore remained undated. In addition, Farrant *et al*. (1995) demonstrated that in the 0–700 ka range, the chronology for formation of cave wall notches and thus aggradational events is closely associated with 11 major interglacial peaks. Palaeoclimatic fluctuations and associated changes in hydrology are therefore considered a major driving force for karst evolution and speleogenesis.

In recent years the discovery of Whiterock Cave opened up a new avenue for research in the higher levels of the Clearwater system. When combined with newly available dating techniques, these new opportunities offered promise for establishment of a complete chronological framework for cave development within the Park. Sampling in Whiterock Cave was the main focus of work by members of the 2009 Mulu Caves Project expedition. However, basing the 2010 expedition at Park Headquarters provided an ideal opportunity to revisit the sites of the 'early' science with modern dating techniques, and thus gain a fuller understanding of Mulu cave development.

Financial support made available by the British Cave Research Association Cave Science Technology Research Initiative (CSTRI) enabled expansion of the existing speleothem U-series record using two approaches. For samples younger than the current limit of U–Th dating, which, due to technological developments, is now c.600 ka, it was possible to add extra dating points to those obtained during the development on a wider scale. Further, for speleothems older than the limit of the U–Th dating method, it was possible to screen and identify speleothems suitable for dating by the newer U–Pb technique (Richards *et al.,* 1998; Woodhead *et al.,* 2006), which is capable of dating materials significantly older than those that can be dated using the conventional U–Th technique.

Methodology

Uranium(U)-238 is the parent isotope of a radioactive decay chain encompassing uranium-234, thorium(Th)-230 and ending with the stable isotope lead(Pb)-206. In the hydrological environment, thorium is adsorbed rapidly on natural colloidal-sized materials. Uranium, however, is readily oxidized and transported in solution in bicarbonate waters as the complexed uranyl ions UO2(CO3)22- and UO2(CO3)34-. During speleothem deposition, uranium in solution in the percolating dripwaters is co-precipitated into the calcite crystal lattice. Thorium concentrations in dripwater and the deposited calcite are, however, typically negligible resulting in extreme fractionation between the parent and intermediate nuclides. The time since deposition may thus be determined by U–Th dating from the ingrowth or decay of intermediate nuclides. U–Pb dating relies on the measurement of cumulative amounts of radiogenic lead. This technique has been shown to be applicable in areas with uraniferous groundwaters (and thus speleothems) and low levels of natural lead (Richards *et al.,* 1998).

Permission to obtain speleothem material from the caves of the Gunung Mulu National Park was granted by the Controller of National Parks and Nature Reserves, Forest Department, Sarawak. Previously-broken speleothems were abundant throughout the caves and thus were readily sampled between elevations of 80 and 535 m asl. All speleothems collected as part of this project were sawn in half and polished in preparation for sub-sampling. In general, the majority of samples display good, dense primary calcite suitable for dating. In total, 15 sub-samples of 80–120mg were obtained from white, dense, crystalline growth layers for ^{230}Th/^{234}U analysis. Chemical separation and multi-collector inductively coupled plasma mass spectrometric (MC-ICPMS) measurement of uranium and thorium isotopic ratios was undertaken in the laboratories of the Bristol Isotope Group using procedures similar to those described in Hoffmann *et al.* (2007). Measurement of one sample (LC-10-14-3), was repeated to test for reproducibility. Ages from this study are quoted in ka (thousand years ago; the datum is 1950 AD).

Results

Analytical data for all samples are provided in Table 1. Ages of sub-samples range from 12.1 ± 0.1 ka (WR-09-02-2) for a stalagmite deposited at an elevation of 110m asl in Whiterock Cave, to six samples that are in secular equilibrium and thus cannot be dated by U–Th dating methods. Repeat measurement of LC-10-14-3 shows the ages to be reproducible. The speleothem calcite is variable in uranium, yielding concentrations between 335 and 9240 ng g-1. Measured (^{230}Th/^{232}Th)$_{activity}$ ranges from 10^1 to 10^4, thus correction for detrital ^{230}Th yields minimal change in the final ages. Uranium–thorium isotopic ratios of samples not dated by the U–Th method all plot upon the line of secular equilibrium (Fig.4), indicating that the system has remained closed since deposition and that the samples are thus older than the effective upper U–Th dating limit of c.600 ka.

Discussion

Identifying speleothems suitable for dating by U–Pb methods required further assessment of the degree of detrital thorium contamination, which can be used to estimate incorporation of common lead into the crystal lattice. Table 1 shows that six samples were beyond the limit of U–Th dating and that these samples contained between 335 and 2000 ng g^{-1} of ^{238}U. Detrital ^{232}Th contamination was between 1 and 9 ng g^{-1} and was suggested as a proxy for ^{204}Pb (Woodhead *et al.,* 2006) using the crustal Pb/Th ratio of 1.6 (Rudnick and Gao, 2003), and a ^{204}Pb abundance of 1.4%. Successful U–Pb speleothem dating requires the presence of high uranium concentrations coupled with low common lead (Richards *et al.,* 1998; Woodhead *et al.,* 2006; Woodhead and Pickering, 2012).

Under these conditions, low Pb/U ratios increase the age resolution, and low common lead reduces the variability in the initial lead isotopic composition (Woodhead *et al.,* 2006). Two of the samples older than 600 ka presented here (WR-09-19-4 and WR-09-23-1) contain less than 1000 ng g^{-1} of ^{238}U, with relatively high predicted $^{204}Pb/^{238}U$ ratios of 6.2 x 10-4 and 1.5 x10-4, respectively, based on a typical crustal Pb/Th ratio. Obtaining geochronological constraints from these samples using U–Pb methods would be challenging. However, the four samples (WR-09-18-3, WR-09-18-4, WR-09-22-1 and WR-09-23-3) that contain high concentrations of uranium (>1000 ng g^{-1}), with low predicted $^{204}Pb/^{238}U$ ($<8x10^{-5}$) are promising. Also, it is encouraging that all samples older than 600 ka display $^{234}U/^{238}U \neq 1$, which enables a direct estimate of the initial state of disequilibrium to be calculated. As observed by others (e.g. Partin *et al.,* 2007), the study found $^{234}U/^{238}U$initial $\ll 1$ for samples < 600 ka, indicating the depositing dripwaters were relatively deficient in ^{234}U.

Details of the new speleothem chronology are shown in Figure 5, plotted against the existing chronology of Farrant (1995). Results from seven out of the fifteen samples plot within the age range of the Farrant (1995) chronology, whereas two older samples from higher elevations of 120 and 166 m asl (WR-09-4-1 and WR-09-23-5) are dateable beyond α-spec limits using the U–Th MC-ICPMS method. Further, six samples (two of which are obscured in Figure 5 due to their similar sample elevations) from between 160 and 275 m asl, and thus the highest elevation cave passages, are too old for the c.600 ka limit of MC-ICPMS U–Th dating. The new dataset, combined with that of Farrant (1995), confirms that the antiquity of cave passages at and above 140 m asl lies beyond the 600 ka limit of U–Th dating. Interestingly, young speleothems growing in what should be older cave passage is a particular problem that needs to be addressed during future work when estimating rates of fluvial incision, which is approximately equal to the rate of uplift. The speleothem data presented here already show promise for extending the Farrant *et al.* (1995) chronology into the higher elevation passages and improving understanding of cave development within the Gunung Mulu National Park.

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Captions

Figure 1: Location of the Gunung Mulu National Park, Sarawak, Malaysia.

Figure 2: Elevation of a cross-section through the Clearwater Cave system, clearly showing horizontal passages extending over a 250m vertical range. Scale on left in metres (Image: Mulu Caves Project.)

Figure 3: Image from Stone Horse Cave showing a cobble bed containing quartz, capped by finely laminated sediment and a thin speleothem layer.

Figure 4. Isotopic composition of speleothems dated in this study, plotted against the $(^{234}U/^{238}U)_{activity}$ evolution curve (Ludwig, 2003).

Figure 5: Speleothem dating results plotted against elevation (m asl). Circles, this study: Closed circles, within the range of U–Th dating; Open circles and arrows, beyond the limit of U–Th dating. Triangles, Farrant (1995): Closed triangles, within the range of α-spectrometric dating; Open triangles and arrows, beyond the limit of α-spectrometric dating. Dotted, dashed and continuous lines highlight the rate of fluvial incision (which is approximately equal to the rate of uplift), as constrained by Farrant et al., (1995).

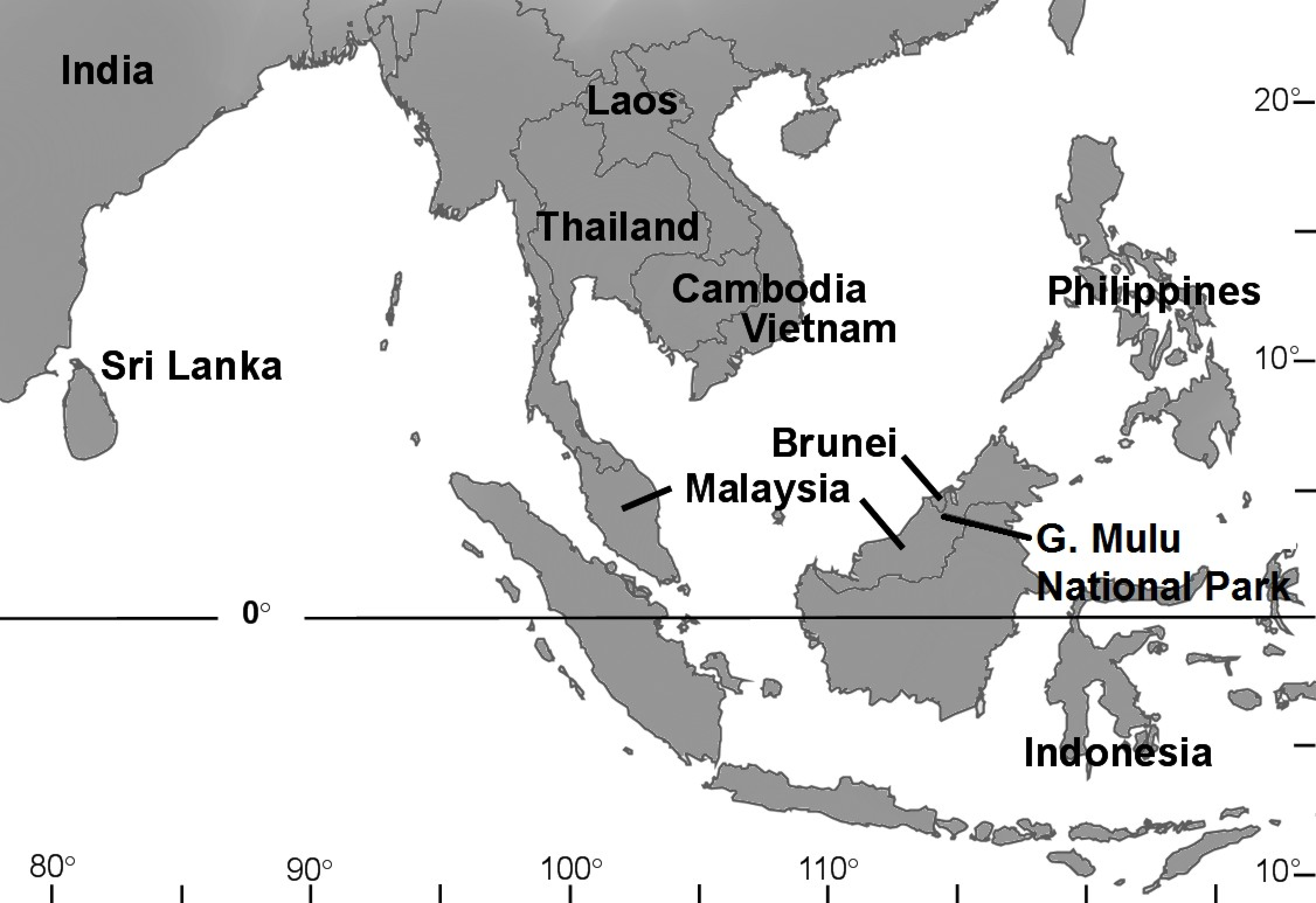
Table 1: U and Th concentrations, isotopic activity ratios, ages of Mulu speleothems and estimated $^{204}Pb/^{238}U$ ratios.

Subscript act denotes activity ratio.Subscript (i) denotes initial. $^{*}(^{230}Th/^{238}U)_{activity} = 1-e^{-\lambda_{230}T} + (\delta^{234}U_{measured}/1000)[\lambda_{230}/(\lambda_{230}-\lambda_{234})](1-e^{-(\lambda_{230}-\lambda_{234})T})$, where T is age in years. $\lambda_{230} = 9.158 \times 10^{-6}$ yr^{-1} (Cheng *et al.* 2000), $\lambda_{234} = 2.826 \times 10^{-6}$ yr^{-1} (Cheng *et al.* 2000), $\lambda_{238} = 1.551 \times 10^{-10}$ yr^{-1} (Jaffey *et al.* 1971). †Thousand years before 1950. $Corrected for detrital Th contamination using the bulk earth value of 0.746 ± 0.2 for initial $^{230}Th/^{232}Th_{act}$. The degree of detrital ^{230}Th contamination is indicated by the measured $(^{230}Th/^{232}Th)$ activity ratio. ‡Repeat measurement. A.D.L denotes above dating limit.

Sub-sample	^{238}U [ng g^{-1}]	^{232}Th [ng g^{-1}]	$(^{230}Th/^{232}Th)_{act}$	$(^{230}Th/^{238}U)_{act}{}^{*}$	$(^{234}U/^{238}U)_{act}$	Age*†	Corrected Age*†$	$(^{234}U/^{238}U)_{(i)\ act}{}^{\$}$	Estimated $^{204}Pb/^{238}U$	Elevation (m asl)
HOTM	1057 ± 6	1 ± 0.01	316 ± 4	0.1031 ± 0.0010	0.6915 ± 0.0019	17.8 ± 0.2	17.7 ± 0.2	0.6755 ± 0.0021		535
LC-09-12-3	843 ± 3	28 ± 0.1	14 ± 0.04	0.1546 ± 0.0008	0.6929 ± 0.0011	28.1 ± 0.2	26.6 ± 0.8	0.6660 ± 0.0021		80
LC-10-14-3	451 ± 2	10 ± 0.05	22 ± 0.3	0.1682 ± 0.0022	0.5319 ± 0.0026	44.3 ± 0.8	43.0 ± 1.2	0.4682 ± 0.0043		80
LC-10-14-3‡	447 ± 2	10 ± 0.04	22 ± 0.1	0.1672 ± 0.0012	0.5306 ± 0.0011	44.1 ± 0.4	42.7 ± 1.0	0.4670 ± 0.0029		80
WR-09-02-2	3028 ± 18	4 ± 0.02	161 ± 1	0.0709 ± 0.0003	0.6782 ± 0.0010	12.1 ± 0.1	12.0 ± 0.1	0.6669 ± 0.0011		110
WR-09-02-4	9237 ± 46	12 ± 0.1	984 ± 7	0.4103 ± 0.0014	0.7476 ± 0.0012	92.7 ± 0.6	92.7 ± 0.6	0.6719 ± 0.0019		130
WR-09-04-1	1375 ± 6	4 ± 0.1	825 ± 36	0.6935 ± 0.0189	0.8234 ± 0.0015	246.4 ± 30.6	246.3 ± 30.6	0.6454 ± 0.0311		120
WR-09-18-3	1998 ± 11	4 ± 0.02	1516 ± 3	0.9621 ± 0.0031	0.9690 ± 0.0018	A.D.L			0.00004	275
WR-09-18-4	1418 ± 6	1.0 ± 0.02	4131 ± 101	0.9768 ± 0.0046	0.9801 ± 0.0018	A.D.L			0.00002	275
WR-09-19-1	1039 ± 4	0.2 ± 0.01	1648 ± 77	0.0966 ± 0.0027	0.9046 ± 0.0020	12.3 ± 0.4	12.3 ± 0.4	0.9012 ± 0.0021		184
WR-09-19-4	335 ± 2	9 ± 0.05	109 ± 0.2	0.9945 ± 0.0037	0.9952 ± 0.0020	A.D.L			0.00062	185
WR-09-20-2	1062 ± 6	1 ± 0.01	513 ± 2	0.1054 ± 0.0005	0.8214 ± 0.0014	15.0 ± 0.08	15.0 ± 0.1	0.8316 ± 0.0015		185
WR-09-22-1	1522 ± 8	3 ± 0.02	1543 ± 3	0.9949 ± 0.0032	0.9952 ± 0.0018	A.D.L			0.00004	248
WR-09-23-1	616 ± 3	4 ± 0.07	412 ± 7	0.9240 ± 0.0046	0.9383 ± 0.0017	A.D.L			0.00015	162
WR-09-23-3	1172 ± 6	4 ± 0.02	760 ± 6	0.9230 ± 0.0038	0.9467 ± 0.0016	A.D.L			0.00008	160
WR-09-23-5	1799 ± 8	4 ± 0.02	1124 ± 6	0.8884 ± 0.0035	0.9263 ± 0.0016	513.6 ± 72.0	513.5 ± 72.0	0.6850 ± 0.0679		166

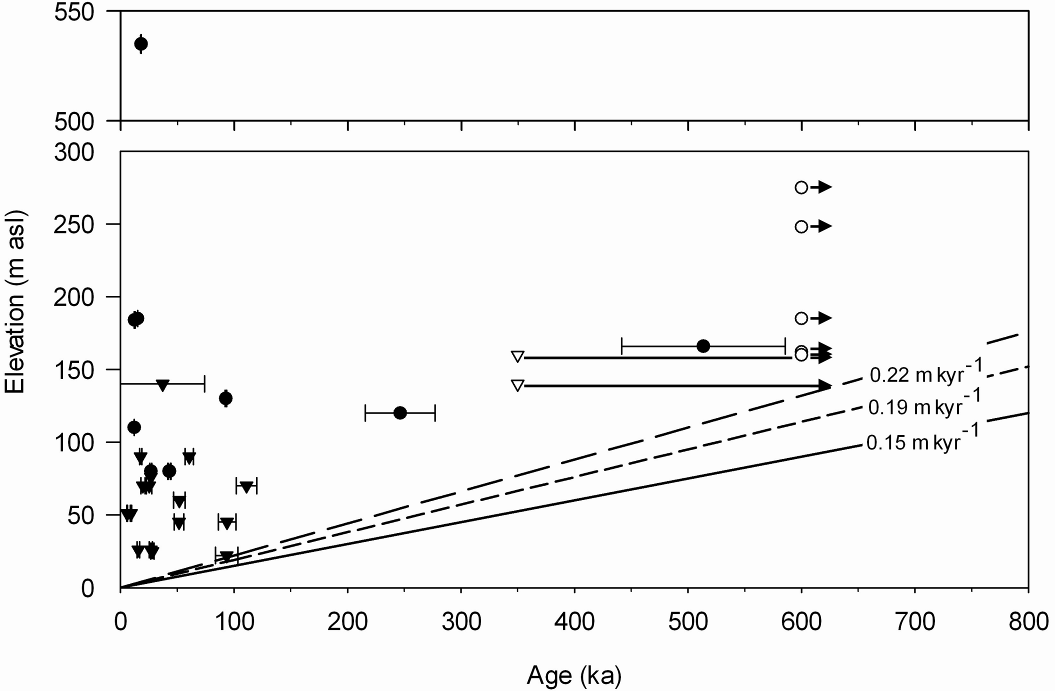
Table 1.

Subscript act denotes activity ratio.Subscript (i) denotes initial. *$[^{230}Th/^{238}U]_{activity} = 1-e^{-\lambda 230T} + (\delta^{234}U_{measured}/1000)[\lambda_{230}/(\lambda_{230}-\lambda_{234})](1-e^{-(\lambda 230-\lambda 234)T})$, where T is age in years. $\lambda_{230} = 9.158 \times 10^{-6}$ yr^{-1} (Cheng *et al.* 2000), $\lambda_{234} = 2.826 \times 10^{-6}$ yr^{-1} (Cheng *et al.* 2000), $\lambda_{238} = 1.551 \times 10^{-10}$ yr^{-1} (Jaffey *et al.* 1971). †Thousand years before 1950. $Corrected for detrital Th contamination using the bulk earth value of 0.746 ± 0.2 for initial $^{230}Th/^{232}Th_{act}$. The degree of detrital ^{230}Th contamination is indicated by the measured $(^{230}Th/^{232}Th)$ activity ratio. ‡Repeat measurement. A.D.L denotes above dating limit.


India
Laos
Thailand
Cambodia
Vietnam
Philippines
Sri Lanka
Brunei
Malaysia
G. Mulu
National Park
Indonesia
0°
20°
10°
10°
80°
90°
100°
110°

250
200
150
100
50
Api Birthday
Reluctant Explorers
Matrimony
Strong Hint of Bigness
Unnamed Bypass
DAYDREAM BELIEVER
Whose Cairn
Lima Pulah
DAYDREAM BELIEVER
Ancestors Passage
Out of Africa
Into Out Of
Down Under
Firecracker
Firecracker
Black Silk Passage


Capping speleothem
Capping laminated sediment fill
Cobble bed containing quartz



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500
300
250
200
150
100
50
0
Elevation (m asl)
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0.19 m kyr^{-1}
0.15 m kyr^{-1}
0
100
200
300
400
500
600
700
800
Age (ka)