

# CONSTRAINING THE AGE OF THE AVELINE'S HOLE 9 CRANIUM BASED ON U-TH ISOTOPIC ANALYSIS OF ITS SECONDARY CALCITE COATING

by

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## ABSTRACT

Sub-samples from two calcite coatings, one adhered to Aveline's Hole 9 (AH9) cranium (housed in Wells and Mendip Museum) and the other expected to be equivalent but of unconfirmed provenance (housed in UBSS Museum), were provided for high-precision mass-spectrometric U-series analysis. The principal aims of the study were to establish (a) whether the UBSS calcite material was originally attached to AH9; (2) the minimum age of AH9 cranium and (3) the original cave setting for calcite deposition. U-Th isochron methods were used to establish the earliest growth of calcite as AD 1824-1955 for both samples. Measured initial  $^{234}\text{U}/^{238}\text{U}$  activity ratios for the authigenic calcite coatings are indistinguishable and equal to 2.47, which very strongly supports their equivalence. The possibility of using this ratio to fingerprint the source of dripwaters and, hence, the original location is suggested. However, there is insufficient supporting evidence and there remains the likelihood that 'Aveline's Hole 9' is a misnomer.

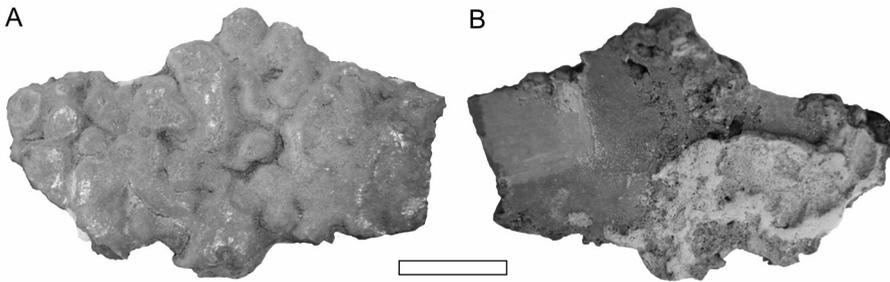
## INTRODUCTION

A cranium (AH9) purported to have been collected from Aveline's Hole, Mendip, UK, and currently housed at Wells and Mendip Museum in Somerset, UK, has been subject to detailed investigation to establish its most likely age and provenance (see full report in Meiklejohn *et al.* this issue). We focus our efforts here on samples of secondary calcite that were deposited on the skull while it was in a cave setting prior to collection. We use mass-spectrometric U-series results on speleothem (Richards and Dorale, 2003) to constrain the minimum age of AH9 and provide further clues to its convoluted history since excavation. Two separate samples were made available for analysis; a small piece of calcite loosely attached to the AH9 cranium provided by Wells Museum, and a much larger piece, from the University of Bristol Spelaeological Society (UBSS) Museum, that was considered highly likely to have originally coated AH9 based on similar morphology and curvature of both the cranium surface and the underside of the calcite layer.

Measurement of U-series isotopic ratios on both samples of calcite made available to us were conducted in order to provide a U-Th age for the earliest calcite precipitation in the coating and thereby constrain the *latest* possible date of deposition for this cranium. In so doing, we could also verify the radiocarbon age of the bone material determined by the Oxford Radiocarbon Accelerator Unit (Meiklejohn *et al.*, this issue). It was also envisaged that ages and U-isotopic ratios could be used to determine whether the two samples were from the same locality, and perhaps more importantly, from Aveline's Hole, because there existed some doubt about the provenance. The use of isotopes to 'fingerprint' the original location is widespread in archaeological and archaeometallurgical studies: Strontium, lead and neodymium isotopes in bones and teeth, for example, have been used in this way to identify the region where an individual lived (for reviews, see Bentley *et al.*, 2006; Pollard, 2009).

## SAMPLES AND METHODS

Both calcite coating samples (from UBSS and Wells) are dense, creamy-white and show no evidence of post-depositional alteration. However, the material contains a significant fraction of detrital material, particularly in the exposed surfaces and initial calcite growth in the sample from the UBSS Museum.



**Figure 1.** Calcite coating from UBSS Museum and believed to have been removed from the calvaria of AH9. Scale bar 20 mm. A: Distal surface B: Proximal surface after removal of detrital-rich layer (upper left) (<0.5 mm) and prior to sub-sampling by scalpel of ~30 mg for U-Th determinations.

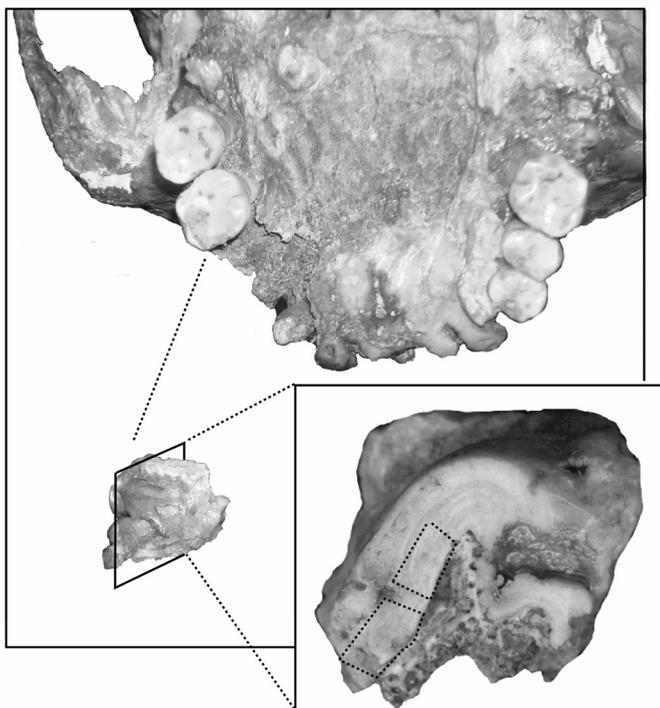
*UBSS AH9 calcite:*

This is believed to have formerly been adhered to part of the outer surface of the AH9 calvarium (or skull cap) and has approximate dimensions of 70 x 45 x 8 mm (Figure 1). This larger calcite sample presented an opportunity to obtain a tight chronological constraint by scraping the underside of the coating (i.e. the face formerly in direct contact with the bone surface) with a clean scalpel. This method has the advantage of higher temporal resolution than drilling powders or cutting thin wafers with a wire saw because a wider surface and smaller width can be sampled to obtain sufficient material (~ 30 mg). After removing a thin layer of detritus-dominated calcite (<0.5 mm), a set of coeval sub-samples was removed for U-Th analysis (including UBSS AH9 calcite\_1, 2, 3, 11; Table 1). A further set of powders were then produced from the next stratigraphically younger layer in the same manner (includes UBSS\_AH9 calcite\_13, 8a and 8b; Table 1). Because the material was contaminated with detrital clay particles and aluminosilicate grains, we required multiple U-Th isotope analyses to estimate the isotopic ratio of the detrital and authigenic (precipitated calcite) components to calculate a U-Th age. Both sample layers were treated as a single coeval population because of the expected large fractional age uncertainties, small sample size and expected calcite growth rate.

*Wells AH9 calcite:*

This was adhering to the cranium at the time of sampling (Figure 2). Much of the bone was coated with a thin layer of calcite, but mechanical removal with drill bit or wire saw was avoided because of likely damage to the skull. Fortunately, ~ 2 g of dense calcite could be loosened from the alveolar process of the inner maxilla, very close to the second molar. This was divided into basal and upper sections (<60 mg) using a diamond wire saw and ultrasonicated to remove cutting debris. The older basal material was subject to analysis (see Figure 2). This calcite material was significantly cleaner (less detritus) than the material from the UBSS Museum.

U-Th determinations were conducted at the Bristol Isotope Group facilities, University of Bristol. For each sub-sample of calcite (n = 9), a  $^{229}\text{Th}$ - $^{236}\text{U}$  tracer was added after total dissolution in a combination of  $\text{HNO}_3$  and HF. Chemical separation of U and Th from the  $\text{CaCO}_3$  matrix was then conducted using AG1x8 ion exchange resin prior to mass-spectrometric analysis. U and Th isotopic analyses were undertaken using a standard-sample bracketing approach on a ThermoFinnigan NEPTUNE, which is an inductively-coupled plasma source multi-collector instrument with Faraday and ion-counting set-up (see Hoffmann *et al*, 2007).



**Figure 2.** Inferior view of AH9 and location of small fragment of calcite coating and bone from alveolar process of maxilla. Inset is section through fragment. Boxes indicate sub-samples cut using drill and diamond wire saw to provide maximum age of calcite.

## RESULTS

Uranium concentrations in the calcite samples vary by a factor of 3 from 0.83 to 2.53  $\mu\text{g}\cdot\text{g}^{-1}$  (Table 1). These values are in excess of all but two samples from Mendip (Atkinson *et al*, 1978; Atkinson *et al*, 1984; Farrant, 1995), where the vast majority of samples (34 out of 37) are < 0.41  $\mu\text{g}\cdot\text{g}^{-1}$ ). It is tempting to suggest that the high concentrations indicate that this

Sample	Sub sample	Measured ratios										
		$^{238}\text{U}$ (ng/g)	$\pm$	$^{232}\text{Th}$ (ng/g)	$\pm$	$(^{232}\text{Th}/^{238}\text{U})$ activity	$\pm$	$(^{230}\text{Th}/^{238}\text{U})$ activity	$\pm$	$(^{234}\text{U}/^{238}\text{U})$ activity	$\pm$	
AH9 calcite (UBSS)	8a	828	8	106.0	10.4	0.04204	0.00011	0.1554	0.0014	2.390	0.004	
	8b	1264	16	103.0	11.4	0.02654	0.00008	0.1003	0.0008	2.390	0.004	
	13	1297	14	64.4	6.6	0.01625	0.00004	0.0482	0.0004	2.452	0.004	
	1	1703	13	126.4	9.6	0.02429	0.00007	0.0791	0.0008	2.467	0.004	
	2	1321	7	33.1	1.9	0.00820	0.00002	0.0317	0.0003	2.452	0.004	
	3	1301	6	76.4	3.6	0.01922	0.00005	0.0668	0.0005	2.428	0.004	
	11	1248	13	74.9	7.2	0.01965	0.00006	0.0643	0.0007	2.426	0.004	
	AH9 calcite (Wells)	b1	1546	4	3.5	0.1	0.000732	0.000001	0.0047	0.0000	2.470	0.002
	b2	2534	6	28.1	0.7	0.003634	0.000005	0.0217	0.0001	2.470	0.002	

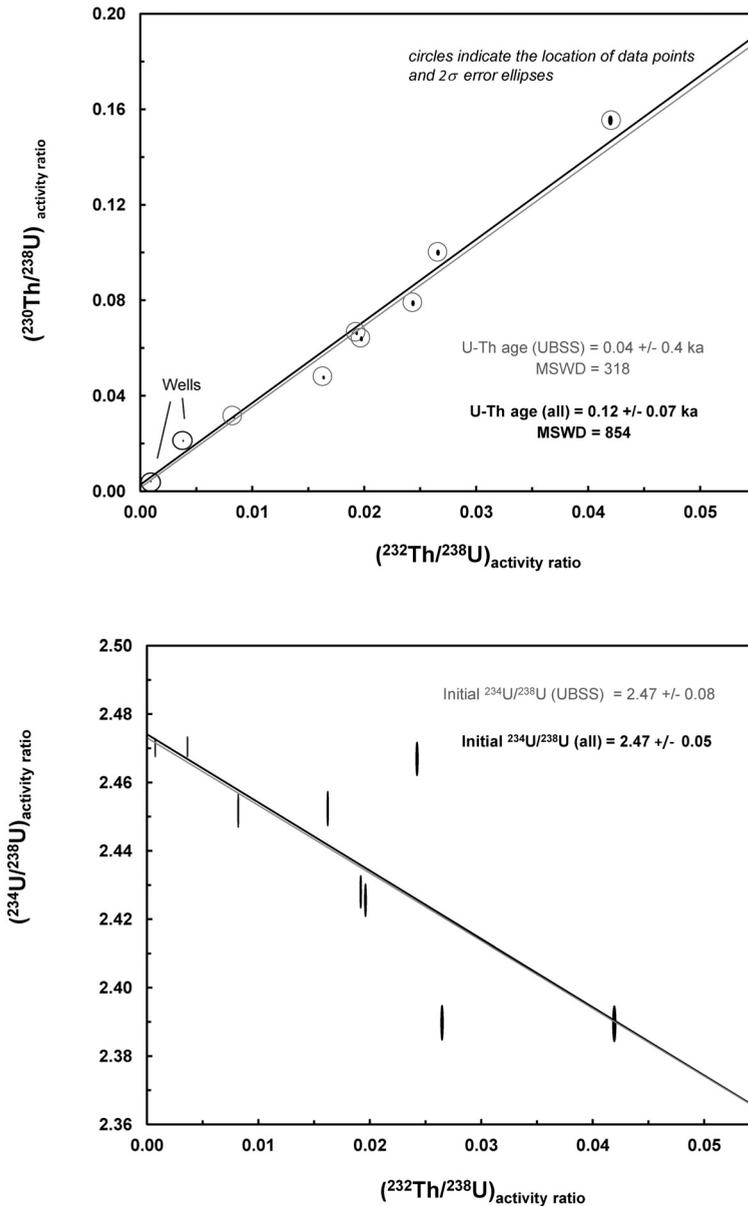
**Table 1.** *U, Th concentrations and isotopic ratios of sub-samples from AH9 (UBSS) and AH9 (Wells). Uncertainties are quoted at the 2  $\sigma$  level.*

sample is likely to be from a location other than Mendip but this cannot be declared with confidence.

U and Th isotope ratios and concentrations provided a sufficient range in values for successful isochron methodology using total dissolution methods (Luo and Ku, 1991; Bischoff *et al.*, 1991). This protocol for calculating U-Th ages assumes a single source of detrital contamination, which can be distinguished by plotting the linear array of results with the full range of measured  $^{232}\text{Th}/^{238}\text{U}$  against  $^{230}\text{Th}/^{238}\text{U}$  and  $^{234}\text{U}/^{238}\text{U}$  results (Figure 3). We used plotting tools and three-dimensional least squares regression tools as implemented in ISOPLOT/Ex (Ludwig and Titterton, 1994; Ludwig, 2001).  $^{232}\text{Th}/^{238}\text{U}$  activity ratios varied by a factor of  $\sim 60$  from  $7.32 (\pm 0.01) \times 10^{-4}$  to  $4.20 (\pm 0.01) \times 10^{-2}$ , which is sufficient to produce a well-defined isochron, albeit with some excess scatter (MSWD > 300), and calculate a U-Th age and initial  $^{234}\text{U}/^{238}\text{U}$  and  $^{230}\text{Th}/^{232}\text{Th}$  activity ratios. This method is preferred over individual corrected U-Th ages because it does not rely on an *a priori* detrital  $^{232}\text{Th}/^{238}\text{U}$  value.

If we assume all material from the UBSS AH9 calcite is the same age and plot the data in  $^{232}\text{Th}/^{238}\text{U}$  vs  $^{230}\text{Th}/^{238}\text{U}$  vs  $^{234}\text{U}/^{238}\text{U}$  space, we observe a linear array with some excess scatter (Figure 3). It defines an age of < AD 1560 ( $2\sigma$ ) and an initial  $^{234}\text{U}/^{238}\text{U}$  activity ratio of  $2.47 \pm 0.07$  ( $2\sigma$ ). Initial  $^{230}\text{Th}/^{232}\text{Th}$  is  $3.4 \pm 0.6$ , which is greater than the bulk earth value of  $0.85 \pm 0.36$  (Wedepohl, 1995). Adopting the same method for the Wells AH9 calcite is not valid because we only have two data points and cannot assess the linearity of fit, but we can confidently constrain the initial  $^{234}\text{U}/^{238}\text{U}$  activity ratio ( $2.470 \pm 0.003$ ), which is the same value as the UBSS sample. Because we obtain the same initial  $^{234}\text{U}/^{238}\text{U}$  activity ratio for both samples, we are in no doubt that both samples analysed come from the same cranium. We can, therefore, pool all results and assume that they represent the same phase of growth on the same sample. We obtain an isochron age estimate for all data of  $120 \pm 70$  bp ( $2\sigma$ , Figure 3), or calendar date of 1824-1954 AD. We have not expanded the age uncertainty to account for the excess scatter observed.

There remains the question 'Where did this sample reside at the time of calcite coating?' In the same manner that Pb isotopic data is used to 'fingerprint' gold or copper artefacts and Sr isotopic values can be used to indicate where an individual lived or migrated, one could also use the initial  $^{234}\text{U}/^{238}\text{U}$  activity ratio to give some indication of the likely deposition locality in certain circumstances. Some have suggested that for some vadose settings, and particularly thermal groundwater-fed cave calcites, consistent initial  $^{234}\text{U}/^{238}\text{U}$  activity ratios, both spatially and temporally, can be predicted for a cave using a 'Regional Uranium Best Estimate' (Gascoyne *et al.*, 1983). However, a survey of  $^{234}\text{U}/^{238}\text{U}$  activity ratios in groundwaters of the Mendip Hills (Burgess *et al.*, 1980; Bonotto and Andrews, 2000) indicates a large range in values from 1.02 to 2.11 (mean = 1.57) for waters draining the Carboniferous Limestone and 1.69 to 3.26 (mean = 2.44) for waters draining the Old Red Sandstone. Also, calculated initial  $^{234}\text{U}/^{238}\text{U}$  activity ratios based on data in speleothems from four Mendip caves; G.B. Cave, Rhino Rift, Charterhouse Warren Farm Swallet and Longwood Swallet; have a wide range of 1.21 to 2.69 (Atkinson *et al.*, 1978; Atkinson *et al.*, 1984; Farrant, 1995). The initial  $^{234}\text{U}/^{238}\text{U}$  activity ratio for Aveline's Hole 9 calcite of  $2.47 \pm 0.05$  is not inconsistent with the wide range observed for secondary calcite growth, but a more comprehensive survey of ratios across the region and beyond is required before we can use such a 'fingerprinting tool' in a convincing manner.



**Figure 3.** Two views of three-dimensional isochrons using  $(^{232}\text{Th}/^{238}\text{U})$  vs  $(^{234}\text{U}/^{238}\text{U})$  and  $(^{230}\text{Th}/^{238}\text{U})$  activity ratios. Ellipses are  $2\sigma$  errors (circles used to identify location of points too small to observe). The data with the lowest  $(^{232}\text{Th}/^{238}\text{U})$  activity ratios are from the Wells AH9 calcite, which has the lowest detrital component. Isochrons are plotted using UBSS Museum calcite data (grey) and all data (black).

## CONCLUSION

We demonstrate here the potential to use U-series data to constrain the age of the secondary calcite coating deposited on AH9 between AD 1824-1954, though we stress that this is the *latest* possible date. Isochron methodology was adopted because one of the available samples from UBSS contained a significant amount of detrital material. It is highly likely that the calcite coating provided from UBSS Museum was sampled from AH9 because it has the same initial  $^{234}\text{U}/^{238}\text{U}$  activity ratio. We suggest that this ratio might be used to determine the original *in situ* location of this cranium, but as yet there is insufficient data from Mendip to suggest a particular cave. We are also aware that the high uranium concentration may indicate that the piece is not from Mendip. Analysis of recent speleothem growth in Aveline's Hole may assist in establishing both the provenance of this enigmatic sample and the issue of whether it is from Mendip or from elsewhere.

## ACKNOWLEDGEMENTS

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