# CHAPTER FOUR URANIUM SERIES DATING OF GLADYSVALE CAVE FLOWSTONES

## 4.1 Introduction

Speleothems are import reservoirs of palaeoclimatic information and are in themselves good palaeoenvironmental indicators as they grow only under specific conditions. The palaeoenvironmental data contained within speleothems are greatly enhanced by their inherent ability to be relatively easily and precisely dated on an absolute timescale via Uranium-series dating. This chapter examines the application of Uranium-series dating and trace element analysis of the speleothems from selected areas of Gladysvale Cave and the results of these data are reported and problems with detrital contamination are addressed.

#### 4.2 Background U screening

In order to determine background U and Th levels in the Gladysvale flowstones, small chips of each flowstone were dissolved in NO<sub>3</sub> and run through the ICP-MS (known as the Neptune) (Chapter 2.2). The samples are numbered RP001, RP002 etc, and a standard, SRM 960, of known uranium concentration (18.7 ppb) was also run. The results of this run are summarised in Table 4.1.

Sample	Sample (g)	Solution (g)	<sup>235</sup> U cps	<sup>238</sup> U volts	<sup>232</sup> Th cps	U ppb	Th ppb
SRM 960	1	1	119174	0.27233	952	18.7	0.001
RP001	0.00245	2.5	584	0.00133	2684	93.4	3.0
RP002	0.00258	2.5	287	0.00064	15994	42.4	17.2
RP003	0.00269	2.5	193	0.00043	1897	27.5	2.0
RP004	0.00245	2.5	299	0.00067	3425	46.7	3.9
RP005	0.00292	2.5	299	0.00067	3425	39.2	3.2
RP006	0.00265	2.5	299	0.00067	3425	43.2	3.6
RP007	0.00236	2.5	299	0.00067	3425	48.5	4.0
RP008	0.00272	2.5	280	0.00061	666	38.7	0.7
RP009	0.00280	2.5	173	0.00038	1456	23.2	1.4
RP010	0.00263	2.5	387	0.00087	2338	56.7	2.5
			Average sample value				4.1

Table 4.1. Background screening of Gladysvale Samples for U and Th levels.

Table 4.1 shows the <sup>238</sup>U levels in the flowstone samples are highly varied, with values ranging from 23.2 ppb to 93.4 ppb, with average values of 45.9 ppb. Low initial levels of

uranium are problematic as there will be corresponding low levels of daughter thorium. Thorium levels were also highly varied and problematically high, with an average of 4.1 ppb. The unusual value of 17.7 ppb for sample RP002 suggests significant detrital thorium contamination in this sample. The standard, SRM 960, produced the expected result of 18.7 ppb uranium, showing that there was no internal drift during the run. Using these background uranium levels and a model age of 200 ka (based on the ESR dates of Curnoe, 1999) and Schmid (2002)), sample and spike masses were calculated to provide optimum uranium and thorium voltages in the Neptune (Table 4.2).

Sample no.	Sample (g)	Spike (g)	U ppb	Th ppb	Estimated age (ka)
RP001	4.0	0.015	93.4	3.0	200
RP002	5.0	0.012	42.4	17.2	200
RP003	5.0	0.006	27.5	2.0	200
RP004	3.1	0.008	46.7	3.9	200
RP005	5.0	0.007	39.2	3.2	200
RP006	5.0	0.098	43.2	3.6	200
RP007	3.2	0.008	48.5	4.0	200
RP008	3.7	0.088	38.7	0.7	200
RP009	5.0	0.088	23.2	1.4	200
RP010	5.0	0.035	56.7	2.5	200

Table 4.2. Calculated samples and spike masses for Gladysvale flowstones

Between 3 and 5g of each sample was needed. In order to obtain a large enough mass of clean flowstone, samples had to be very carefully mechanically prepared, and to aid in this process laser ablation (Chapter 2.2.3) was carried out on a selection of samples.

#### 4.3 Laser Ablation ICP-MS

Six samples were analysed for <sup>238</sup>U, <sup>232</sup>Th and trace elements Sr, Mg, Ba and Ca. Samples RP001 and RP007 are from the two thickest flowstones sampled from Gladysvale, and are from the base and top of the stratigraphy respectively. Samples RP004, RP005, RP006 and RP009 are from throughout the stratigraphy and showed varying visible signs of detrital contamination as thin detrital intercalation (Figure 2.1). Ca values were very stable for all the samples, as the flowstones were predominantly calcium carbonate; therefore the Ca values for each sample were used to normalise the other elements and to convert the raw mass peak data into weight ratios. This was done by dividing the other elements by the Ca levels. These data were then plotted against the time run (in seconds) on a log scale.



Figure 4.1. LA-ICP-MS Trace elements, U and Th data for samples RP001 (A) and RP007 (B). Insert below each graph shows a photograph of the actual flowstone to which the scan data refer.



Figure 4.2. LA-ICP-MS Trace elements, U and Th data for samples RP004 (C), RP005 (D), RP006 (E) and RP009 (F). Inserts are photographs of the actual flowstones to which the scans refer.

#### 4.3.1 U and Th concentrations in Gladysvale Flowstones

# Sample RP001

Flowstone RP001 is from the basal stalagmite in the Porcupine Pit (Figure 2.1) and consists of creamy, white calcite with distinct discoloured layers (Figure 4.1 A). <sup>238</sup>U values fluctuate considerably, and there is no specific correlation between the <sup>238</sup>U concentrations and the nature of the flowstone, as both dirty and clean layers produce elevated U values. The finely laminated layers in general have lower U values, clean, creamy layers have moderate U levels; and very dirty, contaminated layers produce the two major U spikes at 470 and 810 seconds. Thorium values are in general very low, and quite stable along the flowstone. Major peaks at 470, 800, 810, and from 960–1000 seconds correspond to contaminated layers. The area between 900 and 930 seconds was selected for U-series, as although the U levels are reasonably low, Th is at its minimum.

## *RP007*

Sample RP007 is from the flowstone found at its maximum thickness in the extreme proximal reaches of the deposit, up against the front wall of the cave (Figure 2.1). The flowstone is visibly heavily contaminated with detritus (see Figure 4.1 B), and has the highest Th levels (Table 4.1); finding the cleanest possible layer, with the lowest Th was therefore imperative for this sample. <sup>232</sup>Th levels are very high, an order of magnitude higher than for sample RP001, and are equivalent to the <sup>238</sup>U for most of the sample. <sup>238</sup>U levels are lower and track the Th, except between 450 and 500 seconds, where U levels are quite stable and considerably higher than Th. <sup>232</sup>Th levels are lowest between 685 and 700 seconds, with moderate U levels, and was therefore selected for U-series dating.

#### RP004

Sample RP004 is from the stalagmite at the base of section 3 of WF 1 (Figure 2.2). U and Th levels vary greatly, despite the apparent lack of serious detrital contamination (Figure 4.2 C). The flowstone between 840 and 860 seconds has significantly elevated U and the lowest Th concentrations, and was selected for U-series.

#### RP005

Sample RP005 is from the flowstone capping unit Francinah in section 3 of the WF 1 (Figure 2.2). The sample consists of breccia and flowstone and therefore shows massive variation in U and Th values (Figure 4.2 D). U and Th levels are both considerably higher in the breccia than in the flowstone, and are at similar concentrations in the breccia, while the flowstone has much higher U values. The creamy layers around 260 seconds were selected for u-series dating as they display optimum low Th and high U values.

#### RP006

Sample RP006 is from the flowstone capping Francinah in the Peabody Chamber (Figure 2.2), so is stratigraphically the same layer as sample RP005. A combination of breccia and flowstone was lasered for this sample as well (Figure 4.2 E), and huge variations in U, Th and trace elements are seen, but not to the same extent as in RP005. There are flowstone pockets within the breccia layers, which display similar U and Th values as the flowstone, with low Th and significantly high U values. The opposite pattern is observed in the breccias, with slightly lower U and much higher Th. Massive Th peaks are associated with detrital contamination in the flowstones, with creamy calcite layers showing ideal Th and U levels, The layer between 640 and 690 seconds was selected for U-series dating.

#### RP009

Sample RP009 is from the small stalagmite growing on the flowstone at the base of unit SR (Figure 2.2) and consists of clean, creamy calcite (Figure 4.2 F). The U levels are reasonably low, and show major peaks with the creamier levels at 220 and 320 seconds. The Th values are very low, but do show significant peaks corresponding to the dirty layers. The creamy layer from 280 seconds onwards was selected for U-series.

#### Discussion

The U and Th values show good concordance with the measured U and Th concentrations summarised in Table 4.1. In general the U values are of the same order of magnitude for each sample, reflecting the similar ppb values. Sample RP009 has low U and a

correspondingly low measured U ppb of 23.2. RP001 has an anomalously high measured U ppb of 93.4, but reasonably low and highly varied U, suggesting some type of contamination of the solution sample to produce the 93.4 ppb.

The distinct U peaks and Th troughs associated with the calcite layers are due to the differential solubility of U and Th in groundwater – U is highly soluable, while Th is not (Freeze & Cherry, 1979). As a result the calcite layers have predictably high U values and low Th, while the breccias have high U and high Th values, as the Th is trapped in the clay particles within the soil. U and Th levels increase dramatically within the detritus rich layers, as it is probable that the clay minerals within the detritus will have introduced extra U and Th into the speleothem. There is good correlation between Th peaks and the detritus rich layers, meaning that the reasonably high <sup>232</sup>Th ppb of the samples can be avoided by picking layers with low Th values. Because of the generally low U ppb (average 45.9 ppb), layers with elevated U ratios were selected for U-series. These layers were also selected on the basis of no visible detritus and the lowest possible Th levels, and were almost exclusively the creamy calcite layers, except in sample RP001 and RP007 where clear layers met these criteria. The creamy nature of the low Th and high U layers is unusual (Hellstrom, pers. comm.), as in general clear layers are most suitable for U-series. The relationship between the creamy layers and high U is probably caused by organic matter and humic acids, which would give the flowstone the creamy appearance and account for the elevated U values, as the U is concentrated in humic acids in the soil above the cave (Hellstrom, pers. comm.).

## 4.3.2 Trace element distribution in Gladysvale flowstones

#### RP001

The trace element distributions in RP001 show distinct patterns (Figure 4.1 A). The Sr and Mg levels are much higher than the Ba levels, which is the case for all the samples. Ba tracks the <sup>238</sup>U values closely, except for the creamy layer between 650 and 800 seconds where there is a negative relationship between U and Ba. Sr also displays a positive relationship with U, although at much higher concentrations than Ba. Mg shows a negative relationship with Sr, except in the creamy layer from 650 to 800 seconds, where the Mg and Sr levels converge.

#### RP007

Mg and Sr levels are considerably higher than Ba, and remain very constant throughout the sample (Figure 4.1 B). There are slight variations in Mg and Sr and they show a negative relationship. Ba concentrations vary significantly and show a strong positive relationship with Th, with massive peaks corresponding to detrital layers. Ba also appears to have a positive relationship with Sr, but the Sr peaks are much smaller.

# RP004

Mg levels are high and stable, except for some disturbance around 820 seconds, which corresponds to the rim of the sample (Figure 4.2 C). Sr levels are slightly lower than other samples, are reasonably stable, and show a marked negative relationship with Mg. Ba levels are significantly lower than Mg and Sr, but vary greatly, and show a strong positive relationship with Th, with a massive peak at 900 seconds.

## RP005

As with the U and Th values, the trace elements show huge variation between the flowstone and breccia of sample RP005 (Figure 4.2 D). Mg levels are higher and more varied in this sample than in RP004, with troughs corresponding to a thin layer of calcite at 180 seconds and the creamier calcite layers around 260 seconds. Sr levels are relatively stable, with major peaks also corresponding to creamy layers at 260 seconds, showing a strong negative relationship with Mg. Ba values vary substantially, by four orders of magnitude between the breccia and flowstone. Ba levels are an order of magnitude higher than Th (unlike RP004), but still display a strongly positive relationship, with major peaks for the clearer calcite layers around 280 seconds.

## RP006

As in sample RP005, trace elements show a distinct difference between the breccia and flowstone lasered in this sample (Figure 4.2 E). The Mg levels are highly variable, and are an order of magnitude lower for the flowstone in this sample than in RP005. Sr levels are similar to other samples, and show the same strong negative correlation with Mg, with major troughs recorded for detritus-rich layers and the breccia. Ba levels are considerably lower than in sample RP005, but still show a strong positive relationship with Th, and have major troughs corresponding to flowstone layers, and peaks for breccia.

# RP009

Mg and Sr values are very homogenous and stable, with only a very weak negative relationship, which is mirrored by peaks in the U levels (Figure 4.2 F). Ba levels are very low and show a very positive relationship with Th, with peaks corresponding to detritus-rich layers.

# Discussion

Trace element distributions in speleothem calcite is a relatively new aspect of cave studies, and has great potential as a palaeoclimatic indicator. Studies of modern cave systems have aided significantly in understanding the forcing mechanism of various trace element concentrations (e.g. Treble *et al.*, 2003), which has allowed for better interpretation of the ancient systems. Numerous factors are believed to influence the trace element signature in speleothems, the most important being temperature, precipitation and residence time of water above the cave (Roberts, 1997 Roberts *et al.*, 1998; Hellstrom & McCulloch, 2000; Treble *et al.*, 2003). Mg, Sr and Ba are the most abundant trace elements in karstic ground waters (Freeze & Cherry, 1979), a feature clearly seen in the Gladysvale samples (Figures 4.1 and 4.2). The Mg and Sr levels within all the samples analysed do not show any major differences, and are essentially the same throughout the stratigraphy, indicating that there has been no change in the source of the groundwater feeding the cave system (Roberts, 1997).

The partition coefficient of Mg has been shown to be temperature related (Tesoriero & Pankow, 1996), and where sampling frequency is of sufficient resolution, variation is annual (Roberts, 1997; Roberts *et al.*, 1998). Mg levels in speleothems are also related to the residence time of the ground water in the cave roof – ground waters passing through dolomite reach saturation with respect to Ca reasonably quickly, but can still take up Mg (Freeze & Cherry, 1979; Roberts *et al.*, 1998), thus elevated Mg levels are an indication of increased residence time of ground water. Hellstrom & McCulloch (2000) further correlate increased

residence time with periods of reduced effective precipitation. Treble *et al.* (2003) argue further that the sensitivity of Mg to groundwater residence times is a function of the drip water Mg/Ca ratio, and that during dry periods Ca is preferentially lost as it precipitates out before reaching the stalagmite, thus elevating the Mg levels. Therefore, increased Mg levels are a combination of effects produced by drier periods of reduced effective precipitation.

The Mg levels in the Gladysvale samples are generally high, as expected with dolomitic ground waters (Freeze & Cherry, 1979). Mg levels are also relatively stable, with little variation in the samples of clean calcite (RP004 and RP009). There appears to be no relationship between detrital contamination and Mg levels, as RP001 and RP007 have distinct layers of detritus, but RP007 has very stable Mg values. RP001 shows the greatest variation in Mg values, with similar but less well developed variation in RP006. Mg variation occurs predominantly as troughs, and corresponds to the creamy layers of calcite. According to Hellstrom & McCulloch (2000), the lower Mg values indicate a decreased residence time of the ground water within the aquifer above the cave. Therefore, the creamy layer grew during periods of increased effective precipitation within the overall wet period, allowing for speleothem growth in the first place. The lack of real peaks in the Mg values is most likely due to the fact that if there was a decrease in effective precipitation speleothem growth would cease, and thus not record the elevated Mg levels in the ground waters. Samples RP004 and RP009 also consist of creamy calcite, but have stable Mg values, suggesting that there were no changes in the precipitation levels during the growth period.



Figure 4.3. The effect of temperature increase on trace element partitioning in speleothem calcite (Roberts, 1997)

Sr variation in calcite is related to changes in the amount of precipitation, with higher levels of precipitation resulting in elevated Sr levels (Tesoriero & Pankow, 1996). Roberts (1997) correlates increased temperatures with increased calcite precipitation rates, resulting in increased Sr levels, as shown in Figure 4.3. Treble *et al.* (2003) also correlate Sr with Ba (and

Na), which show increased values in relation to calcite growth rates. The interior of southern Africa wet periods are also warm (Holmgren *et al.*, 2003), so periods of increased precipitation should show increased Sr values, as the Gladysvale samples do. The strong positive relationship between Sr and Mg (Figures 4.1 and 4.2), even in samples RP007 and RP009, supports this. The Sr peaks are thus an independent measure of increased precipitation, suggesting that during periods of increased precipitation ground water is flushed through the aquifer above the cave, accounting for the trough in the Mg values. According to Treble *et al.* (2003), the increased Sr values also point to faster calcite growth rates.

Roberts (1997) argues that there is a positive relationship between Mg and Sr, because once the  $Mg^{2+}$  ion has substituted for the  $Ca^{2+}$ , it damages the crystal lattice sites, and makes space for the  $Sr^{2+}$  ion, which is otherwise too large to fit into the lattice (Figure 4.3). Thus an increase in Mg levels should be followed by an increase in Sr. However, this is not the case with the Gladysvale samples, where the relationship between Mg and Sr is negative. It is possible that this negative relationship is due to crystal zoning within the calcite, preferentially allowing for the uptake of Mg or Sr (Hellstrom, pers. comm.).

Barium concentrations are also temperature related, in as much as greater temperatures cause increased calcite precipitation and increased barium levels (Roberts *et al.*, 1998) (Figure 4.3). Sample RP001 shows this, in that the Ba shows a strong positive relationship with Sr. However this relationship is restricted to RP001, as all the other samples display either no relationship with Sr (RP007, RP004 and RP009), or a weak negative relationship, which is restricted to a few Ba peaks (RP005 and RP006). In all the samples except RP001, Ba has an extremely strong relationship with Th, and tracks the Th values with no deviation. Barium is immobile in soil (McBride, 1994). The peaks in Ba and Th correspond with detritus-rich layers, suggesting that these elements have been brought in with the detrital material. According to Moriarty *et al.* (2000), detritus in speleothems is related to caves being slightly open, allowing for material to be brought in during slightly drier phases.

The trace element data for the Gladysvale speleothems would be greatly augmented by similar data from the host dolomites and the regional ground waters. This was, however, beyond the scope of this study. Nevertheless, the results from this small study are encouraging and this is an area that would benefit greatly from further research.

# 4.4 Uranium series

Clean layers of flowstone, identified through laser ablation, were mechanically and chemically prepared according to the protocols developed by Stirling *et al.* (1995), as described in Chapter 2. Solutions were analysed by a Neptune Multi Collector Inductively-Coupled Plasma Mass Spectrometer (MC-ICP-MS). Summarised data are presented in Tables 4.3 and 4.4. Footnotes to these Tables explain how the data were generated.

# 4.4.1 U ppm

Uranium concentrations for half of the samples (Table 4.3) were surprisingly higher than previously measured (Table 4.1). Only samples RP002, RP007, RP008, RP009 and RP004 produced expected uranium concentrations of ~0.040 ppm (~40 ppb), with the remaining samples yielding uranium concentrations from 0.106 ppm (RP010) to 0.740 ppm (RP005), which is at most an increase of 0.700 ppm. These massive differences between uranium values from the initial background screening and the final solutions are most likely due to the addition of U into the solution during the chemical preparation of the samples. Samples RP003, RP005, RP006 and RP010 all also have low <sup>230</sup>Th/<sup>232</sup>Th activity ratios, indicating significant contamination of a <sup>232</sup>Th rich detrital phase. Contained with the detrital phase is additional <sup>234</sup>U, which may account for the extra U in these samples and would have been released from the detrital phases during chemical preparation. Extreme care was taken during the mechanical and chemical preparation of the samples to avoid detritus.

Schwartz (1989) considers only activity ratios of below 20 problematic, and only samples RP003 and RP006 fulfil this condition, with  $^{230}$ Th/ $^{232}$ Th activity ratios of 16 and 3 respectively. Samples RP005 and RP010 have much higher  $^{230}$ Th/ $^{232}$ Th activity ratios of 165 and 169 respectively, but still have increased U ppm, indicating that although activity ratios of 165 and 169 are within accepted values, there is still considerable detrital contamination. However, sample RP007 has the second lowest  $^{230}$ Th/ $^{232}$ Th activity ratios of 5, but produced a U ppm of 0.017, which is considerably *lower* than the initial 0.048 ppm for this sample.

Sample	U ppm <sup>a</sup>	<sup>230</sup> Th ppt	( <sup>234</sup> U/ <sup>238</sup> U) <sub>0</sub> <sup>b</sup>	( <sup>230</sup> Th/ <sup>238</sup> U) <sup>d</sup>	( <sup>230</sup> Th/ <sup>232</sup> Th)	Age (ka) <sup>e</sup>	Initial <sup>f</sup> ( <sup>234</sup> U/ <sup>238</sup> U)⊤
RP 003	0.214	0.393	1.6215 (1.0022) <sup>c</sup>	0.1127 (0.0004) <sup>c</sup>	16	7.804 (0.027) <sup>c</sup>	1.6354 (1.0022) <sup>c</sup>
RP 002	0.022	0.063	1.5710 (1.0018)	0.1780 (0.0009)	3	12.984 (0.070)	1.5924 (1.0018)
RP 005	0.740	2.526	1.6810 (1.0034)	0.2100 (0.0007)	165	14.385 (0.057)	1.7093 (1.0034)
RP 006	0.424	1.981	2.0193 (1.0017)	0.2876 (0.0024)	65	16.501 (0.152)	2.0681 (1.0018)
RP 007	0.017	0.156	1.5197 (1.0016)	0.5676 (0.0022)	5	49.397 (0.239)	1.5978 (1.0017)
RP 008	0.050	0.530	1.5461 (1.0020)	0.6459 (0.0030)	1122	56.766 (0.354)	1.6414 (1.0023)
RP 010	0.106	2.366	1.4062 (1.0013)	1.3759 (0.0038)	169	255.297 (2.510)	1.8377 (1.0054)
RP 001	0.342	7.063	1.2647 (1.0019)	1.2694 (0.0039)	1520	307.516 (4.809)	1.6329 (1.0076)
RP 009	0.025	0.630	1.4260 (1.0014)	1.5384 (0.0038)	226	393.030 (7.584)	2.2982 (1.0259)
RP 004	0.099	2.444	1.3758 (1.0012)	1.5237 (0.0031)	196	571.380 (24.902)	2.8986 (1.1322)

Table 4.3. Uranium series data for Gladysvale flowstones

Table 4.4. Corrected uranium series data for Gladysvale flowstones

Sample	Age (kyr) <sup>e</sup>	Initial <sup>f</sup> ( $^{234}$ U/ $^{238}$ U) <sub>T</sub>	Corrected Age <sup>g</sup> (ka)	Corrected Initial <sup>h</sup> ( <sup>234</sup> U/ <sup>238</sup> U) <sub>T</sub>
RP 003	7.804 (0.0270) <sup>c</sup>	1.6354 (1.0022) <sup>c</sup>	7.45 (0.35) <sup>°</sup>	1.6348 (1.0023) <sup>c</sup>
RP 002	12.984 (0.070)	1.5924 (1.0018)	10.32 (2.68)	1.5879 (1.0048)
RP 005	14.385 (0.057)	1.7093 (1.0034)	14.33 (0.08)	1.7092 (1.0035)
RP 006	16.501 (0.152)	2.0681 (1.0018)	16.33 (0.23)	2.0676 (1.0019)
RP 007	49.397 (0.239)	1.5978 (1.0017)	42.82 (6.77)	1.5868 (1.0114)
RP 008	56.766 (0.354)	1.6414 (1.0023)	56.74 (0.35)	1.6414 (1.0023)
P 010	255.297 (2.510)	1.8377 (1.0054)	254.95 (2.57)	1.8368 (1.0057)
RP 001	307.516 (4.809)	1.6329 (1.0076)	307.46 (5.15)	1.6329 (1.0079)
RP 009	393.030 (7.584)	2.2982 (1.0259)	392.83 (97.3)	2.2976 (1.0253)
RP 004	571.380 (24.902)	2.8986 (1.1322)	571.57 (25.84)	2.9008 (1.1374)

<sup>a</sup> Uranium concentrations determined through isotope dissolution

<sup>**b**</sup> Measured activity ratio,  $(^{234}U/^{238}U)_0 = (^{234}U/^{238}U)/(\lambda^{238}U/\lambda^{234}U)$ , where  $\lambda^{238}U$  and  $\lambda^{234}U$  are the decay constants for <sup>238</sup>U and <sup>234</sup>U respectively.

 $^{\boldsymbol{c}}$  Two  $\sigma$  errors (in parentheses) fully propagated by Monte Carlo simulation

<sup>d</sup> Measured activity ratio,  $({}^{230}\text{Th}/{}^{238}\text{U}) = ({}^{230}\text{Th}/{}^{238}\text{U})/(\lambda {}^{238}\text{U}/\lambda {}^{230}\text{Th})$ , where  $\lambda {}^{238}\text{U}$  and  $\lambda {}^{230}\text{Th}$  are the decay constants for  ${}^{238}\text{U}$  and  ${}^{230}\text{Th}$  respectively.

<sup>e</sup> MC-ICP-MS dates, expressed as 1000s of years before present (ka).

<sup>f</sup> Initial  $(^{234}U/^{238}U)$  activity ratio, calculated by  $(^{234}U/^{238}U)_T = 1 + \{[(^{234}U/^{238}U)-1]_0e^{\lambda 234UT}\}$ , where T is age in years

<sup>**g**</sup> Ages recalculated to account for the effect of detrital Th, assuming an original <sup>230</sup>Th/<sup>232</sup>Th activity of  $0.75 \pm 0.75$  for the detrital phase. Corrected ages (in bold) are used only when there the correction is significant, as the correction introduces addition assumptions to the dating technique.

<sup>h</sup> Corrected initial ( $^{234}U/^{238}U$ ) activity ratio, using corrected ages.

The <sup>234</sup>U/<sup>238</sup>U activity ratios do not add any clarity to the extra U problem, as the activity ratios for the samples in question fall within the range of variability displayed by the whole sample set. It is possible that the final solutions U ppm are higher than those of the initial solutions, as the final solutions were chemically prepared in order to concentrate the U in them, but this still does not fully explain the massive difference. Machine discrepancies and longer measurement times during the run of the final solutions also cannot fully account for the differences. There had also been problems with the Neptune's plasma at the time the initial solutions were run, and solutions may not have been ionised to their full extent, producing lower U values. It is not possible to isolate any one of these factors as the cause of the higher U values, and it is concluded that some combination of these factors, and presently unknown factors (such as those responsible for the low U but high <sup>230</sup>Th/<sup>232</sup>Th activity ratios of sample RP007), is responsible for the increased U ppm in the final solutions.

# 4.4.2 $^{230}$ Th/ $^{238}$ U ages

Ages were calculated using the activity ratio of <sup>230</sup>Th/<sup>238</sup>U and the measured <sup>234</sup>U/<sup>238</sup>U activity ratios. In the literature some U-series ages are calculated using the <sup>230</sup>Th/<sup>234</sup>U ratio instead of the <sup>230</sup>Th/<sup>238</sup>U (e.g. Kaufman *et al.*, 1998). <sup>230</sup>Th/<sup>234</sup>U and <sup>230</sup>Th/<sup>238</sup>U ratios are mathematical equivalents of each other, and the <sup>230</sup>Th age of a sample can be expressed as either. <sup>230</sup>Th/<sup>234</sup>U ratios are used when isotopes are measured using alpha spectrometry, while measurements made using mass spectrometry tend to use <sup>230</sup>Th/<sup>238</sup>U ratios. As isotopes were measured using an ICP-MS in this study, ages are reported using <sup>230</sup>Th/<sup>238</sup>U ratios.



Figure 4.4. Photograph (A) and line drawing (B) of the Western Face 1 showing five of the Gladysvale U-series dates (yellow circles) in their stratigraphic context (white circles are stable light isotope sample points).

The U-series ages of the speleothems at Gladysvale are in perfect stratigraphic order (Figure 4.4) and proved the deposit to be both older and younger than the expected 200-250 kyr age from the preliminary ESR results (Curnoe, 1999; Schmid, 2002). The errors on the uncorrected samples without significant detrital contamination are very low, and are well below 1000 years for the younger samples. Errors increase with the age of the samples, but are still comparably low. Sample RP004 has an age of 571.380 ka, which is approaching the maximum limit of U-series, but shows that with high precision mass spectrometry, such as the Neptune, ages of up to 600 ka can be measured.

# 4.4.3 $^{230}$ Th/ $^{232}$ Th activity ratios and age corrections

The basic assumption behind U-series dating is that the system contains no <sup>230</sup>Th at the time of formation, and that any measured <sup>230</sup>Th is the daughter product of the in situ decay of <sup>234</sup>U. However, in natural systems this is not always the case. The amount of extra <sup>230</sup>Th in a sample can, however, be gauged through the activity ratio of <sup>230</sup>Th/<sup>232</sup>Th. The predominant source of extra <sup>230</sup>Th is in sedimentary detritus, which becomes included in the speleothem, and introduces <sup>232</sup>Th, which can be used to trace the otherwise indiscernible addition of <sup>230</sup>Th. If the measured <sup>230</sup>Th/<sup>232</sup>Th activity ratios are greater than 20 (Schwarcz, 1992), the detrital contamination is considered negligible.

There is considerable detrital contamination in some of the samples, especially RP003, RP001 and RP007, which have measured <sup>230</sup>Th/<sup>232</sup>Th activity ratios (Table 4.3) of below 20. In these cases, a correction of the age must be made, based on the <sup>232</sup>Th present in the sample and on an assumed <sup>230</sup>Th/<sup>232</sup>Th activity ratios (such as Dorale *et al.*, 1992). This form of correction is not ideal, as the degree of <sup>238</sup>U and <sup>234</sup>U contamination in the detritus is not addressed (Hellstrom, 1998), and a better form of correction is the construction of isochrons (Bischoff & Fitzpatrick, 1991). However, in this study each sample was run only once, making it impossible to construct isochrons. Without some type of correction, ages are overestimated because of the additional <sup>230</sup>Th, so some type of correction is needed. Corrections were made for all samples (Table 4.4), by recalculating ages using an assumed initial <sup>230</sup>Th/<sup>232</sup>Th activity ratio of 0.75  $\pm$  0.75, which covers the range of all observed initial <sup>230</sup>Th/<sup>232</sup>Th activity ratios in speleothems (Hellstrom, pers. comm.).

All samples produce younger ages after correction (Table 4.4). Samples which show the greatest difference are also those which had higher than expected U ppm, suggesting that detrital contamination is contributing significantly to the elevated U levels in these samples. The corrected ages of samples RP003, RP001 and RP007 are considerable younger than the uncorrected ages (Table 4.4) and the errors on the ages have also increased considerably. RP003 has an <sup>230</sup>Th/<sup>232</sup>Th activity ratio of 16 and is the least affected by the correction. confirming that once <sup>230</sup>Th/<sup>232</sup>Th activity ratios approach 20, the detrital contamination is negligible. Sample RP002 has the highest detrital contamination with a <sup>230</sup>Th/<sup>232</sup>Th activity ratio of 3 and the age correction is significant in this relatively young sample, with a shift from the uncorrected age of 12.984 kyr to a corrected age of 10.32 kyr. The errors on this sample are a large 2.68 kyr. Ideally RP002 should be re-sampled and re-run, but this was not possible in context of this study. Sample RP007 has the second lowest <sup>230</sup>Th/<sup>232</sup>Th activity ratio of 5, and the corrected age of  $42.82 \pm 6.77$  kyr is a massive ~7 kyr younger than the original age of  $49.397 \pm 0.239$ . As already discussed, this sample is somewhat enigmatic, as the U ppm is extremely low (0.017 ppm). Once again, ideally, RP007 should be re-sampled and re-run to determine if this age is repeatable.

Corrected ages have a built-in assumption of the original <sup>230</sup>Th/<sup>232</sup>Th activity ratio of the contaminating phase, and thus add extra uncertainty to the ages. Because of this, the corrected ages are not used in this dissertation, except for samples RP003, RP001 and RP007 where it is clear that correction of the detrital contamination is necessary.

4.4.4 Initial  $^{234}$ U/ $^{238}$ U activity ratios

In an undisturbed sample of at least 5 Ma, the unstable isotopes <sup>234</sup>U, <sup>238</sup>U and <sup>230</sup>Th will be in secular equilibrium, and will all be decaying at the same rate, giving them all the same activity ratio. Once secular equilibrium has been reached, the measured <sup>234</sup>U/<sup>238</sup>U ratio will be 1. The formation process of speleothems disturbs this equilibrium by removing the insoluble <sup>230</sup>Th from solution, and setting up the U-series disequilibrium, which is used to date speleothems (Ivanovich, 1982), as already discussed. The disequilibrium present in speleothems at their time of formation also reflects the <sup>234</sup>U/<sup>238</sup>U disequilibrium in the natural groundwaters feeding the cave. The <sup>234</sup>U/<sup>238</sup>U activity ratio is not 1 in ground waters as a result of the increased mobility of <sup>234</sup>U in the weathering of the host rocks (Gascoyne, 1982), which adds extra <sup>234</sup>U to the ground waters, thereby raising the activity ratio of <sup>234</sup>U/<sup>238</sup>U

above 1. There is some debate as to the cause of the increased mobility of  $^{234}$ U. Originally Cherdynstev *et al.* (1965) argued that the increased mobility of  $^{234}$ U is due to the presence of extra  $^{234}$ U in the host mineral, occupying sites in the crystal lattice damaged by emission of  $\alpha$  and  $\beta$ -particles emitted by the  $^{238}$ U parent. Osmond and Cowart (1982) later argued that the alpha recoil of  $^{234}$ U in solution is a more important factor in understanding the source of the extra  $^{234}$ U.

Therefore initial  ${}^{234}$ U/ ${}^{238}$ U values are of interest as they reflect the groundwater conditions in the host rock at the time of speleothem formation, and changes in the activity ratio of  ${}^{234}$ U/ ${}^{238}$ U will in turn reflect changes in this ground water system over time. Changes in the groundwater system are most likely driven by climatic change, making the initial  ${}^{234}$ U/ ${}^{238}$ U ratios potentially interesting palaeoenvironmental proxies (Gascoyne, 1982; Kaufman *et al.*, 1998). The initial activity ratio of  ${}^{234}$ U/ ${}^{238}$ U is back calculated for all the samples using the measured age of the samples (Table 4.4, see footnotes of Table 4.4 for equation used to calculate initial  ${}^{234}$ U/ ${}^{238}$ U). For samples RP003, RP001 and RP007 the corrected initial  ${}^{234}$ U/ ${}^{238}$ U ratios are used. Initial and corrected initial  ${}^{234}$ U/ ${}^{238}$ U ratios are plotted against age in Figure 4.5.



Figure 4.5. Initial and corrected  ${}^{234}U/{}^{238}U$  activity ratios against age (ka) of the Gladysvale flowstones. Rough trend lines in  ${}^{234}U/{}^{238}U$  ratios are indicated by dashed dark blue line.

The initial  ${}^{234}\text{U}/{}^{238}\text{U}$  ratios for the Gladysvale samples are all well above 1, with an average value of 1.889. There is an overall trend towards higher initial  ${}^{234}\text{U}/{}^{238}\text{U}$  ratios with age, as illustrated by Figure 4.5. This trend most likely indicates a slow reduction in the excess  ${}^{234}\text{U}$  available in the source rocks.  ${}^{234}\text{U}$  is preferentially extracted from host rocks by groundwaters, and the reduction of  ${}^{234}\text{U}$  may just represent a slow depletion of the easily extracted  ${}^{234}\text{U}$  from the source rocks.

The changes in initial  ${}^{234}$ U/ ${}^{238}$ U ratios with time of the Gladysvale samples can therefore be explained without changes in the palaeoenvironmental controls on the groundwater system. Kaufman *et al.* (1998) however argue that in low rainfall regimes, such as in Israel, the initial U composition of the groundwater is a reflection of changes in the discharge rate of cave drip waters, which are directly controlled by the local soil and moisture conditions (Kaufman *et al.*, 1998). Kaufman *et al.* (1998) also argue that in low rainfall areas, the initial  ${}^{234}$ U/ ${}^{238}$ U ratios may be more significantly affected by the amount of U removed from the soil above the cave than by the dissolution of U from the country rock.

South Africa is, in general, a low rainfall area (Tyson, 1986) and using the argument of Kaufman *et al.* (1998), the initial  $^{234}U/^{238}U$  ratios at Gladysvale can be interpreted as only very general rainfall indicators. The oldest samples, 571 ka and 393 ka yield high initial  $^{234}U/^{238}U$  ratios, with a steady decrease until 255 ka, where there is a slight increase, followed by a decrease until 42 ka. Then there is an increase in the initial  $^{234}U/^{238}U$  ratio at 16 ka, followed by a decrease in values until 10 ka, with a sudden increase at 7.4 ka (Figure 4.5). These data could relate to change in the rainfall regime of the area, with high values suggesting low rainfall (Kaufman *et al.*, 1998) and lower values suggesting increased rainfall. Therefore these data may indicate that this area had relatively low rainfall in the mid Pleistocene, with a slow increase in rainfall until 255 ka, when rainfall levels dropped. This was then followed by a second gradual increased in rainfall until the late Pleistocene. Rainfall levels dropped dramatically at 16 ka, and then increased steadily into the early Holocene, with a slight drop at 7.4 ka. This explanation of the variation in the  $^{234}U/^{238}U$  data will be discussed further later, but it is very general, and more  $^{234}U/^{238}U$  and age data are needed to make any firm palaeoenvironmental interpretations.