

Research paper

# U–Pb geochronology of speleothems by MC-ICPMS

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Received 1 February 2006; received in revised form 2 July 2006; accepted 2 August 2006

## Abstract

Building upon the work of Richards et al. [1998. U–Pb dating of a speleothem of Quaternary age. *Geochimica et Cosmochimica Acta* 62, 3683–3688], we have developed a method for precise dating of speleothems beyond the range of the U–Th technique using the U–Pb decay scheme. By coupling low-blank sample preparation procedures and multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS) analytical methodologies developed for low-level Pb-isotope analysis, we find that, under ideal circumstances (radiogenic speleothems with very low common Pb), U–Pb dating of speleothems is not only possible, but also produces excellent age resolution—often comparable to or better than U–Th studies. Corrections for initial isotopic disequilibrium are necessary and exert a strong control on the achievable age uncertainty.

The technique will be of immediate benefit in extending speleothem-based climate proxy records beyond ~500 ka and will also find other uses, such as the dating of associated sub-fossil remains, and providing constraints on rates of landscape evolution and neo-tectonic processes. Here we present initial results for speleothems from the Nullarbor Plain, Western Australia, and the Alpi Apuane, Italy. The Nullarbor samples provide important new constraints on the development of aridity in Australia during the late Tertiary/early Quaternary, while the Apuane samples offer insights into the landscape history and uplift of that region.

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**Keywords:** Speleothem; U–Pb; U-series; MC-ICPMS; Disequilibrium; Palaeoclimate

## 1. Introduction

Speleothems—stalagmites, flowstones and other cave deposits—are widely used archives of palaeoclimate variation and have yielded some remarkable insights into palaeoclimatic conditions during the late Quaternary (e.g., Ayliffe et al., 1998; Bar-Matthews and Ayalon, 1997; Drysdale et al., 2005; Genty et al., 2003; Yuan et al., 2004). A variety of speleothem properties are proxies for mean annual temperature, rainfall, and surface vegetation (McDermott, 2004) and this information is recorded in successive growth layers, often with annual resolution (e.g., Roberts et al., 1998). Speleothems can respond rapidly to

changing climatic conditions and may remain very well preserved for many millions of years. Uses other than palaeoclimate proxies are also being investigated such as indicators of flooding, seismicity and human occupation (Richards and Dorale, 2003).

While speleothems undoubtedly carry a wealth of important data, a major contributor to their success is their suitability for dating by U-series analysis. The U–Th decay scheme is a highly robust dating method for carbonate materials up to ~half a million years in age, but beyond this time, the value of speleothems is currently limited by a lack of appropriate chronometers. The U–Pb decay scheme offers the possibility to significantly extend the use of speleothems in palaeoclimate and other studies back many millions of years. Since the pioneering study by Richards et al. (1998) of a Quaternary speleothem from

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Winnats Head Cave, UK, however, very few speleothem groups have reported success with the U–Pb technique (e.g., Lundberg et al., 2000; Cliff, 2001).

Potential problems which have hampered the development of this method are likely twofold and stem from: (a) analytical challenges intrinsic to the measurement of the extremely low Pb contents often observed in such materials; and (b) the difficulty in obtaining a range in parent/daughter ratios for isochron construction without encountering variable initial (so-called ‘common’) Pb. The analytical problem is largely related to the need to process samples larger than ~0.1 g in order to obtain sufficient Pb for analysis when, generally speaking, analytical blanks often increase in proportion to the amount of sample being processed. For analysis by thermal ionisation mass spectrometry (TIMS) methods, purity of the Pb separate is also an important consideration since incomplete separation of matrix materials from the sample Pb of interest can result in unpredictable mass fractionation behaviour on the filament or, in the worst case, poisoning of the silica-gel activator, resulting in poor ionisation (e.g. Woodhead et al., 1995). Finally, the Pb isotope system has always presented a special analytical case since internal correction for instrumental mass bias is not possible, and thus usually requires some form of external normalisation. The advent of MC-ICPMS instrumentation has provided a suitable alternative to TIMS for high-precision Pb-isotope analysis. More efficient ionisation in the ~8000 K plasma reduces the need for stringent sample preparation, which, in turn, allows for lower processing blanks and higher throughput. This technology has much to commend its use in speleothem U–Pb geochronology, and our preliminary experiences in this regard are documented in this contribution. The second problem—that of variable common Pb—is largely a sampling issue and thus one which may ultimately find resolution as we learn more about the U–Pb systematics of speleothems. In this contribution, we make some broad observations, which might allow more focussed sampling strategies in future.

## 2. Samples studied and analytical methodology

### 2.1. Speleothem samples

Here we present data for several different speleothems from two regions in order to illustrate the potential utility of the technique (detailed discussion of the results, together with additional data, will be presented in other publications). The first samples come from Leana’s Breath Cave, a small cavern immediately south of Old Homestead Cave beneath the arid Nullarbor Plain of Western Australia. The Nullarbor Plain is one of the largest karst regions in the world at ~200 000 km<sup>2</sup> in area. It is a flat-lying area of shallow marine limestones, which were exposed some 15 million years ago due to a combination of uplift and global lowering of sea level. Despite an arid to semi-arid climate, lack of surface streams and little relief, satellite-derived

digital terrain data show clear evidence of ancient river channels and other landforms indicative of significantly higher rainfall at periods in the past. Large, organic-rich speleothems interpreted as having formed beneath forest and/or swamp vegetation are widespread in caves beneath the plain, and until now have only been shown to be older than the ca. 350 ka maximum age limit of alpha spectrometric U–Th dating (Goede et al., 1990). MC-ICPMS U–Th analyses from our laboratory (Hellstrom, unpublished data) have found some limited calcite deposition in the period 350 to ~500 ka, but confirmed that the majority of Nullarbor speleothems are within measurement uncertainty of secular equilibrium and thus beyond the limit of mass spectrometric U–Th dating. In addition, Caldwell et al. (1982) have observed that the dark brown colouration of many old Nullarbor speleothems is due to organic compounds, suggesting more effective leaching of organic soil matter (hence higher rainfall) at the time of their deposition. The palaeoclimatic importance of these samples then lies in their potential to provide insights into the timing of the onset of Australian aridity during the late Tertiary and early Quaternary.

An additional sample was obtained from a stalagmite (CC16) from Antro del Corchia, a large cave system situated in the Alpi Apuane massif of northern Tuscany, Italy. The Apuane massif rises abruptly above the Tyrrhenian coastal plain and is largely composed of steeply dipping Mesozoic marbles and metadolostones. It is heavily karstified, with over a thousand known caves (Piccini et al., 2003). Stalagmite CC16 was collected from the upper level of a large, well-decorated chamber (Galleria delle Stalattiti) ca. 500 m from the nearest cave entrance. This upper level consists of a stalagmite-covered flowstone sheet which mantles the remnants of a clastic sedimentary deposit laid down during periodic flooding in the chamber’s evolution. Subsequent excavation of the clastics has produced a false floor, which separates the upper level from the lower one. The stalagmite was one of several broken pieces prised from the upper flowstone surface using a chisel. The sample is inferred to be close to its growth position and not moved by cavers because the piece was strongly cemented in place, its external surface is similar to in situ stalagmites (e.g. nodules developed preferentially on one side) and because of the chamber’s geomorphic setting. It is one of a wide variety of stalagmites collected from Corchia whose ages range from 0.5 ka to beyond 500 ka. Initial research has shown the cave (present-day mean annual temperature 7.5 °C) to be sensitive to the severity of Pleistocene glaciations. Variations in  $\delta^{18}\text{O}$  from younger speleothems in the same chamber (Drysdale et al., 2004, 2005) show a close structural similarity to the Vostok ice-core palaeotemperature record (Petit et al., 1999) and regional sea-surface temperatures (Martrat et al., 2004). This may stem from the site’s sensitivity to North Atlantic climate, which is linked to Southern Ocean circulation via the global oceanic conveyor belt (Broecker, 1997).

## 2.2. Sampling and U–Pb analytical methods

Speleothems were sawn into ~5–10 mm thick slabs and from these sub-samples were cut, where possible, from single growth bands with the aid of a dental drill. Individual sample sizes were in the 100–250 mg range, providing between 150 pg and 2.8 ng of Pb, depending on Pb content (see Table 1). After extraction from the speleothem, sub-sample surfaces were cleaned by repeated ultrasonication in 0.5 M HCl, followed by washing in ultrapure water. Samples were then dried and weighed. All material handling subsequent to cutting was conducted in a multiple-HEPA-filtered environment, and all acids utilised in the dissolution and chemical extraction of Pb were (as a minimum) twice distilled in either quartz or Teflon stills. Following Woodhead and Hergt (1997), samples were placed in new, cleaned 30 ml TPX<sup>®</sup> polymethylpentene beakers with ~1 ml of ultrapure water, and dissolved by dropwise addition of 6 M HCl. After complete dissolution (no residues were observed in any of these samples), sample solutions were aliquoted for spiking, using either mixed <sup>235</sup>U–<sup>208</sup>Pb (initial studies) or <sup>233</sup>U–<sup>205</sup>Pb (current work) tracers. Pb and U were purified using conventional anion-exchange chemistry with HBr/HCl media (employing a single column pass only to reduce blank contributions), and EICHRON TRU-resin with HNO<sub>3</sub>/HCl/HF media respectively (Manhes et al., 1978; Luo et al 1997). Total processing blanks were 5–15 pg Pb and <5 pg U; a value of 10 ± 5 pg has been used for the former in the blank subtraction calculations.

Isotopic analyses were carried out on a Nu Plasma MC-ICPMS coupled to a Cetac Aridus desolvation system with a Glass Expansion OpalMist nebuliser (uptake rate ~40 µl/min). At a typical sensitivity of 100–120 V/ppm, Pb samples, dissolved in 0.5 ml of 0.3 M HNO<sub>3</sub>, yielded total Pb signals upwards of 4 × 10<sup>-13</sup> A (40 mV) for a 200 pg sample size, allowing <sup>205</sup>U, <sup>206</sup>U, <sup>207</sup>U, <sup>208</sup>Pb to be measured on Faraday cups (Hg-corrected <sup>204</sup>Pb data were also collected routinely but are not used in isochron construction as documented below). For our initial studies, which employed a <sup>208</sup>Pb tracer, instrumental mass bias was corrected using a variant of the popular Tl-doping technique as described in Woodhead (2002), but with baselines measured by the so-called ‘on-peak-zero’ method. This technique, in which baselines are measured prior to sample introduction on the masses of interest (e.g. *m/z* = 208, 207, 206, 205, 205, etc.), rather than at half mass position, is particularly suitable to MC-ICPMS measurements where backgrounds are compromised by significant contributions from the carrier gases, e.g. Kr on the Sr spectrum or, in this case, Hg on the Pb spectrum. The method also effectively minimises any errors relating to Pb memory in the sample introduction system (which are usually negligible). In later studies (and our current method), we have introduced a <sup>205</sup>Pb tracer and thus the correction for mass bias using <sup>205</sup>Tl–<sup>203</sup>Tl is no longer possible. As an alternative, we correct these analyses by reference to external standards, in

a manner similar to TIMS analysis (but with much improved data since mass bias variation in MC-ICPMS is greatly reduced). This change in protocol was based upon the observation that, at least for radiogenic samples, the error attributable to the mass bias correction is only a minor component of the overall analytical uncertainty, and the fact that use of a <sup>233</sup>U–<sup>205</sup>Pb tracer would simplify and speed up the analytical process. One drawback of this approach, however, for laboratories running a variety of different sample types, is the need to completely separate the sample introduction systems used for (<sup>205</sup>Pb spiked) radiogenic Pbs from those running (Tl-spiked) common Pbs to avoid any issues relating to instrument memory.

As in all small radiogenic Pb samples, <sup>204</sup>Pb is ≪1% atomic proportion and thus must be measured on an ion-counter. Unfortunately, the interference correction for <sup>204</sup>Hg (an impurity in the Ar carrier gas of the ICP) makes <sup>204</sup>Pb difficult to determine accurately at these levels. Although there has been some progress in dealing with the Hg interference (e.g., for laser ablation U/Pb zircon geochronology; Horstwood et al., 2003), the analytical challenge remains considerable. For the more radiogenic samples in this study, the counts observed on mass 204 are the equivalent of only a few hundred femtograms and, of this, the <sup>204</sup>Hg interference may contribute tens of percent. In order to correct for such an interference requires a detailed knowledge of the relative gain on two ion counters, its short and long-term stability, and the mass bias for the Hg transported by the carrier gas. These are not insurmountable issues but, in the case of many organic rich speleothems, we also observe that significant Hg can also be contributed from the sample itself and, in this case, the Hg mass bias is impossible to determine (since the signal is never seen in isolation). Given these demands and the extremely small size of the signal to be measured, we consider isotope ratios involving <sup>204</sup>Pb to be unreliable for dating purposes.

U isotope dilution analyses were initially performed with mass bias correction by standard bracketing, using the SRM 960 and U500 standards. Measured <sup>238</sup>U/<sup>235</sup>U for these standards varied by <0.02% (1σ) during any given analytical session and ratios for unknowns are considered accurate to this level. Subsequently use of a <sup>233</sup>U tracer allowed the natural <sup>238</sup>U/<sup>235</sup>U in the sample to be used for internal bias correction. For some samples the <sup>234</sup>U/<sup>238</sup>U activity ratio, denoted [<sup>234</sup>U/<sup>238</sup>U], was determined on a sub-sample of the same growth layer, using the U–Th method of Hellstrom (2003). Initial <sup>234</sup>U/<sup>238</sup>U ratios were calculated using the following:

$$[{}^{234}\text{U}/{}^{238}\text{U}]_i = 1 + ([{}^{234}\text{U}/{}^{238}\text{U}]_m - 1)e^{\lambda^{234}t},$$

where square brackets indicate the activity ratio, subscripts *i* = initial, *m* = measured, *t* = time in years, and  $\lambda^{234}$  is the decay constant for <sup>234</sup>U, for which we used a value of 2.835E–6. Blank correction and isochron construction were performed using the data reduction software PBDAT

Table 1  
U and Pb data for the samples considered in this study

Sample ID	Sample mass (g)	$^{238}\text{U}/^{206}\text{Pb}$	Per cent error ( $2\sigma$ )	$^{207}\text{Pb}/^{206}\text{Pb}$	Per cent error ( $2\sigma$ )	$^{208}\text{Pb}/^{206}\text{Pb}$	Per cent error ( $2\sigma$ )	$^{238}\text{U}/^{204}\text{Pb}^{\text{a}}$	U ( $\mu\text{g g}^{-1}$ )	Pb ( $\text{ng g}^{-1}$ )	Total Pb (pg)	Per cent radiogenic Pb	$[\text{}^{234}\text{U}/\text{}^{238}\text{U}]^{\text{b}}$
<i>Nullarbor, Leana's Breath Cave</i>													
LBC-MO1-1	0.269	1607	0.38	0.103	5.73	0.143	10.2	416 910	1.44	0.96	259	77	$1.0025 \pm 0.0021$
LBC-MO1-2	0.210	1719	0.32	0.052	22.80	0.010	300	3 893 700	1.33	0.71	148	98	
LBC-MO1-3	0.256	1530	0.31	0.140	5.53	0.238	8.11	245 260	1.20	0.93	239	67	
LBC-MO1-4	0.271	1722	0.36	0.053	6.49	0.012	70	5 159 300	1.40	0.74	201	98	
LBC-MO1-5	0.157	926	0.31	0.426	1.03	0.979	1.09	36 026	1.35	3.06	480	22	
LBC-MO1-6	0.269	1723	0.34	0.051	15.00	0.009	203	14 802 000	1.26	0.67	179	100	
LBC-MO1-7	0.245	1700	0.32	0.062	0.21	0.035	0.48	1 535 300	1.31	0.73	178	93	
LBC-MO5-1	0.209	1447	0.34	0.137	6.89	0.000	9.27	224 120	1.13	0.94	196	66	$1.0012 \pm 0.0023$
LBC-MO5-2	0.229	900	0.31	0.290	1.37	0.662	1.45	52 485	1.09	2.06	472	35	
LBC-MO5-3	0.149	1263	0.33	0.184	5.05	0.380	6.01	128 770	1.20	1.29	192	54	
LBC-MO5-B	0.130	1041	0.38	0.350	1.10	0.770	1.24	50 783	2.02	3.58	466	29	$1.0005 \pm 0.0026$
LBC-MO5-C	0.136	1393	0.32	0.167	3.95	0.309	5.34	170 230	1.91	1.75	239	59	
LBC-MO5-D	0.115	883	0.31	0.435	0.77	0.983	0.85	33 511	1.87	4.46	511	20	
LBC-MO5-E	0.083	1132	0.36	0.293	3.30	0.634	3.78	69 463	1.45	2.14	178	38	
<i>Italy, Antro del Corchia</i>													
C-1	0.269	5061	0.32	0.271	0.41	0.576	0.49	394 510	13.64	4.32	1161	49	$0.9923 \pm 0.0029$
C-2	0.210	5177	0.32	0.260	0.50	0.547	0.59	423 500	13.47	4.08	856	50	
C-3	0.256	5090	0.31	0.269	0.86	0.568	1.01	402 110	12.14	3.80	973	49	
C-4	0.271	2451	0.31	0.540	0.16	1.290	0.17	74 001	10.15	10.23	2771	14	
C-5	0.157	4833	0.31	0.294	0.38	0.640	0.44	293 680	12.88	4.48	702	38	
C-6	0.269	4992	0.31	0.278	0.56	0.598	0.65	324 200	13.58	4.44	1194	40	

All data blank corrected for  $10 \pm 5$  pg Pb as detailed in text.

<sup>a</sup> $^{238}\text{U}/^{204}\text{Pb}$  ( $\mu$ ) values are estimates only due to the analytical difficulties associated with measuring this ratio (see text) and are not used in isochron construction.

<sup>b</sup>Activity ratios  $[\text{}^{234}\text{U}/\text{}^{238}\text{U}]$  were determined on separate sub-samples from the same growth layer as those used in U/Pb isochron construction.

(Ludwig, 1993) and IsoPlot Ex. 3.04 (Ludwig, 2001), although note that the production of disequilibrium concordia diagrams requires some manipulation of the IsoPlot output since the code is normally configured to plot equilibrium concordia.

### 3. Results and discussion

#### 3.1. Isochron formalisations

Because of the problems obtaining accurate  $^{204}\text{Pb}$  data for small radiogenic Pb samples by MC-ICPMS, isochron methods involving this isotope (e.g.  $^{206}\text{Pb}/^{204}\text{Pb}$  vs.  $^{238}\text{U}/^{204}\text{Pb}$ ), or methods requiring  $^{204}\text{Pb}$ -based common Pb corrections (Wetherill concordia), had to be avoided. The approach of Getty and DePaolo (1995), which involves construction of  $^{206}\text{Pb}/^{207}\text{Pb}$  vs.  $^{238}\text{U}/^{207}\text{Pb}$  isochrons after normalisation to an assumed ‘fixed’  $^{207}\text{Pb}/^{204}\text{Pb}$ , is also not applicable because it was designed for young low-U/Pb systems with very small amounts of radiogenic Pb (and thus quasi-constant  $^{207}\text{Pb}/^{204}\text{Pb}$ ). By contrast, measured  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios in our samples vary by a factor of  $\sim 4$ . Getty et al. (2001) used  $^{208}\text{Pb}$  as the reference isotope to generate a  $^{206}\text{Pb}/^{208}\text{Pb}$  vs.  $^{238}\text{U}/^{208}\text{Pb}$  isochron for Pleistocene coralline limestone. Not only is  $^{208}\text{Pb}$  much more abundant than  $^{204}\text{Pb}$ , the extremely low levels of Th found in ‘clean’ low-temperature carbonates mean that any  $^{208}\text{Pb}$  present is overwhelmingly common Pb (like  $^{204}\text{Pb}$ ). In theory, this should make  $^{208}\text{Pb}$  an ideal reference isotope for U–Pb studies of such carbonates (Cliff, 2001; Richards and Dorale, 2003) and we have indeed found the  $^{208}\text{Pb}$  normalisation approach to be useful for samples in which common Pb comprises a small but significant component. However, in very radiogenic samples ( $^{206}\text{Pb}/^{204}\text{Pb} > 500$ ), common Pb contents are vanishingly small and, in such cases, error magnification upon blank subtraction makes the use of the  $^{208}\text{Pb}$  isotope less attractive.

Richards and Dorale (2003) demonstrated the use of the three-dimensional variant of the Tera–Wasserburg plot developed by Wendt and Carl (1985). In the case of MC-ICPMS-generated data, however, when  $^{204}\text{Pb}$  data are of questionable accuracy such an approach is also compromised. For most of our data we have therefore used the conventional Tera–Wasserburg (T–W) diagram (Tera and Wasserburg, 1972), renamed the ‘semi-total Pb–U isochron’ by Ludwig (1998). The T–W diagram, popular with many Sensitive High-Resolution Ion Microprobe (SHRIMP) U–Pb geochronologists, avoids the use of both  $^{208}\text{Pb}$  and  $^{204}\text{Pb}$ , and uses parameters which, for the majority of samples, are well-determined on Faraday cups ( $^{238}\text{U}$ ,  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$ ). In the case of a suite of coeval, cogenetic speleothem sub-samples with differing  $^{206}\text{Pb}/^{204}\text{Pb}$ , plots of  $^{238}\text{U}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  data uncorrected for both blank and common Pb should define a mixing line between common Pb (a combination of blank and intrinsic common Pb) and pure radiogenic Pb located on the T–W concordia (although note that, in the case of

speleothems, the latter curve is influenced by initial isotopic disequilibrium effects, see below). Plots of isotope data determined on different sub-samples from the same horizon show little systematic difference in the resulting ages when calculated either with or without blank-correction, although usually age errors are reduced for blank-corrected data. As a result, and to achieve a more robust protocol, we therefore chose to blank-correct data before plotting and calculating T–W disequilibrium concordia intercepts with IsoPlot Ex (Ludwig, 2001). An example is provided by the Nullarbor sample MO-1 in Fig. 1a. Note that, in this case, the most radiogenic samples have negligible common Pb, and thus both  $^{208}\text{Pb}$  and  $^{204}\text{Pb}$  (as required by other isochron methods) could not be reliably determined. These mixing lines may be ‘anchored’ with some common Pb constrained independently (e.g. from insoluble residues or from present-day cave waters/

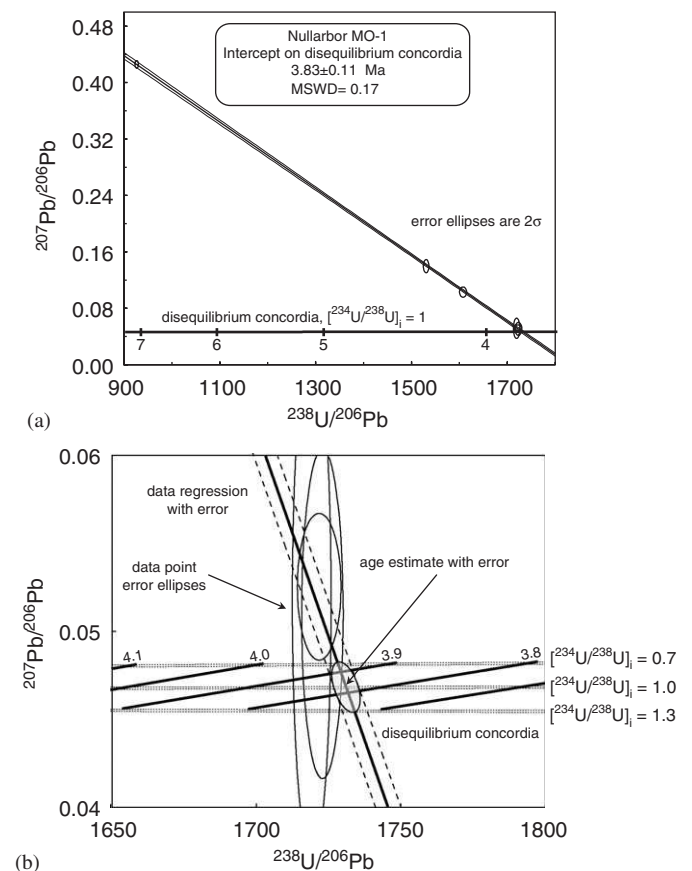


Fig. 1. (a) U–Pb data for Nullarbor sample LBCM01 (‘M0-1’) plotted using the Tera–Wasserburg or ‘semi-total Pb–U isochron’ construction. The quasi-horizontal line in this plot represents a disequilibrium concordia plotted for  $[^{230}\text{Th}/^{238}\text{U}]_i = 0$ ,  $[^{234}\text{U}/^{238}\text{U}]_i = 1$ . Tick marks with numbers on this curve are ages in Ma. A linear regression with its associated  $2\sigma$  uncertainty envelope is also shown passing through the individual blank-corrected U–Pb analyses. The calculated age is derived simply from the intersection of the two. (b) Detail of the area of intersection showing a family of possible disequilibrium concordia representing sample evolution under different  $[^{234}\text{U}/^{238}\text{U}]_i$  conditions and chosen, in this case, to show the best estimate of the true value  $\pm 30\%$ . Parallel lines in bold running across these concordia represent disequilibrium isochrons with ages marked in Ma.

speleothems) that may help to improve resolution, but in this work we have simply used the analyses themselves to define the mixing lines.

The most significant conclusion to be drawn from this analysis is that, under ideal circumstances, U–Pb dating of speleothems is not only feasible, but also capable of providing very precise age estimates. In fact, the errors observed—often less than 1% ( $2\sigma$ ) before correction for initial isotopic disequilibrium (see below)—closely approach those obtained from high-quality U-series analysis, currently the most precise method of dating speleothems younger than  $\sim 0.5$  Ma in age.

### 3.2. The limitations of youth: U-series disequilibrium considerations

Accurate U–Pb geochronology relies on initial secular equilibrium in the U-series decay chains. Ludwig (1977) was the first to consider the possible errors arising from violations of this assumption, and this issue has been reiterated by Richards et al. (1998). The problem is particularly relevant to speleothem studies, since it is well known that cave carbonates are precipitated out of U-series secular equilibrium (in fact, this forms the basis of U-series dating). A wealth of data on both modern and late Quaternary speleothems indicates a wide range of  $^{234}\text{U}/^{238}\text{U}$  activity ratios at the time of formation,  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$ , reflecting the even wider range observed in contemporary groundwaters; most commonly activity ratios are  $>1$  but  $^{234}\text{U}$ -depleted speleothems are also known (and indeed are currently prevalent at both sites under discussion herein). In addition, the time required for  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  ingrowth (clean speleothems are precipitated with essentially no Th or Pa) in the  $^{238}\text{U}$ – $^{206}\text{Pb}$  and  $^{235}\text{U}$ – $^{207}\text{Pb}$  decay chains must also be taken into account. A number of other disequilibrium processes are possible but are either hard to quantify or unlikely to be relevant to the present study due to extremely short half-lives. These include effects in the  $^{238}\text{U}$  chain such as loss of gaseous  $^{222}\text{Rn}$  (which Richards et al. (1998) suggested was unlikely from dense speleothems), incorporation of  $^{222}\text{Rn}$  in areas isolated from substantial atmospheric flushing producing erroneously old ages in very slow-growing materials (see Neymark et al., 2000 for a possible example), mobility of  $^{210}\text{Pb}$  (Baskaran and Iliffe, 1993) and  $^{226}\text{Ra}$ . In the  $^{235}\text{U}$  chain, ‘unsupported’  $^{207}\text{Pb}$  in dripwaters may also be generated by decay of  $^{219}\text{Rn}$  (Dublyansky and Pashenko, 2001).

While a correction for initial  $^{234}\text{U}$  and  $^{230}\text{Th}$  isotopic disequilibrium is achieved relatively easily, for example, using the Isoplot spreadsheet functions of Ludwig (2001), the accuracy of such corrections is rather strongly dependent upon the choice of appropriate input parameters, in particular the initial U-isotope composition, denoted  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$ . For example,  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  for speleothems is inherently difficult to predict (in contrast to marine carbonates, e.g. McCulloch and Esat, 2000;

Getty et al., 2001) and is known to have varied with time in many caves, in response to palaeoenvironmental change and as a long-term drift (Kaufman et al., 1998; Hellstrom and McCulloch, 2000; Richards and Dorale, 2003). Antro del Corchia provides an excellent example of the latter phenomenon: a database of over 100 U/Th analyses for samples  $<400$  ka in age (Drysdales et al., 2004, 2005; unpublished data) clearly shows  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  to have undergone minor fluctuations superimposed on an overall trend of decreasing  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  with time (Fig. 2).

In the case of the Nullarbor materials,  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  was estimated based upon the few available analyses of speleothems within the range of U–Th dating from this region. In such cases, it is suggested that relatively large errors be assigned to these estimates (Fig. 1b shows the  $\pm 30\%$  error we have used and its effect upon the isochron construct). The Corchia speleothem data define an excellent isochron (for such a young system) due to the unusually high U content of these samples (Fig. 3a). In a manner similar to the Nullarbor sample shown above we could use a best estimate of the  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  in deriving the correct age for this sample (in this case a value of 0.8 would be used, consistent with the model derived in Fig. 2). This sample is, however, young enough to still show detectable  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  disequilibrium and this value can be used to help refine the U/Pb age calculation, since  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  no longer has to be estimated. In this case the corrected age is derived from the intersection of the sample regression and curves plotted for the measured  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  rather than estimated  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  as shown in Fig. 3b. The U–Pb age calculated in this way is some 52 ka older than the age resulting from a default assumption of equilibrium  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  and no initial  $^{230}\text{Th}$ , and 17 ka younger than the age calculated using the ‘best estimate’ value of  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$ . The corrected age uncertainty, while still small in relative terms (2%) is  $\sim 9$  times larger than that resulting from the regression alone, meaning uncertainty in  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  overwhelms all other sources of error in this case.

Corrections to the U–Pb age will be most accurate for samples young enough to have measured  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  that is analytically resolvable from unity (typically  $<1$ – $2$  Ma depending on extent of  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  disequilibrium). For older samples,  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  must be estimated and, realistically, this estimate should be assigned relatively large errors. This procedure has two important consequences. Firstly, although it is commonly assumed that disequilibrium effects become negligible after several Ma, such calculations should be performed routinely, irrespective of age, since they often have a significant effect on not just the age estimate itself but, equally importantly, on the error estimate. Secondly, this constraint means that the best age precision may actually be obtained by U–Pb methods on samples in the age range  $\sim 250$ – $750$  ka, where  $[\text{}^{234}\text{U}/^{238}\text{U}]_i$  is most likely to be discernible from the secular equilibrium value. Disequilibrium corrections have been applied to all

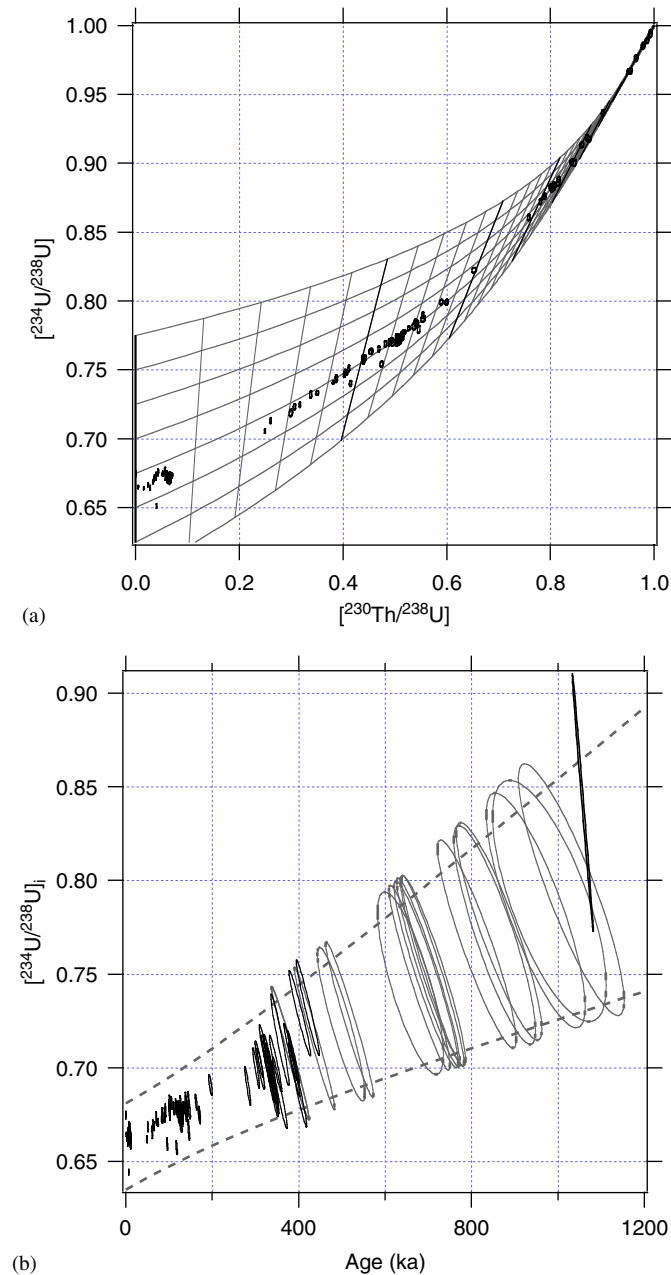


Fig. 2. (a) U–Th isotopic compositions of ca. 100 speleothem analyses from Antro del Corchia (Italy) showing the reasonably consistent evolution of  $[^{234}\text{U}/^{238}\text{U}]$  at this site. Late Holocene speleothems have  $[^{234}\text{U}/^{238}\text{U}]$  of ca. 0.67, and older samples are approximately distributed along the curved evolution path leading from this point (straight lines are isochrons at 20 ka spacing). (b) The same data set showing calculated  $[^{234}\text{U}/^{238}\text{U}]$  vs. age. The grey dashed lines define a model uncertainty envelope for  $[^{234}\text{U}/^{238}\text{U}]$  evolution projected from the measured U–Th analyses (in black). Grey ellipses represent  $^{238}\text{U}$ – $^{234}\text{U}$  ages calculated on the basis of this model for those samples beyond the range of U–Th, and are expected to significantly improve as future paired U–Pb and  $[^{234}\text{U}/^{238}\text{U}]$  analyses reduce model uncertainty (that of sample CC16 is shown as the strongly correlated black ellipse at top right).

the isochrons shown in this paper and, in most cases, result in significant changes to both age and errors.

Finally, we note that the detrimental effect of disequilibrium corrections on age error is likely to be lessened when

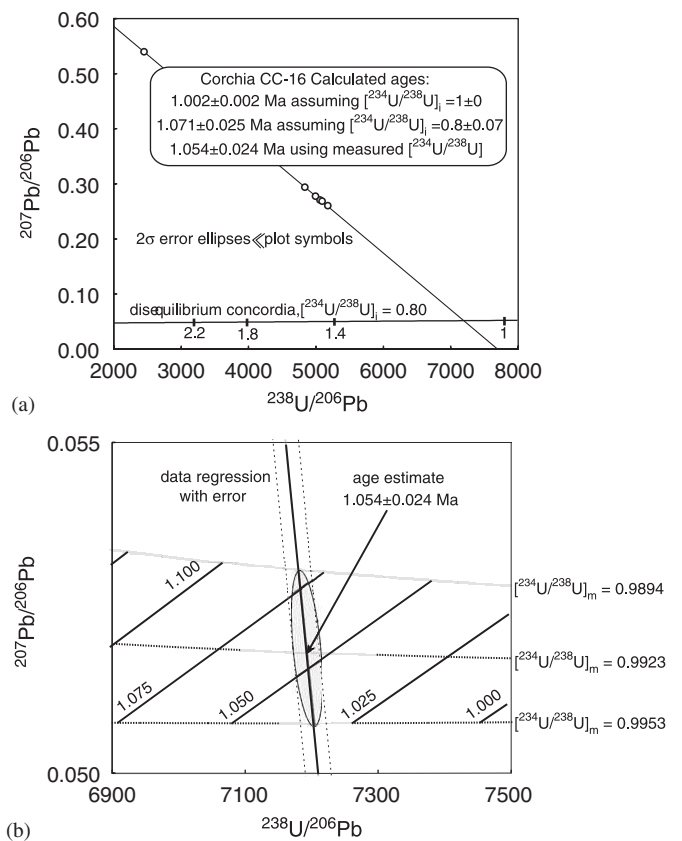


Fig. 3. (a) U–Pb data for Antro del Corchia sample CC16. In this case individual errors are too small to be shown clearly on this diagram due to the high U content of these samples. A very well-defined regression results in an apparent age of 1.071 Ma assuming the best estimate of the  $[^{234}\text{U}/^{238}\text{U}]_i$  derived from the model of Fig. 2. In this case, however, we have a measurable  $[^{234}\text{U}/^{238}\text{U}]$  ratio at the present day of  $0.9923 \pm 0.0029$  in the sample which can be used to further refine the U–Pb age estimate. (b) Detail of the intersection area between sample regression and disequilibrium concordia, providing a preferred age estimate of  $1.054 \pm 0.024$  Ma. Note in this case we have plotted an envelope showing U–Pb isotope ratio variation on the basis of measured, rather than estimated  $[^{234}\text{U}/^{238}\text{U}]_i$  (Note: as a result these do not represent evolution trajectories as would be the case when using  $[^{234}\text{U}/^{238}\text{U}]_i$  as in Fig. 1b).

considering relative ages within any given speleothem as might be obtained, for example, in constraining the growth rate of a climate proxy record. Our observations and a review of the literature suggest that  $[^{234}\text{U}/^{238}\text{U}]_i$  does not usually not shift by more than a few hundred permil during the period of speleothem growth and thus the uncertainty on  $[^{234}\text{U}/^{238}\text{U}]_i$  variation between different horizons of the same stalagmite or flowstone can be reduced. As an example, the disequilibrium corrections for two subsamples shown in Fig. 4 assumed initial  $[^{230}\text{Th}/^{238}\text{U}]$  activity ratios of 0 and an uncertainty of only 10% for  $[^{234}\text{U}/^{238}\text{U}]_i$  of two horizons from the same speleothem, rather than the 30% uncertainty assumed for the correction used in Fig. 1. This allows improved resolution of growth rate and rates of change in other proxies within a speleothem, but comparison of ages with other speleothems would of course require propagation of the larger uncertainties for both samples.

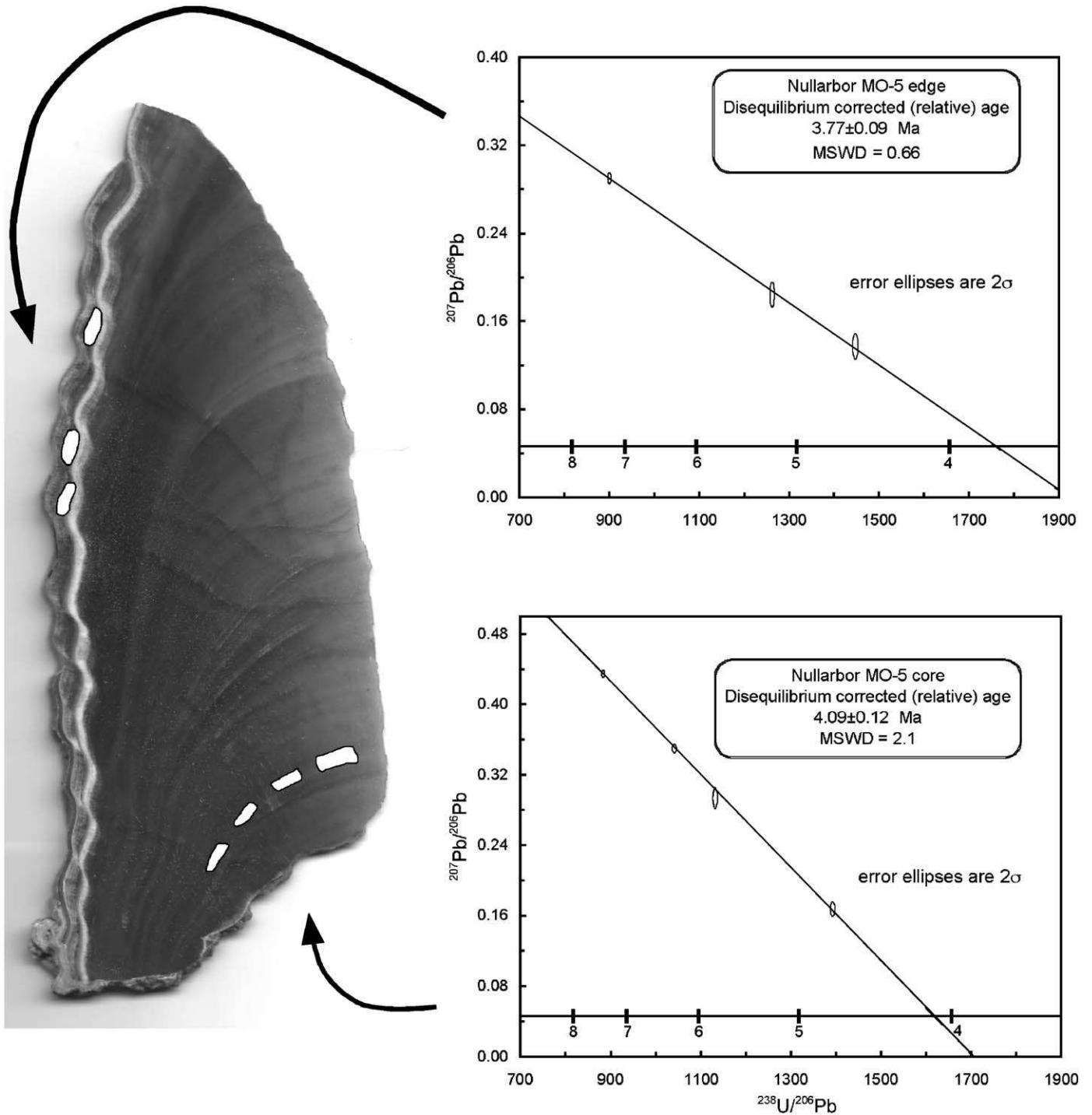


Fig. 4. U–Pb data for Nullarbor sample LBCM05, illustrating the potential effects of a disequilibrium correction for comparison of sub-samples of the same speleothem. In this case, we used a  $[^{234}\text{U}/^{238}\text{U}]_i$  value of  $1 \pm 0.1$  to achieve this correction, assuming less relative shift in  $[^{234}\text{U}/^{238}\text{U}]_i$  ratio between sub-samples of the same speleothem. For the purposes of absolute age determination a greater uncertainty should be applied.

### 3.3. $^{206}\text{Pb}/^{238}\text{U}$ ages vs. isochrons

The highly radiogenic Pb signal in some speleothems raises the further possibility of calculating radiogenic  $^{206}\text{Pb}/^{238}\text{U}$  ages independently for individual sub-samples of speleothem, much as in zircon studies. Obviously, this requires the common Pb composition to be stipulated

individually, because it can no longer be derived from the multi-sample mixing systematics. Despite this uncertainty, the ability to obtain stand-alone single sample ages is certainly of interest, if only as a preliminary screening tool. For example, individual sub-samples from the Nullarbor speleothem MO-1 considered in Fig. 1, which has an isochron age of 3.83 Ma, all provide  $^{206}\text{Pb}/^{238}\text{U}$  ages of

3.72–3.82 Ma (corrected for an arbitrary common Pb having the composition of our average laboratory blank, and disequilibrium effects). Such estimates typically become more inaccurate as common Pb contents (and hence the degree of correction required) increase and so their value remains to be established and will probably depend upon the growth rate of individual speleothems, and the degree to which common Pb contributions have remained constant throughout the growth of any individual sample. Isochron methods are of course far more robust and offer the potential for constraining the timing of proxy records in much the same way as U-series ages but they remain rather labour intensive to employ. Nevertheless, such methods provide the only reliable means of constraining ages in relatively slow-growing samples greater than 0.5 Ma in age, where the full length of a speleothem may represent only a few hundred thousand years (e.g. Fig. 4).

#### 3.4. The utility of the technique and the relative merits of MC-ICPMS analysis

Given the small number of U–Pb isotope data for Pleistocene speleothems available in the literature, an obvious question arises as to why our methodology has been so successful. One simple reason may be sample selection, as the materials we have chosen for analysis were already determined to be free of significant detrital contamination by prior U-series analyses (these analyses provided the initial indications that the samples were likely to be considerably beyond ~500 ka in age and thus suitable for U–Pb study). This is clear from Fig. 5a, in which our

data are compared with literature data presented by Richards and Dorale (2003), their Fig. 14, in which  $^{204}\text{Pb}$  is used as an index of the common Pb content. Both the Nullarbor and Corchia speleothems we have analysed are significantly more radiogenic (i.e. contain less common Pb) than the majority of those previously reported. Indeed, many of the Nullarbor materials have  $\mu$  ( $^{238}\text{U}/^{204}\text{Pb}$ ) values far higher than any yet recorded (Table 1). Unfortunately Pb concentration data for speleothems are rarely reported in the literature, precluding a more detailed survey. Given the extremely low Pb contents of our speleothems, however, it is not clear that standard sample preparation procedures (e.g. for ICPMS determination) performed outside of a clean room environment would necessarily reflect true concentrations and, as a result, the literature data may not always have been obtained under ideal circumstances. Therefore, as an alternative approach to the problem, we have collated Th and U abundance data from the U-series geochronology literature, and employed Th as a ‘proxy’ for common Pb, using the crustal Pb/Th ratio of ~1.6 (e.g., Rudnick and Gao, 2003) to relate Th to Pb contents. Fig. 5b has been drawn using the same scaling as Fig. 5a (since total common Pb is generally  $\sim 100 \times ^{204}\text{Pb}$  content) and reveals that, in this case, our data fall within the broad field defined by literature data, albeit at the low end of the spectrum of Pb contents. Clearly this is not an ideal construct since it relies on the assumption that Pb and Th are incorporated into speleothems in the ratio of their average crustal abundance. As a first order estimate, however, it implies that our data do fall within ‘normal’ concentration limits.

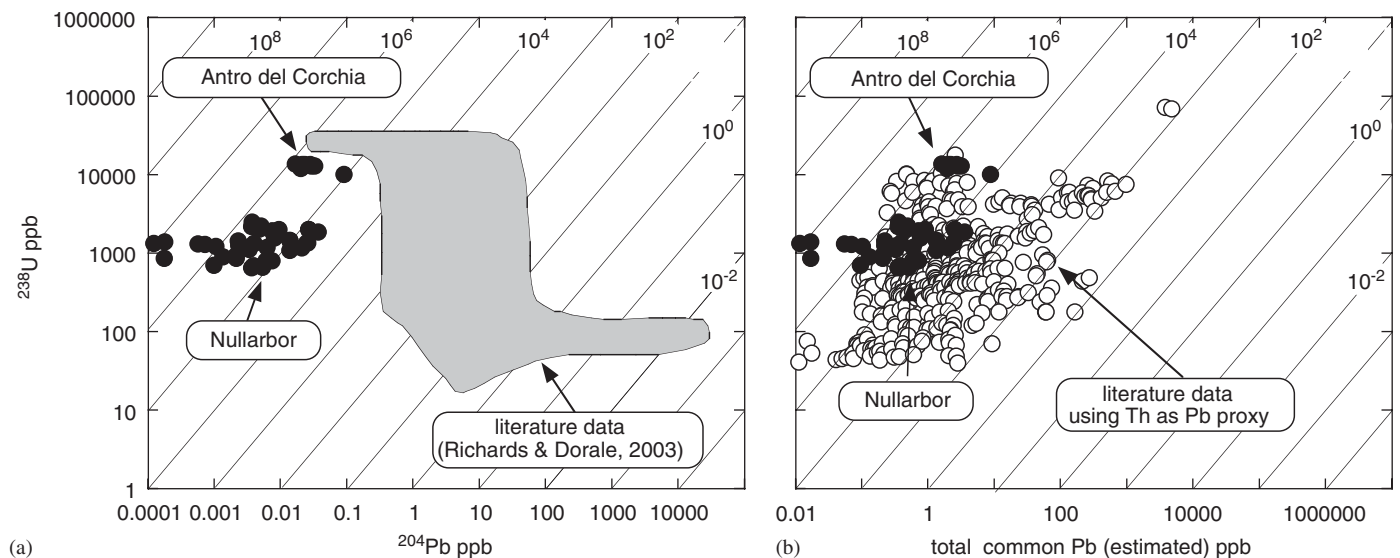


Fig. 5. (a) U vs. Pb concentration diagram, after Richards and Dorale (2003) but with the x-axis extended by two orders of magnitude. On the x-axis,  $^{204}\text{Pb}$  is essentially a measure of the ‘common’ Pb component. Diagonal lines represent the  $^{238}\text{U}/^{204}\text{Pb}$  ratio ( $\mu$ ). Both Nullarbor and Corchia speleothem samples are all characterised by very low common Pb contents (52 samples plotted which include speleothems other than those documented in this paper). (b) a complementary diagram with similar scaling (total common Pb assumed to be  $\sim 100 \times ^{204}\text{Pb}$  content) constructed from a survey of the U–Th geochronology literature (essentially a random selection of 25 papers published since 1998). Thorium has been used as a proxy for common Pb, assuming a crustal Pb/Th ratio of 1.6 (Rudnick and Gao, 2003). Open symbols represent these literature data while closed symbols are our own data. In this case the samples analysed in this study appear comparable with compositional ranges from the literature. See text for further discussion.

The apparent discrepancy between these two figures could be explained by the fact that the data we gathered from the literature represent samples for which some sort of initial screening (suitability for geochronology hence low detrital content) has already been undertaken and thus our literature data set is inherently 'biased'. Resolution of this issue can only await further careful studies of speleothem Pb contents. For the purpose of our present discussion, however, we merely note that a significant proportion of the samples collected for geochronology purposes are apparently clean enough (with only a few ppb common Pb) to be also suitable for U/Pb geochronology. This observation, coupled with our experiences to date suggests to us that the method has widespread applicability.

While a variety of screening strategies have been proposed for U-series (and hence, by inference, U–Pb) sample selection using both petrographic and geochemical criteria (e.g., Railsback, 2002), the most effective method may be Th concentration analysis by quadrupole ICPMS (or Pb if samples are prepared in a clean room environment) or even assessment of the degree of detrital Th contamination by U–Th-isotope analysis. The latter provides the obvious advantage of an approximate age estimate (i.e. are the samples older than 500 ka?) and is also now relatively rapid via modern MC-ICPMS techniques (e.g., Hellstrom, 2003). In terms of sub-sampling, we concur with Richards and Dorale (2003) that the best strategy for U/Pb isochron dating is to follow a single growth band wherever possible. Not only does this ensure that sub-samples conform to a single age population but also helps to minimise the possibility of variable initial Pb isotope compositions so that simple two-component mixing relationships are obtained, and may help to produce a spread in U/Pb ratios through progressive drip water fractionation down the flanks of stalagmites during growth. Although, we have observed systematic variation in Pb content along the growth band in only one speleothem sample, in almost all relatively radiogenic materials we have analysed to date, this strategy produces a reasonable spread in U/Pb ratios. The use of a dental drill makes sub-sampling along individual growth bands several mm in width relatively straightforward and we believe is a major contributor to the success of the method.

As we have shown, MC-ICPMS can be readily adapted to produce high-precision U–Pb isotope data for samples containing quantities of radiogenic Pb (0.2–1 ng Pb) comparable to those encountered in the analysis of old single zircons by TIMS (see below). Further improvements to sensitivity and efficiency may be obtained by applying multi-ion-counting techniques (e.g. Hellstrom, 2003) rather than measuring small Pb signals on Faraday cups, although this would introduce an additional error due to inter-calibration of ion counter gain. In comparison with TIMS, the benchmark technique for low-level Pb isotope analysis, the critical aspects of MC-ICPMS are possibly the more reproducible and predictable Pb signals, more stable (although larger) mass bias, less stringent requirements for

sample purity, and fast throughput. While TIMS can, under ideal circumstances, provide a higher signal for a given sample size than MC-ICPMS, TIMS Pb signals are well known to be strongly dependent on the purity of the Pb sample, the effectiveness of the silica-gel activator, and the filament loading technique. This does not appear to be a problem in modern IDTIMS zircon U–Pb studies (where no ion exchange purification is done), but would undoubtedly be a greater concern for a similar-sized Pb fraction extracted from 200 mg of calcite! By contrast, our results suggest that speleothem Pb's purified with a single pass over a 0.1 ml anion resin column provide consistent and predictable signals in the ICPMS, with a blank of  $\approx 10$  pg. Likewise, estimates of mass bias provided by the spike  $^{205}\text{Tl}/^{203}\text{Tl}$  ratio measured concurrently with each Pb sample show a very limited range (typically less than 0.1% total range in  $^{205}\text{Tl}/^{203}\text{Tl}$  during any given analytical session). This observation suggests that a mass bias correction can be readily accomplished by reference to an external standard where Tl-doping is abandoned in favour of samples spiked with  $^{205}\text{Pb}$ . Obviously, both mass bias correction and isotope dilution requirements would be elegantly solved with the use of a  $^{202}\text{Pb}$ – $^{205}\text{Pb}$  spike (e.g., Todt et al., 1996) but such a tracer is not widely available. Furthermore,  $^{202}\text{Pb}$  measurement by MC-ICPMS is complicated by interference from  $^{202}\text{Hg}$ , mirroring the problems involved in measurement of  $^{204}\text{Pb}$ .

Overall, our observations indicate that MC-ICPMS is a viable alternative to current TIMS methods for low-level radiogenic Pb isotope analysis. Combined with improved sample throughput, we believe that the more predictable mass bias behaviour and ionisation (even in samples containing impurities remnant from the chemical separation of Pb) are significant advantages for the analysis of speleothems, and indeed for all Pb samples. For this reason, despite many years invested in the development of high-precision double-spike methods for TIMS Pb analysis (e.g., Woodhead et al., 1995; Powell et al., 1998), our laboratory has now abandoned TIMS entirely in favour of MC-ICPMS analysis. The most serious drawback of the technique, Hg interference at mass 204, can be alleviated with a variety of specific approaches such as the use of Hg-traps in the carrier gas lines; however, as we have seen, alternative isochron constructs are available which render measurement of  $^{204}\text{Pb}$  unnecessary.

### 3.5. U/Pb ratios and the source of common Pb

It is clear that a key factor in the success of speleothem U–Pb dating is the incorporation of only small amounts of common Pb with uniform isotopic composition into the sample during growth. Unfortunately, while the transport of U as a uranyl carbonate and its subsequent incorporation into the calcite lattice is relatively easily understood (e.g., Gascoyne, 1992), the source of common Pb encountered in speleothems is less clear. This is an important issue because there would be clear advantages

in selecting materials with low common Pb, resulting in higher U/Pb ratios (providing increased age resolution) and diminishing the influence of variable initial Pb isotopic compositions (which produce scatter and degrade isochrons).

In nature, Pb occurs as both divalent and tetravalent ions but  $\text{Pb}^{2+}$  predominates over  $\text{Pb}^{4+}$ . Pb concentrations in continental waters are  $<0.1$  ppb (Patterson, 1980) suggesting a relatively low solubility under surface conditions. Adsorption onto clays, organic particles, and Fe hydroxides, rather than simple solubility considerations may thus be the main factors controlling Pb transport in meteoric waters (e.g. Erel and Morgan, 1992). Furthermore, although no direct distribution coefficient has been determined for Pb in calcite, and it has been demonstrated that Pb can substitute for octahedrally coordinated Ca in calcite (Sturchio et al., 1997; Reeder et al., 1999) it is thought that such a substitution is unfavourable since the difference in size of the cations (ionic radius  $1.19 \text{ \AA}$  for Pb vs.  $1.00 \text{ \AA}$  for Ca) creates considerable lattice distortion. As a result of both these factors (low concentration in surface waters, exclusion from the calcite lattice) it would seem reasonable to expect an extremely low Pb concentration in natural calcites. In this respect, both the Nullarbor and Corchia speleothem samples considered in this study, which contain at most a few ppb Pb (see Table 1), may approach the norm. It is clear, however, that many other speleothems contain much higher Pb concentrations than these simple observations would predict (up to many tens to hundreds of ppm: Richards and Dorale, 2003, Fig. 5 of this report). Two further possibilities exist which may account for the incorporation of this Pb, namely fluid inclusions and particulate Pb.

Many speleothems contain fluid inclusions, trapped at the time of calcite growth; indeed, in some cases these can be so abundant as to impede crystal growth (Kendall and Broughton, 1978). Such inclusions may form an alternative pathway for Pb incorporation in actively growing speleothems although, given the solubility of Pb in typical groundwaters, this would only seem likely in material showing very high fluid inclusion densities. Fortunately, high-densities of fluid inclusions have a tendency to cause calcite to assume a milky white colour (Kendall and Broughton, 1978) and so it may be possible to use such a feature as an initial screening protocol prior to ICPMS analysis (note all of the samples used in this study were transparent to translucent and are thus assumed to have low fluid inclusion densities).

Alternatively, Pb could be incorporated into speleothems as particulates, either as airborne dust or transported in dripwater. Speleothems have been shown to be potential recorders of aeolian dust transport in both temperate maritime and arid climatic regimes (e.g. Frumkin and Stein, 2004). If this is the case then material most amenable to geochronology may be found in the far reaches of many cave systems, remote from the cave entrance and its associated airborne particulate load. Field evidence and

low  $^{232}\text{Th}$  contents in both the Nullarbor and Corchia speleothem samples (measured  $^{230}\text{Th}/^{232}\text{Th}$  ratios are typically greater than 5000 at both sites, and range as high as  $\sim 120\,000$ ) indicate that these grew in areas isolated from external influences. It also seems unlikely that detrital material is incorporated into Corchia stalagmites through dripwater transport, as observed  $^{230}\text{Th}/^{232}\text{Th}$  is at its highest during relatively fast growth intervals in several stalagmites (e.g. Drysdale et al., 2006) i.e. periods marked by increased dripwater flow. Limited U–Th results available for Nullarbor speleothems (Hellstrom, unpublished data) support a similar conclusion for that location.

### 3.6. Regional implications, Nullarbor

Goede et al. (1990) investigated speleothems from a number of caves in the Mundrabilla region using U-series methods and concluded that there had been no significant deposition of carbonate in the area for more than 400 ka. Subsequently, Sesiano and Hedley (1996) determined that a black calcite stalagmite from Koomoolookooka Cave was reversely magnetised and thus at least older than 780 ka. As a result, it has been a widely held belief that the Nullarbor speleothems are of great antiquity, and represent a record of climatic conditions that were much more favourable for speleothem growth than today's arid climate. Our  $\sim 4$  Ma U–Pb ages for some of these speleothems now confirm, for the first time, that many of the Nullarbor speleothems are indeed of Pliocene age despite their often excellent preservation. Further work on stratigraphically older Nullarbor speleothems is now underway and may potentially record climatic signals back to  $\sim 15$  Ma when the area was uplifted, allowing karst formation in carbonate rock newly exposed in the vadose zone. Although it is generally believed that much of the past 15 Ma after the formation of the Antarctic ice sheet corresponds to the onset of aridity in southern Australia (e.g., Bowler, 1982), the degree to which such an event was punctuated by cooler, wetter periods, and the frequency of these environmental fluctuations is largely unknown. Without this detailed information, the origin and nature of this climatic change remains speculative. By analysing a larger number of Nullarbor materials using the U–Pb techniques documented here we aim to provide a significantly clearer picture of this period and, in addition, provide new constraints on the uplift history of the region.

### 3.7. Regional implications, Corchia

The encouraging age result on Corchia stalagmite CC16 provides an unprecedented opportunity to explore climate and landscape history during the Early to Middle Pleistocene. In terms of climate history, the similarity between the  $\delta^{18}\text{O}$  of Corchia speleothems and the Vostok palaeotemperature proxy record (Drysdale et al., 2004, 2005) suggests that the  $\delta^{18}\text{O}$  record of pre-400 ka Corchia

speleothems may allow us to test the chronology of the European Project for Ice Coring in Antarctica (EPICA) ice core (EPICA Community Members, 2004), which extends back to at least 740 ka. Furthermore, the initial confirmation by U–Pb dating that the trend of dripwater [ $^{234}\text{U}/^{238}\text{U}$ ] evolution vs. time observed from U–Th dating continues until at least 1 Ma indicates that precise  $^{234}\text{U}$ – $^{238}\text{U}$  dating over the interval 400 ka to 1 Ma will be possible for this site using rapid MC-ICP-MS analysis, greatly improving the chronological resolution over what is possible using U–Pb alone (Fig. 2). Indeed, about half of the ~25 speleothems dated at this site so far would appear to be between 0.4 and 1.1 Ma on the basis of this model (Fig. 2).

U–Pb ages on Antro del Corchia speleothems are also potentially significant for providing independent chronological constraints on regional landscape history. The cave is one of a small number in the Apuane karst to preserve extensive sub-horizontal phreatic and epiphreatic passages. Such passages are regarded as useful indicators for the topographic position of palaeo-base levels (Ford et al., 1981; Williams 1982; Gascoyne et al., 1983; Piccini et al., 2003; Stock et al., 2005). Stalagmites, the speleothem type most widely used in palaeoenvironmental reconstruction, only grow in dewatered caverns; hence their ages can provide minimum dates for the time of dewatering.

The U–Pb age for CC16 indicates that the cave was dewatered, and thus renewed uplift possibly occurred prior to 1.05 Ma. The chamber from which the stalagmite was collected (~840 m a.s.l.) forms part of almost 2 km of ~sub-horizontal passage within the elevation range of 800–850 m a.s.l. The extensive development of horizontal passages at this level is regarded as evidence for a stillstand in the regional base-level position, for which there is some geomorphic support outside the cave in the form of remnant erosional benches (Piccini, 1998). Although confident interpretations are limited by our single age from this passage to date, this is consistent with what we know of regional uplift history. Fission-track ages suggest major exhumation events in the Apuane at ~6–4 Ma (Balestrieri et al., 2003) and ~2 Ma (Abbate et al., 1994, 1999). Dating the basal units of the flowstone upon which CC16 grew would produce older ages that better constrain the minimum age of dewatering. A careful program of sampling and dating from the full sequence of sub-horizontal passages within Antro del Corchia presents a tantalising opportunity for generating chronological information to compliment that derived from independent methods.

Recently, Stock et al. (2005) demonstrated the extent to which U–Th speleothem ages can grossly underestimate the timing of former base-level positions. Although this is due in part to the time lag between cave dewatering and inception of speleothem growth, the limited range of the U–Th method also constitutes a major constraint. Extension of the age range using the U–Pb technique presented here should reduce uncertainty in speleothem-based cave chronologies.

Carbon isotope ( $\delta^{13}\text{C}$ ) data from pre-400 ka speleothems in the cave may also provide new insights into the region's tectonic history. Currently, the sparse alpine vegetation above the cave produces relatively high speleothem  $\delta^{13}\text{C}$  values (–3 to +3‰). Significantly lower  $\delta^{13}\text{C}$  (–10 to –3‰) of speleothems collected from lower-elevation caves in the region (e.g. Drysdale et al., 2006) are consistent with the mixed beech and chestnut forests that cover these slopes today. Ancient Corchia speleothems revealing similarly low  $\delta^{13}\text{C}$  may allow us to place new constraints on regional uplift, as these would indicate more luxuriant vegetation (and a more significant source of biogenic  $\text{CO}_2$ ) overlying the cave.

#### 4. Conclusions

Our pilot studies, using the new methodology outlined above, have produced a number of speleothem U–Pb ages of high quality. We are confident that this technique has the potential to drive significant advances in continental-based palaeoclimate research, in addition to studies of landscape evolution and palaeo-seismicity.

In terms of sampling, the key factor to obtaining high-quality U–Pb isochrons is the requirement for generating a spread in U/Pb ratios while avoiding significant common Pb. Although the processes by which such Pb is incorporated in speleothems remains unclear, material growing in isolated or remote areas of caves may ultimately prove optimal for this purpose. Ideally, preliminary sample screening using either trace element analysis by quad-ICPMS or rapid determination of detrital Th content (as a proxy for Pb) using MC-ICPMS U-series analysis can identify the most promising dating candidates prior to the more substantial efforts required to produce U–Pb isochrons. A survey of the literature, however, indicates that a significant proportion of the speleothem samples collected for (U–Th) geochronology purposes are already clean enough to be also suitable for U/Pb geochronology suggesting that similar sample selection strategies can be employed.

In parallel with U-series analysis, MC-ICPMS analysis has much to commend its use in the study of U–Pb systematics in speleothems. In addition to rapid throughput, MC-ICPMS is much less sensitive to sample impurities and allows processing of relatively large samples with low blank chemistry. The inability to measure  $^{204}\text{Pb}$  accurately is easily circumvented by using alternative isochron constructs, such as the Tera–Wasserburg or ‘semi-total Pb/U isochron’. Using this methodology, age estimates can be obtained with a precision, which is comparable to those observed in U–Th analyses. A correction for initial isotopic disequilibrium, however, remains essential in all cases and contributes significantly to overall analytical uncertainty.

Preliminary ages for speleothems from the Nullarbor Plain of Western Australia promise new constraints on the critical question of increasing aridity in Australia during the late Tertiary, while new ages on samples from Antro del

Corchia in Italy offer the prospect of a more detailed understanding of the landscape, tectonic and climatic evolution of the region.

### Acknowledgements

Sample collection from the Nullarbor caves has been made possible as a result of an extensive program of exploration and mapping by both the Speleological Research Group of Western Australia and the Cave Exploration Group of South Australia. We gratefully acknowledge the excellent financial and logistical support from the Federazione Speleologica Toscana for our Corchia research. We thank Ken Ludwig for his enthusiasm and advice on matters geochronological throughout this project and Jim Paces, one anonymous reviewer and the editor for detailed comments and suggestions that have greatly improved the manuscript. Isotope Geoscience at the University of Melbourne is partly funded by the Australian Research Council.

*Editorial handling by D.A. Richards*

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