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Editorial

New advances in the dating of speleothems – An introduction

Speleothems are secondary cave mineral deposits formed from meteoric percolation waters. Environmental information held within these waters, via their isotopic, organic and elemental composition, is encoded in the growing cave minerals (usually calcite, occasionally aragonite), producing a natural archive of environmental history. This environmental history is unravelled through quantitative and qualitative studies of the chemical and physical properties of speleothems, which can be measured accurately and precisely using a range of spectrometric, spectroscopic and microscopic techniques.

In the last decade, there has been an explosion of interest in speleothem research. A significant portion of this has been dedicated to understanding the ways in which speleothems record environmental change. This has been achieved through cave-monitoring programs (Genty et al., 2001; Huang et al., 2001; Tooth and Fairchild, 2003; McDonald et al., 2007; Mattey et al. 2008), laboratory experiments (Huang and Fairchild, 2001; Polag et al., 2010; Day and Henderson, 2011) and mathematical modelling (Kaufmann and Dreybrodt, 2004; Mühlinghaus et al., 2009; Dreybrodt and Scholz, 2011). Results of such studies provide a powerful basis upon which we interpret speleothem proxy data. However, the utility of speleothems as palaeoenvironmental archives is fundamentally underpinned by our capacity to date them precisely and accurately (Richards and Dorale, 2003), enabling climate-proxy time series to be developed at time frames ranging from recent decades to millions of years, and at resolutions ranging from subannual to millennial.

The earliest speleothem dating involved the use of radiocarbon methods to verify annual layering in a flowstone entombing a human thighbone (Broecker et al., 1960). Although a number of subsequent studies employed radiocarbon methods (Franke, 1965; Labeyrie et al., 1967; Geyh, 1970; Franke and Geyh, 1971), the technique fell out of favour due to uncertainties over the time constancy of the 'dead carbon fraction'. The most widespread technique of speleothem dating up until today has been based on isotopic disequilibria in the uranium-series decay chain. First applied to corals in the 1950s (Barnes et al., 1956) and subsequently to speleothems in the 1960s (Rosholt and Antal, 1962), U-series dating continues to underpin the majority of speleothem palaeoenvironmental studies. Advances in technology since the mid 1980s have led to dramatically increased analytical precision and progressively smaller sample-size requirements, as U and Th isotope determination by alpha counting was superseded by thermal ionisation mass spectrometry (Edwards et al., 1997) then single- (Shen et al., 2002) and multi-collector plasma mass spectrometry (Luo et al., 1997). Along with the recent refinement of uranium-lead isotopic dating of speleothems (Woodhead et al., 2006), application of these methods has dramatically expanded the scope of speleothem studies and given rise to sophisticated methods for building age-depth models (Scholz and Hoffmann, 2011). Recent years has also seen the re-emergence of radiocarbon dating, as both a chronological tool (especially for young speleothems – Genty and Massault, 1997; Mattey et al., 2008; Hodge et al., 2011) and as a means for calibrating variations in atmospheric radiocarbon (Hoffmann et al., 2010; Southon et al., 2012). Speleothems are now hailed as one of the most important and highly sought-after natural archives of environmental change (Henderson, 2006), and our ability to date them with great precision and accuracy has been fundamental to attaining this status.

It is therefore timely to present a collection of ten research papers in this special issue, representing some of the latest advances in speleothem dating and their applications to speleothem-based palaeoenvironmental problems. The impetus came from two international meetings that took place in 2011. The first, the *6th International Conference on Climate Change: The Karst Record* held in Birmingham, UK, in June, brought together over 200 speleothem specialists from around the world. The second was the *18th INQUA Congress* in Bern, Switzerland, in July, which included an oral and poster session dedicated to speleothem dating.

Many speleothems contain growth laminae that may persist over a large portion of, or more rarely throughout, the sample. The counting of laminae, if demonstrated to be of annual frequency, provides a powerful means by which to verify age models derived from discontinuous radiometric ages (Dasgupta et al., 2010) and to improve the internal chronology of a speleothem, leading to age models with overall uncertainties lower than those of the accompanying radiometric ages (Fleitmann et al., 2004; Scholz et al., 2012). However, as yet there is no agreement regarding how a lamina-counted sequence is anchored in real time using radiometric data and how lamina-count errors are propagated into the final age model. The paper by Domínguez-Villar et al. (2012) addresses these problems. After describing in detail their imaging and lamina-counting technique (well-suited for counting layers in texturally complex speleothems), they identify and estimate all significant sources of error in lamina counting. They recommend anchoring a lamina chronology not to the radiometric age having the lowest 95% uncertainty but rather by using a least-squares fit of the lamina chronology to the U-series age–depth plot, which minimises the residuals between each date and the lamina count. As one would expect, the technique will be more robust as the number of radiometric ages increases. They illustrate their approach using a section of a stalagmite from Kaite Cave, Spain,

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to refine their earlier chronology through the 8.2 ka event (Domínguez-Villar et al., 2009).

Not all speleothems can be layer-counted, which means that age models must be developed based solely on radiometric ages spread along the depth of the speleothem. Until a decade ago, such models were produced using either linear interpolation or spline fits, which often struggled to accommodate speleothem growth characteristics, especially where the density of ages was not high. Recent years has seen the emergence of alternative models (Drysdale et al., 2004; Scholz and Hoffmann, 2011; Breitenbach et al., 2012), yet a consensus has yet to be reached on which style of model is most appropriate. The contribution by Scholz et al. (2012) is therefore very timely: it 'test-drives' five alternative age-modelling approaches using one synthetic and two empirical speleothem age-depth datasets. Each dataset contains a number of 'hurdles' often encountered in speleothems, such as hiatuses, age inversions and abrupt growth-rate changes. The authors compare how each modelling algorithm handles these hurdles, with the conclusion that StalAge, OxCal and the finite positive growth rate model are generally better adapted to the complexities of speleothem growth and age outliers than spline-based algorithms.

When designing a sampling strategy for any speleothem axial-growth model, there is a suite of *a priori* considerations: age, growth rate, U concentration, initial $^{230}Th/^{232}Th$ ratio and sub-sample integrity. The last is a particular problem in slow-growing samples, for which micro-milling and high-precision mass-spectrometric dating techniques are now routinely employed, and this is the focus of Drysdale et al. (2012). The internal fabric, or stratigraphy, of most speleothem samples is evidenced by visible features, such as fluid inclusions, detrital clays and changes in mineralogical composition (see http://www.gly.uga.edu/railsback/speleoatlas/SAintro1.html for examples), however this is not always the case. Drysdale et al. (2012) convincingly illustrate the advantages of trace-element mapping or 'contouring' by laser-ablation ICP-MS to reveal the growth structure in sections of a sub-aqueous speleothem from Italy that do not display visible laminae. For these growth phases, internal architecture is revealed by high-resolution maps of Sr, Ba, Mg and U, which guide micro-milling sampling at the sub-millimetre scale for U-series. The authors carefully consider the contribution to overall age uncertainty from U–Th age determination errors, sampling morphology, resolution and density. These are issues that are going to become ever more prevalent as the community strives for robust growth models to support temporal records of palaeoenvironmental information obtained at higher resolution and density than age determinations.

Despite the large number of speleothem papers published in recent years, relatively few long, high-resolution records have been found. A resulting need to splice shorter, lower-resolution or less well-dated records together has led to varied approaches in the past, none of which has reached wide acceptance. The article by Fohlmeister (2012) provides a much-needed systematic approach to this problem, "intra-site correlation age modelling". Using synthetic and real speleothem datasets comprising U–Th age determinations and oxygen isotope proxy data, the author has demonstrated the use of a Monte Carlo technique through which two closely related speleothem records can be placed on a common timescale. The model begins with simple monotonic linearly-interpolated age-depth models for each of a pair of speleothems, which are then incrementally evolved subject to their constraining age uncertainties. Whenever a new model is found for either speleothem which gives better correlation between the proxy records it replaces the previous best-fit model for that speleothem. Following a suitably large number of iterations, the two records may be placed on a common timescale and spliced together, and additional speleothems can then be merged into this composite record in the same way. The author cautions of a number of limitations with this technique, in particular that it may give spurious results from widely separated caves, and when used on records with low-resolution age control. Intra-site correlation age modelling comprises a powerful new technique, best used only after a very careful reading of the article. A number of possible enhancements to the technique are noted by the author, and their future implementation will be something to watch over the coming years.

Although most speleothems described in the palaeoenvironmental literature are composed of calcite, a number of studies have focused on speleothems formed of aragonite or aragonite-calcite (e.g. Railsback et al., 1994; Frisia et al., 2002). Given that aragonite is metastable at Earth-surface conditions, and readily reverts to the more stable calcite form, speleothems composed of both minerals are highly susceptible to calcitization through their growth history. This has no doubt inhibited researchers from utilising such speleothems more widely, in spite of their abundance in certain environments (e.g. caves developed in dolomite). Focussing on an aragonite-calcite speleothem from Mexico, Lachniet et al. (2012) explore the effects of calcitization on the integrity of U-series chronologies. The U-series results on the (primary) aragonite sections yield precise ages in correct stratigraphic sequence, whereas the corresponding results on the calcite sections not only give less precise ages but also ages significantly older than ages of aragonitic sections from similar or identical stratigraphic positions. Based on petrographic observations, trace-element analyses and U-series measurements, the authors attribute the calcitization to the penetration into the aragonite of conduit-flow percolation waters undersaturated with respect to aragonite, causing dissolution and recrystallization to calcite. They caution against inflating the initial $^{232}Th/^{230}Th$ ratio as a means of bringing the anomalous calcite ages into stratigraphic order.

U-series dating is clearly the method of choice to establish robust age models for speleothems; very few other geochronological techniques rival these chronologies both in accuracy and precision. However, for some speleothems U-series dates may not be useful due to very low uranium concentrations, insufficient radiogenic Th and/or multiple sources of detrital Th. Hua et al. (2012) address these challenges commonly faced in the study of late Holocene stalagmites composed of impure calcite lacking continuous laminae of annual origin. The authors studied two stalagmites using a series of ^{14}C AMS data and identified the 'bomb peak' in both specimens within the uppermost millimetres. The authors then used two approaches to estimate the dead carbon fraction for these stalagmites for the pre-bomb period. These corrected radiocarbon ages were used as input data for age-depth modelling using both non-Bayesian and Bayesian codes. Excellent agreement between the outputs of these models was observed for both stalagmites. This study is one of the first to demonstrate that for those young speleothem samples, where temporal variations in the dead carbon fraction can be well constrained, robust age-depth models can be established. More than half a century after the pioneering study by Broecker et al. (1960) the results presented by Hua et al. (2012) provide new hope for research on young speleothems previously regarded as unsuitable given their unfavourable U-series characteristics.

The article by Griffiths et al. (2012) explores the significance of past radiocarbon values recorded by speleothems from a different angle. The starting point was a robust age model for an Indonesian stalagmite defined by U-series dated for an interval in the late Holocene marked by a prominent excursion in atmospheric radiocarbon content. Using these constraints and a series of radiocarbon analyses the authors derived a time series of varying values of dead carbon fraction. These data were then compared to paleoenvironmental proxies (C and O isotopes and Mg/Ca ratios) to determine the controlling mechanisms. Not too surprisingly the authors found a strong association between the dead carbon fraction and the local karst hydrogeology and climate: more dead carbon was delivered to the speleothem during intervals of strong monsoon (when the karst water feeding system had a higher degree of openness) and *vice versa*. The soil-karst model employed by Griffiths et al. (2012) also showed that it is possible to estimate the initial $\delta^{13}C$ value of dissolved inorganic carbon in the drip water using the combined stalagmite ^{14}C and $\delta^{13}C$ measurements. This finding opens the door to more precisely describe and model isotope fractionation effects that prevailed during calcite precipitation in the past. Or to put it differently: to make better use of one of the most important proxy indicators of speleothems, $\delta^{13}C$.

Breakthroughs in U-series techniques have provided the crucial momentum to position speleothems among today's key paleoenvironmental archives (Henderson, 2006). Yet, the decay constant of ^{230}Th dictates that despite technological advances U-series dates beyond 500–600 ka are progressively less precise and the method effectively approaches its upper limit. The hope for researchers working on speleothems of older (but unknown) age relies on the U–Pb technique, and the article by Woodhead et al. (2012) is a timely attempt to summarize the key aspects of this dating technique. Written by members of a leading U–Pb laboratory, this review discusses the various steps from sample selection to data evaluation. Given the fact that U–Pb dating still belongs to the suite of most time-consuming techniques, sample pre-screening is essential. The authors discuss various methods and recommend autoradiography using beta scanners, ideally in combination with laser-ablation ICP-MS, as rapid screening methods for reconnaissance studies. Following a detailed description of the chemical preparation and the mass-spectrometric analyses using state-of-the-art MC-ICP-MS data, alternative methods for isochron construction are presented. Case studies clearly show the high degree of precision that can be achieved with ancient speleothems of optimum quality. The authors emphasize, however, that even with these technologies the issue of age resolution becomes highly relevant beyond a few million years and it is no longer possible to use U–Pb methods to develop internal chronologies for typical speleothems (showing a growth duration rarely exceeding several tens of thousands of years). Notwithstanding these limitations, this article will certainly contribute to the growing interest in this technique that leads the way for the speleothem community tackling issues of climate change beyond $\sim$500 ka.

To test theories of climate change and human evolution for the Middle Pleistocene and earlier, including phasing relationships between astronomical forcing and climate parameters, we require continuous palaeoenvironmental records with a high density of independent, radio-isotopic ages. As discussed in the review by Woodhead et al. (2012), there exists great potential for U–Th–Pb dated speleothem records to fill the existing gap beyond 500 ka, but to do this effectively requires levels of precision and accuracy of $<$5 ka (i.e. much less than the period of precession of the Earth's axis of rotation). This is challenging, but Bajo et al. (2012) highlight a detailed and robust contribution that achieves such levels using material, with very low common Pb, high U and a residual disequilibrium in $^{234}U/^{238}U$ activity ratio, that grew during three glacial terminations of the Middle Pleistocene ($\sim$970–810 ka). The authors discuss the importance of sample density for age models and also the contribution of various sources of correlated and systematic errors, including spike calibration, decay constants and Th and common Pb corrections that can affect the derived age model. Note the age model discussed here for CC8 from Corchia Cave in Italy is an improvement on that for the same sample illustrated in Woodhead et al. (2012). Importantly, the long record of stable oxygen isotope composition in this speleothem can be linked with past North Atlantic sea-surface temperatures (Drysdale et al., 2009). This will be revealed in forthcoming contributions and is likely to be compared with astronomically-tuned archives of Middle Pleistocene age, such as marine $\delta^{18}O$ (e.g. Lisiecki and Raymo, 2005), loess magnetic susceptibility (e.g. Sun et al., 2006) or ice core $\delta O_2/N_2$ records (e.g. Landais et al., 2012), to make useful observations about the synchroneity and the spatial pattern of climate response to insolation forcing at this time.

Finally, compared to the last two decades, the 1970s and 1980s saw a considerably larger proportion of speleothem research focused on studies of landscape history, where speleothem U-series chronologies were used to help constrain uplift and incision rates (Ford et al., 1981; Williams, 1982). Recent advances in speleothem and sediment burial dating using terrestrial cosmogenic nuclides have led to something of resurgence in this field recently (Granger and Stock, 2004; Stock et al., 2005; Meyer et al., 2009; Polyak et al., 2010). Szanyi et al. (2012) use a suite of single-collector plasma-source mass spectrometric U-series ages on fossil calcite rafts from Hungarian caves to refine the regional uplift history. The rafts were deposited in a series of cave pools thought to have been active at the time when the regional base level occupied similar elevations. Based on the extent of these rafts, the authors argue that they formed in extensive bodies of water coincident with the regional water table, rather than as isolated pools in the karst vadose zone. The authors identify regional variations in uplift rates, the range of which brackets independently derived estimates from nearby travertines.

References

Bajo, P., Drysdale, R., Woodhead, J., Hellstrom, J., Zanchetta, G., 2012. High-resolution U-Pb dating of an Early Pleistocene stalagmite from Corchia Cave (central Italy). Quaternary Geochronology 14, 5–17.

Barnes, J.W., Lang, E.J., Potratz, H.A., 1956. Ratio of ionium to uranium in coral limestones. Science 124, 175–176.

Breitenbach, S.F.M., Rehfeld, K., Goswami, B., Baldini, J.U.L., Ridley, H.E., Kennett, D.J., Prufer, K.M., Aquino, V.V., Asmerom, Y., Polyak, V.J., Cheng, H., Kurths, J., Marwan, N., 2012. Constructing proxy records from age models (COPRA). Climate of the Past 8, 1765–1779.

Broecker, W.S., Olsen, E.A., Orr, P.C., 1960. Radiocarbon measurements and annual rings in cave formations. Nature 185, 93–94.

Dasgupta, S., Saar, M.O., Edwards, R.L., Shen, C.-C., Cheng, H., Alexander, E.C., 2010. Three thousand years of extreme rainfall events recorded in stalagmites from Spring Valley Caverns, Minnesota. Earth and Planetary Sciences Letters 300, 46–54.

Day, C.C., Henderson, G.M., 2011. Oxygen isotopes in calcite grown under cave-analogue conditions. Geochimica et Cosmochimica Acta 75, 3956–3972.

Domínguez-Villar, D., Fairchild, I.J., Baker, A., Wang, X., Edwards, R.L., Cheng, H., 2009. Oxygen isotope precipitation anomaly in the North Atlantic region during the 8.2 ka event. Geology 37, 1095–1098.

Domínguez-Villar, D., Baker, A., Fairchild, I.J., Edwards, R.L., 2012. A method to anchor floating chronologies in annually laminated speleothems with U-Th dates. Quaternary Geochronology 14, 57–68.

Dreybrodt, W., Scholz, D., 2011. Climatic dependence of stable carbon and oxygen isotope signals recorded in speleothems: from soil water to speleothem calcite. Geochimica et Cosmochimica Acta 75, 734–752.

Drysdale, R., Zanchetta, G., Hellstrom, J.C., Zhao, J.-X., Fallick, A.C., Isola, I., Bruschi, G., 2004. Palaeoclimatic implications of the growth history and stable isotope ($\delta^{18}O$ and $\delta^{13}C$) geochemistry of a Middle to Late Pleistocene stalagmite from central-western Italy. Earth and Planetary Science Letters 227, 215–229.

Drysdale, R.N., Hellstrom, J.C., Zanchetta, G., Fallick, A.E., Sánchez Goñi, M.F., Couchoud, I., McDonald, J., Maas, R., Lohmann, G., Isola, I., 2009. Evidence for obliquity forcing of glacial termination II. Science 325, 1527–1531.

Drysdale, R.N., Paul, B.T., Hellstrom, J.C., Couchoud, I., Greig, A., Bajo, P., Zanchetta, G., Isola, I., Spötl, C., Baneschi, I., Regattieri, E., Woodhead, J.D., 2012. Precise microsampling of poorly laminated speleothems for U-series dating. Quaternary Geochronology 14, 38–47.

Edwards, R.L., Chen, J.H., Wasserburg, G.J., 1997. ^{238}U-^{234}U-^{230}Th-^{232}Th systematics and the precise measurement of time over the past 500 000 years. Earth and Planetary Sciences Letters 81, 175–192.

Fleitmann, D., Burns, S.J., Neff, U., Mudelsee, M., Mangini, A., Matter, A., 2004. Palaeoclimatic interpretation of high-resolution oxygen isotope profiles derived from annually laminated speleothems from southern Oman. Quaternary Science Reviews 23, 935–945.

Fohlmeister, J., 2012. A statistical approach to construct composite climate records of dated archives. Quaternary Geochronology 14, 48–56.
Ford, D.C., Schwarcz, H.P., Drake, J.J., Gascoyne, M., Harmon, R.S., Latham, A.G., 1981. Estimates of the age of the existing relief within the southern rocky mountains of Canada. Arctic and Alpine Research 13, 1–10.
Franke, H.W., 1965. Das Wachstum der Tropfsteine. In: Proceedings of the 4th International Congress of Speleology, vol. 3, pp. 97–103.
Franke, H.W., Geyh, M.A., 1971. Radiokohlenstoff-Analysen an Tropfsteinen. Umschau in Wissenschaft und Technik 71, 91–92.
Frisia, S., Borsato, A., Fairchild, I.J., McDermott, F., Selmo, E.M., 2002. Aragonite-calcite relationships in speleothems (Grotte de Clamouse, France): environment, fabrics, and carbonate geochemistry. Journal of Sedimentary Research 72, 687–699.
Genty, D., Baker, A., Vokal, B., 2001. Intra- and inter-annual growth rate of modern stalagmites. Chemical Geology 176, 191–212.
Genty, D., Massault, M., 1997. Bomb C-14 recorded in laminated speleothems: calculation of dead carbon proportion. Radiocarbon 39, 33–48.
Geyh, M.A., 1970. Isotopenphysikalische Untersuchungen an Kalksinter, ihre Bedutung für die ^{14}C-Altersbestimmung von Grundwasser und die Erforschung des Paläoklimas. Geologisches Jahrbuch 88, 149–158.
Granger, D.E., Stock, G.M., 2004. Using cave deposits as geologic tiltmeters: application to postglacial rebound of the Sierra Nevada, California. Geophysical Research Letters 31, L22501. http://dx.doi.org/10.1029/2004GL021403.
Griffiths, M.L., Fohlmeister, J., Drysdale, R.N., Hua, Q., Johnson, K.R., Hellstrom, J.C., Gagan, M.K., Zhao, J.X., 2012. Hydrological control of the dead carbon fraction in a Holocene tropical speleothem. Quaternary Geochronology 14, 81–93.
Henderson, G.M., 2006. Caving in to new chronologies. Science 313, 620–622.
Hodge, E., McDonald, J., Fischer, M., Redwood, D., Hua, Q., Levchenko, V., Drysdale, R., Waring, C., Fink, D., 2011. Using the ^{14}C bomb pulse to date young speleothems. Radiocarbon 53, 345–357.
Hoffmann, D.L., Beck, J.W., Richards, D.A., Smart, P.L., Singarayer, J.S., Ketchmark, T., Hawkesworth, C.J., 2010. Towards radiocarbon calibration beyond 28 ka using speleothems from the Bahamas. Earth and Planetary Science Letters 289, 1–10.
Hua, Q., McDonald, J., Redwood, D., Drysdale, R., Lee, S., Fallon, S., Hellstrom, J., 2012. Robust chronological reconstruction for young speleothems using radiocarbon. Quaternary Geochronology 14, 67–80.
Huang, Y., Fairchild, I.J., 2001. Partitioning of Sr^{2+} and Mg^{2+} into calcite under karst-analogue experimental conditions. Geochimica et Cosmochimica Acta 65, 47–62.
Huang, Y., Fairchild, I.J., Borsato, A., Frisia, S., Cassidy, N.J., McDermott, F., Hawkesworth, C.J., 2001. Seasonal variations in Sr, Mg and P in modern speleothems (Grotta di Ernesto, Italy). Chemical Geology 175, 429–448.
Kaufmann, G., Dreybrodt, W., 2004. Stalagmite growth and paleoclimate: an inverse approach. Earth and Planetary Science Letters 224, 529–545.
Labeyrie, J., Duplessy, J.C., Delibrais, G., Letolle, R., 1967. Études des témperatures des climats anciens par la mesure de l'oxygène-18, du carbone-13 et du carbone-14 dans les concrétions des caverns. In: Proceedings of the International Atomic Energy Agency, Vienna. IAEA-SM87/5, pp. 153–160.
Lachniet, M.S., Bernal, J.P., Asmerom, Y., Polyak, V., 2012. Uranium loss and aragonite-calcite age discordance in a calcitized aragonite stalagmite. Quaternary Geochronology 14, 26–37.
Landais, A., Dreyfus, G., Capron, E., Pol, K., Loutre, M.F., Raynaud, D., Lipenkov, V.Y., Arnaud, L., Masson-Delmotte, V., Paillard, D., Jouzel, J., Leuenberger, M., 2012. Towards orbital dating of the EPICA Dome C ice core using $\delta O_2/N_2$. Climate of the Past 8, 191–203.
Lisiecki, L.E., Raymo, M.E., 2005. A Pliocene-Pleistocene stack of 57 globally distributed benthic $d^{18}O$ records. Paleoceanography 20, PA1003. http://dx.doi.org/10.1029/2004PA001071.
Luo, X., Rehkämper, M., Lee, D.-C., Halliday, A.N., 1997. High precision $^{230}Th/^{232}Th$ and $^{234}U/^{238}U$ measurements using energy-filtered ICP magnetic-sector multiple-collector mass spectrometry. International Journal of Mass Spectrometry 171, 105–117.
McDonald, J., Drysdale, R., Hill, D., Chisari, R., Wong, H., 2007. The hydrochemical response of cave drip waters to sub-annual and inter-annual climate variability, Wombeyan Caves, SE Australia. Chemical Geology 244, 605–633.
Mattey, D., Lowry, D., Duffet, J., Fisher, R., Hodge, E., Frisia, S., 2008. A 53-year seasonally resolved oxygen and carbon isotope record from a modern Gibraltar speleothem: reconstructed drip water and relationship to local precipitation. Earth and Planetary Science Letters 269, 80–95.
Meyer, M., Cliff, R.A., Spötl, C., Knipping, M., Mangini, A., 2009. Speleothems from the earliest Quaternary: snapshots of paleoclimate and landscape evolution at the northern rim of the Alps. Quaternary Science Reviews 28, 1374–1391.
Mühlinghaus, C., Scholz, D., Mangini, A., 2009. Modelling fractionation of stable isotopes in stalagmites. Geochimica et Cosmochimica Acta 73, 7275–7289.
Polag, D., Scholz, D., Mühlinghaus, C., Spötl, C., Schroder-Ritzrau, A., Segl, M., Mangini, A., 2010. Stable isotope fractionation in speleothems: laboratory experiments. Chemical Geology 279, 31–39.
Polyak, V., Hill, C., Asmerom, Y., 2010. Age and evolution of the Grand Canyon revealed by U-Pb dating of water table-type speleothems. Science 319, 1377–1380.
Railsback, L.B., Brook, G.A., Chen, J., Kalin, R., Fleischer, C.J., 1994. Environmental controls on the petrology of a Late Holocene speleothem from Botswana with annual layers of aragonite and calcite. Journal of Sedimentary Research A64, 147–155.
Richards, D.A., Dorale, J.A., 2003. U-series chronology and environmental applications of speleothems. In: Bourdon, B., Henderson, G.M., Lundstrom, C.C., Turner, S.P. (Eds.), Uranium-series Geochemistry Reviews in Mineralogy and Geochemistry, vol. 52. Mineralogical Society of America, Washington DC, pp. 407–460.
Rosholt, J.N., Antal, P.S., 1962. Evaluation of the $^{231}Pa/U–^{230}Th/U$ Method for Dating Pleistocene Carbonate Rocks, US Geological Survey Professional Paper 450-E, pp. E108–E111.
Scholz, D., Frisia, S., Borsato, A., Spötl, C., Fohlmeister, J., Mudelsee, M., Miorandi, R., Mangini, A., 2012. Holocene climate variability in north-eastern Italy: potential influence of the NAO and solar activity recorded by speleothem data. Climate of the Past 8, 1367–1383.
Scholz, D., Hoffmann, D.L., 2011. StalAge: an algorithm designed for construction of speleothem age models. Quaternary Geochronology 6, 369–382.
Scholz, D., Hoffmann, D.L., Hellstrom, J., Bronk Ramsey, C., 2012. A comparison of different methods for speleothem age modelling. Quaternary Geochronology 14, 94–104.
Shen, C.-C., Edwards, R.L., Cheng, H., Dorale, J.A., Thomas, R.B., Moran, S.B., Weinstein, S.E., Hirschmann, M., 2002. Uranium and thorium isotopic and concentration measurements by magnetic sector inductively coupled plasma mass spectrometry. Chemical Geology 185, 165–178.
Southon, J., Noronha, A.L., Cheng, H., Edwards, R.L., Wang, Y., 2012. A high-resolution record of atmospheric ^{14}C based on Hulu Cave speleothem H82. Quaternary Science Reviews 33, 32–41.
Stock, G.M., Granger, D.E., Anderson, R.S., Sasowsky, I.D., Finkel, R.C., 2005. Comparison of U-Th, paleomagnetism, and cosmogenic burial methods for dating caves: implications for landscape evolution studies. Earth and Planetary Science Letters 236, 388–403.
Sun, Y., Clemens, S.C., An, Z., Yu, Z., 2006. Astronomic timescale and palaeoclimatic implication of stacked 3.6-Myr monsoon records from the Chinese Loess Plateau. Quaternary Science Reviews 25, 33–48.
Szanyi, G., Surányi, G., Leél-Ossy, S., 2012. Cave development and Quaternary uplift history in the Central Pannonian Basin derived from speleothem ages. Quaternary Geochronology 14, 18–25.
Tooth, A.F., Fairchild, I.J., 2003. Soil and karst aquifer hydrological controls on the geochemical evolution of speleothem-forming drip waters, Crag Cave, southwest Ireland. Journal of Hydrology 273, 51–68.
Williams, P.W., 1982. Speleothem dates, Quaternary terraces and uplift rates in New Zealand. Nature 298, 257–260.
Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., Zanchetta, G., Devine, P., Taylor, E., 2006. U-Pb geochronology of speleothems by MC-ICPMS. Quaternary Geochronology 1, 208–221.
Woodhead, J., Hellstrom, J., Pickering, R., Drysdale, R., Paul, B., Bajo, P., 2012. U and Pb variability in older speleothems and strategies for their chronology. Quaternary Geochronology 14, 105–113.

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