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Stable isotope microsampling of speleothems for palaeoenvironmental studies: A comparison of microdrill, micromill and laser ablation techniques

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Abstract

Three different techniques are currently in use to microsample speleothem (and tufa) specimens at moderate to high spatial resolution, manual microdrilling using a dentist drill, semi automated micromilling, and laser ablation. While a separate handling step is involved in the first two techniques — transferring the sample powder to an on-line carbonate preparation system linked to an isotope ratio mass spectrometer — the laser is directly interfaced with the mass spectrometer via a gas preparation device. In this study we compare stable C and O isotope results obtained by these three preparation techniques using continuous He-flow mass spectrometry on the same speleothem samples. The overall consistency of the results is satisfactorily high, in particular between the micromill and the laser data. Although the precision of the laser data is slightly lower than analyses obtained by the other two methods (in particular with respect to $\delta^{18}O$), the speed of acquisition renders laser ablation a useful reconnaissance technique for rapidly analyzing long sections of speleothems. Micromilling is the method of choice to obtain highly spatially resolved isotope data of high analytical precision, while microdrilling is still an low-cost alternative for sampling at comparably low resolution, e.g. of fast growing stalagmites.

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1. Introduction

Stable C and O isotope values are among the most widely utilized proxy data in paleoenvironmental studies of continental carbonates that include speleothems, molluscs and tufa deposits. The O isotope values of these carbonates primarily reflect atmospheric and hydrological processes, while C isotope values are related to the terrestrial C cycle and provide information about soil and vegetation (see Dorale et al., 2002, and McDermott, 2004 for reviews on the use of these stable isotopes in speleothem research, and Turi, 1986 and Pentecost, 2005 for summaries of stable isotopes of travertine deposits).

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Previous studies commonly relied on relatively low-resolution data obtained using manually drilling small amounts of carbonate powder from rock slabs. Most studies used an increment between 0.5 and a few millimetres depending on the growth rate of the sample. Recent years have seen a strong demand for higher resolution continuous stable isotope sampling in order to address issues of climate variability on short (i.e. annual to centennial) time scales including rapid changes in the environment. This demand has resulted in an renaissance of semi automated micromill techniques, which have been in use for 25 years in other fields of sediment and rock petrology (Verschure, 1978; Prezbindowski, 1980; Wada, 1988; Dettman and Lohmann, 1995; Wurster et al., 1999; Fouke and Rakovan, 2001). These techniques are capable of continuously sampling sections of speleothems (e.g., Frappier et al., 2002) or tufa deposits (e.g., Matsuoka et al., 2001) at spatial resolutions ranging from a few tens of microns to fractions of a millimetre. This well established technique combines high spatial resolution and high analytical precision, i.e., phosphoric acid reaction and subsequent measurement of the CO_2 by isotope ratio mass spectrometry (IRMS).

Isotope analysis of carbonates conducted on CO_2 liberated by in-situ laser heating is another attractive means of obtaining data at high spatial resolution, developed some 15 years ago (Smalley et al., 1989; Dickson et al., 1990). Decarbonation of carbonate at high temperatures should produce CO_2 with minimal isotopic fractionation between the solid and gas phase. In practice, isotope data were affected by problematic isotope fractionations affecting both C and O. These fractionations seemed to be both laboratory and target specific, caused by partial reactions due to low absorption of 1.066 μm near-infrared laser radiation, and to back reactions of CO_2 with active CaO within the sample chamber (e.g. Powell and Kyser, 1991). Far infra-red radiation from CO_2 lasers (10.66 μm) is far more efficient at coupling with carbonate minerals and Sharp and Cerling (1996) demonstrated that laser heating of carbonate in a sample chamber flushed by a stream of flowing He using a CO_2 laser offered significantly improved reproducibility and performance. The He-flow method minimizes back-reactions between CO_2 and the target and with the usual advantages of on-line gas purification and rapid isotope analysis.

In this article we compare for the first time stable isotope results obtained by micromilling and laser ablation in order to assess the reproducibility of these results and to explore potential problems and biases. In addition, micromill results of different resolution for the same samples are presented and compared to results obtained by manual microdrilling.

2. Samples and methods

We prepared a set of speleothem samples which were micromilled and partially manually microdrilled at Leopold-Franzens-Universität Innsbruck (LFUI). Two samples were subsequently re-analyzed using laser ablation at Royal Holloway, University of London (RHUL). All samples were cut along the growth axis and polished prior to analysis.

OBI 55: A stalagmite from Obir Cave (Carinthia, Austria), Holocene in age, composed of inclusion-poor, dense calcite. The sample shows faint macroscopic growth bands and discontinuous, laminae (30–100 μm) of possibly annual origin. The top 24 mm of this stalagmite were manually microdrilled at c. 1 mm intervals. Subsequently, the top 18 mm were microdrilled at c. 0.5 mm resolution (parallel track 6 mm to the right of the original track) and finally the top 25 mm were micromilled at 0.1 mm resolution (parallel track 2 mm to the left of the original track).

GRI 2: This is a flowstone sample from Marine Isotope Stage 3, obtained from Griffen Cave (Carinthia, Austria — Spötl and Mangini, 2005). It consists of non-translucent, micritic calcite showing fine-scale macroscopic layering on a millimetre scale. A section of about 8 cm was micromilled in two parallel tracks (2 mm apart) at 0.1 and 0.25 mm, respectively.

HOT 1: A flowstone formed during isotope stage 5 in fractures of a carbonate slope breccia near Innsbruck (Austria; Spötl and Mangini, 2006). The layer is 3–4 cm thick and consists of dense, light yellow calcite. Regular lamination (mostly c. 50 μm thin) is visible in two intervals of the flowstone under epifluorescence. The sample was first microdrilled manually at 1 mm resolution and later micromilled at 0.1 mm resolution (track 2.5 mm apart from the original track). Subsequently, a laser profile was shot along the micromill track so ensure direct comparability between the two sets of data.

LAS 5: A late Holocene flowstone from Vinschgau (northernmost Italy; Spötl et al., 2002) composed of orange, dense calcite interlayered with white aragonite. The sample was first micromilled at 0.075 mm resolution. Subsequently, a laser profile was shot along the micromill track to ensure direct comparability between the data sets.

2.1. Microdrilling and micromilling

Microdrilling was conducted using a standard dentist drill (0.3–0.8 mm diameter). Vertical holes down to about 1–2 mm depth were manually drilled at increments specified above. The powder was collected and transferred into auto sampler exetainer vials and analyzed the same way as the micromilled samples (see below). Micromilling was performed using a NewWave Research micromill equipped with 0.3 mm stainless steel drill bits (Brasseler). A trench about 2 mm wide and 0.2 to 0.3 mm deep was micromilled concordant to the lamination/bedding. An important aspect of this type of continuous micromilling is that no material remains between two consecutive samples (cf. microdrilling). The resulting powder was transferred into 10 ml exetainer vials using a small scalpel. The drill bit and the sample surface were cleaned after each milling step using a brush. We optimized the micromilling procedure at LFUI so that a trained person is capable of preparing about 100 microsamples for the mass spectrometer within about 3 h. The stable isotopic measurement is performed using continuous-flow isotope IRMS (Spötl and Vennemann, 2003). In 2004 we upgraded our automated carbonate preparation system to allow a total of 120 samples (including standards) to be analyzed over-night. The results are reported relative to the VPDB standard.

2.2. Laser analysis

In-situ analysis by laser sampling was performed using an automated laser-ablation system built at RHUL which

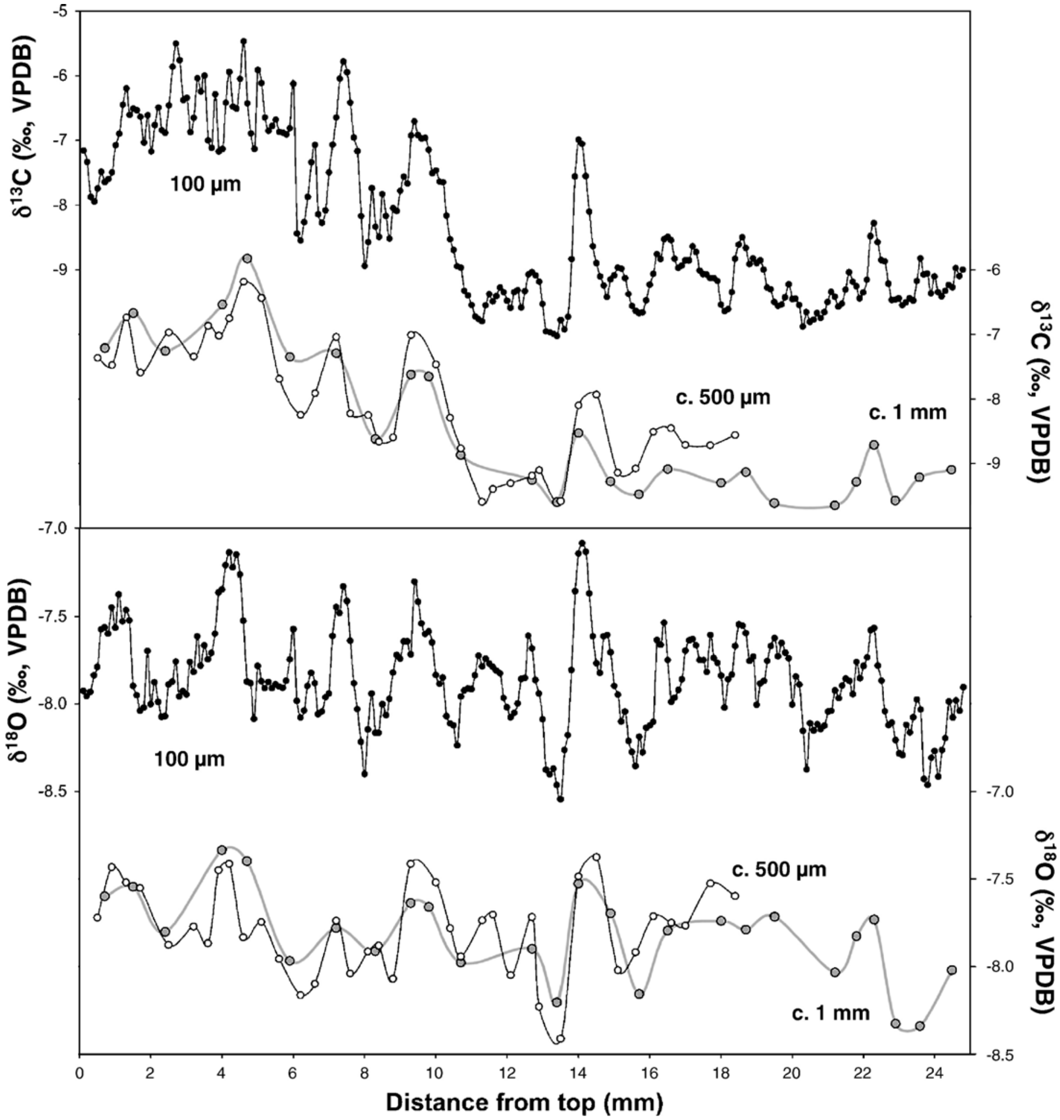

Fig. 1. Comparison of stable C and O isotope profiles across the top part of stalagmite OBI 55. The 1 mm and 0.5 mm incremental data were obtained by manual microdrilling, whereas continuous micromilling produced the 0.1 mm data series. Isotope data are plotted on two different vertical axes to facilitate visual inspection.

consists of a CO_2 laser bench (Synrad 25 w CO_2 laser operating at 10.6 μm, spot size 100–150 μm) and a He-flow sample chamber coupled to a Carlo–Erba NA1500 elemental analyser and a VG Instruments Optima mass spectrometer. The elemental analyser provides the He supply to the flow-through laser chamber and the return flow passes through a magnesium perchlorate water drying column into a 1 m packed GC column, TCD, and via an open split into the mass spectrometer ion source. The sample chamber has an internal diameter of 40 mm (total volume 30 ml) and He is diffused through a porous frit fitted to the base of the chamber at a rate of 40 ml/min. The sample, prepared as a thin slab or pencil (5–10 mm thick) with the surface to be analysed ground flat using 1000 grade grit, sits on the porous frit and the chamber sealed with a BaF_2 window. The laser is fired for 0.5 s at 40–80% power to yield CO_2 pulses with peak heights of approximately 2 nA. Laser damage to the target, resulting in fracturing and spallation, can be a problem and laser power may be decreased for fragile samples. Ablation pits are surrounded by a thermal halo of partially decarbonated (and isotopically fractionated) material which can be 2–4 times the diameter of the laser spot depending on the duration of the laser pulse. Thus, adjacent ablation spots

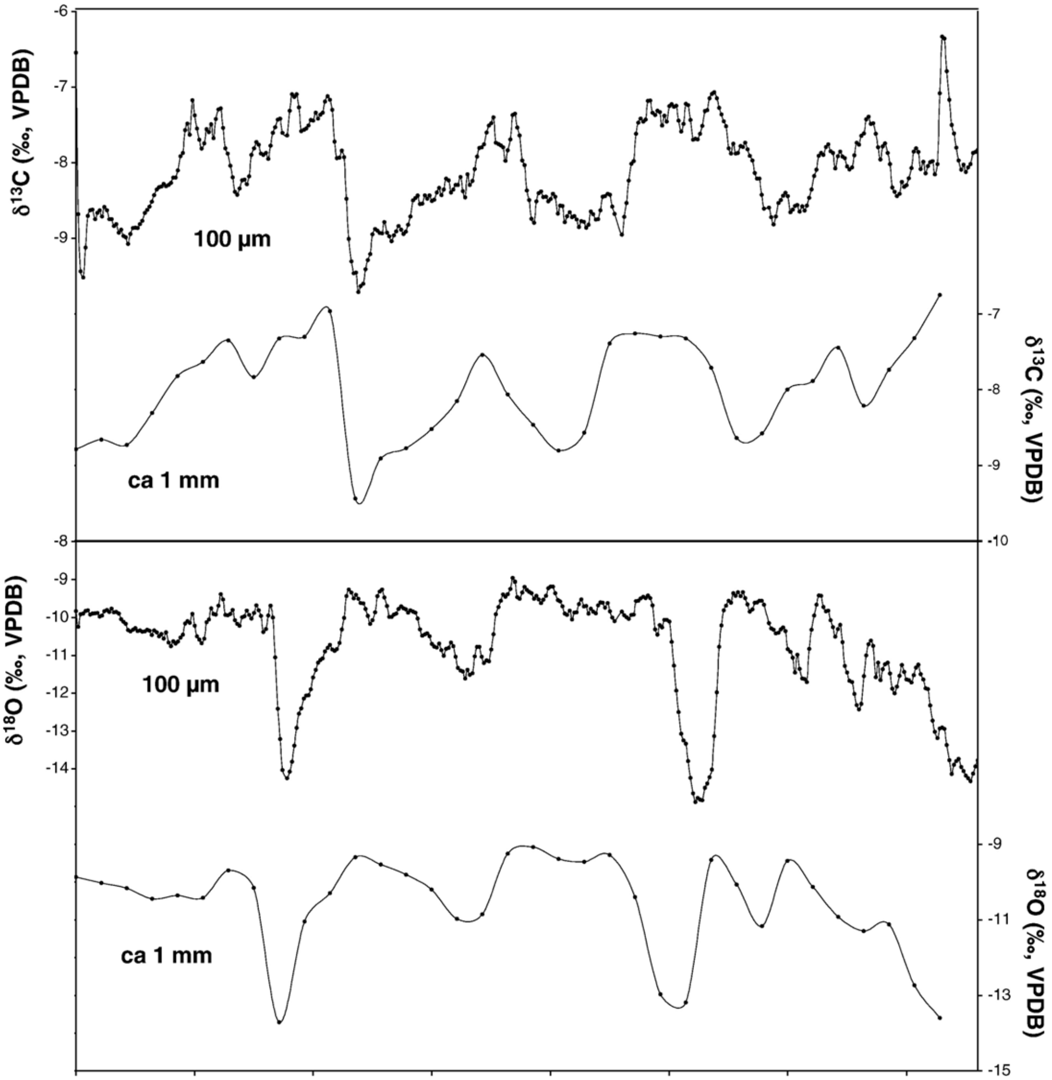

Fig. 2. A microdrill traverse (at 1 mm increments) compared to a 0.1 mm micromilled profile across flowstone HOT 1. Note the lack of second-order isotope variability in the low-resolution data. The slight mismatch of the two profiles above 20 mm reflects nonparallel growth layers.

must be sufficiently separated to avoid these halos thereby limiting the linear spatial resolution to a minimum value of around 300 μm. Resolution can be doubled in laminated calcite by carrying out parallel forward and reverse traverses with staggered laser spots.

A typical analytical run consists of alternating cycles of 20 spot analyses of Carrara marble, and traverses across the unknown sample, finishing with a final block of 20 Carrara analyses. Sample HOT1 was sufficiently robust and underwent parallel forward and reverse profiles giving a net spatial resolution of 338 μm. Sample LAS 5 was susceptible to laser damage and was analysed as a single pass at lower resolution to minimise fracturing. The average values for each block of Carrara data are used as a within-run drift monitor and drift corrected laser data are normalized to VPDB based on the difference in the grand mean of the micromill and laser data for the whole sample. The corrections (+0.14‰ for δ^{13}C and −1.14‰ for δ^{18}O) encompass solid–gas fractionations associated with laser-decarbonation which are constant for a particular set of operating conditions. Reproducibility of laser analyses, measured on Carrara marble 'standard' blocks are better than ±0.2‰ (1 sigma) for δ^{13}C and ±0.3‰ (1 sigma) for δ^{18}O.

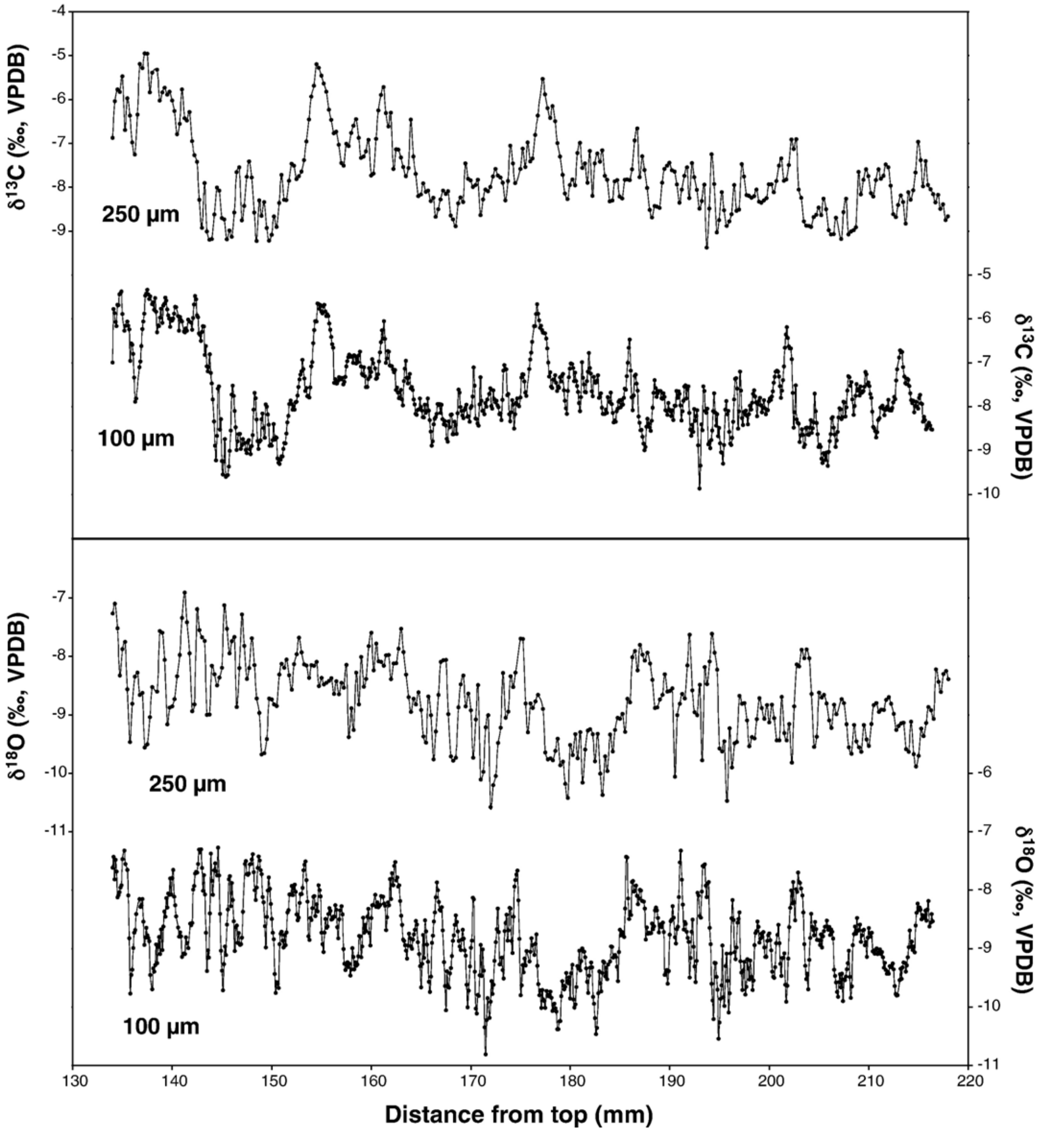

Fig. 3. Comparison of two isotope data series acquired using different micromill increments, sample GRI 2. Note higher degree of reproducibility for the C isotope data because of a higher signal-to-noise ratio.

Variations in CO_2 yield can result from differences in the absorbance of laser radiation by the target, which may be enhanced or attenuated by defects such as holes or cracks, and related to crystallinity and composition. Analytical error causing anomalous yields arises from non-linearity of the ion-source and from changes to the spot-halo geometry affecting the net solid–gas isotopic fractionation that particularly affects $\delta^{18}O$ values. Source linearity is routinely monitored over an order of magnitude range in beam intensity and is typically less than 0.25‰ for both $\delta^{13}C$ and $\delta^{18}O$, so instrumental error induced by yield variations of less than a factor of 2 are negligible. Anomalous yields are usually associated with defects (natural and laser-induced) and isotope data from these spots can be removed from the data set if necessary.

3. Results and discussion

3.1. Microdrill vs. micromill results

The low-resolution microdrill and the high-resolution micromill data series of stalagmite OBI 55 show good correspondence of salient features (Fig. 1). O isotope values exhibit a high variability of centennial origin (based on U-series dates — Spötl and Mangini, unpublished data). Low resolution profiles obviously fail to characterize several features which comprise only 1–2 mm of calcite stratigraphy (Fig. 1). If present — such as the prominent excursion 14.5 mm below the top of the stalagmite (Fig. 1) — they are characterized by one or two data points only. The low resolution data also

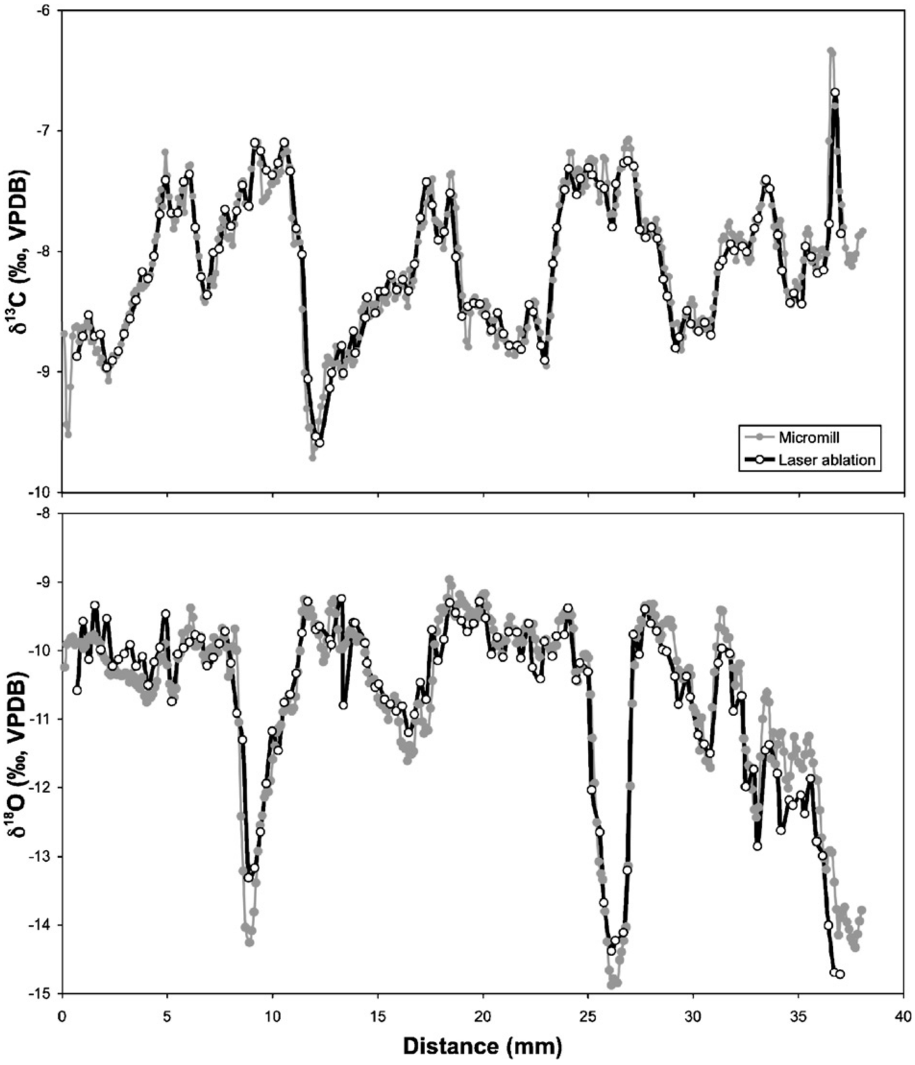

Fig. 4. Comparison of C and O isotope data obtained by micromilling (100 μm resolution) and by laser ablation (338 μm resolution) of flowstone HOT 1.

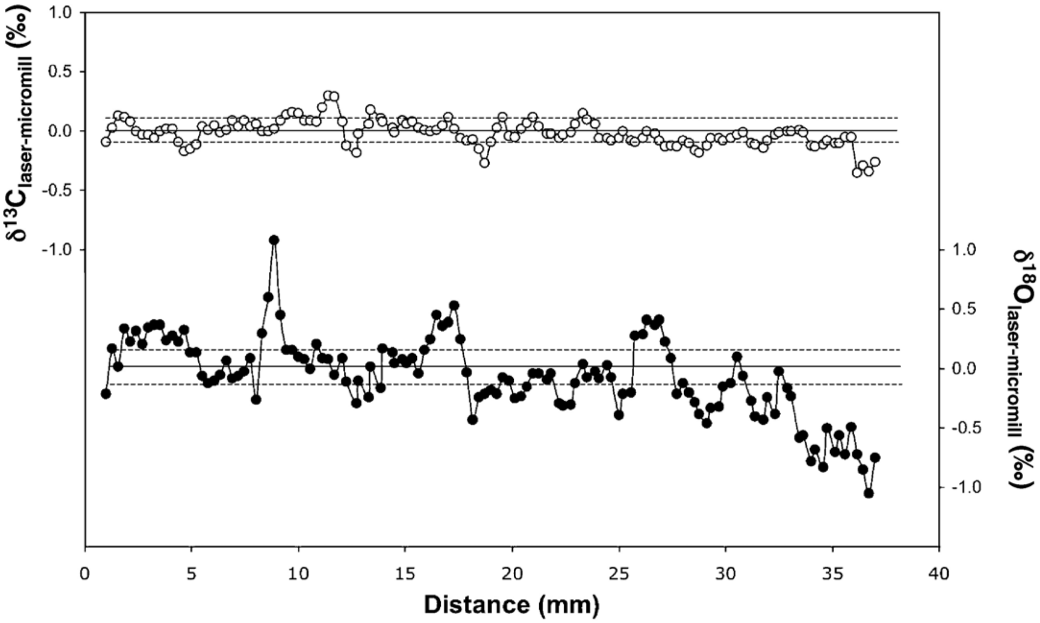

Fig. 5. Difference between the isotopic profiles obtained by micromilling and laser ablation (sample HOT 1), represented as the difference between equally sampled spline fits to each data set. See text for discussion.

tend to miss extreme values, as shown by the peak values for the C isotope maxima at 14.5 and 7.0 mm below the top of the sample: the 1 mm and 0.5 mm resolution data series suggest peak $\delta^{13}C$ values that are lower by about 1.5 and 0.9–1.2‰, respectively (Fig. 1). Similar insights can be gained from comparing microdrill (1 mm resolution) and micromill data (0.1 mm resolution) of flowstone HOT 1. The sample is characterized by large variations in both C and O isotopes. The most significant excursions exhibited by the low-resolution data (Fig. 2) are defined by very few data points. Smaller-scale isotope variability, e.g.

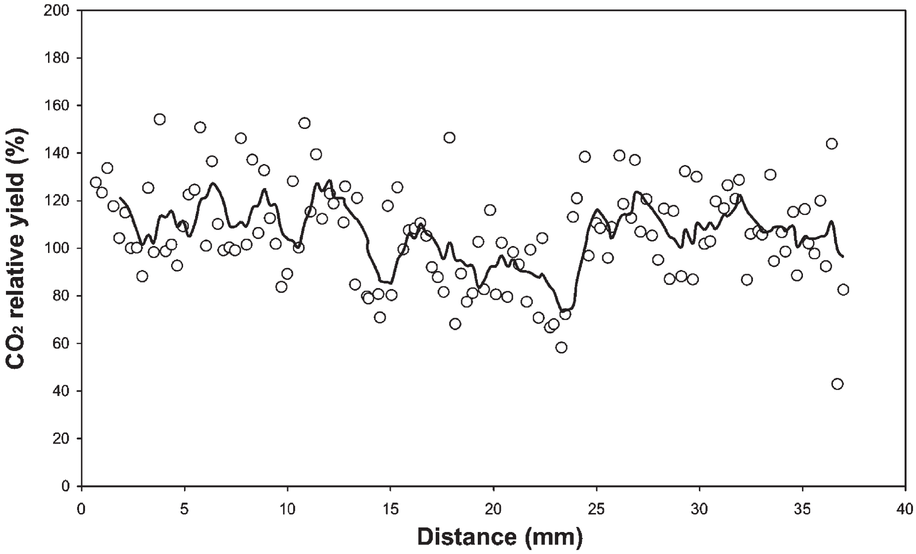

Fig. 6. Variation in relative yield of CO_2 from each laser spot along the length of HOT 1. The black line is a 5-point running mean. See text for discussion.

between 17 and 24 mm above the base in $\delta^{18}O$, are not visible in the microdrill data. Most importantly, the latter give little insights into the structure (and hence rate) of even the first-order isotope excursions that are clearly defined in the 0.1 mm data (Fig. 2).

3.2. Micromill data of different spatial resolution

Two parallel tracks in sample GRI 2 allow to assess the reproducibility of micromill data and to compare results from two different resolutions (0.25 and 0.1 mm — Fig. 3). GRI 2 is a flowstone sample showing fine-scale macroscopic layering. U-series dates suggest average growth rates of 40–80 mm/kyr (Spötl and Mangini, 2005). Although the milling traverse was not always strictly perpendicular to the individual laminae because of slightly irregular lamination, the two isotope profiles compare quite favorably (Fig. 3). C isotope data show a higher signal-to-noise ratio than the O isotope data and each of the larger peaks are present in both the moderate— and the high—resolution data. With regard to the C isotope data the 0.25 mm resolution data capture the salient features of

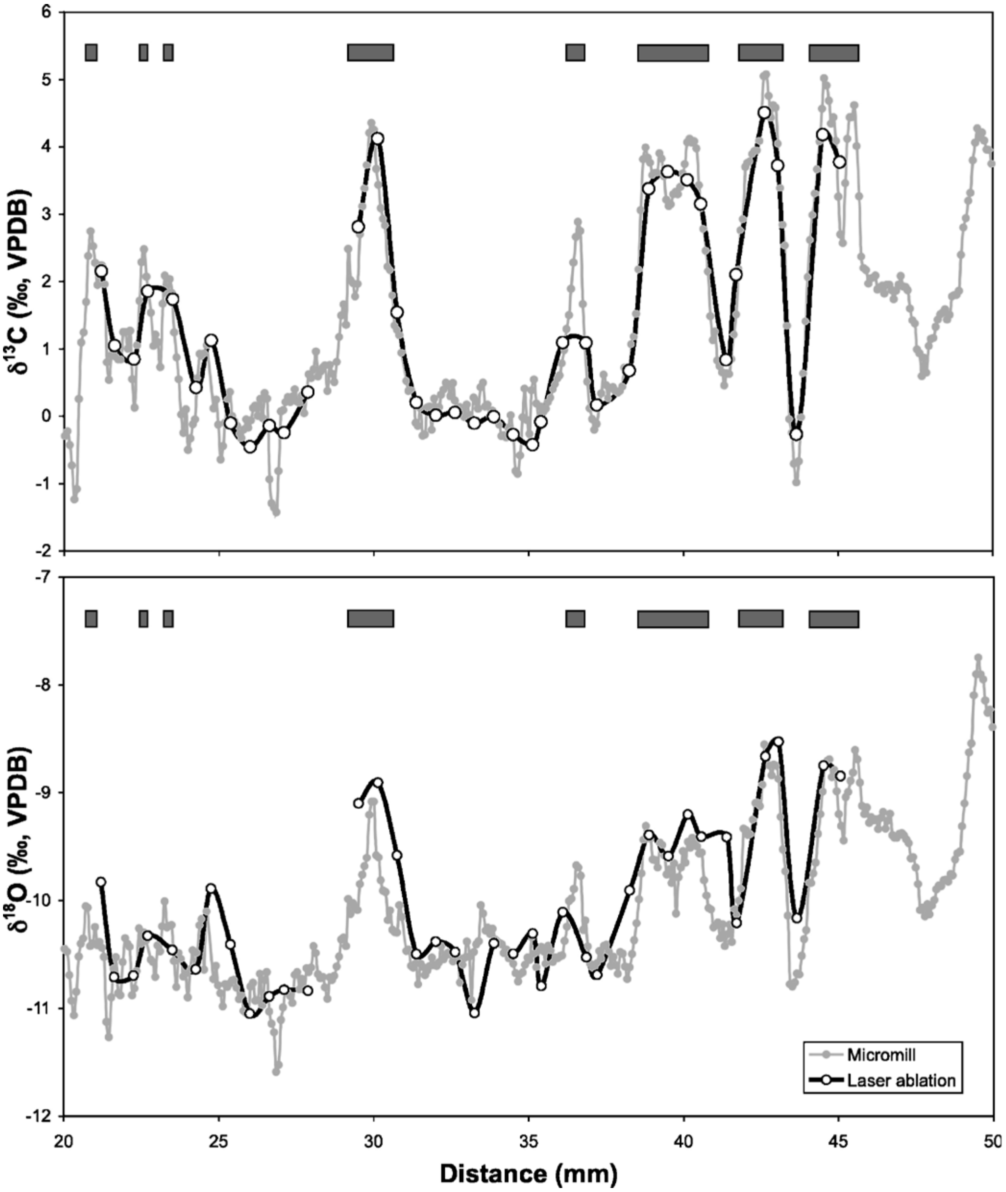

Fig. 7. Comparison of C and O isotope data obtained by micromilling (100 µm resolution) and by laser ablation (630 µm resolution) for a section of composite calcite–aragonite flowstone LAS 5. Dark grey horizontal bars indicate aragonite layers. See text for discussion.

the 8 cm section well. This, however, is not the case with the O isotope data, whose low signal-to noise ratio renders identification of minima and maxima in the 0.25 mm record (Fig. 3) ambiguous. The 0.1 mm resolution is clearly needed to define the high-frequency variability in this record.

3.3. Micromill vs. laser ablation results

Laser analysis were performed along the axis of the micromilled trench of sample HOT 1 to ensure the best possible spatial congruence of the two techniques. Micromill analyses at 100 μm resolution and laser analyses at 338 μm resolution for HOT 1 are shown in Fig. 4. There is a high degree of correspondence between the two methods with the lower resolution laser data showing minimal smoothing of the sharp excursions revealed by the micromill data.

The difference between the micromill and laser data are examined in better detail by fitting cubic spline curves to each dataset, resampling spline fits at the same resolution (338 μm) and then subtracting one from the other. The results of this for HOT 1 are shown in Fig. 5. $\delta^{13}C$ data remain for the most part within analytical error (±0.1‰), and other than at 13 mm, there are no obvious systematic shifts along the sample. The match for $\delta^{18}O$ is close to the limits of analytical error but shows local deviations of up to 0.5‰ at 8 mm, 17 mm and 27 mm. Since these excursions also occur where isotopic gradients are greatest these (and similarly the largest excursion in $\delta^{13}C$ at 13 mm) are likely to be artefacts of slight inaccuracies in the registration of the two datasets. The last 7 mm of the $\delta^{18}O$ profile does show evidence of a progressively larger discrepancy which may be a local target-dependent fractionation. Variation in the relative laser ablation yield in yield CO_2 along the section is shown in Fig. 6. The mean yield is 6% higher than that obtained on Carrara marble and CO_2 generation was relatively constant along the section falling between 100% and 150%, with evidence of a slight increase in yield around 23 mm. Variations in yield result from differences in the absorbance of laser radiation by the target related to crystallinity and composition. However, there is no relationship between variations in yield, including the slight increase in yield seen at 23 mm, and the match between the micromill and laser data shown in Fig. 5. The reason for the difference between the two data sets in the last 7 mm of the section remains unclear and a small target dependent effect cannot be ruled out.

A second flowstone sample, LAS 5, composed of alternating brown calcite interlayered with white aragonite was analysed by laser ablation but suffered fracturing as the laser track advanced a portion of these data are shown in Fig. 7 and compared with micromill data analysed at 75 μm resolution. The laser data for LAS 5 shown in Fig. 7 represent the merger of a forward and reverse profile with small local spatial corrections (<200 μm) to compensate for regions where growth lamellae are not perfectly normal to the axis of the traverse. The laser and micromill data again show that first order variations (c. 2‰ in $\delta^{13}C$ and up to 5‰ in $\delta^{18}O$) on a 5 to 10 mm distance are accurately reproduced. Over smaller distances aliasing errors cause some discrepancies in amplitude and phase of sub-mm isotope variations.

4. Recommendations

4.1. Choice of the method

All three methods utilized in this study have their advantages and disadvantages with regard to resolution, precision, speed and cost. None of the methods can be applied to all types of speleothem samples unless compromises are made. While micromilling is clearly superior to manual microdrilling when it comes of high spatial resolution (e.g. Frappier et al., 2002; Holzkämper et al., 2004; Mangini et al., 2005), the latter is probably the method of choice when it comes to sampling meter-long stalagmites at millimetre-scale resolution without access to laser facilities (e.g., Dykoski et al., 2005). Laser ablation analysis represents the fastest technique, but its spatial resolution — currently in the order of 250 to 500 μm — and precision — typically better than ± 0.2‰ for $\delta^{13}C$ and ±0.3‰ for $\delta^{18}O$ — is second to micromilling (and microdrilling, respectively). Laser spot analyses, however, can be performed at a rate of around 20 spots per hour or 60 linear millimetres per day at 250 mm resolution rendering this approach ideal for reconnaissance analyses of long sections of speleothem.

4.2. Sample orientation and aliasing

When it comes to high-resolution sampling issues it is important to consider issues related to the geometry of sampling. For example, as the trench of micromill traverses have a finite width parallel to the growth layers (typically 2 mm in our samples) irregular laminae will limit the ability to sample at the resolution of individual laminae. In the case of a significant change in isotope values across, e.g. a microhiatus or a sharp boundary between calcite and aragonite layers poor alignment of the trench (or laser spots) will result in an apparently gradual transition. We therefore recommend to gradually re-orient the sample slab whenever visible growth layers change their orientation along the sampling transect, i.e. the micromill trench does not necessarily have to follow a straight line through a given specimen. In such specimens it is then important to refer U-series data not to the distance from the top of the sample (measured along a straight line), but to the specific distance (sample) on the curved isotope transect. In addition to the lateral extent of the trench also its vertical dimension is relevant as non-vertical lamination will also compromise high resolution sampling. This, of course, is also pertinent to micro-drilling. In order to maximize both sample mass and time resolution is was therefore recently suggested that the recommended micromill sampling shape should be approximately 20x by 2x by x, whereby x is the thickness of the growth laminae (Fairchild et al., 2006). For example, micromilling a succession of regularly spaced 100 μm-wide laminae would require a 2 mm wide trench, 0.2 mm deep and results in increments slightly over 100 μg in weight, i.e. samples sizes that can be conveniently analyzed using state-of-the-art IRMS techniques.

Whenever the domain sampled is small relative to the interval between two consecutive analyses aliasing may occur, that is the incorrect recording of high-frequency variation (Weedon, 2003). This phenomenon is strongest developed where (a) regularly spaced laminae of (b) high intralamina (e.g., seasonal) isotope variability are sampled at a constant increment. In the extreme case of a perfectly laminated sequence of large and regular intralamina isotope variability incremental microsampling will give rise to a regular pattern of isotopic variability that is entirely unrelated to the true composition of the sample. In practice it is more likely that partial aliasing will occur, as the thickness of consecutive laminae is typically quite variable. Verification or falsification of (partial) aliasing requires the knowledge of the average growth rate, either by a series of U-series dates or by direct petrographic observations of laminae. Secondary ion mass spectrometry would offer the very high spatial resolution necessary to avoid aliasing (and explore the intralamina variability) in laminated speleothems, but the currently poor precision, slowness, high costs and difficult access prevents the routine use of this technique in stable isotope microsampling (Treble et al., 2005; Fairchild et al., 2006).

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