A high spatial resolution $\delta^{18}O$ profile of a speleothem using an ion-microprobe

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Abstract

The oxygen isotopic composition of a stalactite from the Soreq Cave, Israel has been investigated by in situ high spatial resolution ion microprobe analysis. The $\delta^{18}O$ record obtained on portions of the stalactite, which were deposited during the time interval of 18–14.3, 10.8–8.5 and 1.5–0.2 ka, has a temporal resolution ranging from ~ 1 to 25 years (depending on the deposition rate during the period investigated). Comparison to results obtained by micro-drilling and phosphoric acid reaction gas-phase mass spectrometry indicates that the ion microprobe analyses are precise and accurate at the 0.4–0.5‰ level. The high resolution of the ion microprobe profile enables the detection of short duration excursions toward low $\delta^{18}O$ values during deglaciation (from 18 to 14.3 ka), providing further evidence indicating the instability of the glacial climate.
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1. Introduction

The study of past climates has been a primary raison d'être for the study of variability in the stable isotope abundances of light elements in geochemistry (Urey et al., 1951). During most of the past four decades, the majority of the paleoclimatological studies has been concerned either with investigating the marine record or that contained in ice cores. Recent efforts in reconstructing climate change from conti-

nental records have renewed interest in the use of speleothems as climatic proxies (e.g., Hendy, 1971; Schwarcz, 1986; Gascoyne, 1992; Bar-Matthews et al., 2000). The utility of cave deposits for climate reconstruction has been improved by new capabilities to date young carbonates by U-series disequilibrium as determined by thermal ionization mass spectrometry (TIMS) (Dorale et al., 1992; Kaufman et al., 1998).

Our assumption is that the variations in $\delta^{18}O$ of a speleothem reflect primarily the changes in oxygen isotopic composition of precipitation in the area ($\delta^{18}O_w$) and the temperature of precipitation. The variation of $\delta^{18}O_w$ is in turn determined mainly by the vapor source, the surface air temperature (Dansgaard, 1964; Rozanski et al., 1993), and the total

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amount of rain in the area (Gat, 1996 and references cited therein). The time resolution of speleothem studies is determined by the growth rate of a speleothem, as well as by the sensitivity of the method of isotopic analysis, which determines the amount of calcite sample required. The recent introduction of computer-aided drill samplers (Quinn et al., 1996) and of laser ablation–gas chromatography–isotope ratio mass spectrometry (LA–GC–IRMS, McDermott et al., 2001) has increased this resolution significantly. Utilizing this technique, in the case of a rather fast growing stalagmite from the Shihua Cave in China, Ku and Li (1998) were able to achieve a resolution of 3 years over the last 500 years. Obviously in slower growing speleothems the time resolution is accordingly diminished.

In the present study, a high-resolution $\delta^{18}O$ profile of portions of a well-dated stalactite from the Soreq Cave, Israel was obtained by ion microprobe analysis and compared to a conventional $\delta^{18}O$ profile from the same sample, with the purpose of examining the possibility of increasing the spatial (and thus the time) resolution of $\delta^{18}O$ as climate proxy in speleothems.

2. Sampling and methods

The stalactite chosen for analysis is part of sample 2-N described previously by Bar-Matthews et al. (1997) and Kaufman et al. (1998). The stalactite comes from the Soreq Cave, a karstic cave in the westward-dipping flank of the Judean Hills anticline, about 20-km southwest of Jerusalem. The cave is located in a dolomitic host rock, and speleothem deposition has been practically continuous in it for the last 185,000 years (Bar-Matthews et al., 2000; Ayalon et al., 2002). Since the main purpose of our study is methodological, we chose this well-documented sample. Its mineralogy is rather simple (low magnesium calcite); it is well dated, and a rather closely spaced $\delta^{18}O$ profile of it was already available (Bar-Matthews et al., 1997; Kaufman et al., 1998). This profile could then serve as a check against the ion microprobe results. A slab of stalactite 2-N was prepared by cutting it perpendicular to its length, and polishing it with SiC and commercial diamond paste. The $\delta^{18}O$ profile was performed, using a micro driller (0.5 mm in diameter), by drilling every 0.5 to 1.0 mm and measuring the collected powder by the usual phosphoric acid, common bath, reaction technique (90 °C) using a VG Isocarb system attached to a Sira II mass spectrometer. Fig. 1 illustrates the $\delta^{18}O$ vs. age curve as reported by Kaufman et al. (1998). In order to ensure that the two analytical methods are applied along identical transects, the portion of the stalactite between 0.2 and 1.6 ka was re-drilled after the ion-probe analysis, using the ion-probe craters trace as a guide (Fig. 5C).

For ion microprobe analysis, the polished Soreq samples were mounted within the central 1.5 cm
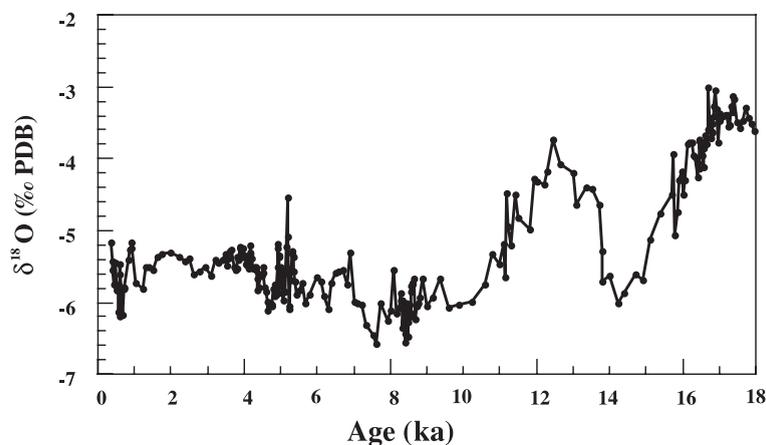

Fig. 1. Profile of $\delta^{18}O$ variations with time back to 18 ka in stalactite 2-N obtained by micro-drilling and conventional acid dissolution analysis (Kaufman et al., 1998).

diameter of a 2.5-cm-diameter sample holder. This central area included a polished crystal of our working standard "Optical Calcite" (OC) with a presumably known $\delta^{18}O_{PDB}$ of -14.4‰ (however, see below). Tests of oxygen isotope ratios measured on a petrographic glass slide demonstrated the importance of maintaining an approximately 2 mm distance from the edge of the sample holder. Outside of this central area, systematic shifts (of a few per mil) in instrumental mass fractionation could be resolved, presumably due to changes in ion extraction geometry caused by distortions in the electric field of the ion acceleration space induced by the edges of the sample holder. Thus, in order to accomplish long traverses, the sections of stalactite to be measured were cut such that they could be mounted in the center of the sample holder with a slight overlap between sequential sections.

Measurements were made with the UCLA CAMECA ims 1270 ion microprobe, using a Cs^+ primary beam. Negative secondary ions were analyzed and a normal incidence electron flood gun was used to neutralize positive charge buildup on the insulating samples (Slodzian et al., 1987). Faraday cup detectors were positioned along the mass focal plane to collect $^{18}O^-$ and $^{16}O^-$ simultaneously at a mass resolving power of ~ 2000, which is sufficient to separate all significant mass interferences. The primary beam was defocused in order to sputter in an aperture illumination mode, resulting in shallow elliptical craters with a long axis of ~ 25 μm and a depth of ~ 1 μm (Fig. 2). The distance between spots was aimed at about 100 μm, trying to avoid cracks, obvious impurities etc. (Fig. 2). The current integrated in each Faraday cup over 10 s was measured by feedback electrometers in an evacuated, thermally controlled housing (manufactured by Finigan); the relative gains of the amplifiers were calibrated with use of a constant current supply.

Measurements typically comprised a fixed presputter time of 2 min followed by 15 to 20 cycles of data acquisition (total time < 5 min per spot). Instrumental mass fractionation was corrected for by repeated analysis of the OC standard. The overall precision of the method can be estimated from these analyses: the standard deviation on 45 measurements of the OC was 1.0‰. This should be considered a lower limit on the achievable precision since slow drift could be further corrected by interpolation of
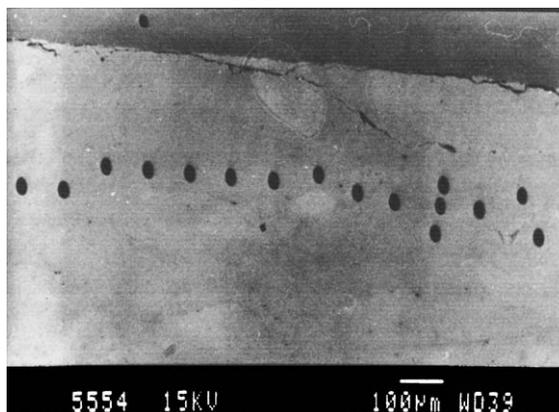

Fig. 2. Microphotograph of a segment of sample 2-N after ion-probing. Note size and elliptical shape of beam spot and spacing between spots. Parallel spots were used where fluctuations in measured standard values were observed (see text).

standard measurements bracketing the time interval for a set of analyses of the Soreq sample, and also because it does not account for possible heterogeneity of the OC standard material. Because the Soreq sample consists of only low Mg calcite, the OC sample is sufficiently close in chemical composition that we may consider any possible matrix effects on the instrumental mass fractionation correction (Fayek et al., 2001) to be insignificant. Thus, accuracy—which in this case has been checked by independent conventional analyses of the same Soreq samples—ought to be good to within the quoted precision estimate or the limitations due to isotopic heterogeneity of the OC standard.

3. Results and discussion

3.1. Standardization

Because the method can only analyze solid samples on a relatively small spatial scale, standardization can be a major problem in ion microprobe analysis. Specifically, it may be difficult to certify that one is dealing with an isotopically homogeneous standard, and to ascribe a constant isotopic ratio to such a standard. Conventional analyses of the "Optical Calcite" (OC) that is being used as a standard at the UCLA laboratory yielded two values for $\delta^{18}O_{PDB}$,

$-14.4‰$ and $-13.6‰$. The two values were obtained by two different laboratories, and it was previously decided to prefer the value of $-14.4‰$ (Mahon et al., 1998). At the outset of the present study, we observed inconsistent agreement between the corrected $\delta^{18}O$ values for the Soreq sample and the values published by Bar-Matthews et al. (1997) and Kaufman et al. (1998). Whereas some parts of the profile obtained after correcting the raw data by comparison with an OC standard value of $-14.4‰$ agreed well with the conventionally obtained pattern, other parts differed by as much as $1‰$. Thus we undertook a series of re-measurements of four aliquots of the OC standard in the laboratory of the Geological Survey of Israel; the same laboratory in which all of conventional isotope measurements of Soreq speleothem were done. To our utter surprise two subsamples of OC (about 20 mg each) yielded $\delta^{18}O_{PDB}$ results of $-13.3‰$ and $-14.4‰$, suggesting that we were all along using a standard that is isotopically inhomogeneous on a millimeter scale. In hindsight such an isotopic variation on a micro scale is not very surprising. Isotopic zoning of similar magnitudes in calcite crystals has been reported before (Dickson, 1997). Obviously such a problem is inherent in using the ion microprobe; the preparation or identification of isotopically homogeneous standards will probably remain a nontrivial obstacle of the method.

Because of the potential ambiguity in the $\delta^{18}O$ value of any given crystal of the OC standard, we developed a second order correction procedure for checking the accuracy of the data. An initial profile was obtained by correcting the measured data for instrumental mass fractionation by the average of five measurement spots on the OC standard made after about every 20 spots of sample profiling. These corrections assumed the previously preferred value for OC. After obtaining the $\delta^{18}O$ profile, we then micro-drilled 14 samples along (parallel to) the ion microprobe traverse and analyzed them by conventional acid reaction gas-source mass spectrometry. By this method, we could in principle adjust the entire sections of the ion microprobe profile so that its mean value would agree with the $\delta^{18}O$ of the drilled samples that we used now as "anchors". Only in one case there was a need for such re-adjustment.

3.2. High-resolution paleoclimate record

In order to compare the ion microprobe data to those obtained by conventional analysis we chose a segment of the record with the most dramatic $\delta^{18}O$ change over a shortest time (distance) interval. This is the segment that corresponds to the transition from the last glacial maximum (LGM) to the Holocene period (18 to 8.5 ka). Indeed this is also the segment that is
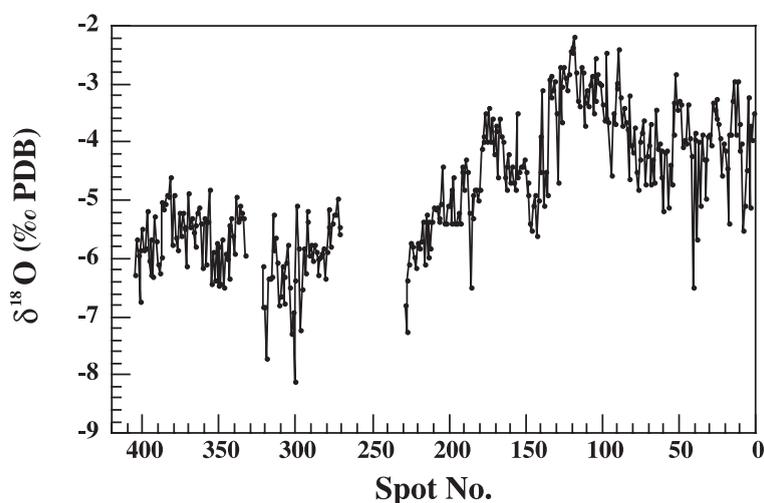

Fig. 3. Sequence of $\delta^{18}O$ analyses vs. ion-probe spot number for two slabs from stalactite 2-N.

potentially the most illustrative for understanding the finer details of climatic change. In addition we also studied the Soreq segment representing the most recent period (1.5 to 0.2 ka).

The instrumental mass fractionation corrected $\delta^{18}O$ values of about 410 spots from the two slabs of stalactite 2-N are represented in Fig. 3. The gap between spots 230 and 270 in Fig. 3 is due to our removal of these results. An unexplained technical problem caused a large (about 12‰) drift of both sample and standard results. The same gap is then propagated into Figs. 4 and 5.

The time interval that a 25 μm size spot covers varies between ∼ 25 years when the deposition rate was 1 mm/ka, between 18 and 17 ka, to ∼ 1 year when the deposition rate was much faster reaching ∼ 30 mm/ka, between 16.5 and 16 ka and 9.5 and 8.5 ka (Kaufman et al., 1998 their Fig. 4). Similarly, the 100 μm distance between sampling spots corresponds to ∼ 4 years at the fast deposition rate and to ∼ 100 years during periods of slow growth.

Fig. 4 shows the $\delta^{18}O$ traverse with the abscissa being transformed from distance into age by assuming a linear interpolation between the ages determined by Kaufman et al. (1998). Obviously the primary difference between the $\delta^{18}O$ drilled traverse and that of ion microprobe is the higher resolution of the latter, in most parts by a factor of 4. Each spot covers 10 and 100 years using ion-probe and 30 to 500 years using micro-drilling (Fig. 4). One way to be able to compare
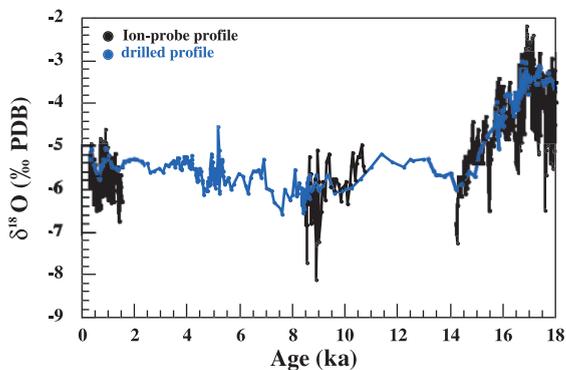

Fig. 4. Superposition of $\delta^{18}O$ vs. age profiles. In blue is sampling by micro-drilling, black is the raw ion-probe data. Note (i) the time span from 14.3 to 10.8 and from 8.5 and 1.5 ka is not represented by ion probe profile; (ii) the noisier glacial profile compared with the Holocene.
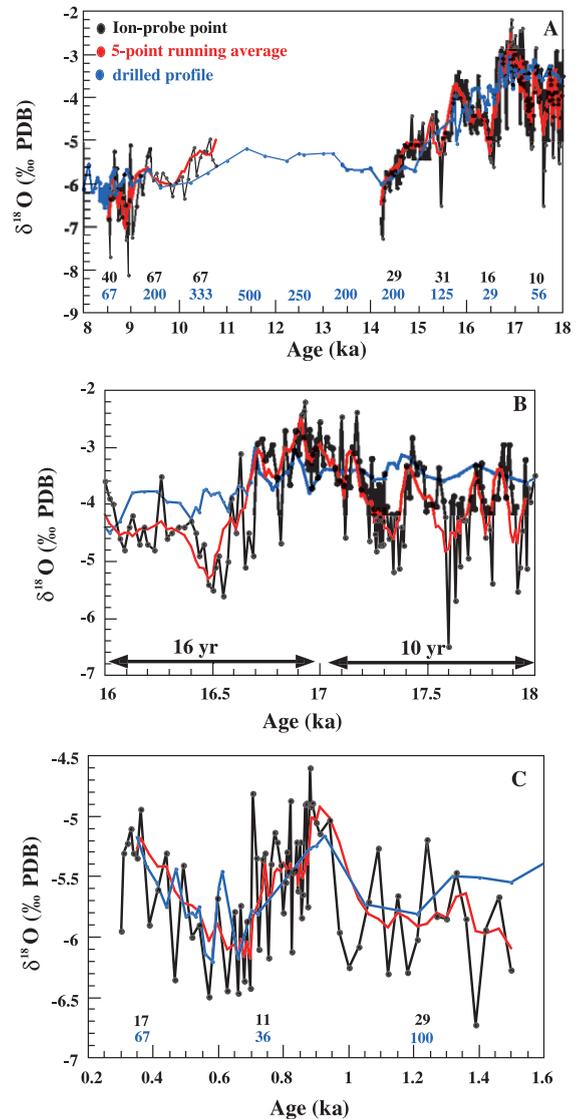

Fig. 5. Enlargement of Fig. 4 for the time period of 18 to 8.5 ka (A), 18 to 16 ka (B), and 1.5 to 0.2 ka (C). The red line added to this diagram is the five-point running average of the ion-probe results. The numbers at the bottom of A and C indicate how many years each data point integrates, (blue for drilled data, black for ion-probe data) calculated for segments of 1000 years in Fig. 5A and 500 years for segments in Fig. 5C. The portion of the drilled transect depicted in Fig. 5C was drilled after the ion probe analysis, using the craters as a guide (see text). Note (i) the larger amplitude $\delta^{18}O$ variations during deglaciation, (ii) the good agreement between the drilled data and the five-point moving average of the ion microprobe (C), the change in frequency of fluctuations between 18 and 17 ka compared with 17 to 16 ka (B).

better the two records is to compare the lower resolution drilled record to an averaged record of higher resolution ion microprobe data. An attempt at such a filter is presented in Fig. 5, which shows a five-point running average of the ion microprobe data. The resultant curve resembles closely the structure of the lower resolution curve, thus confirming in principle the validity of the ion-probe analysis. The ion-probe high resolution profile records the major climatic events that were described before (Bar-Matthews et al., 1998, 1999): the major deglaciation from 18 to 14 ka, the low δ^{18}O event at about 0.6 ka and the onset of the high δ^{18}O event at about 0.4 ka.

Given the basic accuracy of the ion microprobe data, further inspection of the high-resolution traverse reveals a sequence of low δ^{18}O "spikes" that are resolved outside of analytical precision (Fig. 5B, C). These spikes bear similarity to the anomalously low δ^{18}O values (Bar-Matthews et al., 1997; Ayalon et al., 1998), which correspond to the very rainy years that occur several times in a century based on historical records (Bar-Matthews et al., 1998). It is instructive to note that the low δ^{18}O spikes are not seen in the five-point running average curve, thus explaining their absence from the lower resolution drilled profile. This is expected if the rainy periods are only annual excursions (or at most several consecutive years) and not maintained over decadal time scales. Another feature evident in Fig. 5 is the greater variability of δ^{18}O during the LGM and deglaciation (Fig. 5A, B) as compared to the late Holocene (Fig. 5C). Greater instability of the apparent rainfall record in the glacial world has been noted previously (Dansgaard et al., 1993).

A comparison of the drilled profile and our data with GISP2 δ^{18}O record (Fig. 6) demonstrates a comparable resolution and a good match between the three curves within the dating error (Fig. 6A). In particular note the correlation on all three curves between the decrease in δ^{18}O from 16.5–16 to 15 ka, which is probably related to the global deglaciation. The relatively high (cold) δ^{18}O excursions of 17, and 15.8 ka on the ion-probe profile (Fig. 6B) correlate with the low (cold) GISP-profile (Fig. 6C) peaks at 17.1 and 16 ka, respectively. Similarly, the low speleothem δ^{18}O peaks at 17.3 and 16.5 ka match the GISP high δ^{18}O peaks at 17.4 and 16.8 ka. This good match further supports our trust in the ion-probe data.
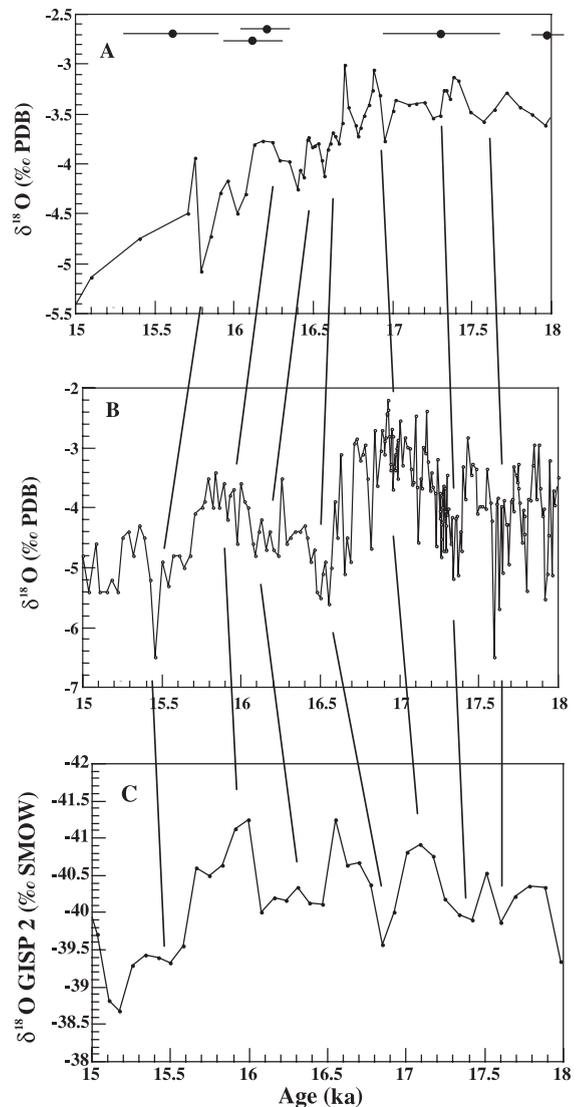

Fig. 6. The drilled (A) and the ion-probe (B) δ^{18}O record compared to the GISP2 record (C) for the time period of 18 to 15 ka. Note the good match of both positive and negative δ^{18}O excursions, both in the general pattern and in the high frequency events. Filled circles at top of (A) indicate thermal ionization mass spectrometer (TIMS) ages as well as the 2σ errors on those.

The main feature evident from both the high-resolution and low-resolution curves is the existence of two isotopic "modes" that are recorded in the cave—the glacial "heavy" mode, and the about 2–3‰ lighter post-glacial mode. These two major modes are overlain by lower amplitude oscillations.

3.3. Evaluation of the method: conclusions and prospects

The need to extract the maximum degree of information from proxy records in order to obtain interpretable paleoclimate data may be discussed in terms of a comparison of ion microprobe vs. conventional $\delta^{18}O$ carbonate analysis. This initial study demonstrates that ion microprobe measurements have an advantage of yielding better spatial resolution, with a possibly increased speed of analysis. With moderate improvements in technique and employing an "offset" sampling strategy for the traverse, the resolution of an ion microprobe traverse can be readily increased by a factor of 2 to 3. On the other hand "wet", conventional analysis has an advantage in achieving better precision and accuracy. It is however not clear that this "cost-benefit" comparison is always valid. It is often the case that the very high precision achieved in conventional measurements is not actually utilized in the interpretation of the data. Thus when considering Fig. 1, and similar figures in Bar-Matthews et al. (1997, 1998, 2000), Kaufman et al. (1998), and Ayalon et al. (2002), use is rarely made of the $0.1-0.2\%_o$ precision.

Considering the advantages of ion-probe analysis, its better spatial resolution shows up strongly in our data set. The fact that spikes undetected with a 0.5 mm resolution can be observed when resolution is increased to 0.1 mm (Fig. 4) is noteworthy.

In summary, this initial investigation has demonstrated that oxygen isotopic microanalysis of carbonates for high-resolution paleoclimatic reconstruction is feasible with the ion microprobe. The advantages of better spatial resolution in ion microprobe analysis may in some instances outweigh the disadvantage of poorer precision by detecting trends undistinguishable when sampling is limited by physical drilling. Possible limitations of accuracy, due to standardization issues including matrix effects, in ion microprobe analysis of carbonates can be successfully overcome in some cases by secondary calibration by micro-drilling, demonstrating the complimentarity of the two methods.

Acknowledgements

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