

RCM

## Letter to the Editor

To the Editor-in-Chief  
Sir,

### Continuous-flow isotope ratio mass spectrometric analysis of carbonate minerals

Stable isotope (C, O) analysis of carbonate minerals (predominantly calcite) is a standard procedure in a wide range of geoscientific research fields, including paleoceanography and terrestrial paleoclimate studies. The classical method used to obtain C and O isotope ratios in calcite<sup>1</sup> is labor-intensive and requires large sample sizes (tens of milligrams) and each sample must be prepared by hand. Recent technical advances have led to the development of online carbonate preparation lines hooked up to dual-inlet isotope ratio mass spectrometers (IRMS). The advent of continuous-flow techniques has significantly simplified and streamlined this method.<sup>2</sup> A recent article<sup>3</sup> described the advantages of this technique, but also noted some problems. It is the purpose of this short communication to suggest improvements which allow for a high sample throughput and good long-term external precision, even for very small samples.

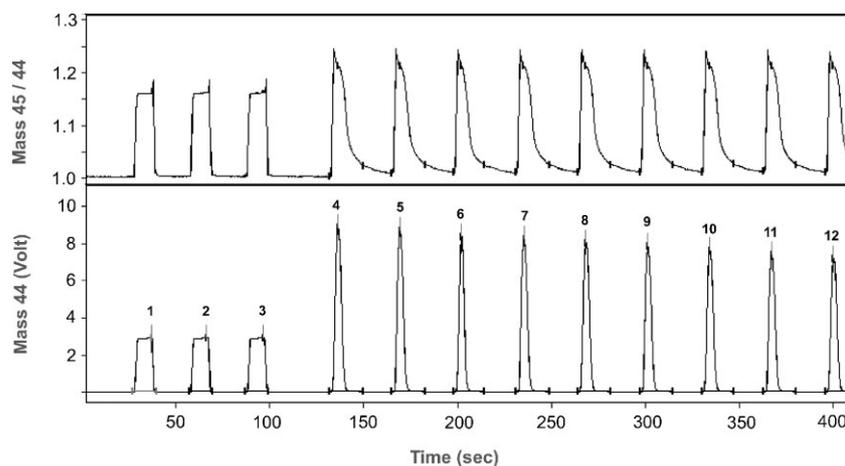
The systems described herein consist of a ThermoFinnigan GasBench II equipped with a CTC Combi-Pal autosampler and linked to either a Delta<sup>plus</sup>XL (University of Innsbruck, UI) and a Finnigan MAT 252 mass spectrometer (University of Tübingen, UT), respectively, which is essentially the same setup as that used in a previous study.<sup>3</sup> Carbonate microsamples are loaded manually into 10-mL round-bottomed borosilicate exetainers and sealed using butyl rubber septa (Labco). 72 exetainers including 12 aliquots of an in-house standard (sieved Carrara marble (UI) or Laaser marble (UT)) and 1 quality assurance

(QA) standard (sieved Laaser marble; always placed in the same position in the sample tray) are routinely loaded for one run. Standards are weighed so that there is a well-defined spread in sample size (routinely about 100–450 µg). This is important for subsequent linearity corrections. The samples are also within the same size range as the standards. Most samples are prepared semiautomatically using a micromill device that produces fairly consistent sample volumes. The exetainers are placed into an aluminum tray kept at  $72.0 \pm 0.1^\circ\text{C}$ . During a first step the exetainers are automatically flushed with 6.0 He by penetrating the septa using a double-hole needle at a flow rate of 120 mL/min. This procedure takes about 3 h for 72 samples, using two flushing needles simultaneously. Afterwards, 4–6 drops of phosphoric acid (density 1.91) are automatically deposited in each exetainer using the autosampler and a stainless-steel capillary needle attached to an acid pump, while the second needle transfers the evolved gas from a neighboring vial into the GasBench driven by a small stream of He (0.5–1 mL/min). As each row consists of eight samples, this procedure ensures identical reaction times (82 min per sample) and represents a significant modification as compared to the manual acid-dosing and long (up to 54 h) reaction times described previously.<sup>3</sup> The reservoir of the phosphoric acid is kept within the heated aluminum block to facilitate pumping of the viscous fluid. Following water removal using Nafion traps, CO<sub>2</sub> is separated from other components using a gas chromatographic column (Poraplot Q with fused-silica tubing, 25 m × 0.32 mm) heated to 70.0°C, and the peak corresponding to this CO<sub>2</sub> is then passed via an open split into the mass spectrometer. The advantage of heating the GC column is a significantly shorter gas retention, yet providing sufficient CO<sub>2</sub>-N<sub>2</sub> separation and good internal precision. Overall analysis time per sample can also be reduced significantly.

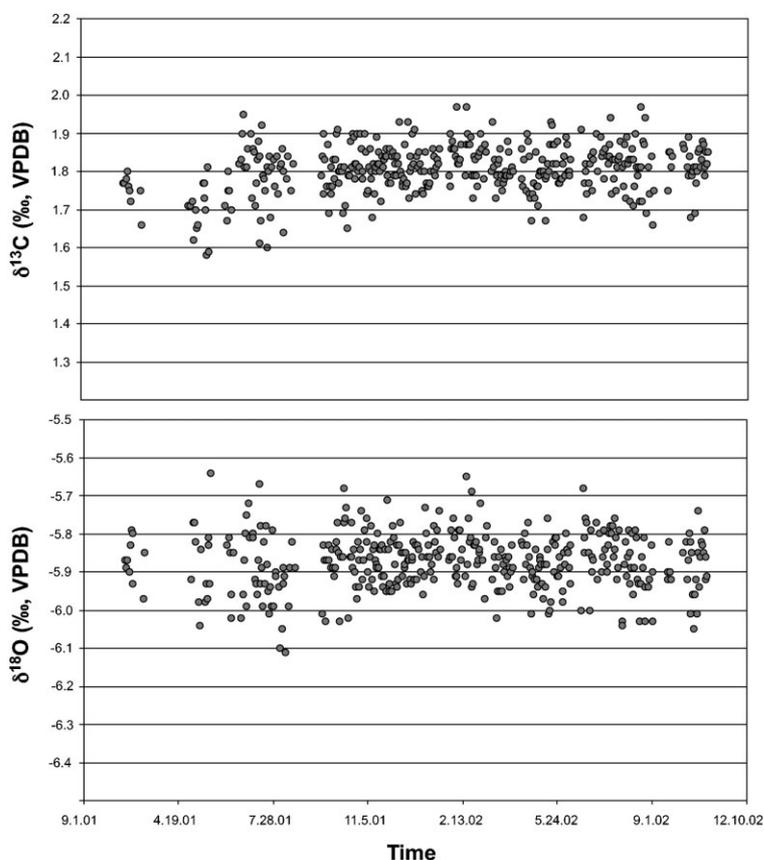
Each sample run starts out with a peak centering, followed by three rectangular-shaped peaks of CO<sub>2</sub> reference gas, after which nine (UI) or ten (UT) successive sample peaks are

produced by delivering nine (or ten) sequential aliquots of pure CO<sub>2</sub> into the ion source (Fig. 1). The internal precision (1 sigma) measured over these nine peaks is typically 0.03–0.06 and 0.04–0.08‰ for raw  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values, respectively, given a sample size above 50 µg. A linearity correction is performed based on the relationship between the intensity of the first (UI) or second (UT) sample peak ( $m/z$  44) and the raw  $\delta^{18}\text{O}$  value of the 12 individual standards. Depending on the conditions of the mass spectrometer, the correction can be negligible or significant (up to a few tenths of a per mil, mostly for  $\delta^{18}\text{O}$ ). Calibration of the raw results versus the VPDB scale is achieved using in-house calcite standards (subsequent to linearity correction) that have been calibrated against NBS-18, NBS-19, CO-1 and CO-8 reference materials. The external precision calculated over 12 standards per run is typically 0.05–0.06 for  $\delta^{13}\text{C}$  and 0.06–0.08‰ for  $\delta^{18}\text{O}$ , again for samples larger than about 50 µg. Since spring of 2001 the system at UI has been used to run a large number of powdered carbonate samples (ca. 28 000 samples until October 2002). The standard deviation (1 sigma) for the QA sample over this 20-month measurement period is 0.065 and 0.075‰ for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively (Fig. 2). While the sample numbers at UT have not been as high (ca. 15 000 since October 2000), a similar external standard deviation has been achieved.

At UT, additional tests have been made to determine the minimum size that can be analyzed using the GasBench system described above. The results for samples between about 10 and 150 µg of calcite (Laaser marble; weighed to a precision of about  $\pm 0.25$  µg using a Mettler Toledo UMT2 microbalance) are summarized in Fig. 3. A comparison of sample weight versus the peak area of the second peak indicates a significant linear correlation (Fig. 3(a)). For samples larger than about 170 µg of calcite (corresponding to about 1.2 µmol of CO<sub>2</sub>), automatic dilution of the sample gas sets in by opening the split. Whether or not the split is left in or taken out is a function of the size of the first peak. If signal intensity of  $m/z$  44 is



**Figure 1.** Chromatogram of carbonate isotopic analysis. Three rectangular reference gas peaks are followed by nine injections of sample gas. The entire sequence takes about 7 min per sample.



**Figure 2.** Chart showing the performance of the QA sample LAAS-1 over a 20-month period. Gaps are due to times when the mass spectrometer was used to run water and gas samples. The 1-sigma standard deviation is 0.065 and 0.075‰ for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively.

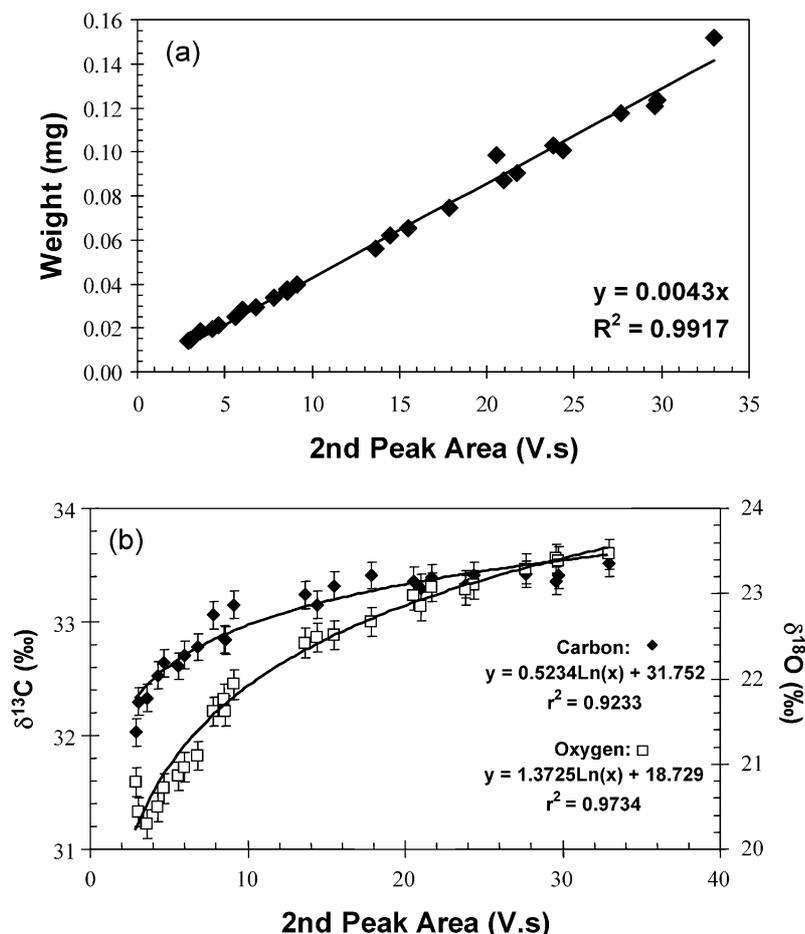
above 10 V, automatic dilution sets in (open split out). For peak intensities larger than 12 V for  $m/z$  44, the signal becomes too large for the collectors of the mass spectrometer. Because of this automatic dilution, the second peak area is used for calibration and linearity

correction purposes at UT, as a different set of linearity correction equations has to be used for the samples analyzed with dilution compared to those analyzed without.

Figure 3(b) illustrates the change in uncorrected  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values as a

function of sample size. With decreasing sample size, the  $\delta^{13}\text{C}$  values decrease by about 1.5‰ while the  $\delta^{18}\text{O}$  values decrease by about 3‰. At the same time the internal precision for the 10 measured peaks decreases from about 0.03 and 0.05‰ for samples bigger than about 50  $\mu\text{g}$  to about 0.21 and 0.22‰ for samples less than 20  $\mu\text{g}$ , respectively, for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. However, the decreasing values change in a significant logarithmic fashion, allowing for a correction to be applied (Fig. 3(b)). The correction is applied using the peak area of the second peak. Corrected values below 50  $\mu\text{g}$  in size have an average precision of 0.12 or 0.16‰, respectively, for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values. External precision for a set of standards as well as unknowns (marine ostracods) of this correction procedure was also tested by analyzing splits of 25 samples with a Kiel carbonate device (analyst: M. Joachimski, University of Erlangen, Germany) and the GasBench at UT. All values in the size range 14–100  $\mu\text{g}$  agreed to within  $\pm 0.2\%$ .

Over the course of the last few years of operation it has been established that this sample-size correction is constant in function and can be incorporated as part of the linearity correction that is performed based on the relationship between the intensity of the second sample peak and the raw  $\delta^{18}\text{O}$  value of the average of the standards in any one run. Given the good linear relationship between sample weight and peak area (Fig. 3(a)) as well as the fact that the



**Figure 3.** (a) Weight of carbonate against peak area of the second peak in the chromatogram for calcite samples between 10 and 150  $\mu\text{g}$  in size. The significant linear correlation allows for determination of yields of  $\text{CO}_2$  from samples of unknown carbonate content. (b) Change in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values of calcite samples less than 150  $\mu\text{g}$  in size. Note the significant logarithmic decrease in values. This change in values can be corrected for resulting in an average precision of 0.12 and 0.16‰ in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively, for samples smaller than 50  $\mu\text{g}$ . For samples larger than 50  $\mu\text{g}$ , the precision is similar to that for samples above 100  $\mu\text{g}$ .

oxygen isotope values show an effect that is twice that for carbon (Fig. 3(b)), we believe that this sample-size correction is largely related to changes in the linearity of the mass spectrometer, including the reference of the raw values against a reference peak of constant size and value. Because of the logarithmic function of the correction, the lower sample-size limits are probably close to 10  $\mu\text{g}$  of calcite-equivalent yield for routine measurements as outlined above. For samples smaller than this, the precision of measurements deteriorates rapidly and becomes unacceptably large for most interpretations of isotopic compositions. However, with a parallel

adjustment of the size of the reference peak, the situation could be improved.

In summary, the continuous-flow technology offers good internal and external precision for online isotopic measurements of calcite (and aragonite) samples. Provided that the reaction time and the amount of acid used per sample are kept constant (i.e., acid dosing performed by an autosampler equipped with two needles) samples can be reacted at temperatures significantly higher than room temperature (e.g., 72°C), which in conjunction with a heated GC column allows fast chromatographic separation of gas phases and hence high sample throughput (e.g., 72 samples in ca. 13 h).

Finally, less reactive carbonate minerals can also be analyzed in the same online mode, e.g., (Fe-poor) dolomite is reacted at 90°C in our laboratories and the results are both precise and consistent with conventional offline preparation techniques. As with calcite runs, the entire calibration is based directly on standard materials that are part of each run (in this case, an isotopically homogeneous dolomite whose isotopic composition was determined using conventional offline dual-inlet techniques), rather than solving fractionation equations for the acid-based reaction. In other words, there is no need to know the stable isotopic composition of the  $\text{CO}_2$  reference gas *a priori*, nor the acid fractionation factor at the given temperature of the reaction.

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