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Perspective Note **PS01**

The Perspective IRMS: Small Sample Carbonate Analysis with the Nu Carb Automated Carbonate Device

Precise carbon and oxygen isotope ratio ($\delta^{13}C$, $\delta^{18}O$) signatures in calcium carbonate ($CaCO_3$) rocks are utilised as a valuable tool for geochemists and marine scientists in a wide range of application areas. These include, but are not limited to, the determination of water/rock interactions during diagenesis of carbonate sediments and rocks, carbon isotope chemostratigraphy for detailed correlation of oil and gas reservoir lithologies, spatial and temporal changes in ocean chemistry, as well as paleothermometers of ocean water and marine habitat through time.

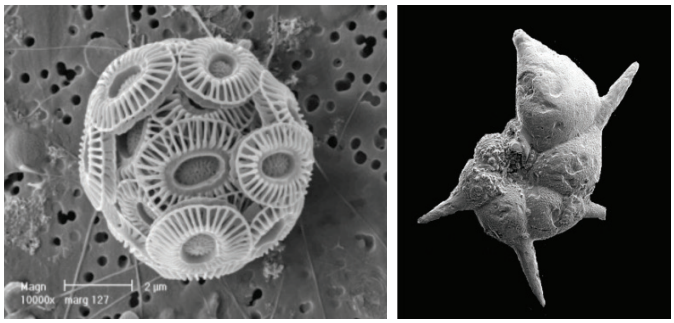
The Nu Instruments Nu carb automated carbonate device, interfaced to the Nu Instruments PERSPECTIVE isotope ratio mass spectrometer precisely determines $\delta^{13}C$ and $\delta^{18}O$ isotope ratios of small amounts (15-150 µg) of calcium carbonate.

Figure 1: nu carb carbonate device

Hardware Description

The nu carb is a bench-top carbonate device contained within a custom built oven, maintained at a user defined temperature typically 70° C (Figure 1). Carbonate samples contained in 50 open top individual vials are reacted sequentially with a controlled amount of added phosphoric acid.

The acid injection system consists of a motor driven syringe that enables control of both the amount, as well as the speed of delivery of the acid injected. Acid is stored in a 40 ml capacity reservoir, from which the syringe is automatically recharged and is sufficient for the analysis of up to 400 samples. A specially designed slow pump system ensures that samples consisting of very fine powder particles cannot scatter during the initial vial pump out sequence.



Scanning electron microscope images of a coccolith (left) and of a foraminifera (right)

An optical vial detection system ensures that either the vial is present, or is clear of the sample block before continuing with a sample preparation sequence. The evolved CO_2 from the acid/carbonate reaction is transferred cryogenically to a dual micro inlet, followed by isotopic measurement on the high resolution and high sensitivity Nu PERSPECTIVE IRMS. The liquid nitrogen consumption rate is typically 250 ml per sample.

The Nu Instruments software controls all of the sample preparation steps. This includes the vial positioning, vial pump out, delivery of acid, collection of the CO_2 generated, sample clean-up and transfer to the micro dual inlet for reference and sample beam balancing prior to data acquisition. All of these functions are under automated control; with user definable parameters associated with each step such as amount of acid delivered, the time to deliver, vial pump-out time and sample transfer time.

A single aliquot of reference gas introduced into the reference gas bellows will be sufficient for the analysis of all 50 samples. An automatic reference gas refill capability is available as an option. Reference gas can be automatically introduced at the start of the batch or during the batch. Parameters, such as the number of samples analysed before a reference gas refill is triggered, or the minimum mass 44 ion beam that the reference bellows should achieve are available within this option. This option provides added flexibility in managing a batch that contains large samples, small samples or a mixture of both.

Results and Discussion

Figures 3 and 4 show plots of sample size versus $\delta^{13}C$ and $\delta^{18}O$ respectively for the analysis of a Carrara marble sample.

Longer term reproducibility:

Table 1 shows the raw data results obtained from analysing the same sample, UCDSM92, over a period of 6 weeks with the same reference gas. The data comprises four batches of fifty samples per batch. The sample weights range from 16 to 160 µg. The raw delta 45 and 46 statistics are shown for each batch. Of the two hundred total results, only one is rejected. The automatic reference gas refill strategy used for all the batches consisted of a reference gas change every ten samples analysed.

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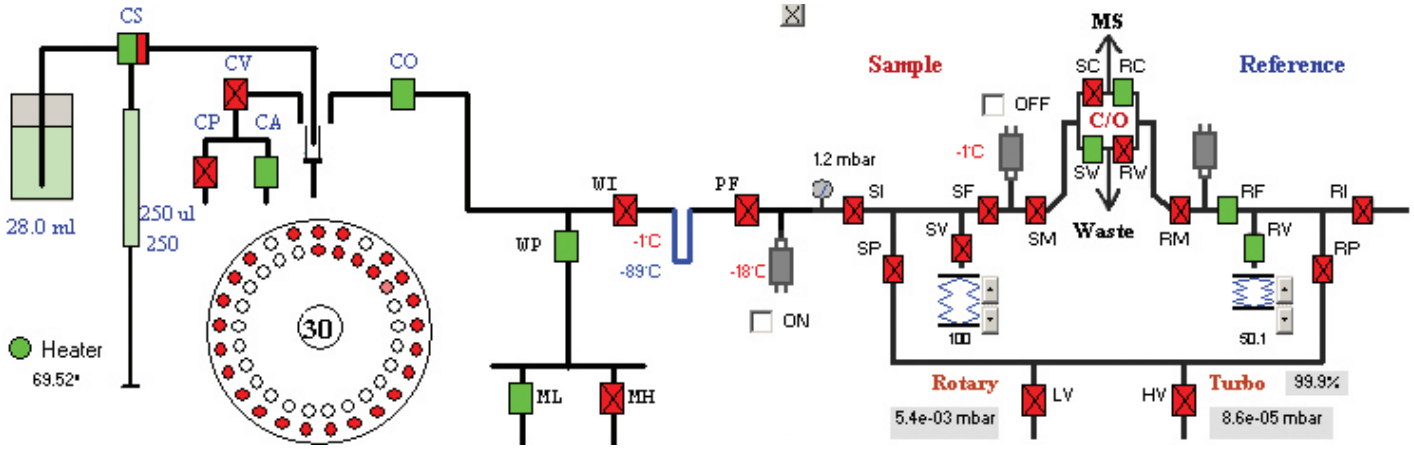

Figure 2: user interface schematic of nu carb

Acquisition Date	raw δ^{45}	1σ ext	raw δ^{46}	1σ ext	Sample size µg	n
2012/01/18	-0.10	0.02	-0.31	0.03	37-87	50
2012/01/19	-0.09	0.01	-0.28	0.03	31-72	50
2012/02/28	-0.10	0.02	-0.34	0.03	16-160	49
2012/03/07	-0.10	0.02	-0.33	0.03	22-74	50
All data	-0.10	0.02	-0.32	0.04	16-160	199

Table 1: Raw data results obtained over a period of six weeks using the same reference gas and sample.

Intersample memory effects:

Any sample preparation system that is designed to sequentially analyse samples with variable isotopic composition has the potential to exhibit memory effects. For example, will a small sample $\delta^{18}O$ measurement of NBS19 be affected by a previously run large sample of NBS18. Before carrying out such a test on the Nu carb, other sources of memory have to be considered and eliminated.

There are two major areas involved with the analysis that have the potential to exhibit memory effects independent of the sample preparation.

1: Changeover valve mixing effects. The rate at which, for example, the reference CO_2 which is normally derived from carbonate clears the C/O valve when it is switched from reference to sample and vice versa.
2: Source mixing effects. Does the reference gas clear the source prior to the arrival of the sample gas, and vice versa.

Test 1: Source and changeover valve mixing

A test that involved the measurement of two gases, very different in isotopic composition, using the Dual Inlet PERSPECTIVE was devised. A tank CO_2 sample gas that is depleted in both ^{13}C and ^{18}O was measured against a carbonate derived reference gas. The C/O delay time when switching from reference to sample was varied from 1 second up to 20 seconds and the results compared. Any source or changeover valve mixing that occurs will be expressed as a change in the raw delta 45 and raw delta 46 values. The results of this test are shown in table 2.

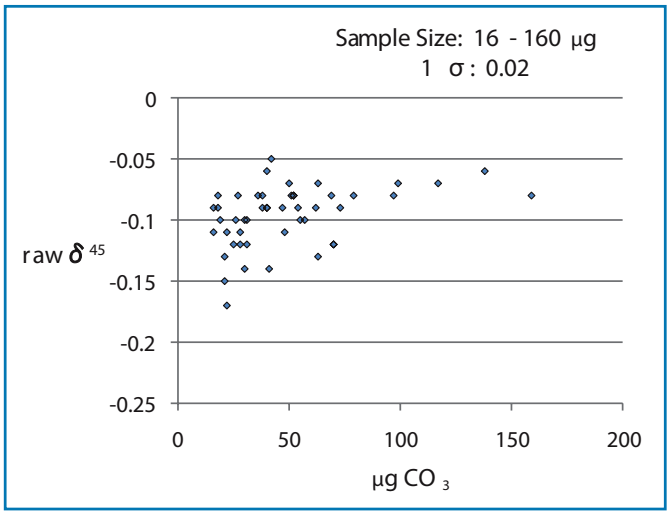

Figure 3: Sample size in µg carbonate versus raw δ^{45} measured.

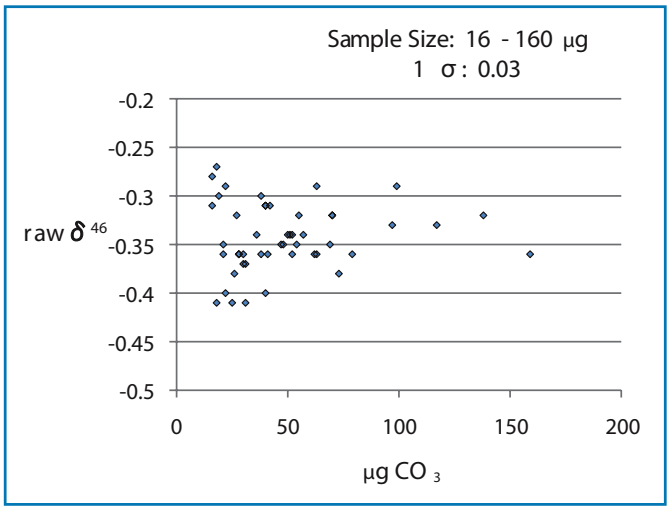

Figure 4: Sample size in µg carbonate versus raw δ^{46} measured.

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Note: the analyses are each generated from a standard cold finger depletion volume measurement equivalent to the analysis of 25 µg calcite.

Changeover valve delay (seconds)	δ^{45}	δ^{46}
20	-35.46	-25.88
10	-35.50	-25.88
5	-35.47	-25.90
2	-35.48	-25.88
1	-35.47	-25.88
mean	-35.48	-25.89
std	0.015	0.009

Table 2: Results of the tests showing the total lack of source/changeover valve mixing effects.

Test 2: Nu carb sample memory test

A series of samples were analysed as part of a calibration measurement for a new Carrara marble sample (NCM) that could possibly be used as a long term laboratory standard. Carbonate standards NBS19 and NBS18 were used for calibration. A Carrara standard from UC Davis (UCDSM92) was used as a check on the accuracy of the calibration. Incorporated into the batch was a sequence of alternate NBS19 and NBS18 measurements. Table 3a is a subset of the total batch.

Sample	mg	$\delta^{13}C_{vpdb}$	$\delta^{18}O_{vpdb}$
ncm-6	42	2.13	-1.86
ncm-7	23	2.10	-1.84
ncm-8	31	2.11	-1.89
ncm-9	27	2.09	-1.88
ncm-10	39	2.08	-1.86
nbs19-1	105	1.95	-2.17
nbs19-2	43	1.95	-2.20
nbs19-3	46	1.97	-2.22
nbs19-4	39	1.93	-2.17
nbs19-5	22	1.94	-2.19
nbs18-1	32	-5.03	-22.83
nbs18-2	84	-4.99	-23.18
nbs18-3	22	-5.02	-23.06
nbs18-4	25	-5.05	-23.11
nbs18-5	54	-4.96	-23.07
ucd-1	112	2.09	-1.91
ucd-2	65	2.09	-1.91
ucd-3	37	2.08	-1.91
ucd-4	19	2.07	-1.96
ucd-5	57	2.08	-1.92
nbs19-6	49	1.95	-2.18
nbs18-6	60	-5.02	-23.22
nbs19-7	37	1.93	-2.19
nbs18-7	30	-4.99	-23.06
nbs19-8	37	1.94	-2.27
ncm-16	19	2.03	-1.94
ncm-17	100	2.12	-1.91
ncm-18	33	2.06	-1.96
ncm-19	73	2.10	-1.90
ncm-20	27	2.10	-1.90

Table 3a: Subset of sample memory/NCM calibration batch

Sample	$\delta^{13}C_{vpdb}$	$\delta^{18}O_{vpdb}$	µg	n
ncm	2.09	-1.91	19-100	19
1σ	0.03	0.04		
ucdsm92	2.08	-1.92	19-112	5
1σ	0.01	0.02		
True value	2.08	-1.94		

Table 3b: The results obtained for the analysis of NCM Carrara. Also the value obtained for the University of California Davis internal standard UCDSM92 Carrara along with its accepted value

Sample	$\delta^{13}C_{vpdb}$	$\delta^{18}O_{vpdb}$	µg	n
nbs19	1.93	-2.22	33-49	4
1σ	0.02	0.04		
nbs18	-4.97	23.10	30-105	4
1σ	0.04	0.16		

Table 3c: Showing the results obtained when measuring a sequence of NBS19 and NBS18 standards measured alternately.

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Conclusions

The data presented addresses a number of analytical characteristics associated with small sample carbonate analysis. Figures 1 and 2 show the relationship between sample size in µg and the $\delta^{13}C$ and $\delta^{18}O$ results obtained.

Table 1 shows the stability of the uncorrected raw δ^{45} and δ^{46} measurements of UCDSM92 Carrara marble, versus the same reference gas taken over a 6 week period. External precision of 0.02‰ and 0.04‰ respectively was achieved on a total data set of 200 samples less 1 rejected.

Table 3a, 3b and 3c presents $\delta^{13}C$ and $\delta^{18}O$ data from a calibration run using mixed standards. The intentions were two fold. To calibrate an internal standard NCM Carrara, and to perform an inter sample memory test, by demonstrating alternate measurements of NBS19 and NBS18. The mixed standard data indicates that there is no memory between samples of grossly different isotopic compositions.

This analysis was prefaced by a test showing that gas mixing effects for both the dual inlet changeover valve and ion source, were negligible for changeover valve switching times ranging from 20 seconds down to 1 second. See table 1 for the results.

The Nu Instruments Nu carb is compact dual inlet carbonate device that offers high precision $\delta^{13}C$ and $\delta^{18}O$ isotope ratio determinations on small carbonate samples. It can be interfaced either with the high sensitivity high resolution Nu PERSPECTIVE or the Nu HORIZON isotope ratio mass spectrometers.

Features of the Nu carb include:

- 50 individual sample vial capacity
- Average sample analysis time = 32 minutes
- Motor driven syringe (0-250 µl) for precise acid delivery to sample vials
- Slow pump mechanism that eliminates sample disturbance during pump out
- Optical vial detection system
- Optional automated reference gas refill system
- Reservoir capacity 40 ml H_3PO_4 (enough acid for 400 samples if 100 µl of acid is used per sample)
- Provision of internal racks for conditioning of the next 50 samples
- 250 ml of LN_2 per sample
- All internal parts held at 70 °C
- Bench top, located on dual inlet bench.

Acknowledgements

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