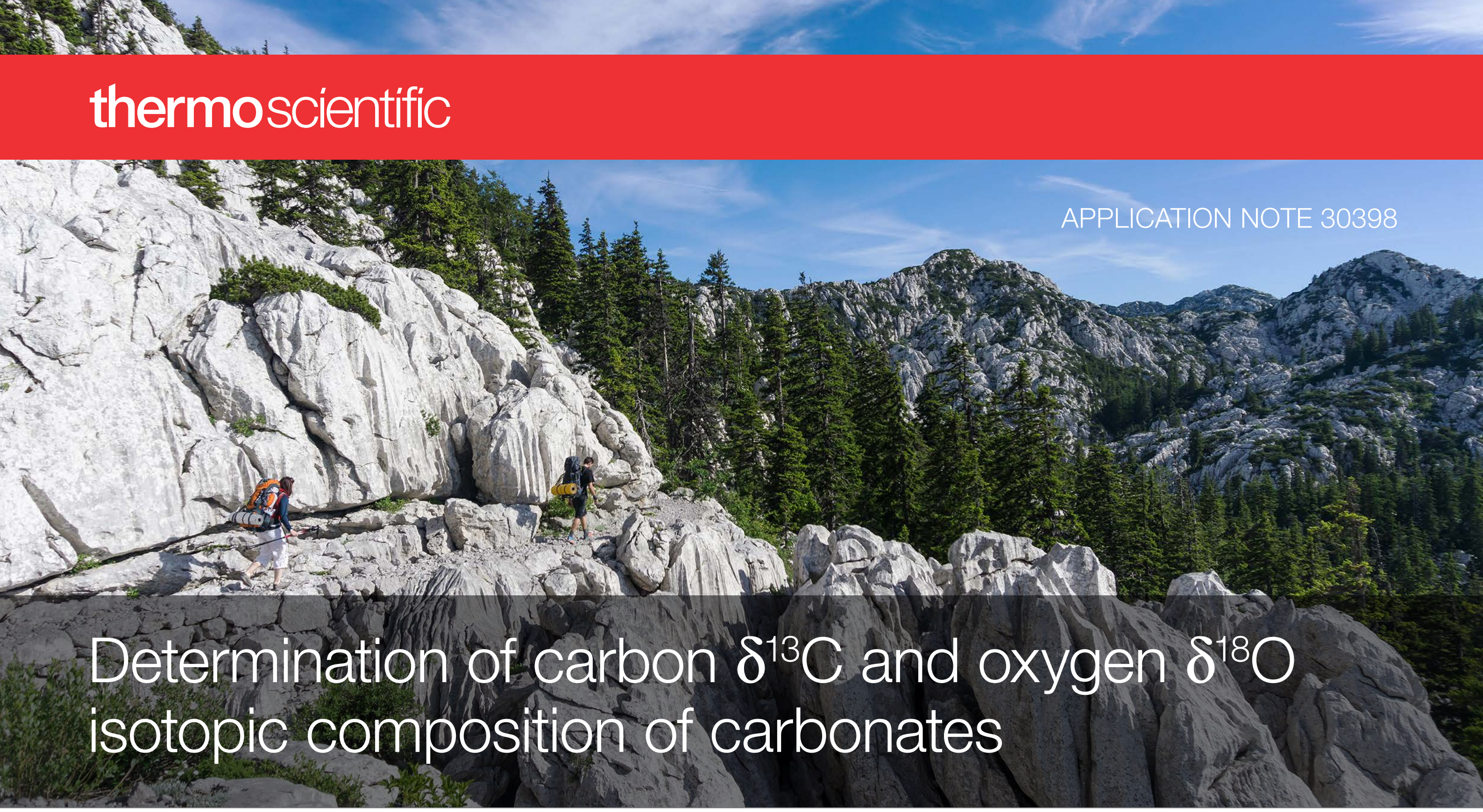


APPLICATION NOTE 30398

Determination of carbon δ^{13}C and oxygen δ^{18}O isotopic composition of carbonates

Authors
Danijela Smajgl, Nils Stöbener,
Magda Mandic
Thermo Fisher Scientific,
Bremen, Germany

Keywords
δ^{13}C, Carbonates, Delta Ray Connect, Isotopic Composition, Oxygen, δ^{18}O

Goal

To demonstrate the automated measurement of δ^{13}C and δ^{18}O from solid carbonate samples using a Thermo Scientific™ Delta Ray™ Isotope Ratio Infrared Spectrometer (IRIS) with URI Connect™. The measurement of certified reference materials confirms the precision of <0.1‰ for both δ^{13}C and δ^{18}O, and the accuracy within the uncertainty of the standards.

Introduction

- Stable carbon and oxygen isotopic composition (δ^{13}C and δ^{18}O) of carbonates has been widely used for the reconstruction of paleoenvironments.
- The isotopic signature of carbon, δ^{13}C is significant as a tracer for the origin of carbon.
- Variations of δ^{18}O in oxygen bearing minerals have been used as proxies for various environmental records, especially temperature.

For many decades, different instrumental methods involving generations of the Thermo Scientific™ Kiel™ Carbonate Device, or the continuous flow Thermo Scientific™ Gas Bench™ II System with the Carbonate Option in conjunction with a CTC GC PAL™ or Combi PAL™ Autosampler, offered the scientifically required high precision and high throughput of samples for these applications.

The Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer (IRIS) with the Universal Reference Interface (URI) Connect and Teledyne™ Cetac™ ASX-7100™ Autosampler (Figure 1) can be moved and installed much easier than mass spectrometers. This enables scientists to measure carbonates directly on a research ship or on-site in the field.

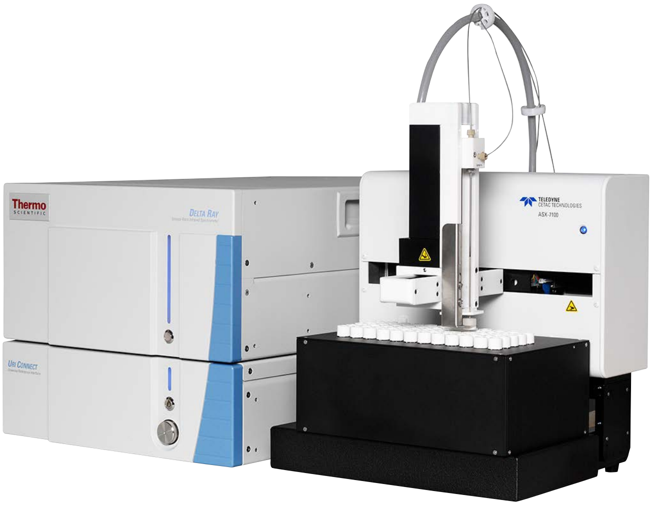


Figure 1. The Thermo Scientific Delta Ray Isotope Ratio Infrared Spectrometer (IRIS) with the Universal Reference Interface (URI) Connect and Teledyne Cetac ASX-7100 Autosampler

The preparation of the samples for analysis on the Delta Ray IRIS with URI Connect is similar to the previously mentioned Gas Bench II method. Samples are put into vials and phosphoric acid is added. The resulting reaction releases CO_2 gas, which is then introduced into the Delta Ray IRIS with URI Connect via the Variable Volume. With this workflow, more than 100 samples in vial can be analyzed per day with a $\delta^{13}C$ precision better than 0.1‰.

Experimental

Setup

The URI Connect contains a Variable Volume of up to 100 mL in size. The CO_2 gas released in the vials by reaction of samples with phosphoric acid is flushed into the Variable Volume through a Nafion™ based built-in water trap. CO_2-free synthetic air is used as a carrier. During measurements, the Variable Volume is compressed, resulting in a continuous gas flow of diluted sample CO_2 into the measurement cell (Figure 2).

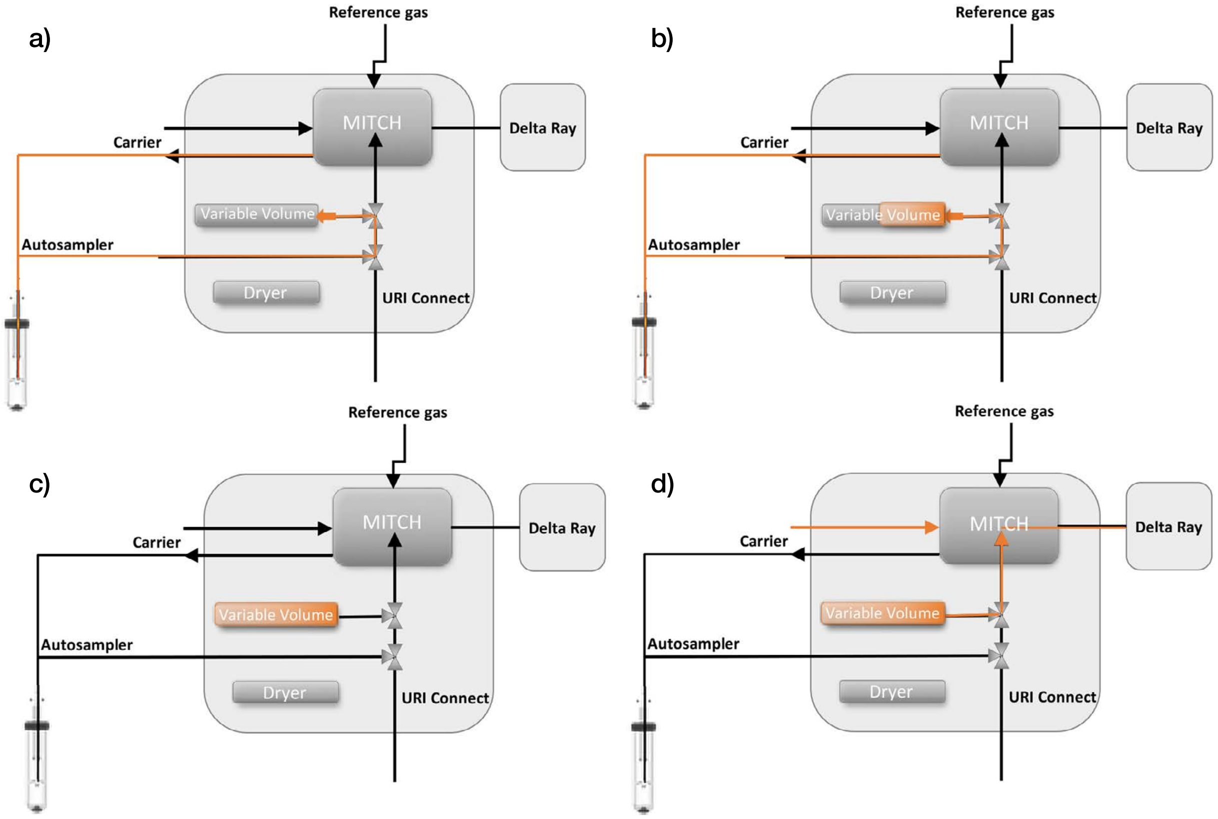


Figure 2. Workflow of the sample handling within the URI Connect: a) Flushing of the vial headspace into the Variable Volume; b) Variable Volume increases; c) Headspace transfer completed; d) Release of sample gas from the Variable Volume into the Delta Ray IRIS with URI Connect and dilution with synthetic air. MITCH™, or gas MIxing and swiTCHing device, controls the flow and concentration of the gases within URI Connect.

Prior to measurement, a fraction of the Variable Volume is used to determinate the present CO_2 concentration. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) automatically adjusts the dilution of the CO_2 to achieve the desired concentration (e.g. 400 ppm) in the Delta Ray IRIS with URI Connect. As part of the workflow, reference gases are regularly measured at the same concentration as the sample to allow for automatic drift correction.

Method

Three international standards of carbonate material (NBS 18, NBS 19, and IAEA-CO-1; Table 1) were analyzed with Delta Ray IRIS with URI Connect. To confirm the high accuracy and precision, NBS 18 and NBS 19 were used as reference materials for calibration, while IAEA-CO-1 was treated as the unknown sample. The Principle of Identical Treatment was applied in sample and standard preparation, in measurement procedure, as well as in the evaluation of the results.

Sample preparation

Borosilicate vials were washed and dried overnight at 70 °C. After adding 400–500 µg of sample, vials were sealed with new septa and residual air was removed from the vials by an automated autosampler-assisted flushing procedure. The flushing procedure was carried out at a flow of 30 mL/min for 3 minutes. Further, samples were manually acidified using 3 droplets of 104% phosphoric acid (anhydrous phosphoric acid; 104% of H_3PO_4 = 0.25 mol H_2O/L H_3PO_4) and placed into a heated tray at a constant temperature of 80 °C. After one hour at 80 °C, the measurement was started (Figure 3).

NOTE: For applications where only determination of carbon $\delta^{13}C$ isotopic composition is of interest, a similar method can be used. For this purpose 104% phosphoric acid is not needed. 43% H_3PO_4 is sufficient, and also sample preparation and measurement can be done at room temperature, but with a longer reaction time.

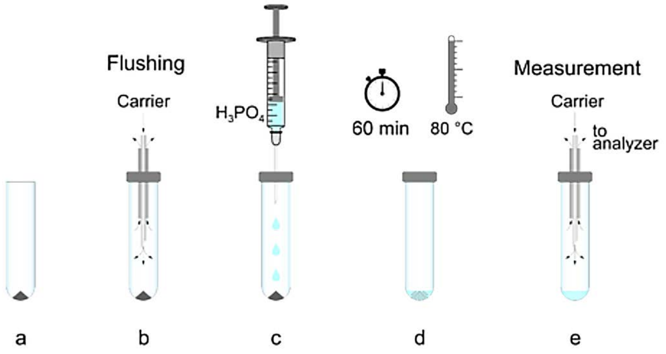


Figure 3. Sample preparation: a) 400–500 µg sample is used for analysis; b) Residual air is removed from the vials by an automated autosampler-assisted flushing procedure; c) Samples are manually acidified using 3 droplets of 104% phosphoric acid; d) Reaction time of 60 minutes at a constant temperature of 80 °C; e) Start of measurement.

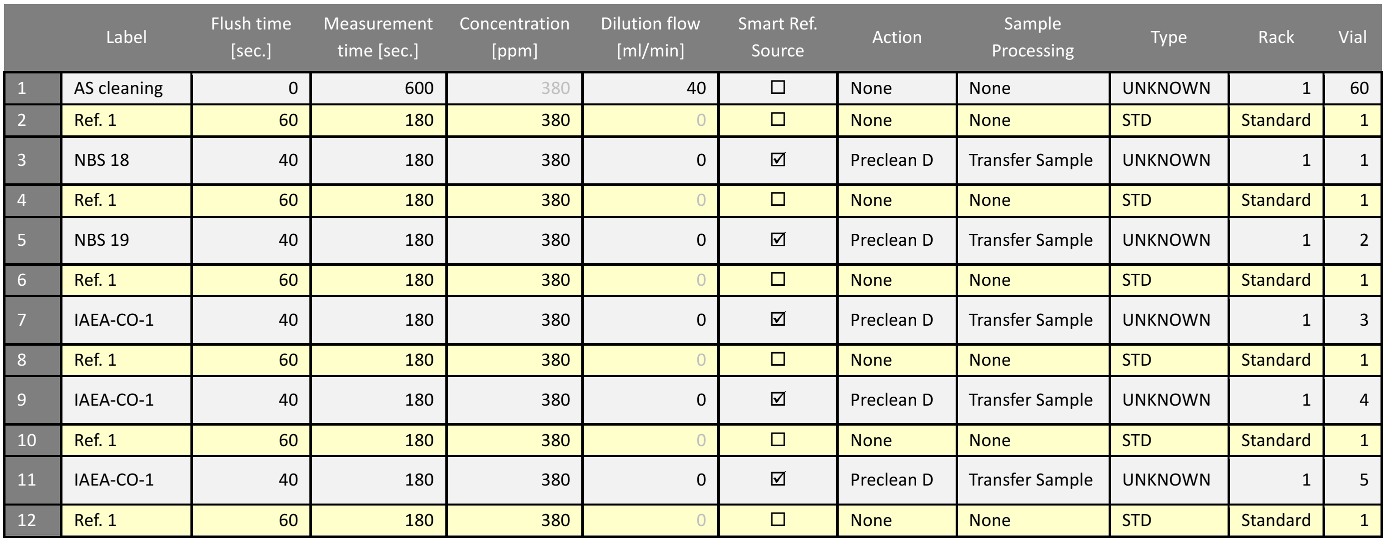
Measurement setup

The sampling and measurement procedures were driven automatically from Thermo Scientific Qtegra Software. The LabBook used for the analysis is shown in Figure 4.

Prior to starting the measurement, reference gas lines were flushed using the Gas Control window of the Qtegra Dashboard. The first sample line in the LabBook contained an autosampler cleaning procedure (Table 2).

Table 1. Isotopic composition of international standard materials given by IAEA. (R/C) Classification assigned to the property value for the analyte (recommended/certified).

Reference Material	Analyte	Value (‰ VPDB)	SD	R/C
NBS 18	$\delta^{13}C$	-5.014	0.035	C
	$\delta^{18}O$	-23.2	0.1	R
NBS 19	$\delta^{13}C$	1.95	By definition	C
	$\delta^{18}O$	-2.20	By definition	C
IAEA-CO-1	$\delta^{13}C$	2.492	0.030	C
	$\delta^{18}O$	-2.4	0.1	R



	Label	Flush time [sec.]	Measurement time [sec.]	Concentration [ppm]	Dilution flow [ml/min]	Smart Ref. Source	Action	Sample Processing	Type	Rack	Vial
1	AS cleaning	0	600	380	40	☐	None	None	UNKNOWN	1	60
2	Ref. 1	60	180	380	0	☐	None	None	STD	Standard	1
3	NBS 18	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	1
4	Ref. 1	60	180	380	0	☐	None	None	STD	Standard	1
5	NBS 19	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	2
6	Ref. 1	60	180	380	0	☐	None	None	STD	Standard	1
7	IAEA-CO-1	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	3
8	Ref. 1	60	180	380	0	☐	None	None	STD	Standard	1
9	IAEA-CO-1	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	4
10	Ref. 1	60	180	380	0	☐	None	None	STD	Standard	1
11	IAEA-CO-1	40	180	380	0	☑	Preclean D	Transfer Sample	UNKNOWN	1	5
12	Ref. 1	60	180	380	0	☐	None	None	STD	Standard	1

Figure 4. Qtegra ISDS LabBook layout

Table 2. LabBook setup for autosampler cleaning procedure

Flush time	0 s
Measurement time	600 s
Port	Sample A
Dilution flow	40 mL/min
Action	None
Sample processing	None
Vial	60

The build-in sample processing method "Transfer Sample" was chosen for sample measurement. This method executes sample collection from the autosampler, sample concentration determination prior to measurement, and optimization of the measurement conditions.

Each sample measurement was followed by a measurement of a working standard gas to correct for instrument drift. To gain maximum precision, both samples and working standards were measured for 180 s. Prior to each sample transfer, the Variable Volume and plumbing was flushed with Carrier by means of an Action Script.

Results and discussion

Two-point data calibration – correction

For correction, data from Qtegra Software were exported to a Microsoft™ Excel™ file. The obtained isotope ratios for NBS 18 and NBS 19 were averaged and used to generate two-point calibration curves for the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios (Table 3). The calibration functions were then applied to the measured isotope ratios of the samples (Figure 5). The resulting numbers are in agreement with certified values (Table 4). Figure 5 shows the obtained $\delta^{13}C$ and $\delta^{18}O$ values for all IAEA-CO-1 standards and mean value.

Table 3. Expected and measured isotope ratios of NBS 18 and NBS 19, as well as derived calibration functions

$^{13}C/^{12}C$	$R_{expected}$	$R_{measured}$
NBS-18	0.0111241	0.0111217
NBS-19	0.0112020	0.0111998
Calibration Function: $R_{expected} = 0.9962625 \times R_{measured} + 4.401301 \times 10^{-5}$		

$^{18}O/^{16}O$	$R_{expected}$	$R_{measured}$
NBS-18	0.00201920	0.0020334
NBS-19	0.00206261	0.0020758
Calibration Function: $R_{expected} = 1.023266 \times R_{measured} + 6.148319 \times 10^{-5}$		

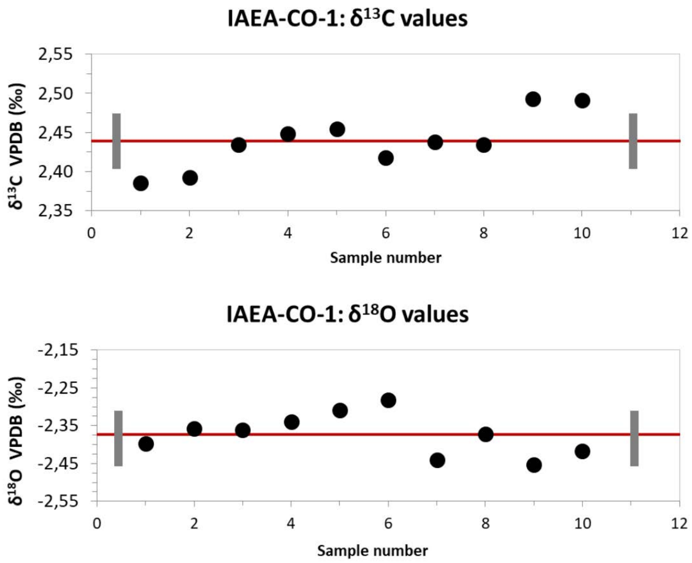


Figure 5. δ^{13}C and δ^{18}C values of ten IAEA-CO-1 standard samples. The gray vertical lines indicate the position of NBS 18 and NBS 19 standards used for scale calibration.

Table 4. Resulting δ^{13}C and δ^{18}O values for the IAEA-CO-1 standard samples based on the calibration data of Table 3

IAEA-CO-1	Measured	1SD	Certified*
δ^{13}C (‰VPDB)	2.44	0.03	2.49 ± 0.03
δ^{18}O (‰VPDB-CO_2)	-2.37	0.05	-2.4 ± 0.1

*Recommendation only for δ^{18}O

Conclusions

The Delta Ray IRIS with URI Connect allows for determination of δ^{13}C and δ^{18}O values from carbonates with a precision comparable to IRMS. In addition, the instrument allows the researcher to obtain these data directly in the field. The workflow for analysis of carbonates and other samples is fully automated.

Reference

1. IAEA Reference Material Online Catalog: https://nucleus.iaea.org/rpst/referenceproducts/ReferenceMaterials/index.htm

Find out more at **thermofisher.com/DeltaRay**