Analysis of $\delta^{13}C$ & $\delta^{18}O$ of carbonate minerals by CF-IRMS

Applied Geochemistry group - Isotope Science Laboratory (AGg-ISL)
Department of Geoscience
University of Calgary

Overview:

Pure carbonate mineral species are analyzed by Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) using a Thermo Finnigan GasBench® coupled to a DeltaV^{Plus} ®.

Sample preparation:

- All carbonate samples must be ground to a powder of ~50 to 100µm. If the material is judged to be too coarse, an extra charge for grinding the sample with a mortar and pestle will be applied
- Although only ~300 to 500 ug are needed for each analysis, it is preferable to send at ***least*** a few milligrams. Clear glass, screw top vials are preferred. Sample vials must be airtight
- Indicate the %C (inorganic) if the sample is an impure carbonate
- Indicate %S or %C (organic) if more than about 1wt%
- A completed sample submission form must accompany the samples https://www.ucalgary.ca/labs/isotope-science-lab/sample-submission

Online (CF-IRMS) technique:

A weight of sample equal to ~0.300mg of pure calcite is weighed into a 12mL Labco Exetainer (p/n: 038W). The exetainers are loaded into a horizontal rack, uncapped. The rack holds 10 vials at a time. Approximately 200uL of specially prepared anhydrous phosphoric acid (Coplen et al., 1983) is then carefully injected just inside the neck of the Exetainer. Because of the horizontal orientation the acid remains near the vial neck in a small droplet, separated from the sample at the bottom of the vial. Vials are kept horizontal, capped and flushed with UHP Helium for 10 minutes at a flow rate of ~70ml/min. The vials are then turned to vertical allowing the acid droplet to run down to the bottom of the vial and react with the sample. Vials are then placed in the heated block of the GasBench at 25°C and left to react for specified times (minimum of 5hrs for calcite and ~48hrs for dolomite). The evolved CO_2 headspace is then sampled automatically by the Gas Bench using a 50µl sample loop and inlet to the ion source of the mass spectrometer for analysis of $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios. The headspace of each vial is sampled 6 times by loop injection. The first peak is discarded and the subsequent 5 injections are acquired. If the first peak is > 30 [V], the subsequent 5 injections are automatically diluted by a factor of ~3:1 by the software.

Selected internal Lab Reference Materials (see table below) are run at the beginning and end of each set of samples and are used to normalize the data as well as correct for any instrument drift. These internal lab standards are periodically calibrated against International Reference Materials (see second table below) to assure accuracy to the VPDB scale. All results are reported in the per mille notation relative to the international VPDB scales for $\delta^{13}C$ and $\delta^{18}O$ respectively.

Stable isotope ratios are expressed as delta (δ) and are measures of a 'per mille' (‰), or parts per thousand difference between the isotope ratio of a sample and that of a known (International) standard material. Values are reported relative to 'Vienna Peedee Belemnite' (VPDB) formation for Carbon and Oxygen (Craig, 1957).

Oxygen isotopic ratios are commonly compared to both the VSMOW and the VPDB references. Traditionally, oxygen in water is reported relative to VSMOW while oxygen liberated from carbonate rocks or other geologic archives is reported relative to VPDB. As in the case of hydrogen, the oxygen isotopic scale is defined by two materials, VSMOW2 and SLAP2. Measurements of sample $\delta^{18}O$ vs. VSMOW can be converted to the VPDB reference frame through the following equation: $\delta^{18}O_{VPDB} = 0.97001*\delta^{18}O_{VSMOW} - 29.99‰$ (Brand et al., 2014)

<u>Reference materials used for data correction</u>:

ISL carbonate standards	**Estimated $\delta^{13}C$ value (VPDB)**	**Estimated $\delta^{18}O$ value (VPDB)**
ISL Cal-I (calcite)	-40.1 ± 0.3‰	-21.4 ± 0.3‰
ISL Cal-II (calcite)	-2.6 ± 0.2‰	-12.6 ± 0.3‰
ISL Cal-III (calcite)	+3.4 ± 0.4‰	-2.0 ± 0.3‰
ISL-NaHCO3	-20.1 ± 0.3‰	-18.6 ± 0.3‰
ISL-Lublin (calcite)	-0.4 ± 0.2‰	-14.6 ± 0.3‰

International RMs	**Accepted $\delta^{13}C$ (VPDB)**	**Accepted $\delta^{18}O$ value (VPDB)**
NBS 18	-5.01 ± 0.06‰	-23.00 ± 0.06‰
NBS 19	1.95 ‰ (b.d.)	-2.2 ‰ (b.d.)
USGS44 ($CaCO_3$)	-42.03 ± 0.10‰	
IAEA CO-9 ($BaCO_3$)	-47.32 ± 0.20‰	-15.28 ± 0.09‰

Note: (b.d.) = by definition

Performance:

Precision and reproducibility using this technique is typically better than ±0.1 per mille (n=10 internal lab standards) for both $\delta^{13}C$ and $\delta^{18}O$.

References:

- USGS Report 01-4222, *Compilation of Minimum and Maximum Isotope Ratios of Selected Terrestrial Materials and Reagents*, 2002

- Coplen et al., *New Guidelines for $\delta^{13}C$ Measurements*, Anal. Chem., Vol. 78, No. 7, pg. 2439-2441

- Coplen, T.B., Kendall, C., and Hopple, J., (1983). Comparison of stable isotope reference samples, Nature, vol. 302, pp. 236-238

- Revez, K. et al., (2001). Measurement of $\delta^{13}C$ and $\delta^{18}O$ Isotopic Ratios of $CaCO_3$ using a Thermoquest Finnigan GasBench II Delta Plus XL Continuous Flow Isotope Ratio Mass Spectrometer with Application to Devils Hole Core DH-11 Calcite. USGS Open-File Report 01-257

- Brand, Willi A.; Coplen, Tyler B.; Vogl, Jochen; Rosner, Martin; Prohaska, Thomas (2014). "Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report)". Pure and Applied Chemistry. 86 (3): 425–467

- Assonov, S. et al., (2020). On the metrological traceability and hierarchy of stable isotope reference materials aimed at realization of the VPDB scale: Revision of the VPDB 13C scale based on multipoint scale-anchoring RMs. Rapid Commun Mass Spectrom. 2021;35:e9018.

- Helie, JF. et al., (2021). Discontinuity in the Realization of the Vienna Peedee Belemnite Carbon Isotope Ratio Scale. Anal Chem. 2021, 93, 10740-10743