$\delta^{13}C$ isotopic analysis of Dissolved Inorganic Carbon (DIC)

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

Overview:

Waters containing dissolved inorganic carbon (DIC) are analyzed by Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS) using a Thermo Finnigan GasBench® coupled to a DeltaV^{Plus} ®.

Sample preparation:

- Water samples should be collected using standard field sampling techniques in 40mL clear glass, screwtop vials with buytl-rubber septa caps (cap liners of silicone rubber or Teflon coated silicone are to be avoided)
- Bottles should be filled to capacity to minimize headspace
- Samples should be filtered to at least 0.45uM, and if possible 0.2uM
- Biocide is not needed if samples are filtered to 0.2uM
- If filtration is not possible, a biocide may be used. The ISL will NOT accept samples preserved with mercuric chloride ($HgCl_2$). Alternative acceptable biocides are: 1) sodium azide (add 10uL of 3.6M solution per vial), 2) Zinc Chloride (add 10 µl of 50% w/v $ZnCl_2$ per milliliter of water sample) or 3) Copper Sulfate (~5mg of crystals in each vial)

- A completed sample submission form must accompany the samples https://www.ucalgary.ca/labs/isotope-science-lab/sample-submission

- Alkalinity (as $CaCO_3$ equivalent in mg/L) is needed to estimate the amount of sample to prepare for isotopic analysis. Please provide alkalinity data with the submission form. If alkalinity cannot be supplied, it can be measured in the ISL. Contact the lab manager for pricing.

Online (CF-IRMS) technique:

Exetainers (Labco p/n: 038W) are loaded with 250uL of 85% H_2PO_4, capped and flushed with UHP helium at ~70ml/min for 10minutes. Based on the alkalinity, an amount of sample equal to ~0.250mg of pure $CaCO_3$ is injected into the vial. Vials are placed in the heated block of the GasBench at 25°C and left to react for ~5 hours. 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 $^{13}C/^{12}C$ 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.

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 (Craig, 1957).

Selected internal Lab Reference Materials (see table below) are prepared in DI water and analyzed through-out the sequence 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.

Reference materials used for data correction:

ISL carbonate standards	**Calibrated $\delta^{13}C$ value (VPDB)**	
ISL A&H ($NaHCO_3$)	-21.8 ± 0.3‰	
ISL Safeway ($NaHCO_3$)	-1.4 ± 0.3‰	
ISL JT Baker ($NaHCO_3$)	-19.8 ± 0.3‰	
ISL-K_2CO_3	-29.2 ± 0.3‰	

International RMs	**Accepted $\delta^{13}C$ (VPDB)**	
NBS 18	-5.01 ± 0.06‰	
NBS 19	1.95 ‰ (b.d.)	
USGS44 (CaCO3)	-42.03 ± 0.10‰	
IAEA CO-9 ($BaCO_3$)	-47.32 ± 0.20‰	

Note: (b.d.) = "by definition"

Performance:

Precision and reproducibility using this technique is typically better than ±0.3 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