

AN026

Fast, Easy $\delta^{13}\text{C}$ from Carbonates Using Picarro's Liaison™ System Coupled to an AutoMate Prep Device.

High-precision, rugged device can even be used for field deployment

Keywords:

Material: Carbonates, paleontology, limestone, marble

Process: Stable isotopes, $\delta^{13}\text{C}$, Liaison



Summary and Relevance:

The stable carbon isotope signatures derived from carbonate rocks and carbonate bearing materials have been used to study a variety of phenomena, including past atmospheric carbon dioxide levels ¹, correlation of rock formations to geological time-scale events² and history of ocean circulation patterns. Until now, scientists obtaining $\delta^{13}\text{C}$ data using traditional IRMS instrumentation have dealt with technical challenge (constant calibration, electronics sensitivity, etc.). A new $\delta^{13}\text{C}$ system from Picarro significantly reduces technical challenges for carbonate sampling. Picarro's Liaison system provide a seamless connection between CO₂ liberation systems, such as the [AutoMate Prep Device](#) from AutoMateFx, Inc.³ and the Picarro Isotopic CO₂ Cavity Ring-Down Spectrometer (CRDS). This novel combination of devices enables the measurement of $\delta^{13}\text{C}$ from both automatic acidification of solid samples (limestones, marine and lake sediments, soils, etc.) and of DIC in water samples (marine and fresh). The system is fast and easy to use. Samples run in 10 minutes and set-up time is less than an hour. The system offers high precision but is capable of



deployments to field stations and other remote locations previously considered unsuitable for isotope measurements.

In this application note we present isotopic data from a series of carbonate standards, processed using the AutoMate Prep Device and analyzed with Picarro Iso-CO₂ analyzer. The precision is excellent and sample replicates were each completed in 10 minutes.

Process:

Three replicates (each ca. 200 µg) of six carbonate standards (NBS-18⁴, a carbonatite from Fen, Norway; NBS-19⁴, reported as TS-Limestone from white marble of unknown origin; NBS-20, Solnhofen limestone from Southern Germany; B1, a marine carbonate; BYM, Brown Yule marble; CM-UF, Carrera marble-University of Florida) were deposited in Exetainer glass vials which in turn were queued on the AutoMate system carousel. On the start signal from the Picarro analyzer, 4ml of 10% phosphoric acid was added to the first vial. During the reaction period of 4min, the CO₂ liberated was flushed from the Exetainer into Liaison using N₂ carrier gas. The gas was allowed to mix in a bellows and was then routed from Liaison into the isotopic CO₂ analyzer, where the ¹³C/¹²C ratio is measured from the ¹²CO₂ and ¹³CO₂ spectral features and δ¹³C value calculated. Simultaneously, during isotopic carbon analysis of the first sample, the second sample is acidified and the evolved CO₂ is collected in a second bellows inside Liaison.

Results:

The results from the Picarro iso-CO₂ CRDS analyzer are shown in Table 1 below. The precision of the carbonate samples analysis is within 0.3 ‰ or better, with an average standard deviation of 0.17 ‰. In addition, the CRDS data analyses match accurately with the standards certified values as recorded with IRMS. The results indicate the Picarro CRDS can achieve high-precision results for carbonates that are sufficient for many research studies.

	CRDS ^{13}C / ‰	S.D.(n=3) / ‰	Certified ^{13}C /‰	^{13}C / ‰
NBS18	-5.22	0.14	-5.01	0.21
NBS19	1.99	0.10	1.95	-0.04
NBS20	-1.02	0.31	-1.06	-0.04
B1	0.62	0.14	0.64	0.02
BYM	-2.33	0.09	-2.29	0.04
CM-UF	2.02	0.23	2.13	0.10

Table 1. Picarro CRDS reported data for each carbonate standard is given in the left hand column. The IRMS certified value for each carbonate is given in the 4th column. The difference between the two values is provided in the final column as 'Delta delta'.

Comments:

A new generation of CRDS-based isotopic analyzers and accompanying front-end automation devices enables simple and fast measurement of carbon stable isotope ratio from carbonate rocks. This data complements earlier work on DIC (AN014, Stable Isotope Ratio Measurement of Dissolved Inorganic Carbon)

References:

1. See for example: Paleosol Barometer Indicates Extreme Fluctuations in Atmospheric CO₂ Across the Cretaceous-Tertiary Boundary, L. Nordt, S. Atchley and S.I. Dworkin, *Geology*, **2002**, 30 (8), 703-706
2. See for example: Silurian $\delta^{13}\text{C}$ Stratigraphy: A view from North America, M.R. Saltzman, *Geology*, **2001**; 29 (8), 671-674.
3. <http://automatefx.com/home.html>
4. Friedman, I., O'Neil, J., Cebula, G. (1982): Two New Carbonate Stable Isotope Standards. *Geostandards Newsletter*, **1982**, vol. 6, No. 1, 11-12.