Advances in sample preparation at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS): Investigation of Carbonate Secondary Standards

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NOSAMS SAMPLE PREP LAB (SPL)

The development of robust sample preparation techniques for ocean science research has been a hallmark of NOSAMS since its inception.

Here we present advances from NOSAMS which include:

- Comparison of pyrolysis of carbonate materials to standard acidification methods.
- Are carbonate intercomparison standards homogeneous?
- Use of the Ramped PyrOx (RPO) system for carbonates.
- Progress on incorporating a Picarro isotope analyzer into our sample preparation stream.

CONTINUOUS $\delta^{13}C$ MEASUREMENTS

- Currently, ~5-6 $\delta^{13}C$ measurements are collected from the fractions of each RPO sample run.
- To achieve greater data density, CO_2 evolved from the RPO sample is delivered to a Picarro G2101-i Isotopic Carbon Analyzer following oxidation (Fig. 5)
- A flow of 19 ml/min (versus 35 ml/min for standard RPO operation) under N carrier gas is used to satisfy the technical specifications of the Picarro analyzer

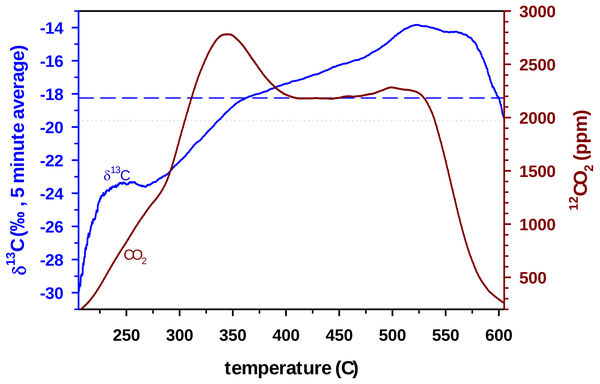

Figure 1. CO_2 and $\delta^{13}C$ data collected with a Picarro G2101-i connected directly to the NOSAMS RPO output flow. The data presented is from a NOSAMS internal standard, with a measured isotope value of -19.6 ‰ (dotted line); mass balance of Picarro isotope data is -18.25 ‰ (dashed line).

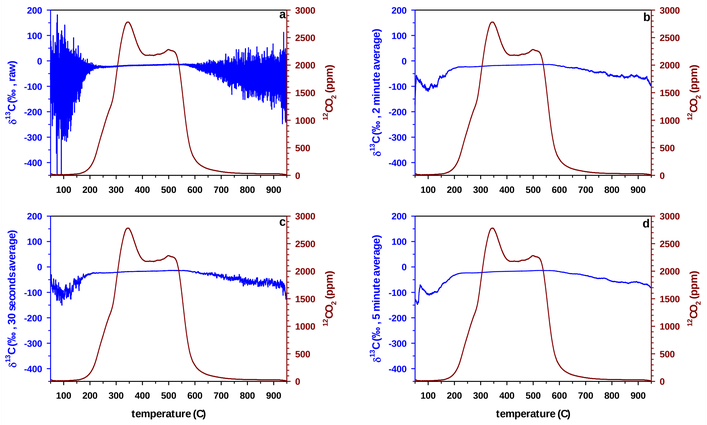

Figure 2. Picarro data averaging and noise distribution for a NOSAMS internal standard (Fig. 1). Values below ~200 ppm do not yield reliable $\delta^{13}C$ data. Thermogram shoulders may require use of the Picarro Liaison.

THERMAL ANALYSIS OF CARBONATES

To explore future thermogravimetric analysis (TGA), carbonate samples under a constant heating regime have been tested. While this disregards the continuous weigh method associated with TGA, these preliminary results support continued investigation of TGA. NOSAMS-2 is an internal secondary standard of <2μm sieved carbonate powder from microsampled quahog shells.

Methods for current experimental setup:

- ~10mg (~100 μmol C) are loaded into a 9mm quartz tube
- sample is heated from 25°C to 850°C degrees at a ramp rate of ~75°C/min
- while maintaining a sample temperature of 850°C, the evolved CO_2 is cryogenically transferred (4min period), quantified, and stored in a finger flask awaiting conversion to graphite.

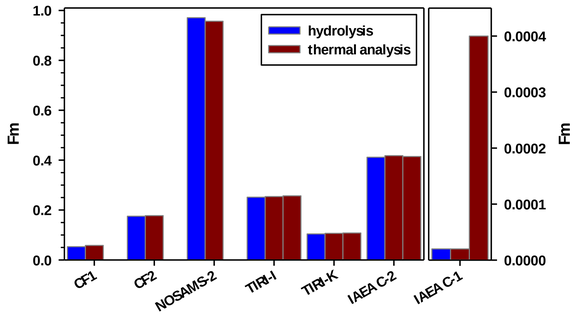

Figure 3. Fm (fraction modern) values for NOSAMS secondary carbonate standards and client foraminifera examples (CF1,2) using traditional hydrolysis and thermal analysis. Traditional hydrolysis (blue bar) values for standards are average NOSAMS consensus.

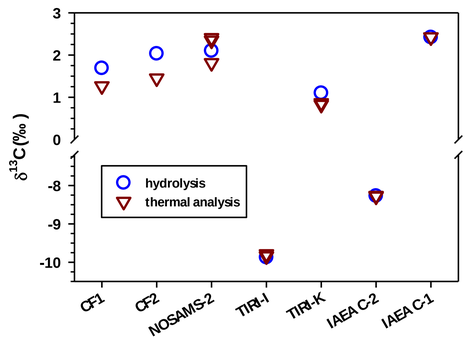

Figure 4. $\delta^{13}C$ values for NOSAMS secondary carbonate standards and client foraminifera examples (CF1,2) using traditional hydrolysis and thermal analysis.

NOSAMS-2 and some client foraminifera failed to make graphite or were slow to react without the addition of silver grains, indicating the inclusion of organic materials.

A method success of 80% and slightly more efficient sample preparation imply the potential for use in daily production of certain sample types.

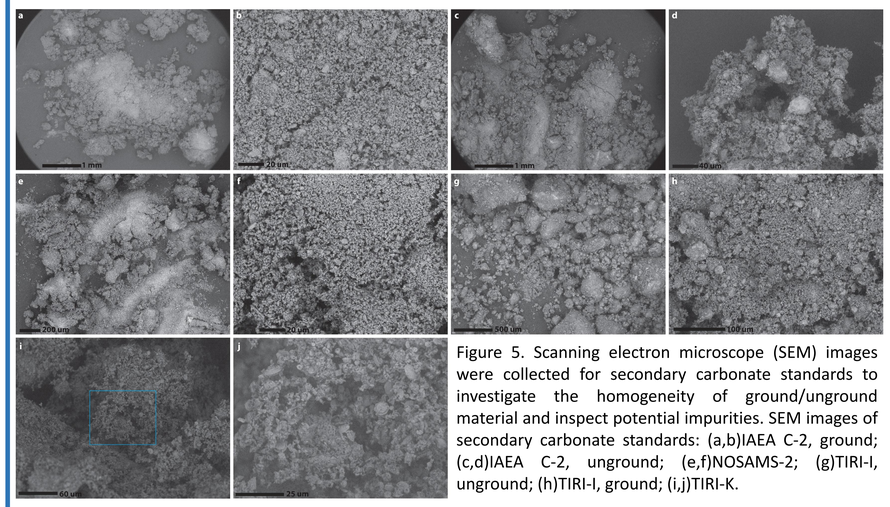

Figure 5. Scanning electron microscope (SEM) images were collected for secondary carbonate standards to investigate the homogeneity of ground/unground material and inspect potential impurities. SEM images of secondary carbonate standards: (a,b)IAEA C-2, ground; (c,d)IAEA C-2, unground; (e,f)NOSAMS-2; (g)TIRI-I, unground; (h)TIRI-I, ground; (i,j)TIRI-K.

Ground secondary carbonate standards demonstrate good homogeneity

Potential impurities (organic particles, etc.) were not observed in any secondary carbonate standards (ground and unground)

RAMPED PYROLYSIS-OXIDATION (RPO)

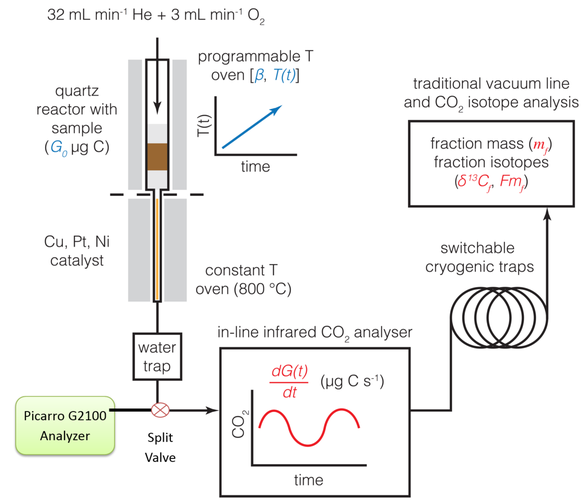

Figure 6. Schematic diagram of the NOSAMS RPO instrument, adapted from Hemingway [2017][1]. The system has been modified for compatibility with the Picarro G2101-i Isotopic Carbon Analyzer at several junctions. Standard RPO operation uses a He+O mixture as depicted, and is directed toward the CO_2 analyzer at the split valve. Picarro operation uses N+O and is directed toward the Picarro at the split valve. The system is currently being adapted to allow for simultaneous continuous Picarro $\delta^{13}C$ measurements in addition to traditional RPO trapping and analysis. [1]Hemingway, J.D., 2017, Understanding terrestrial organic carbon export: A time-series approach: Massachusetts Institute of Technology & Woods Hole Oceanographic Institution, 190 p.

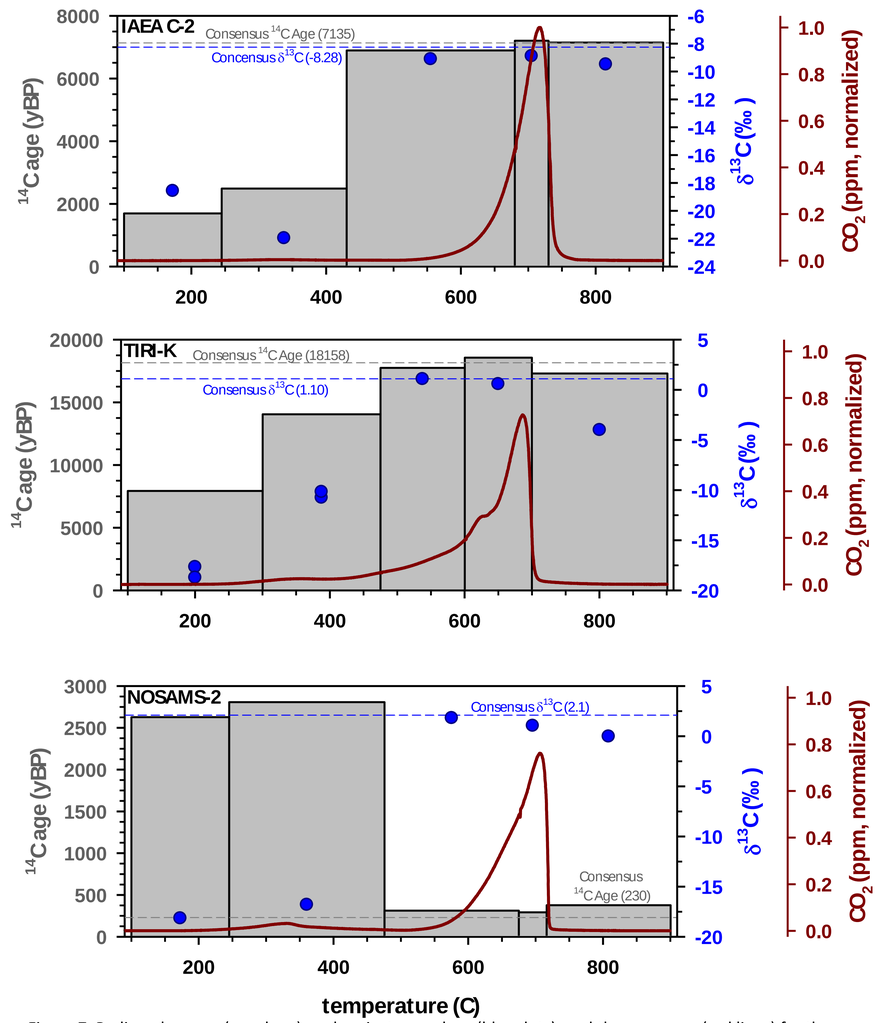

Figure 7. Radiocarbon age (gray bars), carbon isotope values (blue dots), and thermograms (red lines) for three NOSAMS secondary carbonate standards. Consensus age and carbon isotope values are shown by dashed lines, gray and blue respectively. Replicate $\delta^{13}C$ values are shown for the first two fractions of TIRI-K.

RPO fractions with the largest measured vs. consensus value are relatively small in mass, however these differences may account for the slight variability we observe in the age and Fm of material considered homogeneous.

Future RPO studies of IAEA C-1 and TIRI-I, as well as other submitted carbonate types, will investigate evidence of similar patterns/results.

NOSAMS NATIONAL OCEAN SCIENCES ACCELERATOR MASS SPECTROMETRY

Acknowledgements: Peter Landry, Brian Monteleone, Cameron McIntyre and Dr. Xuchen Wang

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