

## Ramped Pyrolysis-Oxidation $^{14}\text{C}$ Preparation Laboratory

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*Ramped pyrolysis-oxidation* (published alternatively as ramped pyrolysis, Ramped PyrOx, or RPO)  $^{14}\text{C}$  dating is a preparation process that aims to separate organic carbon in terms of thermochemical stability through the process of pyrolysis. The process results in multiple  $^{14}\text{C}$  dates for each sample, what is known as an age spectrum. This process is useful in geochronology where geologists are interested in dating organic matter in sediments, rocks, or dissolved in bodies of water. Such interest in dating organic matter usually evolves where there are no other easily identifiable targets for radiocarbon dating (macro- or microfossils, specific compounds, etc.). This process has other applications outside of geochronology as well.

### *Diversity and Equity*

The RPO facility at USF-CMS prides itself in an inclusive atmosphere. We welcome and encourage use of our facility by students from diverse backgrounds, especially those that are currently under-represented in the Earth sciences. As such, all visiting scholars should expect to contribute and benefit from this atmosphere in many ways.

### *Facilities Overview*

The Ramped Pyrolysis-Oxidation (RPO)  $^{14}\text{C}$  dating facility at the University of South Florida College of Marine Science is available for use by visiting scholars. The facility houses materials and apparatuses for pretreatment of samples (freeze-driers, acid treatment manifolds, scales, and muffle furnaces) as well as ancillary analysis (elemental analysis, stable isotope analysis). The RPO system itself consists of a flow system (mass flow controllers, infrared gas analyzer), a furnace system (two tube furnaces with independent temperature controllers, quartz reactor, and quartz sample inserts), and a vacuum separations system (hybrid turbomolecular pump, capacitive diaphragm manometer), controlled partially by LabVIEW graphical control system. Visiting scholars can generate purified  $\text{CO}_2$  from different temperature intervals of their samples. Sealed *in vacuo* in borosilicate glass tubes, these  $\text{CO}_2$  samples can be submitted to radiocarbon measurement facilities.

### *Required Time for Visiting Scholars*

It takes approximately one week to be trained to a point of semi-autonomy on the RPO system. Training can be partially accomplished with samples and blanks that will ultimately comprise the scholar's research. Once trained, scholars can base desired time of residence on the capability to run two samples per day. Scholars are also required to prepare one blank determination sample for each 10 unknown  $\text{CO}_2$  samples that they generate, and to share those data with the laboratory once analyzed for  $^{14}\text{C}$  content. This ensures the best up-to-date understanding of blank corrections necessary to interpret data from this system. Additional time is required if the scholar plans to perform all sample pretreatment at USF-CMS, including removal of carbon-bearing minerals from the sample. Notably, we cannot analyze acid-

fumigated samples from scholars who have performed sample pretreatment at their home institution as those samples destroy our oxidation catalyts. Acid rinsing is necessary, and we can share our protocol with interested parties.

### *Laboratory Costs and Expenses*

Costs for RPO can be divided into two categories: Consumables and analysis. Typically, visiting scholars separate a single sample into five temperature intervals for unique  $^{14}\text{C}$  measurements. The consumables cost for this is \$535 per sample, which includes acid pretreatment at USF-CMS. Scholars who pretreat their samples prior to arrival at USF will only incur charges of \$330 per sample for RPO analysis only. Radiocarbon analysis charges can vary from laboratory to laboratory. The samples we prepare have been handled well by the National Ocean Sciences Accelerator Mass Spectrometer as they have had the most success in graphitizing our samples. Their [prices for  \$^{14}\text{C}\$  determination](#), or those from an AMS laboratory of your choice, must be budgeted into your proposal. Dr. Rosenheim can discuss options with you.

Prior to visiting USF-CMS, students can opt to treat their samples for removal of minerals bearing carbon. RPO dating targets organic matter. Often organic carbon and mineral carbon (e.g.  $\text{CaCO}_3$ ) are present in the same sediment horizons, but are not necessarily concomitant in formation. Removal of minerals such as  $\text{CaCO}_3$  is necessary to result in unambiguous organic carbon dates if the carbon-bearing minerals are not coeval with the age of deposition. **It is important that this is done by means other than acid fumigation!** Acid fumigation samples have disrupted the process of our catalyts for conversion of RPO pyrolysates to  $\text{CO}_2$ . We can share our Standard Operating Procedure if you choose to perform demineralization in your own laboratory. Briefly, we weight each sample and calculate the amount of 10% HCl required to neutralize the mass of sample assuming it was 100%  $\text{CaCO}_3$ . This ensures acid in excess. Samples are either rinsed on a filter or centrifuged until a neutral pH is approached, and ultimately stored in a low-temperature ( $50^\circ\text{C}$ ) until their weight ceases to decrease from loss of water (generally 24 hours, but variable depending on sediment type). Samples contain no added toxic ingredients after this procedure and can likely be safely transported if they had no hazardous ingredients prior to this treatment.

### *Laboratory Staff*

Visiting scholars will be tutored primarily by the laboratory technician. Generally, students in the CMS program that work with RPO analysis will have a role in the tutelage of the visiting scholar if applicable. This benefits in networking visiting scholars as well students matriculated at USF.

### *Data Processing*

Management and processing of the data involves the following steps:

- Submission of samples to qualified radiocarbon analysis laboratory ( $t_0$ )
- Reporting of  $^{14}\text{C}$  results to submitter of samples. ( $t_0 + 14\text{-}28$  days, AMS laboratory-dependent)
- Blank correction of  $^{14}\text{C}$  results, with help from USF-CMS RPO staff (+1 day)
- Data visualization – PI Brad Rosenheim is available to discuss and help with data visualization of RPO results after blank correction (+0.5 days).

### *Lead Time*

Generally, wait times to use the RPO facility are on the magnitude of one month. Between June and October, wait times can increase due to preparation of samples during the summer and for the AGU Fall Meeting, and, likewise, there is more internal student pressure on the facility during the summer months (May-August). To propose work over the summer, it is best to contact Dr. Rosenheim early in the year to plan for a visit.

### *Contact Information*

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