

A reactor for high-temperature pyrolysis and oxygen isotopic analysis of cellulose via induction heating

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A reactor for converting cellulose into carbon monoxide for subsequent oxygen isotopic analysis via continuous flow isotope ratio mass spectrometry is described. The system employs an induction heater to produce temperatures $\geq 1500^\circ\text{C}$ within a molybdenum foil crucible positioned by boron nitride (BN) spacers within a quartz outer sleeve. For samples of a homogeneous working standard cellulose between 300 and 400 μg in size, the blank/signal ratio is $< 5\%$, and the long-term precision is 0.30‰ (N = 232). For samples of 30 to 100 μg in size, a gas pressure sintered silicon nitride (Si_3N_4) outer sleeve replaces the quartz sleeve, the BN spacers are not used, and 6.0-grade carrier He must be used to minimize the blank signal. With these modifications a blank/sample ratio of $< 5\%$ and long-term precision of 0.30‰ (N = 144) are obtained. These results are similar to those achieved using standard high-temperature furnaces, but the reactor is simpler to pack, the system is more economical to run, and samples as small as 30 μg cellulose may be measured. For both reactors memory is significant in the subsequent sample and is believed to be due to exchange with reactor oxygen at temperatures above 1000°C . Further applications might include online preparation of other materials requiring temperatures of 1500–2600°C. Copyright © 2008 John Wiley & Sons, Ltd.

The advent of online continuous flow techniques for oxygen isotopic analysis of organic materials^{1,2} has revolutionized the use of such measurements for ecological and paleoenvironmental studies requiring high throughput, accuracy and precision.^{3–6} These systems employ a conventional high-temperature furnace with silicon carbide elements to maintain an anoxic reactor core with excess elemental carbon at temperatures of 1450–1500°C.⁷ Carbohydrate compounds introduced into these conditions are quantitatively pyrolyzed into carbon monoxide and hydrogen gases, which are then admitted to the stable isotope mass spectrometer via a continuous flow interface for oxygen, carbon and/or deuterium isotopic analysis. Although excellent reproducibility is also obtained in lower temperature systems,⁸ there is good evidence and theory to recommend pyrolysis at temperatures above 1450°C to minimize memory and fractionation effects associated with partial conversion into carbon dioxide.⁹ However, the requirement for high temperatures creates difficulties. These temperatures push the limits of conventional silicon carbide element furnaces, and these expensive components wear out quickly. Furthermore, fragile, precisely packed, multi-component reactors are required, and these reactors must be cooled, cleaned and repacked every few hundred samples, necessitating frequent intervals of downtime.

Induction heating systems provide an alternative means of producing pyrolysis conditions for the analysis of oxygen and deuterium isotopic compositions of organic materials. The basic elements, strengths and weaknesses of such a system were reported as early as 1965.¹⁰ In the system described here a 1 MHz radio-frequency generator is used to inductively heat a conductive crucible inside a reactor under anoxic conditions. A helium (He) carrier gas stream carries pyrolysis products through a gas chromatography (GC) column and then into a continuous flow interface for introduction into a stable isotope mass spectrometer.

The potential advantages of such a system are a simple, robust, energy efficient heater design, and the potential to reach temperatures at or above those commonly attained by high-temperature silicon carbide element furnaces. The disadvantage is that the reactor is heated from room temperature to pyrolysis temperature for each sample, creating the potential for transient leaks and blank signal effects related to the dramatic temperature changes experienced in the system. (In this communication the term 'blank' will be used to describe an apparent sample peak voltage and isotopic signature measured by mass spectrometry in the absence of introduction of a sample into the pyrolysis reactor.) Furthermore, the pyrolysis reactor must meet the following conditions for precise and accurate measurement of oxygen isotopic composition:

- Outer casing that is thermally non-conductive, electrically non-conductive, thermal shock resistant, impermeable to He, CO and H₂, and affordable and obtainable in the required dimension. If these conditions are not met, leaks may occur, either through thermal stress on fluoroelastomeric

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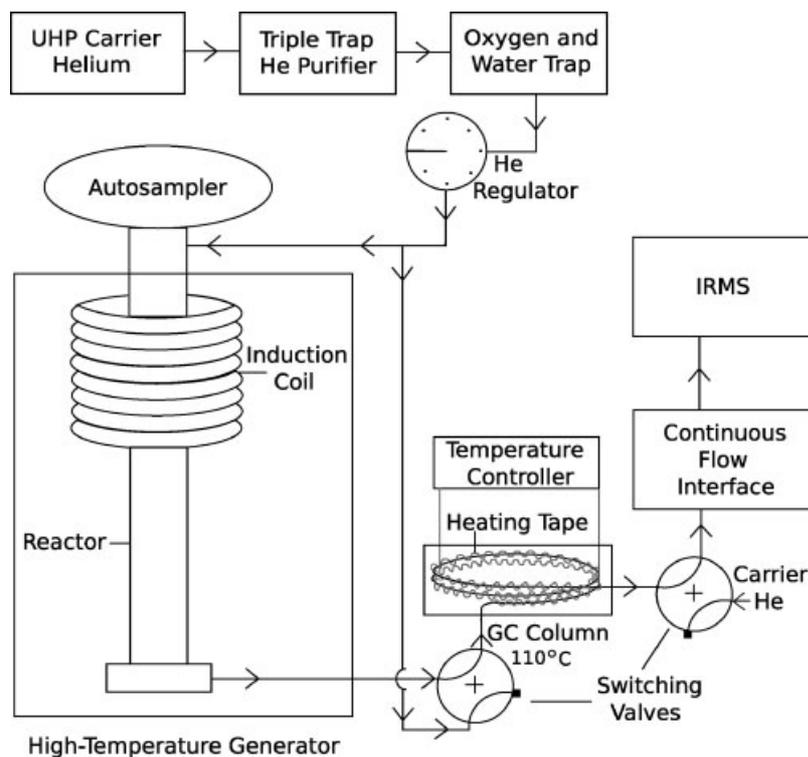


Figure 1. Schematic representation of the induction heater system for pyrolysis of cellulose samples for oxygen isotopic analysis.

seals at either end of the reactor, or through direct leaks through the reactor sleeve. The reactor casing must not electromagnetically shield the crucible from the induction field, or the crucible will not reach pyrolysis temperatures.

- Crucible and packing that is electrically conductive (permits resistance heating to occur), withstands temperatures of at least 1500°C, and catalyzes the quantitative conversion of organic molecules into CO and H₂ for subsequent isotopic analysis. In other words, the crucible must act as an induction susceptor, and it must not melt, degrade, or tear during the required and repeated deep heating and cooling cycles.
- Reactor materials that are otherwise non-reactive with each other and with introduced samples and sample capsules. Production of CO from materials other than the sample itself must be minimized, and isotopic exchange with oxygen species in the system must be minimized.
- Oxygen and water must be minimized throughout the sample preparation system and in the mass spectrometer so that the isotopic compositions of these molecules do not bias the measurement.

Herein the development of two optimized pyrolysis reactors which produce CO from cellulose for oxygen isotopic analysis via mass spectrometry for 50–500 µg samples is described. The system has advantages in cost, efficiency and throughput over conventional pyrolysis furnaces and reactors, and produces similar accuracy and precision for samples as small as 30 µg.

EXPERIMENTAL

Instrumentation

A 1 MHz radio-frequency generating induction heater designed for use in conjunction with a modified elemental analyzer and sealed autosampler (high-temperature generator (HTG)/elemental combustion system (ECS), zero-blank autosampler; Costech Analytical Technologies, Milan, Italy; Valencia, CA, USA) was used for the development of CO samples for isotopic analysis. The basic system and flow path (Fig. 1) consist of a He carrier gas stream running through the autosampler and pyrolysis reactor, into a GC column (1 m, molecular sieve 5 Å), and then via a transfer line to a continuous flow interface (ConFlo III, ThermoFinnigan Bremen, Germany) into a Delta Plus XP stable isotope mass spectrometer (ThermoFinnigan). The HTG is triggered by an electrical signal from the continuous flow interface. The heating intensity at the HTG is controlled by the combination of induction coil voltage and time interval of energization of the induction coil. For the two reactor designs, these parameters can be fixed to produce chromatographic evidence of complete pyrolysis (cf. Results and Figs. 4 and 5).

The HTG/ECS is modified as follows to optimize the system for oxygen isotope analysis (Fig. 1):

- The carrier gas is purified from UHP (5.0 grade) to >6.0 grade using a Supelco Triple Trap (Supelco/Sigma-Aldrich Biotechnology LP, St Louis, MO, USA). An oxygen and water trap is fitted directly downstream (Alltech/Grace, Wakefield, IL, USA). Only the latter is required

for analysis of samples larger than 300 μg using helium dilution at the ConFlo III at the precisions described herein.

- The plumbing of the ECS is largely bypassed by using a Swagelok regulator (Swagelok Corp., Solon, OH, USA) to deliver required He flow rates directly to the reactor. The reactor output is plumbed directly to the GC column, and the GC column is plumbed directly to the transfer line, with stainless steel Swagelok fittings. These modifications may not be necessary, but they reduce the number of fittings (and potential system leaks) from over 24 to seven.
- A closed loop chiller/recirculator (Neslab CFT-33; Thermo Scientific, Newington, NH, USA) running about four continuously filtered liters of one part antifreeze to three parts water is used to cool the HTG electronics and induction coil. A flow sensor (FS-380P, 0.17 gallons/min (GPM) rating, normally open electrical connection; Gems Sensors, Plainville, CT, USA), externally mounted with quick connects, replaces the original flow switch supplied with the HTG and is easily serviced when needed. The HTG is designed such that a coolant no-flow condition opens the HTG main electrical circuit, preventing system operation without cooling fluid – an important safety consideration.
- The ECS GC oven is augmented by heating supplied by two 3-foot lengths of high-temperature heating tape mounted in series, controlled by an electronic ramp and soak temperature controller, which receives temperature data via a T-type thermocouple (all heating and control components by Omega Engineering, Stamford, CT, USA). The heating tape is wrapped around the GC column and permits column conditioning at a temperature of 200–250°C, which drives off water collecting in the molecular sieve. The 1 m molecular sieve 5 Å column (Costech Analytical Technologies) is recurved to fit in a 10-cm diameter space and is spaced away from the walls of the GC oven using ceramics to avoid damaging the oven at the high temperatures required to recondition the molecular sieve column.
- Swagelok two-way crossover switching valves and additional He lines are used to maintain a clean He environment in the GC column when the reactor is open to atmosphere, and when the GC column is being conditioned at high temperatures. These changes minimize downtime, system flushing, and introduction of atmosphere into these sensitive elements, and also into the mass spectrometer analyzer itself. Installation of the valves into the system did not detectably increase mean background levels.

Reactor

Two reactors (Fig. 2) have been developed that meet the material property conditions described in the Introduction. The first is suitable for samples $>300 \mu\text{g}$ and is based on a quartz outer casing (Costech Analytical Technologies), which itself consists of three joined sections of varying diameter. The pyrolysis sector has o.d. 20 mm, i.d. 17 mm and length 13 cm. Below this is a 10-mm taper to a section with o.d. 8 mm, i.d. 5 mm, and length 38 cm. Below this is a 1-cm taper to a 5-cm long section of 5 mm o.d. and 2 mm i.d. quartz, which is joined to the 2-mm stainless steel transfer

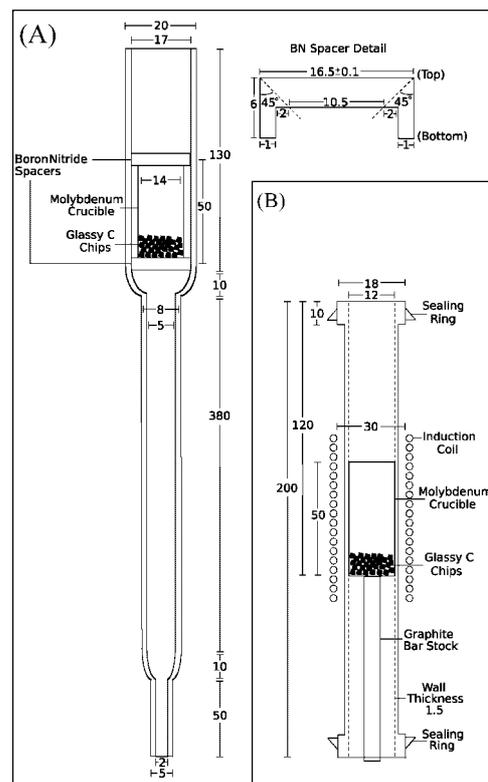


Figure 2. Schematic representation of (A) large sample and (B) small sample pyrolysis reactors. Measurements are in millimeters. Note that drawings are not to scale.

line to the GC column by a stainless steel compression fitting. A similar reactor geometry was previously used in a low temperature system design.⁸ Within the quartz tube, a cylindrical crucible formed from a 50 mm \times 50 mm, 0.002" thickness piece of 3N8 (99.98% pure) molybdenum foil (ESPI Metals, Ashland, OR, USA), with 50 mm length and 14 mm diameter, is held in position by two custom-designed spacer rings made of hexagonal boron nitride, grade AX05 (Ferro-Ceramic Grinding Inc., Wakefield, MA, USA). The spacers are shaped to funnel a dropped sample into the crucible, and to hold the crucible away from the walls of the quartz tube. The crucible is filled with 12 high-temperature conductive graphite or glassy carbon chips 3–5 mm in diameter (ESPI Metals; Hochttemperature Werkstoff GmbH, Thierhaupten, Germany). The lower two sections of the reactor are within the left furnace of the ECS, which is kept at its minimum operating temperature of 500°C.

A second reactor is suitable for samples as small as 30 μg and is composed of an outer casing of Ekasin S silicon nitride (ESK Ceramics, Kempton, Germany; Ceradyne Corp., Costa Mesa, CA, USA) with i.d. 12 mm, o.d. ground to 15 mm (with the exception that the o.d. at either end of the tube is 18 mm), and length 200 mm. The Ekasin S tube is approximately 92% Si_3N_4 , with the remainder primarily SiO_2 . Inside this reactor a molybdenum crucible similar to that used in the quartz reactor is held in a vertical position by friction and by a 75-mm rod of high-temperature conductive graphite (ESPI Metals). About 6–8 graphite or glassy carbon chips are placed inside the molybdenum crucible. In this configuration the left



Figure 3. Left: 'Large sample' reactor composed of molybdenum crucible half-filled with graphite or glassy carbon chips, held in position by boron nitride spacers within a quartz tube. Only the section of the tube subjected to pyrolysis temperatures is shown. Center: 'Small sample' reactor composed of a molybdenum crucible half-filled with graphite chips, supported by a graphite rod within a silicon nitride tube. The o-rings shown just left of the graphite rod are used below the Faraday cage shielding the induction coil to center the reactor within the coil. Right: HTG unit in small sample mode. The HTG coil is located inside the Faraday cage positioned just under the autosampler (center, top). Chiller/recirculator and external flow switch are visible at lower left.

furnace of the elemental analyzer is bypassed and can be switched off (Fig. 3).

RESULTS

Figure 4 shows screenshots of blank and 300 μg cellulose sample chromatograms for the large sample configuration. The blank signal in dilution mode (top panel) is obtained by activating the induction heater but without dropping a sample from the autosampler, and is less than 20 mV, or about 2% of a typical sample peak (bottom panel). It occurs at about the same elution time as a sample signal. The sample peak is derived from dropping a 300 μg , silver-foil-wrapped sample into a crucible preheated to pyrolysis temperature for 33 s at 190 V at the HTG. The total heating time is set to 40 s. Figure 5 shows the respective chromatograms for the system in small sample mode, for which the HTG settings are 210 V, 33 s, and the sample is of mass 100 μg . Again, the total heating time is set to 40 s. In small sample configuration, we can most easily detect two distinct components of the blank signal (top panel). The first is just a few mV in amplitude, has a highly depleted M30/M28 ratio (typically -937%), and elutes well before the sample peak (Fig. 5). The second elutes at about the same time as the sample signal. It is much larger than the early-eluting peak, but typically is less than 100 mV; for a 100 μg cellulose sample, this is about 2% of a typical sample peak (bottom panel). The isotopic composition of the later blank peak varies between the $\approx 10\%$ value for quartz⁷ and the typical values for oxygen in organic materials of about 24–35%. The temperature at which the pyrolysis

occurs cannot be measured directly in an induction heater, but attaining reaction temperatures in excess of 1450°C is critical for the accuracy and precision of the isotopic results. Leuenberger and Filot⁹ showed that substantial amounts of CO₂ were formed when reactor temperatures were 1000–1400°C, and isotopic values were skewed as a result of isotopic partitioning between CO₂ and CO. Although we cannot measure temperature directly, we have melted nickel (melting point (MP) = 1455°C), iron (MP = 1538°C) and titanium (MP = 1668°C) under standard operating conditions. Under system full heating power, we have even melted edges of the molybdenum crucible itself (MP = 2623°C). We have also monitored CO₂, water, and mass 30-only production (presumably formaldehyde; A. Hilbert, personal communication, 2007) at the analyzer via close examination of the sample chromatography (Figs. 4 and 5) and found that these molecules are present only at negligible background levels. (We do reliably observe a late-eluting mass 30-only peak when the heating intensity is not set high enough or when the sample is not dropped into the crucible, and use this as a quality control measure.) Together the indirect evidence suggests that we are achieving temperatures at or above 1500°C.

Table 1 shows results of $\delta^{18}\text{O}$ measurements made on six celluloses prepared as part of the blind European 'Millennium' Project isotope laboratory intercomparison study.¹¹ None of these materials were used in the calibration of the HTG pyrolysis system to international isotope standards. Results averaged from two European high-temperature pyrolysis labs are taken as the known values of these

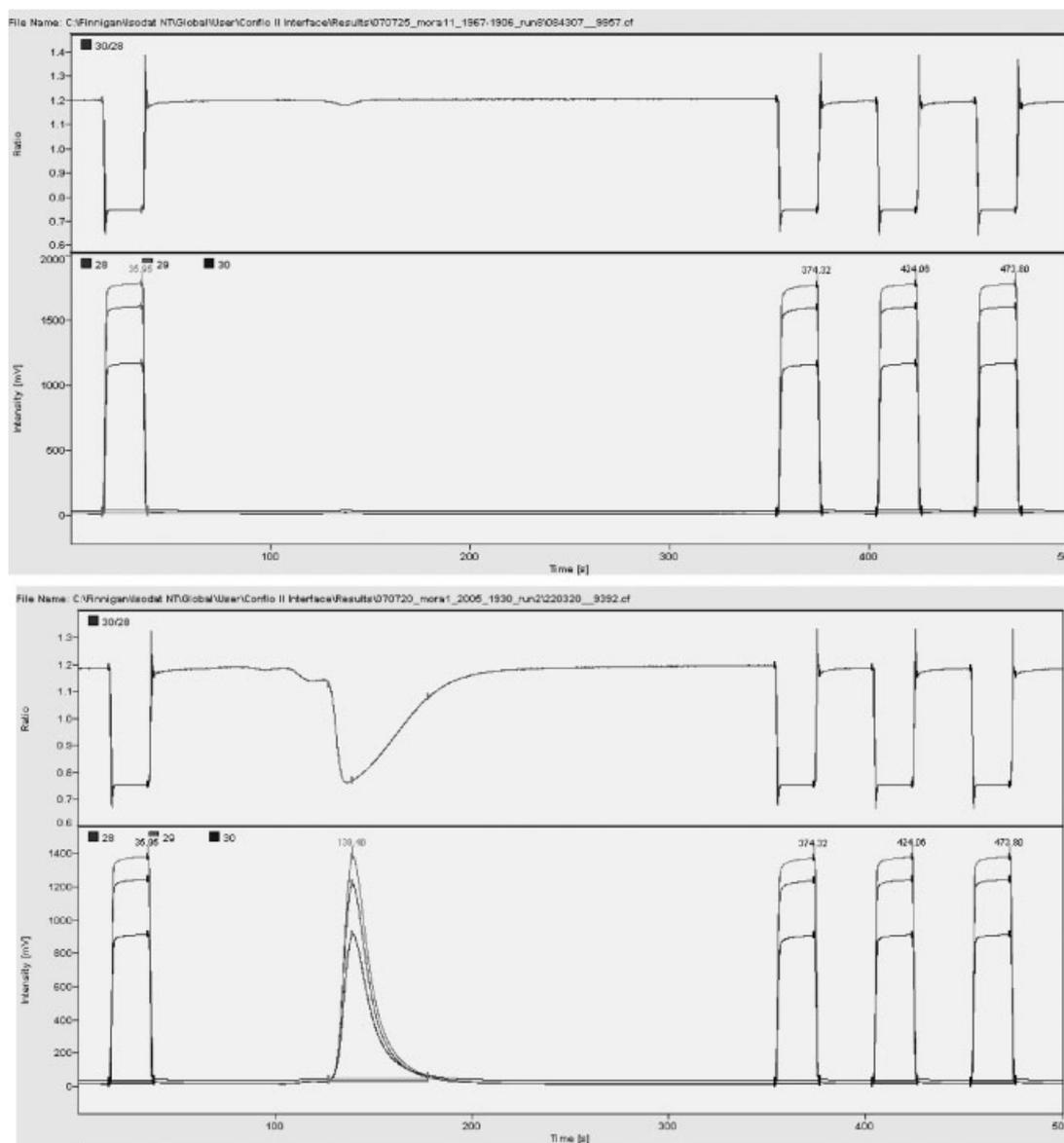


Figure 4. Top: 'Large sample' (dilution on) blank chromatogram. Bottom: 'Large sample' (dilution on) sample chromatogram. In both cases the HTG voltage is set to 190 V, and the coil is energized for 40 s. The sample is dropped into the crucible 33 s following start of coil energization.

materials. They are not statistically distinguishable at the $p < 0.05$ significance level from our observations using either the HTG large or small sample reactors. Table 2 shows the precisions obtained for the in-house α -cellulose working standard, which has a calibrated $\delta^{18}\text{O}$ isotopic value of $31.01 \pm 0.3\%$. For a range of mass classes ranging from 20 to $1550 \mu\text{g}$ measured in large and small sample reactor configurations, we find measurement precisions of about 0.3–0.4%.

DISCUSSION

Blank signal

Because the high-temperature generator impulse heats the reactor from room temperature to 1500°C for each measurement over about 30–50 s, there is a blank 'signal' monitored on masses 30 and 28 and evident in the chromatography. The blank has a slightly variable amplitude and widely

varying isotopic composition. Experiments (not shown) varying the length and/or time of reactor heating reveal a linear increase of the amplitude of the blank peak with increasing crucible heating intensity. The blank appears to be CO formed in the reactor because it elutes at the same time as the CO from actual samples (e.g. Fig. 5). The coincidence in elution time of the blank signal and the sample signal is not altered even if we double the length of the GC column. We can rule out heating-induced leaks: monitoring of mass 40 (argon) during heating indicates that the system is leak-tight despite the deep temperature cycling inside the reactor. We can also rule out the silver sample capsules as the source of the blank signal: tests comparing the blank signal with and without dropping an empty silver capsule indicate that there is no detectable blank signal associated with the silver capsules.

Instead, the blank may be the product of two processes occurring in the reactor. First, under anoxic high-temperature conditions, quartz and carbon react to form

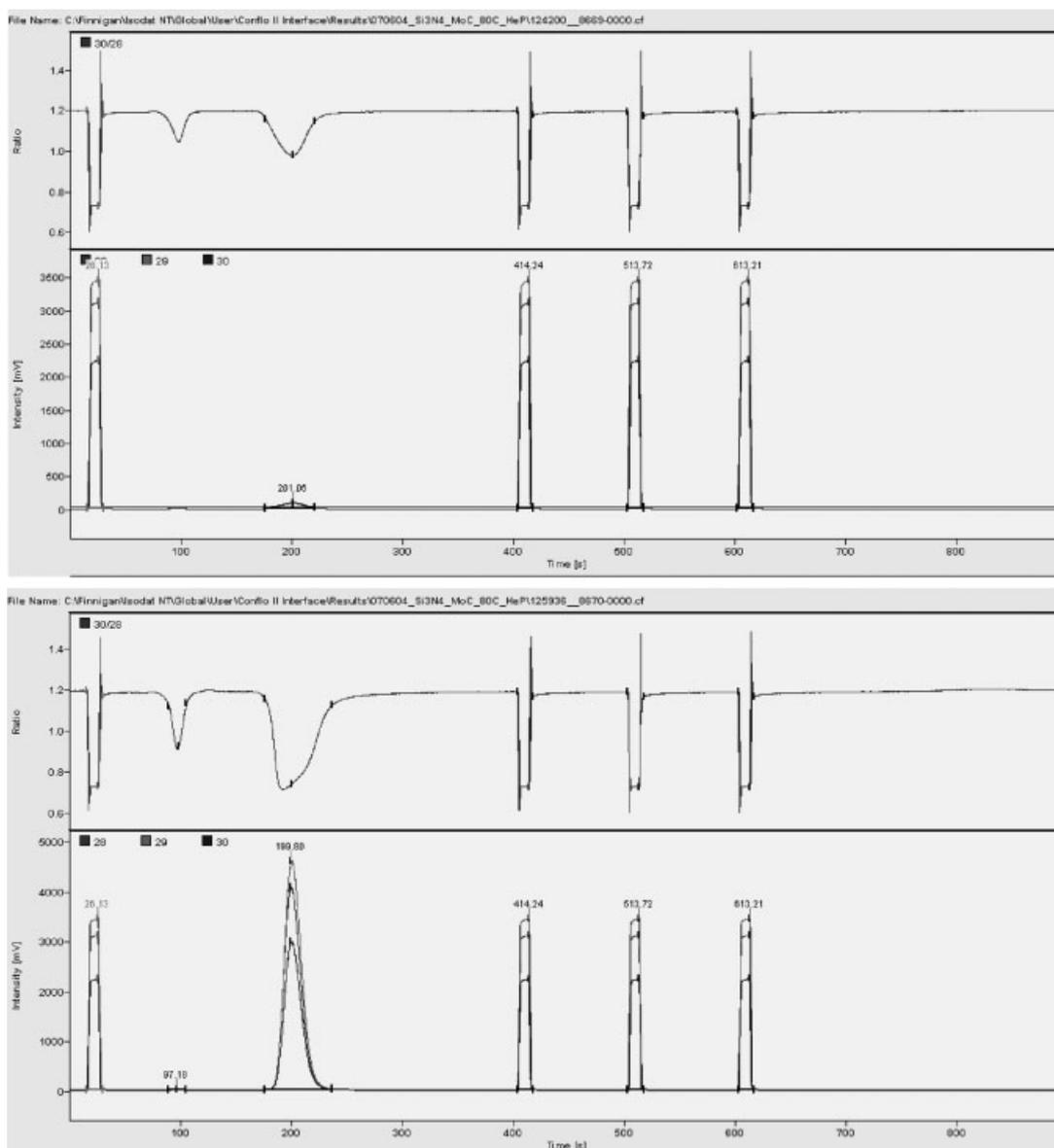


Figure 5. Top: 'Small sample' (dilution off) blank chromatogram. Bottom: 'Small sample' (dilution off) sample chromatogram. In both cases the HTG voltage is set to 210 V, and the coil is energized for 40 s. The sample is dropped into the crucible 33 s following start of coil energization.

CO, via formation of silicon carbide and/or silicon. Secondly, pyrolytic conversion of oxygen and oxygen-containing materials adsorbed onto graphite or glassy carbon surfaces will produce CO. This blank component may include contaminants adsorbed on graphite or glassy carbon surfaces and/or continuously entering the system via the He carrier gas stream. Evidence for the first process is from the observation that the amplitude of the blank signal is directly proportional to heating as estimated temperatures inside the reactor exceed about 1100°C. However, the system still produces a blank in the absence of graphite or glassy carbon in the reactor. Purification of 5.0 carrier He to >6.0 carrier He via the Supelco gas purifier reduces the blank with carbon present to about 40% of that observed without the extra gas purification.

Hence, reactor development was oriented toward minimizing heating of the reactor sleeve, and minimizing the

amount of solid and gaseous carbon in the system. The first requirement is achieved by using an electrical insulator for the reactor sleeve, using the electrically insulating boron nitride (BN) spacers to permit carrier He flow around the crucible, and minimizing the mass of the induction susceptor (i.e. the directly heated component of the reactor; here, the crucible and carbon catalyst) via use of a molybdenum foil crucible. Molybdenum has a very high electrical conductivity (34% I.A.C.S.; resistivity = 5.2 microhm-cm @ 0°C) and high melting point (2617°C), but the foil crucible mass is only about 1.3 g. Together with the graphite, the susceptor materials weigh less than 2 g. Because the thermal mass of the induction susceptor is small relative to the mass of the reactor sleeve and BN spacers, the reactor sleeve is heated less than it would have been in the presence of a more massive susceptor. The BN spacers allow carrier He to stream between the susceptor and the quartz reactor sleeve.

Table 1. HTG pyrolysis $\delta^{18}\text{O}$ (SMOW) results

Standard	Known	Large sample mode		Small sample mode	
		Measured	<i>p</i> -value	Measured	<i>p</i> -value
Earth	31.38 ± 0.12	31.26 ± 0.16	0.47	31.42 ± 0.17	0.71
Wind	27.45 ± 0.15	27.35 ± 0.24	0.56	27.75 ± 0.20	0.12
Fire	32.40 ± 0.11	32.32 ± 0.21	0.59	32.62 ± 0.10	0.23
Land	28.46 ± 0.39	28.86 ± 0.18	0.08	28.51 ± 0.19	0.73
Air	32.58 ± 0.14	32.49 ± 0.28	0.57	32.41 ± 0.16	0.35
Sea	29.66 ± 0.44	29.52 ± 0.15	0.56	30.01 ± 0.43	0.17

'Known' isotopic values are preliminary data averaged from two European high-temperature pyrolysis labs, measured as part of an ongoing laboratory inter-comparison for the EU-funded project Millennium (GOCE-017008). Measured isotopic values and 1σ errors were obtained for $N = 5$, 400 μg mass (large sample mode) and $N = 5$, 100 μg mass (small sample mode). *p*-values for HTG data are with respect to known isotopic values ('Known'), obtained from the Millennium intercomparison study.^{11,12} *p*-values are calculated given 1σ reproducibility of the in-house Sigma-Aldrich α -cellulose standard during the calibration tests: 0.27‰ ($N = 33$) and 0.31‰ ($N = 28$) for large and small sample reactors, respectively.¹³

Although the reactor sleeve is being heated radiatively, and the cooling potential of the He stream cannot be great, use of the spacers appears to further reduce the blank and improve measurement precision to satisfactory levels. These features keep the blank signal to <5% of the signal, such that precision of 0.2–0.3‰ ($N = 10$ –300) can routinely be achieved. For samples larger than 300 μg this noise/signal (N/S) ratio can be achieved in our IRMS system with sample stream He dilution at the continuous flow interface. For smaller samples run without He dilution, the use of the Si_3N_4 outer sleeve and >6.0 grade He minimizes the blank signal further, so that 5% N/S and 0.2–0.3‰ precision can be achieved even with cellulose samples as small as 30 μg (Table 2).

System memory

We performed further experiments in both large and small sample mode to determine the extent to which reactor memory and blank isotopic effects influence the results. We ran series of five replicates of four isotopic standards sequentially, attributing differences between the first and last samples within each set of replicates as resulting from the influence of memory resulting from prior analyses. The isotopic differences between each five-replicate set ranged from 3 to 19‰. We used a simple two-component mixing model $[f\delta_{n-1}(\text{true}) + (1-f)\delta_n(\text{true}) = \delta_n(\text{measured})]$, with n = sequence number] to determine the fraction f of isotopic signature δ attributable to memory. We also ran a randomized sequence of standards with an isotopic range of 20‰ to assess the effect of system memory on the precision and accuracy of results (Fig. 6).

In all cases we found substantial memory in both the small and large sample reactors. For reactors using graphite, the memory effect, expressed as a percentage of the difference between current and prior replicate sample sets, was independent of reactor type, and was about $15 \pm 3\%$ of the isotopic range in the first sample, $7 \pm 3\%$ in the second sample, and $4 \pm 4\%$ in the third sequential sample. Memory effects were about 1/3 smaller for similar experiments with samples running at 6 V rather than 4 V or 1.5 V. In the randomized experiment we found a significant memory effect for samples whose true isotopic value departs substantially from that of previous samples. Sequential small sample mode HTG analyses, which alternated samples of a single standard material with blank measurements, show that the blank isotopic composition may initially be as low as 10‰, but evolves asymptotically toward the value of the standard material being run through the system over the course of 5–10 analyses.

Although lower temperature systems demonstrate memory,^{8–14} negligible memory effect (<2%) is observed in conventional high-temperature pyrolysis systems (Thermo-Finnigan TC/EA; M. Fan, N. English, personal communication, 2008). Since we believe we are achieving crucible temperatures in excess of 1500°C (see Results section), we think that the source of the memory is exchange with oxygen in the reactor.² Conventional high-temperature furnace systems avoid this by isolating sample CO from a ceramic outer reactor sleeve using a glassy carbon liner,^{2,7} and, recently, using a molybdenum sleeve.¹⁵ In the system described here, the oxygen source may be the reactor sleeve and/or oxygen-containing compounds adsorbed on graphite

Table 2. $\delta^{18}\text{O}$ (SMOW) results as a function of sample size

Mass (μg)	all	Small sample mode				Large sample mode		
		20–40	41–60	61–90	90–110	110–130	300–400	1500–1550
N	503	10	25	35	165	24	232	12
Mean	31.05	31.03	31.05	30.99	31.13	31.04	31.01	31.01
Std. err.	0.37	0.38	0.36	0.28	0.47	0.29	0.32	0.36

Isotopic data are for a single house cellulose standard, Sigma α -cellulose, measured between June 2006 and February 2008. Means and errors for all data (first data column) are calculated as the N -weighted averages and root mean square of the N -weighted standard error variances, respectively.

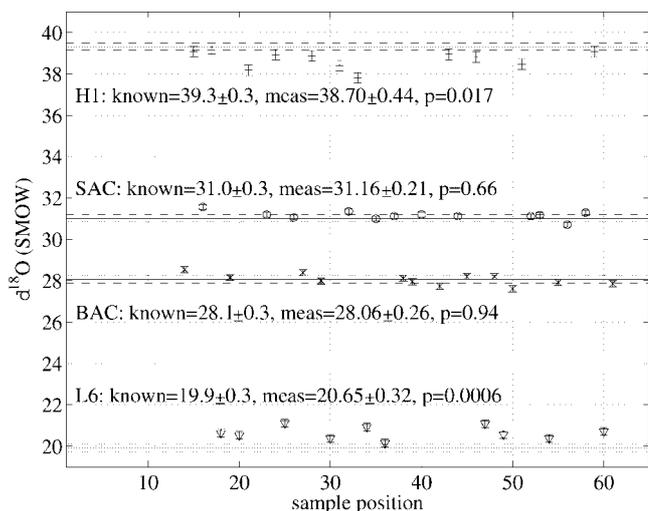


Figure 6. Randomly ordered standard analyses vs. known values for four homogeneous isotopic standards run in large sample mode, with glassy carbon in the reactor. Known values noted in text and given with $\pm 2\sigma$ error bars (solid and dashed lines); values measured in experiment also have $\pm 2\sigma$ error bars. There is a significant memory effect for the lightest and heaviest standards; moderate standards show negligible memory effect, in agreement with the memory model described in the text. The memory effect is reduced by 50–80% compared with the system run with graphite in the reactor.

or glassy carbon surfaces or on the cellulose samples themselves. In this model, oxygen is exchanged between the prior sample and reactor oxygen, which is then exchanged with the oxygen of subsequent samples run through the reactor. This may be true even for the Si_3N_4 reactor sleeve, which is about 8–10% quartz: in the presence of even trace amounts of oxygen, Si_3N_4 is converted into quartz at temperatures above 1000°C (T. Kempf, ESK Ceramics, personal communication, 2006). This would explain the evolution of the blank isotopic signature from near the quartz value of about 10‰⁷ to the organic oxygen isotopic range over the course of ten or more sequential sample analyses.

System memory can be addressed in at least three ways. First, if sequential cellulose samples have a true difference of 4‰ or less, even 15% of the range is within typical 1σ analytical uncertainty for continuous flow oxygen isotope measurements. However, if this is not the case, the two-component mixing model would permit correction based on previous values: $\delta_n(\text{true}) = \delta_n(\text{measured}) - f\delta_{n-1}(\text{true}) / (1 - f)$. Second, memory can be reduced by 50–80% (i.e. to 2–5% of isotopic difference) either by running at higher (4–6 V in large sample mode) sample voltages, or by substituting high conductivity glassy carbon (Hochtemperaturwerkstoff GmbH, Thierhaupten, Germany) for the graphite in the system (Fig. 6). Third, if the hypothesized source of blank and memory is correct, additional experimentation focusing on keeping the reactor sleeve cool and reducing oxygen and reactive carbon in the system should further reduce blank and memory effects.

System operation

The design of the Costech HTG and the modifications that we have introduced allow system consumables to be easily renewed without long wait times after the system is opened to the environment, and without introducing atmosphere unnecessarily into the analyzer. A new molybdenum crucible must be conditioned by running a dozen or so silver-encapsulated samples through the system; the silver helps to seal the crucible seams, which improves inductive heating and ensures complete conversion of the sample into CO. The crucible construction must create a gap-free bottom surface, and occasionally crucibles will fail immediately, due to imperfect shaping. A conditioned crucible will typically last for 300–800 samples, with the limiting factors being the buildup of silver and carbon in the crucible and on the reactor walls, oxidation of graphite chips, and deformation of the crucible with repeated heating cycles. Since the system returns to room temperature within a few minutes of heating, and with the ability to isolate and purge only the reactor, a preformed crucible with new graphite can be swapped into the system in about 15 min. Quartz pyrolysis tubes can be cleaned of carbon residue with dilute nitric acid and heating in a glass furnace at 800°C. We have found that the quartz tubes are reusable an indefinite number of times. The lifetime of a Si_3N_4 reactor tube has yet to be determined, but is in excess of 600 samples. Measurement protocols can be optimized to about 10 min length, and a 99-position autosampler permits samples to be analyzed in automated mode in a daily run cycle. Monthly maintenance of the GC column is carried out *in situ* under He flow and takes about 5 h. Because the reactor sleeves and BN spacers can be cleaned and reused, costs over the past year of use have averaged about \$5/sample, inclusive of consumables, reactor components, crucibles, prorated equipment replacement costs, and technician time. True long-term costs remain to be determined.

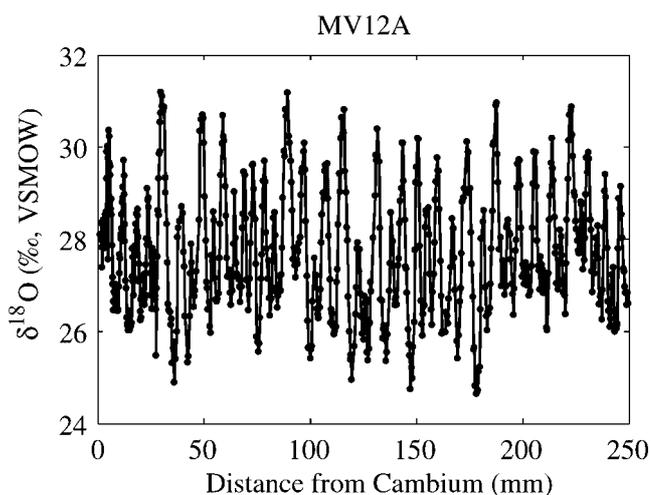


Figure 7. Oxygen isotope chronology from tree core MV12A collected at Monteverde, Costa Rica, plotted vs. distance from the cambium, and showing an isotopic cycle, which is hypothesized^{16,17} to reflect the annual cycle in rainfall amount and humidity at this location.

Applications

Our immediate applications for this system are in high-resolution proxy climate data development based on intra-annual isotopic composition of cellulose from tropical trees, which is interpreted to reflect annual and interannual rainfall variations (Fig. 7).^{16,17} The ability to measure on samples as small as 30 µg may permit us to make intra-annual isotopic measurements on slow-growing trees and/or low-density wood samples. More diverse uses might take advantage of the temperatures reached in the molybdenum crucible ($\leq 2600^\circ\text{C}$), which are not possible in a conventional furnace. The uses cited by Gehre and Strauch⁷ for their high-temperature pyrolysis system include oxygen analysis of sucrose, other organics, sulfates, phosphates, potassium nitrate, carbonates, iron oxides, quartz sand, zeolite and manganese oxide. Lücke *et al.* reported excellent results using an induction heater and glassy carbon reactor to analyze the oxygen isotopic content of biogenic silica.¹⁸ We have not explored any of these other analyses yet.

CONCLUSIONS

Induction-derived pyrolysis of cellulose samples produces precise, accurate and economical oxygen isotopic results on samples as small as 30 µg, as long as blank signals can be minimized via reactor design. Memory effects are evident and influence primarily the first of a sequence of samples having a mean value very different from prior samples.

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