THE KECK CARBON CYCLE AMS LABORATORY, UNIVERSITY OF CALIFORNIA, IRVINE: STATUS REPORT

Robert K Beverly[1,2] • Will Beaumont[1] • Denis Tauz[1] • Kaelyn M Ormsby[1] • Karl F von Reden[3] • Guaciara M Santos[1] • John R Southon[1]

ABSTRACT. We present a status report of the accelerator mass spectrometry (AMS) facility at the University of California, Irvine, USA. Recent spectrometer upgrades and repairs are discussed. Modifications to preparation laboratory procedures designed to improve sample throughput efficiency while maintaining precision of 2–3‰ for 1-mg samples (Santos et al. 2007c) are presented.

INTRODUCTION

The Keck Carbon Cycle Accelerator Mass Spectrometry (KCCAMS) facility was established in 2001–2002 and was set up to use carbon isotopic techniques, primarily AMS, to advance understanding of the carbon cycle and its linkages with climate. The AMS system is a National Electrostatics Corporation compact spectrometer based on a 0.5MV accelerator (NEC 1.5SDH-1).

After an initial series of technical upgrades (Southon et al. 2004, 2007; Southon and Santos 2004, 2007), 2–3‰ precision is routinely achieved for samples with >0.7 mg of carbon (Santos et al. 2007b). The spectrometer has been relatively trouble-free for a system that runs 24/7 and is past 70,000 targets measured, but after 7 yr of operation, it is starting to show its age and consequently a few significant problems have occurred. This paper summarizes recent upgrades and some of the lessons learned during the last 3 yr of spectrometer operation.

Regarding sample preparation, the KCCAMS sample prep laboratory (which provides 60% of all samples measured at the facility) has been upgraded to handle a larger number of samples. This lab routinely produces graphite samples as small as 0.015 mg C for outside submitters and internal research as small as 0.001 mg C, with close to 100% yield (Santos et al. 2007a,c). Recent modifications include the construction of a third 12-headed graphitization line, digital monitoring of reaction vessel pressures during graphitization and catalyst preconditioning, additional pretreatment of the Fe catalyst, and transition from pressing samples with a hammer to a modified pellet press. Storage issues with combusted and graphitized samples, carbonate sample processing, and quality control are discussed.

IMPROVEMENTS TO THE BEAM TRANSPORT SYSTEM AND ACCELERATOR

A significant bottleneck in the design of our spectrometer is that the divergence of the beam in the injection line is limited by the height of the vacuum box in the injection magnet. This in turn limits the size of the beam at the entrance to the accelerator tube, so that the full ion optical acceptance of the stripper canal cannot be used. Since beam emittance increases as ion source outputs increase, this mismatch unnecessarily limits the usable beam output from source.

To alleviate this problem, we increased the ion source voltage from 55.5 to 66.5 kV (58 kV on the source plus 8.5 kV cathode voltage) to reduce beam divergences in the injection line. The main ion source insulator (Ceramaseal 17142–02-W, 6″ ID) was replaced with a larger unit (Ceramaseal

[1]Earth System Science Department, University of California, Irvine, California 92612, USA.
[2]Corresponding author. Email: rbeverly@uci.edu.
[3]NOSAMS, McLean Laboratory, WHOI, Woods Hole, Massachusetts 02543, USA.

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17143-03-W, 8″ ID) for better voltage holding capability and improved source pumping. In addition, the beamline cross for the source pump (downstream of the source) was replaced, allowing a new einzel lens within the cross to be used in conjunction with the existing lens in the source extractor assembly in a "zoom lens" configuration, to better accommodate a wide range of beam divergences.

Additionally, the original injector magnet in the AMS system, a Danfysik 90° double-focusing dipole with 304.8-mm bending radius and 48-mm pole gap (DF01319), was redesigned with new pole pieces to increase the gap by 20 to 68 mm. The purpose of this change was to allow larger (higher divergence) ion beams to be transmitted without introducing excessive aberrations in the beam tail beyond the full width at 10% of maximum. The modified magnet was designed using the finite-element code Infolytica MagNet (Infolytica Corporation, www.infolytica.com). The calculated focal length for this design is ~710 mm, up from 690 mm in the original design. To balance the increasing vertical focal length resulting from the increased gap, the pole tips were rotated by 0.5° to obtain a similar increase in the horizontal focal length.

The finite element calculations showed significant deformation of the field contours near the Rogowski pole edges at the ends of the magnet, but only for extreme angle rays in the vertical: all rays that would pass through the clear 53-mm gap within the vacuum box were essentially unaffected. In the horizontal plane, extreme angle rays encounter distorted fringe fields (weaker than the design values) due to the increased gap, leading to a slight underbending and consequent off-axis displacement, and also to a shorter focal length. Again, for beam divergences corresponding to a circular beam that fills the vacuum box in the vertical (±35 mrad) the calculated effects are very small.

The new magnet poles were fabricated by New England Technicoil (www.technicoil.com) and the new taller vacuum box by NorCal Products, Inc (www.n-c.com). The increased magnet currents required for the larger gap were within the design specifications for the original Danfysik magnet coils and power supply and no other changes were required. The magnet redesign and the extra flexibility provided by the second lens have allowed us to maintain 2–3‰ precision and accuracy in measurements on near-modern samples, while running the ion source routinely at currents of up to 225 μA of $^{12}C^{-}$, –40 to 50 μA higher than previously. We have attempted to estimate the size of the output beam spot by running the full-intensity $^{12}C^{-}$ beam for an extended period on to an internal flange in the beamline, a few cm off-axis and a few cm upstream from the calculated beam waist position. If the outer edge of the visible spot burned into the flange is close the actual edge of the beam, the beam diameter was just 2.5 mm, indicating that any beam aberrations introduced by transport through the redesigned magnet are remarkably small.

Other recent improvements included changes to the accelerator charging system and to the NEC current integrators that measure the stable isotope currents. The rims of the drive pulley and high-voltage terminal pulley in the charging system were replaced with new conductive plastic versions, leading to improved voltage stability, a reduction in the amount of dust generated by arcing and erosion of the pulleys, and a 30% increase in charging currents. The current integrators were checked and recalibrated using a current source (Keithley 220A), which was itself recalibrated using precision resistors and a 5 1/2 digit voltmeter. The resulting improved linearity over the lowest 10% of the ^{12}C and ^{13}C current ranges allows us to measure samples as small as a few micrograms using the same current ranges as full-sized samples. Since very small samples can now be accurately normalized to full-sized standards, fewer small standards are required (Santos et al. 2010) and correspondingly more ultra-small unknowns can be accommodated in a 40-sample wheel.

SYSTEM AGING

As the AMS system nears 7 yr of service, some age-related issues have arisen. In the accelerator, the linear bearings in the steel motor slides have been oxidized due to acidity from SF_6 breakdown products and deformed due to the weight of the motor and the ballast weights that keep tension on the Pelletron chain. In order to keep the slides moving freely, they were lubricated, polished clean, and rotated 180° to the unwarped side. In the past 2 yr, both the terminal georator and generating voltmeter bearings have worn out and needed to be replaced. The pressure seals on the majority of the feedthroughs into the accelerator tank relaxed over time, creating small SF_6 leaks that necessitated retightening.

In the injection magnet, the Fe^- beam from the ion source sputtered the stainless steel vacuum housing, producing magnetic flakes that partially blocked beam transmission. These flakes had to be periodically removed and the Fe^- beam ultimately perforated the vacuum box wall. The leak was welded shut and a removable tantalum shield was inserted to protect the chamber. Although the shield itself is sputtered, the non-magnetic flakes formed do not interfere with beam transmission.

Corrosion in the water-cooling systems for the magnets, power supplies, and tank has caused several minor leaks and required valve and fitting replacement. Photo-oxidation of pneumatic air lines caused the plastic lines to become brittle and fail. This in turn triggered the random insertion of gate valves mid run, requiring the replacement of all plastic air lines.

SAMPLE PREPARATION LABORATORY IMPROVEMENTS

Several improvements have been made to the KCCAMS prep lab to improve efficiency and throughput while maintaining precision of 2–3‰ for samples. A third 12-headed graphitization line was constructed, increasing the number of graphite reactors from 24 to 36. This higher capacity increases the number of samples that may easily be run in a day from 48 to 72, reducing scheduling conflicts.

A customized LabView program was recently implemented to allow real-time monitoring of reaction progress of pressure transducers already connected to each individual graphitization reactor. Live pressure monitoring allows a quick determination of reaction completion, reducing likelihood of fractionation due to methane production (Bottinga 1969) and enabling faster turnaround time for the graphite line.

The KCCAMS prep lab uses a modified hydrogen-reduction method of graphitization onto a Fe catalyst (Santos et al. 2004). Previous tests have shown that the Alfa Aesar mesh –325 lots #J02M27 and #L16P22 is the optimal Fe catalyst for our graphitization procedure (Santos et al. 2007b). In an attempt to reduce its modern carbon blank, the Fe catalyst was baked at 300 °C for 3 hr in air. Post oxidation, the Fe was preconditioned normally (baked in the graphite reactor at 400 °C under an excess of H_2). Aliquots of gas derived from radiocarbon-dead anthracitic coal were then graphitized on both the oxidized/H_2 preconditioned and H_2 only preconditioned Fe (Figure 1). Results show an average of ~0.3 μg per 5 mg Fe of modern carbon is removed by baking the Fe prior to precondition with H_2. This is most likely due to particulate matter removal or oxidation of surface carbon rather than removal of carbon from bulk Fe grains. Currently, the Fe catalyst is baked in air at 300 °C for 3 hr once a month.

For hydrolysis of carbonate samples, we use 3-mL blood vials (Becton-Dickinson) (Santos et al. 2004). Carbonate is placed inside a blood vial, which is then sealed and evacuated via a hypodermic needle. Some 0.8 mL of 85% phosphoric acid is injected through the vial septum and the vial is

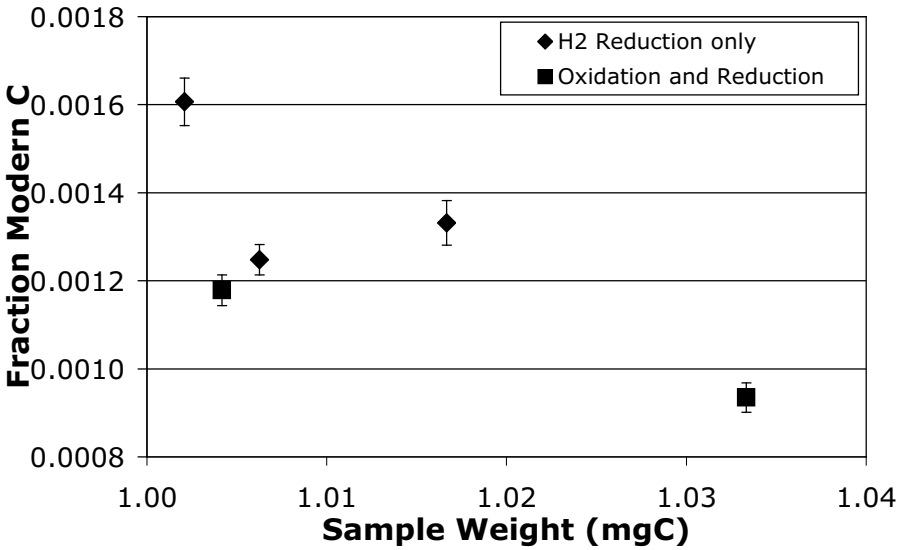

Figure 1 Background measurements of Fe catalyst preconditioned by H_2 reduction, and catalyst oxidized at 300 °C in air followed by preconditioning by H_2 reduction.

placed on a heat block to increase reaction speed. In 2005, the design of the Vacutainers was changed, and the new, redesigned septum was not suitable for this procedure. Kendall Monoject vials were purchased and tested as an alternative, but although the septa on these blood vials appear almost identical to the original Vacutainer design, they were prone to gas leaks around the needle. We only use glass 3-mL Vacutainer® blood manufactured prior to the design change.

An area of concern for ours and other labs (Goslar et al. 2004) is the degradation of graphite quality over time and how this degradation affects measured ^{14}C values. Figure 2 displays fraction modern C versus storage time between graphitization and measurement of all full-size (≥0.7 mg C) OX-I runs over the last 3 yr. Similar to Goslar et al. (2004), a general trend toward more depleted measurements is observed as storage time increases. This trend is not systematically observed in every data point; the 2 samples stored the longest show agreement with the consensus OX-I value. In an attempt to characterize the cause of depletion, systematic tests were performed on OX-I standards stored differently over a period of 3 months. OX-Is were graphitized normally and either pressed and run quickly, stored unpressed with a rubber cap ($^{14}C/C = 0.92 \times$ Modern) in a Lucite cabinet with an NaOH reservoir to reduce ambient CO_2 concentrations (wet cabinet), pressed and stored in the wet cabinet, or capped unpressed with Al foil and stored in air. After ~4 months from the time the first set were run, all storage samples were measured on the AMS using recently graphitized OX-I as normalizing standards. Figure 3 displays the results; error bars have been omitted for clarity and are all <2.5‰. All aliquots of the OX-I graphitized and measured within 2 weeks cluster around the consensus value of 1.040. As storage time increases, samples stored in the wet cabinet show a variable depletion relative to the aliquot of the same sample measured immediately, whereas samples exposed to air (Al cap) remain relatively unchanged. As any mass-dependant fractionation caused by back reaction of stored graphite to (for instance) CO_2 should be corrected by the online AMS $\delta^{13}C$ measurement, it seems that the graphite stored in the wet cabinet is slowly adsorbing depleted carbon outgassed from either the rubber cap, Lucite wet cabinet, or plastic storage trays. Normalizing standards and unknowns that are graphitized and stored together should degrade in the same fashion over time, and therefore, should have no overall effect on measurement. Because we do not

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routinely graphitize our primary standard with our unknowns, we always avoid measurement of samples stored for over a month.

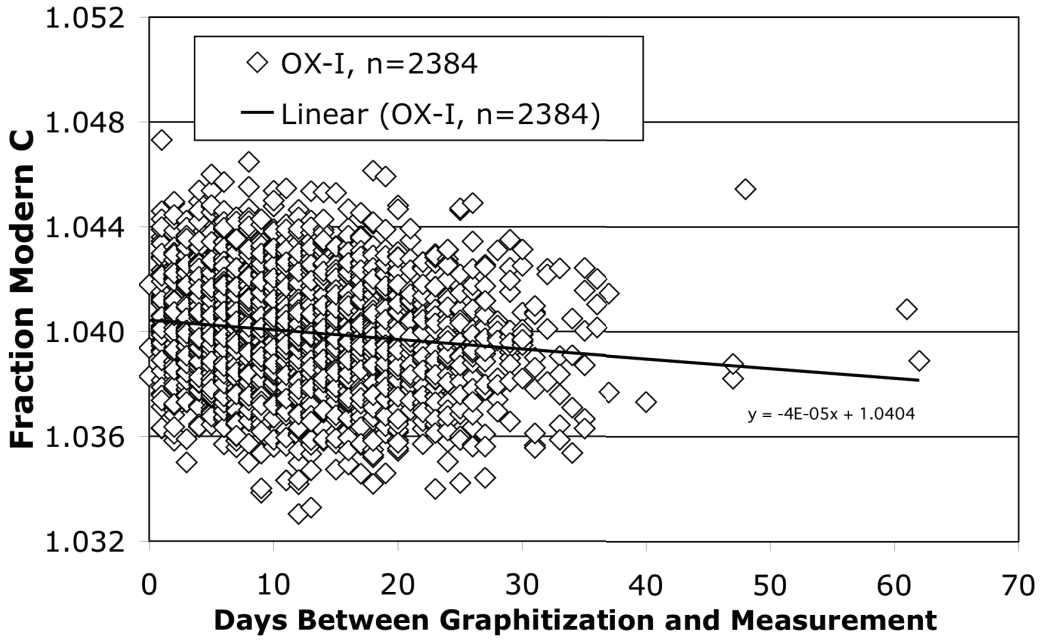

Figure 2 Fraction modern C (Stuiver and Polach 1977) of OX-I standards illustrating the slight downward trend with storage time. Six OX-Is are run with every wheel and each run on an OX-I is normalized to a running mean of the remaining 5.

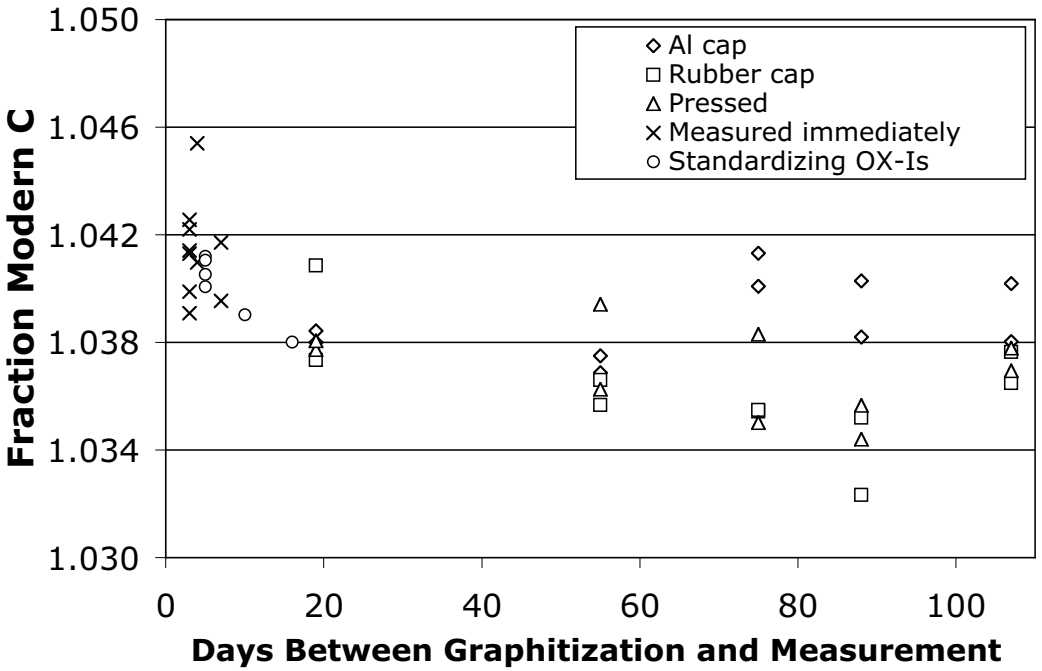

Figure 3 Measured fraction modern C of OX-I standards stored. Samples stored near plastic show depletion with time.

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After switching from the NEC-designed sample holders to our front-loading holders, we pressed samples manually by hammering, but we have recently switched back to using a press. The use of a press fitted with a pressure gauge allows for more consistent pressing between different users and reduces jamming and breaking of pressing pins. Importantly, the pressing pin is part of the sample loading jig, not integral with the press itself. Detaching the pin from the press body enables faster and better cleaning of the pin, and improves the alignment of the pin and sample holder. Overall precision of 2–3‰ has not changed since the pressing method has been modified.

QUALITY ASSURANCE/QUALITY CONTROL

Figures 4–6 show data from primary, the most common secondary standards, and blanks that are run with each set of samples analyzed (Santos et al. 2007c). The secondary standards and blanks are chosen to match the unknown sample type and expected age, and undergo the same chemical steps as unknowns. Monitoring of standards and blanks allows graphite production issues to be resolved immediately. In addition, long-term trends permit analysis of accuracy and precision. All ratios in the figures are corrected by the online AMS $\delta^{13}C$ and normalized to the known value of the primary standards for each individual run, and all ratios except blanks are background-corrected (Santos et al. 2010). Although standards that require more handling or are older in general show more variation, the 1-σ scatter for near-modern standards is between 2 and 3‰.

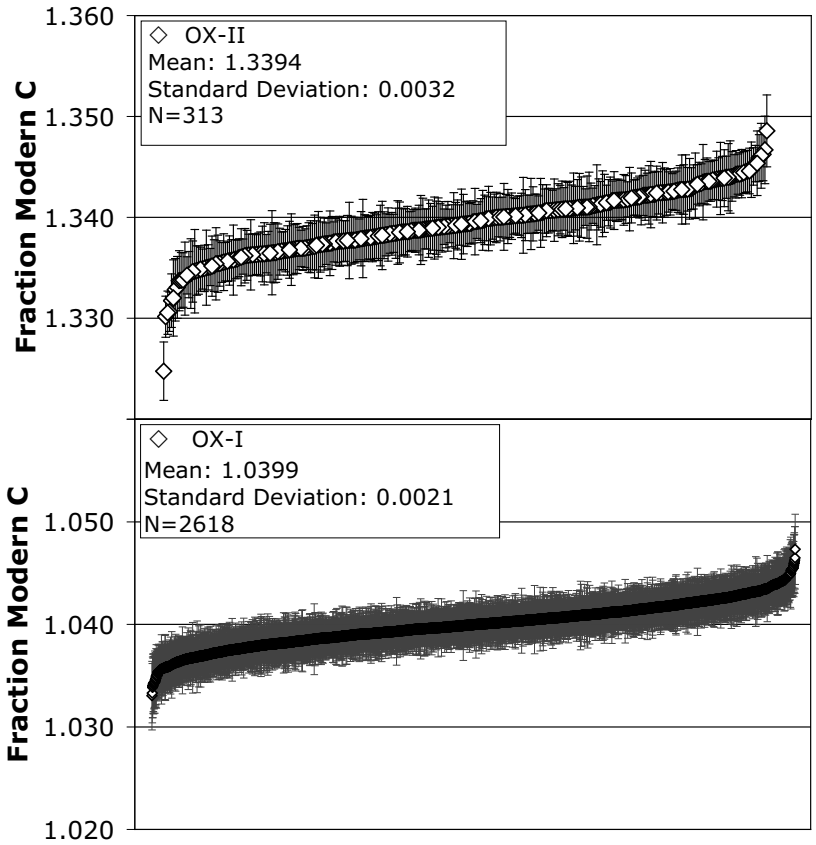

Figure 4 Distribution of Fm values for full-sized (≥0.7 mg C) OX-II (a) and OX-I (b) standards in the past 3 yr. Data normalized to given OX-II and OX-I values, respectively. Error bars are 1 σ.

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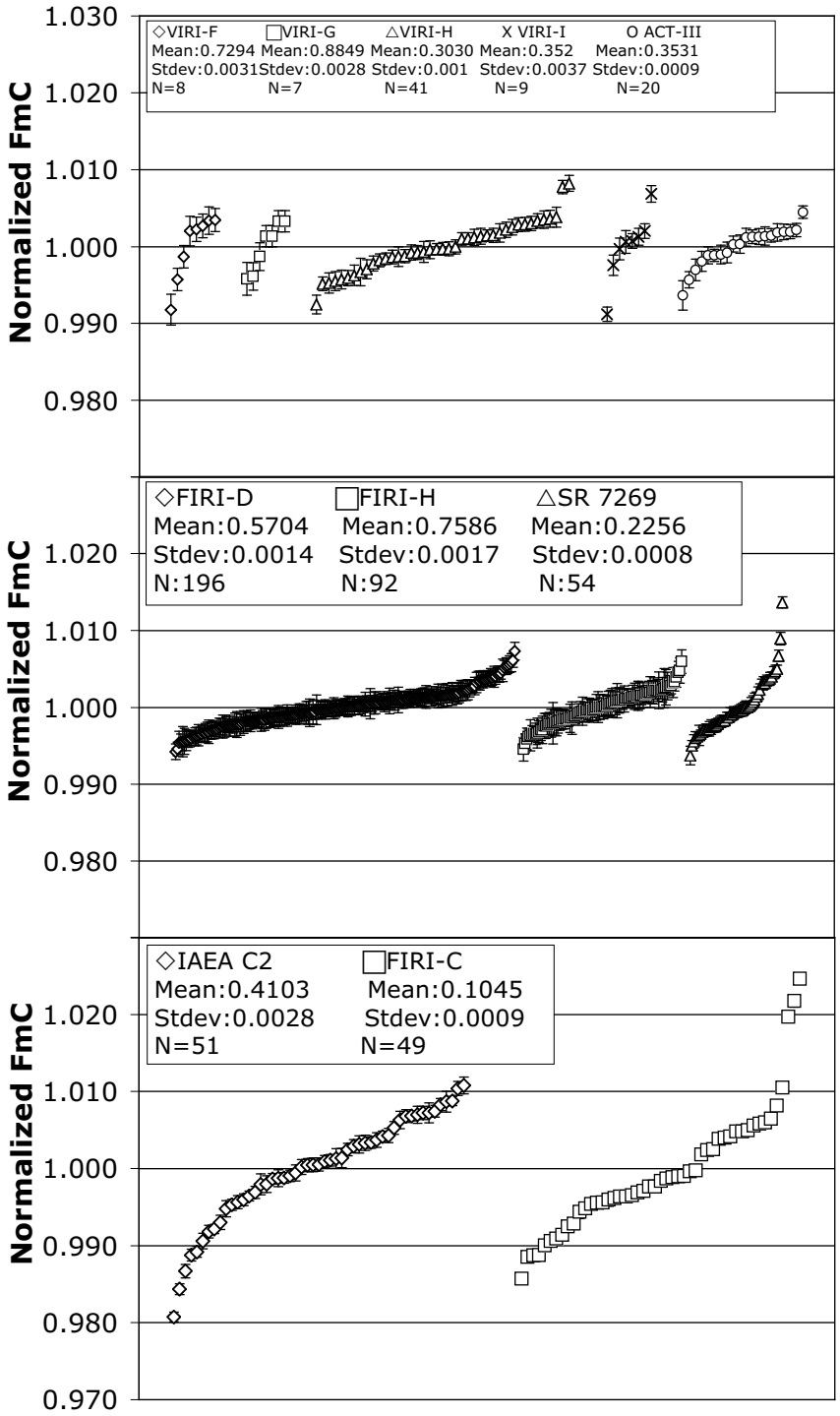

Figure 5 Distribution of Fm values for large (≥0.7 mg C) bone (a), organic (b), and carbonate (c) secondary standards over the past 3 yr. Data have been normalized to 1 by division with the internal laboratory mean value. Error bars are 1 σ.

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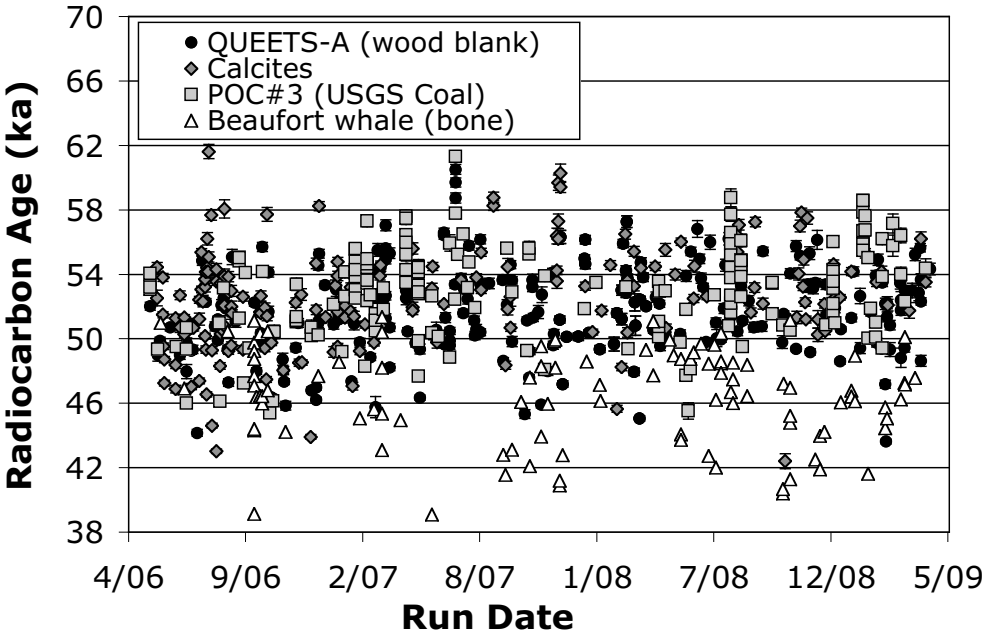

Figure 6 Background measurements of ^{14}C-free full-sized (≥0.7 mg C) ABA-treated wood and USGS coal POC#3, HCl-leached calcite, and ultrafiltered bone.

CONCLUSIONS

The AMS spectrometer at UCI has been operating since 2002 and has run over 70,000 samples. Over the past 3 yr, several improvements have been made to the AMS system to improve system operation and to deal with age-related wear and tear. Sample preparation methods have been upgraded to increase sample throughput. It is important to note that recent method improvements and machine upgrades to increase sample throughput have not changed the overall measured precisions and accuracies.

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