

## MAGNESIUM PERCHLORATE AS AN ALTERNATIVE WATER TRAP IN AMS GRAPHITE SAMPLE PREPARATION: A REPORT ON SAMPLE PREPARATION AT KCCAMS AT THE UNIVERSITY OF CALIFORNIA, IRVINE

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**ABSTRACT.** We present a brief discussion of sample preparation procedures at the Keck Carbon Cycle Accelerator Mass Spectrometer (KCCAMS), University of California, Irvine, and a systematic investigation of the use of  $\text{Mg}(\text{ClO}_4)_2$  as an absorptive water trap, replacing the standard dry ice/ethanol cold finger in graphite sample preparation. We compare high-precision AMS measurement results from oxalic acid I and USGS coal samples using  $\text{Mg}(\text{ClO}_4)_2$  under different conditions. The results obtained were also compared with those achieved using the conventional water removal technique. Final results demonstrate that the use of  $\text{Mg}(\text{ClO}_4)_2$  as an alternative water trap seems very convenient and reliable, provided the  $\text{Mg}(\text{ClO}_4)_2$  is replaced frequently.

### THE KCCAMS PREP LABORATORY

A new sample processing laboratory was constructed and installed at the Keck Carbon Cycle Accelerator Mass Spectrometer (KCCAMS) facility in late 2002 to expand existing University of California, Irvine (UCI) radiocarbon sample handling capabilities. The KCCAMS prep laboratory has provided approximately 1500 unknown samples and quality control standards during the first 10 months of operation.

The prep laboratory is equipped for routine chemical sample cleaning and preparation of organic samples and carbonates. It also contains a sample-combustion system, 2 graphitization lines, and an accelerator target pressing station. The combustion line has 10 pump-out heads, while each graphitization line has 12  $\text{H}_2/\text{Fe}$  reactors (Figure 1a, b), allowing us to graphitize 48 organic or carbonate samples per day. The vacuum lines are made of glass and stainless steel and are pumped by turbo-molecular pumps backed by oil-free diaphragm pumps. Water is removed during graphitization either by using magnesium perchlorate— $\text{Mg}(\text{ClO}_4)_2$ —in the graphite-reactor, or by cold fingers attached to stainless steel thermoses converted to dry ice/alcohol dewars. The progress of the reaction is monitored using pressure transducers (Figure 1b). The design was based on sample graphitization lines from CAMS/Lawrence Livermore National Laboratory (LLNL).

### SAMPLE PREPARATION PROCEDURES

Submitted samples from carbonaceous raw materials are chemically and/or physically pretreated, when necessary, to remove any unwanted material before conversion to carbon dioxide by combustion or acid hydrolysis. Organic samples are pretreated initially by removal of any visually obvious contamination, followed by a standard acid-alkaline-acid treatment. Carbonate samples are leached in dilute HCl. Sample are then rinsed twice with MilliQ water and dried on a heating block at 80 °C.

Carbon dioxide is produced from pre-leached carbonates by acid hydrolysis using 85% phosphoric acid in disposable septum-sealed reactors (Vacutainer blood collection vials, 3 ml) (Figure 2a, b). Carbonates are weighed into the Vacutainers and evacuated using a 1.3-cm-long #26 hypodermic Luer-tip needle adapted to an Ultra-torr fitting in the graphitization line (Figure 2b). Once the Vacu-

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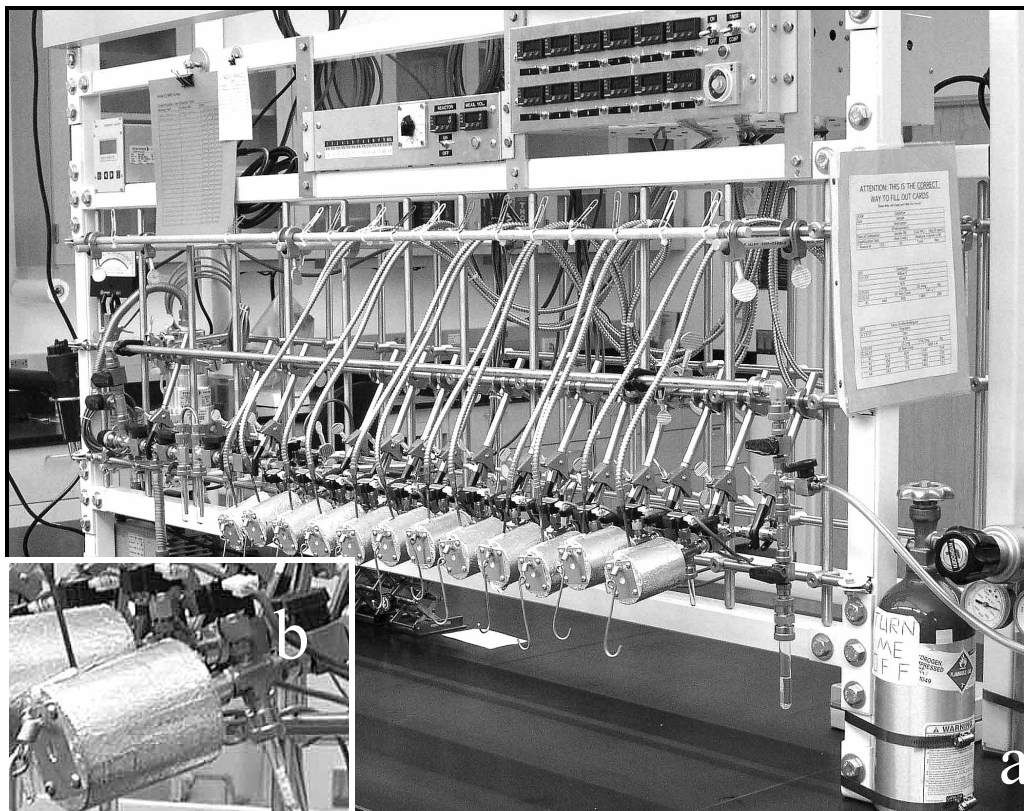


Figure 1 a) Graphitization line for target preparation showing H<sub>2</sub>/Fe reduction reactors. Each 12-head graphitization line can produce 24 samples per day. The design is based on graphitization lines from the CAMS/LLNL laboratory. b) Reduction reactor detail showing Mg(ClO<sub>4</sub>)<sub>2</sub> in the graphite-reactor.

tainers are evacuated, we detach the vial from the line and use a gas-tight Luer-lock syringe with a #26 needle to introduce 1 cc of 85% phosphoric acid (Figure 2a). The Vacutainer reactors are then placed on heating-blocks at 80 °C for at least 20 min. When the reaction ceases, they are returned to the graphitization line to extract the CO<sub>2</sub> via the needle fitting. To ensure complete evacuation of the needle fitting prior to CO<sub>2</sub> extraction, the needle is initially inserted halfway through the Vacutainer septum. The CO<sub>2</sub> is cryogenically purified and reduced to graphite in pyrex 6 × 50 mm culture tubes (Loyd et al. 1991), using hydrogen at 650 °C for 3–4 hr over pre-baked iron. Since the Vacutainer vials are disposable, cleaning and waste handling after sample preparation are minimized.

The carbon dioxide production of organic samples is performed by combustion at 900 °C in evacuated sealed quartz tubes in the presence of CuO and silver wire. After CO<sub>2</sub> extraction and purification, CO<sub>2</sub> is then reduced to graphite as described above.

Samples prepared on these lines have demonstrated 56 ka and 54 ka BP backgrounds for organic and carbonate materials, respectively, for samples containing 1 mg of carbon (Southon et al., these proceedings).

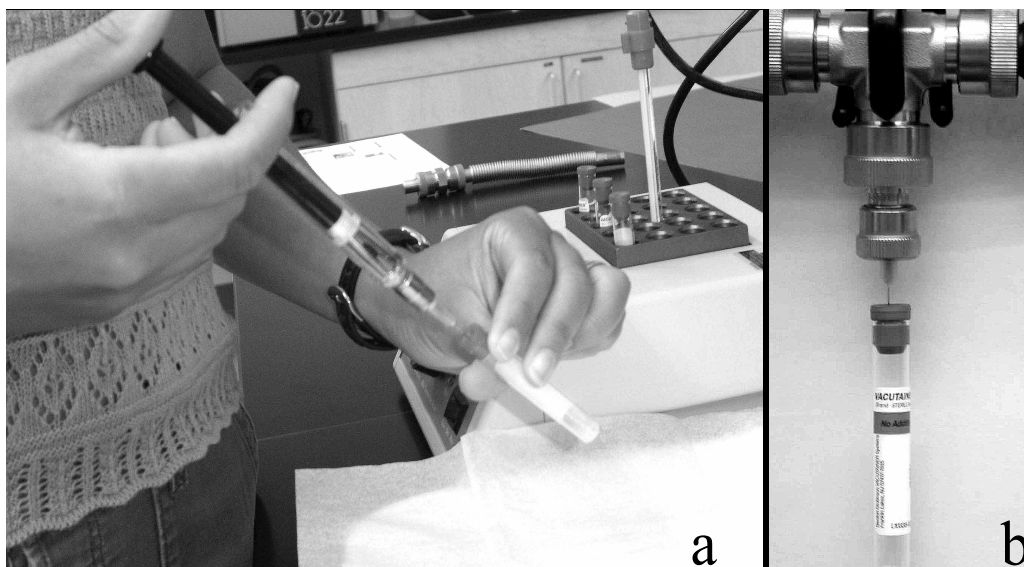


Figure 2 Acid hydrolysis procedure for carbonate sample. (a) 1cc of 85% phosphoric acid being introduced into septum-sealed reactors (Vacutainer vials). (b) Detail of Vacutainer attached to the graphitization line for evacuation. The base of a #26 hypodermic needle is placed in an Ultra-torr fitting, between the Ultra-torr ferrule and the sealing o-ring.

### Use of Magnesium Perchlorate for Water Removal

Magnesium perchlorate is a well-known hygroscopic substance that has been used worldwide in the desiccant columns of stable isotope mass spectrometers. For more than 10 yr,  $Mg(ClO_4)_2$  has been used to trap water during hydrogen reduction for graphite sample preparation at the UCI labs (S Zheng, personal communication).

At that time, UCI graphite was being measured at the LLNL AMS facility, where precision was initially 0.6% (J Southon, personal communication). These first investigations of the use of the substance in the graphitization process demonstrated its suitability, and 3 main advantages were immediately apparent: a) it is a very easy material to handle, allowing the user to replace it easily in the graphite-reactor in a very short period of time; b) it removes the need to prepare dry ice/ethanol slushes for each individual graphite-reactor, which can be time consuming; and c) the  $Mg(ClO_4)_2$  water-trap could be re-used many times (also providing more time saving) without compromising the final measurement precision, as was demonstrated by multiple measurements of standards (S Trumbore, personal communication).

In 2002, UCI installed a compact AMS from the National Electrostatics Corporation (0.5MV 1.5SDH-1 AMS system). AMS  $^{14}C$  precision for measurements performed with this system is currently between 0.2 to 0.5%, based on multiple measurements of oxalic acid-I (OX-I) for hydrogen reduced graphite using Fe or Co catalyst (Southon et al., these proceedings). Accuracy is being evaluated on measurement results of secondary standards, such as oxalic acid-II (OX-II) and ANU sucrose (ANU), where 4‰ fluctuations can be observed.

Since  $^{14}C$  measurement precision has varied and some of the variation may be due to isotopic fractionation during sample preparation, we decided to perform a systematic comparison of the use of cryogenic mixtures or absorption in  $Mg(ClO_4)_2$  to remove water during the graphitization reaction. Unusual variations on background samples beyond 50 ka also indicated a possible memory

or contamination effect from the  $\text{Mg}(\text{ClO}_4)_2$  (or water trapped in the perchlorate), which was typically being used for 10 to 15 graphitizations before replacement based on absorptive saturation of the substance.

## EXPERIMENT AND RESULTS

In the first experiment, 4 independently combusted samples of USGS coal and 4 of oxalic acid I (OX-I) were generated, each with enough material to be split into 3 aliquots. The  $\text{CO}_2$  from each sample was purified and shared equally among 3 graphite-reactors operated under different conditions, generating the graphite-aliquots 981.1, 981.2, and 981.3, for example. We compare the effects of saturated and unsaturated  $\text{Mg}(\text{ClO}_4)_2$ , and pumping on the graphite-reactors for different periods of time before use (6 times previously used perchlorate and 90 min pumping time—group 1; 6 times previously used and 10 min pumping time—group 2; and wet perchlorate and 10 min pumping time—group 3). A set of 12 OX-I samples and 12 coal samples were graphitized and measured by AMS.

In the second experiment, 3 independently combusted samples of USGS coal and 3 samples of OX-I were generated, each with enough material to be split into 4 aliquots. The  $\text{CO}_2$  from each sample was purified and shared equally among 4 graphite-reactors. In this case, we compared the use of cryogenic mixtures (group A), fresh perchlorate (group B), and previously used dry (group C) and wet (group D) perchlorate, for water removal. A set of 12 OX-I samples and 12 coal samples were graphitized and measured by AMS.

In the third experiment, we repeat the same conditions applied to the second experiment (Table 1) for the OX-I samples, but using  $\text{Mg}(\text{ClO}_4)_2$  that had been previously used 8 times. We also pumped the graphite-reactor (i.e. on the perchlorate) for a longer period of time (60 min). A set of 12 OX-I samples were graphitized and measured by AMS.

Table 1 Summary of the water removal conditions in the graphitization reactor for the 3 experiments.

<p><b>First</b>  group 1—<math>\text{Mg}(\text{ClO}_4)_2</math> used 6 times previously; reactor was pumped for 90 min  group 2—<math>\text{Mg}(\text{ClO}_4)_2</math> used 6 times previously; reactor was pumped for 10 min  group 3—<math>\text{Mg}(\text{ClO}_4)_2</math> used 6 times previously and exposed to MQ water vapor; reactor was pumped for 10 min</p> <p><b>Second</b>  group A—Dry ice and ethyl alcohol cold finger; reactor was pumped for 20 min  group B—Fresh <math>\text{Mg}(\text{ClO}_4)_2</math>; reactor was pumped for 20 min  group C—<math>\text{Mg}(\text{ClO}_4)_2</math> used 2 times previously; reactor was pumped for 20 min  group D—<math>\text{Mg}(\text{ClO}_4)_2</math> used 2 times previously and exposed to MQ water vapor; reactor was pumped for 20 min</p> <p><b>Third</b>  group I—Dry ice and ethyl alcohol cold finger; reactor was pumped for 60 min  group II—Fresh <math>\text{Mg}(\text{ClO}_4)_2</math>; reactor was pumped for 60 min  group III—<math>\text{Mg}(\text{ClO}_4)_2</math> used 8 times previously; reactor was pumped for 60 min  group IV—<math>\text{Mg}(\text{ClO}_4)_2</math> used 8 times previously and exposed to MQ water vapor; reactor was pumped for 60 min</p>
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Water removal and pumping conditions from the graphite-reactors from the 3 experiments were designated as groups, and they are summarized on Table 1. AMS results from the 3 experiments are present in Tables 2, 3, and 4, respectively. All results were normalized to an independent set of OX-I samples prepared using fresh perchlorate.

## DISCUSSION

From the first experiment (Table 2), we noticed that all of the  $\Delta^{14}\text{C}$  data from the OX-I “unknown” samples were lower than those of the normalizing standards prepared with fresh perchlorate ( $\Delta^{14}\text{C} = 33.2 \pm 2.2\text{‰}$ ). The difference could not be explained. It was clearly not a fractionation effect since the Fraction Modern and  $\Delta^{14}\text{C}$  values in Table 2 have already been corrected for any graphitization or machine-induced isotopic fractionation (Pearson et al. 1998), using the on-line  $\delta^{13}\text{C}$  values. The differences were too large to be accounted for by memory from the 6 samples (all close to Modern) run previously in each reactor.

In the second and third experiment, there were no significant differences between the AMS  $^{14}\text{C}$  results for OX-I samples prepared using different water removal treatments and the normalizing standards prepared with fresh Mg(ClO<sub>4</sub>)<sub>2</sub> (Tables 3 and 4; Figure 3). At the level of precision of these tests, 3.8 and 3.3‰, respectively, twice or 8 times previously used Mg(ClO<sub>4</sub>)<sub>2</sub> appears to have no effect on  $\Delta^{14}\text{C}$ . However, a larger spread in the results can be noticed when Mg(ClO<sub>4</sub>)<sub>2</sub> was completely wet.

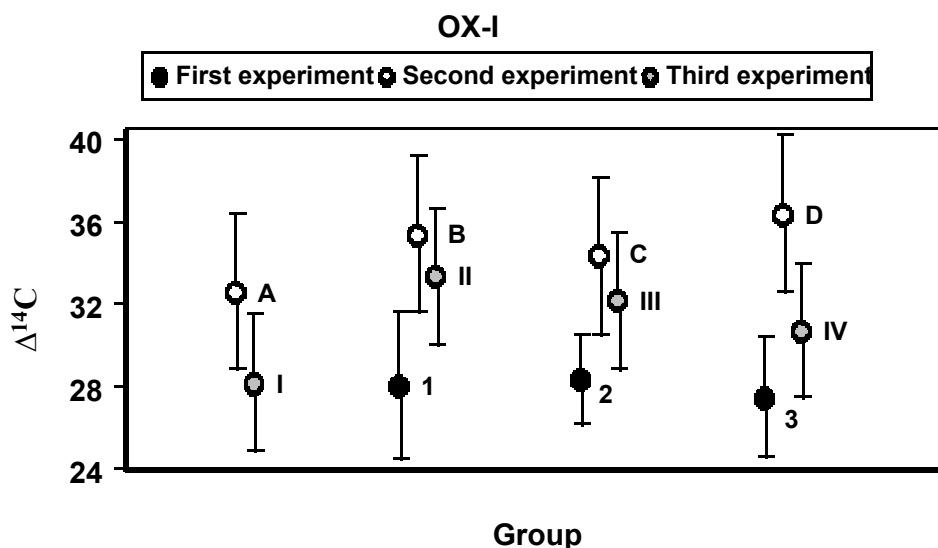


Figure 3  $\Delta^{14}\text{C}$  average and uncertainties of OX-I samples from the 3 experiments. Errors plotted represent the  $1\sigma$  scatter in the results from each group, or the statistical precision, whichever is greater. Groups of samples are shifted to better show the error bars.

In Table 3, we also compare AMS  $\delta^{13}\text{C}$  measurements with  $\delta^{13}\text{C}$  obtained on an Elemental Analyzer (EA) coupled with an IRMS from graphite produced in the second experiment. The EA  $\delta^{13}\text{C}$  results from aliquots of the graphite produced showed that there was no isotopic fractionation during graphitization (Table 3). However, machine-induced isotopic fractionation effects are clear on this second experiment.

For the background samples (USGS coals), the experiments seem more conclusive. We believe that the CO<sub>2</sub> samples have been contaminated by modern CO<sub>2</sub> trapped in water in the perchlorate (or in the perchlorate itself) since the 4 different CO<sub>2</sub> samples all show backgrounds improving as Mg(ClO<sub>4</sub>)<sub>2</sub> wetness decreases and/or longer pumping time was applied (Figure 4). Note that none of these USGS coal samples are as good as the  $54.3 \pm 0.6$  ka (background processed graphite) obtained with fresh perchlorate in the first experiment, for reasons which are unexplained.

Table 2 Results of OX-I and coal samples considered as unknowns. These results were normalized to an independent set of 8 OX-I samples prepared using fresh perchlorate. Measurement precision was 2.2‰ on the 8 OX-I samples and 2.2–4.0‰ on OX-II and ANU secondary standards. AMS system background on synthetic graphite was  $59.2 \pm 0.5$  ka. The graphitization line background obtained on USGS coals prepared with fresh perchlorate was  $54.3 \pm 0.6$  ka. Coal samples were not background corrected. AMS  $^{13}\text{C}$  was measured on-line using offset Faraday cups after the HE analyzing magnet of the spectrometer.

OX-I samples									
UCI AMS#	Sample (lab nr)	AMS $\delta^{13}\text{C}$	Ext. err.	Fraction modern	$\pm$	$\Delta^{14}\text{C}$	$\pm$	Average	STDEV
<b>Group 1</b>									
3479	UCIG_981.1	-17.1	0.4	1.0312	0.0019	24.6	1.9	28.1	3.6
3480	UCIG_982.1	-15.9	0.2	1.0319	0.0020	25.3	2.0		
3481	UCIG_983.1	-16.2	0.3	1.0380	0.0024	31.4	2.4		
3482	UCIG_984.1	-16.0	0.3	1.0375	0.0019	30.9	1.9		
<b>Group 2</b>									
3484	UCIG_981.2	-16.7	0.2	1.0343	0.0022	27.7	2.2	28.3	1.4
3485	UCIG_982.2	-19.5	0.5	1.0367	0.0020	30.1	2.0		
3486	UCIG_983.2	-16.7	0.2	1.0353	0.0022	28.7	2.2		
3487	UCIG_984.2	-18.6	0.4	1.0335	0.0020	26.9	2.0		
<b>Group 3</b>									
3489	UCIG_981.3	-18.3	0.2	1.0343	0.0025	27.7	2.5	27.5	2.9
3490	UCIG_982.3	-18.3	0.3	1.0376	0.0020	30.9	2.0		
3491	UCIG_983.3	-18.2	0.3	1.0306	0.0020	24.0	2.0		
3492	UCIG_984.3	-18.4	0.3	1.0339	0.0019	27.3	1.9		
USGS coal samples									
UCI AMS#	Sample (lab nr)	AMS $\delta^{13}\text{C}$	Ext. err.	Fraction modern	$\pm$	Age	$\pm$	Average	STDEV
<b>Group 1</b>									
3494	UCIG_855.1	-24.0	0.3	0.0013	0.0001	53,360	410	52,010	1905
3495	UCIG_856.1	-23.2	0.3	0.0015	0.0001	52,280	310		
3496	UCIG_857.1	-22.7	0.1	0.0022	0.0001	49,240	230		
3497	UCIG_858.1	-24.4	0.3	0.0013	0.0001	53,160	460		
<b>Group 2</b>									
3499	UCIG_855.2	-23.0	0.3	0.0015	0.0001	52,340	290	50,893	1512
3500	UCIG_856.2	-23.3	0.3	0.0017	0.0001	51,100	330		
3501	UCIG_857.2	-23.6	0.2	0.0023	0.0001	48,770	250		
3502	UCIG_858.2	-23.8	0.3	0.0017	0.0001	51,360	250		
<b>Group 3</b>									
3504	UCIG_855.3	-24.2	0.3	0.0030	0.0002	46,640	410	48,273	1969
3505	UCIG_856.3	-24.1	0.3	0.0027	0.0001	47,420	310		
3506	UCIG_857.3	-24.0	0.6	0.0026	0.0002	47,910	580		
3507	UCIG_858.3	-22.7	0.2	0.0017	0.0001	51,120	500		

Table 3 Results of OX-I and coal samples considered as unknowns. These results were normalized to an independent set of 9 OX-I samples prepared using fresh perchlorate. Measurement precision was 3.8‰ on the OX-I's and 5.0‰ on OX-II secondary standards. The graphitization line background obtained on USGS coals prepared with fresh perchlorate was 52.1 ± 0.6 ka. Coal samples were not background corrected. EA/IRMS <sup>13</sup>C's are measured on graphite aliquots using a Fisons NC 1500 Elemental Analyzer coupled to a Finnigan Delta Plus stable isotope ratio mass spectrometer. AMS <sup>13</sup>C's are measured on-line using offset Faraday cups after the HE analyzing magnet of the spectrometer.

OX-I samples											
UCI AMS#	Sample (lab nr)	EA-IRMS $\delta^{13}\text{C}$	AMS $\delta^{13}\text{C}$	Ext. err.	Fraction modern	Age	$\pm$	$\Delta^{14}\text{C}$	$\pm$	Average	STDEV
<b>Group A</b>											
3777	UCIG_1136.1	-19.1	-21.7	2.4	1.0378	0.0046	31.1	4.6	32.6	2.0	
3779	UCIG_1138.1	-19.5	-19.0	2.2	1.0415	0.0033	34.8	3.3			
<b>Group B</b>											
3781	UCIG_1136.2	-19.9	-25.3	3.7	1.0445	0.0055	37.8	5.5	35.4	2.4	
3782	UCIG_1137.2	-19.3	-18.9	1.8	1.0397	0.0042	33.1	4.2			
3783	UCIG_1138.2	-19.8	-19.8	0.9	1.0419	0.0025	35.3	2.5			
<b>Group C</b>											
3785	UCIG_1136.3	-20.5	-19.7	1.1	1.0405	0.0026	33.8	2.6	34.3	0.8	
3786	UCIG_1137.3	-19.8	-19.7	0.7	1.0419	0.0024	35.2	2.4			
3787	UCIG_1138.3	-18.8	-20.8	0.7	1.0406	0.0030	34.0	3.0			
<b>Group D</b>											
3789	UCIG_1136.4	-19.6	-20.9	1.8	1.0409	0.0030	34.3	3.0	36.4	2.9	
3790	UCIG_1137.4	-20.1	-21.0	1.8	1.0417	0.0033	35.1	3.3			
3791	UCIG_1138.4	-19.6	-23.3	1.4	1.0464	0.0027	39.7	2.7			
USGS coal samples											
UCI AMS#	Sample (lab nr)	AMS $\delta^{13}\text{C}$	Ext. Err.	Fraction modern	Age	$\pm$	Average	STDEV			
<b>Group A</b>											
3793	UCIG_1157.1	-31.9	1.7	0.0019	0.0001	50,210	390	50,367	630		
3795	UCIG_1159.1	-26.2	1.6	0.0020	0.0001	49,830	360				
<b>Group B</b>											
3796	UCIG_1157.2	-28.3	1.2	0.0019	0.0001	50,270	280	50,457	180		
3797	UCIG_1158.2	-28.3	2.7	0.0019	0.0001	50,470	320				
3798	UCIG_1159.2	-25.0	1.3	0.0018	0.0001	50,630	290				
<b>Group C</b>											
3799	UCIG_1157.3	-27.0	2.2	0.0020	0.0001	50,020	400	49,827	729		
3800	UCIG_1158.3	-27.0	2.0	0.0019	0.0001	50,440	480				
3801	UCIG_1159.3	-26.3	1.9	0.0022	0.0001	49,020	210				
<b>Group D</b>											
3802	UCIG_1157.4	-25.9	3.3	0.0029	0.0001	46,840	280	46,850	1535		
3803	UCIG_1158.4	-27.0	2.3	0.0024	0.0001	48,390	300				
3804	UCIG_1159.4	-24.4	1.4	0.0035	0.0001	45,320	190				

Table 4 Results of OX-I samples considered as unknowns. These results were normalized to an independent set of 7 OX-I samples prepared using fresh perchlorate. Measurement precision was 3.3‰ on the OX-I samples and ANU secondary standards. The graphitization line background obtained on USGS coals prepared with fresh perchlorate was  $49.8 \pm 1.4$  ka. Coal samples were not background corrected.

OX-I samples									
UCI AMS#	Sample (lab nr)	AMS $\delta^{13}\text{C}$	Ext. err.	Fraction modern	$\pm$	$\Delta^{14}\text{C}$	$\pm$	Average	STDEV
<b>Group 1</b>									
4329	UCIG_1483.1	-22.7	0.4	1.0338	0.0024	27.2	2.4	28.2	2.5
4330	UCIG_1484.1	-20.3	0.3	1.0329	0.0024	26.3	2.4		
4331	UCIG_1485.1	-17.9	0.4	1.0376	0.0024	31.0	2.4		
<b>Group 2</b>									
4332	UCIG_1483.2	-18.3	0.4	1.0438	0.0024	37.1	2.4	33.4	3.2
4333	UCIG_1484.2	-15.2	0.2	1.0382	0.0024	31.6	2.4		
4334	UCIG_1485.2	-18.2	0.4	1.0381	0.0028	31.4	2.8		
<b>Group 3</b>									
4337	UCIG_1483.3	-17.9	0.3	1.0385	0.0024	31.9	2.4	32.2	0.3
4338	UCIG_1484.3	-17.6	0.3	1.0389	0.0028	32.3	2.8		
4339	UCIG_1485.3	-19.2	0.4	1.0391	0.0036	32.4	3.6		
<b>Group 4</b>									
4340	UCIG_1483.4	-20.1	0.4	1.0380	0.0024	31.4	2.4	30.7	1.1
4341	UCIG_1484.4	-20.4	0.3	1.0379	0.0025	31.3	2.5		
4342	UCIG_1485.4	-18.6	0.4	1.0360	0.0034	29.4	3.4		

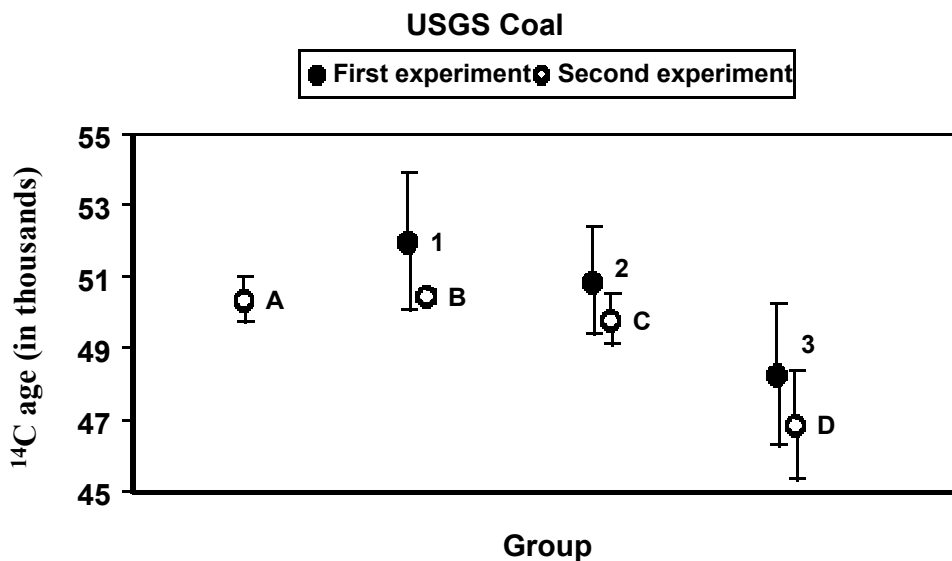


Figure 4  $^{14}\text{C}$  age averages for coal samples and respective errors from the 3 experiments. Errors plotted represent the  $1 \sigma$  scatter in the results from each group. Groups of samples are shifted to better show the error bars.



Overall, backgrounds were not as good at the time of the second experiment (e.g. compare the graphitization line backgrounds for the first and second tests cited in the table captions). Under these conditions, we saw no significant differences between results for coals graphitized using cryogenic mixtures (group A) or fresh mixtures (group B), and only minimal contamination for the twice previously used Mg(ClO<sub>4</sub>)<sub>2</sub> (group C). On the other hand, a large background increase was observed for group D, as for group 3 in the first experiment, where the Mg(ClO<sub>4</sub>)<sub>2</sub> was wet.

These experiments had induced us to use the Mg(ClO<sub>4</sub>)<sub>2</sub> during graphitization only 3 times before replacement. Overall precision has decreased over a period of several months from a range of 0.2–0.5% to 0.2–0.3%. This improvement may not be due to changing the way we use the perchlorate, but it does demonstrate that the use of perchlorate is compatible with high precision. Backgrounds also improved and are frequently as old as 53 ka.

### CONCLUSION

For <sup>14</sup>C measurements that do not require precision better than 0.3% or backgrounds better than 53 ka, the use of Mg(ClO<sub>4</sub>)<sub>2</sub> as an alternative water trap seems very convenient and reliable provided the Mg(ClO<sub>4</sub>)<sub>2</sub> is replaced frequently. Variations in Δ<sup>14</sup>C are not significant when comparing dry-fresh Mg(ClO<sub>4</sub>)<sub>2</sub> with standard dry ice/ethanol cold fingers.

For measurements requiring better precision (<0.2%) and/or backgrounds (>53 ka), the Mg(ClO<sub>4</sub>)<sub>2</sub> should be treated with some suspicion. In such cases, cryogenic mixtures or thermoelectric cooling may be preferable solutions for removing water during the graphitization reaction. As yet, we have no direct evidence to show exactly what mechanism causes the Δ<sup>14</sup>C shifts. However, it seems that the moisture content of the Mg(ClO<sub>4</sub>)<sub>2</sub> is important and we suspect that trapping of CO<sub>2</sub> in wet perchlorate plays a part.

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