

## HIGH-LEVEL $^{14}\text{C}$ CONTAMINATION AND RECOVERY AT XI'AN AMS CENTER

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**ABSTRACT.** A sample with a radiocarbon concentration estimated to be greater than  $10^5$  times Modern was inadvertently graphitized and measured in the Xi'an AMS system last year. Both the sample preparation lines and the ion source system were seriously contaminated and a series of cleaning procedures were carried out to remove the contamination from them. After repeated and careful cleaning as well as continuous flushing with dead  $\text{CO}_2$  gas, both systems have recovered from the contamination event. The machine background is back to  $2.0 \times 10^{-16}$  and the chemical blank is beyond 50 kyr.

### CONTAMINATION LEVEL

Samples that contain high concentrations of radiocarbon (“hot” samples) are a catastrophe for a low-background accelerator mass spectrometer (AMS) laboratory. The memory effect induced by contamination in the sample preparation lines and/or the ion source is very difficult to eliminate. As a national AMS platform in China, the Xi'an AMS Center receives various samples from many differing groups. Though we do our best to inform our colleagues about the dangers of “hot” sample contamination to our multi-element AMS laboratory, a water sample (XA6007) was received last summer that proved to have extremely high  $^{14}\text{C}$  content. The count rate of this “hot” sample was so high that the data acquisition system was grossly overloaded (the dead time was 100%). To make things worse, the data acquisition system unaccountably printed out a falsely low count rate of 968 cps (ratio of  $^{14}\text{C}/^{12}\text{C} = 7.5 \times 10^{-14}$ ) for this sample, while an archaeological sample (XA6008), which immediately followed this “hot” sample, had a count rate of 10 times Modern. We were finally able to determine which sample was hot by lowering the  $^{12}\text{C}$  beam current from microamperes to nanoamperes. Unfortunately, the hot sample was sputtered when in the ion source for 30 min total (this was the time required to complete its analysis). The average beam current in that analysis was  $\sim 30 \mu\text{A}$ . The data from this test yielded an estimated  $^{14}\text{C}$  concentration for the hot sample of greater than  $10^5$  times Modern! It is well known that about 20 years ago, both the LLNL (Vogel et al. 1990) and Arizona AMS laboratories (Jull et al. 1990) were exposed to  $^{14}\text{C}$  contamination of 30,000 and 5000 Modern, respectively. Fortunately, these hot samples were discovered quickly and were only analyzed for 10 seconds and  $< 2$  min, respectively; thus, only their sample preparation lines and not their ion source system were affected by the “hot” samples. In our case, the ion source system was seriously contaminated, as were the sample preparation lines.

In order to check the level of contamination in the ion source system, we remeasured 8 samples (Table 1), 5 of which were standard samples (sugar), 2 were blank samples (charcoal), and the last was a bone sample. All these samples were prepared, prior to the arrival of the “hot” sample, in uncontaminated sample preparation lines and pressed into holders using the same drill stem. Comparing the pre- and post-contamination results for these samples yielded an average difference of  $2.14 \times 10^{-13}$ .

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Table 1 Comparison blank and standard sample measurement before and after contamination of the AMS.

Lab nr	Pre-contamination	Post-contamination	Contamination increment	Average increment
XA5999	$1.41 \times 10^{-12}$	$1.68 \times 10^{-12}$	$2.74 \times 10^{-13}$	$2.14 \times 10^{-13}$
XA6000	$1.37 \times 10^{-12}$	$1.60 \times 10^{-12}$	$2.29 \times 10^{-13}$	
XA6001	$1.40 \times 10^{-12}$	$1.55 \times 10^{-12}$	$1.46 \times 10^{-13}$	
XA6002	$1.38 \times 10^{-12}$	$1.58 \times 10^{-12}$	$2.02 \times 10^{-13}$	
XA6003	$1.41 \times 10^{-12}$	$1.62 \times 10^{-12}$	$2.09 \times 10^{-13}$	
XA6004	$2.56 \times 10^{-15}$	$2.18 \times 10^{-13}$	$2.16 \times 10^{-13}$	
XA6005	$3.05 \times 10^{-15}$	$1.91 \times 10^{-13}$	$1.88 \times 10^{-13}$	
XA6006	$1.07 \times 10^{-12}$	$1.32 \times 10^{-12}$	$2.49 \times 10^{-13}$	

## CLEANING PROCESS

### Ion Source

The entire ion source chamber was dismantled. All disassembled parts from the ion source chamber and all sample-pressing tools were ultrasonically cleaned with distilled water, diluted acid, and ethyl alcohol and baked at 90 °C for 12 hr. All parts too large to fit in the ultrasonic bath were wiped with emery paper, cleaned with ethyl alcohol, and baked at 50 °C for 12 hr. The ionizer, ionizer cover, aperture, and Cs were replaced. After several ion source cleanings and machine background checks, we found the contamination mainly came from the cladding-like material inside the Cs shroud. The Cs shroud was thus polished by a small grinding wheel and with emery paper.

### Sample Preparation Lines

The “hot” sample was prepared in an acid-hydrolysis line (Figure 1) using our standard procedure for water. Phosphoric acid (25 mL) was added to 500 mL of unpretreated water from the sample. The evolved CO<sub>2</sub> was purified in the acid-hydrolysis line and then reduced to graphite in line 9 of the left side of the 24-reactor graphite line (Figure 2).

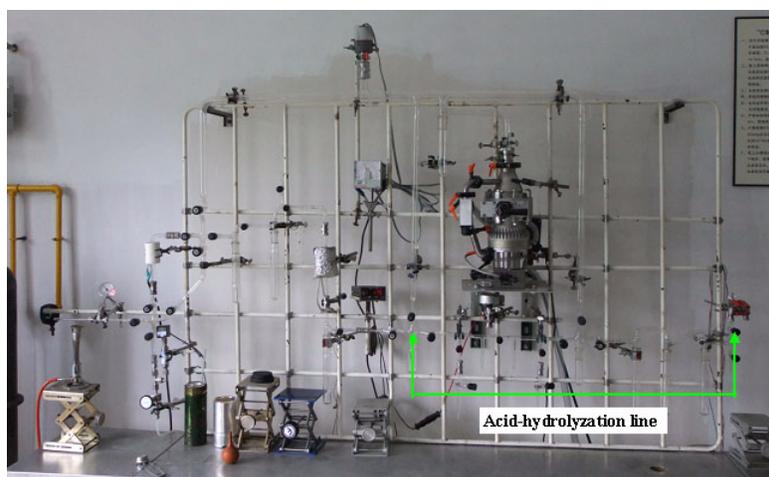


Figure 1 Acid-hydrolysis line at Xi'an AMS Center. The “hot” sample was prepared in an acid-hydrolysis line using our standard procedure for water. Some 25 mL of phosphoric acid was added to 500 mL of unpretreated water from the sample.

Before cleaning the sample preparation lines, all laboratory utensils that had been exposed to the “hot” sample were removed from the laboratory. The cleaning procedure used on parts of the contaminated lines was implemented as follows:

1. The heavily contaminated parts of the line (those that had come in direct contact with the sample/CO<sub>2</sub>) were disposed of and replaced.
2. All lightly contaminated parts of the line (parts attached to the line but never in direct contact with the sample) were rinsed in water and ultrasonically cleaned with detergent for 2 days. The detergent was changed out several times during this process. The parts were then ultrasonically cleaned with distilled water and dehydrated with an ethyl alcohol rinse. The metal parts were baked in a vacuum oven at 90 °C and the O-ring seals and glass valves were air-dried.
3. The gas sample vessels were first cleaned using the same procedures as described above. They were then heated in a muffle furnace at 400 °C for 3 hr.
4. The non-disassembled glass parts were repeatedly cleaned with distilled water, hydrochloric acid, and ethyl alcohol.
5. Once cleaned and re-assembled, the acid-hydrolysis line (Figure 1) was flushed with dead CO<sub>2</sub> and degassed by heating the glassware.
6. Once cleaned and re-assembled, the graphitization line (Figure 2) was flushed through continuous reduction of dead CO<sub>2</sub> produced in an uncontaminated CO<sub>2</sub> preparation line.

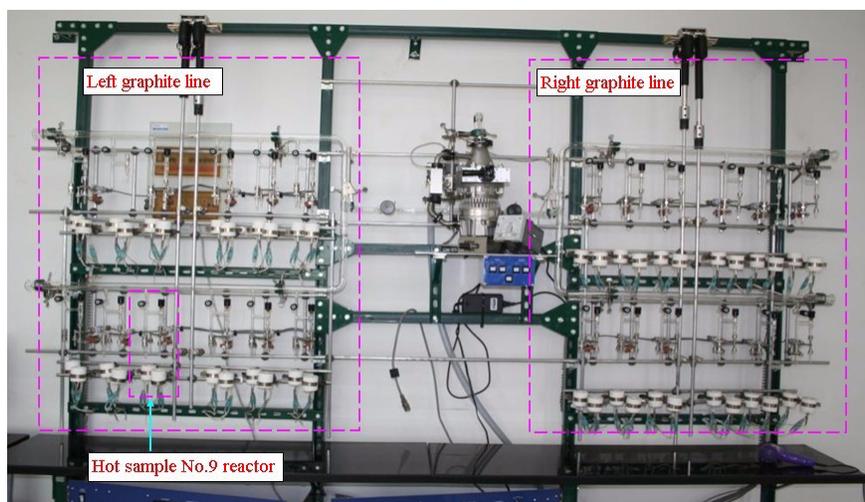


Figure 2 The 24-reactor graphitization line at Xi'an AMS Center. The evolved CO<sub>2</sub> was purified in the acid-hydrolysis line and then reduced to graphite in line 9 of the left side of the 24-reactor graphite line.

## RECOVERY CHECK

### Ion Source Chamber

The ion source chamber, and each of its parts, underwent several cleanings as described above. Table 2 shows the results of the background check after the first and the last cleaning. After the first cleaning, the background was still 1 order of magnitude higher than that measured during the acceptance test. After the last cleaning, we checked the machine background for 4 nuclides, as was done for the acceptance test in 2006 (Zhou et al. 2006). The results were better than the level measured during the 2006 acceptance test (Table 3).

Table 2 The results of the background check after the first and the last cleaning.

Sample	$^{14}\text{C}/^{12}\text{C}$	$^{14}\text{C}/^{12}\text{C}$	Machine background
	after first cleaning	after last cleaning	
3 mm (graphite)	$5.15 \times 10^{-15}$	$3.92 \times 10^{-15}$	$3 \times 10^{-16}$
Alpha (graphite)	$2.84 \times 10^{-15}$	$2.0 \times 10^{-16}$	
Sigma (graphite)	$3.50 \times 10^{-15}$	$1.67 \times 10^{-15}$	
Al with Cu core		$\sim 8 \times 10^{-17}$	

convert into beam current of graphite

Table 3 Comparison of acceptance test in 2006 and the nuclide backgrounds for isotope ratio after the last cleaning.

Nuclide	Machine background (acceptance)	Background for isotope ratio after last cleaning	
		Average value	Best measurement
$^{14}\text{C}$	$3.1 \times 10^{-16}$	$2.0 \times 10^{-16}$	$1.84 \times 10^{-16}$
$^{10}\text{Be}$	$3.6 \times 10^{-15}$	$3.78 \times 10^{-15}$	$1.71 \times 10^{-15}$
$^{26}\text{Al}$	$2.3 \times 10^{-15}$	$1.12 \times 10^{-15}$	$1.12 \times 10^{-15}$
$^{129}\text{I}$	$2.0 \times 10^{-14}$	$1.78 \times 10^{-14}$	$1.02 \times 10^{-14}$

### Acid-Hydrolysis Line

Dead  $\text{CO}_2$  gas, prepared by the Arizona AMS laboratory, was transferred into the contaminated acid-hydrolysis line (Figure 1). The  $\text{CO}_2$  was graphitized in an uncontaminated graphitization line at the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS), Xi'an. The result was  $49,247 \pm 476$  yr BP, which shows that the contamination from the hot sample was successfully removed from the acid-hydrolysis line (vial #1 in Table 4).

### Graphitization Line

Dead  $\text{CO}_2$  gas, prepared by either the Tucson AMS laboratory or in an uncontaminated acid-hydrolysis line at the IEECAS, Xi'an, was transferred directly into the left side of the contaminated graphitization line (Figure 2) and reduced. The graphitized sample was then divided into 2 parts and measured at both the Arizona AMS laboratory and the Xi'an AMS Center for cross-check (Table 4). The data show that the ages of 5 samples measured on 27 September were younger than 50 kyr. Two of them (vials 3 and 4) were  $\sim 28$  kyr because they are from loess carbonate. Results from samples processed on 2–3 October show that background values were greatly improved ( $>50$  kyr). From this set of 11 targets, just 4 samples, 2 from loess carbonate (vials 13 and 14) and another 2  $^{14}\text{C}$ -dead charcoals from the Arizona AMS lab (vials 12 and 17) were younger than 50 kyr. We believe that the loess carbonate samples yielded younger  $^{14}\text{C}$  values due to the carbonate leaching process; however, we do not have an explanation for the results of the charcoal dates.

Table 4 Recovery check of the sample preparation line.

Vial #	Graphite		Material	Gra- phite line	Xi'an age (BP)	Uncer- tainty (BP)	Processing lab	Synthe- sis rate (%)
	date (m/d/yr)	Lab code						
<b><math>\text{CO}_2</math> prepared in Tucson, graphitized on the uncontaminated line in IEECAS, Xi'an</b>								
1	10/1/11	XA6069	Arizona - dead charcoal	Inst. - Line 1	49,247	476	$\text{CO}_2$ transported on contami- nated acid-hydrolysis line	95
<b>Graphitized in left side of 24-reactor graphitization line, Xi'an AMS Center</b>								
2	9/27/11	XA6072	calcite	1	45,377	301	Hydrolyzed at Xi'an AMS	98
3		XA6073	loess carbon- ate (S9)	7	28,875	107		96
4		XA6075		8	28,855	107		98

Table 4 Recovery check of the sample preparation line. (Continued)

Vial #	Graphite date (m/d/yr)	Lab code	Material	Graphite line	Xi'an age (BP)	Uncertainty (BP)	Processing lab	Synthesis rate (%)
5		XA6074	Calcite	9	46,539	567		99
6		XA6071		12	44,242	453		95
7	10/2/11	XA6070	Arizona - dead charcoal	9	52,096	648	CO <sub>2</sub> prepared in Tucson	96
8	10/3/11	XA6083		1	52,051	550	CO <sub>2</sub> prepared in Tucson	97
9		XA6084	Calcite	2	50,085	406	Hydrolized at Xi'an AMS	97
10		XA6085		3	51,899	420		96
11		XA6086		4	50,872	381		99
12		XA6079	Arizona - dead charcoal	5	47,711	381	Combusted at Xi'an AMS	95
13		XA6087	loess carbonate (S9)	6	37,930	164	Hydrolized in IEECAS, Xi'an	97
14		XA6088		7	38,495	167		97
15		XA6080	Arizona - dead charcoal	8	53,959	502	CO <sub>2</sub> prepared in Tucson	98
16		XA6081		9	53,160	462		96
17		XA6082		10	40,220	242		99
18	10/10/11	XA6094	Calcite	1	53,969	633	Hydrolized in IEECAS, Xi'an (CO <sub>2</sub> split into 11 aliquots)	99
19		XA6095		2	54,218	1204		96
20		XA6096		3	55,660	699		95
21		XA6097		4	55,998	851		97
22		XA6098		5	53,106	829		98
23		XA6099		6	45,759	420		98
24		XA6100		7	54,190	915		97
25		XA6101		8	55,571	729		98
26		XA6102		9	57,691	1206		100
27		XA6103		10	49,022	1350		99
28		XA6104		12	52,628	936		100
29	3/18/12	XA6585	Calcite	1	60,428	1442	Hydrolized in IEECAS, Xi'an (CO <sub>2</sub> split into 12 aliquots)	99
30		XA6586		2	57,856	1289		96
31		XA6587		3	56,632	2117		100
32		XA6588		4	59,897	1252		97
33		XA6589		5	59,386	1289		98
34		XA6590		6	55,848	809		99
35		XA6593		7	62,400	1140		98
36		XA6594		8	62,270	1465		98
37		XA6592		9	61,954	1079		100
38		XA6591		10	54,631	617		99
39		XA6595		11	64,097	1298		100
40		XA6596		12	59,951	933		99
41	3/25/12	XA6604	Calcite	1	57,024	1242	Hydrolized in IEECAS, Xi'an (CO <sub>2</sub> split into 12 aliquots)	97
42		XA6608		2	58,369	868		96
43		XA6597		3	60,985	1116		100
44		XA6601		4	59,565	941		98
45		XA6605		5	57,975	999		99
46		XA6600		6	58,973	913		99
47		XA6606		7	56,326	1193		100
48		XA6607		8	60,340	946		98
49		XA6599		9	61,118	991		100
50		XA6598		10	60,858	1053		99
51		XA6603		11	57,256	748		100
52		XA6602		12	59,186	1208		99

Table 4 Recovery check of the sample preparation line. (Continued)

Vial #	Graphite date (m/d/yr)	Lab code	Material	Graphite line	Xi'an age (BP)	Uncertainty (BP)	Processing lab	Synthesis rate (%)
<b>Graphitized in right side of 24-reactor graphitization line, Xi'an AMS Center</b>								
53	10/15/11	XA6106	Calcite	1	54,343	1421	Hydrolized in IEECAS, Xi'an (CO <sub>2</sub> split into 12 aliquots)	98
54		XA6107		2	53,863	1114		99
55		XA6108		3	53,954	2002		99
56		XA6109		4	55,073	1607		99
57		XA6110		5	53,942	710		98
58		XA6111		6	48,543	470		98
59		XA6112		7	50,898	1528		99
60		XA6113		9	55,866	1258		97
61		XA6114		10	56,581	820		99
62		XA6115		11	56,842	1012		98
63		XA6116		12	52,487	2390		98

### Combined Lines

Dead CO<sub>2</sub> gas from a large calcite sample (background material) was processed in the affected acid-hydrolysis line (Figure 1) to limit the errors that can be introduced by material and processing line inconsistencies. The evolved CO<sub>2</sub> was divided into 24 splits and reduced in each of the 24 cleaned reactors on the graphitization line (Figure 2). Figure 3 shows that most of the samples were older than 50 kyr, with some samples measuring beyond 60 kyr. The <sup>14</sup>C results are not corrected for background as these are background samples.

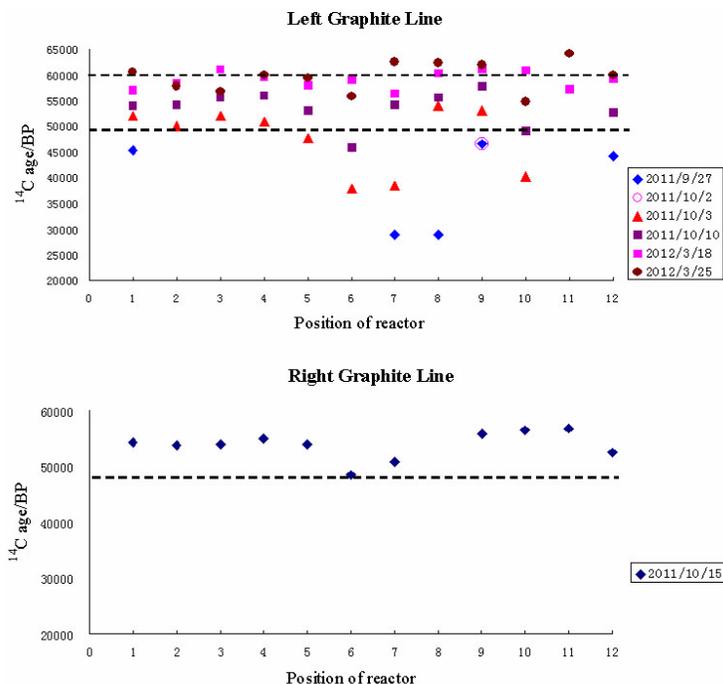


Figure 3 Recovery check of the 24-reactor graphitization line. The results show that most of the samples were older than 50 kyr, with some samples measuring beyond 60 kyr. The <sup>14</sup>C results are not corrected for background.

## DISCUSSION

Based on data collected during the above investigations, it can be concluded that both the contaminated sample preparation lines as well as the ion source chamber have recovered from the contamination event. The data show that recovery from severe contamination of both sample preparation lines and the ion source chamber is possible by careful and repeated cleaning. We also see that flushing the sample preparation lines with dead CO<sub>2</sub> is an essential part of this process. Fortunately, only a few of the parts that came in direct contact to the “hot” sample had to be replaced.

It is not always possible for the chemist and/or submitter to identify a <sup>14</sup>C “hot” sample in advance. If a “hot” sample is measured, the data acquisition system should have a significant signal at the beginning of the run, preceding the overload of the amplifier. Therefore, the AMS operator must pay careful attention to the initial measurement of all <sup>14</sup>C samples. We agree with Jull et al. (1990) that “tracer <sup>14</sup>C should not be allowed in a radiocarbon laboratory.” We also agree with Vogel et al. (1990) that prescreening of some samples with liquid scintillation counters may be necessary.

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