

## THE EFFECT OF N<sub>2</sub>O, CATALYST, AND MEANS OF WATER VAPOR REMOVAL ON THE GRAPHITIZATION OF SMALL CO<sub>2</sub> SAMPLES

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**ABSTRACT.** The effect of nitrous oxide (N<sub>2</sub>O) upon the graphitization of small (~40 µg of carbon) CO<sub>2</sub> samples at the ANSTO and University of California, Irvine, radiocarbon laboratories was investigated. Both laboratories produce graphite samples by reduction of CO<sub>2</sub> over a heated iron catalyst in the presence of an excess of H<sub>2</sub>. Although there are significant differences between the methods employed at each laboratory, it was found that N<sub>2</sub>O has no effect upon the reaction at levels of up to 9.3% by volume of CO<sub>2</sub>. Further, it was systematically determined that more effective water vapor trapping resulted in faster reaction rates. Using larger amounts of the Fe catalyst generally resulted in higher yields or reaction rates (but not both). The effects of changing the type of Fe catalyst on the final yield and reaction rate were less clear.

### INTRODUCTION

Although there are various important intermediary reactions for the H<sub>2</sub>/Fe graphitization process (Verkouteren et al. 1987; Verkouteren and Klouda 1992), the overall chemical reaction for the formation of graphite by the reduction of carbon dioxide (CO<sub>2</sub>) is:



Short reaction times reduce the risk of contamination (through air leaks), and high graphite yields produce more sample for accelerator mass spectrometry (AMS) measurement and reduce the risk of isotopic fractionation, so optimizing this reaction is particularly important for small samples.

The motivation for this study arose from some remarkably slow reaction rates (~days) encountered at the Australian Nuclear Science and Technology Organisation (ANSTO) when attempting to graphitize small (16–40 µg) test samples from the National Institute of Water and Atmospheric Research (NIWA). These test samples were processed in preparation for <sup>14</sup>CH<sub>4</sub> measurements on air extracted from ancient (10–15 kyr BP) Greenland ice. Such measurements have not previously been attempted, and both the small sample sizes and low methane concentrations (~500 parts per billion [ppb], as compared to ~1750 ppb for the modern atmosphere) pose formidable challenges. The problematic test samples were derived from an apparatus used at NIWA (Lowe et al. 1991) to separate methane (CH<sub>4</sub>) from air, which involved oxidation of the CH<sub>4</sub> to CO<sub>2</sub> over a platinum catalyst at 650–800 °C. It has long been known (eg. Olsson and Turkdogan 1974 and references therein) that the presence of nitrogen-bearing gaseous species can have an adverse effect upon graphitization. It was therefore hypothesized that N<sub>2</sub>O may be retarding graphitization, because the platinum catalyst used at NIWA is known to produce small amounts of N<sub>2</sub>O from nitrogen and oxygen in the air stream. N<sub>2</sub>O is cryogenically trapped along with methane-derived CO<sub>2</sub>. Gas chromatography (GC) measurements of samples produced from this apparatus showed that N<sub>2</sub>O was present at levels of up to 0.08% of CO<sub>2</sub> for samples with ambient CH<sub>4</sub> concentrations processed at 800 °C.

In order to investigate the effect of N<sub>2</sub>O on the graphitization reaction, we initially prepared a series of ~25-percent modern carbon (pMC) CO<sub>2</sub> samples containing ~40 µg of C with 0.2% N<sub>2</sub>O added

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volumetrically. These samples were graphitized and measured for radiocarbon at the ANSTO and UC Irvine  $^{14}\text{C}$  laboratories under various conditions. Later, we added additional  $\text{N}_2\text{O}$  to a maximum concentration of 9.3% by volume. We present the results of these trials and our conclusions.

### PREPARATION OF $\text{N}_2\text{O}$ -CONTAINING TEST SAMPLES

Pyrex<sup>®</sup> breakseals of test gas were prepared at the Scripps Institution of Oceanography (SIO) and sent to UC Irvine and ANSTO for graphitization and AMS measurement. A large volume of ~25-pMC pure  $\text{CO}_2$  was prepared by mixing  $\text{CO}_2$  from “modern” and “dead” source cylinders, both supplied by commercial  $\text{CO}_2$  manufacturers in the USA.

The ~25-pMC  $\text{CO}_2$  was decanted from this high-pressure cylinder into vacuum through a partially opened valve to provide aliquots for the breakseals, giving the potential for isotopic fractionation. Five of these breakseals were later analyzed for  $\delta^{13}\text{C}$  at NIWA, with an average of  $-26.34\text{‰}$  and a standard deviation of  $0.44\text{‰}$ . Because the typical standard deviation for a set of replicate  $\delta^{13}\text{C}$  samples at NIWA is  $0.01\text{‰}$ , this must represent the variability associated with the  $\text{CO}_2$  decanting fractionation. Accelerator-measured values of  $\delta^{13}\text{C}$  were available for correction of the  $^{14}\text{C}$  data for this fractionation at UC Irvine, but not at ANSTO.

The  $\text{N}_2\text{O}$ -spiked samples were prepared using a stainless steel vacuum line of known volume fitted with a capacitance manometer (0–1.3 kilo Pascals [kPa] range, 0.13 Pa resolution). Leak checks were performed prior to preparing each sample. Some 1.3 kPa of ~25-pMC  $\text{CO}_2$  was metered into the line and subsequently frozen into an evacuated Pyrex tube with liquid nitrogen. Then, 2.7 Pa of pure  $\text{N}_2\text{O}$  was metered into the same volume (giving an estimated error in the  $\text{N}_2\text{O}$  content of  $\pm 2.5\%$ ), and subsequently frozen into the same Pyrex tube. The Pyrex tube was then allowed to warm up to room temperature for 5 min, ensuring that the  $\text{CO}_2$  and  $\text{N}_2\text{O}$  were well mixed. Following this, 40- $\mu\text{g}$  aliquots of the mixture were metered from this tube into the vacuum line and subsequently frozen and flame-sealed in other Pyrex tubes. Two of these breakseals were subsequently diluted with UHP  $\text{N}_2$  and measured by GC at NIWA, yielding  $\text{N}_2\text{O}$  concentrations of 0.171% and 0.186% of  $\text{CO}_2$ . The lower than expected  $\text{N}_2\text{O}$  concentrations, as well as the larger than expected difference between the two are most likely a consequence of the GC measurement itself, the quality of which was limited by the very small amount of sample gas.

Later, we wished to examine the effect of higher concentrations of  $\text{N}_2\text{O}$ . We prepared these samples at ANSTO using the available 0.2% 40- $\mu\text{g}$  25-pMC breakseals. For each of these test samples, a breakseal was cracked and its size measured in a known volume using a capacitance manometer (0 to 1.3 kPa range, 0.12% reading uncertainty). After cryogenically transferring the  $\text{CO}_2$  into a glass flask, additional  $\text{N}_2\text{O}$  (99.8% purity, instrument grade) from a BOC gas cylinder connected to the mixing line via a needle valve was metered in volumetrically to a required amount and cryogenically added to the glass transfer flask.

### Standard ANSTO Procedure for Small Samples

ANSTO small reaction vessels have an internal volume of 3.5 mL and are fitted with pressure gauge heads to monitor the progress of the reaction. At ANSTO, the standard procedure (Hua et al. 2004) is to use a fixed amount of 1 mg of Cerac -325 Fe catalyst (99.9% purity), regardless of sample size. The catalyst is dispensed with a microcurette. The catalyst is first heated to 450 °C under ~50-kPa  $\text{O}_2$  for 0.5 hr, followed by reduction under ~75-kPa  $\text{H}_2$  at 600 °C for 1 hr. The oxidation step significantly improves the performance of the Cerac catalyst, as described in Hua et al. (2004). Following this pretreatment, the  $\text{CO}_2$  is introduced into the reaction vessel with the  $\text{H}_2:\text{CO}_2$  ratio of typically

2.5:1. The excess of  $H_2$  gives a higher initial pressure, which speeds the graphitization reaction; however, care must be taken to stop the reaction at completion to limit the production of  $CH_4$ .

The reaction proceeds at 600 °C with pressure decreasing rapidly for all samples within 2 hr and a minimum pressure reached for samples >100  $\mu g$  within 4 hr; smaller samples can take longer. During the reaction, the water vapor produced is trapped in a cold finger and chilled to -39 °C by a 2-stage Peltier chiller. The reaction is normally left to complete overnight. The reaction chamber pressure, furnace, and cold finger temperatures are logged throughout by a PC system. Yield efficiencies are calculated on the basis of the residual pressure, knowing the initial amount of  $CO_2$  and  $H_2$  and the stoichiometric factor.

Sample mass is determined on a dedicated line where the breakseal is opened and the  $CO_2$  transferred to a calibrated volume of  $23.03 \pm 0.26$  mL; temperature is recorded and used in the calculation of sample mass. Capacitance (absolute) manometers are used for pressure measurement. Following this, the  $CO_2$  is transferred into a small "transfer flask," which is fitted with its own valve, and taken to the graphitization line. All ANSTO samples produced with 1 mg of catalyst were front-pressed into a 1.00-mm-diameter recess in aluminum cathodes using a steel pin and a hammer. All ANSTO samples produced with 4 mg of catalyst were rear-pressed into a 1.60-mm-diameter recess using a steel pin, integral to the aluminum cathodes.

ANSTO operates 2 machines for AMS, the 10MV ANTARES accelerator (Fink et al. 2004) and the 2MV STAR accelerator, the latter manufactured by High Voltage Engineering Europa (HVEE). Both machines have the same HVEE cesium sputter ion source, which is capable of moving the sample in an XY plane normal to the incident cesium beam, efficiently utilizing the sample carbon contained in the cathode recess. The XY stage is centered on the focused cesium beam (diameter ~300  $\mu m$ ) by scanning an "alignment cathode" containing a 0.3-mm carbon rod and measuring the  $^{13}C$  or  $^{12}C$  beam intensity as a function of position. During AMS measurement on ANTARES, the XY stage moves the cathode in a circular pattern of 0.3 mm diameter. During AMS measurement on STAR, the XY stage moves to predefined positions within the sample recess.

AMS measurement on ANTARES utilizes the 4+ charge state with the terminal at 5.2 MV.  $^{12}C^-$ ,  $^{13}C^-$ , and  $^{14}C^-$  are injected sequentially using an isotope "bouncing" system.  $^{12}C^{4+}$  can be measured, although the normal practice is to measure the  $^{13}C^{4+}$  beam to derive the 14/12 ratio.  $\delta^{13}C$  is measured separately if there is sufficient sample (not the case here). AMS measurement on STAR uses the 3+ charge state with the terminal at 1.8 MV.  $^{12}C^-$ ,  $^{13}C^-$ , and  $^{14}C^-$  are injected continuously with a recombinator system, and  $\delta^{13}C$  is measured on-line. Currently, measured  $\delta^{13}C$  is not of sufficient accuracy to use for correction of the measured sample activity.

Typically, each sample is inserted into the ion source 6–8 times for 200-s measurements, stopping if the current has dropped by ~50%. Samples of ~40  $\mu g$  will often produce much the same current on the sixth insertion as for the first. Samples are normalized to the mean of multiple normal-sized OX1 and OX2 standards, and machine background is subtracted. Following the measurement, procedural background corrections are applied on the basis of previously determined curves for the addition of extraneous carbon from the processing of small standards and blanks of a range of sizes. Corrections for isotopic fractionation during graphitization and sputtering are also applied for small samples, using measurements on a set of commensurately sized standards.

### Standard UC Irvine Procedure for Small Samples

UC Irvine reaction vessels have an internal volume of 3.1 mL and are fitted with pressure gauge heads to monitor the progress of the reaction. The standard procedure (Santos et al. 2004) is to use a fixed amount of 4–5 mg of Alfa Aesar -325 Fe catalyst (98% purity), regardless of sample size. The catalyst is dispensed with a microcurette, and is first heated under ~98 kPa of H<sub>2</sub> at 400 °C for 1 hr. Following this pretreatment, the CO<sub>2</sub> is introduced into the reaction vessel with an excess of H<sub>2</sub> a few percent over stoichiometric. The reaction proceeds at 500 °C with pressure decreasing rapidly and a minimum pressure reached for samples <20 µg within 20–30 min. During the reaction, the water vapor produced is absorbed by anhydrous magnesium perchlorate Mg(ClO<sub>4</sub>)<sub>2</sub> (“dehydrite”), contained in a glass finger. Yield efficiencies are calculated on the basis of the residual pressure, knowing the initial amount of CO<sub>2</sub> and H<sub>2</sub> and the stoichiometric factor. Imprecision in the pressure measurements, in combination with the production of variable amounts of CH<sub>4</sub>, affects the accuracy of this calculation.

Sample mass is determined volumetrically in a common measuring volume of ~2.8 mL in the graphitization apparatus using a 0–196-kPa silicon pressure (absolute) sensor. A convenient estimation of the mass can also be made by using the 0–33-kPa silicon pressure sensors that monitor the reaction pressure. All UC Irvine samples were front-pressed into a 1.00-mm-diameter recess in aluminum cathodes using a steel pin and a hammer.

AMS measurement utilizes the 1+ charge state with the terminal at 0.5 MV, with both <sup>12</sup>C<sup>1+</sup> and <sup>13</sup>C<sup>1+</sup> measured (Southon et al. 2004). AMS measurements involve up to 10–12 runs on each sample. For samples of a few tens of µg, there are typically 150 s or 20,000 counts per run (whichever comes first). Measurement stops when the current reaches 30–50% of the original current, typically 8–10 runs for a 30–40 µg sample. Samples are normalized to the mean of multiple normal-sized OX1 samples. δ<sup>13</sup>C is measured on-line and is used to correct the measured isotope ratios. Several small dead-C blanks and aliquots of OX1 similar in size to the unknowns are also run. These are used to estimate the modern and dead-C contributions to the blank, and those values are used to correct the measured ratios.

### RESULTS

The different graphitization procedures and results are shown in Table 1. All samples were converted to graphite and, with the exception of 1 sample (cathode loading problem), all were measured for <sup>14</sup>C. δ<sup>13</sup>C of the samples was not measured at ANSTO; instead, a value of –25‰ was assumed. The effects of the difference between the assumed and the measured average δ<sup>13</sup>C (–26.34‰) as well as the estimated δ<sup>13</sup>C variability of the samples (=0.44‰) on <sup>14</sup>C of ~25-pMC samples are small (<0.1 pMC) and are not considered here.

Sample masses as measured at UC Irvine and ANSTO are shown in Table 1 and, with 1 exception, were all the expected ~40 µg. The accuracy of UC Irvine masses is limited by the resolution of the pressure gauges at these low pressures. At ANSTO, the internal heater that maintains the sensor at 45 °C for electrical stability results in a temperature gradient in the gas and a slight over-estimation of sample mass.

Table 1 Experimental results for CO<sub>2</sub> samples spiked with N<sub>2</sub>O at both laboratories. Cerac -325 was only used at ANSTO and always had the full oxidation/reduction treatment as described in the text. Alfa Aesar -325 was used at both laboratories and only had the reduction step as described in the text. Section A describes the effect of varying catalyst type and amount, section B the effect of different methods of water removal, and section C the effect of higher N<sub>2</sub>O concentrations. The shaded rows of section A indicate graphitization reactions performed with standard type, amount of catalyst, and pretreatment method for each laboratory. The yield of 102 ± 7% shown for each UC Irvine sample is the average and 1-σ error of the measured yields.

Sample ID	Laboratory	Catalyst		H <sub>2</sub> O removal			Reaction time (hr)	Graphite yield (%)	<sup>14</sup> C pMC (%)		
		Catalyst type	Mass (mg)	Treatment	Mg(ClO <sub>4</sub> ) <sub>2</sub>	Cold trap temp (°C)				N <sub>2</sub> O conc. (%)	Carbon mass (μg)
<b>A: CATALYST TYPE &amp; AMOUNT</b>											
OZI687	ANSTO	Cerac -325	1	O <sub>2</sub> /H <sub>2</sub>		-39	0.2	38.4 ± 0.4	2.5	78 ± 16	24.75 ± 0.46
OZI688	ANSTO	Cerac -325	1	O <sub>2</sub> /H <sub>2</sub>		-39	0.2	61.6 ± 0.7	2.0	75 ± 15	24.23 ± 0.43
OZI689	ANSTO	Cerac -325	1	O <sub>2</sub> /H <sub>2</sub>		-39	0.2	39.4 ± 0.5	4.0	80 ± 15	25.47 ± 0.47
OZI690	ANSTO	Cerac -325	4	O <sub>2</sub> /H <sub>2</sub>		-39	0.2	37.9 ± 0.4	4.0	91 ± 13	25.14 ± 0.60
OZI691	ANSTO	Cerac -325	4	O <sub>2</sub> /H <sub>2</sub>		-39	0.2	37.3 ± 0.4	14.0	98 ± 13	25.03 ± 0.60
OZI692	ANSTO	Cerac -325	4	O <sub>2</sub> /H <sub>2</sub>		-39	0.2	37.9 ± 0.4	3.0	97 ± 13	— <sup>a</sup>
OZI805	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-39	0.2	36.6 ± 0.4	3.0	85 ± 17	24.76 ± 0.71
OZI806	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-39	0.2	36.8 ± 0.4	3.0	88 ± 17	25.48 ± 0.50
OZI807	ANSTO	Alfa Aesar -325	4	H <sub>2</sub>		-39	0.2	37.4 ± 0.4	4.0	87 ± 17	25.65 ± 0.92
OZI808	ANSTO	Alfa Aesar -325	4	H <sub>2</sub>		-39	0.2	37.4 ± 0.4	4.0	87 ± 17	24.46 ± 0.97
22579	UC Irvine	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	39 ± 1	1.0	102 ± 7	25.46 ± 0.21
22580	UC Irvine	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	39 ± 1	1.0	102 ± 7	25.75 ± 0.17
22584	UC Irvine	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	41 ± 1	1.0	102 ± 7	25.57 ± 0.21
22585	UC Irvine	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	39 ± 1	1.0	102 ± 7	25.69 ± 0.20
22586	UC Irvine	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	41 ± 1	1.0	102 ± 7	25.49 ± 0.18
20898	UC Irvine	Alfa Aesar -325	4	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	35 ± 1	0.5	102 ± 7	25.79 ± 0.37
20899	UC Irvine	Alfa Aesar -325	4	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	37 ± 1	0.5	102 ± 7	25.48 ± 0.40
20900	UC Irvine	Alfa Aesar -325	4	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	35 ± 1	0.5	102 ± 7	26.60 ± 0.39
<b>B: WATER REMOVAL</b>											
OZI809	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	37.3 ± 0.4	1.5	88 ± 18	25.35 ± 0.66
OZI810	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		0.2	37.5 ± 0.4	1.7	90 ± 18	25.42 ± 0.58
OZI862	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-58 <sup>b</sup>	0.2	37.0 ± 0.4	1.3	90 ± 16	24.85 ± 0.61
OZI863	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-67 <sup>c</sup>	0.2	37.7 ± 0.4	1.0	90 ± 16	24.81 ± 0.77

Table 1 Experimental results for CO<sub>2</sub> samples spiked with N<sub>2</sub>O at both laboratories. Cerac -325 was only used at ANSTO and always had the full oxidation/reduction treatment as described in the text. Alfa Aesar -325 was used at both laboratories and only had the reduction step as described in the text. Section A describes the effect of varying catalyst type and amount, section B the effect of different methods of water removal, and section C the effect of higher N<sub>2</sub>O concentrations. The shaded rows of section A indicate graphitization reactions performed with standard type, amount of catalyst, and pretreatment method for each laboratory. The yield of 102 ± 7% shown for each UC Irvine sample is the average and 1-σ error of the measured yields. (Continued)

Sample ID	Laboratory	Catalyst		H <sub>2</sub> O removal			Reaction time (hr)	Carbon mass (μg)	Graphite yield (%)	<sup>14</sup> C pMC (%)
		Laboratory	Catalyst type	Mass (mg)	Treatment	Mg(ClO <sub>4</sub> ) <sub>2</sub>				
<b>C: HIGHER N<sub>2</sub>O CONCENTRATIONS</b>										
OZI851	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>	-39	1.2	37.3 ± 0.4	89 ± 18	24.78 ± 0.80
OZI852	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>			1.0	36.9 ± 0.4	85 ± 16	24.86 ± 0.60
OZI853	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub> <sup>d</sup>	-39	1.0	38.1 ± 0.4	89 ± 17	25.14 ± 0.62
OZI854	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>			1.0	36.5 ± 0.4	85 ± 16	25.02 ± 0.60
OZI855	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-39	9.0	37.1 ± 0.4	86 ± 15	24.32 ± 0.67
OZI856	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		9.0	37.3 ± 0.4	90 ± 17	25.16 ± 0.62
OZI857	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-39	9.2	36.6 ± 0.4	86 ± 16	25.06 ± 0.68
OZI858	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-39	9.1	37.4 ± 0.4	87 ± 16	24.82 ± 0.65
OZI859	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>	Mg(ClO <sub>4</sub> ) <sub>2</sub>		9.3	36.8 ± 0.4	87 ± 17	24.76 ± 0.61
OZI860	ANSTO	Alfa Aesar -325	1	H <sub>2</sub>		-39	9.2	37.1 ± 0.4	88 ± 16	24.55 ± 0.64

<sup>a</sup>Sample lost from cathode recess.

<sup>b</sup>Cold trap: -58 °C at start of reaction, -45 °C after 1.25 hr.

<sup>c</sup>Cold trap: -67 °C at start of reaction, -36 °C after 2 hr.

<sup>d</sup>Mg(ClO<sub>4</sub>)<sub>2</sub> previously used for 4 graphitizations.

<sup>e</sup>Data logging failure.

### Effect of Catalyst Type and Amount

Our initial investigations were focused on graphitizing  $CO_2$  samples with 0.2%  $N_2O$ , using the standard procedure at each laboratory for removing water vapor; the experimental results are summarized in section A of Table 1. As can be seen, all 6 samples were graphitized successfully, with reaction times as expected for both laboratories. The ANSTO yields of ~78% were typical for 40- $\mu$ g C samples, and the cathodes gave carbon currents typical for samples of this size. At UC Irvine, the conversion of  $CO_2$  to graphite was 100% efficient and the samples also gave carbon currents typical for samples of this size.

To further investigate the disparity in yields and reaction rates between the 2 laboratories, we tried varying the type and amount of catalyst. At first, we varied the amount of catalyst, increasing to 4 mg at ANSTO and decreasing to 1 mg at UC Irvine. Of the 3 samples prepared at ANSTO, all were converted with higher than normal yields of ~95% in about normal times, with the exception of 1 sample that required an excessive reaction time; we have no explanation for this sample. The generally higher yields are presumably due to the greater surface area of catalyst. The 3 samples prepared at UC Irvine were converted to usual yields of 100% graphite in about twice the time normally required with 4 mg of catalyst. This was also true of some small standards prepared using 1 mg of catalyst. This is consistent with a reduction in catalyst surface area. It was, however, puzzling that increasing the catalyst at ANSTO did not affect the reaction rate, whereas at UC Irvine it was increased. The increase in catalyst improved yields at ANSTO, whereas the yield remained 100% at UC Irvine.

Use of non-standard catalyst amounts presented cathode loading problems and AMS measurement difficulties for each laboratory. At UC Irvine, the 1-mg catalyst samples were hammered into a 1.00-mm recess in aluminum cathodes using a hardened steel pin. This is the normal method of loading cathodes; however, the smaller amount of catalyst made transfers difficult and resulted in a lower sample surface than usual. AMS measurements were normalized to standards prepared with 4–5 mg of catalyst, although some small standards and blanks prepared with 1 mg of cathode were concurrently measured.

At ANSTO, the samples prepared with 4 mg of Cerac -325 catalyst were rear-pressed into 1.6-mm-diameter cathodes using the usual pressure of 350 kPa. This gave sample surfaces that were flush with the cathode, but of poor quality. It was later found that the Fe pellet had fallen from one of the cathodes on loading the ion source, so no AMS result was obtained. Both laboratories found that samples produced with 1 mg of catalyst produce larger currents but do not last as long as samples produced with 4 mg of catalyst in the ion source.

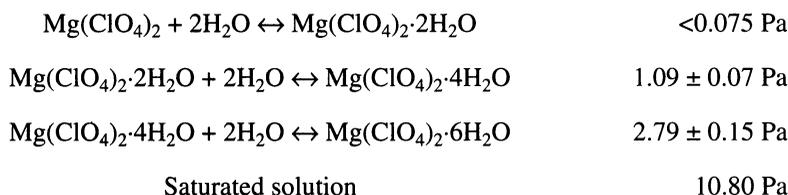
Further trials were conducted at ANSTO following the tests described above. At first, the Alfa Aesar -325 catalyst was tested in 1-mg and 4-mg amounts and pretreated with reduction under  $H_2$  only (at 600 °C for 1 hr). After the cathode loading problems described above, we increased the pressure to 700–800 kPa for these two 4-mg samples. The two 1-mg samples were front-pressed as before. As can be seen in section A of Table 1, all 4 samples graphitized to slightly higher yields and in similar times. We did not see the dramatic improvement in performance that we had expected with this catalyst.

### Effect of Water Removal

As it became apparent that the differences in type and amount of catalyst could not explain all of the disparities in yields and reaction rates seen at ANSTO and UC Irvine, we decided to test different means of removing water vapor at ANSTO, while continuing with the use of 1 mg of Alfa Aesar

-325 Fe catalyst. First, we tested the use of  $\text{Mg}(\text{ClO}_4)_2$  by loading the cold finger with ~100 mg of isotope-grade anhydrous  $\text{Mg}(\text{ClO}_4)_2$  pellets (6–18 mesh) from EuroVector. As can be seen in section B of Table 1, the reactions of the 2 samples produced in this way proceeded to about the same yield—but in half the time of the similar samples that employed the cold trap at  $-39^\circ\text{C}$ . We then produced 2 additional samples with a lower cold trap temperature. For these samples, we surrounded the cold finger with an aluminum heat pipe immersed in a bath of ethanol and dry ice; the starting temperature is shown in Table 1, rising towards the end of the reaction as shown in the footnote. These reactions proceeded at a slightly faster rate, to about the same yield, as those using  $\text{Mg}(\text{ClO}_4)_2$ .

Water removal has been thought to be a critical factor in the graphitization of small samples (Verkouteren and Klouda 1992; Pearson et al. 1998; Pearson 2000:111–112), although no quantitative data exists. Such a strong dependence on the means of water vapor removal for small samples is remarkable in view of the small amount of water involved (about  $6.7\ \mu\text{mol}$  or  $120\ \mu\text{g}$  of  $\text{H}_2\text{O}$  for  $40\ \mu\text{g}$  of C as  $\text{CO}_2$ ). We have not observed this dependency for larger samples. The vapor pressure of ice is strongly dependent on temperature, being considerably reduced from 12.84 Pa at  $-40^\circ\text{C}$  to 0.06 Pa at  $-80^\circ\text{C}$ . Copeland and Bragg (1954) found aqueous vapor pressures for the following  $\text{Mg}(\text{ClO}_4)_2$  equilibria:



Presumably, at both UC Irvine and ANSTO, we initially had anhydrous  $\text{Mg}(\text{ClO}_4)_2$  in the trap. The same charge of  $\text{Mg}(\text{ClO}_4)_2$  was used for a few graphitizations before replenishment, but with the small amount of water produced during the reaction it is fair to assume that the water vapor pressure was always much less than 1 Pa, possibly as small as 0.08 Pa. This is comparable with the water vapor pressure of 0.06 Pa we expect above ice at  $-80^\circ\text{C}$ . With a cold trap at  $-39^\circ\text{C}$ , the water vapor pressure is more than an order of magnitude higher.

A possible explanation for why excess  $\text{H}_2\text{O}$  vapor could inhibit the graphitization reaction follows from an examination of the reaction mechanism. Before the reversible reaction (1) can proceed,  $\text{CO}_2$  must be reduced to CO on the Fe:



Then, graphitization of CO proceeds:



For a constant amount of catalyst, the available Fe surface decreases as the graphite forms. This is quite apparent for large samples, where the catalyst develops a “woolly” appearance as it becomes encrusted with graphite. We speculate that for small samples where there is always a fresh Fe surface, the reverse reactions come into play, with C being oxidized back into CO and CO being oxidized back into  $\text{CO}_2$ . The reactions are forced to the right-hand side when the water vapor is efficiently removed, either with  $\text{Mg}(\text{ClO}_4)_2$  or a cold trap at  $-80^\circ\text{C}$ . This may explain why the small samples prepared with 4 mg of Cerac -325 or Alfa Aesar -325 catalysts took slightly longer to graphitize than those prepared with 1 mg when a  $-39^\circ\text{C}$  cold trap was used at ANSTO.

### Effect of N<sub>2</sub>O Concentration

The effect of spiking CO<sub>2</sub> samples with N<sub>2</sub>O concentrations of up to 9.3% by volume was further tested at ANSTO. These samples were all prepared with Alfa Aesar -325 mesh catalyst, with either Mg(ClO<sub>4</sub>)<sub>2</sub> or a -39 °C cold trap. As can be seen from section C of Table 1, with the exception of sample OZI853, which took 4 hr to complete, no significant changes in either yield or reaction rate were observed. The longer reaction time for this sample may be related to overuse of the Mg(ClO<sub>4</sub>)<sub>2</sub>.

### AMS Performance of Catalysts

The 98% purity Alfa Aesar -325 mesh catalyst contains sufficient Li to be a problem for AMS measurement of the 4+ charge state—for example, with ANTARES. The dilithium ion <sup>7</sup>Li<sub>2</sub><sup>-</sup> is injected along with <sup>14</sup>C, and <sup>7</sup>Li<sup>2+</sup> enters the detector, which, although well-resolved, increases the detector dead time. This is not an issue for the 1+ and 3+ charge states used on the other machines. Note that ICP-AES analysis of the 2 catalysts mentioned above, plus a third, Sigma-Aldrich -400 (99.9% purity), only showed that Li was below the detection limit of 6 mg per kg in these catalysts.

### CONCLUSIONS

Neither laboratory had any problems preparing or measuring 40-μg samples of 25 pMC CO<sub>2</sub>, with 0.2% N<sub>2</sub>O using their respective standard sample preparation conditions. At each laboratory, these samples graphitized at the rates and gave yields typical of N<sub>2</sub>O-free samples of this size. Further, higher N<sub>2</sub>O concentrations of up to 9.3% of CO<sub>2</sub> by volume do not appear to affect either the graphitization or the AMS measurement. We thus conclude that N<sub>2</sub>O does not significantly interfere with graphitization.

In an effort to optimize the graphitization yield and reaction rate for small samples, several other variables—namely Fe type, catalyst amount, and the water-trapping method—were also investigated. The relatively small number of samples involved limits the confidence with which we can draw conclusions; however, some patterns seem clear. ANSTO found that when using a -39 °C cold finger to trap water vapor, 4 mg of Cerac -325 catalyst produced a higher yield of graphite than did 1 mg, but with a slightly longer reaction time. Four-mg and 1-mg amounts of Alfa Aesar -325 behaved similarly in terms of yields, but once again slightly faster reaction rates were found for 1 mg of the catalyst. At ANSTO, we found that 1 mg of Cerac -325, with the full oxidation/reduction treatment, and 1 mg of Alfa Aesar -325, with just the reduction treatment, behave similarly in terms of reaction speed, but with slightly enhanced graphite yield for the latter.

UC Irvine found that 1-mg amounts of Alfa Aesar -325 had twice the reaction time than did 4 mg, but gave the same final yield. Both laboratories found that samples prepared with 1 mg of Fe produce higher currents than those produced with 4 mg, and that the latter last longer in the ion source. There were some difficulties comparing non-standard amounts of catalyst at the 2 laboratories because sample loading techniques had not been optimized for these amounts.

At ANSTO, for 1 mg of reduced Alfa Aesar -325 catalyst, decreased reaction times with similar high final yields were obtained when the cold trap temperature was dropped below the usual -39 °C or when Mg(ClO<sub>4</sub>)<sub>2</sub> was used instead of a cold trap. The reaction time depends significantly on the means used to remove the water vapor produced in the reaction.

This work demonstrated that the presence of up to 9.3% N<sub>2</sub>O in small CO<sub>2</sub> samples does not present any difficulties for the preparation of graphite by reduction over a heated iron catalyst in an excess of H<sub>2</sub>. It confirms that the correct choice of catalyst type and amount is essential for obtaining the

best graphitization performance. It also revealed that more effective water vapor removal significantly increases the rate at which the graphitization reaction proceeds for small samples.

## FURTHER WORK

All of the results presented in this paper relate to small samples to which N<sub>2</sub>O was deliberately added. We need to confirm that small samples without N<sub>2</sub>O present show the same trends as we have reported. We also need to study the dependence of the graphitization reaction on the means of water vapor removal for larger samples.

Despite changing the ANSTO procedure, graphite yields remained less than the 100% yields observed at UC Irvine. This is partly an artifact of the way the yields are calculated at each laboratory. It may also be related to the formation of methane towards the end of the reaction, as found by McNichol et al. (1992). Another possibility is a yield dependence on the different reaction temperatures: 500 °C at UC Irvine and 600 °C at ANSTO. UC Irvine have found that the reaction yields for small samples are sensitive to temperature and more experiments are needed to investigate this.

Although Alfa Aesar -325 offers the advantage of simpler pretreatment over the Cerac -325, due to its Li content it is a poor choice for measurement by the 4+ charge state. At ANSTO, we have begun testing a third catalyst, Sigma-Aldrich -400, which has been previously used at UC Irvine. This catalyst has an acceptable Li concentration, which may even be lower than the Cerac -325. Preliminary results show that it performs as well or better than the Alfa Aesar in terms of reaction yields and times, with just the H<sub>2</sub> reduction step and using a cold trap at -80 °C. Two test samples containing ~40 µg C graphitized on 1 mg of catalyst in <1 hr with a graphite yield of 90%.

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