ILLUMINATION OF A BLACK BOX: ANALYSIS OF GAS COMPOSITION DURING GRAPHITE TARGET PREPARATION

A. P. McNICHOL, A. R. GAGNON, G. A. JONES and E. A. OSBORNE

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543 USA

ABSTRACT. We conducted a study of relative gas composition changes of CO_2, CO and CH_4 during the formation of graphite targets using different temperatures, catalysts and methods. Reduction with H_2 increases the reaction rate without compromising the quality of the AMS target produced. Methane is produced at virtually any temperature, and the amount produced is greater at very low temperatures. The reduction of CO to graphite is very slow when H_2 is not included in the reaction.

INTRODUCTION

The National Ocean Sciences Accelerator Mass Spectrometry (AMS) Laboratory is being established to provide a large number of high-quality ^{14}C analyses to the oceanographic community, particularly in support of such large programs as the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS). The production of uniform, high-quality sample targets is essential to the optimal performance of any AMS system. For the analysis of radiocarbon by AMS, compressed, filamentous graphite is a good material to use in the sputter ion source. The methods currently in use at ^{14}C AMS labs around the world include reduction with H_2 over a transition metal catalyst (Vogel, Southon & Nelson 1987), and reduction with Zn over a transition metal catalyst (Slota *et al.* 1987). The reactions involved in these two methods have been well studied and reviewed (Boudouard 1901; Manning & Reid 1977; Turkdogan & Vinters 1974; Jull *et al.* 1986; Slota *et al.* 1987; Vogel, Nelson & Southon 1987); important reactions are listed in Table 1. Most studies of these reactions were conducted at constant pressures (Boudouard 1901; Manning & Reid 1977; Turkdogan & Vinters 1974), usually around one atmosphere, conditions that do not represent those used during the formation of AMS targets. We describe here the initial results of a study of gas composition changes during graphite target preparation. The results of this study can be used to optimize target preparation methods.

METHODS

We used a residual gas analyzer (RGA) (AMETEK Dycor Model MA 200FG) to analyze the composition of gases produced during the formation of graphite from CO_2. Figure 1 shows the design of the reaction apparatus. Filamentous graphite was produced by both methods described below.

Method A (H_2 Reduction)

We reduced CO_2 to graphite over reduced Co or Fe catalyst using H_2 as the reducing agent (Vogel, Nelson & Southon 1987). We used 325 mesh spherical Co or 200 mesh dendritic Fe. Approximately 12 mg of Co or 2 mg Fe were weighed into the Vycor tube and pre-reduced at 400° C in an H_2 atmosphere. Pure, dry CO_2 was transferred to the reactor and a stoichiometric excess of H_2 gas (≥ 2.5 pCO_2) was added. A cold trap (−80°C) was placed over the Pyrex tube, the oven placed over the Vycor tube and raised to reaction temperature (set point between 500–750°C depending on the reaction). Temperature and pressure were monitored throughout the entire reaction, which lasted 4–24 h. At the end of the reaction, we weighed the graphite that had formed on the metal catalyst. We have produced over 250 graphite targets for which we have pressure *vs.* time and yield data

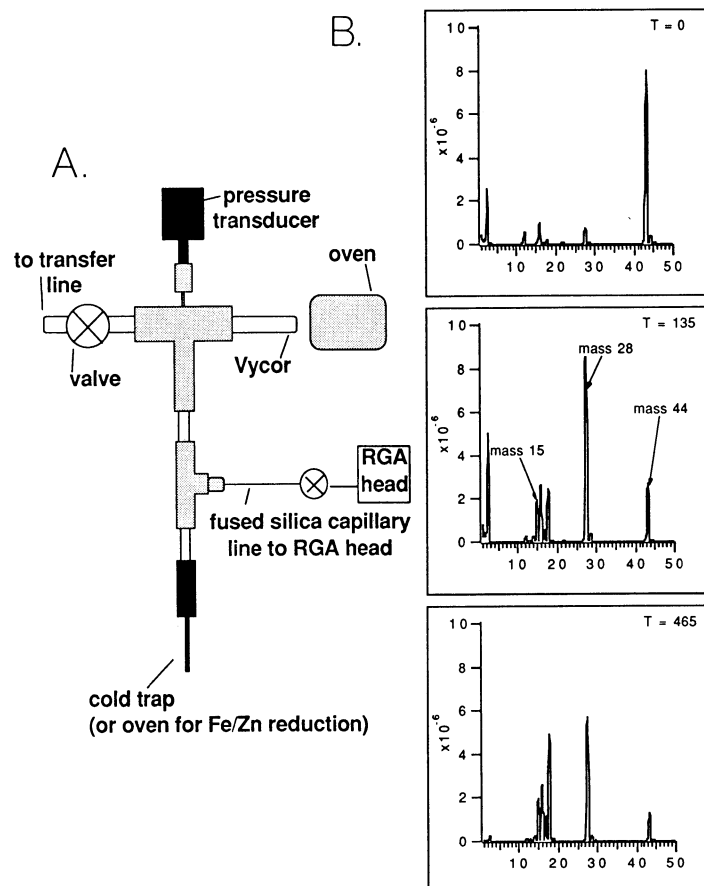TABLE 1. Reactions Occurring Within the Graphite Reactor

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (1)$$
$$CO + H_2 \rightleftharpoons C(gr) + H_2O \qquad (2)$$
$$CO_2 + Zn \rightleftharpoons CO + ZnO \qquad (3)$$
$$2CO \rightleftharpoons CO_2 + C(gr) \qquad (4)$$
$$2CO + 2H_2 \rightleftharpoons CO_2 + CH_4 \qquad (5)$$
$$CO + 3H_2 \rightleftharpoons H_2O + CH_4 \qquad (6)$$
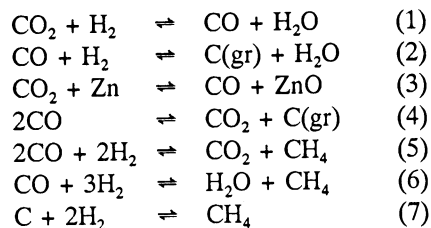$$C + 2H_2 \rightleftharpoons CH_4 \qquad (7)$$

Fig. 1A. The reaction apparatus used in the RGA experiments. The hatched areas represent stainless-steel vacuum fittings and, except for the Vycor tube listed, the rest of the tubing is Pyrex. B. Typical RGA scans from the beginning, middle and end of a graphite reaction. The x axis is in mass units, and the y axis indicates the pressure in torr. The label at the top right of each graph indicates the time in minutes at which the scan was taken.

using this method. All graphitization reactions progressed to a point where the pressure change indicated the reaction had gone to completion. We also analyzed the bulk isotopic fractionation observed in a subset of graphite samples by measuring the $\delta^{13}C$ of CO_2 generated from recombusted graphite in a subset of sample targets. We studied 11 of the reactions using the RGA.

Method B (Fe/Zn Reduction)

We reduced CO_2 to graphite over Fe catalyst using Zn metal as the reducing agent (Slota *et al.* 1987). Approximately 2 mg Fe were weighed into the Vycor tube and 50–70 mg powdered Zn metal were weighed into the Pyrex tube. The Zn metal was precleaned by heating to 435°C under vacuum. The Fe was precleaned by heating to 650°C under vacuum for 20 min. We transferred pure, dry CO_2 to the reactor and prereduced it to CO by heating the Zn finger to 400°C for 30 min. The CO was reduced to graphite by heating the metal catalyst finger to 650°C. Temperature and pressure were monitored throughout the reaction, which lasted for 8 h. At the end of the reaction, we weighed the graphite that had formed on the metal catalyst.

RGA Method

We monitored the gas composition within the reactor during graphitization using the RGA. A fused silica capillary (90 cm long, 50 μm inside diameter) was used to introduce gas samples from the graphite reactor to the RGA. The capillary was required to reduce the pressure in the reactor (up to 3 atm) to $< 1 \times 10^{-6}$ atm, the highest pressure the RGA filament can withstand. We analyzed gas composition between masses 1 and 50 at specific times by opening the valve between the reactor and the RGA only when a sample was desired. Removal of a sample takes gas away from the reaction vessel; thus, a pressure decrease is associated with each sample. This has a greater impact on the samples taken at the end of the experiment when the pressure is low, and is very noticeable in gases whose partial pressure is very low.

Figure 1 shows typical scans from the beginning, middle and end of a reaction. In these scans, a clear peak at mass 44 corresponds to CO_2, and a distinct peak at mass 28 corresponds primarily to CO. The peak at mass 28 includes a small contribution from the fragmentation of CO_2. The peak at mass 16 corresponds to CH_4, but also includes O from fragmentation of CO_2, CO and H_2O. However, a major fragmentation product occurs at mass 15, which is unique to CH_4. For this study, we decided to monitor mass 44 to indicate changes in the concentration of CO_2, mass 28 for CO and mass 15 for CH_4.

It is difficult to use an RGA as an exact quantitative analytical tool, and we decided to use the RGA data as a "semi-quantitative" indicator of the relative proportions of CO_2, CO and CH_4. To interpret the data obtained from the RGA, we made the following assumptions and calculations. We did not adjust the observed peak heights for the differences in the ionization cross-sections. The experimentally observed relative cross-sections normalized to N_2 are 1.36, 1.07 and 1.57 for CO_2, CO and CH_4, respectively (O'Hanlon 1989). We believe we are underestimating the amount of CO_2 and CH_4 relative to CO by approximately 20%. We have not considered the concentration of H_2 in this study, because we were unable to measure the concentration of H_2 well, using the RGA. When the different cross-sections were taken into account, the ratio of H_2/CO_2 at the beginning of each reaction calculated from the RGA data was less than one-half the actual ratio.

An additional factor we needed to consider when analyzing the data was the pressure change that occurred within the reaction vessel during the reaction. In a typical reaction, the pressure decreases from 2.0 to 0.2 atm. The RGA responds in a non-linear fashion to the pressures observed in the reaction vessel. To remove this bias, we made the following calculation:

$$pm = Pt[(\text{mass } m)/\text{totmass}] \tag{1}$$

where

  pm = Partial pressure of gas corresponding to mass m, atm

mass m = Peak area under mass 44, 28, or 15

totmass = Total peak area, mass 0-50

Pt = Total pressure in reactor measured by pressure transducer, atm.

Thus, considering the calculations required, we emphasize that the actual partial pressures reported from an individual experiment are only semi-quantitative, but that the calculated partial pressures have great significance when comparing the behavior of different experiments.

RESULTS

We conducted 12 RGA experiments; the experimental conditions for each are summarized in Table 2. Figures 2 and 3 show examples of the pressure change observed with time; the profile observed in Figure 2A is the most typical. Generally, pressure increases when the ovens are turned on at the beginning of the reaction, and after a short period, the pressure decreases regularly for *ca.* 1–2 h. At this point, the rate of the pressure change decreases until it reaches a constant level. The amount of time it took to reach the slope break varied from experiment to experiment and is listed in Table 2. During Experiments 8 and 9, the observed pressure change was very different from the typical profiles (Fig. 2B, 3A); during these experiments, it was difficult to detect a slope break in the profile. Figure 3B shows the results of Experiment 12, the only RGA experiment using Method B to produce graphite.

TABLE 2. Experimental reaction conditions. The last five columns report the time it took for the concentration of the listed species to reach a minimum or maximum pressure in the graphite reactor in minutes.

Experiment	Reaction date	Temperature (°C)	Catalyst	CO max	CO min	CO₂ min	CH₄ max	Slope break
1	17 Oct 90	600	Co	78	130	133	125	102
2	22 Oct 90	680	Co	72	133	117	117	102
3	30 Oct 90	680	Co	75	*	100	91	102
4	8 Nov 90	575	Co	75	167	150	102	78
5	23 Nov 90	650	Co	64	150	150	95	90
6	27 Nov 90	640	Co	77	183	133	96	84
7	4 Dec 90	625	Co	92	183	150	108	108
8	28 Mar 91	750	Co	67	**	83	83	†
9	1 Apr 91	530	Co	49	150	167	119	60
10	14 Nov 90	625	Fe	47	133	108	75	66
11	22 Mar 91	500	Fe	70	217	233	130	−
12	9 Apr 91	650	Fe	85	**	247	‡	†

*No data available

**No minimum observed

†The phenomena could not be observed

‡Not applicable in this experiment

Figures 2 and 3 also show the changes in the pressures of the individual compounds CO_2, CO and CH_4 with time for four experiments; Figure 2A is representative of most of the experiments. In a typical experiment, the CO_2 pressure decreases rapidly to a relatively constant level; it takes between 90 to 150 min to reach a minimum value (Table 1). During Experiments 9 and 11, it took almost 4 h for the CO_2 pressure to decrease.

In each experiment, the nominal pressure of CO started at a non-zero value because of a contribution from CO_2 (see Methods), but changes after the beginning of the reaction were due to changes
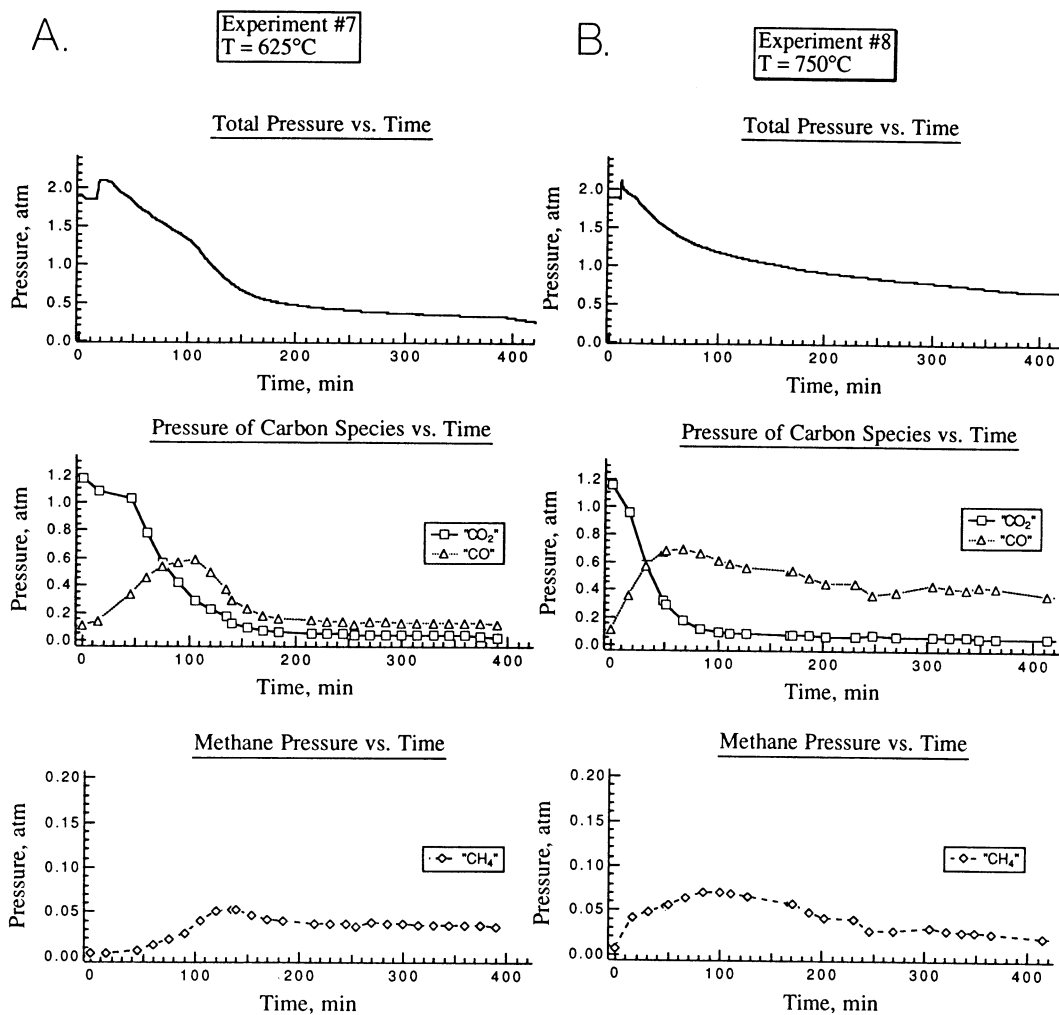
Fig. 2A & B. Change in total, CO$_2$, CO and CH$_4$ pressures with time for Experiments 7 and 8; experimental conditions are listed in Table 2.

in the amount of CO in the reaction vessel. Initially, a CO pressure increase is coincident with the CO$_2$ pressure decrease; eventually, CO reaches a maximum concentration and then decreases to a background level. For most experiments, it took between 65 to 80 min for CO to reach its maximum pressure; during Experiments 9 and 10, it took only 50 min, and during Experiment 7, it took 90 min (Table 1).

The profile of CH$_4$ pressure change with time is similar for all experiments. Figures 2 and 3 show three examples; Figure 2A is most typical. Methane was virtually absent until after the CO pressure had reached a maximum level. Its pressure rose rapidly to a very low pressure (0.03–0.08 atm) at which it remained for the rest of the reaction. During Experiment 9, the pressure of CH$_4$ reached the highest pressure observed in these experiments; Figure 3A shows the profile. Table 2 lists the time at which CH$_4$ reached its maximum pressure.
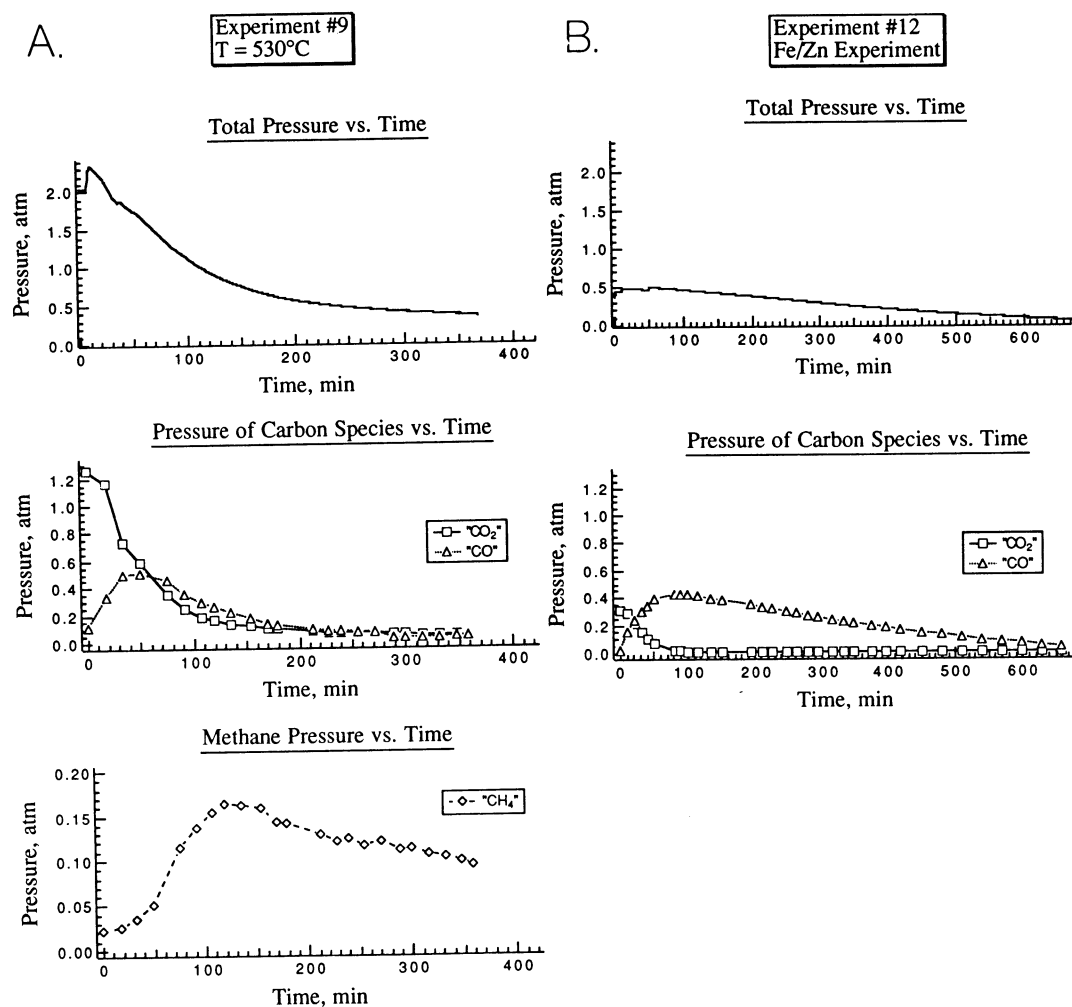
A.   Experiment #9
      T = 530°C

B.   Experiment #12
      Fe/Zn Experiment

Total Pressure vs. Time

Total Pressure vs. Time

Pressure of Carbon Species vs. Time

Pressure of Carbon Species vs. Time

Methane Pressure vs. Time

Fig. 3A & B. Change in total, CO_2, CO and CH_4 pressures with time for Experiments 9 and 12; experimental conditions are listed in Table 2.

Using a gravimetric method to determine yield, we observed variable yields, which differed greatly from those predicted by the pressure change. For the H_2 reduction, when we used Co as the catalyst, we observed an average yield of 72%; when we used Fe, the yield was 87%. For samples produced on Co that we recombusted, we found a bulk stable carbon isotope fractionation of −1.2‰ ± 0.3‰, which was independent of gravimetric yield. This is somewhat less than that observed by Vogel, Southon and Nelson (1987).

DISCUSSION

We analyzed the experimental results to determine the effects of changing reaction temperature, type of catalyst and reducing agent on the gas composition during graphite formation. Our goal is to find the most rapid, reproducible method of forming graphite that performs well in our accelerator. We have chosen to concentrate here on these parameters, even though they are not the

only ones affecting the production of graphite. Table 2 summarizes the different reaction conditions for these experiments.

Effects of Temperature

We conducted 12 experiments with reaction temperatures varying from 500–750°C. We were interested in determining whether the temperature of the reaction influenced the rate of any of the reactions occurring. In analyzing the temperature effects, we considered only the experiments using H_2 as the reducing agent and Co as the catalyst; thus, results from Experiments 10–12 are not included. In order to examine the effect of temperature on reaction rates, we have plotted the amount of time it took for each of the carbon gases to reach a maximum or minimum concentration *vs.* the temperature of the reaction (Fig. 4). The reaction temperature does not correlate with the time it takes to reach the maximum or minimum CO concentration. However, reaction temperature does correlate with the time it takes the CO_2 concentration to reach a minimum with faster disappearance of CO_2 occurring at higher temperatures. Given the relation between temperature and the time to reach the CO_2 minimum, it seems unusual that temperature does not relate to the time it takes to reach the CO maximum. One explanation is that Reaction 1 (Table 1) is rapid and enhanced at high temperatures, and Reactions 4, 5, or 6 act to effectively blur any relationship between the CO maximum and temperature.
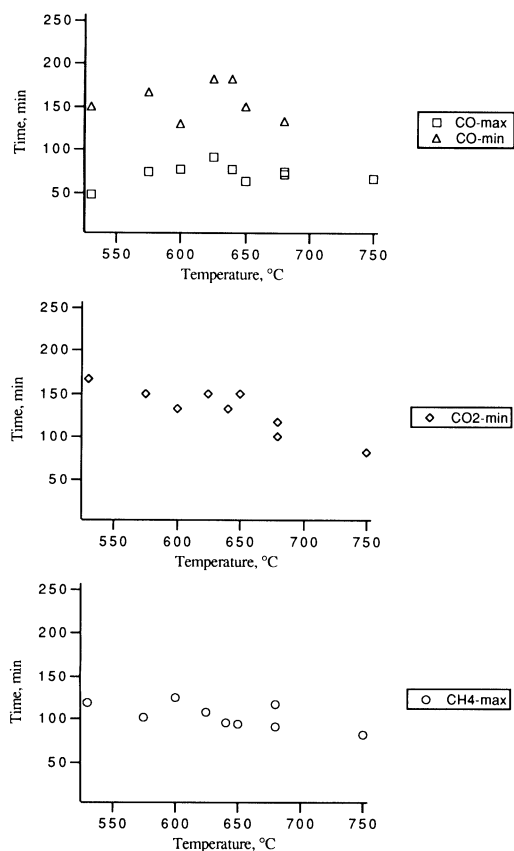
Fig. 4. Relation between the time to reach the observed maxima or minimum and reaction temperature

A small correlation exists between reaction temperature and the time it takes to reach the maximum CH_4 concentration with a quicker appearance of CH_4 occurring at lower temperatures. This is consistent with other studies indicating that the formation of CH_4 is favored at lower temperatures. We were surprised to observe approximately the same amount of CH_4 produced in all the experiments we conducted, because we expected less CH_4 to be formed at higher temperatures. However, these experiments indicate that, within a wide range of temperatures (575–750°C), the amount of CH_4 produced is constant. Also, CH_4 is produced early in the reaction sequence, and then remains at a constant pressure. The small decrease seen at the end of the reactions is from removing gas to introduce into the RGA. This suggests Reactions 5 and 6 are important in producing CH_4 and Reaction 7 is not (Table 1).

The temperature studies indicate the conversion of CO_2 to CO with H_2 is favored at high temperatures. It must also be noted that although CO_2 reacted most rapidly at 750° C, it was virtually impossible to convert the CO produced to graphite at this temperature.

Effects of Different Catalysts

We conducted two H_2 reduction experiments using dendritic Fe as the catalyst (Experiments 10 and 11) in order to investigate the effects of different catalysts on the reaction rates. Experiment 10 was conducted at 625°C and Experiment 11 at 500°C; these experiments can only be directly compared to ones conducted at the same or similar temperatures. Experiment 10 was compared to Experiments 1, 5, 6 and 7; Experiment 11 was compared to Experiment 9. For the reaction at 625°C, the data indicate that all the reactions involved in graphitization are faster when Fe is used as the catalyst. This has been observed before (Vogel, Southon & Nelson 1987) and appears to be related to the form of the catalyst (dendritic *vs.* spherical) rather than the metal. However, for the reactions conducted at the lower temperatures, the reverse is true. It is not clear if the latter observation would remain valid if the low-temperature reactions were conducted at exactly the same temperatures. We have found that graphite produced using Fe or Co behaves similarly in our accelerator (von Reden *et al.* 1992). Thus, for the rapid production of graphite targets, Fe appears to be a better catalyst at temperatures between 575 and 650°C.

Differences with Methods

Our final experiment was to analyze the gas composition changes that occur during the production of graphite using Zn as the reducing agent. Because, in this reaction, the Fe catalyst is heated to 650°C, we compared the results to the H_2 reductions conducted between 625 and 680°C (Table 2). All the data except one point indicate that all the reactions involved proceed more rapidly when H_2 is used as the reducing agent. In comparing the Fe/Zn and Co/H_2 reactions, the biggest difference in the reaction rate is observed during the conversion of CO to graphite. The RGA data clearly indicate that this is a more rapid reaction in the presence of H_2. The data from Experiment 12 suggest that, in the Fe/Zn reactions, the conversion of CO to graphite is a diffusion-controlled process.

Other Observations

Our data also suggest a point in the reaction after which no further changes occur in the concentration of CO, although we still observe a small decrease in the pressure. Continuation of the H_2 reduction beyond this point does not seem worthwhile for improving the reaction yield.

As we noted earlier, CO_2 was rapidly reduced to CO at 750°C, but it was extremely difficult to reduce the CO to graphite. It is possible that the high temperature destroyed the surface of the catalyst and greatly impeded the progress of the reaction.

Based on the results of these experiments, reduction of CO_2 with H_2 using Fe as the catalyst seems to be an appropriate method for rapidly producing graphite targets that perform well in the AMS. However, other important factors that must be considered are the reaction yield and the possibility of isotopic fractionation. Using a gravimetric method to determine the yield, we found that graphite yields from reductions using H_2 varied widely, usually between 60–100% (McNichol, unpublished data). Isotopic analyses of a portion of the graphite samples revealed a constant fractionation of −1.2‰, not one which varied with yield. We were surprised at the absence of a yield-dependent isotopic fractionation and believe this indicates that our gravimetric yield determination is not accurate. Studies have shown that, using the Fe/Zn reduction, yields are more reproducible and higher (Gagnon & Jones 1991), but that the magnitude of the isotopic fractionation is dependent on yield (Jull *et al.* 1986).

CONCLUSIONS

These experiments represent a first attempt at understanding the numerous factors affecting the production of graphite targets for AMS. It is clear from this study that the use of H_2 speeds up the graphitization reaction, yet it is not clear why the yields are so variable. It was surprising, yet encouraging, to discover that there was not a yield-dependent isotopic fractionation using the H_2 reduction. However, until reproducibly high yields can be obtained using the H_2 reduction, it appears that the Fe/Zn reduction remains an attractive method for small, irreplaceable samples.

ACKNOWLEDGMENTS

REFERENCES

Boudouard, O. 1901 Recherches sur les equilibres chimiques. *Annales de Chimie et de Physique* 24(7): 5–85.

Jull, A. J. T., Donahue, D. J., Hatheway, A. L., Linick, T. W. and Toolin, L. J. 1986 Production of graphite targets by deposition from CO/H_2 for precision accelerator ^{14}C measurements. *In* Stuiver, M. and Kra, R. S., eds., Proceedings of the 12th International [14]C Conference. *Radiocarbon* 28(2A): 191–197.

Gagnon, A. R. and Jones, G. A. 1991 AMS radiocarbon results obtained from graphite targets produced at the Woods Hole Oceanographic Institution between 1986 and 1990. Abstract. *Radiocarbon* 32(2): 198.

Manning, M. P. and Reid, R. C. 1977 C-H-O systems in the presence of an iron catalyst. *Industrial Engineering and Chemistry, Process Design and Development* 16(3): 358–361.

O'Hanlon, J. F. 1989 *A User's Guide to Vacuum Technology*, 2nd Edition. New York, John Wiley & Sons: 401 p.

Slota, P. J., Jr., Jull, A. J. T., Linick, T. W. and Toolin, L. J. 1987 Preparation of small samples for ^{14}C accelerator targets by catalytic reduction of CO. *Radiocarbon* 29(2): 303–306.

Turkdogan, E. T. and Vinters, J. V. 1974 Catalytic effect of iron on decomposition of carbon monoxide: 1. Carbon deposition in H_2-CO mixtures. *Metallurgical Transactions* 5: 11–26.

Vogel, J. S., Nelson, D. E. and Southon, J. R. 1987 ^{14}C background levels in an accelerator mass spectrometry system. *Radiocarbon* 29(3): 323–333.

Vogel, J. S., Southon, J. R. and Nelson, D. E. 1987 Catalyst and binder effects in the use of filamentous grapite for AMS. *In* Gove, H. E., Litherland, A. E. and Elmore, D., eds., Proceedings of the 4th International Symposium on Accelerator Mass Spectrometry. *Nuclear Instruments and Methods* B29: 50–56.

von Reden, K. F., Jones, G. A., Schneider, R. J., McNichol, A. P., Cohen, G. J. and Purser, K. H. 1992 The new National Ocean Sciences Accelerator Mass Spectrometer Facility at Woods Hole Oceanographic Institution: Progress and first results. *Radiocarbon*, this issue.