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PRODUCTION OF GRAPHITE TARGETS BY DEPOSITION FROM CO/H_2 FOR PRECISION ACCELERATOR ^{14}C MEASUREMENTS

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ABSTRACT. A method has been developed at the Arizona AMS facility for production of graphite directly from CO_2 by catalytic reduction of CO/H_2 mixtures. The method is a modification of procedures discussed by Vogel *et al* (1984). Currents of $^{12}C^-$ from these targets vary considerably, but have a median value which is 70% of that achieved from spectroscopic graphite. Precisions of ±60 to 100 yr are routinely achieved for ^{14}C ages of 5000-yr-old samples containing one milligram of carbon. The yield of ^{14}C from "blank" targets is 0.6 ± 0.1% of that from modern material.

INTRODUCTION

The reported number of ^{14}C samples studied by accelerator mass spectrometry (AMS) has expanded rapidly from the few available in 1982 to well over 1000 in 1984 (Wölfli, Polach & Anderson, 1984). One of the most important considerations for ^{14}C dating by AMS is the method of target preparation. At Arizona we have performed a large number of measurements (>800) using carbon produced from Mg reduction of CO_2, and melting the carbon with iron powder to make a solid target. These targets give ^{14}C ages to a precision of 150 to 400 yr BP on samples of <10,000 yr BP (Donahue *et al,* 1983; Donahue, Jull & Zabel, 1984), and the precision is limited by the C^- current obtainable from this material in a Cs sputter-ion source (~0.5–2μA).

For higher precision it is necessary to fabricate targets from a material such as graphite, which gives a high C^- current. Several different methods for producing graphite have been used by various groups, including thermal and RF cracking of hydrocarbons (Wand, Gillespie & Hedges, 1984; Beukens & Lee, 1981), DC discharges in CO/H_2 (Andree *et al,* 1984), and high-temperature and pressure treatment of charcoals (Rubin, Mysen & Polach, 1984). Vogel *et al* (1984) at the Zurich AMS symposium reported on the preparation of graphite by the reduction of CO_2 with H_2 over Fe at 600°C. This material reportedly gave C^- beams similar to those from graphite and a ^{14}C background of ~40,000 yr BP. The graphite was formed on the surface of an iron powder, and the mixture was used as the target.

The catalytic decomposition of CO over iron or nickel catalysts has been known for many years (eg, Boudouard, 1901) and has been extensively studied more recently by several authors (Turkdogan & Vinters, 1974; Olsson & Turkdogan, 1974; Walker *et al,* 1959). Three basic reactions occur at pressures of less than a few atmospheres:

$$2CO \rightarrow C + CO_2, \tag{1}$$

$$H_2 + CO \rightarrow C + H_2O, \tag{2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O. \tag{3}$$

The formation of CH_4 (3) is generally more favored at lower temperatures (Wagman *et al,* 1945). Several other gas-phase reactions such as Fischer-Tropsch type formations of organic compounds (Falbe, 1982) can also occur, but should not be significant at conditions important to this discussion. Turkdogan and Vinters (1974) showed that H_2 had an accelerating effect on the rate of deposition of C from CO. The deposition is dominated by reaction (1) below 50% H_2 and the second reaction becomes increasingly important at higher H_2/CO ratios.

In this paper, we discuss the characteristics of carbons produced via these reactions using Ni and Fe catalysts. Ion current, durability and isotopic effects of accelerator targets produced from these carbons are presented, and examples of achievable ^{14}C-age precision and backgrounds are detailed.

METHODS

A measured volume of CO_2 (1.8 to 10cc) prepared from an archaeological or geophysical sample by standard methods (Jull, Donahue & Zabel, 1983) is transferred by cryogenic pumping into a vacuum system that includes two Vycor tubes. One contains zinc powder (50 to 100mg) and the other contains iron powder (10 to 30mg) and a piece of Ni foil (10 to 30mg) ca 3 to 5 cm away from the iron. The system is shown in Figure 1. The finger containing Zn is then heated to about 400°C for two hours to allow most of the CO_2 to be reduced to CO. After this time, hydrogen is admitted in a ratio of H_2/CO between 1.2 and 1.8. The iron-containing finger is then heated to 700 to 750°C. The heater is placed so that the Ni foil is at the top of the oven. The temperature of the Ni is between 500 and 700°C. The cold finger is cooled to $-78°C$ to remove any water formed. After an initial period of ca 2 hours, the pressure starts to decrease and carbon formation on the Ni foil takes place. Typical reaction times are 12 to 24 hours, with overall yields of 40 to 100% carbon. The carbons produced have been identified as graphite by x-ray diffraction and by negative ion current. The material is easily removed from the Ni foil and weighed. Measurements of the $^{13}C/^{12}C$ ratio of the graphite materials are carried out by conventional mass spectrometry. Samples of a number of both starting material and resultant graphites have been analyzed to assess the magnitude of the isotopic fractionation introduced during target preparation.

Yields and Reaction Rate

Yields of graphite have been studied for ca 200 samples as a function of H_2/CO gas ratio and initial gas pressure. For a number of runs, it appeared that less H_2 gas was used than expected for the amount of C produced by reaction (2); this explained by the Boudouard (1901) reaction (1). Both reactions (1) and (2) favor graphite deposition at the temperatures used (Walker *et al,* 1959; Wagman *et al,* 1945). In some cases, low overall yields were observed, suggesting some formation of CH_4; there is a weak correlation of this effect with high H_2/CO ratio. No strong dependence of total carbon deposited was observed as a function of H_2 content. In general, rates of carbon deposition averaged 0.2mg C/hour, with ca 20mg Fe

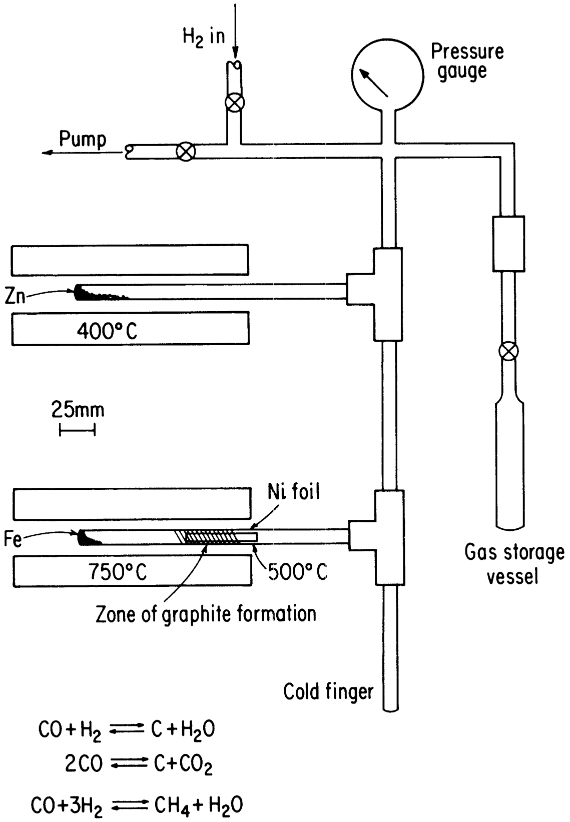

Fig 1. Detail of graphite preparation line

and 30mg Ni foil catalyst. Any dependence on H_2/CO or total pressure is masked to a great extent, presumably by other factors influencing the reaction; however, maximum rates of reaction of ~0.34mg/hr are observed at $H_2/CO \sim 1.5$. For a run with no added hydrogen, carbon was still deposited at 0.11mg/hr. Vogel *et al* (1984) have reported similar reaction rates of about 0.25 to 0.4mg/hr using their method.

GRAPHITE CHARACTERISTICS

$^{12}C^-$ *Ion Currents*

Samples from 0.5 to 0.8mg of graphite are pressed into target holders with a pressure of ca 8kbars. The target holders are designed to ensure that the geometry of the 1-mm-diameter graphite targets is the same for all targets. The $^{12}C^-$ currents obtained from the targets in our cesium sputter-type ion source are plotted for 81 targets (Fig 2). The currents plotted are time averages obtained from the targets during a period of ca 1 hour in the cesium beam. Average currents from various targets range from 2 to 17μA, with a median of ca 7μA. These results can be compared with a current of ca

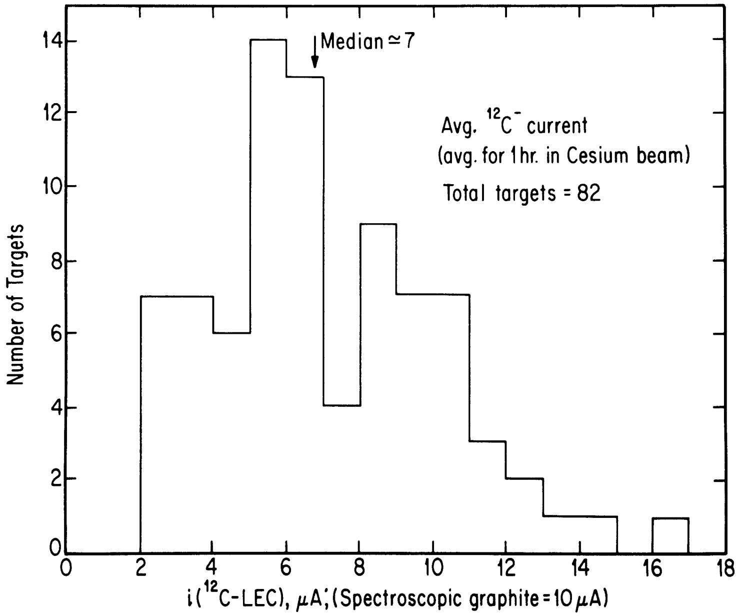

Fig 2. Average $^{12}C^-$ current obtained from 82 targets made from catalytically-reduced graphite. The mean value is ca 7μA.

10μA, obtained from spectroscopic graphite in our standard geometry. In our system, a $^{12}C^-$ current of 1μA results in a ^{14}C rate from modern material of ca 1 count per second.

X-Ray Diffraction

X-ray diffraction (XRD) patterns of a series of graphites which exhibited varying C^- output have been obtained. The diffraction traces show a very consistent broadening of the graphite 002 line of 0.55 to 0.65° (2θ). A d-spacing of 3.35 to 3.36Å indicates well-graphitized material (Walker, McKinstry & Pustinger, 1954). Poorly-crystallized graphites tend to shift d to higher values, along with line broadening (Oya & Marsh, 1982). The XRD results suggest that well-formed crystallites and poorly-crystallized material are both present. An average crystallite size of Lc~150 to 200Å can be calculated from the observed line widths. There is no apparent correlation of C^- output with the small variations in XRD parameters. In some samples, lines of iron carbide have also been observed.

Isotopic Effects

We have studied the $\delta^{13}C$ values of ca 40 samples of pretreated sample material, and the corresponding product graphite. Graphite was converted to CO_2 by standard combustion techniques and analyzed by gas-source mass spectrometry. Results show a variable fractionation of up to −15‰, decreasing with increasing carbon yield. This result is what one expects from a Rayleigh condensation of a solid from a fixed amount of gas phase

(Hoefs, 1980). The average fractionation deduced from our 40 measurements is $\Delta(^{13}C) = -8‰$, and the standard deviation for a single target is $\pm 4‰$.

Background Measurements

Table 1 shows the results of a series of measurements on graphite targets fabricated from material containing no ^{14}C. The weighted average of these measurements is $F_m = (^{14}C/^{13}C)_{Bkgd}/(^{14}C/^{13}C)_{modern} = 0.0058 \pm 0.0013$. The quoted uncertainty is the standard deviation of a single measurement from the weighted average. Using a value of twice that standard deviation results in a maximum ^{14}C age which can be measured; $(Age)_{max} = 47{,}000$ yr.

The fact that our lowest backgrounds measured with natural graphite (Donahue, Jull & Zabel, 1984) are a factor of 6 to 8 lower than the weighted average determined from the data in Table 1, indicates that most of the background in our catalytic graphite targets is introduced during fabrication, and leads to the expectation that this background may be further reduced through improvement in fabrication techniques.

Isotope-Ratio Precisions

In the normal procedure for measuring $^{14}C/^{13}C$ ratios, each wheel of 10 targets contains 2 standard targets. Table 2 shows results of a series of 24 measurements made of the ratio of $^{14}C/^{13}C$ ratios in 2 standard targets mounted in the same wheel. The two standards used were NBS oxalic acid II and AD 1890 bristlecone pine. The results of the measurements were

TABLE 1
Background data

Date	Lab no.	Material	Fraction of modern carbon (F_m)	
5/24/84	3	tank CO_2	0.0088 ± 0.002	
5/29/84	5	tank CO_2	0.0052 ± 0.0004	
7/12/84	12B	tank CO_2	0.0063 ± 0.0026	
6/14/84	14	tank CO_2	0.0092 ± 0.0012	
10/4/84	52	act-5 shells	0.0070 ± 0.0010	
10/4/84	64	tank CO_2	0.0059 ± 0.0007	
12/10/84	74C	$CaCO_3$	0.0084 ± 0.0012	
12/10/84	112C	tank CO_2	0.0088 ± 0.0009	0.0082 ± 0.0007
12/11/84	112D	tank CO_2	0.0074 ± 0.0010	
1/8/85	112E	tank CO_2	0.0078 ± 0.0019	
12/20/84	1737A/B	H_2 treated Ni	0.0061 ± 0.0008	0.0057 ± 0.0006
1/18/85	1737C	"	0.0049 ± 0.0006	
2/13/85	1737D	"	0.0083 ± 0.0013	
3/6/85	1737E	"	0.0058 ± 0.0013	
2/15/85	1915A	tank CO_2	0.0069 ± 0.0007	0.0062 ± 0.0008
	1915B	"	0.0052 ± 0.0008	
4/3/85	1995	$CaCO_3$	0.0047 ± 0.000	
3/6/85	1940	USGS Whalebone	0.0052 ± 0.0004	
	1942	" "	0.0053 ± 0.0005	

Weighted average of all samples = 0.0058 ± 0.0013

TABLE 2

^{14}C ratios of NBS Oxalic II *vs* AD 1890 wood

Date	Fraction modern, (OXII/modern-uncorrected)		$F_m(\delta^{13}C$-corrected)
	*	**	
12/18/84	1.370 ± 0.016	(0.016)	1.373
	1.327 ± 0.025	(0.018)	1.330
	1.351 ± 0.022	(0.018)	1.354
12/19/84	1.348 ± 0.015	(0.014)	1.356
	1.366 ± 0.019	(0.015)	1.374
	1.377 ± 0.019	(0.016)	1.376
	1.350 ± 0.015	(0.015)	1.349
1/3/85	1.351 ± 0.014	(0.014)	
1/7/85	1.383 ± 0.019	(0.019)	1.391
1/8/85	1.336 ± 0.019	(0.013)	1.335
1/15/85	1.366 ± 0.027	(0.015)	
1/18/85	1.351 ± 0.013	(0.013)	
1/23/85	1.379 ± 0.012	(0.012)	
1/30/85	1.350 ± 0.017	(0.017)	1.361
1/31/85	1.350 ± 0.015	(0.014)	1.361
2/6/85	1.343 ± 0.026	(0.015)	1.341
2/8/85	1.385 ± 0.015	(0.015)	1.383
2/13/85	1.335 ± 0.023	(0.019)	1.346
2/15/85	1.329 ± 0.022	(0.022)	1.323
2/26/85	1.310 ± 0.015	(0.014)	1.306
	1.331 ± 0.023	(0.019)	1.327
2/27/85	1.331 ± 0.017	(0.016)	1.327
2/28/85	1.352 ± 0.016	(0.012)	1.346
3/6/85	1.356 ± 0.016	(0.016)	1.350

* Larger of scatter and statistical errors

** Statistical errors

R (weighted mean) = 1.354

σ (weighted mean) = 0.004 (0.3%)

σ (statistical) = 0.004

$$\frac{\text{Measured ratio}}{\text{Known ratio}} = \frac{1.354 \pm 0.004}{1.350 \pm 0.0027} = 1.003 \pm 0.004$$

converted to a ratio R = $(^{14}C/^{13}C)_{oxII}/(^{14}C/^{13}C)_{1950}$ using the calibration curve of Stuiver (1982). Both the numerator and the denominator have been normalized to $\delta(^{13}C) = -25‰$. Results of analyses of the measurements shown in Table 2 are:

1) to a level of 0.3%, the standard deviation of the average of a series of measurements is equal to the statistical uncertainty of that average

2) systematic errors in the measured ratio are <0.4%.

SUMMARY

Various characteristics of graphites produced for $^{14}C/^{13}C$ analysis by TAMS have been reported. The target fabrication method described has allowed us to achieve;

1) $^{12}C^-$ currents time-averaged over 1 hour in the Cs sputter ion source of ca 7μA,

2) ^{14}C age determinations of between ±60 and ±100 yr on material of <5000 yr BP age, using a single target and ca 1 hour of machine time,

3) a ^{14}C background age of 47,000 yr BP,

4) a demonstration of precisions of measurements of the ratio,

$$\{(^{14}C/^{13}C)_{OX\text{-}II}/(^{14}C/^{13}C)_{AD\ 1890}\} \text{ of } 0.3\%$$

limited by statistical uncertainties.

At present we are studying further improvements using smaller samples, different catalysts, and the effect of eliminating H_2 from the process. In the near future we expect to fabricate graphite accelerator targets routinely from samples containing $100\mu g$ of carbon.

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