ing could be the lunar sample described by Brown and Wechsler (*21*) who, to explain the large apparent APD size, suggested that a period of reheating had occurred although this reheating is now clearly not essential.

The isothermal coarsening kinetics of APD's in pigeonite provide good evidence of impurity segregations onto APB's. In metallic alloys, such segregations have given values of *n* between 2 and 4 (*15*). The higher value for pigeonite implies a more severe restriction of APB mobility. There is a fundamental difference between metals, in which the domains arise by atomic ordering, and pigeonite, in which they arise from a displacive transformation. Structural distortions at APB's in pigeonite may provide more suitable sites for the location of particular cations. Ions other than Ca^{2+}, however, may also restrict APB mobility in pigeonite. During heat treatments without graphite, some crystals became slightly oxidized and had smaller domain sizes than those heated for the same time and at the same temperature in the presence of graphite. The slower growth rate could be due to the segregation of Fe^{3+} or vacancies onto the APB's.

Unfortunately, it is not likely that any simple quantitative relationship between domain size and cooling rate can be established on the basis of the results presented here. There appear to be too many variables, particularly relating to the behavior of Ca^{2+}. Even on a qualitative basis, it may be difficult to interpret APD sizes in terms of thermal history without substantial additional evidence.

MICHAEL A. CARPENTER*
Department of Mineralogy and
Petrology, Cambridge University,
Cambridge, England

References and Notes

1. N. Morimoto, *Fortschr. Mineral.* **52**, 52 (1974).
2. P. E. Champness and G. W. Lorimer, in *Electron Microscopy in Mineralogy*, H.-R. Wenk, Ed. (Springer Verlag, Berlin, 1976), p. 174.
3. N. Morimoto and M. Tokonami, *Am. Mineral.* **54**, 725 (1969).
4. G. E. Brown, C. T. Prewitt, J. J. Papike, S. Sueno, *J. Geophys. Res.* **77**, 5778 (1972).
5. C. T. Prewitt, G. E. Brown, J. J. Papike, *Geochim. Cosmochim. Acta* **1** (Suppl. 2), 59 (1971).
6. A. H. Heuer and G. L. Nord, Jr., in *Electron Microscopy in Mineralogy*, H.-R. Wenk, Ed. (Springer Verlag, Berlin, 1976), p. 274.
7. S. Ghose, G. Ng, L. S. Walter, *Geochim. Cosmochim. Acta* **1** (Suppl. 3), 507 (1972).
8. J. S. Lally, A. H. Heuer, G. L. Nord, Jr., J. M. Christie, *Contrib. Mineral. Petrol.* **51**, 263 (1975).
9. M. A. Carpenter, *Phys. Chem. Minerals* **2**, 237 (1978).
10. G. E. Poquette and D. E. Mikkola, *Trans. Am. Inst. Min. Metall. Pet. Eng.* **245**, 743 (1969).
11. M. Sakai and D. E. Mikkola, *Metall. Trans.* **2**, 1635 (1971).
12. D. G. Morris, G. T. Brown, R. C. Piller, R. E. Smallman, *Acta Metall.* **24**, 21 (1976).
13. A. T. English, *Trans. Am. Inst. Min. Metall. Pet. Eng.* **236**, 14 (1966).
14. C. L. Rase and D. E. Mikkola, *Metall. Trans.* **6A**, 2267 (1975).
15. F.-W. Ling and E. A. Starke, Jr., *Acta Metall.* **19**, 759 (1971).
16. H. Kuno, *Proc. Jpn. Acad.* **23**, 111 (1947).
17. R. H. McCallister, *Contrib. Mineral. Petrol.* **65**, 327 (1978).
18. R. Lindner, *J. Chem. Phys.* **23**, 410 (1955).
19. G. Sauthoff, *Acta Metall.* **21**, 273 (1973).
20. R. J. Williams and H. Takeda, *Trans. Am. Geophys. Union* **53**, 551 (1972).
21. G. E. Brown and B. A. Wechsler, *Geochim. Cosmochim. Acta* **1** (Suppl. 4), 887 (1973).

22. I thank my supervisor, Dr. J. D. C. McConnell, for his encouragement and interest, and Dr. D. L. Bish and Prof. C. W. Burnham for their critical comments on the manuscript. The work was undertaken during the tenureship of a Natural Environment Research Council studentship which is gratefully acknowledged.

* Present address: Department of Geological Sciences, Harvard University, Cambridge, Mass.

29 January 1979; revised 25 May 1979

Carbon-14 Dating of Small Samples by Proportional Counting

Abstract. *Conventional carbon-14 dating by means of gas proportional counters has been extended to samples containing as little as 10 milligrams of carbon. The accuracy of the dating procedure has been checked by dating sequoia tree-ring samples of the 1st century A.D. and B.C. and an oak tree-ring sample of the 19th century A.D.*

The advantages of small sample size in carbon-14 dating are evident. In the authentication of works of art, for example, milligram sampling might be permissible in many cases where the removal of as much as a gram of sample would not. In archeological dating it often happens that only small samples are available, which must be totally consumed in order to obtain the data.

Recently a series of studies have demonstrated the feasibility of ^{14}C dating of small samples by means of a procedure consisting of the production of carbon ions in a specially designed source, acceleration of these ions in a Van de Graaff electrostatic accelerator (*1-3*) or a cyclotron (*4, 5*), reversal of the ion charge (in the Van de Graaff) to provide an effective decontamination from ^{14}N, magnetic and electrostatic selection, and finally direct counting. The method has been used for trial dating studies (*2, 5*) and would appear to be of enormous potential, especially for the dating of very old or very small samples. On the other hand, this method does require a machine which is expensive both to purchase [about $500,000 (*3*)] and to operate; for best results it would appear that such a machine should be "dedicated," that is, designed, built, and used for no other purpose (*3*).

We describe here some new develop-

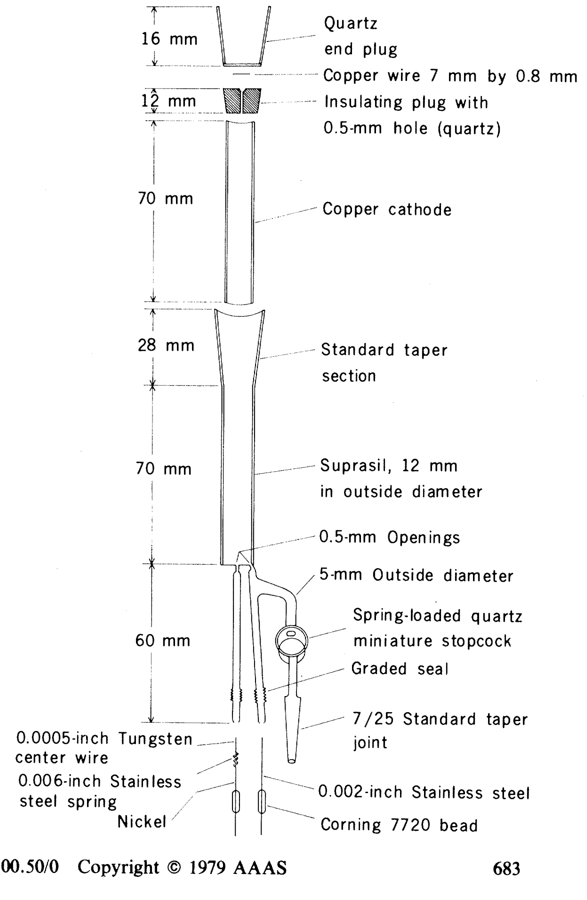

Fig. 1. Construction details for the 5-cm² counter for ^{14}C.

ments in an alternative and very much less expensive method, the extension of conventional ^{14}C dating by proportional gas counters to samples containing as little as 10 mg of carbon (20 cm^3 of CO_2 at standard temperature and pressure). Although we were aware of earlier published accounts of small ^{14}C counters (*6*-*8*; Table 1), we undertook this research project, which was funded by the Conservation-Analytical Laboratory of the Smithsonian Institution (*9*), primarily on the basis of the considerable experience with small low-level proportional counters at the Chemistry Department, Brookhaven National Laboratory. The final step in the solar neutrino detection experiments (*10, 11*) utilizes this technique.

In the small counter designed for the present application, all materials of construction are carefully chosen to be as free of naturally occurring contaminants as possible. The counter envelope is made from optical grade fused silica; all other parts, including the stopcock and the insulating and end plugs, are made of fused silica except for the short lengths of glass used to seal the anode and cathode leads and the electrodes themselves. The cathode is a cylinder formed from 0.013-cm copper foil (99.99 percent pure). Details of the counter construction, diagrams, assembly, and operating procedures are available from the authors (*10*) (Fig. 1).

The counter has design features that make it attractive for measurement of low-level activity. No plastics are used, and so the entire counter may be baked at 300°C during evacuation. Volume efficiencies for ^{14}C in CO_2 have been determined for different individual counters to be between 85 and 90 percent.

We have checked the stabilities of the counters throughout each run by reading out the accumulated counts at least once, sometimes several times, each week during a counting period. The counting data are judged to be acceptable only if a period-to-period comparison of the accumulated counts shows no statistically significant deviations and no progressive change in counting rate during the run.

The quantitative conversion of the carbon within specimens into pure CO_2 was achieved by conventional procedures of combustion and purification (details are available from the authors). The purified CO_2 was collected with a Toepler pump and forced quantitatively into the counter by displacement with mercury. Sample size was such that the final pressure of CO_2 in the counter was about 4 atm.

We judged the purity of this counting gas by analyzing the shape and resolution of the copper Kα x-ray peak (8.07 keV) obtained by exposing the counter to an external iodine-125 source. It has been demonstrated that x-ray peaks from gas counters filled with CO_2 at high pressures become significantly broadened and skewed when even minute amounts of electronegative impurity gases are present. Tests of the combustion and purification system with standard samples of National Bureau of Standards (NBS) oxalic acid, Standard Reference Material (SRM) 398-benzoic acid, SRM 5i-cast iron, and SRM 33-d nickel steel yielded greater than 99 percent recovery in every instance.

Two different kinds of background-reduction apparatus were available. In the first, the counter is placed in a low-level shield consisting of a guard ring of proportional counters (5 cm in diameter) inside a passive shield of 30 cm of iron. In the second, the counters are inside the well of a large cylindrical NaI crystal (25 by 25 cm), whose scintillation pulses are in anticoincidence with the counter pulses. If appropriate routers are used, the first apparatus can handle up to eight counters simultaneously; the second, up to four. From each counter the router directs the pulses into a specified 256-channel memory block in the first half of a 4096-channel analyzer. The optimal conditions for pulse height analysis and ^{14}C signal to background were arrived at

Table 1. Characteristics of small ^{14}C dating counters.

Volume (cm^3)	Pressure (atm)	Counting gas	Weight of carbon (mg)	Counts per day (net) of modern carbon	Counts per day of background	Modern carbon/background ratio	Days to reach 2 percent counting accuracy*		Reference
							Modern carbon	5730 years	
				Earlier small ^{14}C counters					
35	1	CO_2	18.8	288	403	0.72	33.0	114.5	(*6*)
30	1	$C_2H_4 + C_2H_2$	32.2	446	360	1.2	14.7	47.4	(*7*)
40	1	C_2H_6	42.9	439	360	1.2	15.0	48.7	(*7*)
40	0.6	C_2H_4	25.7	288	173	1.7	19.1	59.1	(*8*)
				This work					
5†	4	CO_2	10.7	186	56	3.3	21.5	59.3	Ring shield
5†	4	CO_2	10.7	186	21	8.9	16.5	39.0	NaI shield
7.5	4	CO_2	16	269	77	3.5	14.6	39.9	Ring shield

*Defined as the days of counting necessary to reduce the factor square root of the sum of the net counts plus twice the background counts divided by the net counts to 0.02. †Average response of detectors of this size.

Table 2. Test of dating procedure with tree-ring samples of known age. Ring shields were used for these counters.

Tree-ring date	Net radiocarbon activity* (count day^{-1} mg^{-1})		Radiocarbon date (years)	Equivalent dendrochronological range†	$\delta^{13}C$ relative to PDB‡	Counter number
	Sample	NBS oxalic acid				
31 to 37 B.C., sequoia	13.06 ± 0.24	17.20 ± 0.22	32 A.D. ± 190	130 B.C. to 305 A.D.	−21.2	C-4
31 to 37 B.C., sequoia	13.09 ± 0.22	17.20 ± 0.19	44 A.D. ± 160	100 B.C. to 276 A.D.	−21.2	C-6
36 to 42 A.D., sequoia	12.74 ± 0.24	16.96 ± 0.19	69 B.C. ± 190	380 B.C. to 200 A.D.	−20.6	C-5
1844 to 1850 A.D., oak	15.80 ± 0.13	16.75 ± 0.19	1870 A.D. ± 120	Not available	−24.1	C-12

*Corrected for background; error includes errors in background. †Taken from (*13*). Maximum ranges reported. ‡Values relative to the Pee Dee belemnite (PDB) standard were measured by A. P. Irsa.

by a lengthy series of trial counting measurements (the authors can supply details).

As a test of our overall method and instrumentation, tree-ring samples of known age from sequoia (31 to 37 B.C. and A.D. 36 to 42) and oak (A.D. 1844 to 1850) were dated (*12*). Four counters designated C-4, C-5, C-6, and C-12 were used. The first three counters had volumes of 5 cm^3; the fourth, 7.5 cm^3. The proportional counter guard ring was used for background suppression.

The results of these dating measurements are given in Table 2. In all cases, the measured age agrees with the known age to within the limit of error at the level of 1 σ.

We have not as yet dated any samples of known age with the counters placed in the second (NaI well-crystal) anticoincidence shield. We have, however, measured dead CO_2 counter backgrounds in that shield and have found them to be one-half to one-third of those observed in the first shield (Table 2). The actual counting data for modern carbon and background are given in Table 1, where our pressurized counters in the two shields are compared with previously reported small ^{14}C counters.

The data in Table 2 were derived from counts of 45 days each for the oxalic acid and wood samples and 30 days for background in counters C-4, C-5, and C-6. We now feel that a reasonable counting time is 10^5 minutes for each, that is, about 70 days. Although 7 months are thus needed for an overall experiment, as noted above eight (or four) samples are measured simultaneously, and we may hope that with experience it may not prove necessary to redetermine modern carbon and background each time a date is measured.

It is perhaps premature to compare the use of small counters with Van de Graaff accelerators and cyclotrons in the dating of small samples—in the latter cases the state of the art is rapidly advancing, and the machines in use are not at all optimized as yet for dating studies. For very old or very small samples, or both, it would appear that the accelerator may have greater potential. The accelerator will certainly be the quicker, but also the more expensive, way to date samples of carbon in the 10-mg range. In addition, the accelerator consumes the carbon sample during the dating process.

Using a counter of 5 cm^3 containing CO_2 at 4 atm, counted for 69.4 days, we calculate that, for samples of age 0, 1, 2, and 3 times the ^{14}C half-life, the errors are $\pm$ 90, 150, 270, and 510 years if the ring shield is used and $\pm$ 80, 130, 200, and 350 years if the NaI crystal is used.

We estimate that a complete counting system set up for the simultaneous operation of eight proportional counters would cost on the order of $40,000. However, most conventional ^{14}C dating laboratories now functioning could probably adapt such small detectors to their existing equipment at much less expense.

GARMAN HARBOTTLE
E. V. SAYRE, R. W. STOENNER
Department of Chemistry,
Brookhaven National Laboratory,
Upton, New York 11973

References and Notes

1. D. E. Nelson, R. G. Korteling, W. R. Stott, *Science* **198**, 507 (19 → C. L. Bennett, R. P. Beukens, M. R. Clover, H. E. Gove, R. B. Liebert, A. E. Litherland, K. H. Purser, W. E. Sondheim, *ibid.*, p. 508.
→ C. L. Bennett, R. P. Beukens, M. R. Clover, D. Elmore, H. E. Gove, L. Kilius, A. E. Litherland, K. H. Purser, *ibid.* **201**, 345 (1978).
→ T. H. Maugh II, *ibid.* **200**, 635 (1978).
4. R. A. Muller, *Lawrence Berkeley Lab. Rep. LBL 5510* (1976); *Science* **196**, 489 (1977).
5. ———, E. J. Stephenson, T. S. Mast, *Science* **201**, 347 (1978).
6. T. P. Kohman and P. S. Goel, in *Radioactive Dating* (International Atomic Energy Agency, Vienna, 1963), p. 395.
7. M. A. Geyh, in *Radioactive Dating and Methods of Low-Level Counting* (International Atomic Energy Agency, Vienna, 1967), p. 575.
8. H. Oeschger, *ibid.*, p. 13.
9. Funded by the Conservation-Analytical Laboratory of the Smithsonian Institution under contract FC-5-53083 (Dr. R. M. Organ, laboratory director).
10. F. H. Kummer, R. W. Stoenner, R. Davis, Jr., *Brookhaven Natl. Lab. Rep. 16972* (1972).
11. R. Davis, Jr., *Brookhaven Natl. Lab. Rep. 24674* (1978).
12. Tree-ring samples were supplied by the Applied Science Center for Archaeology, University of Pennsylvania.
13. E. K. Ralph, H. N. Michaels, M. C. Han, *Mus. Appl. Sci. Center Archeol. (Univ. Pa.) Newsl.* **9** (No. 1), 1 (1973).
14. Research performed at Brookhaven National Laboratory under contract with the U.S. Department of Energy.

1 March 1979; revised 29 May 1979

Chrysotile Asbestos in a California Recreational Area

Abstract. *Dustfall along roads and trails being used recreationally in the Clear Creek area of San Benito County, California, located in the New Idria serpentinite, was found to be 90 percent or more chrysotile asbestos. Personal samplers worn by motorcyclists using one of the trails showed concentrations of airborne fibers ranging from 0.3 to 5.3 fibers per milliliter, according to methods prescribed for monitoring occupational exposures. The present workplace standard for brief exposures to asbestos is 10 fibers per milliliter; 5 fibers per milliliter is the proposed standard. The average total dust concentration estimated from personal samplers was approximately 20 milligrams per cubic meter of roughly 90 percent chrysotile. To our knowledge, this is the first demonstration of asbestos exposures of this magnitude, in size ranges known to be pathogenic, resulting from natural deposits not associated with mining, milling, or industrial use.*

Analysis of a sample of rock from the Clear Creek area in San Benito County, California, submitted by the Bureau of Land Management (BLM) of the U.S. Department of the Interior in mid-1977, showed a high concentration of chrysotile. The area is in a serpentine massif, part of the New Idria–San Benito body, known to contain this form of asbestos (*1, 2*). A warning sign was posted, and additional studies were requested to determine whether chrysotile fibers were present in the air and water of the area. These studies were made during the spring and summer of 1978 and are the subject of this report.

The BLM supervises some 60,000 acres of federally owned land located in the southern Diablo Range, about 115 miles southeast of San Francisco. A portion of this land, comprising the Clear Creek watershed, has been designated a recreational area. Among its major attractions are sparsely vegetated and erosion-resistant slopes in one of the serpentine-rich areas. These attract adventurous cyclists. Of the 41,150 users of the area in 1975, about 85 percent were operators of off-the-road vehicles, principally motorcycles; the others were campers, hunters, or rock collectors. Most of the motorcyclists were weekend users and included many families with children.

The geology and mineralogy of the New Idria–San Benito serpentinite have been described by a number of observers (*2–4*). It is one of the larger of several major ultramafic complexes in California and appears as an outcropping more than 6 km wide and 20 km long at the southern end of the Diablo Range. In 1958, Rice and Matthews of the California Division of Mines (*5*) identified the white, fibrous, matted material that covers many hillsides in the area as chrysotile; its commercial development began in the early 1960's. Mumpton and Thompson (*2*) have reported on the mineralogy and possible origin of what has been called the Coalinga asbestos deposit. Their analyses of a large number of samples collected on the surface, in mine pits,

0036-8075/79/1109-0685$00.50/0 Copyright © 1979 AAAS