each year the equivalent of 0.8×10^9 to 1.3×10^9 tons of shale assayed at 20 gallons of oil per ton. The corresponding annual release of carbon as CO_2 from retorting and burning the shale oil could range from about 0.06×10^9 tons (for low-temperature retorting, 100 percent recovery as measured by modified Fischer assay) to 0.17×10^9 tons (for high-temperature direct retorting, 60 percent recovery as measured by modified Fischer assay). For comparison, burning 1 million barrels of conventional crude oil per day generates about 0.04×10^9 tons of carbon as CO_2 each year.

The present rate of production of carbon as CO_2 from conventional fuels is close to 5×10^9 tons per year; hence, if 1 million barrels of shale oil were consumed each day in addition to present consumption of conventional fuels, the annual global production of CO_2 from fossil fuels would increase by 1 to 3 percent. If 1 million barrels of shale oil were substituted each day for the same amount of conventional oil in the present worldwide fuel mix, the corresponding increase in CO_2 production would be 0.5 to 2.5 percent of the present annual global flux of CO_2 from utilization of fossil fuels.

Although extrapolation into the future is quite speculative, recent government reports suggest an upper limit for the cumulative production of CO_2 from western U.S. oil shales by the year 2000 (*11*). Loosely based on commercialization projections, our estimate for this limit is the equivalent of production by high-temperature retorting of 1 million barrels per day for 20 years. During this time, retorting and burning that much shale oil would produce 3×10^9 to 4×10^9 tons of carbon as CO_2, or 1 to 2 percent of the 150×10^9 to 300×10^9 tons anticipated from utilizing conventional fossil fuels between 1980 and 2000 (*12*). The total identified resources (*2*) in the Green River Formation amount to about 1.8×10^{12} barrels contained in 5×10^{12} tons of rock. If half of these resources is eventually recovered with high-temperature techniques and subsequently burned, the total release to the atmosphere of carbon as CO_2 could be about 300×10^9 tons. The rate of CO_2 release from oil shales will ultimately depend on the method and rate of exploitation which could last for more than a century.

ERIC T. SUNDQUIST
U.S. Geological Survey,
Reston, Virginia 22092

G. A. MILLER
Area Oil Shale Supervisor's Office,
U.S. Geological Survey,
Grand Junction, Colorado 81501

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12. This range of conventional fossil fuel consumption corresponds to an increase in the concentration of atmospheric CO_2 of 30 to 60 parts per million by the year 2000, assuming that half of the CO_2 produced will remain in the atmosphere.
13. We thank numerous reviewers, particularly J. W. Smith and P. B. Barton, Jr., for their constructive comments and criticisms.

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Soot in Urban Atmospheres: Determination by an Optical Absorption Technique

Abstract. *We have used the high optical absorptivity of urban and source particulates to trace their "graphitic" component. The optical absorptivity and the particulate carbon loading show a strong correlation. Analyses of the data indicate that primary soot emissions compose a major fraction of the carbonaceous aerosol and put a low limit on secondary organic material produced in correlation with the ozone concentration.*

Carbon-, sulfur-, and nitrogen-containing particles account for most of the anthropogenically generated particulate burden in urban areas. Considerable attention has been devoted to understanding the origin and speciation of the sulfur and nitrogen components, but until recently relatively little effort has been directed toward the carbonaceous aerosol, which is often the single most important contributor to the submicron aerosol mass and is expected to have a large impact on visibility and health.

The major cause of these carbon particles is fossil fuel combustion, which produces both primary particulate carbonaceous emissions (soot) and gaseous hydrocarbons, which can be transformed in the atmosphere by gas-to-particle conversion processes to secondary organic material. There has been considerable uncertainty and debate over the relative importance of primary and secondary carbonaceous particles in the urban air (*1*). It is important to resolve this issue since it is obvious that a control strategy and technology for particulate carbon pollution abatement will depend on which of these alternatives prevails.

We describe here the application of a new analytical method which uses the unique optical properties of "graphitic" (*2*) soot to trace the primary component of the carbonaceous particulates under widely different atmospheric conditions over a wide geographical area. Our results are consistent with the earlier work of Novakov *et al.* (*3*) and indicate that primary soot emissions compose a major fraction of the urban carbonaceous aerosol.

Soot consists of a graphitic component and an organic component. The graphitic component can be conveniently monitored because of its large and uniform optical absorptivity, which has recently been shown to be responsible for the gray or black appearance of ambient and source particulate samples collected on various filter media (*4, 5*). The graphitic content of the aerosol can be measured by an optical attenuation method developed in our laboratory (*4*). We have also determined the total particulate carbon, which enables us to study the correlation between the graphitic and the total carbon content of the aerosol (*6*). The correlation or lack of it should depend on the relative amounts of primary and secondary material.

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Measurements have been obtained of the optical attenuation and the total carbon content of over 1000 ambient samples collected in two California air basins and in the Chicago area. These samples were collected daily from 1 June 1977 at Lawrence Berkeley Laboratory, Berkeley, California; from 15 July 1977 at the Bay Area Air Quality Management District monitoring station, Fremont, California; and from 19 August 1977 at the South Coast Air Quality Management District monitoring station, Anaheim, California. Samples were also taken from 23 March 1978 to 9 April 1978 and then from 19 February 1979 on at Argonne, Illinois. At all these sites two samples were collected in parallel on Millipore filter membranes 47 mm in diameter (1.2-μm nominal pore size, type RATF), which were used for the optical attenuation measurements, and prefired quartz fiber filters (Pallflex type 2500 QAO), which were used for the carbon determinations. The monitored flow rates varied between 1.0 and 2.6 $m^3\ cm^{-2}\ day^{-1}$ (that is, 0.24 to 0.62 cubic feet per minute for the total exposed filter area of 9.6 cm^2), corresponding to face velocities of 11.6 to 30.1 cm sec^{-1}. The samples were not segregated by size. A number of representative source particulates have also been sampled and analyzed,

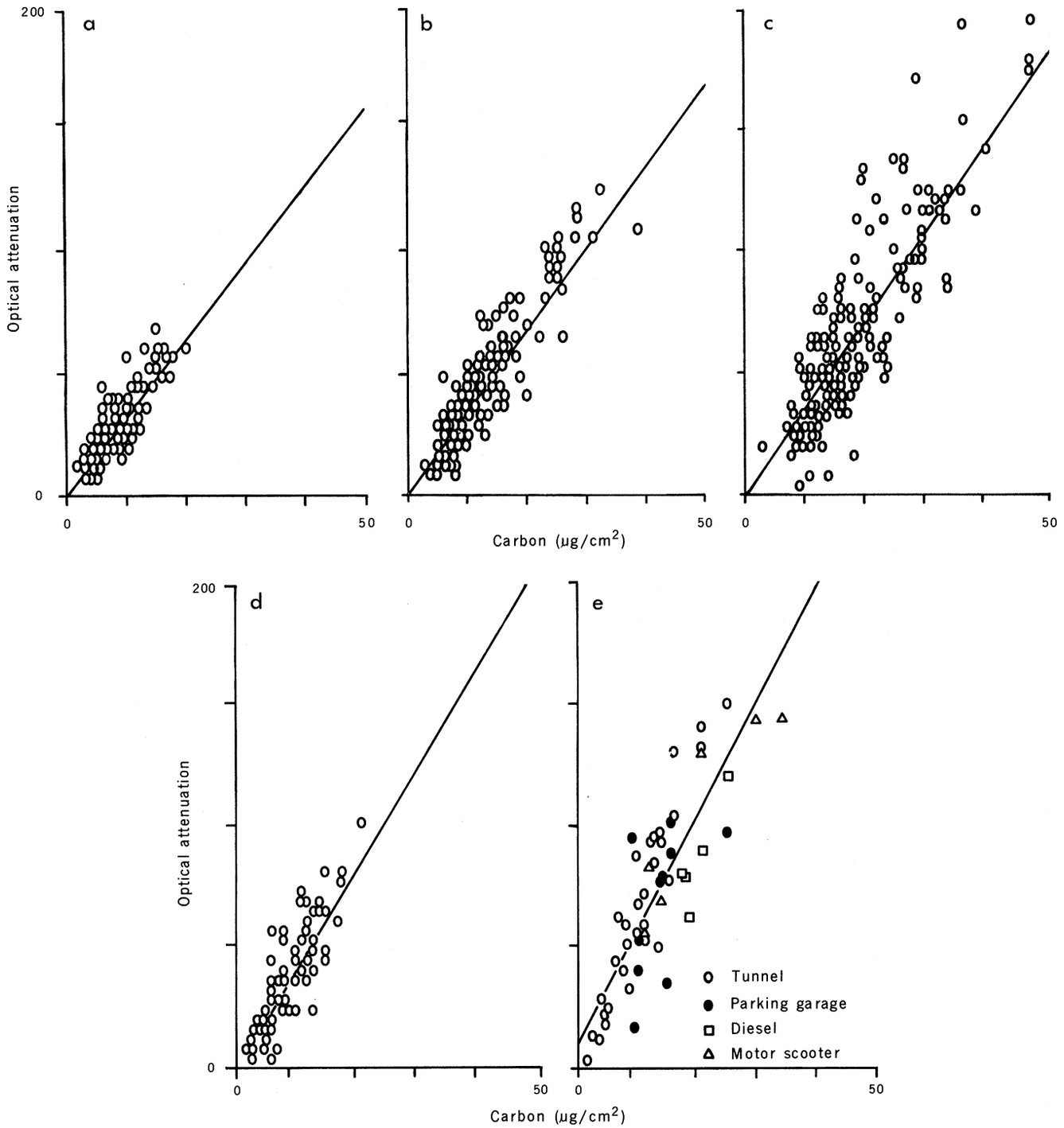

Fig. 1. Plots of optical attenuation versus carbon loading for particulate samples collected at (a) Berkeley, (b) Fremont, (c) Anaheim, and (d) Argonne and (e) from various combustion sources. The solid line represents the least-squares fit of the data points.

including particles collected (i) in a freeway tunnel, (ii) in an underground parking garage, (iii) from a small two-stroke engine, and (iv) from a four-stroke diesel engine.

The optical attenuation is defined as

$$A = -100 \ln (I/I_0)$$

where I_0 is the intensity of the light (wavelength = 0.63 μm) transmitted through a blank Millipore filter and I is the intensity through a loaded filter. If we assume fixed optical constants, this quantity should be proportional to the graphitic content of the aerosol. The carbon loading on the quartz fiber filters was determined by a total combustion–carbon dioxide evaluation method (*7*). The quartz filters were prefired overnight at 800°C to remove all combustible carbon before sample collection. Periodic analysis of blanks typically yielded about 0.5 μg of carbon per square centimeter, as compared with loadings after exposure in the range of 20 to 100 μg cm^{-2}.

Photochemical gas-to-particle conversion reactions should be most pronounced in the summer in the Los Angeles air basin, whereas in the winter in Argonne or Berkeley these reactions should play a much smaller role and the primary component should be much more important. These different photochemical conditions should manifest themselves in the ratio of the graphitic soot to the total carbon content of the particles. That is, under high photochemical conditions one would expect this ratio to be significantly smaller than under conditions heavily influenced by sources. In view of the above, the graphs of optical attenuation versus carbon loading shown in Fig. 1 for samples collected at Berkeley, Fremont, and Anaheim, California, and Argonne, Illinois, as well as various combustion sources, are unexpected. Analyses of the data show the following:

1) There is a strong correlation ($r >$ .85) between optical attenuation and total suspended particulate carbon at every site.

2) The least-squares fit of the data shows relatively small regional differences with a trend toward increasing slope (enrichment in primary carbonaceous matter) for samples collected, respectively, at Berkeley, Fremont, Anaheim, and Argonne.

3) There is a strong correlation between the optical attenuation and the carbon loading for the source samples, and the slope of the least-squares fit is comparable to that found in the ambient samples.

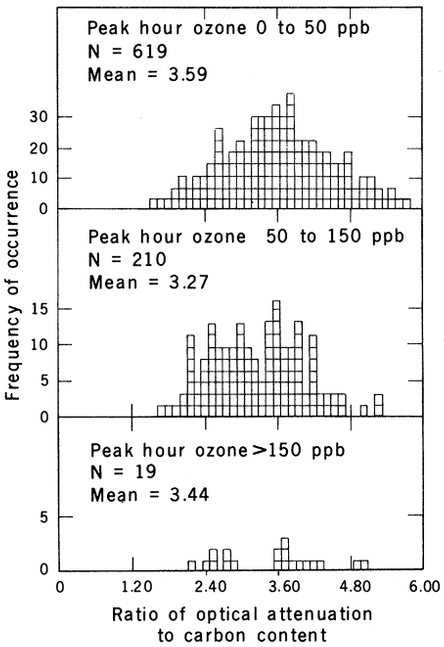

Fig. 2. Distribution of the ratios of optical attenuation to total carbon content (in micrograms per square centimeter) subdivided according to the peak ozone concentration (*ppb*, parts per billion). The means of the distributions are only marginally smaller at larger ozone concentrations, which puts a rather low limit on secondary organic material produced in correlation with ozone.

Result 1 shows that it is possible to predict the total amount of particulate carbon with a root-mean-square deviation of 30 percent by means of a simple measurement of optical attenuation. This implies that the fraction of graphitic soot to total particulate carbon is approximately constant under the wide range of conditions occurring at a given site. On specific days there can be large variations in the ratio, but no large systematic differences are found as a function of the ozone concentration, which has been viewed as a monitor of the photochemical activity.This is graphically demonstrated in Fig. 2, which shows the distribution of the ratios of the optical attenuation to total carbon content for ambient samples from all the California sites taken together, subdivided according to peak hour ozone concentration. Clearly, there is no trend for high-ozone days to be characterized by aerosols which have a significantly reduced graphitic fraction. This places a rather low limit on the maximum importance of secondary organic particulates formed in correlation with the ozone concentration.

The least-squares fit of the data in Fig. 1 shows regional differences which are presumably related to the fraction of the carbonaceous aerosol due to primary emissions. These differences would suggest an increase in the relative importance of the primary component for samples collected, respectively, at Berkeley, Fremont, Anaheim, and Argonne. From the photochemical viewpoint, the results for Argonne are quite reasonable since many of the samples were collected in the winter. However, the trend of the California sites is surprising and indeed is opposite to what would be expected if a significant secondary component was produced as a result of photochemical activity, which should be at its highest level in Anaheim and its lowest in Berkeley.

A strong correlation is also observed between the optical attenuation and the carbon content of the source samples (Fig. 1e). The slope of the least-squares fit of the source data is somewhat larger than that found for the ambient samples, but there is still considerable overlap between the two data sets. This similarity in the absorbing properties of the ambient and source samples strongly suggests that a large component of the carbonaceous aerosol studied is of primary origin. However, because of the spread in both the ambient and the source data, these results do not exclude the possibility of significant secondary species produced in nonozone-related reactions. The results of Grosjean (*8*), Gundel *et al.* (*9*), and others (*10*) suggest that the polar component of the carbonaceous aerosol cannot be accounted for directly from primary emissions. The trend of the sources to have higher optical attenuation per unit carbon than that found in urban air may also be indicative of a secondary component. An analysis based on a comparison of the least-squares fit of the source and ambient data at all sites is consistent with a secondary component, which ranges between 15 and 35 percent of the carbonaceous mass. The data presented here from two California air basins and the Chicago area may raise serious questions about the present control strategy for the carbonaceous aerosol. The generality of these results to other areas across the United States and some areas of Europe is presently being tested. Preliminary data obtained on samples from New York City, Denver, Seattle, Washington, D.C., and Portland are in agreement with the findings outlined in this report.

H. ROSEN
A. D. A. HANSEN
R. L. DOD
T. NOVAKOV
Lawrence Berkeley Laboratory, University of California, Berkeley 94720

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Clarkforkian Land-Mammal Age: Revised Definition, Zonation, and Tentative Intercontinental Correlations

Abstract. *New faunal and stratigraphic evidence documents the validity of the North American Clarkforkian Land-Mammal Age. Its limits are defined by the initial appearances of immigrant taxa. In the type area (northwestern Wyoming), the Clarkforkian is subdivided into three zones. Clarkforkian faunas are approximately correlative with latest Paleocene–earliest Eocene faunas of the Paris Basin of Europe and in part with the Gashato–Naran Bulak faunas of Mongolia.*

Wood *et al.* proposed the Clarkforkian as the last of the North American Paleocene provincial ages—now more widely termed land-mammal ages (*1*, *2*)—and based it "on the Clark Fork Member (and faunal zone) of the Polecat Bench Formation" (*3*, p. 9) (type area in the Clark's Fork Basin, northern Bighorn Basin, Wyoming). Their faunal characterization of the Clarkforkian, including first and last appearances, index fossils, and characteristic taxa, was drawn mainly from earlier studies that had suggested the presence of a distinctive Clark Fork assemblage in this basin (*4–7*).

Until recently, collections of Clarkforkian age were small and few in number, and precise stratigraphic data for most specimens were inadequate. As a result, the original definition of the Clarkforkian (*3*) included inaccuracies both in faunal indicators and stratigraphic details [for example, the "Clark Fork" is not a valid member of the Polecat Bench Formation, nor is the Clarkforkian fauna restricted to that formation (*8*)]. In addition, the misconception that the limits of the Clarkforkian should coincide with epoch or formation boundaries led to dispute over the exact age of the Clarkforkian. For these reasons, the validity of the Clarkforkian came into question (*9*), and a reassessment became mandatory.

Since 1975, personnel of the University of Michigan (UM) Museum of Paleontology, Ann Arbor, under the direction of P. D. Gingerich, have conducted intensive paleontological and stratigraphic investigation in the Clark's Fork Basin. Vertebrate fossils have been systematically collected from a richly fossiliferous section approximately 1000 m thick. The lowest part of the section yields fauna of late Paleocene (late Tiffanian) age (*6*, *10*); the upper part, mammals of early Eocene (early Wasatchian) age (*5*). Clarkforkian mammals occur in the intervening interval, about 450 m thick, in the uppermost Polecat Bench Formation and the lower part of the Willwood Formation (*8*, *11–14*). Thousands of mammalian fossils have now been collected from nearly 300 UM localities, about half of which are Clarkforkian in age (*8*). Although the Clarkforkian fauna is dominated by mammals of Paleocene aspect, it also contains taxa characteristic of the early Eocene. Thus it is an important transitional fauna that spans the time during which many archaic mammals were supplanted by mammals of more modern aspect, including the earliest members of several extant higher taxa.

The beginning of the Clarkforkian can now be defined by the first appearance of Rodentia (*Paramys*) and the mutual first occurrence of Tillodontia (*Esthonyx*), the pantodont *Coryphodon*, and the condylarth *Haplomylus*. The end of the Clarkforkian (beginning of the Wasatchian) is indicated by the first appearance of Artiodactyla (*Diacodexis*), Perissodactyla [*Hyracotherium (15)*], adapid and omomyid primates, and hyaenodontid creodonts, and by the first common occurrence of the condylarth *Hyopsodus* (*8*, *12*, *14*). The suites of taxa that define the boundaries of the Clarkforkian appear essentially simultaneously in the fossil record, suggesting that they represent waves of immigrants (Fig. 1). Several species of Clarkforkian index fossils are now known (*8*), including the common primate *Plesiadapis cookei* [listed by Wood *et al.* (*3*) but now known to be restricted to middle Clarkforkian]. Stratigraphic ranges and precise stratigraphic occurrences of all Clarkforkian mammal species from the Clark's Fork Basin are detailed by Rose (*8*).

Assemblages of definite Clarkforkian age are now recognized from several localities in Wyoming, Montana, and Colorado (*8*, *16*). More than 80 species of mammals are recorded in these assemblages; of these, 70 were found in the Clark's Fork Basin (*8*, *17*, *18*). Most are new records for the Clarkforkian, and about 25 percent are new species described since the inception of the UM project.

Ranges of Clarkforkian mammals in the Clark's Fork Basin permit subdivision of the type Clarkforkian into three biostratigraphic zones. According to Gingerich's zonation of the middle and late Paleocene of North America (based on evolution of plesiadapid primates), the late Tiffanian *P. simonsi* Zone was followed by the *P. cookei* Zone, then believed to occupy all of Clarkforkian time (*11*, *19*). A new species of *Plesiadapis* is now known from strata of latest Tiffanian and early Clarkforkian age, above beds yielding *P. simonsi* and below those yielding *P. cookei* (*8*). The new species is part of the *P. simonsi–P. cookei* lineage but is easily distinguished from both. Thus the stratigraphic range of the new species defines a new *Plesiadapis* zone of latest Tiffanian–early Clarkforkian age. This zone

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