LBL-16147 c. 2
Preprint

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY
AUG 3 1983
LIBRARY AND
DOCUMENTS SECTION

ENERGY & ENVIRONMENT DIVISION

Submitted to Nature

IDENTIFICATION OF COMBUSTION GENERATED CARBON PARTICLES IN THE ARCTIC ATMOSPHERE

H. Rosen and T. Novakov

May 1983

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.

ENERGY
AND ENVIRONMENT
DIVISION

LBL-16147 c. 2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

IDENTIFICATION OF COMBUSTION GENERATED CARBON PARTICLES IN THE ARCTIC ATMOSPHERE

H. Rosen and T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Recent studies in the Alaskan Arctic[1-3] show the presence of substantial concentrations of carbon- and sulfur-containing particles that seem to be characteristic of the Arctic region as a whole.[4-6] These particles are effective scatterers and absorbers of visible radiation[3,7] and appear to be responsible for the phenomenon of Arctic haze first reported by Mitchell.[8] On the basis of trace element analyses, it has been suggested that these particles originate from anthropogenic sources at mid-latitudes.[1,4] Direct substantiation of combustion-generated particles in the Arctic atmosphere has been provided by the identification of large concentrations of graphitic carbon particles at the GMCC-NOAA observatory near Barrow, Alaska.[3] The concentrations of these particles during winter and spring is only about a factor of 4 less than typical urban concentrations in the United States.[3] These graphitic particles, which can only be produced from high-temperature combustion processes, have been identified on a molecular level using Raman spectroscopy. If one excludes natural burning processes that are not expected to be a significant source term during winter and spring when the Arctic haze is at a maximum, then one can attribute these graphitic particles directly to anthropogenic activities. These particles, which have large absorption cross

*This work was supported by the Director, Office of Energy Research, CO_2 Research Division of the U.S. Department of Energy under contract DE-AC03-76SF00098 and by the National Oceanic and Atmospheric Administration under contract NA81RAG00254, Mod. 1.

sections ($\sim 10\ m^2/g$) in the solar spectral region, can lead to significant heating effects over the high surface albedo polar icecap.[9-11] The magnitude of these effects largely depends on the vertical and horizontal distributions of the graphitic particles as well as their concentrations as a function of time of year.[10,11] In this letter, we report on an extension of our studies of carbon particles in the Alaskan Arctic to the Canadian Arctic and the Norwegian Arctic. These studies, using the Raman scattering technique, identify substantial concentrations of graphitic carbon particles at ground-level stations throughout the western Arctic.

The Raman spectroscopy apparatus uses a Coherent Radiation argon ion laser producing 1 W of power at 514 nm. The laser beam is focused by a 75-mm focal length cylindrical lens to a spot 0.06 mm x 2 mm on the sample surface via a small mirror, and the backscattered radiation is collected and imaged by an f/1 lens onto the slit of a 1-m Jarrell Ashe double monochromator equipped with two 1180-grooves/mm gratings blazed at 5000 Å. The output of the spectrometer is detected by an FW130 photomultiplier cooled to -20°C and used in a photon-counting mode. The pulses, after appropriate shaping, are counted and displayed on a multichannel analyzer. A computer-controlled grating drive made by RKB, Inc., allows a given spectral region to be scanned many times and added to the memory of the multichannel analyzer, greatly improving the SNR. In order to minimize heating effects, the highly absorbing samples used in these experiments are rotated at 1800 rpm by a motor, which increases the area illuminated by the laser beam by a large factor with almost no loss in signal level. The focal spot of the laser is located approximately 5 mm below the axis of rotation so that the effective illuminated area is an annulus of 5-mm radius and 2-mm width, resulting in the low power density of $\sim 1\ W/cm^2$.

The Raman spectra are obtained directly from aerosol particles collected on various filter media without any pretreatment procedures. These spectra are observed on top of a large fluorescent background, which is due both to the filter media and the highly fluorescent material in the sample. Irradiation of the sample with the argon laser for 24 hr reduced this background by about an order of magnitude. The intensity of the Raman spectra were typically about 1% of the fluorescent background. Aerosol samples were obtained from six Arctic sites: Barrow in the Alaskan Arctic; Mould Bay, Igloolik, and Alert in the Canadian Arctic; and Bear Island and Spitzbergen in the Norwegian Arctic. The samples from the Alaskan Arctic were collected on prefired quartz-fiber filters (Pallflex 2500 QAO) with a sampler installed at the NOAA-GMCC observatory in cooperation with B.A. Bodhaine of the GMCC program. The samples from the Canadian and Norwegian Arctic were collected on Whatman 41 filters and were provided respectively by L.A. Barrie of the Canadian Atmospheric Environment Service and B. Ottar of the Norwegian Institute for Arctic Research.

Raman scattering and infrared absorption spectroscopy are complementary techniques that measure the vibrational spectra of gases, liquids, and solids. Often vibrational modes that are infrared inactive are Raman active and vice versa. Graphitic structures in which trivalent carbon atoms occupy lattice sites in a two-dimensional hexagonal honeycomb network have intense Raman modes but very weak infrared vibrational spectra. These Raman modes, which were first observed by Tuinstra and Koenig,[12] enable the identification of graphitic structures even in the presence of a complex mixture of substances. Solvent extraction, heat treatment, optical absorption, and morphology studies[13] can provide indirect evidence for a graphitic component; but Raman spectroscopy appears to be the only presently available method for making unambiguous

identifications on a molecular level.

The Raman scattering technique has been applied to identify substantial concentrations of graphitic particles in combustion effluents, urban air,[14,15] and the Alaskan Arctic.[3] These results are shown in Fig. 1, where the spectrum of a sample collected in December 1979 at the NOAA-GMCC observatory in the Alaskan Arctic is compared with spectra of urban particulates, various source emissions, carbon black, and polycrystalline graphite. All spectra show the presence of two intense Raman modes that have been attributed to phonons propagating within graphitic planes.[12] The Raman spectrum of a single crystal of graphite consists of a single band near 1575 cm^{-1}, which has been identified as an E_{2g} vibration of the hexagonal layers.[12] Polycrystalline graphite shows another band at 1355 cm^{-1}, which is not fully understood but has been attributed to the breakdown of selection rules.[12] A small shift in the frequency of the 1575 cm^{-1} Raman mode has also been observed, which apparently depends on the degree of order in the aromatic structures.[16] Such a shift is evident in comparing the spectra of polycrystalline graphite to the other spectra presented in Fig. 1. It is also evident from the figure that the frequency of the vibrational modes in carbon black and those in particles collected from various sources, urban air, and the Alaskan Arctic are coincident to ± 10 cm^{-1}, which is the estimated experimental error. This close correspondence has been used to show the presence of graphitic particles in urban air[14] and in the Alaskan Arctic.[3] In Fig. 2 these measurements are extended to samples collected from three sites in the Canadian Arctic (Mould Bay, Igloolik, Alert) and two sites in the Norwegian Arctic (Spitzbergen, Bear Island). All samples were collected at similar times of the year; but due to sample availability, some samples are from 1980 and others from 1981. It is clear from the spectra that all sites show the presence of significant

concentrations of graphitic particles. There are some differences in the relative intensities and line shapes of the two Raman modes, but these could be due to systematic errors in fluorescence subtraction for the 1350^{-1} mode, which is located on a highly sloping background. If one assumes fixed optical constants (Raman cross sections, absorption cross sections), one can use the integrated intensity of the 1600 cm^{-1} Raman mode as a measure of the relative concentrations of graphitic particles at these sites. These analyses indicate that the concentrations at all these sites are quite comparable with the largest and smallest within about a factor of 3 of each other. The relative ordering of these concentrations for Spitzbergen, Bear Island, Barrow, Mould Bay, Alert, and Igloolik are: 2.1/1.7/0.8/0.8/0.7. It should be emphasized that this analysis is for a particular time interval, and the relative contributions could vary considerably from one time period to the next.

In summary, these results show that the large concentrations of graphitic particles found at the Barrow, Alaska, site are not a local phenomenon but are characteristic of ground-level stations across the western Arctic. If these highly absorbing particles occur at substantial concentrations throughout the Arctic troposphere, then they may have a significant impact on the Arctic radiation balance and climate.

Acknowledgements

I would like to acknowledge Dr. B. A. Bodhaine of the N.O.A.A. - G.M.C.C. program, Dr. L. A. Barrie of the Canadian Atmosphere Environment Service and B. Ottar of the Norwegian Institute of Arctic Research for providing samples respectively from the Alaskan, Arctic; the Canadian Arctic and the Norwegian Arctic.

References

1. Rahn, K.A. and McCaffrey, R.J., Ann. N.Y. Acad. Sci. 338, 486-503 (1980).

2. Shaw, G.E., Atmos. Environ. 15, 1483-1489 (1981).

3. Rosen, H., Novakov, T., and Bodhaine, B.A., Atmos. Environ. 15, 1371-1374 (1981).

4. Barrie, L.A., Hoff, R.M., and Duggupaty, S.M., Atmos. Environ. 15, 1407-1419 (1981).

5. Ottar, B., Atmos. Environ. 15, 1439-1445 (1981).

6. Heintzenberg, J., Tellus 32, 251-260 (1980).

7. Bodhaine, B.A., Harris, T.M., and Herbert, G.A., Atmos. Environ. 15, 1375-1389 (1980).

8. Mitchell, J.M., Jr., J. Atmos. Terr. Phys., Special Suppl., 195-211 (1957).

9. Shaw, G.E., and Stamnes, K., Ann. N.Y. Acad. Sci. 338, 533-539 (1980).

10. Porch, W.M., and MacCracken, M.C., Atmos. Environ. 16, 1365-1371 (1981).

11. Cess, R.D., Atmos. Environ., accepted for publication (1983).

12. Tuinstra, F., and Koenig, J.L., J. Chem. Phys. 53, 1126-1130 (1970).

13. Wolff, G.T., and Klimisch, R.L., eds. Particulate Carbon: Atmospheric Life Cycle (Plenum, New York, 1982).

14. Rosen, H., Hansen, A.D.A., Gundel, L., and Novakov, T., Appl. Opt. 17, 3859-3861 (1978).

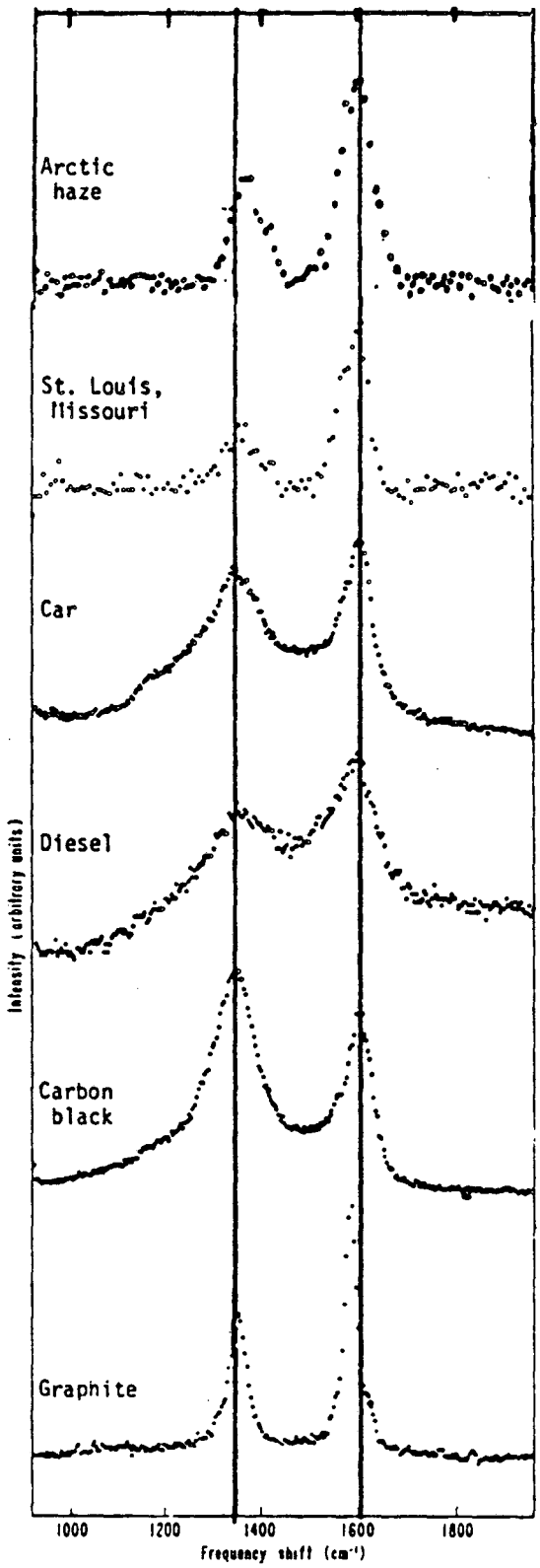
15. Rosen, H., Hansen, A.D.A., Dod, R.L., and Novakov, T., Science 208, 741-743 (1980).

16. Angell, C.L., and Lewis, I.C., Carbon 16, 431-432 (1978).

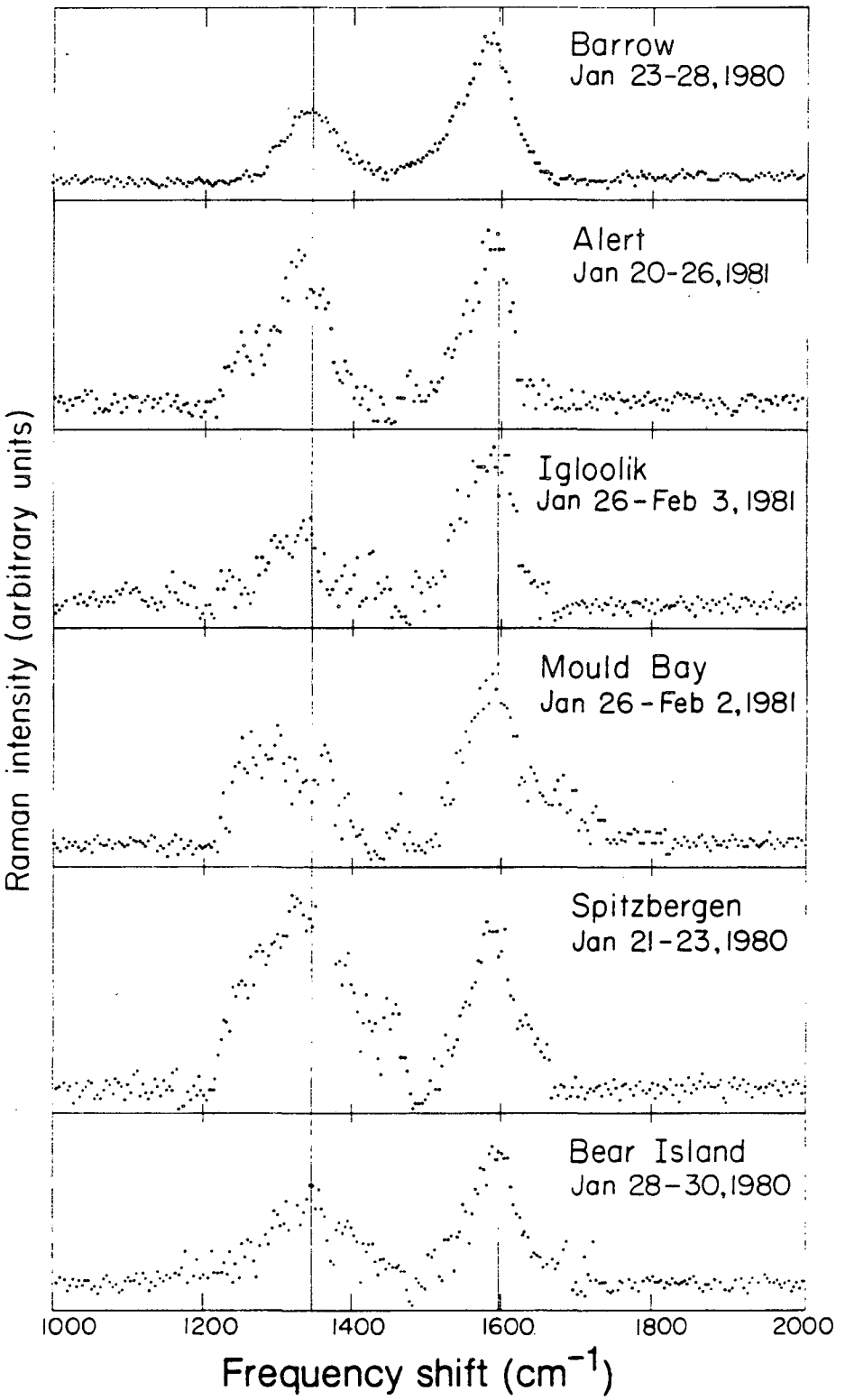
Figure Captions

Figure 1. Raman spectra of particles collected in the Alaskan Arctic compared with spectra of urban particles, various source emissions, carbon black, and polycrystalline graphite.

Figure 2. Raman spectra of particles collected in Alaskan Arctic (Barrow) compared with samples collected in the Canadian Arctic (Alert, Igloolik, Mould Bay) and the Norwegian Arctic (Spitzbergen, Bear Island).



XBL 767-3091B


Barrow
Jan 23-28, 1980
Alert
Jan 20-26, 1981
Igloolik
Jan 26-Feb 3, 1981
Mould Bay
Jan 26-Feb 2, 1981
Spitzbergen
Jan 21-23, 1980
Bear Island
Jan 28-30, 1980
Raman intensity (arbitrary units)
1000
1200
1400
1600
1800
2000
Frequency shift (cm^{-1})

XBL 822-137

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720