Title
RAMAN STUDY OF GRAPHITIC CARBON CONCENTRATIONS IN THE WESTERN ARCTIC

Authors
Rosen, H.
Novakov, T.

Publication Date
1983-08-01

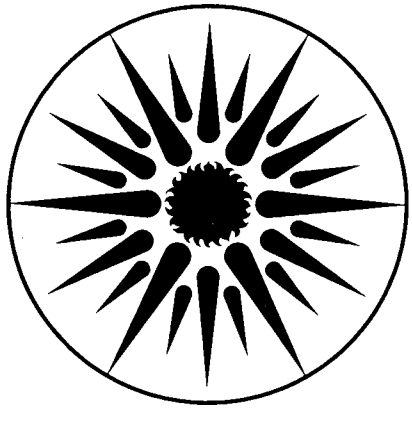
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

RAMAN STUDY OF GRAPHITIC CARBON CONCENTRATIONS IN THE WESTERN ARCTIC

H. Rosen and T. Novakov

August 1983



APPLIED SCIENCE DIVISION

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

DISCLAIMER

RAMAN STUDY OF GRAPHITIC CARBON CONCENTRATIONS IN THE WESTERN ARCTIC*

H. Rosen and T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Recent studies at ground level 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 analysis, it has been suggested that these particles originate from anthropogenic sources at midlatitudes.[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 NOAA-GMCC observatory near Barrow, Alaska.[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 sections ($\sim 10\ m^2/g$) in the solar spectral region, can lead to significant heating effects.[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

* 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.

of time of year.[10,11] In this paper, we report on an extension of our studies of carbon particles in the Alaskan Arctic to the Canadian 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. These results show that the large concentrations of graphitic particles found at the NOAA-GMCC observatory at Barrow are not a local phenomenon but are characteristic of ground-level stations throughout the western Arctic.

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 hours reduced this background by about an order of magnitude. The intensity of the Raman spectra was 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 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] The spectra from these samples show the presence of two Raman modes located at $\sim$ 1350 cm^{-1} and 1600 cm^{-1} that have been identified as due to phonons propagating with graphitic planes.[12] In Fig. 1 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 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 cm^{-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 from each other. The relative ordering

of these concentrations for Spitzbergen, Bear Island, Barrow, Mould Bay, Alert, and Igloolik are 2.1/1.7/1/0.8/0.8/0.7. 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.

Acknowledgments

I would like to acknowledge Dr. B.A. Bodhaine of the NOAA-GMCC program, Dr. L.A. Barrie of the Canadian Atmospheric Environment Service, and Dr. B. Ottar of the Norwegian Institute of Arctic Research for providing samples respectively from the Alaskan Arctic, the Canadian Arctic, and the Norwegian Arctic. 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.

References

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

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

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

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

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

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

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

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

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

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

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

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

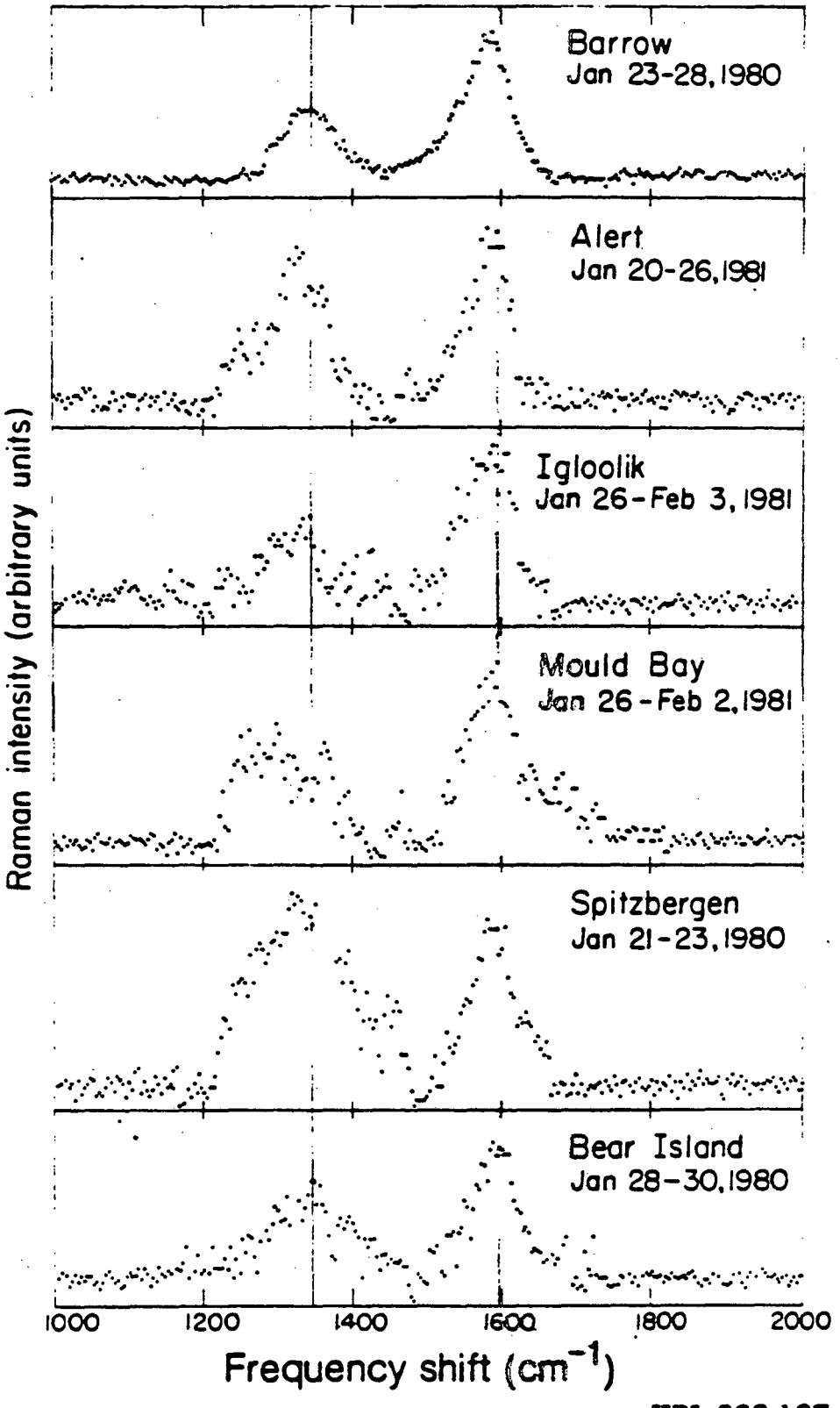
13. G.T. Wolff and R.L. Klimisch, eds., Particulate Carbon: Atmospheric Life Cycle (Plenum, New York, 1982).

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

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

Figure Caption

Figure 1. Raman spectra of particles collected in the Alaskan Arctic (Barrow) compared with samples collected in the Canadian Arctic (Alert, Igloolik, Mould Bay) and the Norwegian Arctic (Spitzbergen, Bear Island).


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