which we have studied, the lowest ^{39}Cl and ^{38}Cl to ^{24}Na ratios were observed near the beginning of the storm. The ^{39}Cl and ^{38}Cl to ^{24}Na ratios observed in the various storms are compared in Table 2 with "meteorological qualifiers" which were used in subjectively classifying the sampling period within the rainstorm.

An apparent relationship between the ratios of ^{39}Cl and ^{38}Cl to ^{24}Na, and the period in the storm when the sample was collected is clearly evident. The two entries of 26 January in Table 2 are especially interesting because these were successive samples 1 hour apart near the end of a rain. The concentration of the longer-lived ^{24}Na was the same, but the short-lived ^{39}Cl and ^{38}Cl increased by about a factor of three.

An explanation for this change in ratio and for the range of ratios shown in Table 2 is evident if one views the storm cloud system as a filter, with unwashed, saturated air entering at the upwind end and moving through the storm cloud with a wind speed V relative to the earth. This unwashed air could contain condensation nuclei which have the cosmic ray–produced radionuclides attached to them in a ratio approaching their steady-state production rates. At the same time, the storm cloud moves with a slower speed v relative to the earth. Then precipitation sampled at the earth at times Δt apart is actually from times in-cloud which are ΔT apart, where $\Delta T = [v/(V - v)] \Delta t$.

For the storm of 26 January 1967 approximate values of $V = 35$ and $v = 25$ could be used along with the known Δt of 1 hour, to give $\Delta T =$ 2.5 hours. If this were the actual in-cloud period, changes in the ^{39}Cl to ^{24}Na and ^{38}Cl to ^{24}Na ratios of about 8- and 16-fold respectively could occur. The observed ^{38}Cl and ^{39}Cl to ^{24}Na ratio changes of about threefold suggest a shortened in-cloud period or perhaps that other processes are important. This possibility, that aerosols do spend a substantial period of time in the cloud after their incorporation in cloud droplets, was offered as an explanation for the nonequilibrium ratios of ^{214}Bi to ^{214}Pb in rains in India (*8*).

This group of short-lived cosmic ray–produced radionuclides has a great potential in studying short-range vertical atmospheric transport rates and in-cloud precipitation-scavenging mechanisms. Their value for many applications will of course increase when their absolute production rates as a function of altitude and latitude have been determined. It is likely that on a careful observation of the absolute and relative concentrations of these radionuclides at several periods during storms, it will be possible to define the processes responsible for changes in radionuclide ratios and to learn a great deal about in-cloud residence time of aerosols, and the efficiency of in-cloud and below-cloud scavenging of aerosol particles by precipitation.

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Urban Haze: The Extent of Automotive Contribution

Abstract. *Observation of the correlation between nitrogen oxides and the extinction coefficient of atmospheric air suggests that the automobile exhaust aerosol (nonphotochemical) may be important to visibility in cities.*

It is frequently difficult to ascribe in a logical fashion the chemical composition of urban air to specific emissions. Besides the difficult-to-describe mesoscale meteorological mixing process, the heterogeneity of sources and pollutants and a sometimes nearly random pattern of human activities pose serious difficulties for the scientist. Our purpose is to describe one case in which some simplification seems justified: the case of automobile-related urban haze.

With an instrument described (*1, 2*), the extinction coefficient (due to scatter) of a sample flow of atmospheric air was monitored continuously for about 9 months (*3*). Because the scattering coefficient is determined on a sample of a few liters, the resultant data are appropriate for studies of correlation of aerosol and gas pollutants, where the gas (such as SO_2 or NO_x) is measured in the same sample of air. These correlations are particularly pertinent since the light-scattering coefficient can be used to infer the mass of particulates per volume of air (μg/m^3) (*2*). Although the correlation coefficient of SO_2 with the scattering coefficient (and hence with particulate mass) was only 0.27 for about 3 months (between September and December 1966) of hourly averages, a higher and perhaps significant correlation of NO_x (0.53) resulted from a similar number of hourly averages during the same period. Sulfur dioxide was measured with a Scientific Industries conductimetric instrument; NO_x, with Saltzman reagent in a Beckman Acralyzer. Air was sampled 13 m above a little-used street, and tests ascertained that local traffic was unimportant to this study (*4*).

This relation between NO_x and scattering coefficient is also suggested by similar time dependencies of the average of hourly values for each, especially on weekdays (Fig. 1). A wind-rose pattern of scattering coefficient (Fig. 2a), corresponding closely to the asymmetric shape of Seattle, suggests a uniform production of particulate matter rather than by a few point sources. The NO_x wind-rose pattern (Fig. 2b) has some similar features: a concentric pattern, with high values toward the northwest and low values to the southwest, corresponding to the shortest trajectory over populated areas for clean maritime air masses. Meteorological data were obtained from Sand Point Naval Air Base, Seattle, which is about 5 km northeast of the sampling site. Once again, study of systematic influences of this distance found them unimportant to the results of this report (*4*).

Although not conclusive, our data suggest a source of part of the urban haze in some cities: the automobile. Although no estimates were made of sources of NO_x other than traffic, Fig. 1 and previous work (*5*) indicate that such were probably unimportant. The data in Fig. 1 resemble results obtained in California towns (*5*) in which automobiles clearly dominate the diur-

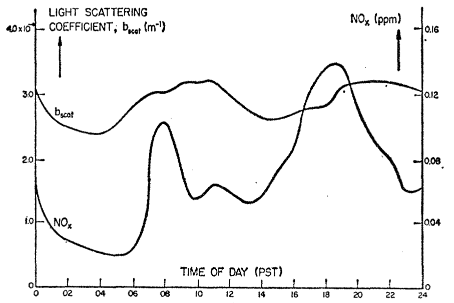

Fig. 1. Averaged hourly average values of b_{scat} (m^{-1}) and NO_x (ppm) on weekdays between 21 September and 22 December 1966.

nal variation of NO_x. Inasmuch as the weather during much of the data period was cloudy or rainy, or both, there is the question of whether or not the aerosol observed was formed or even affected by photochemical reactions. Unfortunately no record of oxidant (a usual indicator for photochemical reaction) was made. One can, however, roughly estimate the amount of haze and light-scatter to be expected in the absence of either photochemical reaction or aerosol agglomeration, from measurements of the composition of automobile exhaust and estimates of atmospheric dilution.

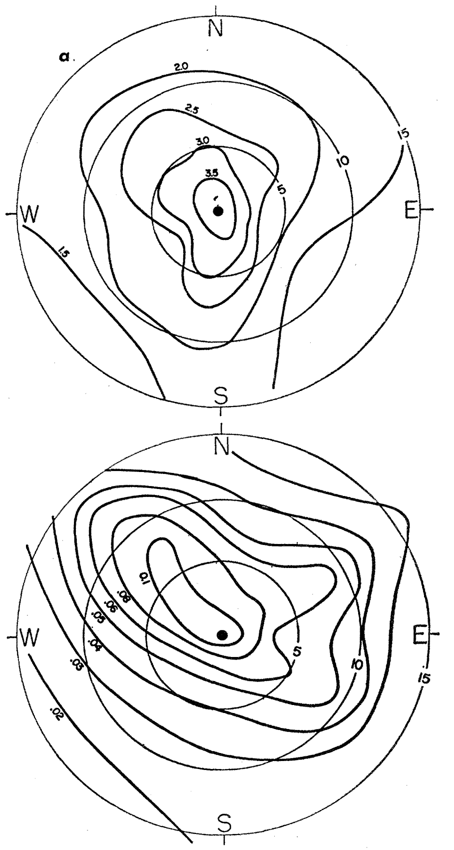

Fig. 2. (a) Smoothed, isoplethed mean values of b_{scat} (m^{-1}) × 10^4 as a function of wind direction and speed; wind speed in knots is the radial coordinate. (b) Similar plot for NO_x data (ppm).

Typical tailpipe concentrations of nitric oxide range from 1000 to 3000 parts per million (ppm), depending on both the design of the engine and its mode of operation (*5*). Less material seems to be available on the aerosol produced by automobiles, but one series of measurements on three automobiles (*6*) yielded typical exhaust concentrations of 50 to 100 μg/liter. The size distribution of this particulate matter was surprisingly close to what is frequently observed in the atmosphere; that is, approximately equal masses in the size class between 2 and 0.2 μ and in the size class below 0.2 μ, with almost no particles of diameter greater than 2 μ.

Assuming that this size distribution can be represented by Junge's equation (*7*), $dN/d \log r = cr^{-3}$, one can calculate an approximate value for the light-scattering coefficient for car exhaust at any given dilution. The resultant relation, which has been discussed in detail (*2*), is in the form of a ratio:

$$[b_{scat}\,(m^{-1})]/[m(\mu g/m^3)] \simeq 3 \times 10^{-6}$$

where b_{scat} is the scattering coefficient and m is the mass of the aerosol. If one assumes from the above auto-exhaust properties that the ratio of mass of aerosol to concentration of nitric oxide in the tailpipe is

$$[m(\mu g/m^3)]/[NO](ppm) \simeq 10^5/10^3 = 10^2$$

(since 100 μg/liter is 10^5 $\mu g/m^3$), then the relation of light-scattering coefficient to nitric oxide, for any dilution of automobile exhaust, becomes approximately

$$[b_{scat}\,(m^{-1})]/[NO]\,(ppm) \simeq 3 \times 10^{-4}$$

if the size distribution remains close to the Junge distribution. The ratio of data seen in Fig. 1 is of the same order of magnitude as is this estimated ratio. Interestingly, two cases of very high correlation between NO_x and light-scattering coefficient were observed on the mornings of 30 January and 23 February 1967. Such a period should provide data for checking the calculated ratio if the particulates and NO_x came from the same vehicular source. Data periods of 4 hours each, with 5- and 10-minute averages, respectively, yielded values of 0.9 in both cases for the correlation coefficient of NO_x with the scattering coefficient. The data for 30 January are reproduced (Fig. 3) to illustrate that the peak readings (about 1 ppm and 5×10^{-4} m^{-1}) occurred just after the peak of rush-hour traffic on main roads adjacent to the campus (about 0800 hours P.S.T.). Local winds on both of these occasions were very light under similar high-pressure systems. At about 0830 hours on 30 January, this ratio was 5×10^{-4} (m^{-1}) $(ppm)^{-1}$, the magnitude of which is surprisingly close to what is expected from diluted car exhaust.

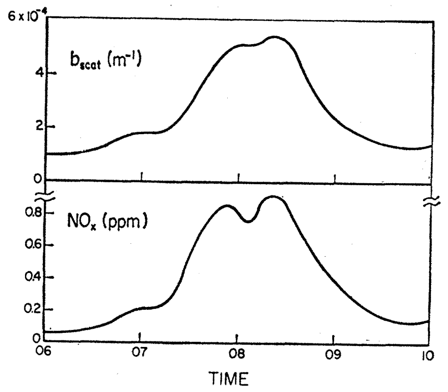

Fig. 3. Ten-minute averages of b_{scat} (m^{-1}) and NO_x (ppm) on the morning of 30 January 1967; Pacific Standard Time.

At this time, the observed concentration of NO_x, 1 ppm, indicated that the exhaust-dilution factor was apparently about 10^3, while the minimum meteorological range (an objective measure of visibility) was about 10 km. Inasmuch as the air before and after the peak at 0830 hours was quite unpolluted, it seems possible in this instance to assign a single vehicular source to the bulk of both the NO_x and the aerosol. Since such degree of reduction in visibility is in the range observed in typical urban areas, these results suggest that the aerosol primarily produced by automobiles should be studied in parallel to investigation of photochemically related particulate matter. Such studies should help to test an estimate (*8*) that half of the aerosol produced by automobiles is primary emission and half is photochemically generated. Finally, the correlation of light-scattering coefficient with concentrations of lead and carbon monoxide should help to confirm or refute the implications of the above data, because of the presence of both of these substances in car exhaust.

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26 November 1967

Pyrite Group: An Unusual Member: $Cu_{0.60}Ni_{0.14}Co_{0.03}Fe_{0.23}S_2$

Abstract. *An investigation of villamaninite from the type locality indicates that former analyses were of aggregates rather than of individual minerals. A redefinition embraces a larger range of solid solution, the end-member of which has the highest content of copper so far attributed to a member of the pyrite family.*

In 1963, during a brief reopening of the Providencia mine near Carmenes in the province of Léon, Spain, material was collected for study of the poorly defined mineral species villamaninite. The mineral has been analyzed chemically by Schoeller and Powell (*1*) as $Cu_{0.39}Ni_{0.36}Co_{0.14}Fe_{0.11}S_2$ and by Hey (*2*) as $Cu_{0.51}Ni_{0.27}Co_{0.09}Fe_{0.13}S_2$, and x-ray spectrometrically by Moh and Ottemann (*3*). Their data made it apparent that because of the extremely fine intergrowths only microprobe analysis could provide chemical definition of the species.

By means of x-ray powder patterns and ore-microscopical investigations, three Cu-bearing members of the pyrite family can be distinguished: one having cell-edge values between 5.59 and 5.62 Å, corresponding to cuprian bravoite, with a mean composition of $Cu_{0.12}Ni_{0.22}Co_{0.11}Fe_{0.55}S_2$; another having cell-edge values between 5.65 and 5.67 Å, corresponding to villamaninite as described by Ramdohr (*4*), with a mean chemical composition of $Cu_{0.28}Ni_{0.35}Co_{0.11}Fe_{0.26}S_2$; and a third compound having cell-edge values between 5.69 and 5.705 Å and a composition of $Cu_{0.60}Ni_{0.14}Co_{0.03}Fe_{0.23}S_2$.

This last composition is beyond that of the Cu-rich end-member of synthetic villamaninite from Moh and Kullerud's (*5*) experiments; their solid-solution gap between NiS_2 and $Cu_{0.4}Ni_{0.6}S_2$ may be reflected by the multiple fine and zonal intergrowths between our Cu-rich villamaninite and cuprian bravoite (Fig. 1). The experimental decrease of the solid-solution range in villamaninite with increase in temperature points to a low-temperature metastable formation similar to that of bravoite (*6*).

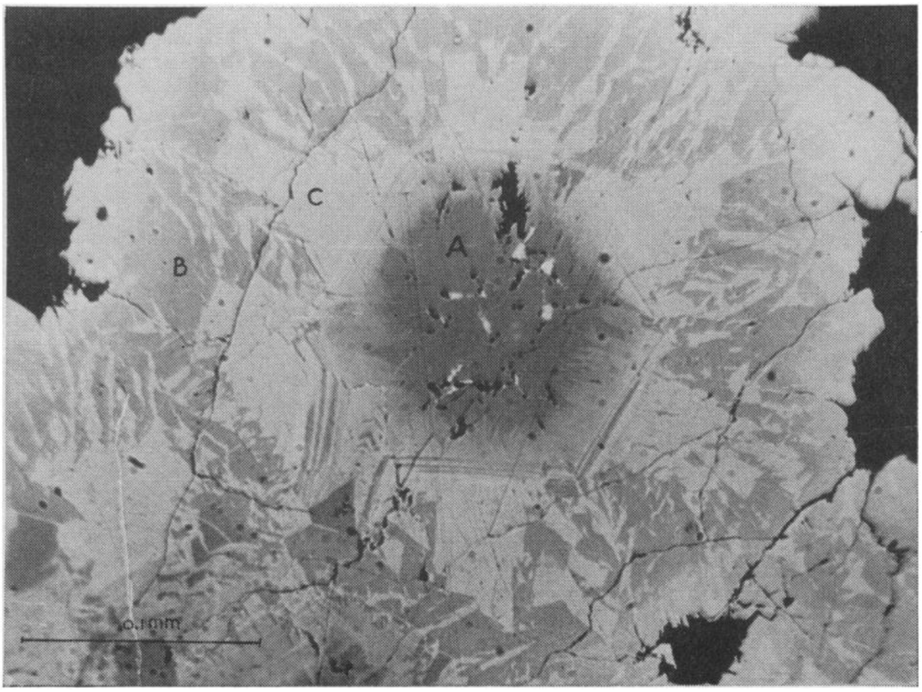

Fig. 1. Copper-rich villamaninite (dark-gray, *A*) intergrown with cuprian bravoite (light-gray, *C*), forming the core of nodular villamaninite (intermediate, *B*).

Ore-microscopically the three phases are easily distinguishable: The cuprian bravoite has a cream color, a reflectivity of about 37 percent (green filter), and Vickers hardness numbers in the 890 to 965 range, so that it is appreciably softer than copper-free bravoite. The intermediate villamaninite invariably occurs in nodular aggregates, has a blue-gray color, reflectivity of about 30 percent, and a Vickers hardness of 535 to 700. The Cu-rich villamaninite occurs as idiomorphic cubic or cuboctahedral crystals with perfect cubic cleavage; it has a violet tinge, a reflectivity of about 27 percent, and a Vickers hardness of 440 to 520. The Cu-rich villamaninite and the cuprian bravoite are the least variable in composition. The optical properties of the nodular villamaninite grade into either one; intermediate members, however, are very rare.

Weissenberg photographs indicated a *Pa*3 space group for both cuprian bravoite and the Cu-rich villamaninite, although the latter is distinctly anisotropic. This feature, and the fine rhythmic alternations of members of the villamaninite group in the spherulitic aggregates, point to low-temperature crystallization. The nodular villamaninite could not be used for single-crystal studies. Cuprian bravoite, nodular villamaninite, and Cu-rich villamaninite are all primary minerals. The Cu-rich variety is the least stable and is replaced by linneite, bornite, chalcopyrite, and Cu-free bravoite.

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6 December 1967