Composition analysis of particles from noctilucent clouds

By G. WITT, *Institution of Meteorology, University of Stockholm*, C. L. HEMENWAY, *Dudley Observatory, Albany, N.Y., and Union College, Schenectady, N.Y.*, N. LANGE, *Institute for Metal Research, Stockholm*, S. MODIN, *Institute for Metal Research, Stockholm*, and R. K. SOBERMAN, *Air Force Cambridge Research Laboratories, Bedford, Mass.*

(Manuscript received December 15, 1963)

ABSTRACT

Composition analysis has been performed on particles collected from noctilucent clouds by a rocket sounding experiment in northern Sweden during August 1962. Electron diffraction, neutron activation, and electron beam microprobe techniques were applied to give information about chemical composition and possible crystal structure of the particles. Results obtained to date are presented in this paper which also discusses the applicability of the above methods to small particle analysis.

Introduction

During August 1962 four identically instrumented Nike-Cajun sounding rockets were launched from Kronogård in Sweden for *in situ* sampling of noctilucent cloud particles. Technical details of the experiment, as well as of the sampling apparatus, are fully described in Refs. A & B of this series.

The sampling surfaces, as described in Ref. A, were partially covered by a lucite hold-down plate with eight openings, machined to the shape of a wheel and coated with an evaporated layer of aluminum.

After the flights, before the sampling containers were opened, the gas inside the containers was withdrawn and analyzed by a mass spectrometer to determine the presence of possible volatile products alien to the normal atmospheric composition. Changes in concentration of molecules normally found at sea level were found as expected, but this was attributed primarily to outgassing and gradual leakage of the containers. Only the presence of traces of ethyl alcohol and acetone was established by this technique. Both these substances were used in the cleaning of the nose cone.

Before the application of a method for chemical analysis of the collected particles two criteria must be kept in mind. First, the method must be sensitive and it must offer a possibility to discriminate the particles from the background, or the substrate. This is particularly important in view of the fact that the total collected mass amounts to less than 10^{-5} grams. This material is distributed over a relatively large area in form of discrete particles whose mass is in general less than 10^{-12} grams. Second, the method must be non-destructive since the amount of matter accessible to analysis is limited. Miarochemical spot-testing which is extensively used in small particle analysis was, for example, rejected for latter reason. Methods which fulfill the above requirements and which were utilized in the present work are electron diffraction, neutron activation and electron beam microprobe analysis.

Electron diffraction analysis

Electron microscopic samples from the aluminum and the fuchsine coated surfaces were used for selected area diffraction analysis. The work was carried out in a Siemens Elmiskop I electron microscope with a 100 kV electron beam. Approximately 100 particles of varying size were found to yield diffraction patterns. The patterns were calibrated with the aid of the (200) ring of chromium. This metal had previously been deposited on the surfaces for shadowcasting (Ref. B.) To investigate possible changes in the diffraction pattern, prolonged heating of the particles by electron bombard-

TABLE 1. *Sensitivity of neutron activation analysis for some elements. The table refers to a length of irradiation of two half-lives, or maximum of one week in a neutron flux of 4 × 10¹³ neutrons/cm². (90 % thermal, 10 % fissionspectrum.)*

Atom	half-life	neutron cross-section	appr. minimum detectable quantity
Al^{28}	2.27 min.	0.21 barns	1.5×10^{-11} g
Au^{198}			
Ca^{45}	165 days	0.016	5×10^{-8} g
Fe^{59}	45 days	0.0033	10^{-7} g
In^{116m}	54 min	148.0	5×10^{-13} g
Mn^{56}	2.58 hrs	13.3	5×10^{-12} g
Na^{24}	15 hrs	0.54	2×10^{-11} g
Ni^{65}	2.56 hrs	0.016	2×10^{-9} g
Si^{31}	2.62 hrs	0.0034	5×10^{-9} g
S^{35}	87 days	0.30	5×10^{-8} g

ment was applied in a number of cases. In many of these cases the diffraction pattern vanished upon heating. The heating also caused recrystallization of the chromium and aluminum coatings of the substrate. Aluminum (111) and (200) rings or traces of rings were clearly identified in eight of the analyzed patterns. Typical diffraction patterns from the samples exposed to noctilucent clouds together with electron micrographs of the corresponding particles are shown in Fig. 5. The accuracy in determination of the crystallographic d-values is approximately 0.5 to 1 % for distinct reflections.

Unambiguous interpretation of the obtained diffraction patterns is not possible as the chemical composition of the particles is not known and only one orientation of the particle can be examined. Moreover, the particles might consist of a mixture of substances or the reflections might even originate from a coating on the surface of the particles. A feature which was observed in 5 to 10 % of the cases was a pattern with hexagonal symmetry for which the largest d-value ranged from 4.43 to 4.47 Å. An example of this pattern is shown in Fig. 5*a*. Such patterns did in most cases vanish upon heating. In one case, however, the pattern remained after prolonged electron bombardment and showed only increased d-values. The increase amounted to about 1.8 %, the largest d-value becoming 4.52 Å. Unfortunately a similar pattern with similar d-values and identical intensity distribution has been observed in other laboratories which were studying objects of entirely different origin, and even objects with known amorphous structure. The possibility that these reflections might originate from a coating of oriented molecules of vacuum oil on the surface of suitable particles has been pointed out. (Brosset, private comm.) A pattern with cubic symmetry and [001] orientation is shown in Fig. 5*b*. Here the largest d-value is 3.14 Å. If both the patterns above originate from the same type of crystal, then this crystal would be cubic with $a_{cu} \approx 6.28$ Å. Lastly, Fig. 5*c* shows a particle containing dark circular inclusions, opaque to 100 kV electrons and believed to be of metallic composition, which did not yield a diffraction pattern.

Neutron activation analysis

If a sample containing certain elements is placed in a flux of neutrons, artificial radioactivity will be induced in it. The energy spectrum of the induced radioactivity is characteristic of the elements composing the sample. The intensity of the radiation is also a function of the length of irradiation, the half-life, and the neutron cross-section. The latter two properties are characteristic of a given element. Table 1 shows these properties and the smallest detectable quantities of some elements in question. The indicated sensitivity is for a length of irradiation of two half-lives, or a maximum of one week in a neutron flux of 4 × 10¹³ neutrons/cm² (90 % thermal, 10 % fis- sion spectrum). (Christell, priv. comm.)

The sample was prepared from the hold-down plate by stripping the surface with a thin Formvar film coated with nitrocellulose of about 200 Å thickness. The area of the replica was about 2 cm². This replica with the particles attached was enclosed in a polyethylene vial and placed in the reactor. After irradiation the sample was transferred to a non-radioactive vial. To avoid contamination the samples were handled in a miniature dry box. Following irradiation the radioactivity was measured by a scintillation gamma ray spectrometer. The activation analysis indicated the presence of the elements Al, Au, Mn, In, and Na. Of these, aluminum was expected to be present in the samples in the form of the coating of the hold down plates. The approximate amount of the metal found (about 10^{-6} g) is in accord with the mass expected from a surface of about 2 cm². Gold, sodium and manganese have high activa-

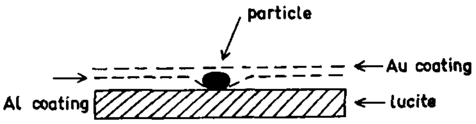


FIG. 1. Schematic drawing of the lucite hold down plate prepared for microprobe analysis. The aluminum coating was applied during the manufacturing while the gold coating was applied prior to analysis. The thickness of the gold layer is approximately 150 A.

tion cross sections and are known to be likely contaminants. Indium was present on one of the sampling surfaces and is likewise labelled as contamination. None of the elements Fe, Ni, Si, Ca and S, all with poor activation efficiencies could be detected with this technique. These results point out the drawbacks of this method of analysis. The drawbacks are, different sensitivity for different elements and if the entire sample is analyzed at one time, there is poor background discrimination. Thus for the present studies, neutron activation analysis is not suitable unless particles can be found which are large enough to be transferred to a nonradioactive substrate after irradiation. Since only a very few such particles are in the existing sample, the analysis of these large particles may not be representative.

Electron Beam Microprobe Analysis

This method is the spectrometric analysis of x-rays emitted from an object illuminated by a finefocused beam of electrons with energies from 10 to 30 kV. The electron beam illuminates a spot approximately 1 micron in diameter. The object thus acts as an x-ray target (as in a Roentgen tube) and yields both x-rays and back-scatter electrons. The emitted x-rays are analyzed by a proportional counter x-ray spectrometer and the spectra are displayed on a potentiometer recorder or on an oscilloscope screen. The display can be obtained in form of an x-ray spectrum of a fixed spot on the sample or of the intensity variation produced by mechanical or electronic scanning of a given area with the electron beam (the spectrometer being set for a fixed wavelength). In the latter case an image of the sample may be obtained on the oscilloscope screen, formed either by the back-scatter electrons or by the x-ray spectrometer output. A back-scatter electron image of a portion of a noctilucent cloud sample is shown in Fig. 2. Particles are found either visually by an optical microscope system, by electronic scanning, or acoustically by connecting a loudspeaker to the pulse counter output. This latter device proved to be almost indispensable in the analysis of particles too small to be detected with the optical microscope. The samples for the present analysis were prepared from the hold down plate previously exposed to noctilucent clouds as well as from identically prepared laboratory control surfaces. In one case the sample was covered by a thin Formvar layer and a nitrocellulose coating on which a gold coating was vacuum deposited. In the other case the gold was applied directly (Fig. 1). The purpose of the metal coating was to make the surface a better electrical and thermal conductor and thus prevent excessive heating and charge accumulation due to the electron bombardment. Because of the particular character of the sample, a special method of search for particles has been developed. The surface was first scanned with the spectrometer set for elements such as Fe, Ni or Si. Once a particle was detected, the substrate was slowly moved back and forth under the electron beam and the x-ray intensity from the particle and background was recorded alternately. The latter

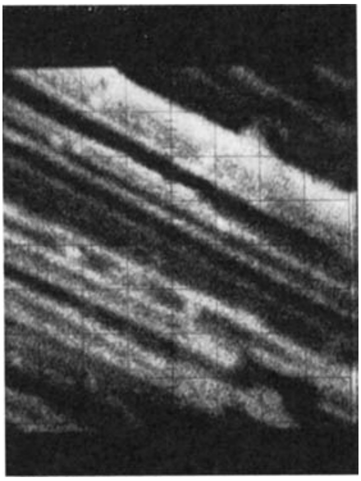


FIG. 2. Back-scatter electron scanning of portion of the lucite plate from a noctilucent cloud sample. The grooves in the picture are due to uneven deposit of gold because of poor surface finish. The area shown is 90 by 90 μ.

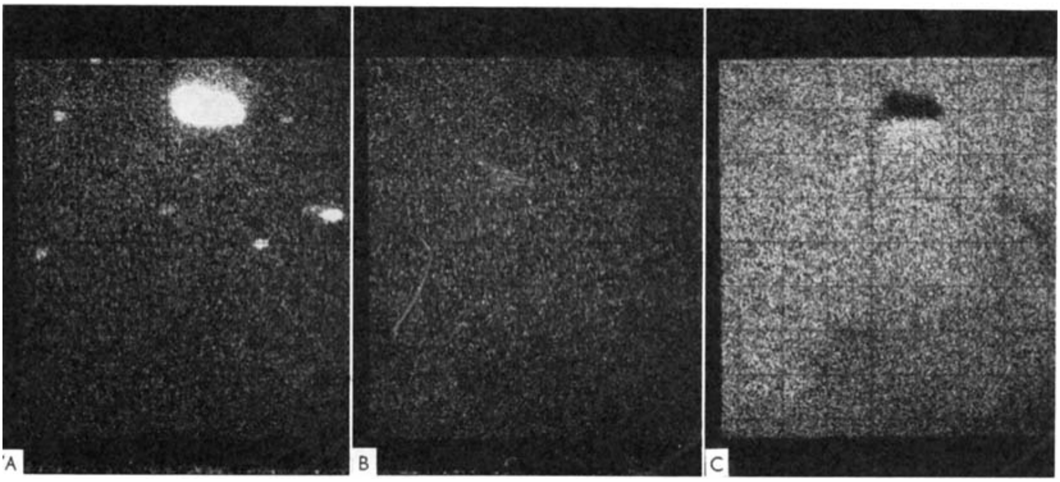
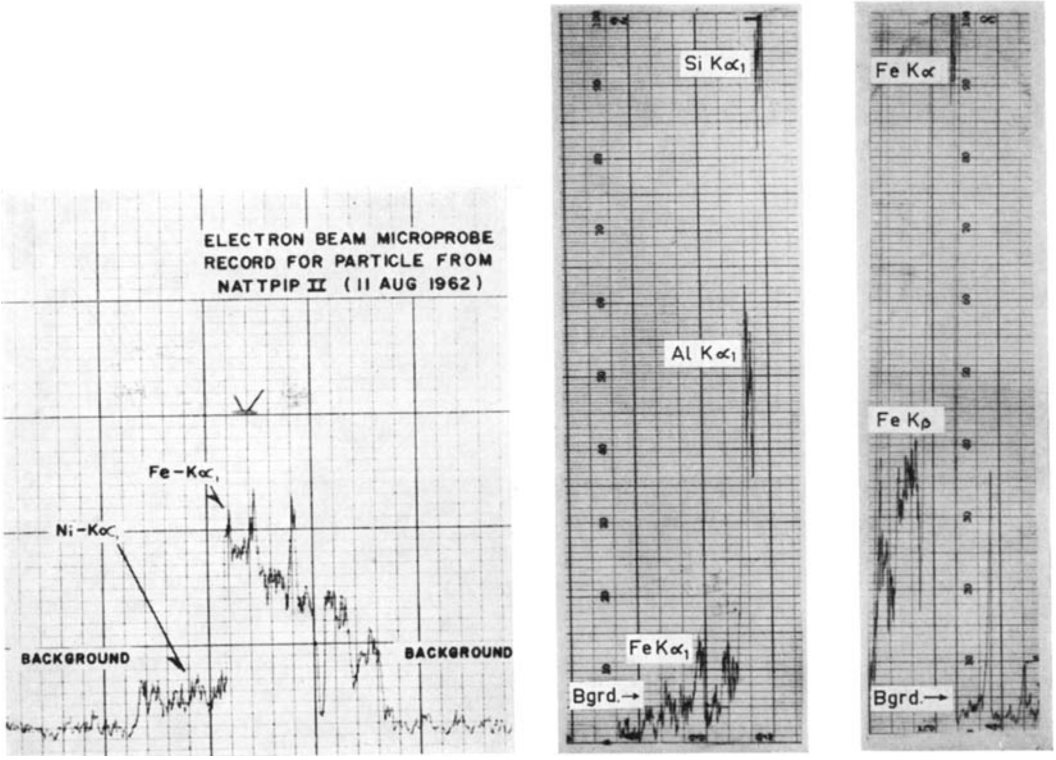


FIG. 3. X-ray spectrometer scanning of portion of the same sample as in Figure 2. The photographs reveal the presence of some micronsize iron particles with no measurable nickel content. The copper radiation is caused by fluorescence from parts of the analyzing instrument or from impurity of the gold coating. The area is 360 by 360 μ. Spectrometer set at (*a*) Fe $K\alpha_1$; (*b*) Ni $K\alpha_1$; (*c*) Cu $K\alpha_1$; (Such particles were also found on laboratory controls and were classified as contaminants.)

procedure was repeated for other emission lines of the same element and those of other elements present. The electronic scanning facility permitted simultaneous analysis of a larger portion of the sample. Fig. 3 shows a series of x-ray scans of part of the noctilucent cloud sample for the $K\alpha$ lines of (*a*) Fe, (*b*) Ni, and (*c*) Cu. The photographs show micron size iron particles with no measurable nickel content. A few such particles were discovered on the exposed surfaces as well as on the laboratory controls and are labelled as contaminants, probably originating from the processing of the surfaces. Copper was generally found evenly distributed on the surfaces. This is believed to originate from fluorescence of the copper parts of the analyzing instrument and possible also from impurities in the gold coating. Figs. 4*a* to *c* show x-ray intensity records obtained from various particles of submicron size, while Fig. 4*c* refers to a particle similar to that shown in Fig. 3 (i.e., one believed to be a contaminant). The most interesting of these records is the one shown in Fig. 4*a* which refers to an iron particle with a Ni/Fe ratio exceeding 15 %. The quantitative determination is approximate, primarily because of movement of the particle in the electron beam. Of some 40 particles which contained iron, three particles with relatively high Ni/Fe ratios (exceeding 5 %) were found by analysis of a total area of approximately 3 cm^2. Indications of nickel were found in a number of other cases. It is pointed out that a nickel content of a few percent is at the limit of discrimination against background noise. The particles with the relatively high Ni/Fe ratio (found in different samples in separate laboratories) showed no detectable amounts of other elements. These high Ni/Fe ratios are uncommon to terrestrial contaminants but can be found in meteoric matter; for example, taenite (Ni/Fe$\approx$10 to 30 %), kamacite (Ni/Fe$\approx$5 %) and schreibersite (Ni/Fe$\approx$14–60 %). Other particles were found to contain silicon and iron, silicon and calcium,

TABLE 2. *Metallic particles found by electron beam microanalysis of 0.5 cm^2 of a surface exposed to noctilucent clouds.*

Particle	Fe	Ni	Remarks
1	+	–	
2	+	–	Weak Al emission from the substrate.
3	+	–	
4	+	+	Ni/Fe 10 %
5	+	+	Ni/Fe small
6	+	–	
7	+	+	Ni/Fe very low
8	+	–	
9	+	+	Ni/Fe 5 %



4 *a* 4 *b* 4 *c*

FIG. 4. Electron beam microanalyzer scans of the lucite plate from a noctilucent cloud sample. The scans were obtained by manually moving the particles back and forth in the electron beam at fixed settings of the x-ray spectrometer. Curves referring to different kinds of submicron size particles are shown and the relevant elements are indicated. The aluminum indication originates from the substrate coating. (*a*) Particle with Ni/Fe ratio greater than 15%. (*b*) Particle containing Si and Fe. (*c*) Pure Fe particle; probable contaminant.

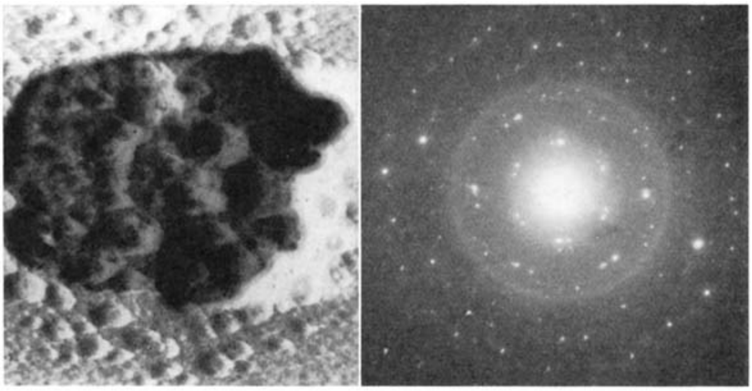
only silicon. An x-ray intensity record for a silicon-iron particle is shown in Fig. 4*b*. The curves are recorded in arbitrary units as it was not possible to obtain quantitative data from particles of the size collected. Table 2 shows the results of the x-ray microanalysis of an area of approximately 0.5 cm². This area is from a hold down plate exposed to noctilucent clouds.

Conclusions and Future Work

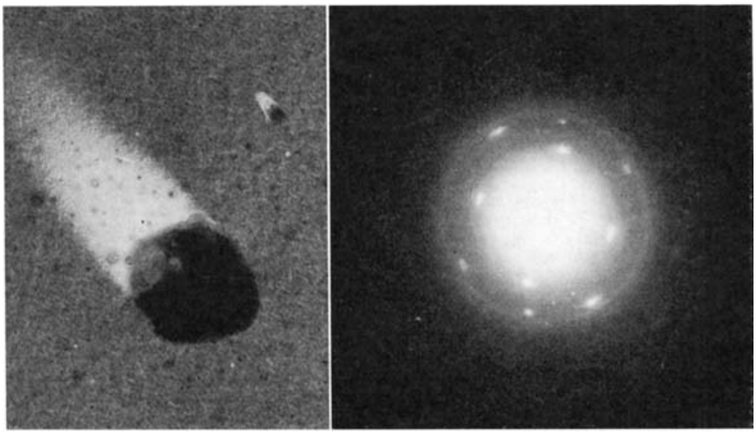
Three msethod have been utilized for composition analysis of the collected particles.

Of these only electron beam microanalysis has yielded useful results. The presence of submicron particles of a possible meteoric origin has been established. Further conclusions will be found in (HEMENWAY, SOBERMAN and WITT, 1964). The results of this partly exploratory work suggest continued samplings experiments such as are presently being planned.

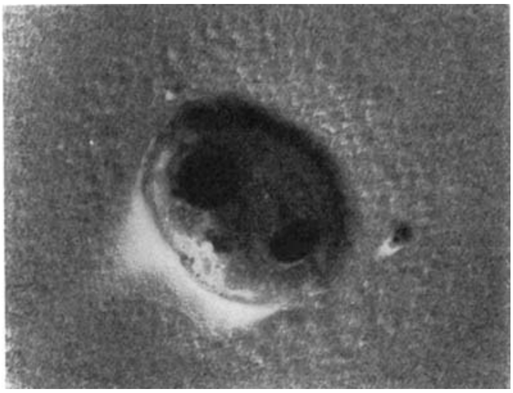
Experience indicates that the impact surfaces for electron beam microanalysis in the future should be made of high purity metals of low atomic number such as Al or Be, both with low background radiation. To minimize chances for contamination the number of handling operations prior to analysis is to be reduced by shaping the surfaces to fit the sample holder of the analyzing instrument without previous cutting. A method for particle identification combining electronic scanning with a low angle shadowcasting technique is presently being investigated.



5 *a*



5 *b*



5 *c*

FIG. 5. Selected area electron diffraction patterns of particles from a noctilucent cloud sample. The solid rings are due to reflections from chromium which was used to shadow-cast the samples. The (200) ring of Cr was used for calibration. Scale of the electron micrographs is 1 micron. (*a*) Sixfold symmetry, double crystal with sporadic reflections not belonging to the pattern. Traces of the Al (111) ring can be observed. The reflections vanished upon heating by electron bombardment. D-values corresponding to the regular pattern: 4.45 Å, 2.58 Å, 2.23 Å, 1.68 Å etc. Similar patterns were found in several particles. (*b*) Fourfold symmetry, zone axis (001), $d_{100} = 3.14$ Å. Complete pattern found in two particles. (*c*) Particle containing dense circular inclusions, opaque to 100 kV electrons and unaffected by prolonged heating by bombardment. The inclusions are believed to be of metallic composition. Such particles did, in general, not yield diffraction patterns. Scale = 0.5 micron.

Acknowledgements

The major part of the analysis has been carried out in instruments at the Institute for Metal Research, Stockholm, the Institute for Silicate Research in Göteborg, the Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass., and Advanced Metals Research of Somerville, Mass. The authors are deeply indebted to Professors R. Kiessling, C. Brosset and R. Ogilvie of the above institutions for generously having placed their instruments at our disposal. The authors are also indebted to Licentiat Roland Christell who was responsible for the activation analysis; the U.S. Quartermaster Corps of Natick, Mass., for the mass spectrometric analysis; Mrs. H. Modin for valuable help in the preparation of the samples; Mr. R. Carnevale and Mrs. K. Willborg for their technical assistance; as well as Professor L. Katz of Renselaer Polytechnic Institute, Troy, N.Y., for helpful discussions.

REFERENCES

HEMENWAY, C. L., SOBERMAN, R. K., and WITT, G., 1964, Sampling of noctilucent cloud particles, *Tellus*, **16**, pp. 84–88.

A. Techniques for Rocket Sampling of Noctilucent Cloud Particles, by R. K. SOBERMAN, S. A. CHREST, J. J. MANNING, L. REY, R. A. SKRIVANEK and N. WILHELM. *Tellus*, **16**, I.

B. Electron-microscopic Studies of Noctilucent Cloud Particles, by C. L. HEMENWAY, E. F. FULLAM, R. A. SKRIVANEK, R. K. SOBERMAN and G. WITT. *Tellus*, **16**, I.

D. Calcium Film Indicator of Moisture Associated with Noctilucent Cloud Particles, by I. LINSCOTT, C. L. HEMENWAY and G. WITT. *Tellus*, **16**, I.

E. Simulation of Ring Patterns observed with Noctilucent Cloud Particles, by R. A. SKRIVANEK and R. K. SOBERMAN. *Tellus*, **16**, I.