

Ferromagnetic particles and ice nuclei

By FRANCO PRODI and ENDRE WIRTH,¹ *Osservatorio Scientifico Sperimentale, IFA-CNR
Verona, Italy*

ABSTRACT

Airborne ferromagnetic particles ($20 - 0.1 \mu\text{m}$ in diameters) have been collected by different methods. Their ability to form ice crystals has been investigated by means of direct and indirect observations. No big ($d > 5 \mu\text{m}$) particles ("black spherules"), placed on filters, have been found to initiate ice phase at -12 and -15°C . Millipore filters, located behind a magnetic and a geometrically identical reference precipitator, have shown no characteristic differences in their ice nuclei concentrations when "developed" in a small diffusion chamber at -18°C . The results show that also the smaller ferromagnetic particles cannot probably be considered as effective ice nuclei.

Introduction and experimental part

The hypothesis of Bowen (1953; 1956) that the world wide precipitation may be influenced by ice nuclei of meteoric origin has been extensively investigated from several standpoints in the past 15 years. Nevertheless no convincing evidence has been found for the effectiveness of meteoric particles: laboratory tests, for instance, have given controversial results. Schaefer (1957) found that they are unable to nucleate above -25°C , while Bigg & Giutronich (1967) evidenced a nucleation threshold as high as -8°C . The formation of secondary particles from meteor vapors has been investigated by Rosinski & Pierrard (1964) in connection with rainfall anomalies. However no attempt has been made, to our knowledge, to separate that fraction of the natural atmospheric aerosol which can be supposed to originate from the ablation of meteoric matter, and to study its nucleation effectiveness. This separation is, in fact, very difficult because by chemical composition, size distribution, shape, several kinds of particles of surface origin are very similar to extraterrestrial ones. This separation is even harder for particles below $1 \mu\text{m}$.

However there is a kind of particles, the so-called "black spherules", that can be found

in deep sea sediments, polar ice, volcanic dust, snow crystals and in the troposphere and stratosphere as well (for instance: Crozier, 1960; Wright et al., 1963; Hodge & Wright, 1964; Kumai, 1966; Vittori, 1968; Soberman & Hemenway, 1965) and authors tend to agree in their meteoric origin. These particles are mostly of ferromagnetic material and can be easily separated from other particles. The instrument for collecting the airborne ferromagnetic aerosol has been described elsewhere in detail (Wirth & Prodi, 1972). It consists of two sets of permanent magnets, arranged in lines and columns, with polarities alternating in the neighbouring magnets. The collection efficiency of the precipitator is 32 % for particles with radii $0.1 \mu\text{m}$, 75 % for particles with radii $0.3 \mu\text{m}$, and 100 % for particles with radii $1.0 \mu\text{m}$. In the present work the ice forming ability of ferromagnetic particles in the size ranges $r \geq 5 \mu\text{m}$ and $0.1 \leq r \leq 2 \mu\text{m}$ is investigated.

A suitable sampling of ferromagnetic particles was performed for us at the top of Mt. Cimone, Italy, by means of an electromagnet. The particles were deposited on silicon grease-coated mylar surface. To directly study their nucleating ability they were washed away from the mylar surface with tetrachloromethane and filtered through Millipore filters (nominal pore size: $0.45 \mu\text{m}$); these were thereafter tested as to the nucleating ability of the particles. This part of the experiment was restricted to particles above $5 \mu\text{m}$ and was aimed at directly

¹ On leave from the Central Institute for Atmospheric Research, Meteorological Service of Hungary, Budapest.

observing the possible nucleation on the particles, by means of an optical microscope. Therefore there was no requirement of knowing the actual particle concentration in air and then no need of assessing the collection efficiency and the yield of transfer to the membrane filters.

The ferromagnetic particles below $5\text{ }\mu\text{m}$ have not received a great deal of attention. Our experimental arrangement was constructed to meet two different requirements. First, to measure the size distribution and total concentration of this fraction of atmospheric aerosol, and at the same time, to give a possibility to determine at least indirectly its nucleating ability. From the point of ice nucleation, this magnetic precipitator served as a filter for ferromagnetic particles, a certain fraction of which can be regarded as of meteoric origin. Membrane filters, capturing the particles which had not been deposited by magnetic and other forces on the walls, were located downstream of each precipitator.

In spite of the numerous attempts there is no absolute method available for measuring the real concentration of atmospheric ice nuclei as a function of the temperature. According to the recent findings of the Fort Collins Workshop (Grant, 1970) the most reliable instruments were the ones in which a good control of supersaturation and temperature could be accom-

plished. According to these findings, a slightly modified version of the Stevenson-Gagin thermal diffusion chamber has been built, having the advantages of good reproducibility in concentration measurements and the accurate determination of the necessary parameters (Fig. 1). The chamber was placed into a normal deepfreezer the temperature of which was maintained between -18 and -19°C ; the filters were developed at -18°C and 2–10 % supersaturation to water. No dependence in ice nuclei counts from supersaturation in this range has been found. The small, unavoidable changes in temperature around the diffusion chamber were compensated by two metal blocks of large thermal capacity. The most important improvement of our arrangement seems to be the control of supersaturation by a heating coil embedded in the bulk ice; the change in the temperature of ice has supplied the desired excess of vapour; both the temperatures of this and the filter support could at any time be checked and were recorded at the beginning and at the end of each measurement.

The two filters below the magnetic and the reference precipitators processed the same volume of air, that was kept between 100 and 500 liters; they were subsequently tested for their ice nuclei counts. Further, to eliminate the minor differences in temperatures (and supersaturations) from run to run which could af-

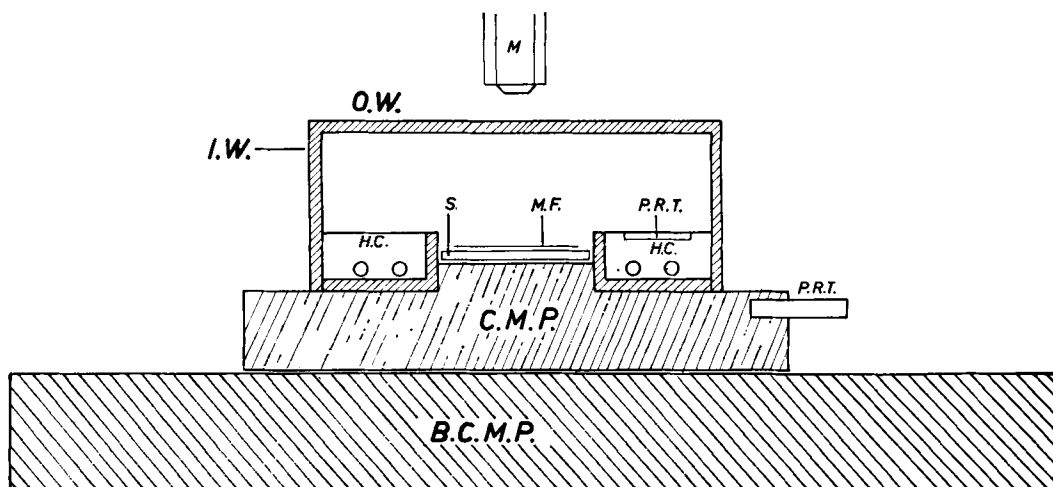


Fig. 1. The thermal diffusion chamber used for the development of the filters. *M*, microscope; *O.W.*, observation window; *I.W.*, insulating walls; *H.C.*, heating cables embedded in ice; *M.F.*, membrane filter; *P.R.T.*, platinum resistance thermometer; *S*, support of the filter; *C.M.P.* and *B.C.M.P.*, metal blocks.

fect the statistics in an unpredictable way, the two filters of each sampling were cut to half and developed together in complementary pairs.

For particles larger than about $5\text{ }\mu\text{m}$, the diffusion box was kept at -12°C and the process of ice crystal development was continuously observed through an optical microscope.

Results and discussion

The apparent example of ineffectiveness in ice nucleation of the large black spherules is clearly demonstrated by the pictures (Fig. 2a and b). The several attempts to identify particles in the visible range in the centers of growing and later evaporating crystals in the close vicinity of discernible black spherules of different sizes all have proved to be unsuccessful. A few tens of black spherules either collected as airborne at Mt. Cimone and transferred from the mylar to filters or found among the residues of thin hailstone slices after melting them thorough Millipore filters (Prodi & Nagamoto, 1971), were developed and inspected with the same result.

For small ferromagnetic particles the direct investigation of the ice nucleating ability is no more possible. Therefore, the counts of the filters below the magnetic and the reference precipitators have been compared. Several runs of measurements have been made at different locations in Italy during June, July and August, 1971. As an example of a rather unusual case of the daily variation in the ice nuclei concentrations, the results of hourly measurements on June 24, 1971, downtown Bologna (Italy) will be presented in Fig. 3. A peak in the concentration of ice nuclei (measured at -18°C) has appeared at about 4.00 p.m. (local time), when the number of nuclei exceeded 15 per liter of air. The pattern of this diurnal variation is out of phase with that of the average aerosol content (in mass concentration) for situations with no low level inversion, this latter having its maximum at the early morning and a minimum during the hours of maximum ventilation that is in the early afternoon. The meteorological factors involved in the dilution of aerosol concentration, on the other hand, are affected by the production rate of the ice nuclei, which, in our case, might be connected with

local urban sources. It should be noted that two other daily runs have been performed in subsequent days showing no more such a definite peak and, once more, no differences in ice nuclei concentrations on the filters in the two cases.

Other samplings have been taken also on a hill close to Bologna (Mt. Cuccolino, 200 m a.s.l.) and at the Osservatorio Scientifico 200 m above Verona and at about 5 km north of the town center.

The results of ice nuclei measurements, together with wind and cloudiness observations, are shown in Fig. 4. Each plot refers to sampling of 500 liters of air during two hours. The difference between the two series has been checked by a simple *t*-test, applying the 0-hypothesis that both of them are originated from the same population. The test has shown a difference at the 5 % significance level in an opposite sense of that it had been expected: in an average, as it is also seen on the picture, slightly higher numbers were recorded on filters placed behind the magnetic precipitator. It seems imaginative to speculate about the possible physical effects acting in this direction, except, may be, the polarization of paramagnetic particles passing through the magnetic precipitator without being captured, but preserving the polarization while collected on the Millipore filters. Considering the experimental errors, connected with ice nuclei counting in general, this difference cannot be considered as meaningful.

In comparing the concentrations of ice nuclei in air at -18°C with those of ferromagnetic particles, it is to be remarked that the latter is about two orders of magnitude higher than the former. It means that, taking into account also the errors of ice nuclei measurement, the possibility that a small fraction of the ferromagnetic material show nucleating ability at the given conditions (and in the size range of the captured particles) cannot be absolutely ruled out; however, no direct indication of their effect could be derived from these measurements. Instead, the measurements seem to indicate the ineffectiveness of the captured ferromagnetic particles as ice nuclei.

In evaluating the results of comparison between the concentrations of ice nuclei precipitated on filters behind the different samplers, the following possibilities exist:

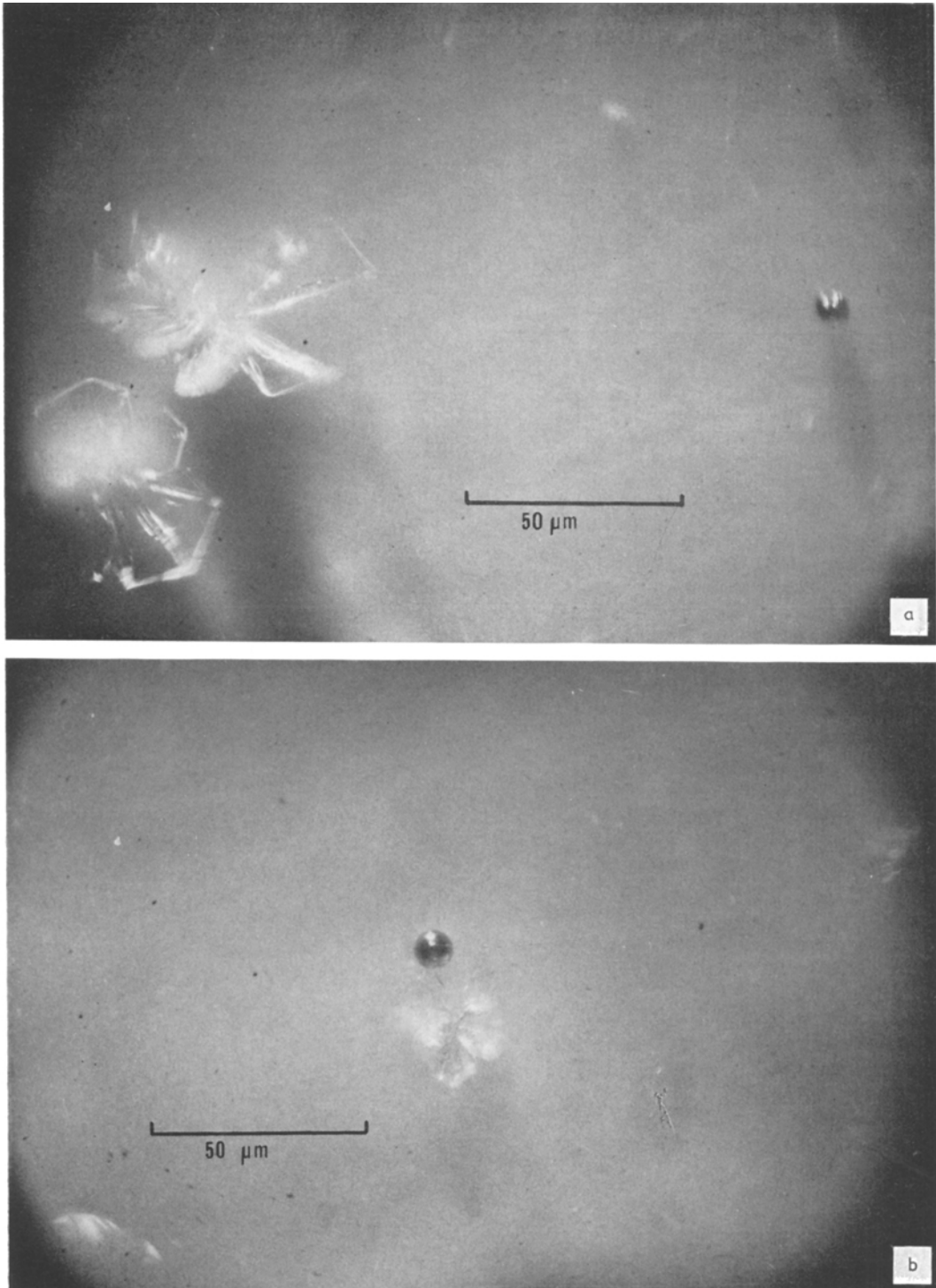


Fig. 2a and b. Examples of apparent ineffectiveness in ice nucleation of two black spherules of diameters $\approx 7 \mu\text{m}$ (a) and $8.5 \mu\text{m}$ (b).

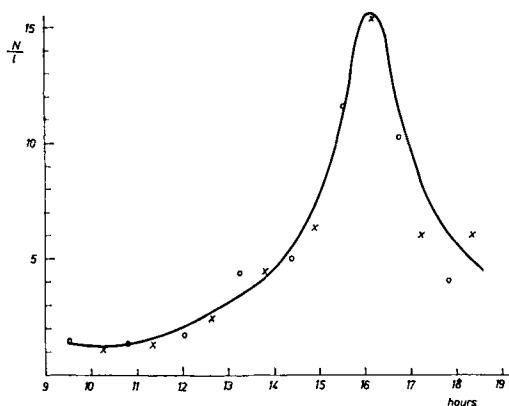


Fig. 3. An unusual case of daily variation in ice nuclei concentration (N/liter) on June 24, 1971 downtown Bologna (Italy).

1. The ferromagnetic aerosol in the size range investigated does not act as an effective nucleating agent;

2. Only small fraction of it plays part in the nucleation process; this fraction remains indistinguishable for instrumental difficulties;

3. The majority of ice nuclei comes from the smaller ($r \leq 2 \times 10^{-5}$ cm) particles for which the collection efficiency of our instrument practically drops to zero.

In the first two cases no special attention should be paid to the ferromagnetic particles from our point of view. It would mean, considering the findings for the big, black spherules that, in the background of a normal, continental aerosol population the meteoric originated matter can play only an unimportant role in the initiation of ice phase: there will be probably always other particles acting in this way. It is not so trivial, however, in the case of smaller ferromagnetic particles. First, the only indication of the extraterrestrial origin of the particles, namely, the ratio of black spherules to those of other shapes steadily increases with

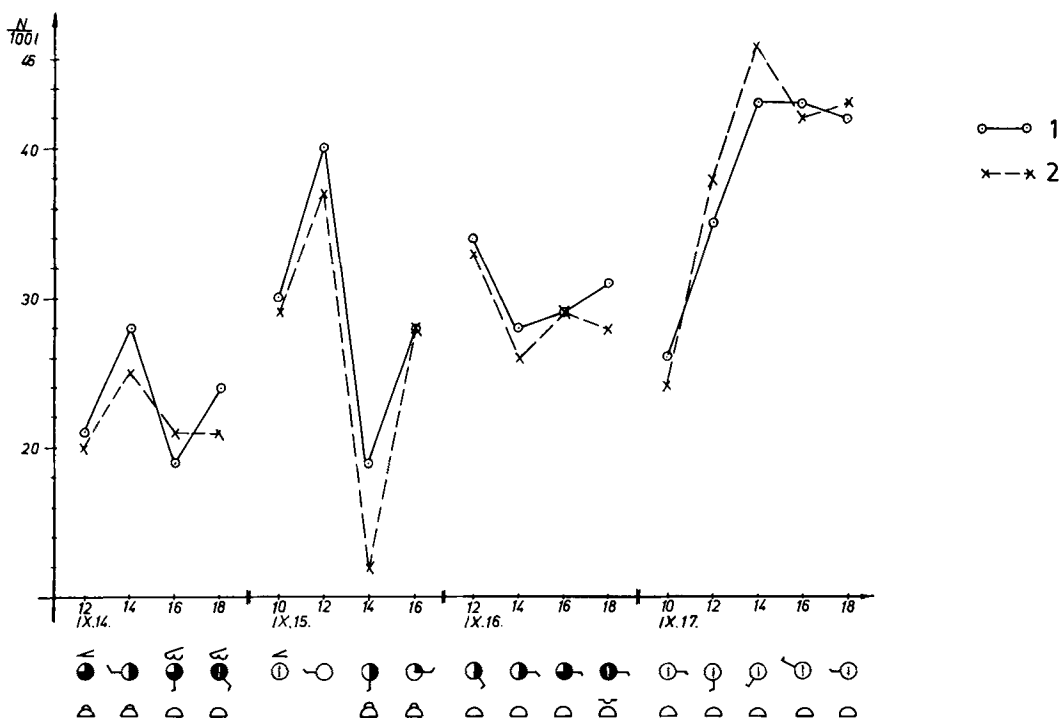


Fig. 4. Ice nuclei concentrations ($N/100$ liters) during a four day (14–17 September 1971) period at the Osservatorio Scientifico, Verona, Italy. —, filters placed downstream of the magnetic precipitator; . . . , filters placed downstream of the reference precipitator without magnets.

decreasing radius. Around, and mainly below $r = 2 \times 10^{-5}$ cm, the vast majority of the particles have round shapes probably due to condensation processes of their formation. There are, though, no investigations on the relationships between the shape of particles and their possible origin, or chemical composition in this range. So it is possible that the excess of this fraction has nothing to do with extraterrestrial dust but comes from industrial activity. In both cases, however, the metal compounds, whether they had originated from the ablation of meteors or not, have proved surely to be poor nucleants in the size range mentioned by Bowen (1956) and very probably so between the 0.1 and 1.0 μm radii.

As to the most likely third case, one has to consider that in ice nuclei measurements by membrane filters the assumption is made that they capture practically all the particles on the front surface. Recent theoretical investigations by Pich (1966) demonstrate that particles smaller than the pore size can really be deposited on the filter's surface but this effect of

inertial deposition decreases very quickly with diminishing sizes, and the capture takes place mostly in the capillaries. Preliminary calculations demonstrate (submitted for publication to the JAM) that only a very small fraction of the total aerosol concentration will be retained on the surface of the membrane filters of different types, which could be taken into account by calculating the collection efficiencies on the bases of Pich's theory. On the other hand, recent experimental (Vali, 1968) and theoretical (Bonis, 1972) investigations support the hypothesis about the existence and efficiency of very small ($d \leq 0.01 \mu\text{m}$) ice nuclei. If this is the case, all of the results, including ours described here, have to be re-evaluated.

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ФЕРРОМАГНИТНЫЕ ЧАСТИЦЫ И ЯДРА КРИСТАЛЛИЗАЦИИ

Ферромагнитные частицы, в диапазоне 20–0,1 $\mu\text{м}$ диаметров, были уловлены с различными методами и их способность для создания ледянных кристаллов исследовалась непосредственными и посредственными наблюдениями. Большие частицы ($\alpha > 5 \mu\text{м}$) помещенные на фильтрах, не играли роль в формировании кристаллов при -12 , -15 °C. «Милли-

пор фильтры», устроены за магнитными и геометрично идентичным контрольным преципитаторами, и «проявиты» в маленькой диффузионной камере при -18 °C, показали подобные концентрации ледянных ядер. Результаты так демонстрировали неспособность ферромагнитных частиц как эффективные ядра кристаллизации.