the starting points. Absorption corrections were made with tabulated data (*18*) for spheres [$\mu r = 0.58$ ($\mu$ is the absorption coefficient and $r$ is the radius)]. Using the correction formula of Zachariasen (*19*), we made extinction corrections iteratively with the least-squares refinement cycles in separate passes.

Observations of the intensities of 28 $k$-odd reflections at both room temperature and $\sim 50°\mathrm{C}$ verified that the monoclinic structure also exists at body temperature (that is, 37°C).

The final cycle of least-squares refinement of the structural model yielded $wR_2$, the weighted "reliability" factor based on $|F|^2$, equal to 3.9 percent and the structural parameters given in Table 1. Although certain anomalies in the temperature factors remain (those for $\mathrm{O}_{\mathrm{IIIA}}$, $\mathrm{O}_{\mathrm{IIIC}}$, and $\mathrm{O'}_{\mathrm{IIIA}}$ are nonpositive definite, possibly because of the assumption discussed in footnote (*16*) or the fact, commented on below, that only part of the specimen was monoclinic), the structure refinement has successfully proceeded far enough to confirm the monoclinic structural form and to permit discussion of its main features. The positions of the hydrogen atoms have been deduced from the positions (in twofold disorder) found in the neutron diffraction studies of Holly Springs hydroxyapatite (*5*). The monoclinic cell is related to the usual one used for hexagonal apatites by a translation of $b$(hex)/2 as well as by doubling of one of the hexagonal axes ($b$). The notation for the atoms follows that used for hexagonal apatite structures with additional designations to allow for atoms that are not symmetry-related in the monoclinic structure although they are in the hexagonal structure.

The most interesting feature of the monoclinic hydroxyapatite structure, and that which had been expected by analogy with monoclinic chlorapatite, is the ordered arrangement of the hydroxyl ions. This is illustrated in Fig. 1. There is a close similarity between the distortions from hexagonal symmetry found in this structure and those found in monoclinic chlorapatite (*4*), including the (unforeseen) fact that the $\mathrm{O}_{\mathrm{III}}$ triangle which is enlarged by having a chlorine ion near its center in chlorapatite is also the one which contains the hydroxyl hydrogen in hydroxyapatite.

Not all of the specimen was in the monoclinic phase. Analysis of the separately refined scale factors for the "monoclinic" ($k$-odd) reflections and the hexagonal ($k$-even) reflections led to the conclusion that the specimen was approximately 63 percent hexagonal and 37 percent monoclinic. Preliminary data for another crystal suggest that this ratio may vary greatly from specimen to specimen and may, therefore, be a point of interest for future studies.

This confirmation of the existence of a monoclinic phase of hydroxyapatite has potential significance in several fields. For example, interest is heightened in exploration of the dielectric properties of the monoclinic phase both in terms of fundamental solid-state properties (probably analogous to those of monoclinic chlorapatite) and in terms of possible involvement in bioelectric effects on bone growth. The existence of monoclinic hydroxyapatite also removes a previously apparent inconsistency between the morphological symmetry (tape-like) of developing dental enamel crystals and their crystal symmetry, which was previously thought to be constrained to hexagonal but is now recognized to have the possibility of being monoclinic.

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14. Three distinct crystal positions occur in the twin, related by 120° rotations about the $c$ axis; none of the more than ten specimens so produced was free of twinning.
15. Details of the technique, which employed both Zr-filtered and unfiltered radiation, have been described elsewhere [see (*4*); P. E. Mackie, thesis, Georgia Institute of Technology (1972)].
16. Although this assumption was satisfactory for the present purpose of confirming the existence of monoclinic hydroxypatite, it clearly does not hold in principle and will have to be abandoned in more detailed refinements of the monoclinic structure. Some confidence in its acceptability here is imparted by the fact that the final $wR_2$ based on the $k$-even reflections alone was 4.0 percent, whereas that for the $k$-odd reflections was 13.9 percent.
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20. This work has received financial support from the U.S. Public Health Service through National Institute of Dental Research grant DE 01912 and from the United Kingdom Science Research Council.

6 October 1972; revised 15 February 1973

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## Ice Nucleation: Elemental Identification of Particles in Snow Crystals

Abstract. *A scanning field-emission electron microscope combined with an x-ray analyzer is used to locate the ice nucleus within a three-dimensional image of a snow crystal and determine the chemical composition of the nucleus. This makes it possible to better understand the effect of nuclei in cloud seeding.*

Information about the elemental composition of atmospheric nuclei is necessary for a quantitative evaluation of deliberate and inadvertent weather modification. In seeding experiments on supercooled clouds, AgI is most often used as the seeding agent. Because the presence of silver in seeded snow can be due to nucleation, scavenging, or sedimentation, analyzing the silver concentration in the snow provides information about the spatial and temporal distribution of AgI in a particular seeding area. However, this method provides little information about the effectiveness of the seeding agent in any weather modification attempt. Only by examining individual AgI particles in relation to individual snow crystals and identifying AgI as the nucleus is it possible to make an objective analysis of seeding experiments.

Using the principle that a particle can act as a nucleus in its own supersaturated solution, Parungo and Rhea (*1*) developed a technique for growing AgI crystals smaller than a micrometer but large enough to be analyzed with an optical microscope and thereby identified as ice nuclei. However, this

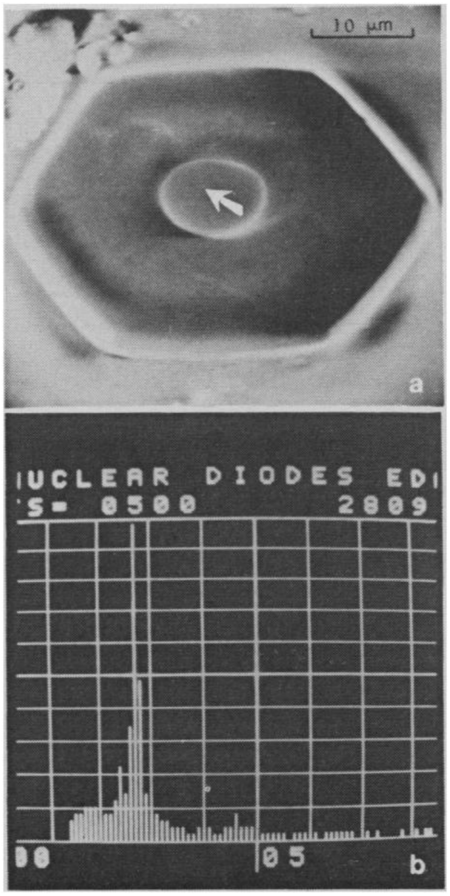

Fig. 1. (a) Image of an ice crystal seeded with AgI and (b) energy-dispersive x-ray spectrum of a particle (arrow) in its center.

method is tedious and its accuracy is limited.

A transmission electron microscope can easily detect ice nuclei smaller than a micrometer (*2*). However, it cannot be used to determine the elemental composition of the nuclei or to isolate the artificial ice nuclei from those provided by nature in a seeding operation in the field. This means that a transmission electron microscope cannot be used to determine the actual seeding effect.

It is possible to use a scanning electron microscope (SEM) to visualize directly the replicas of ice crystals at high magnifications. If the SEM utilizes field emisssion as the electron source, combining the high intensity of the electron beam with excellent spatial resolution, it is possible to locate nuclei of submicrometer sizes in relation to the crystal. Since the SEM operates by bombarding the specimen with a beam of electrons, characteristic x-rays are generated at the point of impact and can be used to determine the elemental composition of nuclei within the ice crystal. Therefore, by combining an energy-dispersive x-ray analyzer with the SEM it is possible to obtain data about the shape of an ice crystal and the exact location and chemical composition of potential nuclei within the crystal in one operation. With this information, it is possible to evaluate quantitatively the effect AgI has on ice nucleation.

In a cold chamber, ice crystals seeded with AgI were collected on sampling studs coated with 3 percent Formvar in ethylene dichloride. Chloroform vapor was applied to replicate the ice crystals. The replicas were then studied with a Coates & Welter field-emission scanning electron microscope, with a magnification of 10 to 88,000 (*3*). The rapidly scanning electron beam produced an image of the surface of the ice crystal. Particles enclosed in the replica were detected by the appearance of changes in surface features. When a particular feature was of interest the electron beam was focused on it, and a complete analysis of the elements was obtained by using a Nuclear Diodes energy-dispersive x-ray analyzer (*4*). Within minutes, the analyzer produced a spectrum of counts as a function of energy between 0 and 8 kev corresponding to all the major and minor elements at that feature.

Figure 1a shows the SEM image of an ice crystal that originated from the droplet in its center. The spectrum obtained with the x-ray analyzer (Fig. 1b) identifies the chemical composition of a particle (arrow) enclosed in the droplet. In Fig. 2, the spectrum is from the particle (arrow) located off center inside the ice crystal. The long lines in column 02 in both spectra correspond to the $K\beta$ transition of silver and show that the element is present; the short lines in column 04 indicate iodine through its $L\gamma$ transition. Although both elements are equimolar in AgI, the heights of the intensity peaks are not a direct measure of their concentrations because the elements are not excited with the same efficiency. (The peaks in column 01 correspond to the composition of the sampling stud.) For a quantitative analysis, the spectrum for the sample is compared with the spectra for a set of standards of the pure elements. Masses as low as $10^{-17}$ and $10^{-18}$ g can be detected.

The field-emission scanning electron microscope coupled with the x-ray analyzer provides a simple and accurate way to identify AgI in seeded snow crystals. This method can also be used for elemental analysis of natural ice nuclei and condensation nuclei. Figure 2 shows two particles at the left edge of the ice crystal; they contain silicon (not documented) and may be quartz ($SiO_2$) that has been scavenged by the ice crystal. The low ice-forming ability of $SiO_2$ compared to AgI eliminates these particles as competitive nuclei in initiating the ice phase in our experiment. This method of analyzing ice crystals will provide a way to study many scavenging problems occurring in precipitation.

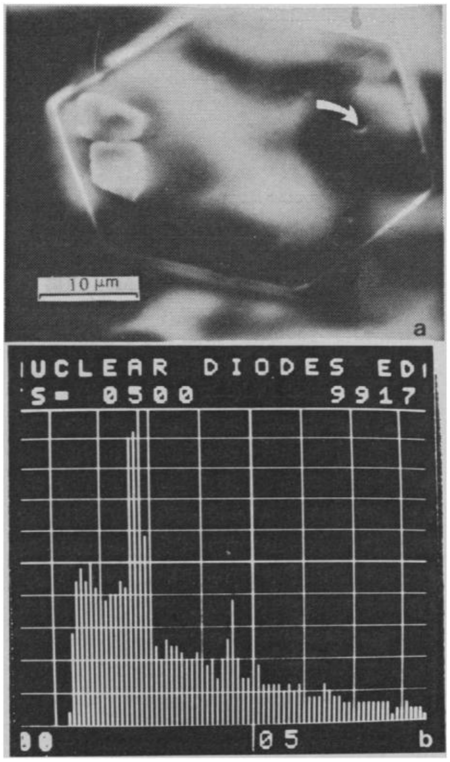

Fig. 2. (a) Image of an ice crystal seeded with AgI and (b) energy-dispersive x-ray spectrum of a particle (arrow) off center.

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5. We thank T. E. Brickman and W. Roth of Coates & Welter Instruments for their valuable assistance during this investigation, and Dr. H. K. Weickmann, Environmental Research Laboratories, Boulder, Colorado, and Dr. J. P. Lodge, Jr., National Center for Atmospheric Research, Boulder, Colorado, for their helpful comments.

12 February 1973; revised 16 March 1973