

Natural Tracer Distribution in Hailstones¹

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ABSTRACT

Preliminary results of a chemical analysis of hailstone slice residues are reported. The radial pattern of Fe particles shows a marked outer ring of relatively high concentration. The possible causes are discussed and it seems reasonable to attribute it to a final freezing of contaminated liquid water contained in the hailstone outer layer.

1. Introduction

The interpretation of hailstone cross sections in terms of environmental growth (temperature, liquid water content and crystal concentration in the mother cloud) is the aim of several laboratory studies. At present, however, rigorous classification of hailstone types in terms of radial ice structure, type of core or embryo, size and distribution of bubbles, etc., seems to be premature. Moreover, the storage of hailstones at different temperatures must contribute to some extent to details observed in the structures. So far, from the analysis of the principal features of hailstone ice produced in the laboratory, it appears that clear ice made up of radial crystals cannot have been formed under dry growth (Kidder and Carte, 1964).

A further contribution which seems promising in clarifying this complicated picture is the study of the sizes and distributions of contaminating materials inside the hailstones. Particles of various chemical composition and different physical characteristics are scavenged by the growing stone and the radial distribution pattern can be interpreted on the basis of studies performed in the laboratory on ice formed from contaminated water.

Although in some respects this new type of analysis undoubtedly enlarges the range of problems to be solved, we believe that some of the more evident aspects of the results obtained by such "chemical" means may help to clarify some of the controversial aspects which are derived from purely physical and optical analyses.

An attempt in that direction was published some years ago (Vittori and Pesaresi, 1964). More recently, Rosinski (1966) presented a series of observations of radial distributions of insoluble particles inside hailstones. Both works show that there are marked variations in contaminant concentration within the hailstone.

The method used by Rosinski allows a quantitative estimation of the distribution pattern but does not

allow a good comparison with the actual structure of the hailstone examined. His results indicate, apart from small-scale fluctuations, that a radial distribution of large insoluble particles within the hailstone, with concentration increasing with radius, appears to be typical of most of the samples he examined.

This paper presents an attempt to precisely localize the observed fluctuations of particle patterns with respect to the gross internal features of the hailstones.

2. Experimental approach

The contaminant analyzed in our previous work was chloride (always present in cloud water), as we could apply a very sensitive chemical reaction for Cl^- ions to the residues of sublimated hailstone slices. In the present approach, in order to follow Rosinski's line, we have undertaken an analysis for other tracers present in the atmosphere as insoluble compounds. Although no cation or anion can be *a priori* assumed to be present in the atmosphere in insoluble compounds, iron appeared to closely satisfy our requirements. In fact, a large fraction of its airborne compounds is expected to be fairly constant, of the order of 10^{-12} gm cm^{-3} (Junge, 1963; Pettersson, 1958; Vittori, 1968). The chemical literature already offers some reactions for Fe which can be used as spot tests of fair sensitivity (Feigl, 1958), and, in addition, since our investigation was concerned with localizing very small Fe particles in the hailstone residues as colored Fe precipitates, the great variety of colorimetric reactions for Fe, generally giving soluble products, has been studied in the laboratory for applicability to our problem.

The great variety of hailstone structures is well documented, with hailstones collected from the Great Plains of North America and the Po Valley in Italy showing marked differences in structure. It appears that the main characteristic of the most frequent type of the former is the presence of a thick outer layer of apparently dry (or crystal plus droplets) growth following a wet or spongy inner layer of moderate thickness. In

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the Po Valley a large portion of hailstones (especially those occurring in the middle of summer) show a structure mainly composed of apparently wet (or spongy) growth. At this point it is best to make clear that the apparently dry outer layer can also be observed in many of the Po Valley hailstones but to a much lesser extent. The above generalization is not based on a statistical evaluation, however, but on our qualitative impression formed from handling many samples of hail from both regions and from observations of published pictures of hailstone cross sections, the latter being admittedly unrepresentative to some extent. The observed difference appears to be limited to stones of moderate size (3–4 cm in diameter).

The samples examined in the investigation reported in this paper are from a Colorado hailfall (1 July 1967); this allows us to assume that the hailstones examined are not very much different, at least in chemical composition, from those analyzed by Rosinski (on the other hand, no relatively large hailstones from the Po Valley were available).

3. Experimental technique

A critical description of the method for preparing and sublimating thin hailstone slices and for determining the distribution of chloride particles in the residues is contained in Vittori and Pesaresi (1964). The analysis for iron particles presented some difficulties, as the residues must be previously treated with acid and brought to the valence required for the reaction. Tests using ferrocyanide reagent for Fe^{3+} (Feigl, 1958) gave fair results, relatively large particles being easily visible as blue-green spots. In order to detect smaller particles, the very sensitive reaction for Fe^{2+} based on α , α' dipyridile reagent (the reaction product is soluble in water) has been modified to yield an insoluble complex of a bright red color. The details of the chemical technique are published elsewhere (Vittori, 1969). Particles in the micron size range are detectable.

Slices² 1–1.5 mm thick are sublimated at -20 to -25°C at vacuum pump pressures (to speed up the sublimation and to minimize local airborne contamination) to a colder surface. The residues distributed upon the surface of the support (a glass plate) are transferred to a photographic type gelatine for the reactions. The transfer operation is accomplished by superimposing the gelatine surface (containing the reagent) upon the glass, making use of a press of such a precision that no microscopic relative displacements take place. Prior to the iron analyses, the residues are placed for some 15 min in a large Petri dish containing a high concentration of HCl vapor.

The complete series of operational steps is long and laborious and some phases of the program require close attention. Thus, 1) the series of pictures prior to sub-

² In order to avoid any specific contamination in the samples, a pure gold wire has been used as cutting element.

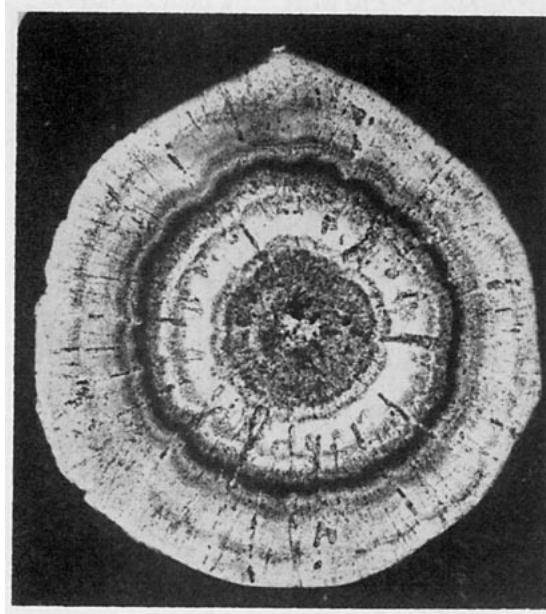


FIG. 1. 1–2 mm hailstone slice in cross polarized light.

limination of the sample should include at least one taken at the last moment when the sample has been placed in the sublimation chamber with good reference points (scale, orientation, etc.), and 2) after the ice has disappeared from the sample, the sublimation chamber should be brought to room temperature equilibrium, and air bled in very slowly (these precautions assure that no condensation occurs on the slide and the residues are not disturbed).

4. Results

Improvements in the measurement technique were made concurrently with the hailstone examinations. All the stones examined turned out to be, in their gross features, of the Great Plains type described above; our analysis, therefore, concerns a homogeneous set of samples.

We cannot yet present an exhaustive documentation of all the details of the findings; much further study is required in comparing the “chemical” and “physical” pictures of the stone. The following facts are the most evident:

- 1) The Fe particle distribution shows sharper fluctuations than does that of the soluble chlorides.
- 2) A ring of relatively high concentration of large particles is found at the periphery of the residues, confirming the sharp radial distribution reported by Rosinski (Figs. 1 and 2).
- 3) The accurate comparison of the Fe particle distribution with the visual structure of the hailstone slice shows that the outer Fe ring is located some 1–3 mm inside the actual outer surface of the hailstone (Fig. 3); chlorides show the same, though with less definition.

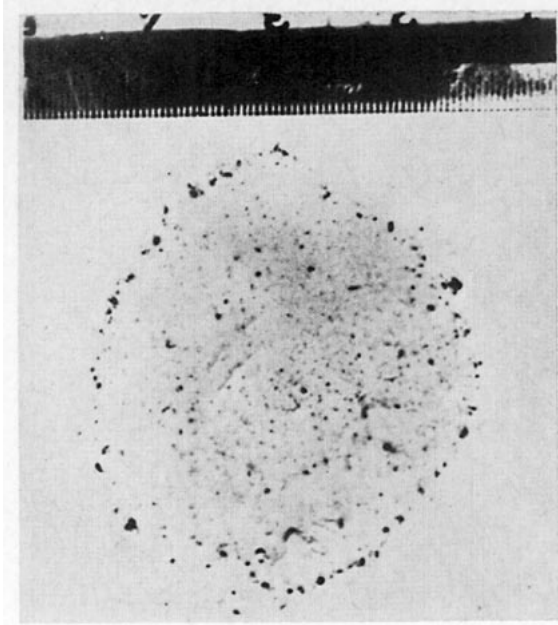


FIG. 2. Distribution pattern reactions involving Fe particles.

4) There are some variations of the concentration of contaminants inside the hailstone which appear to be related in some way to the gross features of the stone (Figs, 4a,b); note the iron particles around the dry growth following the core).

5) Among the common features in the "chemical" and optical patterns, it seems worth noting that

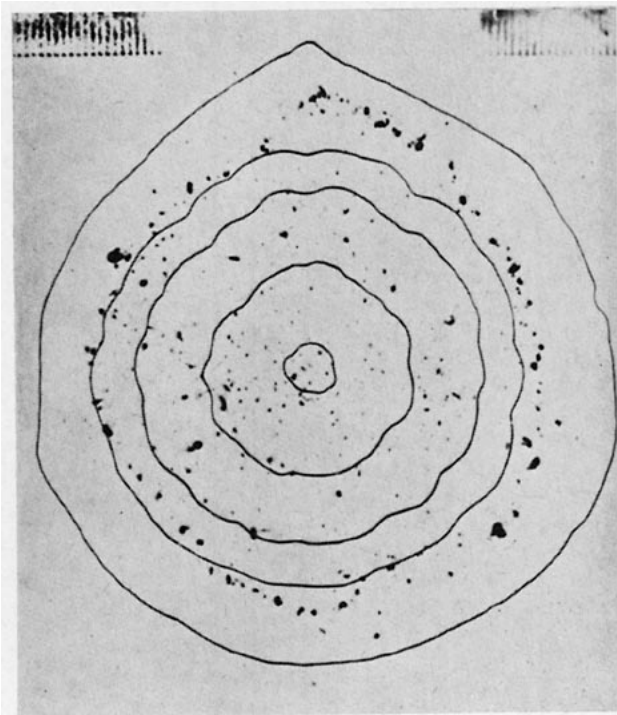


FIG. 3. The Fe particle distribution pattern of Fig. 2 superimposed on an outline drawing of Fig. 1.

localized reactions in the small-scale structure of the chloride distribution correspond exactly with certain details visible at the end of the "wet" layer (Figs, 5a,b).

In addition to the above the following tests were performed:

1) The total amount of Fe in some hailstones, as measured with the atomic absorption spectrometer, gave a fairly constant concentration of around 10^{-6} gm ml⁻¹.

2) Although the technique is not new, we were able, by freezing water containing suspensions or soluble salts in polyethylene cylinders, to confirm that contaminants are pushed by the freezing and are concentrated toward the center; the suspension (colloidal Ag) shows a very sharp ring boundary. A scatter in the micron range can be observed in the soluble material ring.

5. Discussion

A test was performed in order to establish that there is no transport of particles from the border of the slice toward the center during the sublimation phase. To the water used in the run for welding the slice border to the glass, a small amount of fluorescent material was added. Pictures taken in the ultraviolet before and after sublimation showed no displacement. In addition, the residues were analyzed for iron, confirming that the

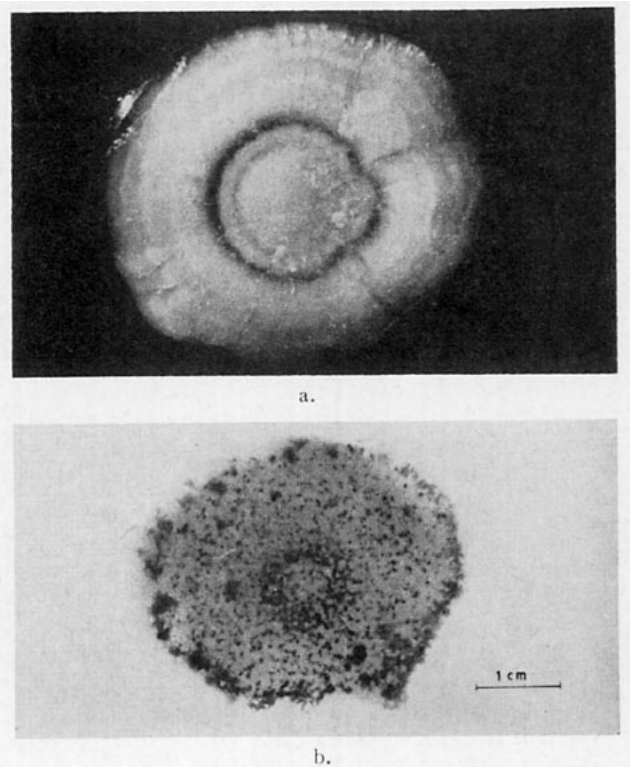


FIG. 4. Hailstone slice (3 mm) in ordinary transmitted light, a, and corresponding distribution pattern of Fe particles, b. The thicker slice shows better detail in the particle distribution pattern.

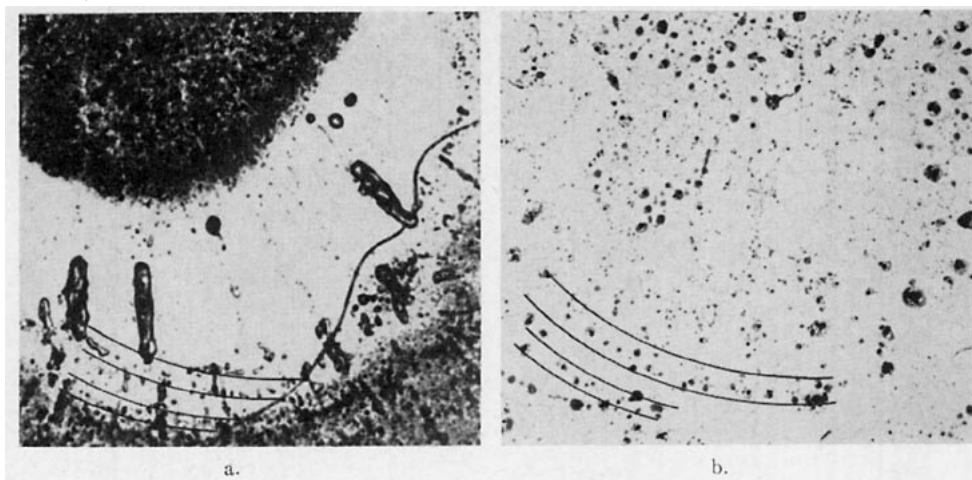


FIG. 5. A portion of a hailstone slice in ordinary transmitted light, a., and the detail of the distribution of chloride reactions, b., the reactions within the marked strips showing an exact correspondence with certain of the visible microstructures of the hailstone in transmitted light. They appear as very small enclosures distributed as parallel lines at the end of the "wet" growth. A superimposition of the two pictures in color (the reaction particles are colored) would show that there is also some correspondence between certain linear radial distributions of the smallest reaction particles and the boundaries between long radial crystals.

intense ring of Fe particles was internal to the slice border.

We think at this preliminary stage of the work that the following possible interpretations (some of them already considered by Rosinski) of the above findings can be advanced:

1) In the growth stage corresponding to the observed high concentration of iron, the stone grows very slowly (presumably because of a low ambient liquid water content), while capturing a great amount of airborne material.

2) Assuming that ice crystals growing at water saturation are very good scavengers of airborne materials (Reiter and Carnuth, 1965; Vittori and Prodi, 1967), the iron ring could correspond to a stage of growth within a mixed cloud.

3) The particles inside the hailstones migrate within the ice phase under the influence of strong temperature gradients.

4) The outer layer of apparently dry growth in the growing hailstone actually contains a small amount of contaminated water which is pushed toward the center during a final low temperature freezing from the outside.

Since there have been no investigations on Fe particle concentration as a function of altitude, we have no indication as to the possible stratification or anomalous concentration gradients of that contaminant in the high troposphere.

Hypothesis 1), however, should require that those portions of the hailstones containing low Fe concentration must have grown in regions of very high liquid content. In fact, the observed wash-out ratio is consistent with the previously mentioned Fe concentration in air, assuming that the atmospheric Fe particles are

scavenged by the hailstone in its growing stage. Accordingly, the calculated concentrations of scavenged Fe in the hailstones lie between 10^{-6} and 0.2×10^{-6} gm ml⁻¹ for an average liquid water content in the range 1–5 gm m⁻³ (collection efficiency taken to be unity).³ Only a low capture efficiency of the droplets for these particles can account for the relatively high water content in the hailstorm clouds.

Hypothesis 2), assuming very high scavenging efficiency of ice crystals for airborne particles, suggests that the Fe ring could correspond to the vertex of the hailstone trajectory in which it could be growing in a mixed cloud. However, the small thickness of the Fe rich shell would imply a very brief residence time in the mixed cloud (the mixed growth proceeds very rapidly). Hypotheses 1) and 2) would both imply rapid changes in the environmental conditions of the growing hailstones.

The migration velocity of particles inside the ice as a function of temperature gradient [hypothesis 3)] is so low that the separation between the outer Fe ring and the hailstone surface could not have been due to the effects of a temperature gradient on the hailstone, either in the cloud (where its residence time is short) or in storage.

Hypothesis 4) seems to find some support from what is already known about hailstone growth mechanisms. Assuming that the outer layer, which polarized light reveals to be composed of very small crystals, is formed by dry growth, the size of the hailstone indicates that

³ The high average concentration of β activity (10^{-10} curie ml⁻¹) in hailstones observed by Blifford *et al.* (1957) as compared with average value of air activity in that period and in that locality (Joint Committee on Atomic Energy, 1959) yields wash-out ratios much higher than the average. A high concentration of fission products in the local high troposphere (Nevada tests) probably accounts for the anomaly.

even in a cloud of relatively low liquid water content and very low ambient temperature, the regime of the growing hailstone should not be far from the Schumann-Ludlam transition line, i.e., where the relatively high temperature of the hailstone surface prevents complete freezing of the supercooled cloud droplets (Vittori and Pesaresi, 1964).

The amount of unfrozen water depends on the temperature of the hailstone surface and on the concentration and nature of the soluble contaminant in cloud droplets. Taking 50 mg liter⁻¹ as the concentration of soluble compounds in cloud droplets collected by the stone (the total amount of soluble substance in rain falling at some distance from contaminated localities contains more than 20 mg liter⁻¹), and 50 as an average molecular weight of the soluble contaminant, we can deduce that of the water collected by a hailstone having a -2C surface temperature a portion of the order of 10⁻³ should remain liquid. Higher temperatures of the growing hailstone should lead to a higher concentration of unfrozen water. Moreover, there is no absolute certainty that the outer layer is of the dry growth type; even a "small crystal" structure may be produced by a spongy or wet growth.

Particles are pushed by the freezing interface and there are some indications that this process can discriminate particles in size (Hoekstra and Miller, 1967). A cooling proceeding from the outside can concentrate and probably agglomerate particles up to 2000 μ in diameter (Rosinski, 1966), contained in a small portion of the outer contaminated layer, into a ring-like distribution. Any process which leads to a warming of the hailstone before the ultimate freezing could play the same role.

6. Conclusions

The results seem to offer considerable substance for continued investigations requiring further laboratory work.

We believe that an investigation of the last interpretation presented would not imply a new model of environmental conditions of the hailstone in the cloud. Since the amount of unfrozen water in the proposed "contaminated dry growth" mechanism can be a function of hailstone radius, assuming its surface temperature increases with size, the radial size distribution

of the solution pockets could play an important role, during a final freezing, not only in radially differentiating the transport of particles but in producing some of the sharp concentric fluctuations in features observed in natural hailstones.⁴

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⁴ Dorsey (1940) reports that "J. Y. Buchanan has shown that the crystals of ice formed from a dilute salt solution are themselves free of salt, but that some of the solution is retained in the interstices between the crystals; at the same time he called attention to the pronounced effect this intercrystalline material may have upon the physical properties of the ice, even when the amount of salt present is excessively minute. The presence of such intercrystalline material should always be remembered when ice in bulk is being studied. In many cases it profoundly affects the results obtained."