SULFATE AEROSOL GENERATION
In the
MARINE ATMOSPHERE

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1, INTRODUCTION

The generation of maritime cloud condensation nuclei (CCN) through the ejection of jet and film droplets from bursting whitecap-produced bubbles on the ocean surface has been well documented. The processes involved in the transformation (evaporation and crystallization) of these liquid droplets into their solid form under varying conditions, however, has not previously attracted much attention from researchers. A set of laboratory investigations and field observations of the characteristics, both physical and chemical, of seawater droplets during phase change in a controlled environment has revealed the following startling and very significant phenomena:

1, Ejection of micro-size sulfate aerosols from the crystallizing droplet.

2, Formation of hollow sphere of sea-salt particles.

3, Shell structure of chlorides ($MgCl_2$ and KCl) on the surface of the ejected aerosols and seasalt particles.

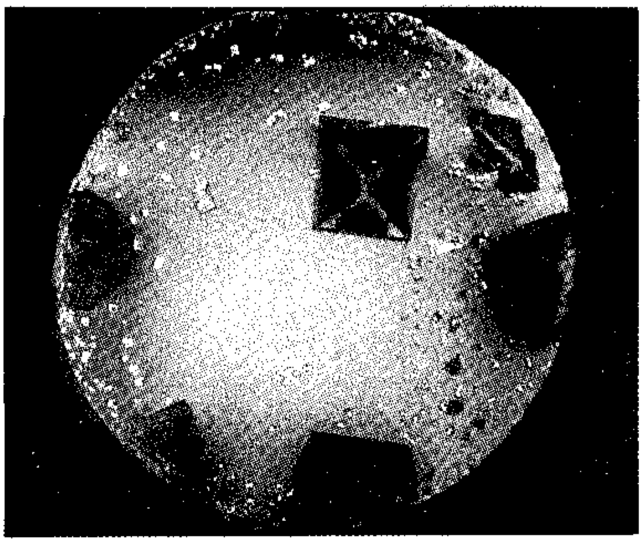

Figure 1, An Evaporating Sea Water Droplet.

2, EXPERIMENTS

For this investigation, samples of seawater and marine aerosols were collected at Cape Cod, Massachusetts (Woods Hole Oceanographic Institution). Droplets of various sizes (from a few μm to 200μm) were generated by an atomizer and also by an ultrasonic humidifier. Individual droplets were produced by a hypodermic needle attached to a disposable syringe. For the observation of phase change, droplets were placed on microscope slides coated with a silicone compound (Dri-film) that produced a contact angle of 90 degrees between the droplet and the slide. Consequently, all droplets formed hemispheres. A small environmental chamber was constructed under a polarizing microscope and the relative humidity (RH) in the chamber was controlled by the solution of $CaC1_2$ in different concentrations. Scanning electron microscope (SEM) studs or microscope slides were placed 2 mm above the experimental droplets in order to intercept any aerosols generated in liquid-microdroplet or solid-crystal form during the evaporation and subsequent crystallization of the droplets. Elemental analyses were performed via energy-dispersive x-ray spectroscopy (EDXS) on individual ejected aerosols and on ocean-generated marine aerosols. Every precaution was taken throughout the experiment to avoid possible contamination either by gaseous or by particulate.

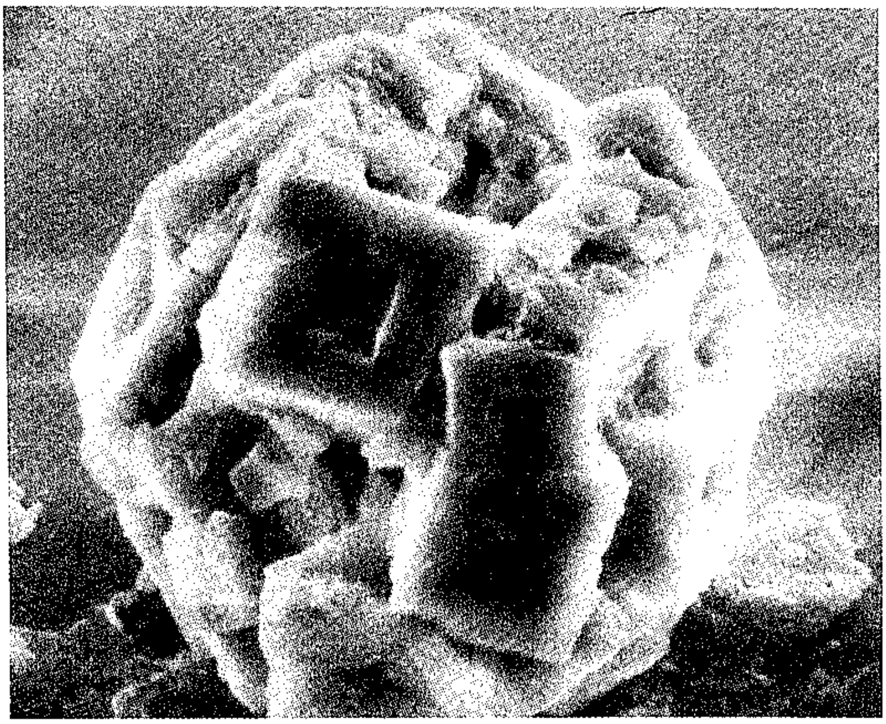

Figure 2, A Hollow Sphere of Sea-Salt Particle.

3, RESULTS AND DISCUSSION

Close examination by a polarizing microscope of an individual seawater droplet in an environment of relative humidity (RH) less than *75%* and temperature of 25°C have resulted in the following observations: Evaporation of water increased the salt concentration. At first, a thin layer of brine formed at the surface of the evaporating droplet; this was followed by a clearly sequential precipitations of numerous microcrystals of sulfates ($CaSO_4$, $MgSO_4$), and by a crust of many relatively larger cubic NaCl crystals beneath the droplet surface correspondent with their individual solubilities and concentrations in the droplet (Fig.1). During this process, solution of chlorides ($MgC1_2$, KC1) mixed with microcrystals of sulfates or NaC1 were expelled by the rising internal pressure generated by the rapid phase changes of many NaC1 crystals in conjunction with the evaporation of water, through interstitial spaces of much larger NaC1 crystals situated beneath the surface of the droplet. Brine-film bursting at the interstices of cubic NaC1 crystals was also observed and followed by the formation of a hollow sphere of sea-salt particles with many holes (Fig.2)(Ref. 1).

Water-droplet formation proceeded rapidly via condensation onto the surface of microscope slides when subjected to RH of 50-60% , indicating the presence of aerosols generated by the crystallization of the experimental droplets. The numbers of ejected aerosol particles were dependent upon temperature and RH and the sizes of the original droplets; from few to 20 aerosol particles per droplet were detected. There were no detectable ejections at RH higher than 70%, or with droplet size smaller than 5 μm in diameter. A larger number of aerosol particles were generated from rapid evaporation followed by crystallization of seawater droplets on a hot (35-45°C) rock surface.

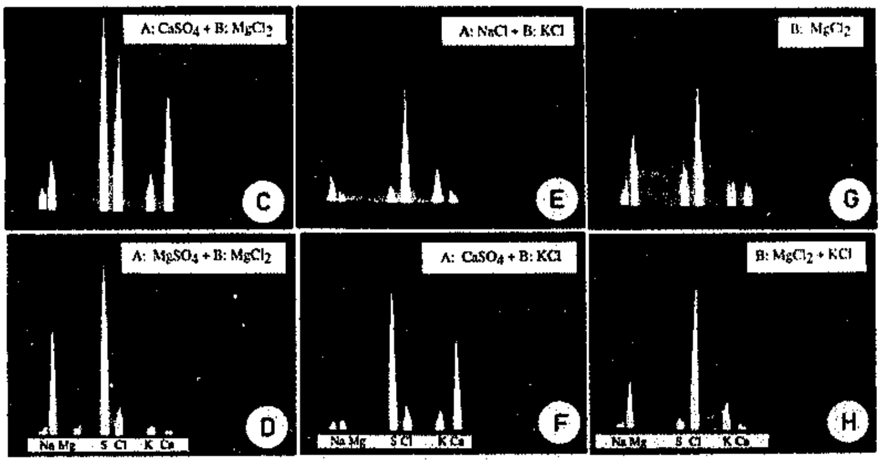

Figure 3, Classification of Marine Aerosol.

The most important mechanism for the generation of a larger number of secondary aerosols was found during the phase change occurring through the bursting of many air bubbles which formed when hollow sea-salt particles were moved into a high-moisture environment or were dissolved into a water drop. Ejected aerosols ranged from 0.1 μm to 10μm in diameter characterized individually by SEM+EDXS system, could be classified into three categories: (A) NaC1 crystals, (B) crystals of sulfates ($CaSO_4$, $MgSO_4$), and (C) chloride droplets ($MgC1_2$, KC1) (Fig.3). Examination of SEM micrographs of sea-salt particles formed after phase change during the free-fall of seawater droplets indicated that more than 50% of the particles larger than 5μm in diameter exhibited as hollow spherical structures with many holes on their surface, or as clusters of cubic salt crystals.

The shell structure of chlorides ($MgCl_2$, KC1) (Fig.4) present on the surface of the ejected aerosols and the sea-salt particles was confirmed via optical and electron microscopy. Under examination with polarized light, the colorless NaC1 crystals (amorphous) and sulfate crystals were found to be consistently coated with a thin layer of crystalline chlorides having very high solubilities. Moving experimental particles into an environment with RH higher than 40% resulted in the gradual disappearance of crystalline substances and the concomitant condensation of water vapor. The end result was liquid droplets containing cubic NaCl crystals at their centers. Only when the RH reached 75% did the NaCl crystals begin to dissolve into the water drops. The shell structure of particles was readily evident upon examination; by varying electron beam intensity or by increasing the acceleration voltage in SEM operation, elemental spectra were obtained from surface and from inside of the particles.

Examination of samples of marine aerosols collected from the coast of Massachusetts by SEM+EDXS confirmed the presence of hollow spheres of many sea-salt particles (Ref. 1) and microcrystals of sulfates possessing a shell structure of chlorides. Hollow sea-salt particles were also observed from aerosol samples collected near McMurdo Station Antarctica (Ref. 2).

4, CONCLUSIONS

Although fractionation during crystallization of sea-salt particles was first proposed by Dessens (Ref. 3), laboratory experiments have not previously provided consistent results (Ref.4-8).

The microscopically investigations reported here confirm that microaerosols are ejected from seawater droplets during crystallization and are followed by the formation of hollow spherical particles. Most notably, secondary ejection of many aerosols is also observed during the phase transition of the hollow particles to liquid form by dissolution into other water droplets. This phenomenon has obvious significance for determining contributions to the population of cloud condensation nuclei (CCN) in the marine atmosphere.

The detection of a chloride ($MgCl_2$, KCl) shell structure on the surface of ejected aerosols and sea-salt particles is of extreme importance to understanding the fundamental nucleation processes of cloud formation in the atmosphere. A chloride film presents a highly hygroscopic surface and was found to initiate the condensation of water vapor to form cloud droplets in an environment with RH as low as 40%. Sodium chloride ($NaCl$-RH 75%) crystals, on the other hand, play only a minor role in initiating condensation.

Recent reports have indicated that high concentrations of sulfates are present in marine aerosols (Ref. 9-14); these were suggested to be the products of the photochemical reaction of SO_2 originating from biological activities (DMS) at sea or from continental and distance authropogenies origins. The ejection of sulfate aerosols during the crystallization of seawater droplets in this investigation may present a new pathway for a better understanding of the generation of sulfates in the marine atmosphere (Ref. 15,16).

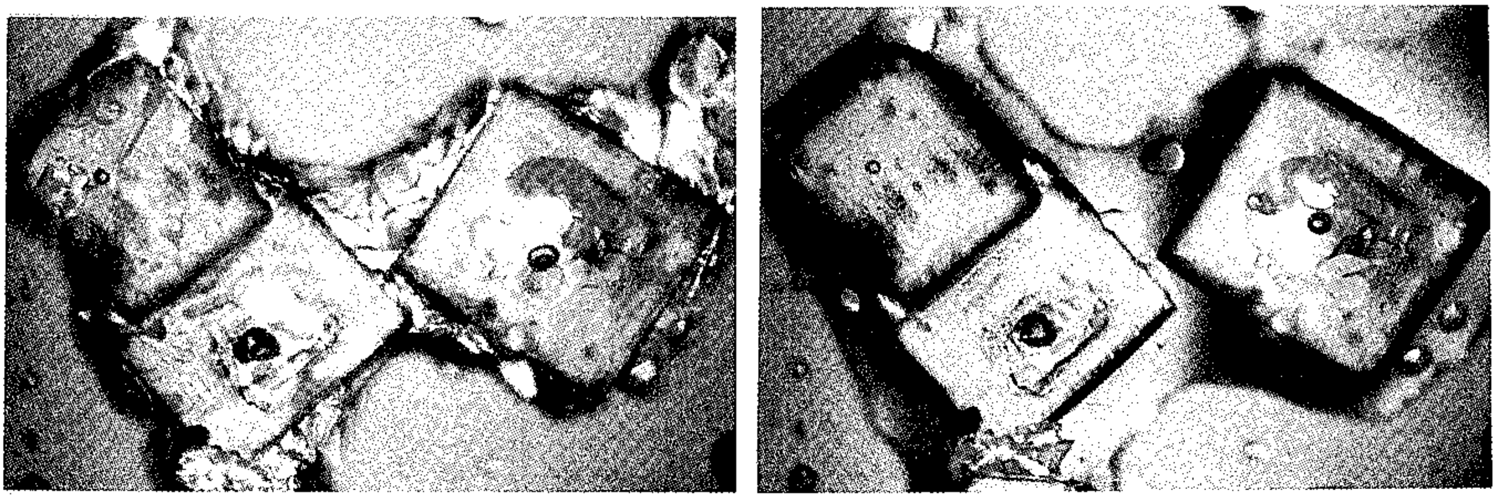

Figure 4, Sea-Salt Aerosol with Chlorides Film in an Environment of : L: 30% RH. R: 50% RH.

5, REFERENCES

1, Cheng, R. J. et al, 1988: The formation of hollow sea-salt particles from the evaporation of drop of water. Atmos. Res. 22,15-25.

2, Murphey, B.,1988 (private communication).

3, Dessens, H., 1946: Les noyaux de condensation dr l'atmosphere. C.R.Acad. Sci. (Paris). 223,915.

4, Facy, L., 1951: Embruns et nuyaux de condensation. J. Sc Meteorol. 3, 86-98.

5, Lodge, J.O. et al, 1954: An experimental investigation of the shatter of salt particles on recrystallization. J. Meteorol. 11,420-421.

6, Twomey, S. et al, 1955: Production of condensation nuclei by crystallizing salt particles. Tellus, 7,458-461.

7, Blanchard, D. C. et al, 1964: Condensation nuclei and crystallization of saline drops. J.Atmo s. Sd., 21, 182-186.

8, Radke, L.F. et al , 1972: The shattering of saline droplets upon crystallization. Atmos. Res *.6,447-455.*

9, Bonsang, B. et al, 1980: Sulfate enrichment in marine aerosols owing to biogenic gaseous sulfur compounds. J. Geophys. Res.,85, 7410-7416.

10, Andreae, M.O. et al, 1986: Internal mixture of salt, silicates, and excess sulfate in marine aerosols. Science. 232, 1620-1623.

11, Parungo, F.P. et al, 1986: A study of marine aerosols over the Pacific Ocean. J..Atmos. Chem. 4, 199-226.

12, Miller, D.F. et a! 1987: SO_2 oxidation in cloud drops containing NaCl or sea salt as condensation nuclei. Atmos. Environ. 21,991-993.

13, Clarke A.D., 1987: The pacific marine aerosol: evidence for natural acid sulfates. J. Geophys. Res. 92,4179-4190.

14, Cheng, R.J., 1988: The generation of secondary marine aerosols. Lecture Notes in Physics, Springer, 589.

15, Cheng, R.J., 1989: Sulfate aerosols generation in the marine atmosphere: The evaporation of seawater droplets, International Conference on Global and Regional Environmental Atmospheric Chemistry, Beijing,China