a controlling factor in all of the extensive long-period fluctuations of the general circulation.

No real attempt has been made as yet to explain how this solar variability directly affects the circulation patterns. However, if the effect is there in the long-period variations, and since the shorter-period variations are similar in character and the sun is known to undergo quite violent short-period variable activity, the possibility is by no means excluded that the irregular short-period variations of solar activity also affect the changing index patterns of the general circulation. If this is the case, it might help to explain the fact that the ordinary cycles of index change of the general circulation are so variable and erratic from cycle to cycle, and between different years, that statistical analysis fails to yield significant indications either of regular periodicity or of regular lag effects in the change of the general circulation pattern.

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TECHNICAL PAPERS

Some Experiments in the Freezing of Water

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Although the supercooling of water is recognized as a very common occurrence, numerous reports have recently been published about it.

In our research we have found that the freezing of water without supercooling would be much more surprising, since we have so far been unable to find anything which will cause freezing at 0° C, except in contact with ice. Normally, water will not freeze until it is cooled to about − 20° C.

Lately, Rau (*8*) claimed to have cooled water to − 72° C before it froze. He accomplished this by means of a "system of successive sterilization of the nuclei of solidification." After the publication of this work, Bangham (*1*), Frank (*4*), and Ubbelohde (*10*) attempted to explain this phenomenon and also to predict certain properties of water in the low-temperature range. Since then, Cwilong (*2*) has tried to repeat Rau's experiment and has proven Rau's measurements to be invalid.

Another reported case of the low-temperature freezing of water is stated by Oltramare (*7*). He reported that R. Pictet and L. Dufour had cooled water to − 40° C, but no paper by either Pictet or Dufour gives this value.

Martin (*6*) cooled water to − 26° C by repeated distillation *in vacuo* without ebullition.

The above experiments were carried out on water in bulk. On the other hand, Vincent J. Schaefer (*9*) found that a supercooled water-droplet cloud dispersed in air, in the absence of sublimation nuclei, spontaneously changes to an ice-crystal cloud when any portion of the cloud is cooled to − 38.9° C or lower. A few ice crystals can be observed at a slightly higher temperature, but the above temperature may be regarded as critical.

Bernard Vonnegut (*11*) found a number of foreign particles, most notably silver iodide, which cause the transformation from a water-droplet cloud to an ice-crystal cloud at considerably higher temperatures. He obtained varying results, depending not only on the material of which the particles were composed but on their crystalline structure, size, etc.

Cwilong (*3*) has also made measurements of the sublimation temperature in the atmosphere and claims a value of − 41.2° C for spontaneous ice-crystal formation in pure air and about 9° warmer for impure air.

In Cwilong's experiment in a Wilson Cloud Chamber, the minimum temperatures reached were calculated and not measured. Furthermore, the presence of ice crystals was shown by their seeding action on a sample of supercooled water. In Schaefer's experiment, the temperature was measured directly and held constant, and the ice crystals observed visually and samples obtained. The validity of his results seems beyond criticism, and his temperature of − 38.9° C should, therefore, be accepted as more exact.

Cwilong's assumption that ions act as sublimation nuclei has not received support from our experiments. In a forthcoming paper, Schaefer will describe a number of foreign-particle sublimation nuclei and their relative effectiveness at various temperatures.

I. Langmuir, in a paper not yet published, reports that he has conceived of a mechanism for the spontaneous nucleation of a supercooled cloud. His explanation is based on the existence of an air-water interface. According to the Langmuir hypothesis, it should be possible, therefore, to cool water out of contact with the air below the critical temperature found by Schaefer and in contact with air down to this temperature.

In an effort to test this hypothesis, the following freezing experiments were carried out. These, although not yet complete, are significant. The apparatus used is shown in Fig. 1.

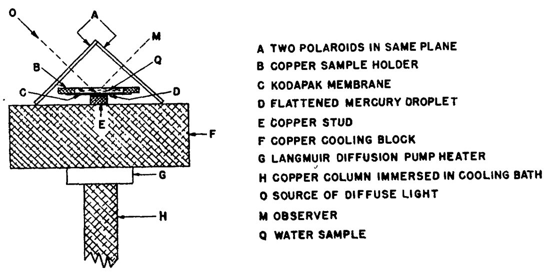

FIG. 1

The water sample to be frozen was supported on a Kodapak membrane (a certain type of cellulose acetate) stretched across a ¾″ hole in a ⅛″ copper plate. Originally it was planned to eliminate the air-water interface by laying another Kodapak film across the water surface, thereby completely enclosing it. The first experiments described below were done, however, without this cover, and the water sample was exposed to the air. The sample was then lowered onto a mercury-covered copper stud about ¼″ in diameter and in thermal contact with a cooling system whose temperature could be accurately controlled. In this way no air-solid interface, below 0° C, was in contact with the liquid. The presence of ice, clear or opaque, could be recognized by means of a polarized beam of light which passed through the sample, was reflected from the mercury surface, and reached the observer through another polarizer with its plane of polarization parallel to the first. The presence of ice caused birefringence which could be easily detected.

Considerable work was done in devising techniques for satisfactorily cleaning the surfaces and purifying the water. It was found that loosely adhering dust on the fresh Kodapak surface could best be removed by simply rolling drops of distilled water across it. Examination under a microscope was used to make sure no dust or dirt remained. Various methods of purifying water were tried, among them distillation, condensation, diffusion through a Formvar membrane, and pressure filtering.

Many freezing runs have shown the crystallization temperature to be independent of the rate of cooling, the previous history, such as previous freezing, and the temperature to which water has been raised to between freezing cycles.

Data from four sets of experiments give an average crystallization temperature of −19.2° C, with a maximum of −18.0° C and a minimum of −20° C: (1) −19.0, −18.0; (2) −19.5, −20.5; (3) −20.0, −19.2; (4) −18.0, −20.0.

These results show that the supercooling of water is not at all an unusual phenomenon. The normal temperature at which water freezes is, therefore, in the absence of any known foreign nucleating materials, very close to −20° C and not, as is commonly believed, at 0° C. It might also be mentioned that considerable vibration was present during all of the above tests but had no observable nucleating effect. Various means were employed to make sure that the exact temperature in the sample was known, and they all showed that the readings were reliable. One way was to check on the melting point of the ice when the temperature was rising; another[1] was to bombard the sample surface continuously with ice nuclei streaming from a tiny piece of dry ice held directly above it and observe when freezing took place.

A number of powdered materials were introduced to the sample in an attempt to make the water freeze at 0° C. So far, nothing has been found which can effect this. Some results follow:

Material	*°C*				*Average °C*
Aquadag	− 7.2,	− 6.8,	− 6.8		− 6.9
Silver iodide	− 8.0,	− 9.5,	− 9.0,	− 9.0	− 8.8
Graphite "280"	− 8.8,	− 9.8,	− 9.8,	− 9.8	− 9.5
Zinc sulfide	− 11.0,	− 11.6,	− 12.2,	− 12.3	− 11.5
Zinc oxide	− 13.0,	− 13.5			− 13.3
Iodoform	− 13.7,	− 13.7,	− 13.2		− 13.5
Lead sulfide	− 11.8,	− 12.3,	− 14.3		
	− 13.8,	− 15.3,	− 13.9		− 13.9
Sulfur	− 15.0,	− 14.8,	− 15.6		− 15.1
Zinc oxide (dri-filmed)	− 18.0,	− 17.0,	− 16.5		− 17.1
Pepsin (surface)	− 20.3,	− 16.5,	− 17.0		− 17.9
AgI ppt from acetone	− 18.0				− 18.0

There is one interesting conclusion to be drawn from the above observations. Graphite has been tried in many ways as a sublimation nucleus for ice and is found to be practically without effect. However, as a freezing nucleus (in water), it seems to be even more efficient than silver iodide. This means that we must distinguish between "sublimation" nuclei and "freezing" nuclei and recognize that the mechanism of nucleation in each case is different.

The possibility immediately suggests itself that very often crystallization in bulk water may be started by a chance contact with a "sublimation" nucleus rather than by a "freezing" nucleus already contained in the liquid. It also suggests the possibility of cooling water considerably below 0° C and keeping it there indefinitely when care is taken to eliminate the introduction of sublimation nuclei as well as freezing nuclei. Having pure water is not enough.

Recently LaMer and Yates (*5*), at Columbia University, conducted experiments on the precipitation of sulfur from dilute solutions of sodium thiosulfate and HCl. They found that ultrasonic irradiation of the water of which the solutions were subsequently made caused a delay in detectable precipitation of approximately four times the normal. This technique was tried in our experiments, and we found that irradiating a sample in a methyl methacrylate container, at one megacycle for

[1] This method of preventing supercooling was suggested by Vincent J. Schaefer.

30 sec, had a pronounced effect on the crystallization temperature of the water. This water retained this property even after standing two months in a bottle.

Five measurements of crystallization temperature were made on this water, each measurement being made on a new surface using a new sample of water: (1) $-38.5°$ C, (2) $-28.7°$ C, (3) $-28.5°$ C, (4) $-30.0°$ C, (5) $-29.0°$ C.

All these measurements were made with the water sample in contact with air, and in each test the temperature was checked by noting the melting point with rising temperature.

It was found that freezing took place in two different ways at low temperature. Often the water seemed to freeze with great rapidity from many locations to form an opaque, milky ice easily recognized by the naked eye. The freezing sometimes took place in an altogether different manner, however, and could be observed only through polaroids. In these cases, single, beautifully colored crystals could be seen to grow slowly out from widely separated nuclei. Sometimes only one crystal developed in a whole water sample.

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Internal Suberization of Plant Tissues

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Suberization of the internal surface, *i.e.* of the intercellular spaces, has been reported in the leaf of the Valencia orange, *Citrus sinensis* (*4*). Intercellular spaces in the mesophyll of the lamina and in the tissues of the petiole and of the basal and laminar abscission regions are lined with a thin film, $\pm 1\ \mu$ in thickness, which resembles the cuticle in its refringence. A similar but more tenuous pellicle lines the inner surface of the cell wall and resembles a tertiary lamella. The films were first identified during the investigation of plasmodesms and cell walls while using a standard cellulose test, 1Kl followed by irrigation with H_2SO_4 ($\pm 80\%$). Both films, extracellular and intracellular, stain yellow with 1Kl and darken on irrigation with H_2SO_4. During and after the blue coloration, the swelling, and ultimate solution of the cellulose of the cell wall, the films remain more or less intact. The degree of persistence depends on film thickness and therefore on the age and, to some extent, on the region of the leaf, since the swelling of the cellulose naturally disrupts all except the heavier coatings and impregnations.

The results obtained in citrus and other plants with 1Kl-H_2SO_4 may be confirmed by the use of other reagents. When sections of fresh material are mounted directly in glycerin, lactophenol, or similar media, suberin pellicles are clearly visible. Staining with Sudan III or Sudan IV proves effective in some cases, particularly if preceded by treatment either with phloroglucin and HCl or with chromic acid ($\pm 50\%$). Irrigation of sections with strong chromic acid dissolves wall materials such as pectic substances, cellulose, and lignin, but leaves suberized membranes alone intact. In the examination of lignified tissues this method is therefore indispensable, since lignin is not broken down by H_2SO_4.

The leaves of sycamore, avocado, castor bean, and squash were examined at the same time and with the same techniques as used in citrus, and the results obtained were similar. It therefore appeared probable that suberization might occur generally in all tissues of vascular plants throughout the plant kingdom. The present survey of more than 50 species[1] confirms this surmise. The plants selected differ in habit and habitat, and incidentally in phylum and family, and include annuals and perennials, xerophytes, mesophytes and hydrophytes, pteridophytes and spermatophytes.

In this and in the previous paper the term suberin is used in preference to cutin, since by current microchemical methods these substances cannot be distinguished satisfactorily. Suberin is more widely distributed than cutin, and it is identifiable macrochemically in deep-seated tissues such as endodermis. It also occurs in the wound cork which may differentiate in parenchymatous tissues after deep or surface wounds, and it is in the principal component in the walls of normal cork cells (*1, 2*).

Suberin appears first in the intercellular spaces of differentiating tissues such as leaf mesophyll, and the parenchyma, cortex, and pith of stem and root. When first observed the films are at the limit of visibility and thereafter, during tissue growth, increase in thickness. Suberization may extend sooner or later along the middle lamellae but does not interrupt the plasmodesms between adjacent cells.

Suberin films are not confined to intercellular spaces but occur also within the cell. A tenuous film which resembles a tertiary layer of the cell wall may be identified soon after the first appearance of the intercellular suberin. It is similar in translucence and in chemical

[1] Some of the species examined were: *Pteridium aquilinum, Selaginella Bigelovii, Araucaria imbricata, Pinus Coulteri, Potamogeton* sp., *Clivia miniata, Iris Pseudacorus, Musa nana, Eichhornia crassipes, Nymphaea alba, Macadamia ternifolia, Annona cherimola, Persea americana, Crassula arborescens, Bergenia cordifolia, Platanus racemosa, Vicia Faba, Cercidium floridum, Dalea spinosa, Citrus sinensis, Ricinus communis, Mangifera indica, Acer macrophyllum, Aesculus californica, Jussiaea repens, Primula polyantha, Asclepias subulata, Acanthus mollis, Cucurbita Pepo, Echinocystis macrocarpa, Venegazia carpesiodes, Cynara scolymus.*