and not a recent contamination of the sample, the pyrite sample was immersed in weak nitric acid for several minutes. This treatment is known to etch pyrite, but has no effect on organic matter. Additional replicas of the same areas clearly showed that both the pyrite and bacterial remains are etched to a similar extent. This demonstrates that the bacteria were to a large extent replaced by pyrite. The darker textures of some of the bacterial remains on the replicas in Figs. 2 to 5 indicate that some organic matter persists in the remains.

It seems reasonable to assume, in view of the fact that the bacteria are intimately associated with an iron sulfide nodule, that these microorganisms were probably similar in function to contemporary types which they also resemble in appearance. This assumption has been made for the several cases of fossil bacteria previously observed (*4, 5*). Contemporary iron-producing bacteria cause $Fe(OH)_3$ to form within the sheath. Hydrogen sulfide, which would be accessible in organic decay processes, could react with the bacterial remains to form pyrite.

One question to be answered is whether this is a freak demonstration, or whether microbiological inclusions may be expected in most coal measures. Probably an abundant microbiological record is preserved in some types of authigenic deposits such as pyrite, but special techniques are needed to disclose it. The resolution required for observation is provided by the electron microscope, but a very delicate etching and replication technique must be used or the evident structure of the fossils will either remain invisible or be destroyed. There is every reason to believe that a wider search for the remains of microorganisms by appropriate similar methods would be successful (*5*).

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1 February 1965

Cryogenic Cooling by Noncondensible-Gas Injection

Abstract. *Temperature control of various cryogenic liquids in the range from their boiling points to near or below their freezing points has been achieved by injecting a noncondensing gas, helium. The process is more easily accomplished than the usual vapor-pumping technique and is applicable in the range from 15° to 300°K. Interesting ice formations were observed in liquid argon.*

Cooling of liquids by evaporation into bubbles of an injected noncondensing gas is a well-known concept that has not been widely applied in laboratory cryogenics. However, Larsen *et al.* (*1*) and Schmidt (*2*) have discussed the theory and presented experimental data on the injection of helium gas into liquid hydrogen or oxygen in a rocket-motor environment.

We present data on the cooling of various liquids by injection of helium gas. Our results indicate that temperature control below the boiling point of the coolant can be achieved more simply by injection of helium than by the usual vapor-pumping technique. The coolants available limit the temperature range of application from 15° to 300°K. The evaporative-cooling effect is strikingly demonstrated by ice formations in liquids having narrow liquid-temperature intervals, such as argon.

The experiments were conducted in a conventional, glass, double-Dewar flask that was strip-silvered to permit visual examination of the inside. The inner flask is shown schematically in Fig. 1; the central container held about 2 liters and was half-filled with coolants for the experiments. The outer flask was filled with a coolant having a boiling point the same as or higher than that of the content of the inner flask in order to make the thermal shielding as neutral as possible. To minimize inflow of ambient heat, the inlet and outlet tubes were constructed of thin-walled stainless-steel tubing or glass. The significance of the (optional) heat exchanger will be noted later. Temperatures were measured with calibrated copper-constantan thermocouples to an accuracy within about 0.1°K. The injection gas was supplied from storage bottles equipped with standard gauges and regulators. Gas flow could be measured accurately within 20 percent. The outlet gas was vented to the atmosphere.

Although any noncondensing gas will produce cooling when bubbled through a liquid, helium is the best for cooling by injection because it has a lower condensation temperature than any other gas, low solubility, low heat-capacity, and good heat-conductive properties; it is also readily available, nontoxic, and nonexplosive. The data reported here were all obtained with helium.

When a noncondensing gas is injected into a liquid, part of the liquid evaporates into the gas bubbles. The change of state of the liquid, from liquid to gas, extracts heat from the liquid; the heat passes into the vapor

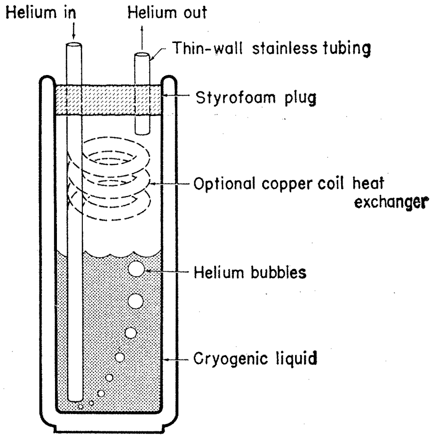

Fig. 1. Schematic drawing of inner flask assembly.

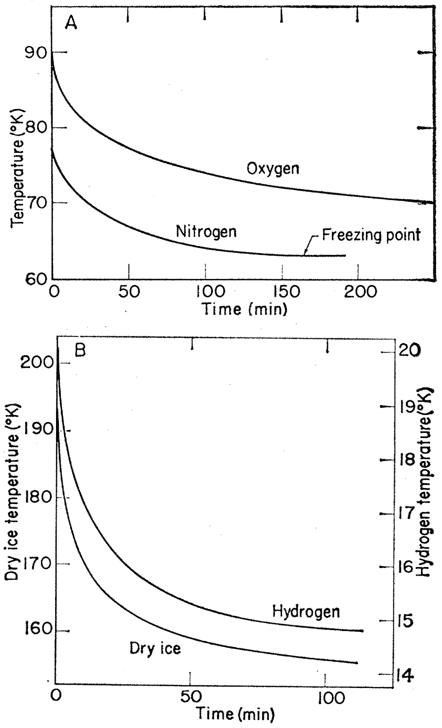

Fig. 2. Temperature versus time for liquid oxygen and liquid nitrogen (*A*) and liquid hydrogen and solid dry ice (*B*) cooled by helium flow at 40 cm^3/sec.

Table 1. Temperature data on coolants (*3*).

Coolant	Freezing point (°K)	Boiling point (°K)	Temperature range with He injection (°K)	Vapor pressure* (atm)
Hydrogen	13.9	20.3	14.8 to 20.3	0.12
Nitrogen	63.3	77.4	63.3 to 77.4	.12
Oxygen	54.8	90.2	69.0 to 90.2	.05
Argon	83.9	87.3	83.9 to 87.3	.68
Dry Ice	Sublimed at 194.7		156.0 to 194.7	.02
Carbon tetrachloride	250.4	350.0	264.4 to ambient	.02
Water	273.2	373.2	285.7 to ambient	.02

* At the lower temperature attained with helium injection.

and the liquid cools. The rate of cooling is determined by the vapor pressure of the liquid. Normally, the liquid is at boiling point when bubbling begins; cooling is thus initially rapid and then gradually decreases, together with the vapor pressure, until the cooling due to evaporation just balances the incoming heat flux or until the liquid freezes and destroys the gas-liquid interface. In Fig. 2 the cooling rates of liquid nitrogen, liquid oxygen, liquid hydrogen, and solid carbon dioxide (dry ice) are illustrated; the helium flow in these instances was 40 cm^3/sec (1.8×10^{-3} mole/sec). Liquid nitrogen was easily cooled to the freezing point. Liquid hydrogen was not frozen but probably could be in a better cryostat. Liquid oxygen could not be cooled to its freezing point. The dry ice was crushed to a coarse powder and loosely packed into the Dewar.

Table 2. Estimated temperature range of coolants with helium injection (*4*).

Coolant	Formula	Temperature (°K)
Fluorine	F_2	60 to 85
Methane	CH_4	89 to 112
Freon 14	CF_4	128 to 145
Freon 13	$CClF_3$	144 to 192
Freon 13 B1	$CBrF_3$	166 to 215
Freon 115	$CClF_2$-CF_3	177 to 234
Freon 11	CCl_3F	219 to 250

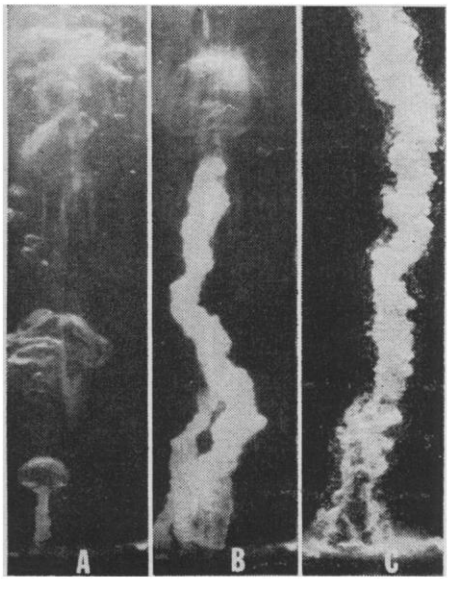

Fig. 3. Hollow tubes of argon ice in liquid argon, produced by injection of helium gas: *A* and *B*, initial growth process; *C*, tube venting above the surface, but enlarging in diameter.

As an example, consider the experiment with liquid nitrogen. From an initial volume of nitrogen of 1000 ml, 2 hours of injection of helium at 40 cm^3/sec evaporated approximately 110 ml and reduced the temperature of the remainder to the freezing point, 63.3°K. The (negative) heat of vaporization produced by evaporation of 110 ml of liquid nitrogen was approximately 5000 cal and equal to the heat removed from the remaining liquid nitrogen in cooling it to its freezing point. Since the incoming helium was precooled by the outgoing cold helium and nitrogen vapor, the initial temperature and heat capacity of the injection gas need not be considered in the effect. At the flow rates used, a few centimeters of copper coil allowed sufficient heat exchange; the coils of tubing shown in Fig. 1 were completely effective for precooling. However, if very large flow-rates or gases other than helium are used (below 100°K, helium is the best gaseous heat conductor), precooling may be more demanding.

After the liquid nitrogen reached its freezing point, the temperature remained constant, with an evaporation rate of approximately 10 ml/hr. About 15 hours were required to extract the heat of fusion and completely freeze the remaining nitrogen. Temperatures as low as 58°K were measured near the helium-inlet tube in solid nitrogen. Varying the helium flow by factors from 0.25 to 4.0 caused proportionate changes in the cooling rate. This fact and approximate calculations based on nitrogen consumption indicated that near-equilibrium was established between each helium bubble and the liquid nitrogen; that is, the bubbles emerged from the liquid almost saturated with vapor. Varying the bubble size had no effect except that the very small holes in the injection tube became blocked with frozen coolant.

The experimental results are summarized in Table 1. Water and carbon tetrachloride were also tested in order to determine more accurately the ultimate pressure of the helium bubble "pump." The data suggest that helium injection will reduce the temperature of any liquid until the vapor pressure equals 0.02 atm or until the liquid freezes. This rule of thumb enables one to predict the temperature range for any liquid from vapor-pressure data. However, it is probable that the 0.02-atm threshold depends on our experimental apparatus and must be used with caution in nonidentical systems. The fact that hydrogen could not be cooled below 14.8°K probably reflected the large heat-leak into our flask through the unsilvered viewing strip. The temperature range possible with dry ice is considerable and covers an interesting area for many experiments.

In Table 2 a low-vapor-pressure limit of 0.02 atm is assumed, and the temperature range for a variety of liquids is estimated. Along with their well-known stability and ease of handling, the freon compounds offer a wide temperature range and should be useful for temperature control in the laboratory in the range from 128° to 250°K.

At atmospheric pressure, argon is liquid only between 83.9° and 87.3°K. Because of this narrow liquid-temperature interval, the evaporative-cooling effect is dramatically demonstrated by the formation of argon ice. To photograph this effect the helium-inlet tube of Fig. 1 was bent so as to extend across the viewing window of the flask and to inject the helium bubbles upward through a number of 1/16-inch (1.5-mm) diameter holes. As the helium bubbles formed in the liquid argon, evaporation into the bubble was so rapid that a sheath of argon ice was formed around each bubble. The ice attached itself to the hole in the tube where the bubble was ejected and a hollow tube of argon ice began to grow (Fig. 3*A*). By varying the rate of flow of the helium the growth rate of the ice tube could be varied between 1 and 10 cm/sec. After the ice tube reached the surface of the liquid and vented the gas there was no further bubbling. However, the ice tube continued to grow in diameter by formation of a layer of transparent argon ice on the outside (Fig. 3*C*); this occurred because the solid argon on the inside of the tube had a high vapor pressure (0.68 atm) and sublimed into the helium-gas stream to furnish additional cooling. The initially formed tube contained many trapped bubbles of helium that gave it a more opaque, white appearance. When the helium flow was increased markedly, small ice particles dispersed throughout the liquid, which rapidly became full of mushy ice and finally froze solid.

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5. We thank G. D. Halsey, Jr., University of Washington, for helpful discussion; M. Grosser, H. Harrison, and G. L. Hollingsworth, Boeing, for discussion and technical assistance. A 16-mm color film showing formation and growth of the argon ice tubes is available from the authors.

29 March 1965

Carbonates: Association with Organic Matter in Surface Seawater

Abstract. *Carbonate mineral particles suspended in surface seawater in tropical and subtropical areas do not interact measurably with the water. Identical complex mineral assemblages occur in waters in various states of saturation. Drastic alterations of temperature and* pH *in the laboratory do not affect the composition of the suspended carbonates. It appears that the mineral grains are protected from the water by resistant organic coatings.*

Surface seawater in tropical and subtropical areas contains carbonates and other minerals in suspension. The amount of suspended matter is variable. A concentration of five or more milligrams of $CaCO_3$ per liter is common near the shore, and far less occurs in the open sea. The mineralogy of the suspended carbonates is normally complex, with aragonite and a variety of magnesium calcites being present.

Samples of surface water from five areas in Bermuda, Jamaica, and western Florida have been studied. One to eight liters of water were filtered through an 0.8-μ Millipore filter. The filter was usually rinsed with a small amount of distilled water to remove sea salts, and was then dried and dissolved in acetone. The resultant slurry was centrifuged, and the centrifugate smeared on a glass microscope slide for x-ray diffraction analysis.

Over 100 samples from the different study areas were analyzed. One striking conclusion can be drawn from the data—there is no obvious evidence of chemical interaction between the carbonates and the seawater.

Aragonite and magnesium calcites exhibit a wide range of solubilities at constant temperature and pressure (*1*). In surface seawater, solubilities are further influenced by changes in temperature, salinity, and CO_2 pressure. However, in Bermuda, for instance, there is no significant change in the mineralogy of the suspended carbonates from summer (29° to 30°C) to winter (15° to 19°C). Surface water in summer has been demonstrated to be supersaturated with respect to all but the most soluble suspended phases of carbonate by use of *p*H-sensing techniques (*2*). By means of similar techniques, water in winter has been shown to be undersaturated with respect to the mineral phases present in the water. Thus it appears that the suspended particles are not acting as nuclei for selective precipitation, nor are they being selectively dissolved.

Off Cedar Key, in northwestern Florida, water in late summer (20° to 22°C) contains suspended aragonite, magnesium calcites, and quartz. Waters from this area with salinities about 30 per mill are oversaturated with respect to most of the carbonate phases present. However, near the mouth of the Suwannee River, where salinities are below 10 per mill and the water is undersaturated with respect to all calcium carbonate species, suspended carbonates are still abundant.

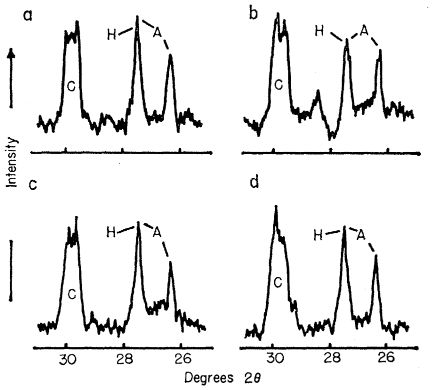

Fig. 1. X-ray diffraction patterns (CuKα) of carbonates suspended in samples (3 liters each) of nearshore Bermuda seawater as the water is cooled. *A*, aragonite peaks; *H*, halite (from dried salts); *C*, Mg-calcites, more magnesium at higher angles. (*a*) Fresh seawater 26.5°C; *p*H, 8.26. (*b*) Cooled 2.5 hours to 16°C; *p*H, 8.23. (*c*) Cooled 5 hours to 13°C; *p*H, 8.20. (*d*) Cooled 10 hours to 9°C; *p*H, 8.17. (*H* and one *A* peak overlap. These four samples were not rinsed with distilled water and thus the halite peak is large.) Samples obtained in September 1964.

Laboratory experiments were conducted in Bermuda in which attempts were made to induce interactions between the suspended carbonates and the water. Cold waters were warmed to above 30°C in an attempt to induce precipitation. Warm waters were cooled to below 5°C to favor solution. Waters were bubbled with air and stirred while being warmed and cooled in order to speed equilibration with atmospheric CO_2. Waters were acidified with HCl to a *p*H of 7.25, at which point reagent calcite that was added dissolved readily; yet as shown in Figs. 1 and 2, no changes in the mineralogy of the suspended carbonates could be detected.

The seawater used in these studies contains abundant organic aggregates (*3*). Microscopic examination of Millipore filters, cleared with oil having a refractive index of 1.500, showed that the aggregates, which ranged in size from 10 μ to 50 μ, contained abundant carbonate material. This material occurred as fine crystal clusters or as individual grains up to 20 μ in diameter. Mineral grains not in aggregates had a brownish coating, similar

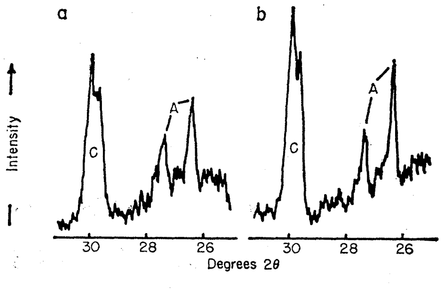

Fig. 2. X-ray diffraction patterns of carbonates suspended in samples (1.5 liters each) of nearshore Bermuda seawater, fresh and acidified. Diffraction peaks identified as in Fig. 1. (*a*) Fresh seawater at 17.3°C; *p*H, 8.21. (*b*) Acidified to *p*H 7.25 with HCl (17.3°C). Stirred for 10 minutes on magnetic stirrer after acidification. Samples obtained in March 1965.