solubility of the product. Under these conditions one may expect that the crystal-growth process is somewhat unorganized and produces large vacancy and defect populations; moreover, crystallite size is expected to be small, as observed, and aggregation probably results from surface charges on the grains. Measurements of gas adsorption of the zinc sulfide precipitate reveal extremely high porosity of the aggregate (2) and suggest that almost the entire surfaces (including the inner) of the constituent grains are active in adsorption.

After 1 minute at 1200°C in the presence of a NaCl flux constituting 2 percent of the total weight, some coalescence of adjacent grains has taken place (Fig. 1*B*). After 2 minutes, total surface area is sharply reduced, although average aggregate diameters, as determined by measurement of air sedimentation rates, are unchanged (Fig. 1*C*); rapid intra-aggregate growth is clearly indicated, although interaggregate mass transport has not occurred to a measurable extent. The coalescence process is considerably advanced after 3 minutes (Fig. 1*D*); individual grains are of the order of 1 μ in size, while average aggregate diameters are approximately 6.5 μ and relatively unchanged from diameters at time zero.

After 4 minutes, the coalescence process is essentially complete and the limiting identity of grain and aggregate has been attained (Fig. 1*E*). Because of obvious problems of heat transfer, clearly the exact stage of coalescence for a given sample depends on sample size and geometry. In our experiments, sample sizes were of the order of 5 g and the thermal treatment was carried out in covered silica crucibles.

The smooth, rounded particles of Fig. 1*E* are typical of those observed in many electron micrographs corresponding to thermal treatments of long duration. Also observed in the longer-term samples are many particles exhibiting sharp step characteristics (Fig. 1*F*). The difference in the morphologies is readily appreciable in the light of two facts: First, such mesa patterns are never observed in particles during the period of intra-aggregate coalescence; secondly, particle growth, after coalescence is completed, must proceed by intergrain attrition. The grain in Fig. 1*F* has clearly been etched thermally, and just before quenching of the sample it was in the process of supplying nutrient to other grains. Interesting is the extent to which single-crystal properties are suggested by the edges and discontinuities revealed in Fig. 1*E*; prominent topographical features can generally be traced backward linearly to the point of origin of the defect. X-ray studies with single grains of recrystallized zinc sulfide powder also indicate that each grain is a single crystal (see *3*).

Figure 1*G* illustrates a rare event in the process of recrystallization of precipitated zinc sulfide. The large central grain exhibits crystal-growth characteristics that have not been observed in hundreds of other electron micrographs of zinc sulfide particles. A number of platelets of hexagonal symmetry are observed in the process of developing from the precipitate grains, in contrast with the usual process of coalescence into grains without well-defined geometries. What the later development of such an aggregate would be is not suggested by any of our observations of numerous particle surfaces. The partially coalesced sample to the side of the aggregate in question shows that not all intra-aggregate processes in a given sample proceed identically; this is because of the variation of rate of heating with particle position within the sample. The micrographs in Fig. 1, *A–E*, represent an average state of development for small samples.

Recrystallization of precipitate at 1000°C proceeds with morphological changes identical with those observed at 1200°C, except that the process is somewhat slower. The inclusion of copper at 1000°C, which is known to favor additionally the cubic modification, also fails to affect the coalescence process although the degree of polytypism is reduced.

In summation, the electron microscope was used to demonstrate intra-aggregate grain coalescence during thermal recrystallization of zinc sulfide precipitate. It was clearly shown that the first few minutes of the thermal treatment are a time of dynamic activity, contrary to projections based on the slow rates of increase of particle diameters. The electron micrographs also explain the differences in morphologies of crystallite types that are observed in samples in which interparticle growth has occurred.

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References and Notes

1. Although the literature reports the transition temperature as 1024°C, the small energy difference between the crystalline modifications allows polytypism on both sides of that temperature. Impurities also may strongly influence the degree of transformation.
2. Details of particle-size measurements, luminescence development, and x-ray crystallography corresponding to the short-term morphological effects described in this report have been published: L. Bodi, "Some aspects of the thermal recrystallization of precipitated zinc sulfide," in *Proc. Intern. Conf. Luminescence Budapest 1966*, in press.
3. G. Gashurov, General Telephone and Electronics Labs., Bayside, N.Y., private communication.

19 May 1966

Undersea Air Supply

Abstract. *The interior air of a simulated underwater habitation was continuously washed or scrubbed with sea water by means of a gas exchanger of the venturi type. The sole method for supplying oxygen and removing carbon dioxide was the scrubbing process. A microburner placed inside the experimental habitation chamber continued to burn until it was intentionally extinguished. Two rats maintained in the chamber for 8 hours suffered no discernible ill effects.*

The gases dissolved in sea water are a potential source of air for men to breathe underseas. Similarly, the carbon dioxide–absorbing capacity of sea water is a potential means for disposing of respiratory wastes. These potentialities were partially verified in experi-

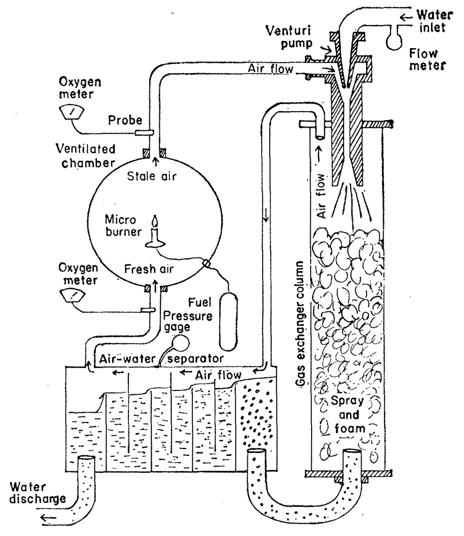

Fig. 1. Apparatus for scrubbing interior atmosphere of metabolic combustion chamber with sea water, thereby replenishing the chamber with oxygen and freeing it of carbon dioxide.

ments at the U.S. Naval Civil Engineering Laboratory (NCEL) (*1*). Stale air from a simulated undersea habitation was brought in contact with sea water in such a way that carbon dioxide from the stale air was exchanged for dissolved oxygen from the sea water. Two rats survived comfortably in the habitation chamber for periods of up to 8 hours.

The feasibility of utilizing sea water to regenerate breathing mixtures underseas is confronted by the fact that, especially at intermediate depths (*2*), the ocean contains numerous pockets of water deficient in oxygen and laden with carbon dioxide. However, even at extreme depths (*3*), much of the ocean is well oxygenated and contains only traces of free carbon dioxide.

Another consideration is that the concentration of oxygen dissolved in sea water (even when air-saturated) is only 1/30 as great as the concentration of gaseous oxygen in air. However, the partial or diffusion pressures of oxygen and carbon dioxide are the same in air-saturated sea water as in moist air. Hence, approximately equal areas of functioning respiratory surface are required to collect oxygen at a given rate with either gills or lungs, even though the volume of water processed by the gills is many times greater than the volume of air processed by the lungs (if oxygen-withdrawing efficiencies are equal).

One of the earliest attempts to utilize sea water for revitalizing breathing mixtures was made in 1953 when it was demonstrated that sea water is an efficient solvent for removing carbon dioxide from submarines (*4*).

A very thin but strong silicone-rubber membrane which readily permits passage of gases and vapors but prevents passage of liquids (*5*) has been developed at the General Electric Research Laboratory where laboratory animals have been maintained underwater for periods of up to 2 weeks in a submerged chamber covered with this membrane. Independently, Ayres has studied membrane processes for revitalizing breathing mixtures with sea water (*6*).

The advantages of the membrane processes are simplicity and economy in energy consumption. The sea water is merely circulated past a membrane. A disadvantage is that the respiratory gases must diffuse through a membrane —a slow process regardless of how thin the membrane is. For example, even a monomolecular film of oil on the surface of the water markedly retards evaporation.

In the undersea air supply experiments at NCEL, no membranes are used. Air from the compartment being ventilated is brought into intimate and agitated contact with sea water in the form of a finely dispersed mixture. Unhampered by membranes, diffusion of gases takes place almost instantly, and occurs through minute distances and over the large surface area of droplets and bubbles. Hence, large volumes of sea water can be processed with relatively compact equipment.

Apparatus assembled for the NCEL studies (Fig. 1) consists of a gas exchanger of the venturi type, a baffled tank for trapping bubbles, and a ventilated habitation or combustion chamber, as if submerged in the ocean. Stale air is pumped from the ventilated chamber through the gas exchanger where it is continuously scrubbed in a stream of sea water. The scrubbing process consists of washing the air by vigorously mixing it with sea water and then separating it from the water again.

During the scrubbing, excess carbon dioxide in the stale air dissolves in the stream of sea water; oxygen dis-

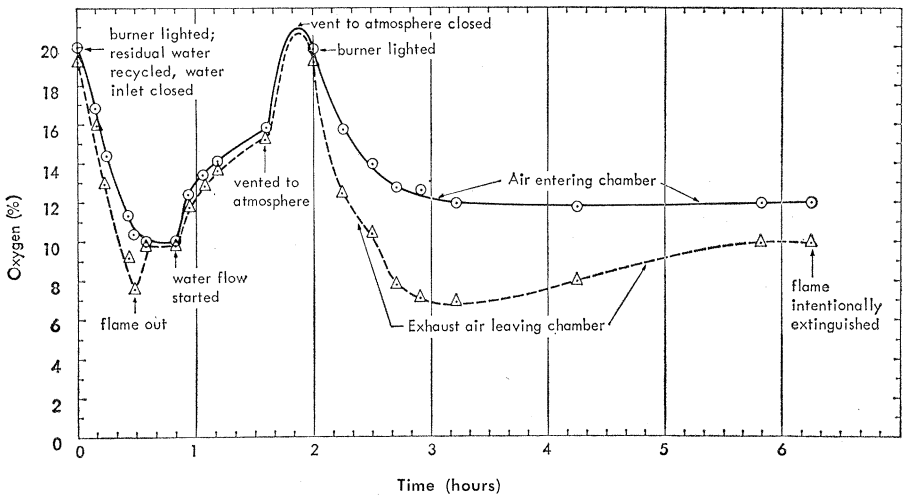

Fig. 2. Concentrations of oxygen in the air entering and leaving a chamber in which a flame is sustained by oxygen recovered from sea water.

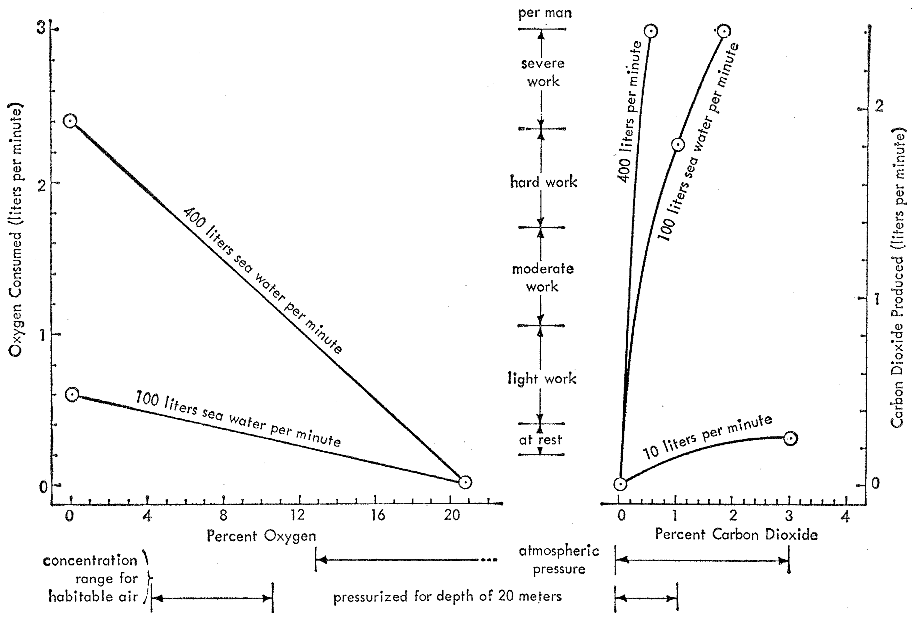

Fig. 3. Limiting concentrations of oxygen and carbon dioxide that can be maintained via a gas exchange process with sea water. It is assumed that the sea water is saturated with air and contains 6 ml of oxygen per liter. Curves for carbon dioxide were constructed from the data of Kathan and Webster (*4*). Positions of the oxygen lines were deduced.

solved in the sea water diffuses into the oxygen-deficient stale air. Before being discharged, the sea water passes through the baffled tank where entrained air is recovered. The scrubbed air, recharged with oxygen, is returned to the combustion chamber where it is again used by a flame or by a laboratory animal. The oxygen concentrations of the streams of air entering and leaving the chamber are continuously measured with a pair of oxygen analyzers (Beckman Model 777).

A microburner consuming only the oxygen confined within the apparatus burned for 31 minutes (Fig. 2). When aerated sea water was supplied at a rate of 30 liter/min, the flow of water forced the air to circulate rapidly through the apparatus. The concentration of oxygen in the air immediately began to increase. The increase having been demonstrated, the return to atmospheric concentration was hastened by briefly venting the system to the atmosphere, and the burner was again lighted. The flame burned for a period of 4 hours and 15 minutes and was then intentionally extinguished. All indications were that it would otherwise have continued to burn indefinitely.

An experiment with two small rats demonstrated that the air in the habitation chamber could sustain life. In one of these experiments the rats were maintained in the chamber for 8 hours without apparent discomfort. They were examined 2 weeks later and were in good health.

In the foregoing experiments, oxygen was recovered from the sea water and was supplied to the rats (or to the flame) at a rate of approximately 0.1 liter/min. A scuba diver resting in an undersea shelter might, if he had been working strenuously, require an oxygen supply 30 times greater than that; a supply only 5 to 10 times greater should more than satisfy his average needs.

A venturi gas exchanger, operating at the same efficiency as the gas exchanger described, would probably have to process 200 to 300 liters of air-saturated sea water per minute to supply one diver with oxygen. To depths of approximately 20 m, sea water can be pumped economically (1 to 3 hp per man) at such rates with conventional pumps, but at greater depths an energy-conserving pumping system (*7*) is required.

The maximum concentration of oxygen that can be maintained in a chamber ventilated by means of a sea-water scrubbing process is limited by the amount of oxygen dissolved in the water and the rate at which the water is processed and the oxygen is consumed (Fig. 3). Similarly, the limit of control of carbon dioxide is restricted by the absorbing capacity of sea water and the rate at which the water is processed and carbon dioxide is produced. Actual operating levels should not be much different from the theoretical limits, since scrubbers are very efficient.

The apparatus described was not designed to function underwater. Pressures were essentially uniform throughout the apparatus and were approximately equal to that of the atmosphere. Different pressures will be required in the various compartments of similar apparatus designed to function underwater.

The pressure in an underwater gas exchanger (as distinguished from a habitation chamber) must not exceed 1 atm owing to the fact that, since sea water and air are in contact only at the ocean surface, the total pressure of dissolved gases in sea water is approximately 1 atm at all depths. If air and sea water were brought together in the gas exchanger at pressures greater than 1 atm, more air would dissolve into the sea water than would diffuse from it, and the net amount of air in the system would decrease.

A net gain in the amount of air in the system could be achieved by maintaining a partial vacuum in the gas exchanger. Air lost as fine bubbles in the exhaust sea water (or air used for such purposes as operating air locks and charging scuba tanks) could thereby be replaced. Removal of carbon dioxide would be less efficient but, nevertheless, would be adequate if the vacuum did not exceed about ⅓ atm.

For efficient recovery of oxygen, pressure in the habitation chamber must be greater (preferably several times greater), than 1 atm. Since the purpose of the scrubbing process is to strip fresh air from sea water with stale air, the lower the oxygen concentration of the stripping air, the more efficient the process. The oxygen concentration of the air in a pressurized habitation chamber can be "breathed down" to relatively low levels (Fig. 3), thereby aiding efficient recovery of oxygen from the sea water.

The interior of the gas exchanger of new apparatus under construction at NCEL will be maintained under a slight vacuum and the habitation or combustion chamber will be slightly pressurized. The apparatus will be tested while submerged.

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References

1. H. P. Vind, M. J. Noonan, A. Langguth, *NCEL Tech Notes 543 and 734* (Port Hueneme, California, 1963–65).
2. Y. Mujake and K. Saruhashi, *Deep Sea Res.* **3**, 242–247 (1956).
3. H. U. Sverdrup, M. W. Johnson, R. H. Fleming, *The Oceans* (Prentice-Hall, Englewood Cliffs, N.J., 1942).
4. R. H. Kathan and A. P. Webster, *U.S. Navy Medical Field Res. Lab. Quart. Rep. NM 007 083.03* (Camp Lejeune, N.C., 1953).
5. W. L. Robb, as reported by Gardner Soule in *Sea Frontiers* **11**, 102 (1965).
6. W. Ayres, U.S. Pat. 3,228,394; reviewed in *Science News Letter* **89**, 54 (1966).
7. W. B. Plum and H. P. Vind, U.S. Navy Dept. Patent Application Case 38,365 (Port Hueneme, California, 1965).

23 May 1966

A Chemically Stratified Lake in Alaska

Abstract. *A meromictic (chemically stratified) lake occupies a thawed depression in a pingo in interior Alaska, near Circle City. Increased salt concentration and anaerobic conditions characterize the zone extending from a maximum depth of 3 to 8.8 meters. The concentration of strontium and lithium is unusually high for lake water.*

Meromictic lakes offer unique systems for studies in limnology and geochemistry because of their permanent chemical stratification and incomplete

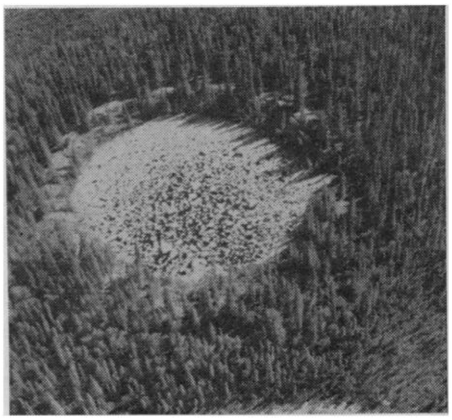

Fig. 1. Pingo Lake in July 1965. The surface bloom of *Cladophora* sp. was unusual for lakes in this part of Alaska.