

Reports

Observations on the Solubility of Skeletal Carbonates in Aqueous Solutions

Abstract. Carbonate skeletal materials of marine organisms exhibit a wide range of solubilities in aqueous solutions. In most cases, the dissolution of the carbonate mineral is irreversible and therefore the material can have no true equilibrium solubility. Relative solubilities have been measured in distilled water and in sea water. The least soluble mineral appears to be calcite with low magnesium content; the most soluble is calcite containing 20 to 30 percent MgCO_3 in solid solution. Aragonite has an intermediate solubility.

Carbonate skeletal materials of marine organisms are composed of the minerals calcite, aragonite, and a spectrum of magnesium calcites (1). Phase equilibrium studies (2) have shown that only the mineral calcite, low in magnesium, is stable at all terrestrial near-surface, pressure-temperature conditions. Aragonite and calcite containing more than about 4 percent MgCO_3 in solid solution are metastable phases. Aragonite and high-magnesium calcite are common skeletal materials.

A solid has a clearly defined equilibrium solubility only if reversible dissolution and precipitation can take place at the solid surface. Some of the skeletal carbonate materials, particularly the high-magnesium calcites, probably cannot be produced by inorganic precipitation at room temperature from sea water. One possible interpretation of the behavior of these materials in a solution is that a steady state is reached

only when the rate of dissolution of the organic calcite is equal to the rate of growth of new inorganic calcite. The steady-state composition of solutions in contact with various skeletal carbonates has been measured by the method of Garrels, Thompson, and Siever (3) in distilled water plus carbon dioxide, and in sea water and distilled water by the saturometer method of Weyl (4).

In the distilled water experiment, about 2 g of finely ground skeletal carbonate was added to 100 ml of water saturated with CO_2 at 1 atm by continuously bubbling CO_2 through the solution. The sample was kept at $25^\circ \pm .05^\circ\text{C}$ in a constant-temperature bath and stirred constantly with a magnetic stirrer. Runs averaged 22 hours, during which pH was measured at regular intervals. A plot of pH change against the reciprocal of the square root of the time approached an asymptote and permitted estimation of

a pseudoequilibrium pH and therefore an apparent solubility. The values obtained by this method are shown in Fig. 1.

In the saturometer experiments in sea water, carbonate particles of sand size were allowed to settle around the submerged pH electrode. Carbon dioxide was not added to the system. The pH reached a steady level in 10 to 60 minutes and the final pH was converted to an apparent solubility, as discussed by Weyl (4). There was somewhat more scatter, and the relative differences in solubility were larger than in the more slowly equilibrated water-carbon dioxide measurements reported in Fig. 1. As in the previous experiments, calcites with very high magnesium content appeared most soluble, low-magnesium calcites least soluble, and aragonites intermediate. Examples of calculated ratios of apparent solubility of typical skeletal materials to the solubility of pure calcite are: *Goniolithon*, calcite with about 30 percent MgCO_3 , 160; *Lytechinus*, calcite with 11 percent MgCO_3 , 66; *Diploria*, aragonite, 17; *Spisula*, aragonite, 6; *Balanus*, calcite with about 3 percent MgCO_3 , 2.

The differences between the measurements made with sea water in the saturometer, where only the interstitial water between the grains is equilibrated, and those made with more dispersed grains in the distilled water-carbon

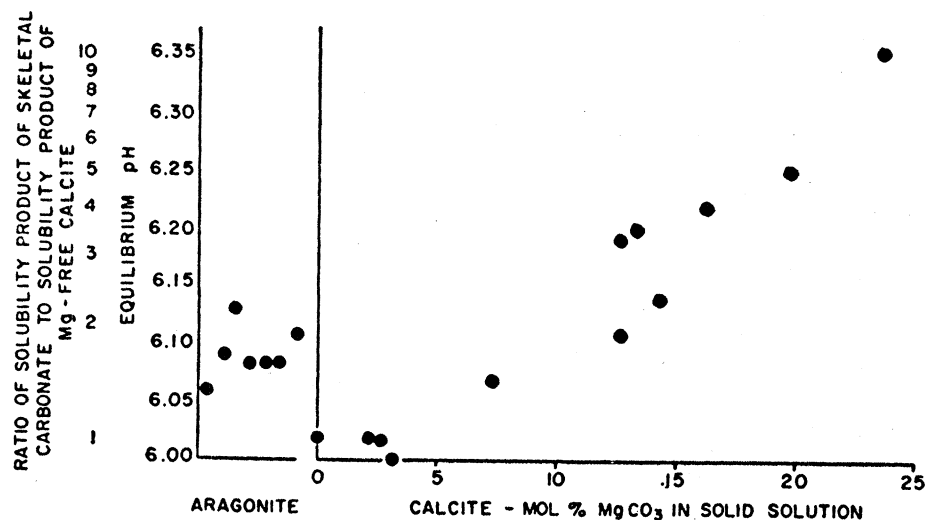


Fig. 1. Equilibrium pH (solubility) of skeletal carbonates in distilled water at 25°C , saturated with CO_2 at 1 atm. Samples from left to right on the graph are: Aragonite-C.P. CaCO_3 ; *Millipora*, Campeche Bank; *Millipora*, Campeche Bank; *Halimeda*, Florida; *Acropora*, Campeche Bank; *Spisula*, New Jersey; Calcite-C.P. CaCO_3 ; *Crassostrea*, New Jersey; Spar calcite, Lehigh Valley; *Aequipecten*, New Jersey; *Dendraster*, So. California; *Lytechinus*, Bermuda; alcyonarian spicules, Bermuda; *Diodema*, Campeche Bank; *Thessea*, Bermuda; *Lithophyllum*, Challenger Bank; *Lithophyllum*, Challenger Bank; *Goniolithon*, Florida. Note: MgCO_3 values for the two highest samples are approximate. Samples of the same species from the same areas have shown values for MgCO_3 comparable to those plotted.

Instructions for preparing reports. Begin the report with an abstract of from 45 to 55 words. The abstract should not repeat phrases employed in the title. It should work with the title to give the reader a summary of the results presented in the report proper.

Type manuscripts double-spaced and submit one ribbon copy and one carbon copy.

Limit the report proper to the equivalent of 1200 words. This space includes that occupied by illustrative material as well as by the references and notes.

Limit illustrative material to one 2-column figure (that is, a figure whose width equals two columns of text) or to one 2-column table or to two 1-column illustrations, which may consist of two figures or two tables or one of each.

For further details see "Suggestions to contributors" [*Science* 125, 16 (1957)].

dioxide system raised the question of whether the variations were due to the differences between techniques or whether they were due to a difference between sea water and distilled water. In order to resolve the problem, a number of samples were re-run by the satrometer technique in a distilled water-carbon dioxide system, and the results were much closer to the results obtained with sea water and satrometer than to those obtained with stirred, distilled water. The probable interpretation is that in the satrometer system the solution concentration rises rapidly until new growth of more stable carbonate can equal the rate of dissolution of the unstable carbonate. In the stirred system, where the grains constitute about 1 percent of the solution volume, the calcium and carbonate concentration in the solution rises much more slowly and hence there is more time for the new inorganic surfaces to grow. At steady state, the ratio of new to original surface is therefore higher in the distilled water experiment than in the satrometer experiment. At steady state one would therefore expect smaller apparent solubility differences in the distilled water experiment.

Some of the geologic and oceanographic implications of these differences in skeletal solubility have been discussed by Chave (5). The distribution of minerals among the various-sized fractions of modern carbonate sediments suggests that the more unstable, more soluble minerals are being dissolved on the sea floor in many areas. Studies of the mineralogy and type of preservation of fossil assemblages indicate that skeletons with more soluble carbonates are being selectively dissolved by groundwater in ancient rocks.

The chemical problem of the solubility of skeletal carbonates is not solved. It is hoped that the presentation of the information which we have to date will stimulate others to work on the problem, and that more precise data will eventually be obtained.

K. E. CHAVE

Department of Geology, Lehigh University, Bethlehem, Pennsylvania

K. S. DEFFEYES

P. K. WEYL

Research Division, Shell Development Company, Houston, Texas

R. M. GARRELS

M. E. THOMPSON

Laboratory of Mining Geology, Harvard University, Cambridge, Massachusetts

References

1. K. E. Chave, *J. Geol.* **62**, 266 (1954); H. A. Lowenstam, *ibid.* **62**, 284 (1954).
2. J. C. Jamieson, *J. Chem. Phys.* **21**, 1385 (1953); R. I. Harker, and O. F. Tuttle, *Am. J. Sci.* **253**, 274 (1955); D. L. Graf and J. R. Goldsmith, *Geochim. Cosmochim. Acta* **7**, 109 (1955).
3. R. M. Garrels, M. E. Thompson, R. Siever, *Am. J. Sci.* **258**, 402 (1960).
4. P. K. Weyl, *J. Geol.* **69**, 32 (1961).
5. K. E. Chave, *Limnol. Oceanogr.*, **7**, 218 (1962). ———, *Paleoecology*, N. D. Newell and J. Imbrie, Eds. (Wiley, New York, in press).

5 February 1962

Preliminary Results of Recent Deep Drilling on Cape Cod, Massachusetts

Abstract. In 1961 a 1000-foot drill hole near Harwich on Cape Cod, Massachusetts, penetrated 435 feet of Pleistocene deposits above 50 to 60 feet of crystalline limestone and phyllitic schist, and more than 500 feet of phyllitic schist with abundant quartz veins. Similar rock is known in the Pennsylvanian and Precambrian (?) sections of Massachusetts and Rhode Island. Material of Eocene age was found in earlier drilling near Provincetown, but none was identified from this hole.

A 1000-foot hole, the first to penetrate crystalline rock on Cape Cod, was completed late in 1961 in the town of Harwich, Massachusetts. The hole was started at about 25 feet above sea level.

The overburden here is 435 feet thick, and is of Pleistocene age. The upper 160 feet is a fine sand, with scattered coarser grained layers. This is underlain by 153 feet of bluish-gray, coarse to clayey silt, which also has scattered coarser grained layers, of possible lacustrine or marine origin. Below this is 116 feet of bouldery till with a matrix of silt similar to that of the overlying material. The majority of the boulders are crystalline rocks, for the most part granites. The lower 6 feet of overburden, also interpreted to be till, is stained brown by iron oxide, perhaps as a result of groundwater movement along the bedrock surface.

Eocene material was found in earlier drilling near Provincetown, Massachusetts (1), but no material of this age was identified from the hole at Harwich. However, recovery of samples from the 6-foot brownish zone above the bedrock was poor, and the zone may contain some unrecognized Eocene material.

The bedrock, penetrated for a dis-

tance of 565 feet, is a fine-grained, sericitized micaceous phyllitic schist. It is medium to dark gray, and has a bluish to greenish cast. The upper 50 to 60 feet contains as much as 30 percent greenish-gray to gray crystalline limestone in beds as much as 3/8 inch thick. Below the carbonate-bearing zone, quartz veins bordered by chloritic alteration products are abundant. Pyrite is the most noticeable accessory mineral. A 15-inch core taken 593 feet below the surface shows the rock to be thinly bedded and to have a good foliation that dips about 80°.

The age of the bedrock has not been established. The samples show lithologic similarities to the Rhode Island Formation of Pennsylvanian age in the Narragansett basin as well as to the Blackstone Series of Precambrian (?) age in Rhode Island (2).

CARL KOTEFF

JOHN E. COTTON

U.S. Geological Survey,
Boston, Massachusetts

References and Notes

1. J. M. Zeigler, W. S. Hoffmeister, G. Geise, H. Tasha, *Science* **132**, 1397 (1960).
2. Publication authorized by the director, U.S. Geological Survey.

13 April 1962

Enhanced Afterglow in Neon by Removal of Electrical Excitation

Abstract. An unusual increase in light output results when a neon strobe tube is suddenly short-circuited during the transient. Experimental measurements have been made of the emitted light from the discharge when the capacitor is short-circuited at different times after the initiation of the discharge.

It has long been observed experimentally that the light-time output from the neon Strobotron tube (type SN-4) shows a sudden increase of light when the current ceases. This lamp is used as a stroboscopic light source in the General Radio Strobotac type 631 where a capacitor discharges into the neon gas (1 cm), causing a peak current of several hundred amperes. The light output versus time curve resembles roughly the current versus time curve until the end of the current pulse, and then the light suddenly rises in a few microseconds to a higher value of light than was reached during the actual discharge. The subsequently exponential type of decay has small ripples, probably caused by surg-