FOSSIL SENSORS

by Heinz A. Lowenstam

The history of life in the oceans during the last 600 million years is recorded by fossils in the sedimentary rocks of the earth's crust. Mineralized tissues in the form of skeletons are more commonly preserved as fossils than the soft parts of organisms, which are found occasionally as impressions or as degraded organic compounds. Hence, fossil skeletons have been the primary objects of paleontologic studies, and they have provided a wealth of information on the kinds of organisms that populated the paleo-oceans. By tracing changes in skeletal designs through geologic time, we have uncovered a rich new source of information on the evolution of marine life.

Questions arose early about the nature of the environmental conditions under which life evolved in the oceans in the last 600 million years and about the possibility that the environmental framework may have undergone evolutionary changes of its own. Two methods employed by students of ecology were found to be applicable in investigating these questions in fossils—adaptive morphologic traits and biogeography. These studies have provided a great deal of information on environmental conditions, such as relative degrees of water turbulence, the physical nature of the sea floor, current directions, and paleotemperature.

The relationships derived from these studies are still largely of a qualitative nature. John Wells has recently noted that the surface markings of coral skeletons show daily increments which are grouped in annual cycles. Extending the investigation to fossil corals, he found that the number of daily increments in an annual group has decreased in the last 600 million years from 424 to 365. These data are in agreement with the rate of deceleration of the rotation of the earth around its axis, calculated earlier by Walter Munk and Gordon McDonald.

Though much remains to be learned about the meaning and precision of biologically recorded geochronometry, the significance of this discovery is obvious, for it uniquely documents and quantitatively defines a significant change of the major variable in the environmental setting of life in the oceans during the course of its evolution.
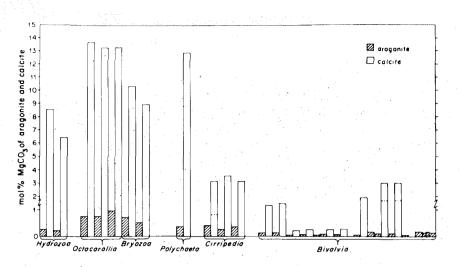
Skeletons are composed of mineral aggregates set in an organic matrix. The minerals, their chemistry, and the chemistry of the organic matrices are the products of biosynthesis by the organisms which elaborate them; hence they should embody basic information on the biochemistry and the environmental factors which affect them. This kind of information should be complementary to that which one derives from the skeletal morphology. These different source areas of information on biology, evolution, and paleoecology have been the subject of our studies.

Carbonate minerals are the most common biochemical precipitates in invertebrate skeletons of the recent marine biomass and of marine fossils. For this reason, carbonate skeletons have been more thoroughly explored than skeletons composed of other minerals. Studies to date indicate that skeletal carbonate minerals and their chemistry embody a wealth of biochemical and ecologic information. In most cases, several factors, through interaction, affect the biogeochemical properties of the carbonate minerals.

Biologic systems precipitate crystalline compounds of carbonate in the form of calcite and aragonite. Most species deposit only one of the two minerals. However, species in six classes of the animal kingdom precipitate both minerals in their skeletons. Elevation in environmental temperatures generally results in preferential increase in aragonite deposition, so that the aragonite-calcite ratio of the skeletal precipitates becomes higher.

This effect is best demonstrated by the mineralogy of the protective tubes of certain annelids (worms), which add carbonate only to lengthen the tube at the opening as the animal grows (right). Determinations of the aragonite-calcite ratios of consecutive growth increments of a species living at Bermuda, where the water temperatures fluctuate widely between winter and summer (from 16°C to 29°C), show cyclic changes of increasing and decreasing aragonite-calcite ratios over a range of 30 percent.
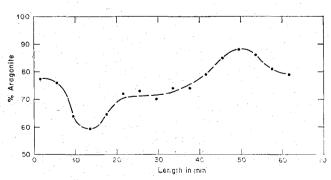
At the outer barrier reef of Palau in the Caroline Islands, the water temperatures are 28°C ± 1°C throughout the year. All other environmental factors remain similarly constant. If temperature were

Histograms showing that the mol% of magnesium is always lower in aragonitic than in calcitic parts of the shells of organisms that lived in a nearly constant water temperature.

the only factor to control the aragonite-calcite ratio of skeletal carbonate precipitates, one would expect to find the same ratios in all temperature-sensitive species. Instead, we find widely differing ratios in the skeletal carbonates that occupy the same micro-environment at Palau. These data indicate that the biochemistry of the species acts as a filter for modifying the effect of temperature on the aragonite-calcite ratios of their carbonate precipitates.

A temperature effect on the magnesium contents of skeletal carbonates is always shown by an increase of the concentration of this element with elevation in environmental temperatures. This relationship has been found in calcitic and aragonitic precipitates of skeletal carbonates from all species of carbonate-secreting metazoa investigated to date. This contrasts sharply with the species-defined selectivity in temperature effect on the carbonate mineralogy. Where temperature is the only ecologic variable, and where the water temperatures are the same throughout the year, as at Palau, the organic calcitic precipitates are always higher in magnesium than aragonitic precipitates (above).

Strontium uptake by skeletal carbonates in response to temperature is like that of magnesium

Aragonite-calcite ratios in consecutive growth increments of annelid worms, showing cyclic changes in the ratios over a range of 30 percent owing to temperature fluctuations.

in reflecting the modifying effects of the crystal chemistry of the mineral phase and of the biochemistry of the species. There are, however, some basic differences when compared to the uptake of magnesium. Strontium is preferentially accommodated in the crystal structure of aragonite as compared to calcite. Consequently, we find that the aragonites precipitated by species of all phyla, with the exception of three classes of mollusca, have noticeably higher Sr contents than the calcitic precipitates. Temperature tends to have an inverse effect on the Sr uptake of all species examined so far; the Sr concentrates decrease with elevation in environmental temperatures.

Another property known to be affected by environmental temperatures is the O^{18} content of the skeletal carbonates. The O^{18} content of carbonates laid down in isotopic equilibrium with the surrounding waters is dependent on the O^{18} content of the water, and on temperature. Since the isotopic composition of mean ocean water is by definition 0, temperatures can be calculated from the O^{18} content of samples derived from the well-mixed oceanic reservoir without requiring a water correction. The O^{18} content of isotopic-equilibrium precipitates decreases with elevation of temperature by about 0.2 percent per degree Centigrade. Only two biologic systems—Coelenterata (which includes corals) and Echinodermata (including sea urchins and starfish)—are known to precipitate skeletal carbonates out of isotopic equilibrium with their surrounding waters.

Another variable of the external environment that determines the isotopic composition of the skeletal carbonates is the chemical composition of the sea water. It has been known for some time that the shells of some molluscan species decrease in size and degree of calcification with decrease or increase in salinity as compared to mean ocean

water. It has also been shown that the dwarfing caused by decrease in salinity in some species is accompanied by an increase in the aragonite-calcite ratios, with values in excess of those found in shells grown at the same temperatures in habitats with water of mean ocean salinity. Similarly, there are data—for brachiopods, among others—which show that shells from highly saline and fresh-water-diluted sea waters have Mg and Sr contents which differ—in some cases radically—from those grown at the same temperature in habitats of mean ocean salinity. We are currently growing a variety of marine species under controlled conditions in our laboratory at Caltech to determine the effects of changes in salinity over the range found in the oceans, and to test the influence of Mg/Ca and Sr/Ca ratios in sea water on the ratios of these ions in skeletal carbonates.

Most investigators of deep sea organisms are inclined at present to attribute the depth zonation of marine biota in the intermediate and low latitudes to a decrease in water temperatures with an increase in depth, and to assign to increases in hydrostatic pressure a minor, ill-defined role. This seems justified in the case of species which range from shallow water at high latitudes to increasingly greater depths in low latitudes, for some species are known to occupy a depth range of 9000 meters—which corresponds to a range of change in ambient pressures equivalent to 900 atmospheres. Environmental temperatures over the entire range differ at most by 3° to 4°C.

It seems clear that, in these particular cases, the limiting factor of their depth distribution is temperature rather than differences in ambient pressures. It has been pointed out also that the upper limit of the deep sea biota in general coincides more closely with the 4°C isotherm than with any particular depth. Yet only a few of these deep sea species range into the shallow waters at high latitudes where the temperature regime is similar to that of their habitat range. Hence, there is the possibility that hydrostatic pressure may be the limiting factor in the depth distribution of many species. An independent measure of depth would be most desirable in the study of fossils, and hence the question of a possible pressure effect on one or several of the skeletal properties is of major significance for paleo-depth determinations.
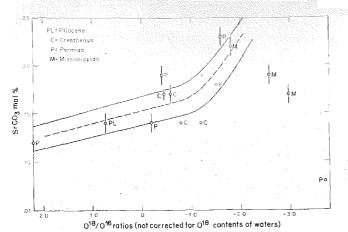
For this purpose we have initiated laboratory studies of the biogeochemistry of skeletal carbonates from multicellular organisms which have a wide depth distribution, in order to determine tolerance ranges in hydrostatic pressure of species from moderate depth. Considering samples from

nature with a wide depth distribution, we selected bottom-dwelling organisms which have either calcitic or aragonitic skeletons in all species of the same class under all known environmental conditions. Their Mg and Sr contents show either poor or no correlation with environmental temperatures, whereas there are systematic changes in concentrations when these data are related to the depths from which samples were taken.

Our pressure experiments have been conducted in an open, high-pressure apparatus that permits injection of food, and the pressure chamber has a plastic window for observing the animals. The system was designed by James Westphal, senior research fellow. Individual gastropods, recovered by dredging from a depth of 800 meters, were found to tolerate gradual increase in pressurization from atmospheric conditions to pressures equivalent to 80 atmospheres, as well as instantaneous depressurization back to 1 atmosphere—as we discovered when the pressure system accidentally failed. The maximum pressures tolerated by the individuals are near the maximum depths from which the samples were taken. Lack of records of this gastropod in the surface waters of the area where these individuals lived indicates that factors other than hydrostatic pressure prevent the species from occupying shallower depth habitats.

Thus, while we still know very little about the subject, it seems that hydrostatic pressure is an important environmental control. It may limit the distribution of species, and, within the range that they occupy, it may affect their biochemistry, which in turn finds an expression in the uptake of the major trace element of skeletal carbonates.

It is becoming clear that the minerals and their chemistry from skeletal carbonates monitor a wealth of information, ranging over the characterization of certain biochemical responses of the organisms to the temperature, the salinity, the sea water chemistry, and the hydrostatic pressure conditions of their environment. The biochemistry of the species basically determines the kinds of minerals precipitated by an organism. It regulates the levels of the trace-element concentrations at different body sites and, in particular, in the tissues which are involved in mineral precipitation. The ability of some biochemical systems to discriminate strongly against certain cations from the external medium explains why there is no apparent crystal chemical partitioning shown by them between the calcite and aragonite phase in the mineral precipitates.

The effects of environmental factors on the biochemistry of the organisms are transmitted invari-

PL = Pliocene
C = Cretaceous
P = Permian
M = Mississippian

SrCO₃ mol %

O¹⁸/O¹⁶ ratios (not corrected for O¹⁸ contents of waters)

The relationship between O^{18}/O^{16} ratios and $SrCO_3$ is depicted here in modern shells (lines) and in fossil forms (letters) as old as 250 million years. Conformity of the relationships shows that no marked change has occurred in the biochemistry of the organism or in the environment. The two M points to the right indicate post-depositioned alteration of these two samples.

ably to the trace-element concentrates of the mineral precipitates, and less frequently to the kinds of mineral phases which are precipitated by certain tissues. There are noticeable differences in the responses by different biochemical systems to environmental controls. These differences are reflected by differences in concentration levels and by the magnitude and direction of deviation on these levels of the trace-element contents and the aragonite-calcite ratios in the different systems.

Methods for applying all this information to the study of the environmental conditions of marine life in the geologic past by means of fossils require proof that we are dealing with the original mineralogy and its chemical properties. In the case of the mineral phases and their trace-element contents, one may ask whether these have undergone changes strictly in response to biochemical evolution, and, in turn, to ecologic variables. There is also the distinct possibility of changes in time in the chemistry of the oceans.

In the face of the large number of unknowns, the only recourse available at present is to compare the relationships of at least two geochemical properties in fossils which show no physical evidence of mineralogic change, with those of related living forms where these relationships have been defined. If relationships in fossils are the same as in recent species, their biogeochemistry is considered the original one, and the factors affecting the particular properties have remained the same. If the original composition is preserved, and one or several of the ecologic variables which affected them underwent evolutionary changes, one would expect systematic changes in their relationships with increase in geo-

logic age. This method of multiple approaches has been applied by us to articulate brachiopods, because fossils of this class are amply represented in the sedimentary rocks of the last 600 million years.

The relationships of the oxygen isotopes to the strontium contents for samples ranging back from the present to 250 million years ago are illustrated at left. The samples numbered by the letter M indicate that one can detect by this method even small diagenetic changes in the isotopic composition and in the strontium contents of the shells. All three samples are shells of the same species from the same deposit at the same locality. The samples showing the greatest divergence from the relations shown by the living forms were found loose on the weathered surface of the deposit; the one of lesser deviation from the weathered zone of the deposit, and the one showing agreement with the relations for living forms was derived from depths in the fresh shale of the deposit. We can also show that the changes in relationships among the samples are precisely what one would expect on grounds of theoretical considerations when shell carbonate becomes altered under the influence of fresh water.

The fact that some of the samples ranging back 250 million years in geologic age show similar relationships in their O^{18} and Sr concentrations indicates that the biochemistry of these brachiopods has not changed and that the isotopic and strontium contents of the ocean were similar to those of the present. Comparison of their Mg content with the O^{18} content indicates that only two low-magnesium samples show agreement in their relation to the O^{18} and Sr content with those in living species. In other samples the Mg content is lower than in living species. This is in agreement with observations on other fossil samples—that the Mg contents in high magnesium calcites in fossil skeletons are more susceptible to alterations in the rocks than are the O^{18} and Sr contents. Because it is highly improbable that three biogeochemical properties with different behavior should agree in their relationships with living forms, the Mg contents of the two samples with low concentrations are considered unaltered. This would indicate that the Mg contents of the oceans have not changed in the last 200 million years.

These examples indicate that it is possible to get a variety of biologic and environmental information about the chemistry of skeletons. There are numerous examples to show that this can be applied to fossils, and, with the aid of such information, we expect with more data to get a better picture of the evolutionary history of life in the ocean and of the changes in the oceanic environment.