# Research in Progress

Signs of Life

When Heinz Lowenstam, professor of paleoecology, discovered the first evidence of biologically produced magnetite ("The Case of the Iron Teeth," *E&S*, June 1964), many scientists found the idea too far-fetched to accept. But in the nearly 20 years since Lowenstam first noticed the gouge marks made by the teeth of chitons (a group of the mollusks) on rocks in a Bermuda tidepool, the iron oxide mineral magnetite has been discovered in numerous other forms of life — from bacteria to honeybees and dolphins. Recent research has also shown that magnetite in the tissues of homing pigeons acts as a compass utilizing the earth's magnetic field (*Caltech News*, August 1980).

Lowenstam and others have also found many more organically produced minerals besides magnetite, and more are being discovered all the time. Although he hasn't counted lately, Lowenstam says there are, for example, many more phosphate and carbonate minerals than previously thought, as well as numerous iron and manganese oxide minerals. Furthermore, organisms that make minerals are widely distributed throughout the five kingdoms of life — bacteria, protozoa, fungi, plants, and animals.

What is particularly striking about finding many of these organically produced minerals is that they shouldn't exist at all where they are formed. They are either not ever produced by inorganic processes in the biosphere or are there only in a particular environment. Magnetite, for instance, is found only in material extruded from the earth's mantle and is not actually precipitated in the biosphere except by such biomineralization processes as the chiton's teethmaking. The animal apparently accomplishes this by an enzyme-conversion process from hydrous iron oxide (ferrihydrite), which is easily produced inorganically in the biosphere.

If certain mineral compounds cannot be easily formed inorganically, how can animals manage it? The answer seems to be that some organisms have "ion pumps," and they can concentrate and localize elements that exist in low concentrations in the external environment. The mineral compounds must be formed in an internal chemical milieu isolated from the outside environment. Some of these compounds, when exposed to the external world, dissolve in minutes. For example, the strontium sulfate mineral celestite produced in the biosphere only by the planktonic Acantharia, which create a beautiful lattice structure of the mineral, has left no
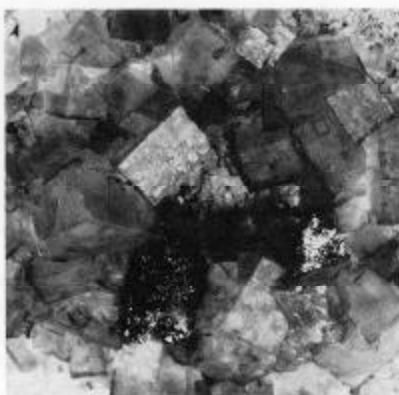
Naturally occurring fluorite (CaF_2) crystals, such as these precipitated from ore-bearing fluids, are formed only at very high temperatures and have a characteristic cube shape.
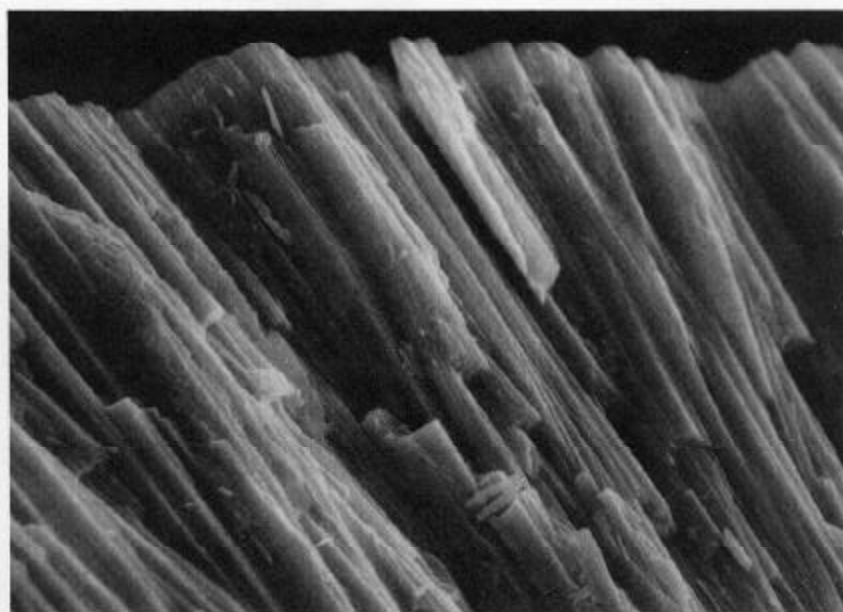
Needle-shaped fluorite crystals (magnified 250 times in this scanning electron micrograph) are biologically formed in the balancing organs (statoliths) of the opossum shrimp at less than room temperature.

fossil record because the surrounding unsaturated seawater dissolves it.

Because of the organic matrix into which these minerals fit as they are formed, they end up with crystal habits distinct from their counterparts in the physical world. They can then be distinguished from inorganically produced minerals by their morphology and, as a rule, also by their chemistry.

As a paleoecologist, Lowenstam is chiefly interested in studying the history of the evolution of life, and these biologically formed minerals often provide important clues — benchmarks at which life started to elbow its way into competition with inorganic processes in the biosphere. His recent paper, written with Lynn Margulis, professor of biology at Boston University and Sherman Fairchild Distinguished Scholar at Caltech in 1977,

challenges the commonly held view that solidly mineralized structures suddenly appeared at the end of the Precambrian Era, 580 million years ago. The two hypothesize that skeletal mineralization was initiated earlier in the late Precambrian in the form of "pinpoint" mineralization of organic hard parts. The oldest fully mineralized hard parts were calcareous throughout, indicating that this process was somehow related to improvements in calcium modulation, transport, and sequestering. The appearance of predators produced selection pressure on prey to develop more efficient nerve and muscle action, which required improvements in calcium modulation and reserves. This may have led to overshooting in calcium supply, with the excess transported to or near the body surface to initiate and later perfect skeletal mineralization.
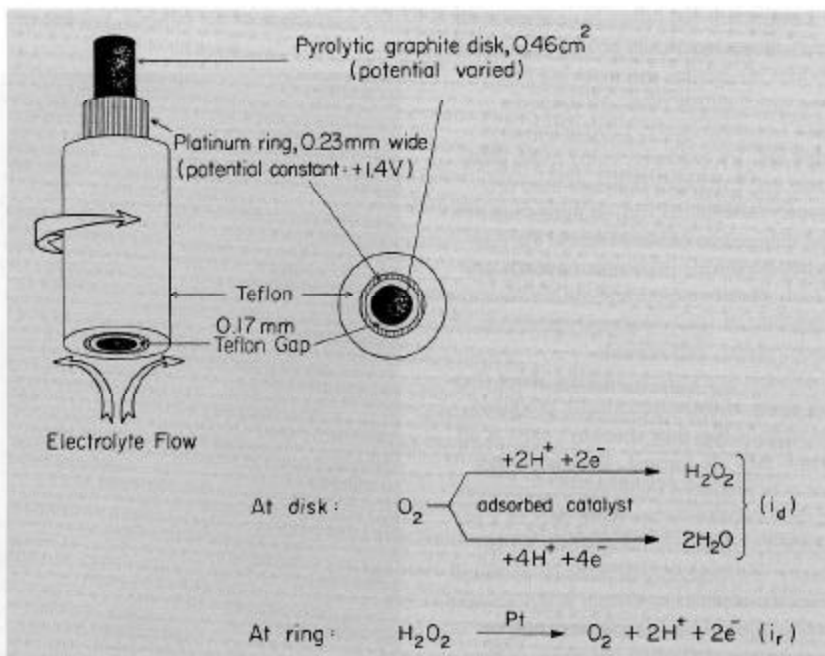
Other recently published research puts forth Lowenstam's theory that organically produced magnetite contributes significantly to the ocean floor sediments that have retained the magnetic pattern of the earth's reversing polarity.

But the applications of his work in biomineralization are not limited to the ancient history of our planet. Lowenstam also suggests that the presence of certain minerals might give a hint of the existence of some sort of life on other planets. Instead of just looking for life as we know it, scientists should perhaps instead look for minerals that "shouldn't be there." Further analysis, if it is possible, might show the presence of characteristic crystal shapes of biologically formed minerals, proving that some kind of biological process is at work in these seemingly "hostile" environments. □

Catalyst Converter

The fuel cells that powered the Apollo and Gemini spacecraft (at a cost of about $100 per watt) were efficient, nonpolluting, and easily located near the site of their use; they had no moving parts and responded well to large changes in demand. Unfortunately, $100 per watt is somewhat steep for the average consumer of electric power. But improvements since the 1960s and the rising cost of fuels make fuel cells increasingly attractive as alternative power generating systems.

One of those improvements has been the discovery of better catalysts for the electrode reactions that occur in fuel cells. Professor of Chemistry Fred Anson and his students have been testing some of the complex molecules that have been fashioned to act as catalysts. Although these molecules may be complex, the fuel cell itself is quite simple in concept, similar to a battery. It has positive and negative electrodes immersed in an electrolyte;

Pyrolytic graphite disk, 0.46 cm^2 (potential varied)

Platinum ring, 0.23 mm wide (potential constant = +1.4V)

Teflon

0.17 mm Teflon Gap

Electrolyte Flow

At disk: O_2 → adsorbed catalyst
$+2H^+ +2e^- \rightarrow H_2O_2$
$+4H^+ +4e^- \rightarrow 2H_2O$ (i_d)

At ring: $H_2O_2 \xrightarrow{Pt} O_2 + 2H^+ + 2e^-$ (i_r)

A rotating ring-disk electrode assembly was used to determine catalyst efficiency. As the rod rotates, the electrolyte flows upward and outward across the electrodes. The reactions at the ring and the catalyst-coated disk are shown at right.

at the cathode (positive pole) it consumes oxygen from the air, and at the anode (negative pole) it consumes hydrogen produced from hydrogen-rich fuels such as hydrocarbons. The electrochemical transformations occurring at both electrodes cause oxygen and hydrogen to combine to form water, and electrons flow spontaneously from the hydrogen to the oxygen electrode through an external circuit to deliver electricity.

Problems occur in this neat arrangement at the oxygen electrode, where the chemistry is somewhat complicated. The bond must be broken between the two oxygen atoms in gaseous oxygen, and four new bonds between oxygen and hydrogen must be formed. Unfortunately, instead of proceeding to water, the reaction often stops at the point where hydrogen peroxide (H_2O_2) has been formed, which avoids breaking the oxygen-oxygen bond; but this is a wasteful reaction pathway that yields only half as many electrons. Better catalysts are needed to induce the reaction to go along the more energy-rich path to water.

Catalysts, such as the finely divided platinum used in the Apollo fuel cells and in a 4.8 megawatt pilot plant being built in New York, are expensive. A high initial cost of a catalyst might be tolerated, however, if it retained its activity while present on the surface of the electrode — where all the action is. But platinum does eventually become less active.

Devising ways to attach catalysts to the surface of the electrode was one of the first problems attacked by Anson's group at Caltech. They found that aromatic molecules (containing benzene rings) bind strongly to graphite electrodes. As a group of chemists in J. P. Colllman's laoratory at Stanford synthesized possible catalyst molecules, Anson's group tested them to determine how well they clung to the graphite electrode and whether they directed the oxygen reduction reaction toward the production of water rather than hydrogen peroxide.

To break the bond in the oxygen molecule, the researchers hoped to stabilize the oxide ions being formed by letting them interact with positive metal ions. The Stanford group prepared a series of metalloporphyrins — flat, ring-shaped, aromatic molecules with a hole in the middle where metal ions, specifically cobalt, could be placed. Two of these flat molecules were strapped together "face to face" with chemical bridges.
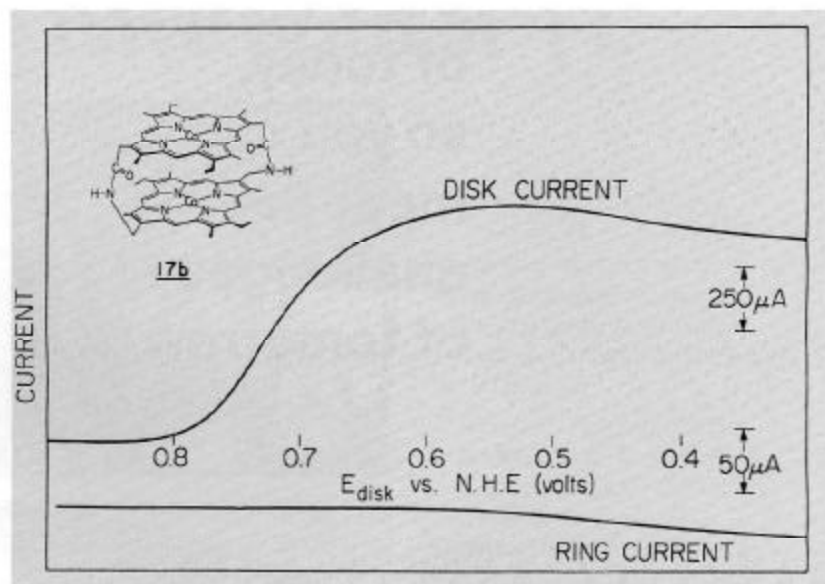
Disk and ring current versus the potential of the graphite disk coated with catalyst — the double porphyrin molecules containing two cobalt ions and strapped together face to face by four bridge atoms. The flat curve of the ring current indicates that little H_2O_2 is being formed (and reoxidized to produce current) and the main product is the desired end, water, which gives no response at the ring.

Having aromatic character, these porphyrins stick to the graphite electrodes very nicely. To determine how efficient they are as catalysts, Anson's group used an instrument with a graphite disk electrode (coated with the catalyst) and a concentric ring electrode, both mounted on a cylindrical rod. The two electrodes are insulated from each other so that electrochemistry can be carried out separately at each electrode. Rotation of the rod about its axis causes the electrolyte to flow up and then radially across the disk and ring. Since the voltage at the ring and disk can be independently controlled, the product of oxygen reduction at the disk can be monitored at the ring. Water gives no response at the ring, while hydrogen peroxide is reoxidized so that an anodic current is detected.

The single, unbridged porphyrin molecule, when tested, yielded only hydrogen peroxide; the face-to-face molecule connected by six bridge atoms and containing two cobalt ions was an improvement but still produced a substantial amount of peroxide. But the same double porphyrin connected by only four bridge atoms produced very little H_2O_2, most of the reaction proceeding directly to the desired product, water.

Anson and his colleagues speculate that the four-bridge porphyrin catalyst works as it does because the two cobalt ions react rapidly with both of the oxygen atoms in the oxygen molecule as it moves inside the cavity separating the bridged porphyrin molecules. This happens only if the separation of the cobalt ions is precisely correct. There is evidence that the active form of the catalyst is that in which the oxidation state of each cobalt ion is $+2$. A perfect catalyst would allow each fuel cell to yield about 1.2 volts; Anson's best value is about 0.7 volt, while the target voltage for the platinum catalyzed fuel cell is 0.6 volt.

Many more experiments are necessary to improve the catalyzed reaction, but the recent progress coming from Anson's laboratory and his associates at Stanford is quite encouraging. It suggests that fuel cells may be able to supply a larger portion of our power needs in the future. □