60 milliradians is almost eliminated, and the agreement with experiment is considerably improved. However, the recent calculations indicate that a Holley model—with two arms in close contact, pointing up, and the other two in close contact and pointing down—is in satisfactory agreement with our measurements. Thus the x-ray data alone do not distinguish between this model and the three-up and one-down model suggested in the text.

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Lepidocrocite, an Apatite Mineral, and Magnetite in Teeth of Chitons (Polyplacophora)

Abstract. *X-ray diffraction patterns show that the mature denticles of three extant chiton species are composed of the mineral lepidocrocite and an apatite mineral, probably francolite, in addition to magnetite. Each of the three minerals forms a discrete microarchitectural unit of the chiton denticles. This is the first indication that lepidocrocite is precipitated by marine organisms and an apatite mineral by chitons.*

Occurrences of magnetite ($Fe_2O_3 \cdot FeO$) in marine sediments have been attributed in the past to volcanic sources or were thought to be derived from cosmic spherules. However, this mineral is also a biological precipitate (*1*). The organisms now known to synthesize magnetite are chitons, which are common in the intertidal zone of rocky shores on the continents and oceanic islands, while a few species are known to occupy ocean deeps up to 4200 m (*2*). Magnetite in chitons is localized in the mineralized denticles of the mature major lateral teeth; the identification of the mineral is based on study of denticle samples by x-ray diffraction, on determination of the ferric-ferrous ration, and on the hardness on the Mohs hardness scale (*1, 3*). Denticles from ten species of chitons were investigated, and magnetite was found in all cases (*1, 4*). However, the x-ray diffraction photographs for a number of chiton species showed not only the magnetite pattern but, in addition, several weak lines (*1*). These additional lines indicated the presence of other minerals which could be either goethite, lepidocrocite, or carbonate apatite, or a combination thereof (*1*).

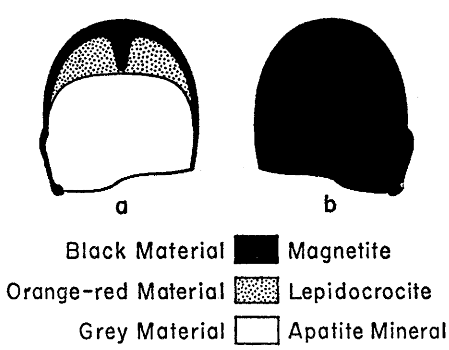

Fig. 1. Distribution of the three microarchitectural units on the denticle surfaces of the teeth of *Acanthopleura echinatum.* (a) Anterior surface view; (b) posterior surface view. Denticle dimensions: height and width, 0.7 mm.

In mollusca, the mineral goethite (αFeOOH) is known to occur in the mineralized denticles of one gastropod family (*5*), and dahllite possibly occurs in the larval shells of one bivalve species (*6*). There is no reliable record of lepidocrocite (γFeOOH) as a biologic mineral precipitate. Hence, it is important to define these unidentified minerals that occur in some chiton teeth and to determine their distribution relative to the magnetite in the mineralized denticles.

We selected species of the Chitonidae for the study, because three of the species that indicated unidentified minerals in addition to magnetite belong to the genera *Chiton* and *Acanthopleura* from this family. The denticles of mature mineralized teeth (major laterals) were mechanically separated from specimens (preserved in alcohol) of *Chiton tuberculatus* from Barbados, West Indies, of *Acanthopleura echinatum* from Viña del Mar, Chile, and of *A. spiniger* from Fiji and Palau, Caroline Islands (*7*). A sample of entire denticles from each species was examined under the microscope for their surface colors, and thin sections were prepared from another sample to compare the colors of their interiors with those on the surfaces.

The denticles of all three species have several features in common. They are similar in shape, and their surfaces show differently colored regions; one of these regions is characterized by a black shiny material and is always found in a homologous position on the denticle surfaces. Species-defined differences are marked by minor color variations in the area unoccupied by the black material. In *Acanthopleura echinatum*, the remainder of the denticle surface is characterized by two distinct color regions, one with bright orange-red and the other with a light gray color. The distribution and boundary relations of the black, orange-red, and gray materials on the denticle surfaces of *A. echinatum* are shown in Fig. 1.

The region occupied by the bright orange-red material in *A. echinatum*

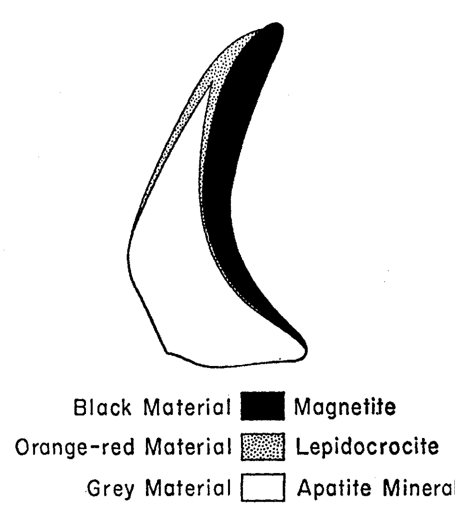

Fig. 2. Distribution of the three microarchitectural units in the inside of the denticles of *A. echinatum*, as seen in the median longitudinal cut through the denticle.

is represented in the two other Chitonidae by a lighter orange-colored material. A light gray material is similarly developed in *A. spiniger* in the region where it is found in *A. echinatum*, whereas the same region is marked by a paler orange-gray material in *Ch. tuberculatus*. In *A. echinatum*, the boundary between the orange-red and gray-colored areas is sharp, whereas in the two other species it appears to be gradational when viewed in reflected light. In transmitted light, the color differentiation of the orange and gray to orange-gray-colored regions becomes more pronounced, but the boundary relations still remain obscure. Figure 2 shows the distribution and boundary relations of the black, orange-red, and gray materials, which are seen on the surface as they appear in thin sections on the inside of the denticles in *A. echinatum*. The black material is developed only thinly in depth, and the remainder of the denticles is composed of subsurface extensions of the orange-red and particularly of the gray material. Hence, the orange-red and gray materials are more extensive in their development than their surface distribution alone indicates. When the areas occupied by the three differently colored materials on the surface and on the inside of a denticle are integrated, the total area is about 63 to 65 percent gray, 33 percent black, and, at most, 2 percent orange-red. The subsurface borders of the three different colored materials are as sharply defined as on the surface. Thin sections show that the distribution of the different colored materials in the denticles of the two other species of the Chitonidae is similar to that of *A. echinatum*. The orange-colored material is sharply bounded peripherally, but its thickness decreases rapidly toward the distal borders of its surface development, where it wedges out. The underlying material in the denticles of *Ch. tuberculatus* and *A. spiniger* is light gray. Hence, the apparent color gradation seen on the surface between the orange material and the materials bordering it distally can be related to an increase in transparency of the underlying gray material as the layer of the orange material on the surface becomes thinner. In *Ch. tuberculatus*, thin sections of the gray material show that it contains a pale-yellow pigment at the surface of the denticles, which tends to accentuate the impression of a color gradation toward the orange-colored material which borders it.

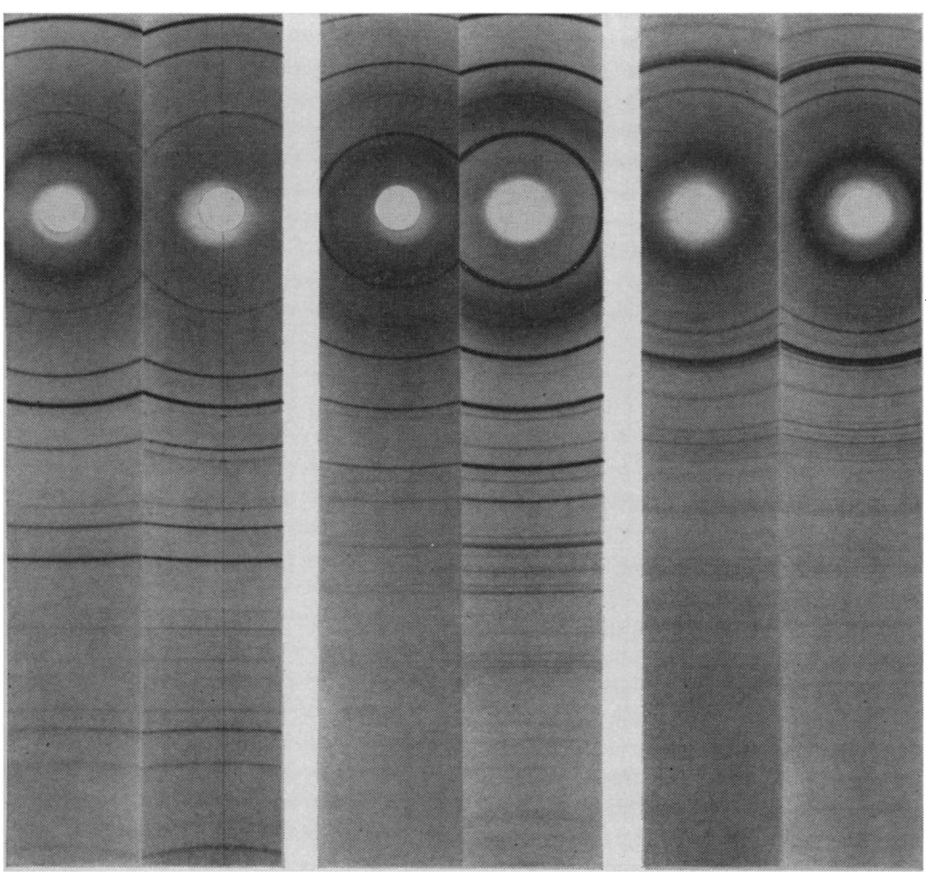

Fig. 3. X-ray diffraction photographs. (A) Black material from denticle of *A. echinatum;* (B) reference magnetite; (C) orange-red material from denticle of *A. echinatum*; (D) reference lepidocrocite; (E) gray material from denticle of *A. echinatum*; (F) reference dahllite.

Samples of each of the differently colored materials were mechanically separated from the denticles of mature lateral teeth of each of the three chiton species. These samples were finely ground, and the powders were investigated separately by x-ray diffraction (Norelco instrument) with a Debye-Sherrer camera and iron-filtered cobalt radiation and nickel-filtered copper radiation. Reference samples of magnetite, lepidocrocite, and dahllite were included for comparison (*8*).

The diffraction photograph of the black material (Fig. 3) checks that of magnetite and of the orange-red material, lepidocrocite, in both spacing and intensity of lines (*9*). The diffraction photograph of the light gray material resembles that of dahllite but shows minor differences in spacing and intensity. Calcium, phosphorus, and fluorine determinations were made with an Applied Research Laboratories electron-probe microanalyzer on the gray material from three denticles of *A. echinatum*. The gray material contained, on the average, approximately 31.9 percent Ca, 15.9 percent P, and 2.3 percent F (*10*); it liberates carbon dioxide when treated with hydrochloric acid; and hence it is composed of an apatite mineral with a carbonate component and a high fluorine content. The mineral is probably a carbonate fluorapatite, francolite. The x-ray diffraction patterns of the similarly colored materials which occupy homologous sites in the mature denticles of *A. spiniger* and *Ch. tuberculatus* were found to be the same as those in *A. echinatum*.

These data show that the denticles of mature major lateral teeth in three species of the Chitonidae contain three different minerals: magnetite, lepidocrocite, and an apatite mineral, probably francolite. Each of these minerals is localized in a discrete microarchitectural unit in the denticles (Figs. 1 and 2). The magnetite, lepidocrocite, and apatite mineral-bearing units occupy homologous sites in the denticles of the three species examined. For this reason, the magnetite unit is always separated spatially from the apatite unit by the lepidocrocite unit. The apatite unit in all three species is the largest (63 to 65 percent), the magnetite unit comprises about 33 percent, and the lepidocrocite unit consists of, at most, 2 percent of the mineral fraction of the denticles. However, the magnetite is the most extensively developed mineral on the denticle surfaces (Fig. 1), occupying about 60 percent, while the apatite mineral covers, at most, 38 percent of the surface area. The minerals recovered from the denticles of all mature teeth on the radula of adult individuals of *A. echinatum* consist, on the average, of 12 mg of the apatite mineral, 6 mg of magnetite, and 0.7 mg of lepidocrocite.

The minerals found in the denticles of the Chitonidae species have biologic and geologic implications. Magnetite was found in the denticles of two Chitonidae species (*1*), whereas the apatite mineral and lepidocrocite are new to chiton precipitates. The identification of lepidocrocite is of particular interest, because this is the first time that this mineral has been observed as a biologic precipitation product.

The Chitonidae in our study have shell plates composed of aragonite. The spicules in the two *Acanthopleura* species, as well as the girdle scales in the *Chiton* species, consist also of aragonite. When the denticle precipitates, namely magnetite, lepidocrocite, and the apatite mineral, are added, the chitons emerge as a rather unique group of organisms, in which as many as four different minerals can be precipitated by the tissues of a single individual.

Chitonidae are common intertidally on rocky shores of the tropical and subtropical seas; for instance, at Barbados, Chitonidae average 30 individuals and as many as 60 individuals per square meter. The mineral fraction of the mature denticles of the standing crop of Chitonidae per square meter is estimated to consist, on the average, of 300 mg of the apatite mineral, 150 mg of magnetite, and 10 mg of lepidocrocite—and of twice those amounts in the more densely populated areas.

The significance of chitons as possible contributors of magnetite to marine sediments has been noted (*1*). The apatite fraction of shallow-water marine sediments has been attributed to skeletal remains of fish and crustaceans. However, our data indicate that, in the tropics and subtropics, the apatitic fraction of the shoal-water sediments should be, in part at least, derived from Chitonidae denticles. Sedimentary occurrences of lepidocrocite were formerly attributed to inorganic sources. My work indicates that this mineral also is a product of biosynthesis. The amounts contributed by the Chitonidae to the sediments are likely to be small. Nevertheless, it is necessary to distinguish in sedimentary lepidocrocites between the biologic and inorganically derived fractions.

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8. P. E. Desautels of the U.S. National Museum supplied the reference sample of lepidocrocite (cat. No. R9593) from Horhausen, Germany. The dahllite standard, supplied by D. McConnell, consists of dental enamel from a post-Wisconsin mastodon tooth (Bluffton, Ohio) which has been chemically analyzed [D. McConnell, *Amer. Mineralogist* **45**, 209 (1960)].
9. The 2.004-Å line shown in the x-ray diffraction pattern of the reference sample (Fig. 3B) is not a recorded magnetite line.
10. The Ca and P contents were determined with the use of the chemically analyzed dahllite as a standard; the F content was determined with a fluorite standard.
11. Contribution No. 1445 from the Division of Geological Sciences, California Institute of Technology. Supported by grants GP-321 and G-20187 from the National Science Foundation. I thank M. Dekkers and A. Chodos for technical assistance.

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Polonium-210: Removal from Smoke by Resin Filters

Abstract. *Use of a mixed ion-exchange resin as a filter for cigarettes markedly reduces both the total amount of polonium-210 in mainstream smoke and the picocuries per milligram of smoke. This procedure effectively minimizes exposure of the lungs of smokers to alpha irradiation.*

Since the publication of Radford and Hunt's report on the presence of ^{210}Po in the mainstream smoke of cigarettes, many have investigated the presence of alpha-particle activity in tobacco (*1*). Although alpha activity in tobacco smoke is relatively low, much interest has been aroused in possible carcinogenic effects on the lung of the resultant irradiation, because of either the cumulative alpha dose or possible synergistic carcinogenic action with nicotine and tars.

We have extensively investigated the concentration of ^{210}Po in various domestic and foreign tobaccos. Our principal goal was reduction of alpha activity in mainstream smoke, with consequent reduction of the exposure of smokers' lungs to the activity, by seeking species of tobacco plants having naturally low contents of polonium. Also we attempted to determine the form in which ^{210}Po appears in the smoke, so that it could be controlled otherwise. In one experiment we used a mixed-bed ion-exchange resin in an attempt to remove ionized polonium from the smoke; all polonium apparently was removed. Other experiments indicated that commercial cigarette filters (cellulose, charcoal-impregnated material, granular charcoal, or combinations of these) removes 50 percent or less of the polonium. The following procedure was designed to investigate more fully the unexpected efficiency of the resin filter.

We used a domestic brand of filter cigarettes, the filter consisting of a chamber containing granular charcoal, with rolled-cellulose elements above and below the chamber. All samples were smoked by machine (*2*). We used a set of parameters that we have adopted as our standard; they consist of eight puffs, each of 35 cm^3 and 2-second duration, taken 58 seconds apart. The mainstream smoke was trapped by a 0.45-μ membrane filter and a flask containing 0.5*N* HCl. Earlier experiments in our laboratory had indicated quantitative removal of ^{210}Po by the membrane filter alone.

Our procedure was to smoke cigarettes first with the normal filter intact and then with the filter removed. Finally, cigarettes were smoked in which the granular charcoal of the normal filter had been replaced with