CHAPTER 6

INTERNAL CHARACTERISTICS

R. K. SOREM and R. H. FEWKES

INTRODUCTION

The concretionary and encrusting nature of modern marine manganese deposits has been recognized for many years. It is therefore somewhat surprising that the details of the layering of these nodules and crusts are still so poorly understood. Although Hamilton (1956) and Mero (1962) clearly showed the variety of nodular structures present, it was Cameron (1961) and Arrhenius (1963) who first showed the complexity of the layering by means of photomicrographs. Burns and Fuerstenau (1966) were among the first to show that chemical variations exist from one layer to the next in a single nodule, and Sorem (1967) emphasized the mineralogical and textural features, as well as large structural features which indicate non-uniformity of deposition, now known to be typical of individual nodules the world over.

In the past few years it has become clear that a thorough understanding of nodule origin and the many natural factors affecting the economic use of nodules requires much more data than are presently available. It is therefore fortunate that recently many workers in diverse disciplines have undertaken the detailed research necessary to obtain the needed information on physical features, mineralogy, and chemical composition of nodules. The outlook for new developments in this field in the next few years is indeed bright.

It is the purpose of this chapter to present information currently available on the internal features of manganese nodules, to offer genetic interpretations of these features, and to suggest new lines of research. To judge from the limited data available on ocean floor crusts rich in manganese and iron (see, for example, Aumento et al., 1968), much of what is learnt about nodules may be applied eventually to an understanding of the origin of these more continuous masses. A genetic relationship between these two is likely.

METHODS OF STUDY

Manganese nodules are complex heterogeneous three-dimensional objects, and a thorough understanding of the internal character of a nodule cannot be obtained by using any single research method. Not only must a variety of details be studied, but the scale of the details must cover a range from
megascopic to sub-microscopic. Furthermore, interpretation of many internal characteristics must commonly depend upon knowledge of the modern external habit of the nodule, so a complete investigation of nodule structure must include an examination of the exterior as well as the interior. For these reasons, a thorough study requires the use of a variety of special equipment, including the ore microscope, the scanning electron microscope (SEM), electron probe microanalyzer, X-ray macroprobe spectrograph, X-ray diffraction apparatus, and a wide assortment of analytical techniques. Although a discussion of the technical operation of the various instruments is beyond the scope of this chapter, the general application of those methods most commonly used is described briefly below.

**Ore microscope**

The familiar concentric shell structure of nodules is commonly visible on broken or sawn nodule surfaces, but a good quality polished section is necessary if the microscopic details of the internal structure are to be studied. The structure of a whole nodule is best revealed by a complete section through the centre, and photographs of whole nodule sections form excellent "maps" with which to control all analytical work on nodules (Fig. 6-1) (Sorem and Foster, 1972a). Many microscopes and other analytical instruments will not accept whole sections of large nodules, however, and parts of nodules must be sectioned separately for many studies.

Preparation of good polished sections of nodules is more difficult than with most common ores, but with experience it is relatively straightforward if modern mounting, impregnating, and diamond polishing methods are used (Sorem and Foster, 1972a). Generally the larger the section the more difficult and time-consuming the preparation. Ideally, a scratch-free section should result so that the specimen may be studied with the polarizing ore microscope at even the highest magnification. If a nodule contains non-opaque minerals of interest, a matching thin-section may be prepared. Polished thin-sections are particularly valuable for some work.

For best results, polished sections should be examined using vertical illumination, like that of the ore microscope, so that both physical relationships and optical properties may be determined. With a good instrument, objects as small as 0.1 micron in size can be resolved, but low to moderate magnification is generally used. Numerous properties may be observed to aid in mineral identification, including colour, reflectivity, bireflectance, and anisotropism, as well as physical properties like habit, cleavage, grain size, texture, hardness, and to a lesser extent chemical reactivity and magnetism.

*All photographs in this chapter are of polished sections using vertical illumination. Opaque minerals appear light, non-opaque minerals appear dark. Near outer edge of nodules is at top in all photomicrographs.*
Fig. 6-1. Polished section. Photomacrograph showing whole nodule structure. Accretion has produced crustal zone of thin continuous shells (layers) around older diversely oriented nodule fragments. Reflectivity of different layers ranges widely and is dependent primarily upon mineralogy and texture. Layers prominent at this magnification are called "gross layers". Photograph courtesy of D. M. Banning. Nodule DH 7-4, East Pacific Ocean, depth 3,660m. (Inset: exterior view of nodule before sectioning.)

The investigation of polished sections of manganese nodules is particularly challenging because of the extremely small grain size and intricate mineral relationships, but the work is very fruitful. Anyone who undertakes this kind of research, however, should be sure that he has a modern ore microscope in good adjustment and an adequate background in its use. Reference to the text by Cameron (1961) would be helpful. Only good quality sections should be used.

Useful optical properties
In the study of nodule sections, the single most useful property in plane-polarized light is reflectivity. Most nodule minerals lack colour but differ in reflectivity, with resulting differences in appearance which range from white to dark gray. Fortunately the eye is sensitive to very small differences in reflectivity, so that adjacent mineral layers less than one micron thick which differ in reflectivity by only a few percent can commonly be distinguished. In the future, it is expected that quantitative measurements of reflectivity will be useful in estimating the approximate chemical composition of nodule minerals.
An important related property is *bireflectance*, which is characteristic of the crystalline oxide minerals in nodules and is accompanied by *anisotropism* between crossed nicols. Detection of these effects permits the instant distinction between crystalline and amorphous nodule minerals, since thus far no crystalline isotropic mineral has been found in nodules. The importance of this distinction cannot be overemphasized, for recognition of crystalline oxides is tantamount to identifying the nodule material richest in manganese, copper, and nickel. To our knowledge, no well-crystallized iron minerals have yet been found in marine nodules.

*Other properties*

The relative hardness of different minerals in nodule sections, as revealed by polishing behaviour and as detected by the pseudo-Becke line method, is also useful in identifying intricate intergrowths of fine-grained minerals. The scratch hardness (*Talmage*) is also of interest and should be estimated, along with an evaluation of tenacity, whenever a microsample is extracted for X-ray diffraction analysis.

Additional characteristics to aid in mineral identification are being sought. Among the techniques currently being explored are chemical etching, magnetic testing, and monochromatic photography. At present, however, we know of no available reference data usable on a microscopic scale.

Other nodule characteristics which have attracted interest in the past include specific surface area, which is uncommonly great (*Weisz, 1968*), specific gravity, and solubility (*Raab, 1972*). Although data on these properties may not be of general use for mineral identification, it would seem very desirable to investigate microsamples of known optical character so that the findings may be applied to the solution of problems of nodule origin if possible. Information of this kind may also be of interest in the development of the most efficient commercial uses of manganese nodules.

Available data on major nodule minerals are presented in Table 6-1.

*Scanning electron microscope*

The SEM is unsurpassed for the study of *undisturbed* nodule material at any magnification beyond that of a medium-power binocular microscope. Whether the subject is the external habit or a fracture surface from within the nodule, preparation is simple and the operator can see and photograph objects less than one micron in size with remarkable depth of focus. Under suitable operating conditions, gold vapor-coating of the sample may be omitted (*Margolis and Glasby, 1973*), or a carbon coating may suffice if an electron microprobe is used in the SEM mode (C. Knowles, personal communication, 1973). Although the SEM generally shows little when a polished section is examined, study of an etched nodule section may be of value for certain problems (*Margolis and Glasby, 1973*).
TABLE 6-1
Properties of chief nodule minerals in polished sections

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Colour</th>
<th>Reflectivity *1</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Todorokite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Mn, Ca)Mn$_3$O$_7$·2H$_2$O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>White to</td>
<td>475 14.0</td>
<td>Randomly oriented microcrystalline intergrowths, appearing fibrous in</td>
</tr>
<tr>
<td></td>
<td>light gray</td>
<td>547 12.7</td>
<td>places. Takes a fair polish.</td>
</tr>
<tr>
<td></td>
<td>(bireflectant)</td>
<td>591 13.7</td>
<td>Anisotropic, colours bluish gray to bluish black. Talmage hardness B.</td>
</tr>
<tr>
<td>Birnessite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Na, Ca)Mn$<em>7$O$</em>{14}$·2.8H$_2$O</td>
<td>651 13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Opaque amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>material</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Impure Mn and Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxides)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>White to</td>
<td>475 14.8</td>
<td>Massive, fine-grained, amorphous. Colour and reflectivity vary with</td>
</tr>
<tr>
<td></td>
<td>gray</td>
<td>547 14.0</td>
<td>composition. Sensibly isotropic. White takes a good polish. Talmage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>591 13.7</td>
<td>hardness B+. Gray polishes with some difficulty. Talmage hardness B.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>651 13.4</td>
<td></td>
</tr>
</tbody>
</table>

*1 Measured by D. L. Banning, Washington State University, using Leitz MPV-1 Photometer with calibrated glass standard.
*2 After Larson (1962).
*3 After Brown et al. (1971).

X-ray diffraction

The mineralogical composition of manganese nodules is as yet poorly understood (see Chapter 7). At present, the most useful information is based on X-ray diffraction analysis of microsamples weighing less than a milligram (Sorem and Foster, 1972a) but much remains to be done. Serious problems of recognition and nomenclature (Sorem, 1972), which were discussed recently at a workshop seminar sponsored by the National Science Foundation (Battelle Seattle Research Centre, June 1973), will not be overcome easily. Work with very small microsamples, for which optical and chemical data are known, seems to hold the greatest promise for the development of routine mineral recognition criteria and for providing
mineralogical data related to nodule origin. Crystal structure determinations based upon single crystal analysis are desirable, but the outlook for this work is not bright in view of the cryptocrystalline and amorphous nature of most nodule material. Electron diffraction analysis has been attempted (J. Zussman, personal communication, 1970), but as yet no useful results have been published.

Inter-laboratory standardization of X-ray diffraction methods and nomenclature has recently been recommended (Sorem, 1972), and round-robin analysis of standards was begun in 1975 among a number of laboratories.

*Chemical analysis*

The chemical composition of manganese nodules has been reported by many investigators. The results represent a wide spectrum of sample types and analytical techniques, however, and therefore all are not directly comparable. Both partial and complete analyses have been made, and both whole nodules and parts of nodules have been used as samples. The most common methods of bulk analysis are X-ray fluorescence and atomic absorption, although other techniques are also reported. Emission spectrography and neutron activation analysis seem to offer special advantages for small sample work.

Recently the importance of analyzing very small parts of nodules has been recognized, and several non-destructive probe methods of analysis have become popular. Not only do these methods permit the analysis of very small samples, but they are essentially non-destructive and leave the sample in condition for optical study. Both spot analyses and concentration variation curves along selected paths have been published. The finest spatial resolution reported thus far is obtained by use of the electron microprobe, with which areas as small as 1–3 microns across on polished sections may be analyzed quantitatively. Greater resolution (e.g., 100 Å) is claimed by several SEM manufacturers who are now marketing energy dispersive analyzing units, but quantitative work is difficult. Analyses of nodule materials by this method have not yet been published. As with the microprobe, both traverses and spot analyses should be possible eventually. At the other extreme of resolution is the X-ray macroprobe spectrograph, which can be used to determine major element composition of areas from 100 to 500 microns in size on polished sections and is especially well-suited to traversing distances of several centimetres across layered specimens relatively rapidly (Sorem and Foster, 1972b).

Semi-quantitative element distribution in polished sections can also be shown by characteristic X-ray scanning photographs obtainable with both microprobe and SEM instruments. This method effectively shows the spatial inter-relationships of numerous elements in an area of microscopic size.
General

The emphasis in this chapter is on mineral recognition in polished sections of manganese nodules. For this purpose both crystalline and X-ray amorphous materials are termed minerals, for both are abundant in nodules and generally are closely intergrown (Fig. 6-2). Although hydrous manganese and iron oxide minerals predominate in most nodules, minor amounts of silicates and other minerals are commonly present. All deserve careful study.

Fig. 6-2. Photomicrograph. Plain light. Typical colloform interlamination of iron-rich amorphous material (medium gray) and crystalline manganese minerals todorokite and birnessite (light gray). Dark gray and black irregular areas are fine-grained detritus, synthetic resin, and surface pits. Outer edge of nodule is just beyond field of view at top. Nodule NP 2–1B, East Pacific Ocean, depth 4,570 m.
**Minerals identified**

The most common crystalline oxide minerals in marine manganese nodules are apparently todorokite and birnessite. Almost without exception, these minerals are intimately intergrown, even in microsamples weighing less than a milligram. Proportions vary from place to place in a single nodule, however, and rarely monomineralic specimens are found (Banning, 1974). The optical properties of these minerals are poorly known, although some data have been presented for both the marine minerals and for specimens from terrestrial manganese deposits (Cameron, 1961; Larson, 1962; Sorem, 1967, 1972). At present the most useful optical properties are reflectivity, bireflectance, and anisotropism. Reliable chemical analyses are reported for terrestrial specimens (Straczek et al., 1960; Larson, 1962; Brown et al., 1971), and the general chemical formula for each mineral is well established, as noted in Table 6-1. Extensive cation substitution has been documented in todorokite.

Other crystalline oxide minerals rich in manganese which reportedly have been found in the growth layers of marine nodules include nsutite (Manheim, 1965), psilomelane, pyrolusite, woodruffite, and vernadite (Andruschenko and Skornyakova, 1969), and ranciéite (Sorem, 1967). Details of the habit and occurrence of these minerals in nodules have not been described, however, and their significance cannot be evaluated at present. In any event, these minerals would be expected to be very fine-grained and difficult to recognize optically without prior identification by X-ray diffraction analysis of microsamples.

Non-crystalline or X-ray amorphous oxides are abundant in nodules and in fact commonly predominate. Poorly crystallized goethite or a related ferric hydroxide has been reported as a nodule constituent by several investigators (Arrhenius, 1963; Glasby, 1972c), but it has not been widely observed. Detailed X-ray diffraction study of iron-rich material in many eastern-Pacific nodules failed to reveal the presence of any crystalline iron compounds (Carr, 1970), even where the material was interlaminated with crystalline manganese minerals. These materials cannot be ignored in research on the origin of manganese nodules, however, and they deserve far more attention than has been reported in the literature. Thus far the only attempt to classify the amorphous oxides microscopically is that of Foster (1970), who used the general term “opaque amorphous material” and recognized both iron-rich and manganese-rich types.

The very fine-grained non-opaque minerals which form an essential but minor part of the oxide shells of most manganese nodules (Fig. 6-3) are poorly known, and in most published reports they are ignored or treated in only a cursory way. Arrhenius (1963) reported “crystallites” of opal, rutile, anatase, barite, and nontronite. Various authors have reported such minerals as montmorillonite, illite, and other less precise species, but identification criteria and mineral relationships are usually not described. According to D.
Pitzl and J. A. Kittrick (personal communication, 1973), both amorphous and finely crystalline minerals are present in the material usually characterized as “clay”, but identification of the mineral species present is a difficult and tedious task. Pitzl has attacked this problem by applying mineral treatment techniques and X-ray diffraction analysis successively to standard API clay minerals, bulk concentrates of non-opaque nodule material, and finally to microsamples extracted from well-documented sites in a single nodule. He concludes that the minerals montmorillonite, illite and chlorite, as well as amorphous silica are present in the eastern-Pacific nodules he studied, and he believes that several other silicates (smectites?) will eventually be substantiated. Apparently there is not as yet any rapid method of identifying microsamples of these minerals with assurance.
Carbonate minerals are evidently rare in manganese nodules, probably because of the great depths at which most nodules form. Even in the relatively shallow deposits of the Blake Plateau, the only calcareous mineral recognized is manganocalcite, which forms thin veinlets which cut the oxide layers.

Clastic grains of many kinds of material have been reported in nodules, including minerals, rock fragments, fossils, and glass shards. Little detailed work has been reported on the detrital minerals, however, and there are as yet no good criteria for distinguishing between authigenic and detrital grains of clay-size or less except textural features revealed by SEM (Pitzl, 1974). Carr (1970) identified large angular grains of quartz, feldspar, and ilmenite by X-ray diffraction, and both he and Foster (1970) illustrated glass shards. Nodules from the Drake Passage show unusual textural features inherent in growth where influx of detritus is especially rapid (Fig. 6-4; Fewkes, 1972). Metallic spherules of cosmic origin have been concentrated from nodules by Finkelman (1970, 1972), and Jedwab (1970) described a number of similar spherules in a *Challenger* nodule. In our experience, metallic spherules are rare in nodule sections, for we have seen only a few in the hundreds of sections we have studied (Fig. 6-5). Their occurrence is of more than passing

Fig. 6-4. Photomicrograph. Plain light. Abundance and angular shapes of clastic silicate grains (gray, smooth appearance) are typical of debris accumulated during nodule growth in region of high sedimentation rate and strong currents. Matrix layers are highly reflective where iron and manganese content is relatively great (approximately 16% Fe, 6% Mn). Nodule DP 11–2, Scotia Sea, depth ca. 1,980 m.
Fig. 6-5. A. Photomacrograph. Partial view of concentric shell structure, outside surface of nodule at top, showing location (arrow) of micro-spherule shown in B. White layers are rich in manganese; gray areas are rich in iron. White line shows probe traverse path. In places this nodule contains more than 1% nickel, yet only this one metallic spherule is visible. Spherules are not a likely source of nickel in manganese nodules. Nodule BR-1-1, Bermuda Rise, Atlantic Ocean, depth 5,390 m.

B. Photomicrograph of spherule indicate by arrow in A. Primary nature is shown by conformability of oxide layers (dark gray) around spherule. Microprobe analysis shows at least 4% nickel content for spherule (C. Knowles, personal communication, 1974).

interest, for the contribution of such particles to the nickel content of nodules has been speculated upon in the past. The paucity of metallic spherules and the unaltered character of the spherule illustrated, which is similar to those shown by Finkelman and Jedwab, suggest, however, that dissolved spherules are not a likely source for the nickel disseminated in the oxide portion of most marine nodules. Jedwab described spherules partially altered to hematite, but the absolute amount of nickel presumably liberated by such alteration would be very small unless many spherules were completely decomposed.
Mineral habit

Disregarding some of the included clastic debris, nodule materials are without exception extremely fine-grained. With the optical microscope it can be seen that botryoidal or colloform habit is predominant, both in material that is amorphous to X-rays and that which is crystalline. The opaque crystalline minerals are concentrated in relatively pure discrete layers in many places, but microscopic seams and patches of these minerals commonly appear also in dominantly amorphous masses in most nodules, and vice versa. In contrast, the non-opaque minerals rarely if ever form continuous layers but instead seem to fill interstices of opaque mineral aggregates.

In sections, even the crystalline minerals cannot generally be resolved microscopically as individual crystals, but their optical behaviour suggests that they generally form partially oriented intergrowths of platy or fibrous crystallites (Fig. 6-6). Crystallite size is commonly less than 0.2 μ to judge from the diffuse nature of X-ray patterns produced by single chips removed from polished sections. Rarely, tabular crystals a few microns across are revealed in polished sections, but crystals of this size are so fragile that they are likely to be destroyed when a nodule is sectioned, and their abundance is therefore difficult to estimate. Fortunately, the SEM does not require sectioning of specimens, and patient study of natural surfaces and fresh fractures with this instrument reveals well-formed crystals not otherwise visible.

Using micro-X-ray diffraction techniques to establish identification, it has been shown that birnessite is characterized by rounded clusters of thin slightly curved radiating lamellae forming a loose open structured array (Fig. 6-7A). In some areas individual clusters coalesce, resulting in large aggregates or continuous layers. Todorokite has been described by some authors as being in the form of fibrous aggregates (Levinson, 1960), as lath-like, flattened on (010) and elongate (001) with terminal edges inclined ca. 60° and 70° to (001) (Frondel et al., 1960a), or in columnar aggregates (Straczek et al., 1960). Crystallites with a morphology similar to todorokite have been observed in nodules (Fig. 6-7B), but because of their small size a positive identification has not been made. Phillipsite crystals are formed in nodules in association with oxides and non-oxides and can be recognized by their acicular or blocky habit and interpenetrant-twinning. (Fig. 6-9A).

Investigation of X-ray amorphous oxide material with the SEM is also of interest because not only is the lack of symmetrical crystals evident, but textures are revealed which strongly suggest deposition by flocculation. Undisturbed recent accumulations are commonly characterized by tiny flocs which occur on external nodule surfaces in the form of continuous layers and as small globular protrusions (Fig. 6-8A). The amount of admixed detritus is variable. Floccule protrusions (Fig. 6-8B) and loosely aggregated
Fig. 6-6. Photomicrographs. A. Plain light. Encrustation of crystalline todorokite and birnessite (bireflectant, speckled white and gray) along fracture wall. Fracture cuts dense mass of nodule oxides, largely medium gray amorphous material. Very thin contorted white seams may be cryptocrystalline. Main fracture is filled with synthetic resin.
B. Crossed polarizers. Anisotropism of todorokite and birnessite is clearly visible. Wavy extinction suggests aggregates of preferentially oriented crystallites. Nodule NP 2-1B, East Pacific Ocean, depth 5,300 m.

Fig. 6-7. Scanning electron photomicrographs of crystalline minerals along an open fracture in a manganese nodule. Nodule NP 2-4.
A. Birnessite in radiating clusters of thin lamellae.
B. Blocky crystals of phillipsite and todorokite (?) (lower right centre) intergrown with birnessite.
Fig. 6-8. Scanning electron photomicrographs of amorphous material found on external and internal nodule surfaces. This amorphous material is thought to consist primarily of iron and manganese hydroxides which have flocculated onto the nodule during nodule growth. The floccules may form a continuous layer covering everything on the outer surface of the nodule (A), occur as tiny protrusions within the protected environment of nodule cavities (B), form loosely aggregated clusters along open fracture surfaces (C), and agglomerate into larger botryoidal masses (D). Nodule NP 11–4 (A and B), Nodule NP 2–4 (C and D), East Pacific Ocean, depth ca. 4,570 m.
 clusters (Fig. 6-8C) also occur within nodules along open cavities and fracture surfaces. The general appearance of the clusters suggests they resulted from the agglomeration of minute colloidal size masses, which in turn probably consist of even smaller particles tightly held together. The coalescing of the clusters may form larger botryoidal masses (Fig. 6-8D).

Clay minerals are also amenable to study by use of the SEM, and the habit of these minerals and their intricate relationship to the opaque minerals is clearly revealed in no other way. In places, birnessite, phillipsite, and todorokite (?) appear to have grown on a crystalline montmorillonite substrate (Fig. 6-9A), whereas elsewhere montmorillonite seems to have crystallized in cavities in the oxides (Fig. 6-9B; Fewkes, 1973).

Distribution of minerals

Considering the problems discussed in a preceding section concerning the identification and classification of nodule minerals, it is clear that published estimates of mineral abundance and distribution in nodules are difficult to evaluate. The most widely published estimates have to do with relative abundance of todorokite and birnessite (or the various "manganites" of Buser) and X-ray amorphous material. Among the earliest estimates are those
of Barnes (1967a) and Cronan (1972c), who concluded, as have others more recently, that nodules from certain regions or depths contain predominantly one mineral or the other. The basic data for these estimates were obtained by diffractometer analysis of bulk powder samples, often by use of copper radiation (Glasby, 1972a). There are dangers in sampling, sample preparation, and contamination with this method, and it would be wise to use the estimates so derived with caution.

It is recommended that estimates of mineral abundance hereafter be made chiefly on the basis of microscopic study, combined with camera X-ray powder diffraction analysis of microsample chips. Any diffractometer work should involve carefully documented sampling, crushing under liquid nitrogen (Burns and Brown, 1972), and use of Fe radiation or some sort of monochromatization to avoid fluorescence. In addition, some means must be found to determine the proportion of amorphous material present.

Published illustrations of manganese nodule sections and diffractometer charts suggest that most manganese nodules contain a large proportion of amorphous material, that crystalline oxides are both randomly dispersed and in well-defined segregations, and that the distinction between the various possible oxide minerals is not an easy task.

COMMON INTERNAL FEATURES OF NODULES

Megascopic

Much detail can be seen in a good polished nodule section megascopically, especially if vertical illumination is used to emphasize variations in reflectivity and improve contrast (Fig. 6-1). Useful observations include thickness and continuity of major layers (shells), the number of major layers and the nature of their relationships, large textural features characteristic of certain layers, and the general distribution of oxide and non-oxide materials. In addition, other structures such as fractures and unconformities and the general nature of the nodule nucleus often can be clearly seen. Significant common megascopic internal features of manganese nodules are summarized below (after Sorem and Foster 1972c, pp. 192–194). (Figures referred to are in the original text and are not repeated here.)

Most nodule sections display prominent conformable layers, each ¼ to 1 mm thick, which represent the concentric shell structure so commonly visible on broken nodules. This gross layering, so-called to distinguish it from the much thinner and more delicate laminations always present in nodules, is visible chiefly because of reflectivity differences between adjacent layers or because of the presence of thin clay-rich partings between layers.* It is especially interesting that gross layers form a number of patterns which are not random and are found repeatedly in nodules from many localities.

*See Fig. 6-1.
In a single nodule, individual layers are generally extensive, but the pattern of the gross layering is rarely uniform throughout. The inner layers tend to conform to the shape of the core, which is commonly a fragment of an older nodule or a rock. Passing outward from the core, layers tend to follow the core shape less and less closely, but even in large nodules the exterior shape commonly reflects the shape of the core. Angular cores generate angular nodules, and equant or very small cores result in spheroidal ("cannonball") nodules (Fig. 1, 2, 3, 4).

Other common patterns of layering include crenulations, pinch-outs, facies changes and angular unconformities. Crenulated layers in the outer margins of a nodule show the internal structure of knobs or botryoidal forms common on most nodule exteriors. They are not restricted to the outer parts, however, and may be found at any level within the nodule. The other features mentioned actually result in the disappearance of a layer or group of layers. Layers may gradually thin and ultimately pinch out between adjacent layers, or they may change texture gradually as they are traced laterally, with or without a change in thickness (Fig. 3). The most striking termination of layers, however, is shown where the broken structure of an older nodule fragment is overlain at a sharp angle by successive layers which encrust the entire fragment (Fig. 5). These structures commonly pass into scarcely recognizable disconformities where the layers in the core fragment lie parallel to those of the encrusting material. The significance of these and similar features in working out the complex history of nodule growth has been summarized by Sorem and Foster (1968) and described in detail by Foster (1970).

Another striking feature of gross layering is the similarity in thickness from one layer to the next (Fig. 1, 2 and 3), and in many nodules there is in addition a similarity in the internal laminations of contiguous layers which suggests regular repetition or even cyclic deposition. A study of the fine details of the laminations has led to the recognition of texture zones, as described in the next section.

Microscopic

When one first views a polished manganese nodule section with the ore microscope, perhaps the most striking characteristic is the complex texture of many layers which megascopically appear to be structureless and homogeneous. As mentioned earlier, the predominant habit of nodule material is botryoidal, which is seen in polished cross-sections as colloform layering. Under the microscope, it is found that most gross layers have a complex colloform internal texture and are non-uniform mineralogically. Microscopically homogeneous layers are rarely thicker than 0.1 mm and most are as thin as 0.001 mm or less. Furthermore, a wide variety of layering patterns exists, ranging from broad arcs with a radius much greater than the thickness of an individual layer to intricate branching patterns where the radius of curvature is of the same order of magnitude as the thickness of the layers involved. Lateral changes in texture are common and correspond to the megascopically facies changes and unconformities previously described.

The layers vary greatly in denseness and continuity as well as in purity. Contacts between different materials are in places sharp, in others diffuse. Dense layers generally take a good polish, whereas impure or porous layers commonly are pitted. Either type of layer may be crystalline or X-ray amorphous, but in many if not most nodules amorphous material appears to
predominate. It should perhaps be re-emphasized that the recognition of crystalline material optically may be difficult because of the extremely fine grain size in many aggregates and the lack of visible euhedral crystals.

In view of these complexities, it may appear that sorting out the mineralogy and structure of manganese nodules in an orderly fashion so that nodules may be characterized microscopically on a routine basis is a hopeless task. Fortunately, however, the fine details and the larger features upon which they are superimposed are not completely random in character, and certain patterns can be found repeatedly in many nodules. This accounts for the recurring use of terms like rind, core, cusp, and nucleus by different authors. At least two important difficulties attend the use of terms like these, however; first, no good definition of the terms is available, and, second, not all common nodule features are included. Probably the introduction of new terms should and can be kept to a minimum, and established petrographic and mineralogical terms will generally be adequate if used with care. To minimize confusion, however, it may be worthwhile soon to compile a glossary of nomenclature for nodule research.

Another approach to systematic usage is to try to categorize certain common major internal nodule features, so that a minimum of detailed description is needed to convey observations to others. The only attempt to do this that has come to our attention is Foster's zone classification, which is based largely on textures visible in sections at magnifications less than 100 X. Foster's research (1970) revealed that a clear relationship exists between many textural features, mineralogy, and chemical composition. The following summary of this classification was presented recently (Sorem and Foster, 1972c) (Corresponding figures in this chapter are noted in square brackets).

In detailed studies of nodules collected west of Baja California, five distinctive textural patterns called zones were recognized in the sequences of laminae. The zones, which differ in homogeneity, textural patterns and composition, are classified as massive, mottled, compact, columnar and laminated. The columnar and mottled zones are the most abundant; the massive, compact and laminated zones are less common. A detailed discussion of the origin and textural interpretations of the various zone types has been given by Foster (1970), from which the following descriptions are abstracted. Comparable zones have been observed in many nodules from a wide range of sampling localities.

**Massive and Mottled Zones**

The massive and mottled zones contain the greatest proportion of crystalline material, but they differ in textural pattern and content of clay and amorphous material (Fig. 6 and 7). These zones contain the greatest concentrations of Mn, Ni and Cu. The massive zone [Fig. 6-10A] is a dense unit composed predominantly of regular but diffuse laminae of intergrown microcrystalline todorokite and birnessite, with minor amounts of clastic debris. Where analyzed, the massive zone contains approximately 32% Mn, 4% Fe, 2% Ni and 0.8% Cu, and in places Mn may be as great as 60%, Ni as high as 7% and Cu as high as 2% (A. C. Dunham, personal communication, 1971). The mottled zone [Fig. 6-10B] differs in that it contains approximately 15% clay and amorphous material in which the
laminae show a chaotic and discontinuous pattern. This zone type contains approximately 21% Mn, 12% Fe, 1% Ni and 0.5% Cu.

The other three zones are made up mostly of laminated opaque amorphous material and differ chiefly in clay content and prominence of intricate colloform layering. These zones contain the greatest concentrations of Fe, Ca, Ti and Si.

**Compact Zone**

The compact zone [Fig. 6-10C] is texturally similar to the massive zone, except that it is composed mostly of well-defined X-ray amorphous laminae (Fig. 7). However, lenses and pods of birnessite and todorokite intergrowths generally account for approximately 3% of the zone. The compact zone contains approximately 19% Mn, 17% Fe, 0.6% Ni and 0.2% Cu. This zone commonly contains the most highly reflective laminae found in the nodules.

**Columnar and Laminated Zones**

The columnar zone [Fig. 6-10D] consists of radially oriented columns of laminated X-ray amorphous material (Fig. 8). Clay fills the space between adjacent columns. The laminae composing the columns display a colloform texture and each column characteristically shows a delicate branching pattern. In places the radial columns are short, densely packed and relatively uniform laterally, giving a concentrically layered appearance. These units are called laminated zones (Fig. 7) [Fig. 6-10E]. The columnar and laminated zones are chemically similar, containing approximately 16% Mn, 16% Fe, 0.4% Ni and 0.25% Cu, but composition may vary greatly.

Foster (1970) also pointed out several other unique features which are common in internal nodule zones. Massive layers of todorokite and birnessite typically contain abundant replaced fossil remains, as well as angular fragments interpreted as volcanic glass shards, which are generally scarce elsewhere in the same nodule. The dense amorphous oxide layers (compact zones) contain a different kind of inclusion, however, which Foster termed "globules". He suggested (1970, p. 53) that these objects were possibly arenaceous fossil tests or perhaps "fossil bubbles" related to submarine volcanism (Fig. 6-11). Additional polished-section and SEM research in our department has since shown that many of these structures are tubular rather than spheroidal and strongly suggests an organic origin.

Another characteristic of massive and compact zones is the very irregular contact with older layers toward the nodule core, which contrasts strongly with the more regular broadly curved outer contact (with younger layers). Close examination shows that in places older laminations are actually truncated by the later material, and partial replacement of the older layers seems to be well documented (Fig. 6-12).

In his discussion of the zonal character of manganese nodules, Foster (1970) also mentioned the common occurrence of a group of well-developed broadly concentric layers which form an outer crustal zone a few millimetres thick on many nodules (Fig. 6-10F). This feature has been observed repeatedly since Foster's work and is present in many nodules from points as distant as several thousand kilometres in the Pacific Ocean and even in the Atlantic (Sorem, 1973).
Common internal features of nodules

Fig. 6-10. Typical internal features of North Pacific Ocean manganese nodules. A, B, C, D, and E courtesy of A. R. Foster. Plain light.

A. Photomicrograph. Dense layer of crystalline todorokite and birnessite, with abundant very fine-grained mineral and fossil detritus, finely laminated cusplate oxides above and below. This is Foster’s (1970) “massive zone”. Irregular lower contact and even upper contact are typical. Crystalline layer was probably deposited as a primary coating on exterior of finely botryoidal nodule surface. Nodule DH 7–2A, depth 3,660 m.

B. Photomicrograph. Chaotic layering of crystalline todorokite and birnessite (white) and amorphous iron-rich oxides (gray). Some areas are pitted (black). This is called the “mottled zone” by Foster (1970). Nodule DH 7–1, depth 3,660 m.

C. Photomicrograph. Very dense white oxide zones roughly conformable with thinly laminated oxide matrix (gray). Both units are iron-rich and amorphous. Diffuse contacts and included pod-like features are characteristic of the highly reflective “compact zone” (Foster, 1970). Nodule DH 5–3, depth 3,840 m.

D. Photomicrograph. Intricate curved laminae of oxides of iron and manganese representing sections through botryoidal nodule structures. Thin white or light gray seams are partly todorokite and birnessite, darker gray seams are iron-rich and amorphous. Black areas are clay or pits filled with synthetic resin. This type of layering is called the “columnar zone” by Foster (1970). Nodule DH 7–2B, depth 3,660 m.

E. A variety of thinly-layered oxides similar to D but with well-developed larger-scale layering upon which the small colloform structures seem to be superimposed. This was recognized by Foster (1970) as the “laminated zone”, in allusion to the thicker set of parallel layers. Nodule DH 7–2A, depth 3,660 m.

F. Photomacrograph. Part of a double-core nodule, emphasizing the parallel layers which form the outer shell, a few millimetres in thickness. Recent layers like these are so commonly recognizable as a discrete unit of structure that they are here called the “crustal zone”. Fine structure of the zone varies from region to region. Here close examination reveals the texture is that of a “laminated zone”. Nodule NP 15–1B.
Fig. 6–11. Photomicrograph. Typical "fragment-rimmed pod" in oxide layer containing alternating laminae of amorphous iron-rich oxides (gray) and crystalline manganese oxides (light gray, pitted). Angular clastic grains (dark gray) are commonly associated preferentially with the manganese-rich minerals, whether they form pods or irregular masses. Pods are probably cross-sections through tubular organic structures. Fragments may be of volcanic origin. Nodule SP 2–2B, South Pacific Ocean, depth 4,570 m.

For discussion purposes, it is proposed to term this the "crustal zone". The layers represent the most recently deposited growth shells and deserve careful study.

In many nodules both oxide-rich and clay-rich shells a few microns thick alternate in this zone, suggesting that deposition was influenced by a crudely regular variation of environment with time. In some nodule sections, similar zones of great age may be observed virtually unchanged within nodules, but commonly the original fine structure appears to have been destroyed by diagenetic processes. In many nodules, however, ancient growth habit seems to have been quite different from that of the modern crustal zone.
In many nodules several or all of the above zone types may be found stacked one upon the other (Fig. 6-13), and Foster attempted to show a correlation in the sequence of occurrence of zones in nodules from the same dredge haul. He suggested that nodules from localities as distant as 300 km might show comparable similarities. Later work has shown that certain textural features are indeed comparable in nodules from Pacific Ocean localities separated by as much as 7,000 km (Sorem 1973), but correlation of zone succession in nodules on a broad scale has not been established. However, there is ample evidence that the general internal structural pattern of nodules is unique in several regions, and correlation of structure with
Fig. 6-13. Photomacrograph. Outer layers of large nodule showing a wide variety of structure. Close examination reveals most of the zones described by Foster (1970). Columnar, massive, and laminated zones are especially prominent. Relatively low reflectivity of columnar zone across centre of photograph, as compared to the thick zone below, is probably due to the presence of considerable amounts of dispersed clay. Even gray at top is synthetic resin in which nodule is imbedded. Photograph courtesy of A. R. Foster. Nodule DH 7-2A, North Pacific Ocean, depth 3,660 m.

geography or bottom topography may eventually be established. For example, very thin broad shells of clay-poor oxides seem to be typical of Blake Plateau nodules in the Atlantic Ocean, while crenulated oxide shells with appreciable clay are typical of Carlsberg Ridge nodules in the Indian Ocean.

The practicability or desirability of using Foster's terminology or a similar one is debatable, particularly when the internal features of nodules are examined at high magnification. Although "massive zone" logically describes a relatively thick continuous layer of todorokite and birnessite, it would not be a reasonable term for the thin seams and irregular patches of these
minerals found in masses of colloform amorphous oxides. This sort of situation is not unusual in geology, however, and an analogy can be drawn with nomenclature problems with sedimentary rocks as an example. The terms sandstone, shale, and limestone are widely used to convey certain textural and mineralogical attributes, and they permit a sort of shorthand description of common rocks. Their wide usage, however, does not prevent the geologist from using more restrictive terms when describing features of special interest, like sandy lenses, shaly partings, and calcite veinlets. Clearly, there are definite advantages in the use of special terms if they are widely accepted. Whatever terms are developed for nodule materials, and there is already a good assortment in the literature, it is strongly urged that they be as truly descriptive as possible and not be based upon genetic interpretations.

In addition to the features already described, nodule growth also results in the development of open spaces, but these have so far received little attention in the literature. Recently, attention was called to the general nature and significance of pores and fractures which are associated with much oxide material (Sorem and Foster, 1967; Sorem, 1973). Pore spaces are commonly very irregular openings interstitial to oxide structures. They are extremely abundant and range from megascopic to sizes smaller than 100 Å. Fractures, which are both parallel to and transverse to the structure of the oxides, are less abundant and generally larger scale features than the pores. In many nodules, pores and fractures are wholly or partially filled with clay or oxides similar to those of the growth shells (Fig. 6-14). In Blake Plateau nodules, manganocalcite occupies some fractures. Fracture-filling minerals are properly called veinlets and clearly indicate late deposition within an existing nodule.

CHEMICAL COMPOSITION

General

Although the general chemical composition of marine manganese nodules has been known for many years, interest has recently been increasing in systematic sampling and analysis. Mero (1962, 1965a) published the first extensive compilation of analyses, which he used to delineate several ocean floor regions on the basis of major metal content of nodules. The areas rich in copper, nickel, cobalt, and manganese which Mero outlined in the Pacific Ocean have since been sampled extensively by both scientific groups and mining companies. Recent compilations of the analytical data now available (e.g., Frazer and Arrhenius, 1972; Horn et al., 1973a) provide additional details of the geographic variation of nodule composition and generally support Mero's original conclusions. A strong economic interest in the recent research is indicated by the fact that most of the analyses published since
Mero’s work have given only the content of the major metals, whereas Mero presented essentially complete analyses. From the scientific point of view, it seems unfortunate that so few complete analyses are available.

Intra-nodule variations

Most nodule analyses published to date represent single whole nodules or a group of nodules from the same dredge haul. The results are useful for many purposes, both economic and scientific, but they camouflage the fact that most nodules are no more homogeneous chemically than they are...
texturally or mineralogically. Burns and Fuerstenau (1966) were perhaps the first to demonstrate that chemical variations on a microscopic scale exist in nodules, and their conclusions have been supported and amplified by later work (e.g., Cronan and Tooms, 1968; Friedrich et al., 1969; Foster, 1970; Raab, 1972; Sorem and Foster, 1972a; Dunham and Glasby, 1974; McKenzie, 1975). While others used non-destructive probe analysis methods and emphasized major element concentrations, Raab excavated small samples from selected layers of sawn nodules and analyzed them for as many as 12 elements by atomic absorption methods. Later, Piper (1972) and Rancitelli and Perkins (1973) also used small samples from parts of nodules for neutron activation analysis. All of the research cited showed that variations in composition within a single nodule are commonly great, far exceeding the variations in average composition of nodules from different bottom localities in the Pacific basin.

In spite of the fact that intra-nodule chemical variations are now well-documented, there is as yet no agreement on the general pattern of elemental distribution and associations, if any, and the cause of the variations. Certain relationships among concentrations of the major metals are found repeatedly, however, and these are now considered typical of nodules by many investigators. In summary, it can be said that iron and manganese are the most abundant metals, and concentration of each varies from place to place inversely with respect to the other, although in some materials they are present in about equal concentrations. In addition, there is a strong sympathetic variation of copper and nickel with manganese content and a definite antithetic relationship between iron and the concentration of copper and nickel, as described earlier by Arrhenius (1963). Burns and Fuerstenau recognized the same variations, and they also suggested a positive correlation between iron and concentrations of cobalt, titanium, and calcium. This correlation is still the subject of study and debate and must be considered uncertain. Most recently, Friedrich et al. (1973) have shown data which in general support the covariance of iron and cobalt within Pacific nodules, but exceptions are noted. Analysis of much smaller samples will probably be needed to establish the true pattern, if one exists.

Relation to mineralogy

It is one thing to establish the fact that certain chemical associations are characteristic of manganese nodules, and it is another thing to explain them. Although there are still gaps in our knowledge, several lines of evidence indicate that chemical variations within nodules are directly related to mineralogical variations. This would come as no surprise to petrologists, for this is the general case in most rocks. The chief reason that it has taken so long to establish the same idea in manganese nodule research lies in the underdeveloped state of nodule mineralogy and petrography.
Suggestions relating chemical composition to mineralogy in nodules have appeared sporadically in the literature for at least 15 years. The first convincing evidence was presented by Burns and Fuerstenau (1966, p. 901), who showed probe analyses relating high manganese, copper, and nickel content to "7-Å manganite", and suggested "isomorphic substitution" as a cause for this relationship. Barnes (1967a), also choosing to use Buser's terminology, concluded that nodules richer in "manganites" contain higher concentrations of nickel and copper than those containing only "δ MnO₂", but he also admitted to serious difficulty in estimating mineral proportions. Cronan (1972c), evidently using similar methods to establish mineral proportions in bulk samples, concluded that todorokite-rich nodules contained greater concentrations of copper and nickel than those rich in birnessite. He proposed that nickel and copper substitute for Mn²⁺ in todorokite and, further, that cobalt and lead substitute for either Mn⁴⁺ in birnessite or Fe³⁺ in FeOOH. He also noted a strong covariance of cobalt and lead. Since none of these investigators except Burns and Fuerstenau analyzed pure mineral samples of todorokite or birnessite but, rather, bulk samples which included unknown proportions of amorphous oxide material, the experimental results must be considered somewhat less than conclusive. The mineralogical identifications may also be open to questions, since evidently diffractometer charts were used and represent samples which were probably mixtures and may have suffered deleterious effects on mineral structure during grinding.

In any case, several investigators have recently attempted to improve the situation by extending the work of Burns and Fuerstenau by probe analysis of microscopic areas of known mineralogy (Carr, 1970; Foster, 1970; Sorem and Foster, 1972c). This work is especially valuable where analyzed material is also characterized optically and the relationships and proportions of the various minerals are known. To obtain the analytical data necessary for individual minerals, an electron probe microanalyzer with a 1-μ beam is essential, and in some instances greater resolution, such as that claimed for new SEM analyzers (100 Å), would be an advantage.

As an example of the capabilities of the electron microprobe analyzer, consider the small nodular feature shown in Fig. 6-15. This body was found in a fracture during a routine optical microscope examination of a polished section prepared from a Blake Plateau nodule. Obviously the mass is heterogeneous, and physical sampling for conventional analysis is impossible. An analysis of each component is desirable, for the relationships visible at high magnification indicate that alternating thin layers of crystalline material (todorokite and birnessite) and amorphous oxides developed by growth about a tiny nucleus. Analytical traverses with an ARL microprobe across the layering reveal that variations in composition are clearly related to the minerals present (Fig. 6-16). The crystalline material is rich in Mn, Cu, Ni, and K, as compared to the amorphous layers, which are rich in iron. The
Fig. 6-15. Photomicrograph. The complex nature of internal nodule features is well illustrated by this cross-section through a micronodule-like body found within a nodule fracture. An electron microprobe traverse was run perpendicular to the thin concentric layers of crystalline and amorphous material in order to determine element distribution (Fig. 6-16). Crystalline layers are light gray in colour with a mottled appearance whereas amorphous layers are more uniform light to dark gray. Nodule BP-1, Blake Plateau, Atlantic Ocean, depth 730 m.
Fig. 6-16. Results of electron microprobe analysis of nodule layers. Variations in metal content along line \( A-A' \) of the nodular structure illustrated in Fig. 6-15. Metal variations can be correlated with optical properties by use of the photomicrograph at the top of the chart. Note that the crystalline layers are rich in Mn, Cu, Ni, and K as compared to the amorphous layers. This may suggest that Cu and Ni were incorporated into the crystal lattices by ionic substitution during nodule growth. Nodule BP–1.
value of the photomicrograph of the analyzed material is obvious. Without the optical data, it would be impossible to recognize the mineralogical units in the specimen. A back-scattered electron probe photograph cannot serve the same purpose, although it is a convenient way of recording the major structures analyzed.

In specimens where chemical variations on a larger scale are of interest, more rapid analyses for major metals can be made with the X-ray macroprobe (Fig. 6-17). Especially when the results are accompanied by a photograph of the section analyzed, much can be learned of the general distribution of major elements in the whole nodule structure. Note that even with the much coarser resolution of the macroprobe (spot size $250 \times 450 \mu m$) elemental and mineralogical relationships are clearly revealed. From this type of macro-analysis it has been learned that manganese-rich and iron-rich alternations are common not only in stacks of microscopic layers but also on a larger scale (Sorem and Foster, 1972a). It therefore appears that the so-called gross-layering in many nodules is not simply a reflection of textural features but represents chemical variations as well. Whether the large and small variations can be correlated from one nodule to the next is not yet known, but it is expected that nodules with similar textural zone sequences will show similar major chemical zonation.

**NODULE CORES OR NUCLEI**

It has often been reported that nodules commonly have a core or central zone which is in general different from the outer parts. This nucleus or core may be of igneous, sedimentary, or metamorphic rock, or it may be a fossil fragment or even a man-made object. Mero (1962, p. 750) concluded that the “... chemical nature of the nucleus does not seem to affect the deposition of manganese or the composition of the manganese and iron phases of the nodule.” This opinion still seems to prevail, although there seems to be little doubt that nuclei of different kinds can affect the accumulation rate of oxide material. The extreme example of rapid growth is accretion about iron bolts, brass shell fragments, and sparkplugs, all of which have been reported in recent years.

It has long been assumed that nodule growth may begin on any relatively large or angular object on the ocean floor, and this is supported by the examination of many nodules from a wide variety of localities. In some areas certain types of core or nucleus seem to predominate over others. For example, nodules from the east-central Pacific Ocean commonly have a fragment of an older nodule as a nucleus, nodules from the Drake Passage have rock pebble nuclei, and nodules from the Carlsberg Ridge region of the Indian Ocean are often found to have a core of altered igneous rock. Local bottom topography, relief, geology, and currents, among other things, also
Fig. 6-17. Results of X-ray macroprobe analysis across whole nodule section.
A. Photomacrograph. Nodule shows well-developed layering in crustal zone but relatively
massive core. Analysis of nodule material along line C-C' was obtained by traversing
across stationary X-ray beam. A path about 450 μ wide was irradiated. Nodule BR-1-1,
Bermuda Rise, Atlantic Ocean, depth 5,390 m.
B. Variations in metal content along line C-C'. Portion of nodule is shown at bottom to
scale. Note traverse relationship of Fe and Mn, and generally sympathetic variation of Mn,
Cu, and Ni. By projecting peaks vertically downward, it is found that manganese content
is greatest where reflectivity is greatest. Highly reflective material also contains
appreciable iron, but highest iron content is found in material of low reflectivity (medium
gray). Nearly all oxide material in this nodule is amorphous.
seem to control the nature of the nucleus, however, and it is not surprising that a variety of types of nuclei are often found within a small area.

The relationship between the encrusting oxides and the nucleus in manganese nodules is of special interest, especially from the point of view of nodule genesis. In particular, close examination of the contact between the two may reveal evidence that basalt, palagonite, or other rocks supply some of the iron and manganese for crust formation. This might be expected in view of the work of Park (1946) and Krauskopf (1957) on spilitic rocks. Burns and Brown (1972) have proposed that the close study of nucleus-crust contacts may lead to a better understanding of the mechanics of crust formation, and Morgenstein (1973a) described a dating method ("hydration-rind") which involves determining the rate of crust accretion by a study of palagonite nuclei in nodules. As yet, however, there is no compelling published evidence that the relationship between nodule and nucleus has any more than very local importance. In polished sections, some nodules show veinlets of oxide material which cut both the oxide crust and the nucleus. Especially where the nucleus is rock, the only explanation for such a relationship seems to be migration of iron and manganese from the crust inward during diagenesis.

From the economic point of view, it is clear that rock nuclei decrease the value of nodules and must be considered waste material. It is also possible that nuclei consisting of old nodule fragments may, at least in some areas, have a different average metal content than the outer portions, and some sort of separation may be desirable before mining or extraction of metals. To date, however, there are apparently few data available on this problem.

DISCUSSION

Significant nodule features

We have tried to emphasize the conviction that microscopic features of manganese nodules are complex and deserve detailed study. All features of nodules are significant, however, if they provide an insight into problems of nodule genesis or economic use of nodules. The chief danger that exists if we do not study the fine structure is that we may try to interpret associations found in bulk samples or large units as if they were products of a single reaction or environment, whereas a sample a few grams in weight may represent a million years of the earth's history. If we assume an average rate of accretion of 10 mm/million years, for example, even a layer or shell 1 μ thick may record seafloor reactions over a period of 100 years. Unfortunately, chemical analyses are rarely reported for pure samples of shells even ten times that thickness.
If the fine details of nodule structure are to be used to understand nodule growth, however, it is clear that we must distinguish primary features from those formed later during diagenesis. It appears fairly certain that the gross layering, and much of the textural detail visible at low magnification in the layers, reflects growth conditions in the past, for many of these textures found in the older interior shells are very similar to those present in the crustal zone. In some nodules old shells have unique textures, however, and their origin is problematical. Some changes clearly do occur following accretion, as shown by cracks, veinlets, and replacement features. The generally high porosity of nodules would indeed be expected to promote secondary changes, but the true extent of diagenetic alteration is difficult to estimate. It seems safe to assume that most nodules have experienced changes to some extent in texture, chemical composition, and mineralogy, however, but not in overall structure.

Dynamic hypothesis of nodule origin

A satisfactory hypothesis of nodule origin must account for all significant nodule characteristics, large or small, primary or secondary. We must look at the physical, chemical, and mineralogical features of nodules as the end products of deep-sea processes and then try to visualize appropriate processes operating on a geologic time scale. The following suggestions attempt to outline some major concepts to consider in the development of such a genetic hypothesis, with the expectation that revisions will be made as new data on nodules and the marine environment become available.

The source of the chief metals is a major problem, since Fe, Mn, Cu, and Ni occur in very low concentrations in sea water. Various authors have appealed to sea water as a source, however, as well as substrate pore waters and igneous rocks and emanations on the sea floor, using chiefly chemical data for evidence. Agreement has not been reached, and one wonders, therefore, if there is any evidence in nodules that has so far been overlooked which might help clarify the situation. We suggest that the nature and distribution of very fine-grained detritus in nodules should be given closer attention; the genetic significance of this material has not been fully explored as yet.

Minute glass shards and mineral fragments have been reported dispersed in nodules in the past, but it is the unusual concentrations of these particles which may be of special interest. It seems reasonable to believe that these particles rain down slowly but continuously on the sea floor as a result of the settling of windborne dust, but how does this explain the origin of unusually rich concentrations of detritus in thin shells at many levels in a nodule? Since the actual relationship is simply an increase in the ratio of detritus to oxides, two possibilities exist; either the rate of infall of detritus increased periodically, or the rate of oxide accretion relative to the rate of
detritus infall decreased from time to time. If the cause is a sporadic increase in the supply of detritus and glass shards and igneous minerals are abundant, then a logical source may be local volcanism (Carr, 1970, pp. 86–87). This explanation may also account for the ubiquitous association of crystalline manganese minerals with the plentiful detritus; igneous sources may at the same time supply solutions rich in manganese, copper, nickel. On the other hand, if the detritus-rich layers indicate periodic abatement of normal oxide accretion, it remains to be explained how at those times the iron oxide deposition is reduced to essentially zero while manganese deposition continues. A solution may be found by a careful study of the iron-rich material which immediately overlies such layers, but no data are presently available to resolve the problem. At present, it appears likely that the iron-rich material is deposited, probably from "normal" ocean bottom water, more or less uniformly with time.

The suggestion has been made in the past that solid state diffusion rather than primary deposition may account for the common layered colloform structures in nodules. The wide occurrence of very sharp textural and chemical boundaries between adjacent layers, among other things, seems to limit this possibility greatly.

In summary, we believe that not only chemical, mineralogical, and structural data on oxide shells are still needed, but that much more must be learned of the detrital particles as well. To dismiss them as "the insoluble fraction" is probably throwing good evidence away. We may speculate, in fact, that our data thus far indicate that many pulsations, both physical and chemical, occur during nodule growth. The scale ranges from that of the gross layers to that of micron-thick layers in many places. The key to understanding the cause of these pulsations may lie in examining the sequence of layers in many nodules from the same locality, as proposed by Foster (1970). If chemical as well as physical correlations can be found, variations in the general environment may well be indicated. Absence of a correlation would suggest, on the other hand, that other factors, perhaps very local in nature, cause the variations in question in nodule layers.

With this tentative picture of long-term deposition, we must consider the problem of the mechanism of deposition. Both inorganic and organic processes have been proposed in the past, but there are few real data. Many investigators who have touched on the problem have suggested colloidal deposition of one kind or another. We wish to emphasize that there is evidence in nodules that colloidal deposition and direct crystallization both probably occur. Iron-rich shells are essentially non-crystalline, even in the inner recesses of nodules, and the sub-microscopic textures revealed by the SEM suggest deposition by flocculation, presumably of colloidal particles. Botryoidal aggregates are common. The manganese-rich shells are crystalline, however, even on the modern exterior of some nodules, and it appears that todorokite and birnessite form largely by ionic crystallization from solution.
In protected cavities, relatively large euhedral crystals are formed, but in general crystals are sub-microscopic. It is possible that associated glass shards or minor elements catalyzed crystallization, but as yet this is pure speculation.

Rate of deposition cannot be judged quantitatively from nodule features, but as better dating methods are applied to small samples from well-documented nodule layers (so that periods of non-deposition can be taken into account), a relationship between rate of deposition and textures may be established. To judge from the textures in nodules and observations of the outer surface, it may be speculated that the familiar delicate botryoidal surface of many nodules represents very slow deposition. Where this is seen as columnar structure in section, the interlamination of oxides and clay seams suggests that there may have been some sort of cyclic pattern in the primary deposition. One might also propose, however, that the clay seams represent periodic exclusion of impurities by gel-like oxides soon after accretion. It seems likely that the dense and less irregular shells rich in manganese, in contrast, may represent short periods of relatively rapid deposition.

Space is too limited to try to account for other common events in nodule history, such as nodule diagenesis, movement, growth in the substrate, and causes of regional geographic variations, but all evidence points the same general way. We must consider nodule growth as a dynamic process, constantly changing, even on a small scale, and never really coming to a halt. Even after many shells have accreted, post-accretion adjustment and internal circulation and deposition of oxides continues. Other changes probably occur upon aging. For example, manganese-rich laminations within iron-rich shells, here interpreted as primary, may actually be in part due to filling of shrinkage cracks.

In spite of the many uncertainties which remain, we believe that it must be concluded that nodules several centimetres in size record the evidence of variations in sea-bottom environment over periods of millions of years. Furthermore, each nodule has probably been responsive to minor influences above, below, and around it, just as it has to major environmental changes.

In summary, nodules reveal a very complex growth history over a long period of time, and we call upon interested investigators to view their data in this context. Ancient environments are probably the key to understanding the general problem of nodule origin, and we must learn about them largely by the methods of historical geology and perhaps, palaeogeochemistry. Modern environments are important but may be of real significance in understanding only the crustal zone of most nodules.