Marine Manganese Nodules:
Importance of Structural Analysis

RONALD K. SOREM and
ALLAN R. FOSTER,
U.S.A.

ABSTRACT

Manganese nodules collected off Baja California have layers (zones) which are texturally and compositionally distinct. Massive and mottled zones consist mostly of cryptocrystalline todorokite and birnessite containing relatively high concentrations of Mn, Ni and Cu. Compact, columnar and laminated zones consist mostly of more iron-rich opaque amorphous material. Within these two groups the individual zones can be distinguished in part by their clay content. These results indicate that systematic research on nodule chemistry, mineralogy, growth rates and beneficiation should include careful analysis of individual layers within the nodules.

INTRODUCTION

M A R I N E  M A N G A N E S E  N O D U L E S form by long-continued accretion, but growth is not uniform in rate or in character, even within a single nodule. The result is an internal structure that is complex and heterogeneous texturally, mineralogically and chemically. If these characteristics are not taken into account when a nodule is sampled for any kind of quantitative work, misleading interpretations of research data are likely. A review of recent nodule literature reveals little mention of this problem, and one must conclude that most investigators fail to observe or understand the complexities of nodule structure.

This paper calls attention to the non-homogeneous nature of manganese nodules by illustrating many of the common internal features visible in polished sections and by presenting general mineralogical and chemical data. It is hoped that some of the dangers inherent in the use of random samples will thus be made clear and that other investigators will be encouraged to incorporate textural studies into their research programs.

In this sort of study, sections of whole nodules are used so that relationships over wide areas can be observed, thereby permitting the growth history of the nodule to be better understood. All of the photographs shown were made with vertical illumination, so that opaque materials are bright and non-opaque materials appear dark. This procedure emphasizes the features of the oxide compounds, which are abundant in most nodules and are of great interest from both the scientific and economic point of view.

The chemical data presented below are based chiefly upon X-ray fluorescence analyses made with a macroprobe attachment. A. C. Dunham provided several microprobe determinations. Because of present instrumental limitations, numerical values can be provided only for Mn, Fe, Cu, and Ni at this time. The zone compo-

Authors' addresses are given at the back of this book.
sitions reported are believed to be representative of nodules in the regions off Baja California, but there are no corresponding data for nodules from other localities. Analytical work on nodule zones in samples from other areas is in progress.

GROSS LAYERING IN NODULES

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.

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 and 4).
Other common patterns of layering include crenulations, pinchouts, 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.

FIGURE 3 — Section of angular nodule, eastern Pacific Ocean, Lat. 21°27'N, Long. 114°07'W. Arcuate core, a segment of an older nodule, has determined nodule shape. Note sharp truncation of core layering at ends of core and conformable contact with younger layers above. Hiatus at conformable contact is unknown. Textural facies change as younger layers pass around ends of section, probably reflecting differences in microenvironment on sea bottom during growth. The nodule rested on the sea bottom in position shown, partially imbedded in bottom sediment. Secondary crack fillings (white, gray) cut core layers transversely.
INTRALAYER TEXTURAL FEATURES

Individual laminae vary in color, reflectivity, structural pattern, composition and thickness. Most laminae are from 0.0001 mm to 0.1 mm thick. They may be crenulated or fairly regular and concentric about the core, and they may or may not conform to gross layering above and below. Boundaries between laminae may be either sharp or diffuse, depending on their composition and texture.

Most laminae are composed of opaque X-ray amorphous material, but an appreciable number are composed of intimate intergrowths of cryptocrystalline tobermorite and birnessite (Carr, 1970). Inclusions and partings of clay and dust-size fragments of quartz and glass occur in both types of laminae. Clastic hematite and magnetite grains occur primarily in the crystalline laminae.

Optical properties of laminae in vertical light are summarized in Table 1.

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

FIGURE 4 — Section of conglomeratic nodule, Drake Passage, near Lat. 58°S, Long. 59°W. Oxide layers enclose many small clastic grains, indicating continual oxide accumulation and intermittent clastic sedimentation. External shape reflects angular shape of large rock fragments. Prepared and photographed by R. H. Fewkes. Nodules supplied by the late D. F. Hewett.

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FIGURE 5 — Textural zones and complex structure in nodule from eastern Pacific Ocean, Lat. 21°40'N, Long. 114°09'W. Core is an older nodule fragment, with layering truncated at (a). Zone b (massive zone) pinches out laterally between adjacent zones. Zone c (mottled zone) grades laterally to a thinner facies which is a texturally and mineralogically different zone (d, compact zone) on the opposite site of the nodule.

TABLE 1 — Optical Properties of Laminae — Vertical Light

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Color</th>
<th>Reflectivity</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Todorokite (Mn,Ca)MnO_2·2H_2O b</td>
<td>White to light gray (bireflectant)</td>
<td>25 to 20</td>
<td>Randomly oriented micro-crystal-line inter-growths, appearing fibrous in places. Takes a fair polish. Anisotropic, colors bluish gray to bluish black. Talmage hardness B.</td>
</tr>
<tr>
<td>Birnessite (Na,Ca)MnO_4·2.8H_2O c</td>
<td>White to gray</td>
<td>25 to 10</td>
<td>Massive, fine-grained, amorphous. Color and reflectivity vary with composition. Sensibly isotropic. White takes a good polish; Talmage hardness B+. Gray polishes with some difficulty; Talmage hardness B.</td>
</tr>
</tbody>
</table>

*Estimated reflectivity in per cent.

bAfter Larsen, 1962.

cAfter Brown, Pabst and Sawyer, 1971.
FIGURE 6 — Massive and mottled growth zones in part of a Pacific Ocean nodule, Lat. 22°N, Long. 113°30'W. The main dense layer (white, gray) is a massive zone, showing typical diffuse lamination and transverse cracks. The laminations consist of intimately intergrown cryptocrystalline todorokite and birnessite. The mottled zone above this layer consists of todorokite and birnessite (white), opaque amorphous material (white to gray) and clay (dark gray). Below the massive zone are poorly defined mottled and laminated layers.

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 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 differs in that it contains approximately 15% clay and amorphous material in which the laminae shows 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 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 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). 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.

SUMMARY

Polished sections of nodules from several geographic regions shows that non-uniform internal structure is common. In addition, analytical work reveals complex mineral relationships and large differences in chemical composition from one part of a nodule to another. Obviously, a detailed study of only one part of a nodule is not likely to reveal representative data on the nodule as a whole. Similarly, analyses of a crushed whole nodule will tell nothing of the complex variations which may have existed within the original specimen. Clearly, any attempt to understand the chemical and mineralogical composition or the growth history and growth rate of most nodules must be based upon carefully selected samples.

Specifically, where anything but bulk analytical results are desired:
(a) samples for chemical analyses should be taken carefully from discrete zones or layers of known extent;
FIGURE 8 — Extensive columnar zone in outer part of spheroidal nodule, Carlsberg Ridge region, Indian Ocean. Note delicately branching radial columns with internal colloform laminae of opaque amorphous material. Concentric gross layering is defined by slight differences in reflectivity. Dark areas are clay. Compare whole nodule photograph, Figure 1.

(b) samples for mineralogical analyses should be taken from optically homogeneous and distinct sites, with optical properties and extent recorded;
(c) samples for age dating by radiometric methods should be taken from layers which surely represent continuous deposition, avoiding unconformities of unknown hiatus at all cost;
(d) beneficiation tests should be based at least in part on the physical and chemical properties of separate zones, and the feasibility of mechanical separation of zones should be explored with a view toward selective processing.

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R. McQuillan
United Kingdom

ABSTRACT
A brief review of recent years on the sampling methods and the results of the North Sea and the Moray Firth

INTRODUCTION
This account principally involves continental studies engaged by the North Sea. A brief introduction outlines of North Sea (1967, 1968) and Sorgenfrei picture has come from the North Sea area of the Pleistocene. The area has been extensively by government-financed researches and the Institute de Recherche.

The area...