FE-MN OXIDATE CRUSTS IN ONEIDA LAKE, NEW YORK

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Abstract. Saucer-shaped iron-manganese crusts occur adjacent to gravel shoal areas in Oneida Lake in central New York. The crusts usually have a crude concentric banding owing to an alternation of orange, iron-rich layers and black, iron-poor layers. Materials from both types of layers are x-ray amorphous. The Oneida Lake crusts, like most other freshwater "manganese nodules," contain about the same Mn concentration as marine manganese nodules, but are usually higher in Fe and lower in trace metals than their marine equivalents.

Although Fe and Mn may be precipitating directly from the lake water, it is more likely that the oxidate crusts are the result of precipitation of Fe and Mn when reduced sediment pore water comes in contact with well oxygenated bottom waters. Organisms, particularly bacteria, may play a role in the formation of the crusts, but to date no evidence for this has been found. (Key words: Sedimentology; geochemistry; sediment-water interaction; New York State.)

INTRODUCTION

Oneida Lake is a large, shallow eutrophic lake approximately 10 miles (16 km) northeast of Syracuse in Oneida and Oswego Counties in central New York state (Fig. 1). The biology, chemistry, and hydrology of Oneida Lake are well known as a result of an intensive study of the lake by the U.S. Geological Survey in cooperation with the New York State Conservation Department (Greerson and Meyers, 1969).

Shallow water and elongation of the Lake in the direction of prevailing winds keep the lake water well mixed most of the time and prevent thermal stratification during the summer months. Although the Lake does not stratify thermally, Greerson and Meyers (1969) report that dissolved oxygen does stratify at an average depth of about 9 m with maximum oxygen depletion of the bottom waters occurring during periods of peak phytoplankton activity. However, where water depths are less than 9 m (approximately 60% of the Lake area), bottom waters are usually well oxygenated.

The intense blue-green algal blooms during the summer months are a graphic indication that Oneida is a eutrophic lake. Contributions of nutrients from industrial, municipal, and agricultural sources have served only to accelerate the Lake's natural eutrophication. Oneida itself is but a small remnant of a once much more extensive lake, Lake Iroquois, which was impounded between retreating Lake Wisconsin (Port Huron) ice sheets and the Helderberg Escarpment approximately 12,500 years ago (Karrow, Clark and Terasmae, 1961). Lake Iroquois was subsequently drained into the St. Lawrence Valley before the end of the Two Creeks Interstadial (approximately 10,500 years ago) leaving behind numerous undrained depressions in the lake plain which covers much of central New York (Muller, 1965; Karrow et al. 1961). Oneida Lake occupies one of these undrained depressions.

IRON-MANGANESE NODULES

Nodules, or concretions rich in iron and manganese, were first collected on the sea floor during the Challenger Expedition in the 1870's. Since then,
they have been the subject of numerous investigations dealing mainly with their origin and geochemistry. With rapid advancement of marine technology, these nodules are considered potential ores, not only of iron and manganese but also of certain trace and minor elements (especially Co, Ni, and Cu) often concentrated in the nodules (Mero, 1962).

Iron-manganese concentrations from freshwater environments, referred to as nodules, concretions, or oxidate crusts by different authors, have been known to exist for many years, but reports of them are few. They have been reported from several Canadian lakes (Kindle, 1932, 1935, and 1936; Harriss and Troup, 1969), from several English lakes (Gorham and Swaine, 1965), from Fennoscandian lakes and streams (Ljunggren, 1953), from Lake Michigan (Rossman and Callender, 1968), and from Lake Champlain (Hunt and Henson, 1969). The occurrence of iron-manganese concretions in Oneida Lake has been known for a number of years and have been termed “Oneida Lake pancakes” by local residents. However, they were not described in the literature until 1961 (Gillette, 1961). In the spring of 1969, I began a study of the Oneida Lake pancakes using scuba divers in an attempt to determine their distribution on the bottom of the Lake.

Description

Figure 1 shows several shoal areas in Oneida Lake where water depths are less than 14 ft (4.3 m). The shoal areas in the center of the Lake are the result of gravel mounds which rise as much as 40 ft (13 m) above the surrounding lake floor. Adjacent to these shoal areas, the hard sandy lake bottom is strewn with pebbles, cobbles, and boulders of varying lithology from the shoals. Many of these rocks are surrounded at the sediment-water interface by a rim-like crust rich in iron and manganese (Fig. 2). In some areas, almost every rock exposed at the sediment-water interface shows some degree of crust development. Although most of the crusts have rock cores, some do not (Fig. 3). The average diameter of the uncored crusts is about 15 cm with a maximum of at least 60 cm. Regardless of the size or shape of the rock core,

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FIG. 1. Index map of Oneida Lake showing depth of water and locations of preliminary dives (from N. Y. State Conservation Dept., Div. of Conservation Education).
FIG. 2. Photographs and drawings of rock-cored iron-manganese crusts from Oneida Lake.
FIG. 3. Photographs of typical iron-manganese crusts without rock cores from Oneida Lake.
FE-MN OXIDATE CRUSTS

the crusts tend to develop a saucer shape with the convex side upward. Most of the crusts show a coarse concentric banding in both horizontal and vertical sections (Figures 2 and 3). Where well developed, the banding can be seen to be the result of alternations of orange iron-rich layers and black iron-poor layers. These two materials together give an overall brown to black color to the crusts.

The crusts are apparently most abundant adjacent to the shoal areas. In the past when the crusts have been accidently caught in dredges and nets or actually hooked by fishermen, they have been collected in the shoal areas. In fact, one shoal area is appropriately called Pancake Shoal by local residents. For this reason, the preliminary dives were made adjacent to the shoal areas (Fig. 1). Crusts were found on all five dives but they were best developed and most abundant adjacent to Dakin and Shackelton Shoals (Fig. 1).

Concentration ranges for 27 elements from four typical Oneida Lake crusts are given in Table 1. Concentrations of these elements in iron-manganese nodules from other freshwater localities and in marine manganese nodules are provided for comparison. The Oneida crusts resemble other freshwater nodules in that they contain more Fe than Mn, whereas most marine nodules contain more Mn than Fe. In addition, the freshwater nodules do not contain the relatively high concentrations of certain trace metals usually characteristic of marine nodules. This is particularly evident for Co, Cu, and Ni, and to a lesser extent for B, Mo, and V. On the other hand, the concentrations of Ag and Cr are generally higher in the Oneida Lake crusts than in marine nodules.

The mineralogy of the iron and manganese phases in the Oneida crusts is not known. X-ray diffraction patterns of several samples using Ni-filtered Cu Kα radiation and V-filtered Cr Kα radiation failed to reveal peaks due to Fe-Mn crystalline compounds such as todorokite, birnessite, or δMnO₂ reported from some marine nodules (Cronan and Tooms, 1969).

Freshwater nodules have been referred to as concretions, nodules, or oxidate crusts by different authors reflecting, in part, variability in their shapes. The Oneida Lake pancakes resemble very closely the oxidate crusts described by Gorham and Swaine (1965) from the English Lakes, (E. Gorham, personal communication) and the concretions from Canadian lakes illustrated and described by Kindle (1932) and described by Harriss and Troup (1969). I prefer the terminology of Gorham and Swaine because it gives a better verbal picture of their mode of occurrence and physical properties and emphasizes the fact that they only occur under oxidizing conditions. Some of the nodules from Lake Champlain (Hunt and Henson, 1969) resemble the Oneida Lake crusts but most are nodular or subspherical in form (Hunt, personal communication). The nodules in Lake Michigan (Rossman and Callender, 1968) are also mostly spherical. Nodules from Lake Ontario resembling those from Lake Michigan have recently been found (D. S. Cronan, personal communication).

Reports of the discovery of manganese nodules in the freshwater environment are becoming more and more common. Of the few reports in the literature, most have appeared in the last decade. This recent surge undoubtedly reflects the long overdue interest in the freshwater environment. As most reports come to light, I am certain that freshwater iron-manganese nodules will prove to be much more common than presently suspected and may, in some localities, be economically important. Freshwater nodules have much in common with marine nodules but are much more accessible so that lakes, such as Oneida, provide ideal laboratories for the study of manganese nodule formation.
TABLE 1. Elemental composition of freshwater and marine iron-manganese nodules.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oneida Lake</th>
<th>English Lakes</th>
<th>Swedish Lakes</th>
<th>Lake Michigan</th>
<th>Canadian Lakes</th>
<th>Pacific Ocean</th>
<th>San Clemente Basin</th>
<th>Atlantic Ocean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (ppm)</td>
<td>6-10</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>0-6</td>
<td>1.4-5.8</td>
<td></td>
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<tr>
<td>Al (%)</td>
<td>0.7-0.95</td>
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<td></td>
<td></td>
<td>0.8-6.9</td>
<td>70-600</td>
<td>40</td>
<td>50-500</td>
</tr>
<tr>
<td>B (ppm)</td>
<td>&lt;10</td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td>0.02</td>
<td>0.1-0.36</td>
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<tr>
<td>Be (ppm)</td>
<td>0.5-5.8</td>
<td>0.08-0.8</td>
<td>0.01-0.2</td>
<td>50</td>
<td>0.5-4.4</td>
<td>1.4-8.2</td>
<td>n.d.</td>
<td>50-6800</td>
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<tr>
<td>Ca (%)</td>
<td>20-60</td>
<td>20-40</td>
<td>&lt;10-50</td>
<td>133-230</td>
<td>140-23,000</td>
<td>50</td>
<td>10-70</td>
<td>10-30</td>
</tr>
<tr>
<td>Cr (ppm)</td>
<td>6-16</td>
<td>4-12</td>
<td>&lt;10-50</td>
<td>50</td>
<td>10-70</td>
<td>10-30</td>
<td>500</td>
<td>500-2100</td>
</tr>
<tr>
<td>Cu (%)</td>
<td>0.04-0.3</td>
<td>0.1-0.62</td>
<td>&lt;10-50</td>
<td>95-373</td>
<td>160-20,000</td>
<td>200</td>
<td>n.d.</td>
<td>200-1400</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>10-29</td>
<td>10-300</td>
<td>30-8000</td>
<td>200-3600</td>
<td>200-3600</td>
<td>130-500</td>
<td>3100-5400</td>
<td>500-6400</td>
</tr>
<tr>
<td>Ga (ppm)</td>
<td>10</td>
<td>1.25</td>
<td>n.d.</td>
<td>1.5-4.7</td>
<td>1.5-4.7</td>
<td>1.5-4.7</td>
<td>1.5-4.7</td>
<td></td>
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<tr>
<td>K (%)</td>
<td>0.05-0.1</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.3-3.1</td>
<td>0.3-3.1</td>
<td>0.3-3.1</td>
<td>0.3-3.1</td>
<td></td>
</tr>
<tr>
<td>La (ppm)</td>
<td>200</td>
<td>20-60</td>
<td>20-40</td>
<td>0.07-0.73</td>
<td>0.07-0.73</td>
<td>0.07-0.73</td>
<td>n.d.</td>
<td></td>
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<tr>
<td>Mg (%)</td>
<td>0.12-0.17</td>
<td>1.4-13</td>
<td>0.6-3.2</td>
<td>6-16</td>
<td>6-16</td>
<td>6-16</td>
<td>6-16</td>
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<tr>
<td>Mn (%)</td>
<td>13.4-15.4</td>
<td>1.4-13</td>
<td>0.2-17</td>
<td>15.7-35.9</td>
<td>15.7-35.9</td>
<td>15.7-35.9</td>
<td>15.7-35.9</td>
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<tr>
<td>Mo (ppm)</td>
<td>30-50</td>
<td>&lt;10-10</td>
<td>&lt;10-30</td>
<td>100-1500</td>
<td>100-1500</td>
<td>100-1500</td>
<td>100-1500</td>
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</tr>
<tr>
<td>Na (%)</td>
<td>0.1</td>
<td>0.18-1.0</td>
<td>n.d.</td>
<td>1.5-4.7</td>
<td>1.5-4.7</td>
<td>1.5-4.7</td>
<td>1.5-4.7</td>
<td></td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>20-60</td>
<td>10-40</td>
<td>10-50</td>
<td>160-20,000</td>
<td>160-20,000</td>
<td>160-20,000</td>
<td>160-20,000</td>
<td></td>
</tr>
<tr>
<td>P (%)</td>
<td>0.04-0.3</td>
<td>0.1-0.62</td>
<td>&lt;10-50</td>
<td>10-29</td>
<td>10-29</td>
<td>10-29</td>
<td>10-29</td>
<td></td>
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<tr>
<td>Pb (ppm)</td>
<td>5-10</td>
<td>0.1-0.60</td>
<td>n.d.</td>
<td>1.3-20.1</td>
<td>1.3-20.1</td>
<td>1.3-20.1</td>
<td>1.3-20.1</td>
<td></td>
</tr>
<tr>
<td>Sn (ppm)</td>
<td>5-10</td>
<td>0.1-0.60</td>
<td>n.d.</td>
<td>0.03-0.85</td>
<td>0.03-0.85</td>
<td>0.03-0.85</td>
<td>0.03-0.85</td>
<td></td>
</tr>
<tr>
<td>Ti (%)</td>
<td>100-200</td>
<td>2-100</td>
<td>50-100</td>
<td>50-100</td>
<td>50-100</td>
<td>50-100</td>
<td>50-100</td>
<td></td>
</tr>
<tr>
<td>Y (ppm)</td>
<td>&lt;10-25</td>
<td>10-60</td>
<td>50-100</td>
<td>330-450</td>
<td>330-450</td>
<td>330-450</td>
<td>330-450</td>
<td></td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>&lt;100-300</td>
<td>10-150</td>
<td>250-1940</td>
<td>400-800</td>
<td>400-800</td>
<td>400-800</td>
<td>400-800</td>
<td></td>
</tr>
</tbody>
</table>

Sources of data
1 Ranges of four analyses supplied by Kennecott Copper Corp. Research Center; Ag, Al, B, Ba, Be, Ca, Cr, Ga, K, La, Mg, Mo, Na, Si, Sn, Ti, V, Y, Zn, and Zr were determined by semi-quantitative spectrographic analysis; Co, Cu, Fe, Mn, and Ni were determined by atomic absorption.
2 Gorham and Swaine, 1965.
3 Rossmann and Callender, 1968.
4 Harriss and Troup, 1969.
5 Mero, 1962.

Origin of iron and manganese on the ocean floor: A review of the literature.
Origin

The origin of the Oneida Lake crusts is not known. Any theory regarding their origin must explain the following observations: 1) they apparently form only at the sediment-water interface, 2) most develop around a rock core or nucleus, 3) they form under oxidizing conditions, and 4) they are composed of interlaminations of different materials. A comparison of the Oneida crusts with other freshwater and marine occurrences reveals other factors which must be considered in the origin of manganese nodules in general; some of these factors will be discussed briefly below:

Role of organisms. Manganese nodules from both the marine and freshwater environments usually do not contain appreciable amounts of organic material. Gorham and Swaine (1965) found that oxidate crusts from several English lakes contained considerably less organic material than the underlying sediments. Kindle (1932) suggested that algae (especially diatoms), by removing CO₂ from the water, would favor the precipitation of carbonates of iron and manganese. Precipitation of iron and manganese oxides would then form rapidly on the initial carbonate surface. Gillette (1961) noted that the Oneida crusts grossly resembled blue-green algal structures from the Bahamas. He found no remains of algal filaments in the crusts but did find what he thought to be bacterial cells. Zapffe (1931) and Krauskopf (1957) have suggested that bacteria may act as catalysts in initiating the precipitation of iron and manganese. These observations suggest that although the crusts themselves are not organic, organisms, particularly bacteria, may play a role in their formation.

Rate of formation. Both marine and freshwater manganese nodules are characteristically laminated. Harris and Troup (1969) suggested that laminae in iron-manganese concretions from some Canadian lakes may represent annual growth increments. Based on this assumption, they calculated growth rates ranging from 0.1 mm/year to 1.5 mm/year. The average Oneida Lake crust is approximately 15 cm in diameter. Assuming that a crust of this size began to form at the end of the Wisconsin (approximately 10,000 years ago), then the crust would have grown at a minimum average rate of 0.015 mm/yr. In any case, the rate of accretion of freshwater nodules is considerably greater than the average rate of 1.0 mm/1000 yrs postulated by Goldberg and Arrhenius (1958) for the formation of marine manganese nodules. Gorham and Swaine (1965) and Rossmann and Callender (1968) found iron-manganese crusts growing on buoys, further evidence for the rapid rate of formation of freshwater crusts.

Regardless of the rate of formation, it is obvious that manganese nodules can only form where sedimentation is very slow or absent. For example, Gorham and Swaine (1965) found that crusts in English lakes formed only where the normal organic-rich lake muds were thin or absent. The Oneida crusts, as well as concretions from Canadian lakes (Kindle, 1936; Harris and Troup, 1969), are found on hard sand or gravel bottoms where wave action is fairly strong and normal fine-grained lake sediments are absent. In the marine environment, manganese nodules are most abundant in areas of slow pelagic sedimentation (Mero, 1962).

Chemical composition. The faster rate of formation of freshwater nodules may also explain why they usually contain lower concentrations of trace metals than marine nodules (Table 1). Goldberg (1954) indicated that high concentrations of trace metals in marine nodules are most likely due to the ability of hydrated oxides and hydroxides of iron and manganese to absorb ions from solution (a process he termed "scavenging"). Krauskopf (1956) also pointed out the importance of adsorption in the removal of metals from sea water and stated that hydrated manganese dioxide and hydrated ferric oxide were the...
most efficient adsorbers in sea water. According to Goldberg (1954), the efficiency of the scavenging process is a function of the length of time the solid phase is in contact with the solution containing the ions to be adsorbed. As an example of the control of time on adsorption efficiency, Goldberg and Arrhenius (1958) report finding a 5 cm thick iron-manganese crust in the San Clemente Basin around a fragment of a naval gun shell approximately 50 years old; this suggests a rate of formation on the order of 1 mm/yr. This crust contained considerably lower concentrations of trace metals than most marine nodules (Table 1), and also contained a much higher content of iron than manganese.

Several investigators (e.g., Gorham and Swaine, 1965; Goldberg and Arrhenius, 1958) have suggested that ferric oxides catalyze the formation of manganese oxides and hydroxides and that the amount of manganese precipitated therefore is a function of the length of time of exposure. This would explain the high Fe:Mn ratio for rapidly formed crusts (e.g., freshwater nodules and the San Clemente nodule) and the low Fe:Mn ratio for slower formed crusts (e.g., most marine nodules). Krauskopf (1957) points out that iron oxides and hydroxides are less soluble than those of manganese and therefore would precipitate from solution before manganese. Earlier precipitates would thus tend to be enriched in Fe; the actual oxidized product formed would be largely dependent on Eh and pH conditions.

Source of iron and manganese. It is usually assumed that the iron and manganese in both freshwater and marine manganese nodules were precipitated from the overlying waters. However, sediment pore water is potentially a more important source and therefore study of the exchange of ions across the sediment-water interface is of great importance in attempting to determine the origin of iron and manganese concentrations. In most lakes the zero redox potential line falls at or above the sediment-water interface, i.e., the sediments are reducing. However, in some lakes the upper few centimeters of sediment are oxidized forming an oxidized microzone (Mortimer, 1941-42; Gorham, 1958). Sediments in the oxidized microzone characteristically contain higher concentrations of iron and manganese (by as much as an order of magnitude) than the reduced sediments, and are usually orange in color due to the presence of ferric hydroxide (Mortimer, 1941-42; Gorham, 1958; Gorham and Swaine, 1965). Mortimer (1941-42) postulated that the oxidation of the sediment was the result of molecular diffusion of oxygen into the sediment. However, Gorham (1958) indicated that the depth of oxidation is controlled not by oxygen diffusion but by turbulent displacement of the upper few centimeters of sediment up into oxidized bottom waters of the lake. Thus, sediment pore water containing ferric and manganese ions is oxidized near the sediment-water interface precipitating the less soluble oxides and hydroxides of iron and manganese by the mechanism suggested by Krauskopf (1957). Rossmann and Callender (1968) found that Mn in interstitial water increased below the sediment-water interface at most stations in Lake Michigan where they found iron-manganese nodules. Upward migration of manganese through the sediment column has also been suggested by Delfino and Lee (1968) in their model for the geochemistry of manganese in Lake Mendota. The fact that the Oneida Lake oxidate crusts occur right at the sediment-water interface suggests that oxidation of reduced sediment pore water may be important in their formation. However, additional factors not operating in the formation of the oxidized microzone might also be needed to explain why the crusts tend to form about a nucleus and attain iron and manganese concentrations about an order of magnitude higher than normally found even in oxidized sediments (Gorham and Swaine, 1965).
FE-MN OXIDATE CRUSTS

Water chemistry and lake productivity. The chemical composition of lake water and the productivity of the lake do not appear to be controlling factors for the formation of freshwater iron-manganese nodules. They have been found in hardwater and softwater lakes, in oligotrophic and eutrophic lakes. However, water chemistry may be a factor in controlling variations in trace element concentrations in iron-manganese precipitates from different lakes (as suggested by Harriss and Troup, 1969), and perhaps even the amount of iron and manganese precipitated.

Geographic distribution. Harriss and Troup (1969) suggested that any theory regarding the origin of freshwater iron-manganese concretions should take into account the fact that they only occur in temperature and subarctic latitudes. Krauskopf (1957, p. 76) states "It is perhaps not by accident (D. F. Hewett, personal communication) that bog-ores of manganese, both in North America and in Scandinavia, are concentrated in areas underlain by the latest Pleistocene till." He was suggesting that glacial till would be more permeable and therefore solution of iron and manganese would proceed more rapidly. The restriction of freshwater iron-manganese deposits to north temperature latitudes may be fortuitous or it may indeed be a necessary condition for their formation.

ACKNOWLEDGMENTS

I would like to thank Kennecott Exploration, Inc. for providing the elemental analyses of four Oneida Lake crusts which appear in Table 1.

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