Reports

Deep-Sea Iron Deposit from the South Pacific

Abstract. *Along with specimens of manganese oxides and basalt, rocks containing more than 30 percent iron by weight and consisting mainly of poorly crystallized goethite have been dredged from the flanks of a seamount located on the East Pacific Rise. The Fe-Mn ratio varies widely among the various oxide rocks deposited at this locality and at another seamount in the same area. The deposit was probably formed by fractional precipitation of iron and manganese which had been introduced locally into the bottom water by hydrothermal solutions of volcanic origin, and by leaching from deep-sea basaltic lavas.*

Iron deposits have never been reported in the deep sea, with the exception of a recent discovery at the bottom of the Red Sea, where iron oxides are associated with hot brines probably discharged through the sea floor (*1*). It is therefore of interest to describe a rock assemblage recovered by the research vessel *Argo* of the Scripps Institution of Oceanography from the flanks of a seamount located in the South Pacific (10°38′S, 109°36′W, station Amph D2), close to the crest of the East Pacific Rise.

This seamount rises from a softly rolling bottom approximately 3000 m below sea level; at the shallowest point at which the vessel crossed the mount the depth was 1790 m. A chain dredge was operated on the flank of the mount between depths of 2130 and 1790 m, and several kilograms of material were recovered.

More than 80 percent of the dredge haul consisted of red-yellow fragments of a friable and powdery rock, some as much as 30 cm in width. Chemical analyses of three such fragments by x-ray and optical spectroscopy (*2*) showed the iron content of this rock to be over 30 percent by weight (Table 1). The mineralogy of the rock was studied by x-ray powder diffraction using FeKα radiation. The pattern of the untreated material revealed only a very weak and broad reflection in a region between 4.3 and 3.8 Å; this was probably due to the (110) planes of a poorly crystalline goethite. After keeping the sample in air at 500°C for ten hours, well-developed reflections of αFe_2O_3 (hematite) appeared, confirming the supposition that cryptocrystalline $\alpha FeO(OH)$ (goethite) is the main component of the rock. The silicon content of these rocks (Table 1) suggests that some disordered silicates, and possibly some amorphous silica, are also present even though such phases are not clearly detectable by x-ray diffraction.

A few pebbles from the dredge haul consisted of black porous manganese oxides (Table 1). One small fragment of relatively fresh basalt was also recovered. Part of the surface of the fragment was covered by a crust of maganese oxides less than 1 mm thick (Table 1). The basalt has porphyritic texture with phenocrysts of labradorite and olivine in a groundmass of plagioclase laths, iddingsite-serpentine, and glass (Table 1).

Any hypothesis on the origin of the iron deposit of station Amph D2 should explain also the occurrence, at the same location, of precipitates rich in iron and manganese but with different Fe-Mn ratios (see Table 1). A purely sedimentary origin implies either the transport of particulate iron from land masses and its slow deposition at the seamount, or the slow chemical precipitation of iron from sea water. The first alternative is very unlikely. No close land masses are present as possible sources of particulate iron; if long-distance transport from continents were responsible, the iron hydroxide particles would be mixed with and diluted by fine terrigenous clays. Terrigenous minerals are exceedingly scarce in this region where local volcanics and their alteration products as well as carbonates, are the main components of the sea floor (*3*).

Slow chemical precipitation from normal seawater is also an unlikely explanation of our findings. Dissolved iron species introduced into the ocean are preferentially oxidized and precipitated close to the continent; the Fe-Mn ratio of deep-sea hydrogenous precipitates decreases away from land masses, and is close to one in pelagic areas. Such a mechanism, therefore, can barely account for deep-sea rocks abundant in iron, and even less for the processes which appear to have locally separated iron from manganese.

The extensive local fractionation of the ferride elements (Table 1) suggests that, at least in part, they were

Table 1. Spectrochemical analyses of samples from dredge haul Amph D2. Three different fragments of red ferruginous rock are designated by a_1, a_2, and a_3; b, black porous manganese oxide rock; c, black manganese oxide crust on basalt; d, olivine basalt fragment. Percent H_2O indicates the loss in weight of the moisture-free sample after 24 hours at 600°C.

Fractions	Amounts															Ratios	
	Oxides					Elements											
	SiO_2 (%)	Al_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Fe (%)	Mn (%)	Ni (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ba (ppm)	B (ppm)	Sr (ppm)	H_2O (%)	Fe/ Mn	Ni/ Co
a_1	17.6	1.0	2.6	1.5	0.39	32.5	1.94	400	35	26	74	115	290	470	13.6	16.7	2.81
a_2	13.9	<1	2.3	0.85	0.45	28.8	2.43	460	120	20	120	100	210	800		11.8	15.5
a_3	12.4	1.0	2.7	0.80	0.38	31.1	0.58	90	32	20	60	100	330	480		51.9	0.47
b	8.1	0.4	2.5	5.9	1.29	5.5	38.72	4500	290	210	>500	1700	85	420		0.14	1.3
c	12.4	3.1	5.2	0.40	3.8	17.8	19.67	3200	6800	87	220	670	230	940		0.9	11.4
d	49.7	15.8	12.3	9.0	0.16	7.7	0.18	83	63	290	140	100	57	145		42.7	3.8

Table 2. Spectrochemical analyses and Fe-Mn ratios in three samples from dredge haul Amph D1. Sample A is black iron-manganese oxide crust on surface of a basalt fragment; sample B is hyaloclastic rock with ferruginous matrix; sample C is hyaloclastic rock with black manganese oxide matrix.

Constituents	Percentage of concentration by weight		
	A	B	C
SiO_2	25.8	38.8	40.0
Al_2O_3	6.5	11.6	10.2
CaO	6.35	11.6	10.2
MgO	5.0	7.0	10.0
K_2O	0.65	0.43	0.16
TiO_2	1.47	1.2	1.0
Fe	13.0	11.7	5.7
Mn	5.59	1.86	7.12
Fe-Mn	2.3	6.3	0.8

supplied by a local source. Volcanic activity is an obvious suggestion for such a source, because the seamount from which the rocks in question were obtained was a submarine volcano, as proved by the presence of basalt.

Krauskopf (*4*) noticed that basalts of submarine origin from various localities and geologic ages are frequently associated with deposits of manganese and iron. To explain such association he suggested that during some submarine eruptions, sea water (possibly acidified by gases derived from magma) may extract a portion of iron and manganese from the lava. Subsequent oxidation by oxygen contained in sea water would cause precipitation and partial separation of the two elements, iron being less soluble than manganese. A similar process has been advocated to explain the formation of some deep-sea iron-manganese oxide deposits associated with basalts which were shattered and hydrated by sea water during their eruption on the sea floor (*5*). In fact, hydrated lava fragments (hyaloclastites) from South Pacific seamounts and adjacent abyssal areas are greatly impoverished in manganese and other ferrides relative to the original unaltered basalt (*6*).

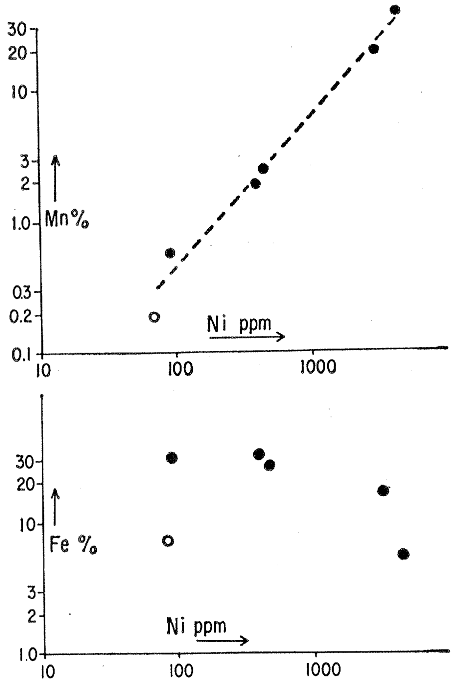

Fig. 1. Mn-Ni and Fe-Ni in samples from dredge haul Amph D2. Open circle, basalt fragment; full circles, oxide samples listed in Table 1.

The above mechanism, and the direct introduction into the bottom water of hydrothermal solutions bearing iron and manganese, are probably the main source of iron for the deposit under discussion. A similar situation can be observed within the submerged caldera of the volcanic island of Santorin, Greece, where an iron hydroxide deposit is being formed near the mouth of a submarine hydrothermal spring. Spectrochemical analysis of a sample from this deposit (collected in 1965) showed the following percentages by weight: SiO_2, 23.50; Al_2O_3, 0.23; CaO, 2.50; MgO, 0.50; K_2O, 0.27; Fe, 40.50; Mn, 0.45; H_2O, 13.50. The percentage of water indicates the loss in weight of the moisture-free sample after 24 hours at 600°C. It also showed the following parts per million: Ni, 13; Co, < 5; Cr, < 10.

The rate of precipitation of iron after its introduction into the sea water depends on the supply of oxygen for its oxidation. Boström (*7*) points out that according to the reaction:

$$4\,Fe^{2+} + 6\,H_2O + O_2 \rightarrow 4\,FeO(OH) + 8\,H^+$$

four moles of FeO(OH) are formed for each mole of oxygen supplied. Accordingly, about 2000 liters of water are necessary to produce one mole of FeO(OH), assuming sea water contains 10^{-4} mole/liter of dissolved oxygen. The presence of a source of heat due to the volcanic activity should locally cause thermal instability of the deep-water masses, resulting in convection currents and a continuous supply of oxygenated water to the site of eruption. The oxidation and precipitation of iron should be rather rapid under such conditions.

The gradual oxidation of the solutions should give rise to fractionation of iron and manganese and to a set of precipitates with various Fe-Mn ratios; namely, a ratio which is high in the early precipitates, and gradually decreases due to the longer residence time of manganese in solution. Variability in the Fe-Mn ratio similar to that found in Amph D2 (Table 1) was found in rocks dredged from another seamount in the same region (7°50′S, 180°08′W, station Amph D1, about 2000 m below sea level). In addition to massive basalt, hyaloclastic rocks recovered at this station consisted of basaltic glass grains up to 1 mm in size, cemented in some samples by a red ferruginous matrix, and in others by a black matrix rich in manganese. Chemical analyses of these rocks and of black iron-manganese oxides encrusting the surface of some of the massive basalt boulders, suggest elemental fractionation of the type described above (Table 2).

Among the minor elements, nickel appears to follow manganese quite closely and to behave independently of iron at Amph D2 (Fig. 1), while the Ni-Co ratio (Table 1) seems rather erratic. Chromium is lower in the iron and manganese oxide rocks than in the basalt, probably because after its introduction in sea water it is oxidized and maintained in solution as $(CrO_4)^{2-}$ (*8*).

Processes of the type described here should not be uncommon in this region, where evidence of extensive submarine volcanic activity is ample (*3*). The areal distribution of iron and manganese dispersed in pelagic sediments of the southeast Pacific is influenced by such processes; for instance, it was shown recently (*9*) that both elements are enriched on the East Pacific Rise due to volcanic-hydrothermal activity along the Rise.

It is possible to explain why iron deposits are not found as commonly as manganese deposits in the southeast Pacific even if it is assumed that volcanism is the main source of ferrides at this area of the ocean floor. One has to consider that the bulk of the iron rapidly precipitates on restricted areas within sites of volcanic activity; on the other hand, much of the manganese is maintained in solution for a longer time and precipitates above the deposits rich in iron at volcanic sites, as well as on wide areas of ocean floor around them. In addition, in areas of volcanic activity, some manganese contained in the sediment is mobilized preferentially to iron, and is reprecipitated near the top of the sedimentary column (*10*). Present deep-sea sampling techniques such as dredging and coring provide areally scattered samples from surface layers of the ocean floor only; under such circumstances manganese minerals are sampled preferentially to iron minerals both in terms of area and depth.

While the present findings tend to support the volcanic theory on the origin of oceanic iron–manganese oxide minerals, there is also clear evidence in favor of similar minerals being formed elsewhere by other mechanisms, namely: (i) the slow chemical precipitation of iron and manganese derived from continental weathering, especially in areas close to land as on the Blake Plateau (*11*) or on banks off the California coast (*12*); and (ii) the diagenetic migration of dissolved manganese in buried reduced hemipelagic sediments and reprecipitation near the interface of water and sediment, as in the Guatemala basin (*13*) or in the Baltic Sea (*14*). One theory cannot be a general explanation for all occurrences of deep-sea iron–manganese oxide minerals; it is becoming increasingly clear that one or the other of the aforementioned mechanisms is dominant in different areas of the ocean floor.

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Maya Blue: A Clay-Organic Pigment?

Abstract. *Maya Blue, a pigment used by the Mayas in Yucatan, is remarkably stable: the color is not destroyed by hot concentrated mineral acids or by heating to about 250°C. The principal constituent is the colorless mineral attapulgite. It is proposed that the pigment is an adsorption complex of attapulgite and natural indigo; a synthetic equivalent may be prepared from attapulgite and either indoxylester or indigo, or by applying the vat-dyeing technique, with reduced indigo. The low dye content of the pigment (less than 0.5 percent) indicates that the dye is absorbed only on the external surfaces of the attapulgite particles and not throughout the channels in their structures. The complex as such is not stable to acids, but the stability displayed by Maya Blue is achieved simply by heating the complex to from 75° to 150°C for several days. An analogous stable pigment can be prepared from sepiolite and indigo. No stable pigments could be prepared from clays with platelike structures or from zeolites.*

Maya Blue, a pigment used by the Mayas in Yucatan, most commonly during the late pre-Spanish period, is found in both pottery and murals; it is exceptionally stable against hot concentrated mineral acids, including aqua regia. The color cannot be extracted with acetone. Upon heating, the blue color persists to about 250°C before it becomes grayish. This exceptional stability caused Maya Blue to be thought an entirely inorganic pigment (*1*). Later the principal constituent proved to be the colorless mineral attapulgite, and it was proposed (*2*) that the pigment might be an attapulgite-organic complex. However, attempts to identify completely the organic material and to synthesize an attapulgite-dye complex having this remarkable chemical stability failed (*1, 2*).

Indigo being one of the most stable blue dyes available to the Mayas, I studied the formation of attapulgite-indigo complexes. Shepard (*2*) mentioned that traces of indigo had been identified in the pigment, but, since no stable attapulgite-indigo complex could be prepared, it was thought that indigo had been merely added to intensify the color.

The following observations were made in collaboration with C. T. Deeds. A blue attapulgite-indigo complex is easily obtained in this manner: When a slightly alkaline solution of synthetic indoxylacetate contacts attapulgite, the clay becomes blue; apparently, indoxyl is oxidized on the surfaces of the clay particles. The blue clay is filtered and washed with water. The resulting pigment is not stable to hot acids, and the color is extractable with acetone. The secret in achieving stability to acids is that the pigment must be heated at moderate temperatures—for example, for several days at 75°C or preferably at 105° to 150°C; the pigment is now stable to hot concentrated mineral acids, the dye cannot be extracted with acetone, and the color is not changed by heating to 250°C. In all these tests, the synthetic attapulgite-indigo complex thus behaves like Maya Blue. No tristimulus values have been obtained for the synthetic pigment, but to the eye the color matches Maya Blue.

Any excess of indigo in the reaction mixture can be removed by extraction with acetone or nitric acid. The dye content of the washed complex is very low (less than 0.5 percent), but nevertheless the color is rather intense.

Two alternative methods of preparing the indigo complex of attapulgite are:

1) Heat a mixture of indigo powder and attapulgite, and remove any excess of indigo by washing with acetone.

2) Reduce indigo with a solution of sodium hydrosulfite, contact attapulgite with this solution, and expose them to air; this procedure is the vat-dyeing technique. Heating is still required for stability to acids.

It seems reasonable to assume that Maya Blue is basically an attapulgite-indigo complex prepared according to one of these procedures or some modification thereof. Since natural indigo contains small quantities of other dyes, the color of the synthetic pigment may not be expected to match Maya Blue exactly.

A product quite analogous in behavior to the attapulgite-indigo complex is the sepiolite-indigo complex that can be prepared in the same way. Both attapulgite and sepiolite have crystal structures featuring parallel channels of molecular dimensions. The particle size of the attapulgite is rather critical: a fraction small as to particle size is required for achieving the intense coloring.