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A MAGNETIC MINERAL FROM THE INDIAN OCEAN[1]

C. G. A. HARRISON AND M. N. A. PETERSON, *Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California.*

ABSTRACT

A high concentration of a magnetic mineral was found near the top of two cores from the Indian Ocean. Magnetic properties of the sediment suggest an *in situ* formation. *X*-ray and magnetic data show that the mineral is between magnetite and maghemite in structure, and the formation of such a mineral in the deep sea environment is considered.

During the Scripps Institution of Oceanography's Monsoon expedition a piston core and trip gravity core were taken at lat 23°56′S, long 73°53′E, in a depth of 2022 fm. The region was one of abyssal hills having maximum heights of about 200 fm, the depth of water ranging from 1700 fm to 2340 fm. The maximum slope of the hills, measured from the PDR record, was about 14°. The record shows few places where there are flat portions between the abyssal hills. The tentative position of the Indian Ocean rise (R. L. Fisher, pers. comm.) puts the position of the core 225 miles east of the center of the ridge.

In the uppermost portion of both cores, there was an anomalously high value of the magnetic susceptibility. In the piston core, measurements of magnetic susceptibility on samples taken at 2 cm, 30 cm, 41 cm, and 57 cm, from the top of the core, were all in the region of 300 micro emu/cc, whereas samples from 64 cm, 72 cm, 91 cm, and further down had magnetic susceptibilities of the order of 10 micro emu/cc (Fig. 1). In the gravity core, samples from 16 cm and 23 cm had a high susceptibility of about 1000 micro emu/cc, and samples from 6 cm, 28 cm, and 45 cm had more normal susceptibilities of between 10 and 25 micro emu/cc.

It seemed likely that a sharp contact from grayish buff to light buff calcareous ooze at 58 cm in the piston core would be diagnostic of the sediment type changing from one of high magnetic susceptibility to one of low magnetic susceptibility, and this was verified with an astatic magnetometer system. Over the portions of the core where the magnetic susceptibility was very high, the deflection of a spot of light from the magnetometer mirror was several centimeters, but over the other portions, little or no deflection was observable. All of the sediment above 58 cm gave large deflections, whereas that below 58 cm gave only small deflections.

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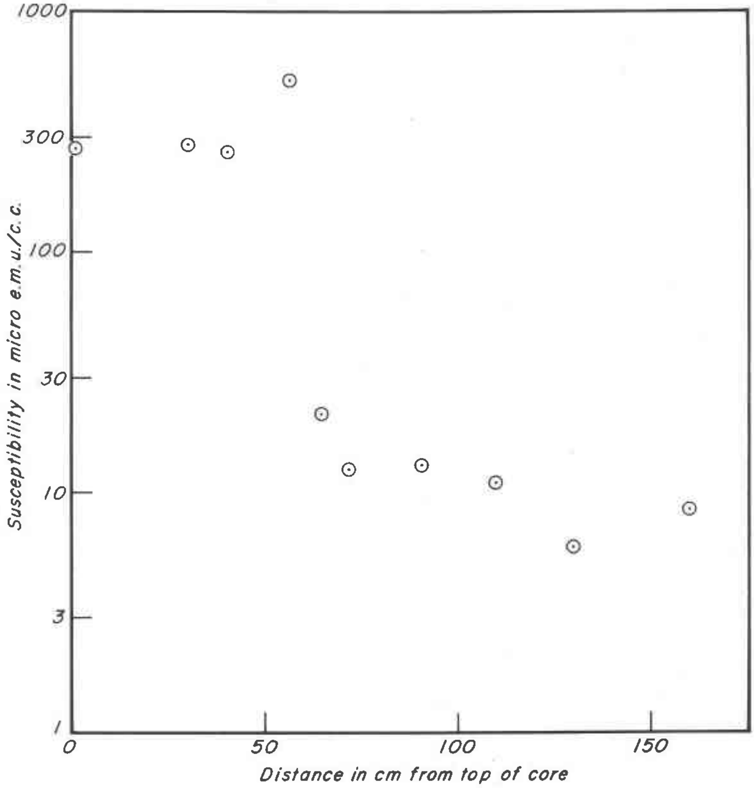

FIG. 1. Magnetic susceptibility of MSN 56 in micro emu/cc for various depths.

The gravity core (buff calcareous ooze, somewhat darker and slightly zeolitic in the lower part) was 58 cm long and only five samples were taken. The sediment in the gravity core apparently has a weakly magnetic section above as well as below the strongly-magnetic section, as the sample at 6 cm had a normal susceptibility. The two boundaries of the more magnetic section were thus between 6 and 16 cm, and between 23 and 28 cm.

The difference between the thickness of the strongly-magnetic portion in the gravity and piston cores is probably due to a shortening produced by the gravity coring process. This would also obscure the lithological boundary, which is only seen in the piston core.

The magnetic mineral occurring in the top 58 cm of MSN 56 P has been carefully studied by several methods, which are now described. The Curie temperature was determined by measuring the saturation magnetization of a small sample as a function of temperature. The heating was done in air, allowing easy oxidation of the mineral. The Curie temperature was found to be 640° C. (Fig. 2). The magnetic susceptibility in a small field was 0.045 emu/gm/oersted. From these two observations, we can say that the mineral is neither magnetite (having a Curie point of 585° C. which is lowered by the presence of impurities), nor hematite, which has a very low initial susceptibility. The only other mineral which would seem likely is maghemite or a mineral with maghemite structure. Maghemite is unstable towards heat, being converted to hematite at a temperature between 200° and 800° C. (Mason, 1943). The Curie point of pure

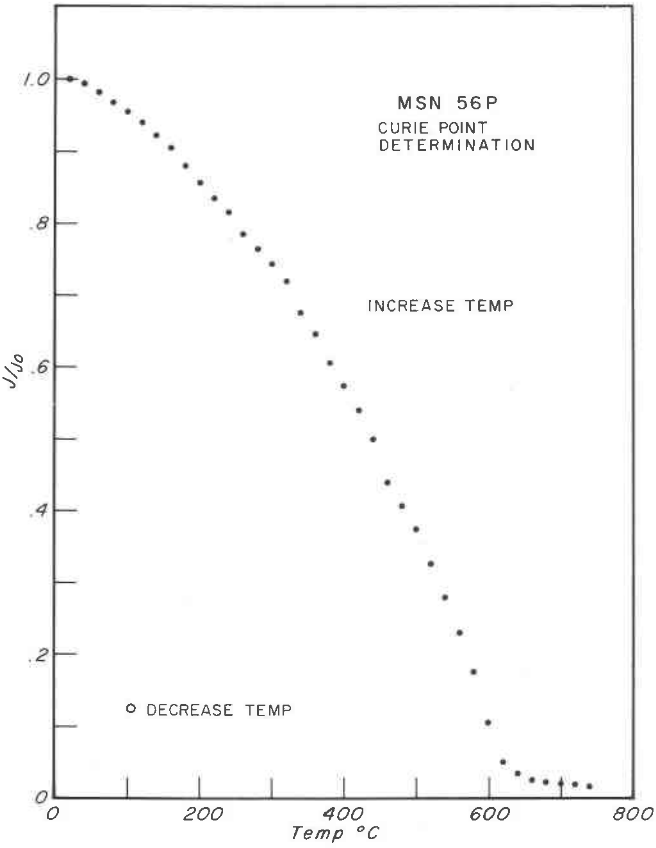

FIG. 2. Saturation magnetization of magnetic "mineral" from MSN 56 P for increasing temperature. The saturation magnetization is plotted as the fraction of the saturation magnetization at 0° C., remaining at T° C. The dots are for increasing temperature. The open circle is the fraction of saturation magnetization at 100° C. after cooling had taken place.

maghemite has never been directly determined, but by measurement of the Curie point of solid solutions of maghemite with another cation, and by extrapolation to pure maghemite it has been quoted as 680° C. (Michel and Chaudron, 1935).

This particular form is quite stable toward heat; when the Curie point was being determined, the material was kept at certain constant temperatures for periods of up to twenty minutes, in order to see if any change from maghemite to hematite (manifested by a fall in saturation magnetization) was occurring. As no such change took place below the Curie point, the material needed a temperature greater than 640° C. for the change to occur; the change from maghemite to hematite had undoubtedly occurred by the end of the experiment, as the saturation magnetization only rose slightly during cooling. It may also be that more time was needed, because of the possibility that structural water may contribute to the stability of maghemite. It should be noted that this mineral was kept wet in fresh, refrigerated core material until separated for study.

X-ray examination of the mineral confirms the above theory. The *x*-ray diffraction pattern (Table I) is generally that of maghemite (γFe_2O_3), and shows most of the important superstructure lines. Spacings are intermediate between magnetite and maghemite, suggesting that the mineral is an incompletely oxidized magnetite, in which the ordering of existing vacancies is only partial. At low angles 2θ the unit cell in the cubic system has a = about 8.34 Å. At higher angles, the pattern becomes more nearly that of magnetite than of maghemite; a is about 8.38 Å. This probably results from differences in diffraction efficiency between the magnetite that is relatively unoxidized, and retains relatively good crystallinity, and the maghemite, in which crystallinity may be considerably less perfect. Small amounts of both lepidocrocite and geothite are also present. There is no observable hematite, although the presence of a very small amount cannot be precluded, because of interference of the two strongest *x*-ray reflections of hematite (104) and (110, hex) with reflections from geothite (130) and magnetite (311) or maghemite (313, tet).

Attention was first brought to this mineral because of the possibility of its *in situ* formation. Texturally, it does not appear to be in rounded grains, which would suggest a detrital origin, nor does it have the octahedral crystal shape of magnetite that is typical of residual magnetite from altered basic volcanic material. Rather, the surface of the individual fragments is druzy, being formed of many closely crowded crystals. A slight ochre stain in places on the surface is probably the lepidocrocite and goethite observed by *x*-ray.

The magnetic anisotropy of the five highly magnetic samples from

TABLE I. COMPARISON OF X-RAY DATA FOR MAGNETIC "MINERAL" FROM MSN 56, WITH THAT OF OTHER IRON MINERALS OF WHICH IT IS COMPOSED

Observed Pattern	Observed Intensity	Magnetite[1]	Maghemite[1]	Lepidocrocite[1]	Goethite[1]
—	—		7.91 (1)		
6.94	VW		6.94 (2)		
6.26	W			6.27 (100)	
5.90	VVW		5.90 (6)		
5.31	W		5.33 (1)		
—	—				4.98 (10)
4.83	M	4.85 (10)	4.82 (6)		
—	—		4.29 (2)		
4.18	W				4.18 (100)
—	—		3.73 (6)		
—	—		3.40 (7)		
—	—				3.38 (10)
3.27	W			3.29 (60)	
3.20	VVW		3.20 (3)		
2.96	S	2.97 (30)	2.95 (30)		
2.78	M		2.78 (3)		
2.69	VVW				2.69 (30)
—			2.638 (4)		
—					2.58 (8)
2.524	VVVS	2.532 (100)	2.514 (100)		2.520 (3)
2.49?	VVW?				2.490 (15)
—				2.473 (30)	
2.45?	VVW?				2.452 (25)
2.419	W	2.425 (8)	2.408 (2)		
—				2.362 (15)	
2.307	W		2.315 (2)		
—					2.252 (10)
—			2.230 (2)		
—					2.192 (20)
2.095	S	2.100 (20)	2.086 (15)	2.086 (12)	
—					2.009 (2)
—				1.935 (30)	
—					1.920 (6)
—			1.865 (1)		
—				1.848 (10)	
—			1.820 (3)		
1.799	W				1.799 (7)
—					1.770 (2)
—				1.733 (15)	
—					1.721 (20)
1.712	W	1.714 (15)			
1.70?	VVW		1.701 (9)		
—					1.694 (10)
—			1.670 (2)		
—					1.661 (4)
1.613	M	1.617 (25)			
—			1.604 (20)		1.606 (6)
—				1.567 (8)	1.564 (15)
—			1.550 (2)		
—				1.532 (7)	
—			1.525 (3)	1.523 (15)	
1.483	S	1.485 (35)			1.509 (10)
—			1.474 (40)	et cetera	et cetera
1.326	VW	1.327 (6)		et cetera	et cetera
—			1.318 (6)	et cetera	et cetera
1.279	W	1.280 (10)		et cetera	et cetera
—			1.272 (8)	et cetera	et cetera

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[1] Data from Brown, 1961, 38b. Data obtained with a Norelco wide angle diffractometer, using Mn filtered Fe radiation, scanning speed of $\frac{1}{4}°$ 2θ per minute, chart speed of $\frac{1}{2}''$ per minute, divergent, scatter and receiving slits of 1°, 1° and .006″ respectively.

MSN 56 P and MSN 56 PG were measured on a suspended sample torque magnetometer built by Dr. A. Rees (King and Rees, 1962). The results (Fig. 3) show that all the samples have maximum magnetic susceptibilities grouped around the vertical, the first time, to our knowledge, that consistent results of this nature have ever been found in a sedimentary deposit. Normally the maximum and intermediate susceptibilities tend to lie close to the horizontal plane (Rees, 1961). Another surprising fact is that, in all cases, the form of susceptibility is that of a prolate ellipsoid, rather than an oblate ellipsoid, which is normally found in sedimentary deposits. On artificially depositing some of the highly magnetic portion (*i.e.*, the entire sediment) of MSN 56 P it was found that the magnetic

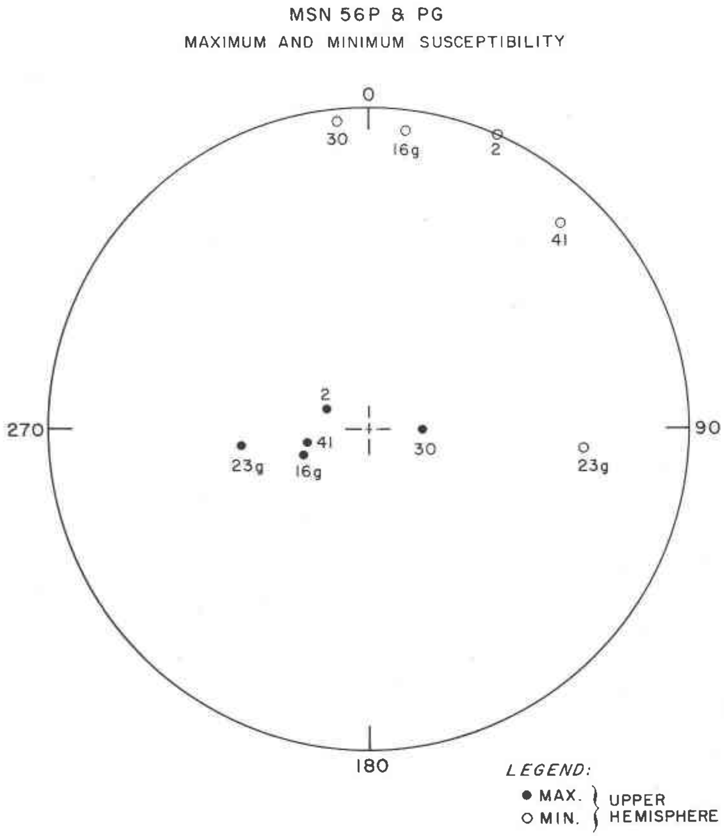

FIG. 3. Maximum and minimum susceptibility directions plotted on an equal area net. The closed circles are maxima, the open circles are minima. A "g" by the side of a number denotes that that specimen came from the gravity core.

susceptibility had a strong maximum in the horizontal plane and that the form of the susceptibility was that of an oblate ellipsoid, These two observations suggest that the magnetic mineral in the cores under discussion was not deposited by usual detrital processes, and that the most likely alternative is that it was formed *in situ*.

The formation of this magnetic mineral by diagenetic processes, or by volcanic-associated processes, or by some combination of these, is suggested. Textural evidence has already been mentioned against the possibility that the mineral is directly residual from the submarine alteration of volcanic debris, and also against the detrital origin for the mineral.

Several possibilities for *in situ* formation are conceivable. A number of ways of forming maghemite are listed by Bernal *et al.* (1959). Natural counterparts of some of these methods exist. Dehydration of pre-existing lepidocrocite will form maghemite that is missing the "ordering" reflections. Inasmuch as the material from MSN 56 has many of these "extra" reflections, it is considered unlikely that it has been formed in this way. Direct precipitation of maghemite and magnetite was shown to be possible, the product depending on whether there was or was not an excess of oxidizing agent, respectively. Oxidation of pre-existing magnetite can form maghemite; most natural maghemites appear to have formed in this manner. This mechanism also yields good ordering of vacancies.

The pelagic sediments of the deep sea would seem especially suited to the possible formation of authigenic magnetite or maghemite, particularly if they contain iron-rich volcanic debris. Slow deposition in oxygenated bottom waters effectively removes all easily oxidized organic material. In the resulting very small content of dissolved sulfide, Fe^{2+} would not precipitate as a sulfide. Berner (1964) has shown the stability fields of iron minerals for some typical sedimentary situations. Little is known about compositions of solutions in pelagic sediments; however, recently, on expedition "Amphitrite" (second leg) of Scripps Institution, measurements were made of pH of solutions squeezed, at 400 psi in a closed system, from red clay cored in 2500 fathoms of water near the Austral Islands. A rather dense and strong crust, composed mostly of manganese oxide material, was present at the surface of the sediment, and a typical carbonate-free red clay was beneath. The pH of the solutions was 6.9 to 7.0. If left open to the atmosphere, the pH climbed quickly to 7.3–7.4 (within minutes), and ultimately to 8.0–8.1 (within hours). Surely out-gassing of CO_2, as a result of changes in temperature and pressure, is responsible for this pH change. At high P_{CO_2}, the field of stability of magnetite becomes smaller, or vanishes completely, as it is supplanted by siderite (Berner, 1964). No siderite, however, is present in these red clays, so it would appear that sufficient CO_2 is not dissolved in these solutions to form this mineral at the pressure and temperature involved. The sediment from the Indian Ocean, in which the maghemite was found, contained about 50% $CaCO_3$.

In a red or brown clay that is buried sufficiently to be effectively isolated from additions of oxygen, and which contains Fe^{2+} bearing minerals, such as olivine, that would be subject to further alteration, the Eh would be controlled by reactions such as:

$$\underset{\text{magnetite}}{2Fe_3O_4} + \underset{\text{liquid}}{H_2O} \leftrightarrows \underset{\text{hematite}}{3Fe_2O_3} + 2H^+ + 2e$$

involving both Fe^{2+} and Fe^{3+}. Other minerals, such as the hydrated ferric oxides, might be important in these reactions, but adequate thermodynamic data are not available. However, it is certainly permissive that magnetite could form. Once formed authigenically, it might then be further oxidized to maghemite, or possibly, in view of the direct precipitation of maghemite demonstrated by Bernal, *et al.* (1959), maghemite might form directly, howbeit, metastably. It may also be that, in some way, volcanic emanations or hydrothermal solutions have played some role. Evidence for recent volcanism, fresh glass at the surface, is present 240 miles south of the location of this magnetic mineral. If secondary oxidation has occurred, there must have been no attendant erosion and redeposition of the magnetite-maghemite bearing mud, because the maximum magnetic susceptibility direction has remained vertical. The formation of lepidocrocite and geothite is probably a still later event, being a coating on the outside of the fragments of magnetite-maghemite.

SUMMARY

1. An unusual abundance of a highly magnetic mineral occurs in one core site from the central Indian Ocean.
2. Its magnetic and *x*-ray properties indicate that it is mostly maghemite, with some aspects of magnetite.
3. For the most part permissive arguments lead to the conclusion that it formed *in situ*.
4. The directions of maximum magnetic susceptibility of the sediment are generally vertical and the form of the susceptibility is that of a prolate ellipsoid.

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