LETTER TO THE EDITOR

**Magnetic Properties of Manganese Nodules Associated
with Dredged Submarine Basalts**

(Received June 3, 1967)

In order to approach some of the most challenging problems in earth sciences such as the interpretation of the magnetic anomaly lineation pattern of the ocean floor, it is essential to study the magnetic properties of submarine rocks. Rocks dredged from the ocean floor are usually found to be coated by a manganese nodule crust. Hence, it was felt that the study of manganese nodule would be important in the interpretation of the magnetic properties of submarine rocks. The present short note reports some of the magnetic properties of manganese nodules which originally constituted the crustal layer of a few cm thickness of submarine basalts dredged from the western Pacific.

A manganese nodule is a massive, layered black material and has been known to be a precipitation product of sea-water. It is well known that manganese nodules are constituted mainly of manganese and iron oxides and hydroxides (Buser, 1959). Major chemical compositions are Mn, Fe, and Si etc. (Menard, 1964).

The present investigation revealed that the manganese nodule sample had a weak remanent magnetization ($\sim 3 \times 10^{-6}$ emu/g). J - H measurement shows that the manganese nodule is paramagnetic at room temperature (χ at room temperature $\approx 1 \times 10^{-5}$ emu/g). When a manganese nodule is heated both in air and in vacuum ($\sim 10^{-3}$ torr), it becomes irreversibly ferromagnetic. This change in magnetic properties is always accompanied by dehydration, in which the weight is reduced to about 3/4 of the original. The transition from the paramagnetic phase to the ferromagnetic one occurs at about 550°C. The heat-treatment of manganese nodules at 900°C for 5 hours seems to complete the change in magnetic properties. The intensity of the saturation magnetization (J_s) of manganese nodules changes with the temperature of heat-treatment. When heat-treated at 700°C for several minutes, J_s at room temperature is 8 emu/g, whereas it becomes 16.3 emu/g after heated at 900°C for 5 hours. There is no change in J_s in further heating at higher temperatures. J_s of the latter sample at liquid nitrogen temperature (-196°C) is 43 emu/g and the extrapolated value of J_s of the latter sample at 0°K is about 50 emu/g. Fig. 1 shows the J_s - T curves of the sample which was heat-treated at various temperatures.

In Fig. 2, the X-ray diffraction pattern of the sample is shown. It is seen from the figure that heat-treatment also leads to a change in crystal structure, i.e., from an amorphous form in the original state to a spinel form in the heated state. Lattice parameter of the sample heated at 900°C is determined as $a=8.492$ Å.

Chemical composition of the sample was estimated with the aid of an X-ray microanal-

yser. The analyses indicate that the ratio of Fe to Mn is generally 1:1. However, small regions were also observed where Mn is significantly enriched and Fe is depleted resulting in smaller ratios of Fe/Mn ($\text{Fe}/\text{Mn} \approx 0.9 \sim 0.5$).

In conclusion, from all the experimental results, it is deduced that the iron-manganite $(\text{Fe}, \text{Mn})\text{O}_2 \cdot n\text{H}_2\text{O}$, amorphous form in the case of this sample) in the manganese nodules studied here is transformed to Jacobsonite (cubic form of $(\text{Fe}, \text{Mn})_3\text{O}_4 + n\text{H}_2\text{O}$ on being heated in air and in vacuum, the latter being ferromagnetic. This conclusion is in complete accordance with the result of petrographic and magnetic studies on synthesized $\text{Mn}_3\text{O}_4\text{-Fe}_3\text{O}_4$ series by Yun (1958) and Eshenfelder (1958). The change from iron-manganite to Jacobsonite indicates a reduction process, showing that the redox condition at ocean bottom is a rather oxidizing one.

Finally, it is proposed that the magnetic properties of manganese nodules can be used as a geother-

Fig. 1 Thermomagnetic curves (J_s - T) of the manganese nodule sample (WP DR-3') heated at various temperatures.

Fig. 2 X-ray diffraction pattern of the manganese nodule sample (WP DR-3') by Fe K radiation.

momenter: if the manganese nodule is ferromagnetic, the sample must have been heated up to 550°C after the formation. Furthermore, the intensity of the saturation magnetization should indicate the temperature at which the sample was heated in the past.

References

- Buser, W., The nature of the iron and manganese compounds in manganese nodules, *Internat. Oceanog. Cong. Preprints*, 962-964, 1959.
- Eshenfelder, A.H., Ionic valences in manganese-iron spinels, *J. Appl. Phys.*, **29**, 378-380, 1958.
- Menard, H.W., *Marine Geology of the Pacific*, McGraw-Hill, 171-190, 1964.
- Yun, I., Experimental studies on magnetic and crystallographic characters of Fe-bearing manganese oxides, *Mem. Coll. Sci. Univ. of Kyoto*, **B 25**, 125-137, 1958.

Mituko OZIMA

Geophysical Institute, University of Tokyo