

Minor Element Composition of Ferromanganese Nodules

Abstract. Mineralogical and chemical analyses performed on 67 ferromanganese nodules from widely varying locations and depths within the marine environment indicate that the minor element composition is controlled by the mineralogy, and that the formation of the mineral phases is depth dependent.

Several attempts have been made to explain the minor element composition of the oceanic ferromanganese minerals. Goldberg (1) pointed out correlations of manganese with nickel and copper and of iron with titanium, zirconium, and cobalt. Goldberg assumed sorption reactions on particulate iron and manganese species to account for these covariances. Riley and Sinhaseni (2) criticized the correlations between iron and zirconium, and between manganese and copper on the basis of a statistical analysis of the data. However, the correlation between manganese and copper has been upheld more recently by Burns and Fuerstenau (3) and by Skorniakova and Andurshchenko (4). Burns and Fuerstenau (3) also pointed out relationships of iron with cobalt, titanium, and calcium, and between nickel, copper, zinc, and magnesium. Their explanation for the inter-element relationships is isomorphic substitution in the different mineral phases.

Skorniakova and Andurshchenko (4), Menard (5), and Mero (6) have pointed out areal groupings of nodules in the Pacific Ocean on the basis of the concentration of various elements in the nodules. The possibility of various supply mechanisms was mentioned as an explanation for this zoning. Menard also showed a depth dependence for the concentration of cobalt.

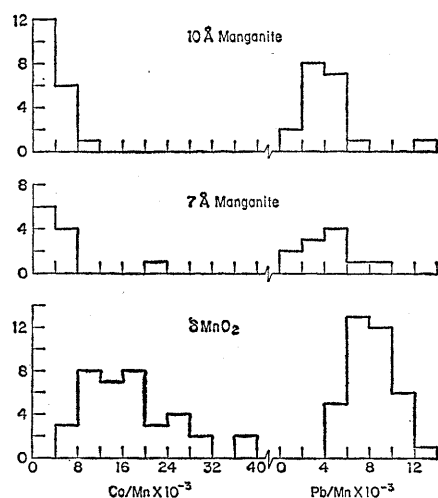


Fig. 1. Distribution of number of samples versus Co/Mn and Pb/Mn, both times 10⁻³.

Still another attempt to use inter-element relationships was made by Arrhenius, Mero, and Korkisch (7), who employed the manganese to cobalt ratio in ferromanganese nodules to distinguish between those nodules formed by volcanism and those inorganically precipitated from seawater. Their major assumption was that cobalt goes into the highly disordered manganite structures found in ferromanganese nodules by Buser and Grütter (8).

This present study aims at a better definition of the minor element relationships in ferromanganese nodules through simultaneous analyses both of the mineralogy and of the chemical compositions of the nodules, as was suggested by Goldberg (9). Sixty-seven different nodules were analyzed by x-ray fluorescence for the elements Mn, Fe, Co, Pb, Cu, and Ni, and for the Ce/La ratio, and mineral compositions of the nodules were estimated by x-ray diffraction techniques.

The mineralogy of manganese nodules has been examined previously by Buser and Grütter (8), by Hewitt *et al.*, by Murata and Erd, and by Manheim (10). Buser and Grütter give a reasonably simple picture of the mineralogy involving three manganese phases. The other authors, mentioned above, give a more complicated picture involving the minerals todorokite, ramsdellite, and birnessite. The simpler picture of Buser and Grütter will be utilized for the purposes of this paper.

Buser and Grütter (8) found three mineral phases in ferromanganese nodules: δMnO₂, 7-Å manganite, and 10-Å manganite. They show that δMnO₂ forms under stronger oxidizing conditions than 7-Å manganite, which in turn reflects higher oxidizing conditions than 10-Å manganite. The nodules in the present study were classified into groups on the basis of the appearance of these three phases in the x-ray diffractograms. All of the nodules contain δMnO₂, some of the nodules contain δMnO₂ and 10-Å manganite, and some of the nodules contain all three phases. Thus, the group labeled δMnO₂ contains only δMnO₂. The group labeled 10-Å manganite contains both 10-Å manganite and δMnO₂. The group labeled 7-Å manganite contains all three

mineral phases. It was not possible to determine the contributions of the amorphous iron phases or to make quantitative measurements on the manganese phases by the techniques employed.

There is an apparent discrepancy between the redox relationships suggested by Buser and Grütter (8) for the three manganese phases and the observed joint occurrence of these minerals; δMnO₂ and 10-Å manganite exist together without the 7-Å manganite, which should be intermediate between the two, according to the redox relationships. No explanation of this observation can be offered as yet.

Figures 1 and 2 show element to

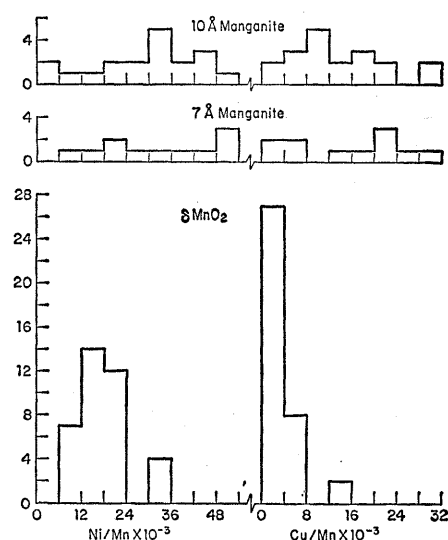


Fig. 2. Distribution of number of samples versus Ni/Mn and Cu/Mn, both times 10⁻³.

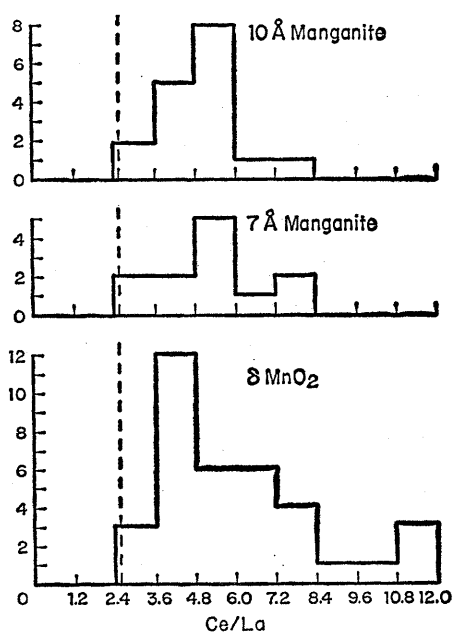


Fig. 3. Number of samples versus Ce/La.

manganese ratios versus frequency of occurrence for each of the mineralogical groups. The ratios, rather than the absolute abundances, were used in these histograms in order to remove the effect of detrital minerals such as quartz and feldspars which were seen in the x-ray diffractograms. From Fig. 1 it is evident that cobalt is enriched in those nodules containing only δMnO_2 . Since no determination of the iron phases was made, no conclusions can be drawn concerning the distribution of the cobalt between the iron and δMnO_2 phases. The assumption made by Arrhenius, Mero, and Korkish (7), that the cobalt is found primarily in the manganite phases, is apparently not valid. The lead (Fig. 1) behaves in a similar way to cobalt. Both lead and cobalt can exist at higher oxidation states than those in which they are normally found in seawater as oxides, and perhaps can be accommodated in the mineral phases in solid solution (9, 11). Nickel and copper, however, do not possess this ability. The histograms (Fig. 2) for these two elements show depletion of these two elements from the δMnO_2 phase with respect to the manganite phases. The spread of the elemental abundance ratios in the man-

ganite groups in Fig. 2 may result from the varying percentage of the manganite phases, and the concentration of the element in the water at the site of formation. This spread in the manganite phases can be contrasted with the considerably more peaked histograms for the δMnO_2 phase.

The ratios of copper and nickel to manganese are 1.5 and 2.7, respectively, in seawater, while in ferromanganese nodules they are 0 to 6×10^{-3} and 1 to 3×10^{-3} , thus showing a depletion of nickel and copper in ferromanganese nodules with respect to seawater. On the other hand, the ratios of cobalt and lead to manganese are 14×10^{-2} and 15×10^{-3} in seawater, while in ferromanganese nodules they are 1 to 2×10^{-2} and 6 to 10×10^{-3} respectively. These ratios are approximately equal in seawater and in ferromanganese nodules. The depletion of copper and nickel, but not cobalt and lead, supports the arguments presented above concerning the inclusion of minor elements in ferromanganese nodules.

The histograms for Ce/La (Fig. 3) show no preferential or distinct values for any of the phases. It is of interest to note that the Ce/La ratio of 2.5 for crustal rocks (12), represented in

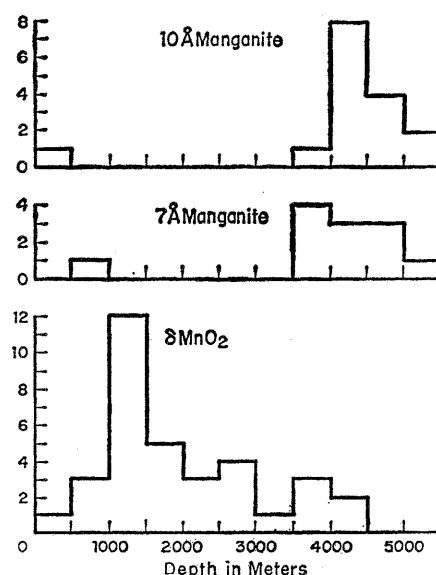


Fig. 5. Number of samples versus depth in meters.

Fig. 3 by the dotted line, is at the lower extreme of the Ce/La ratios for ferromanganese nodules. This is consistent with the idea of the enrichment of cerium in ferromanganese nodules put forth by Goldberg (9).

Minor-element concentrations in ferromanganese nodules are primarily controlled by the mineralogy. Therefore, parameters which may govern the formation of the different mineral phases are sought. Figure 4 shows the distribution of samples taken from the Pacific Ocean. A sampling bias favoring the eastern half of the Pacific Ocean can be seen and it is in this area only that sampling is sufficiently large to determine an areal distribution. There is no apparent pattern in the distribution of samples in the various groups. Figure 5 indicates a depth dependence for the mineralogy. Comparing Figs. 1 and 5, we can see that the Co concentration decreases with depth, in agreement with Menard's finding (5).

The data show that the concentration of the various minor elements in ferromanganese nodules is controlled by the mineral forms present in each given nodule, and that the occurrence of these mineral forms is in turn governed by depth, or some parameter directly related to depth.

The ultimate control of the ferromanganese nodule formation will be found in thermodynamic and/or kinetic considerations of the chemical system defined by nodule formation. The free energy change, ΔG , will vary with the activities of the reactants and products, with the temperature, and with

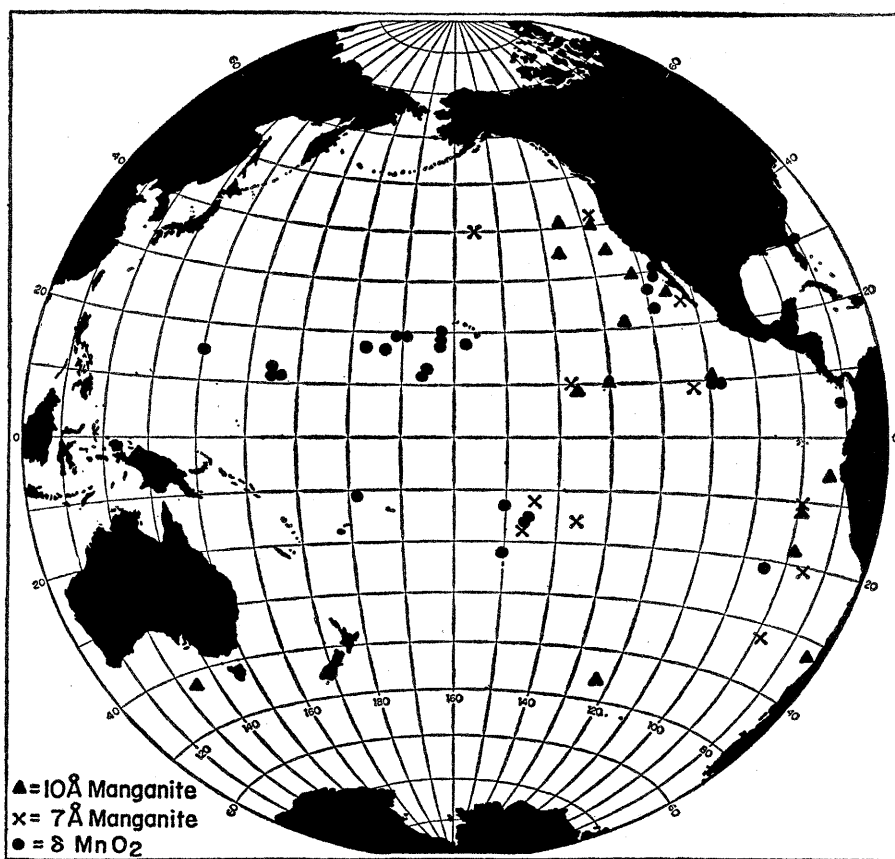
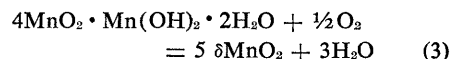
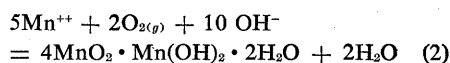
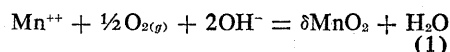


Fig. 4. Sample distribution in the Pacific Ocean, showing variation with mineral form.

the pressure. The chemical reactions involved in the formation of ferromanganese nodules are of the type:



The formula $4\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ represents the 7-Å manganite phase as suggested by Feitknecht and Marti (13) and by Buser, Graf, and Feitknecht (14). The 10-Å manganite can be represented by $3\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ (8).

It can be seen that the only species whose activity is subject to change with depth in Eq. 3 is oxygen. The equilibrium partial pressure of oxygen will increase with increasing hydrostatic pressure (15). Also, the oxygen content of seawater tends to remain constant or increase with depth between 1000 and 5000 m in the Pacific Ocean (16). As a result of these factors, the formation of δMnO_2 would be favored at greater depths. This is contrary to the data presented here.

The two other parameters which can cause ΔG to change as a function of depth are temperature and pressure. The change of ΔG with temperature is given by:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

where ΔS refers to the entropy change of the reaction. Figure 5 shows that the most probable occurrence of δMnO_2 is at 1000 to 1500 m, and that of the manganite phases is at 4000 to 4500 m. The temperature difference represented by this depth difference is usually 3° or 4°C. Therefore, the entropy change must be large for this free energy change to be of significance.

On the other hand, the pressure change is 300 atm. The effect of pressure on ΔG is:

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta \bar{V}$$

where $\Delta \bar{V}$ is the partial molal volume change during the reaction. This latter parameter seems to be the most promising for consideration of controlling the mineralogy of ferromanganese nodules. It has sufficient magnitude and universality to control the mineralogy on an ocean-wide basis. At present this hypothesis cannot be tested because of a

lack of molal volume measurements of the reactants and products.

It should be noted that the measured rate of accumulation (17) roughly corresponds to rates which can be calculated from laboratory kinetic studies (18). However, at present there exist inadequate data to ascertain the effect of temperature and particularly pressure on reaction kinetics of nodular formation.

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Hemoglobin Portland 1: A New Human Hemoglobin Unique in Structure

Abstract. *A new hemoglobin (Hb), Portland 1, has been found in a newborn infant having multiple congenital anomalies and complex autosomal chromosomal mosaicism. The new hemoglobin has a unique tetrameric structure (molecular weight, 66,000) composed of two pairs of different types of chains, neither of which is α , γ_2x_2 . The x-chain of Hb Portland 1 may be a new type of hemoglobin chain, but the available evidence suggests that it may be identical with the ϵ chain. We suggest that Hb Portland 1 is an embryonic hemoglobin that persisted until after birth in relatively large amounts in this patient.*

A new hemoglobin (Hb), Portland 1, was discovered (1) in a female Chinese infant having multiple congenital anomalies; chromosomal studies of lymphocytes revealed complex mosaicism (normal/trisomy 16/short arm 17-18 deletion) (2). The blood sample used by us was obtained immediately after the infant's death at 20 days. The washed erythrocytes were hemolyzed with distilled water and toluene (3), and the clarified hemolyzate was subjected to starch-gel electrophoresis in tris-ethylenediamine tetraacetic acid-borate buffer, pH 8.15 (4). Comparison of the electrophoretic pattern of this hemolyzate with those of several other hemoglobin specimens (Fig. 1) shows that a hemoglobin component having an electrophoretic mobility greater than Hb-A but less than Hb Bart's is present in the

hemolyzate from the propositus. The name Portland 1 is proposed for this previously undescribed hemoglobin, which represented approximately 5 percent of the total hemoglobin; the remainder included Hb Bart's (5 percent), Hb-F_I (11 percent) (5), Hb-F_{II} (55 percent), and Hb-A (22 percent). It is important to note that no Hb Portland 1 was demonstrable in the parents of the propositus.

Structural characterization of Hb Portland 1 was carried out by initial isolation of the hemoglobin components by use of IRC-50 ion-exchange chromatography (phosphate buffer, pH 6.7, 0.05M Na⁺, 0.01M KCN) (6) followed by further purification employing starch-block electrophoresis (barbital buffer, pH 8.6, 0.5M) (7).

The $s_{20,w}$ (4.45S) and $D_{20,w}$ (6.54 ×