

## MINERALOGICAL NOTES

### ELECTRON-PROBE DETERMINATION OF INTER-ELEMENT RELATIONSHIPS IN MANGANESE NODULES

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#### INTRODUCTION

Manganese nodules have attracted considerable attention in recent years as a potential source of Mn, Fe, Co, Ni, Cu and other minor elements. These elements are enriched in manganese nodules relative to igneous rocks, sea-water, and deep-sea clays (Willis and Ahrens, 1962).

The nodules consist of an intimate mixture of crystallites of several minerals, together with organic, colloidal, and detrital matter (Mero, 1962; Arrhenius, 1963). Frequently, the nodules form about a nucleus of pumice, altered volcanic glass or rock, pebble, or skeletal remains. Previously, inter-element relationships were deduced from bulk chemical analyses of manganese nodules (Goldberg, 1954; Riley and Sinhaseni, 1958; Mero, 1962; Skorniakova *et al.*, 1962; Willis and Ahrens, 1962). In view of the complex mineralogy of the nodules, and the obscure definition and difficulty of separation of extraneous material, element correlations derived from bulk chemical analytical data are sometimes ambiguous.

With the development of the electron-probe *x*-ray microanalyzer, it is now possible to analyze minute amounts of material (down to one cubic micron or 1 micro-microgram) on the surface of a solid specimen, and to examine submicroscopic phases. In particular, examination of selected characteristic *x*-radiation during electron-beam scanning of a selected area of a manganese nodule produces a picture of the relative concentration of a specific element throughout the area and allows inter-element relationships to be established directly. *X*-ray intensity profiling of one, two, or three elements simultaneously enables chemical variations of elements to be compared across a nodule. Inter-element relationships obtained from electron-probe measurements are phase correlations and these may differ from correlations deduced from bulk chemical analyses.

The present paper describes methods by which element correlations may be determined with the electron-probe, and summarizes the results obtained by electron-beam scanning and specimen traversing.

PREVIOUS WORK ON THE MINERALOGY AND  
CHEMISTRY OF MANGANESE NODULES

The manganese oxide phases which dominate the mineralogy of manganese nodules have been characterized principally by Buser and coworkers (Buser *et al.* 1954; Buser and Graf, 1955 a,b; Buser and Grütter, 1956; Grütter and Buser, 1957; Buser, 1959). These phases consist of  $\delta$ - $\text{MnO}_2$  and two "manganites,"<sup>1</sup> possessing layer structures. Amorphous hydrated  $\text{FeOOH}$  is also present, frequently as a major constituent. The three manganese oxides, which represent different degrees of oxidation of manganese, possess high specific adsorption properties and undergo rapid isotopic exchange. Minor elements (Mg, Ni, Co, Zn, Ca, Al and Fe) are believed to be concentrated in the "manganite" phases (Buser, 1959).

Numerous trace element studies have been made on manganese nodules. On the basis of bulk chemical analyses, Goldberg (1954) deduced correlations between Co, Ti, Zr and the iron-rich phase and between Ni and Cu and the manganese-rich phase. Riley and Sinhaseni (1958), after re-examining Goldberg's (1954) data, believed that only Fe-Co-Ti and Mn-Ni correlations are shown by the data. Mero (1962) showed that trace element concentrations in the nodules are subject to geographical variations. In the Pacific Ocean, manganese-rich nodules with or without Cu and Ni occur near the American continents, and iron-rich nodules containing Ni, Cu, and especially Co are found in the Central Pacific. Willis and Ahrens (1962) believe that the presence of iron in substantial amount is necessary for the enrichment of certain trace elements. An inverse correlation between iron and manganese was observed, and direct correlations were established between nickel and copper, and between iron and cobalt.

## EXPERIMENTAL METHODS

A radial block (0.5 cm  $\times$  0.5 cm  $\times$  2-4 cm), cut from a hemispherical section of each nodule, was mounted in epoxy-resin and polished. The polished specimens were coated with a thin layer of carbon and stored in a vacuum desiccator. The phases in the nodules were identified by x-ray powder photograph ( $\text{Fe}_{K\alpha}$  radiation, Mn filter; and  $\text{Cu}_{K\alpha}$  radiation, Ni filter) of samples drilled from the matching surface of the other half of each nodule.

<sup>1</sup> The term "manganite," which is prevalent in oceanographic literature, is a chemical name applied to manganese oxide phases found in manganese nodules. The so-called "10 Å manganite" and "7 Å manganite" possess the approximate empirical formulae  $3\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  and  $4\text{MnO}_2 \cdot \text{Mn}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , respectively. The phases should not be confused with the mineral manganite,  $\gamma$ - $\text{MnOOH}$ , which has a different crystal structure.

An ARL electron-probe microanalyzer was used to obtain information on inter-element relationships in the sectioned nodules. Three techniques were used:

1. Wavelength scanning at various points throughout the specimen. This identifies the elements present and yields a semiquantitative analysis at each point.
2. Specimen traversing (96 $\mu$  per minute) under a stationary beam. With appropriate calibration, this technique allows one, two, or three elements to be analyzed simultaneously by ratemeter and provides a graphical means of comparing variations in element concentrations across a nodule.
3. Electron-beam scanning. The electron beam, focussed to a diameter less than one micron, is swept in a regular manner across a square area of sample while a synchronous oscilloscope display indicates the two-dimensional intensity distribution of back-scattered electrons or a selected characteristic  $x$ -radiation. Photographs of the oscilloscope screen provide pictures of textural features and phase relationships (back-scattered electrons) and the relative enrichment of a particular element (characteristic  $x$ -radiation) throughout the area. A comparison of photographs taken during electron-beam scanning enables inter-element relationships to be recognized at a glance, provided the element is present in sufficient concentration not to be obscured by continuous radiation.

## RESULTS

Measurements have been made on manganese nodules from fourteen widespread localities and inter-element relationships were found to be the same in each of the nodules examined. To illustrate the type of results that can be obtained by wavelength scanning and electron-beam scanning, measurements on a representative specimen (DWHD-16) are presented. This nodule was dredged from a depth of 1270 meters from an area approximately 250 miles north-east of Tahiti, which is classified as a region in which the cobalt concentration of manganese nodules is unusually high (Mero, 1962).

The principal phases constituting specimen DWHD-16 are  $\delta$ -MnO<sub>2</sub> and an iron-rich  $x$ -ray amorphous phase believed to contain hydrated FeOOH. Traces of the "7 Å manganite" are also present. Chemical analysis by electron-probe, using metal (Mn, Fe, Co, Ni, Cu, and Zn), oxide (Ti), clinopyroxene (Ca, Mg, and Si), and muscovite (K and Al) standards, yields the following average concentrations (wet weight per cent of total nodule): Mn: 24.5; Fe: 11.5; Co: 1.15; Ni: 0.70; Cu: 0.25; Zn: 0.10; K: 0.4; Ca: 2.1; Ti: 1.1; Mg: 1.0; Al: 1.5; Si: 2.0. The calibration error arising from differences in average atomic number between specimens and the standards limits the accuracy of the analyses to the range plus 10 per cent of minus 5 per cent. A wet chemical analysis gave a water loss at 110° C. of 21.2 wt. per cent.

Electron-beam scanning photographs of an area of specimen DWHD-16 are reproduced in Fig. 1. The picture at top left is a photograph of an

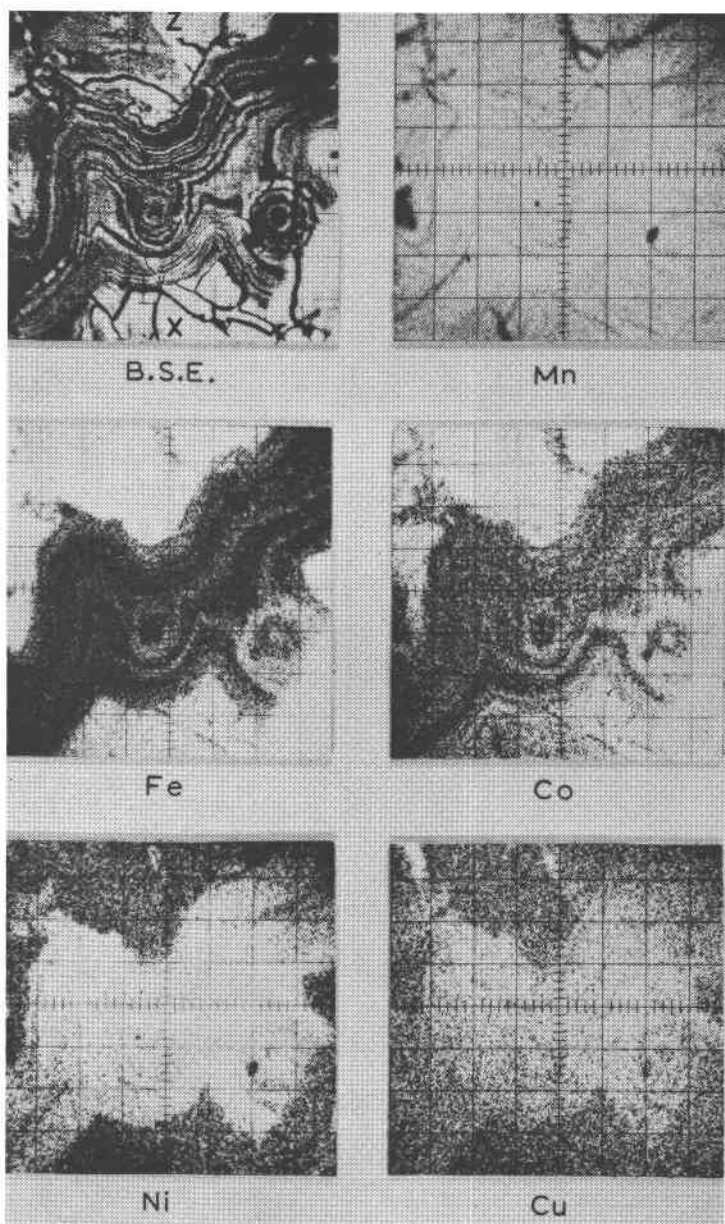
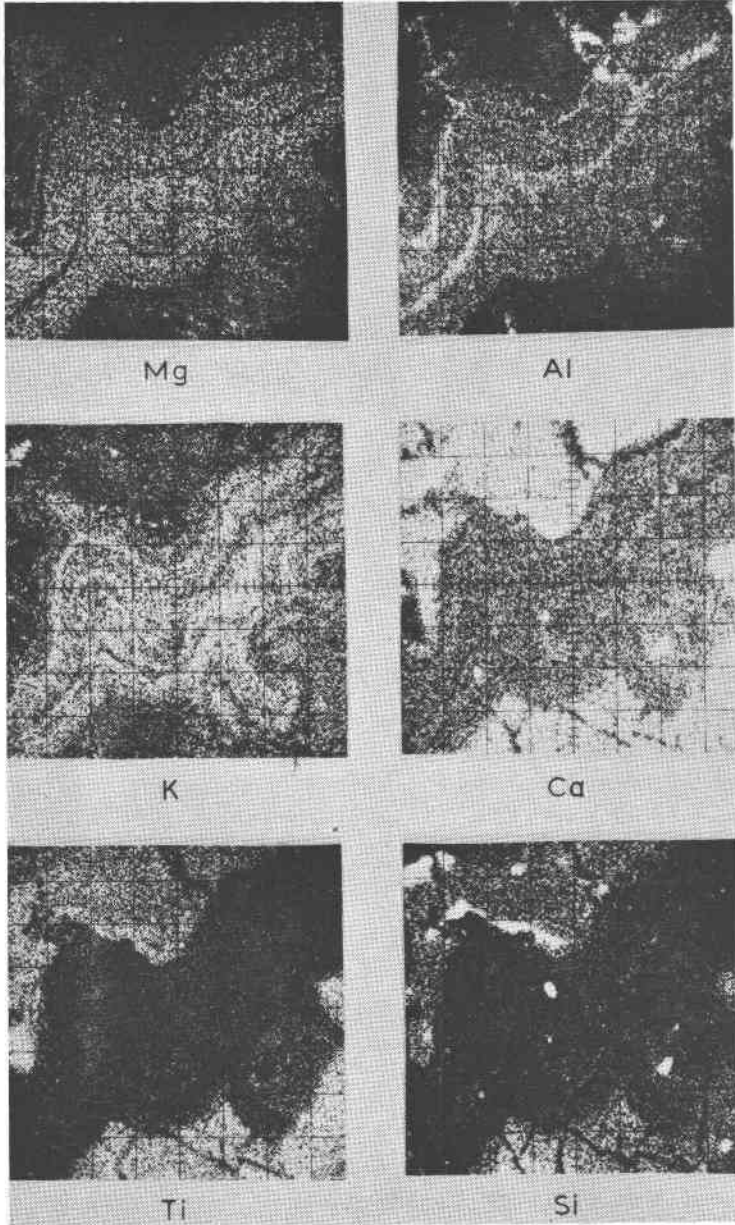


FIG. 1. Electron beam-scanning photographs of back-scattered electrons (B.S.E.) and selected characteristic  $K\alpha$  radiations from a  $360 \times 360$  micron section of a manganese nodule (specimen DWHD-16). Accelerating potential 25 kV. Average concentrations in the bright areas and banded region, respectively, were determined by making traverses along



the vertical section XZ of photograph B.S.E. (wt. % of total nodule) to be: Mn: 23, 31; Fe: 12, 2; Co: 1.2, 0.2; Ni: 0.6, 3.0; Cu: 0.2, 0.5; Mg: 0.7, 2.0; Al: 1.1, 3.0; K: 0.3, 1.2; Ca: 2.2, 0.8; Ti: 1.2, 0.2; Si: 2.5, 0.5; Zn (not shown): 0.1, 0.3.

oscilloscope screen displaying back-scattered electrons (B.S.E.) and illustrates the characteristic textural features in manganese nodules of concentric and fluted banding, and accumulations of micro-nodules. The bands, which are 10–150 $\mu$  wide and rather sporadic in specimen DHWD-16, are narrower and more continuous in some of the other nodules examined. The brighter areas in photograph B.S.E. (Fig. 1) are regions of higher mean atomic number, a contrast control having been adjusted to accentuate the differences. The bright areas consist of an intimate mixture of hydrated  $\delta$ -MnO<sub>2</sub> (average atomic number <29) and hydrated amorphous FeOOH (average atomic number <22), the cracked appearance resulting in part from dehydration of the surface by heating under the electron beam. The darker, banded areas are composed mainly of hydrated "7 Å manganite" (average atomic number of 4MnO<sub>2</sub>·Mn(OH)<sub>2</sub>·2H<sub>2</sub>O is 20).

The remaining pictures in Fig. 1 are photographs of the oscilloscope screen displaying K $\alpha$  radiation of various elements. Bright areas are regions of higher element concentrations relative to dark areas. Exposure times for the minor elements (Co, Ni, Cu, K, Ca, Ti, Mg, Al and Si) are variable and are longer than those for manganese and iron with the result that continuous radiation contributes significantly to the signal and tends to obscure details of minor element enrichment (for example Cu). Nevertheless, minor element correlation is very evident from inspection of Fig. 1, which shows that Ni, Cu, Mg, Al and K occur with Mn in the banded areas, and Co, Ti, Ca and Si occur with Fe in the regions of higher average atomic number. Wavelength scanning at various points in the bright and banded areas (photograph B.S.E.) indicate that Zn is enriched with Ni and Cu, Ba with K, and Mo, Pb, Ce and Zr are enriched with Ti in the bright, iron-rich areas containing  $\delta$ -MnO<sub>2</sub>.

Analyses taken during the specimen traverses along the vertical section XZ in photograph B.S.E. of Fig. 1 are illustrated in Fig. 2. The inter-element relationships and phase enrichments shown in Fig. 2 complement those portrayed in the beam-scanning photographs in Fig. 1, even to minor fluctuations.

Element correlations similar to those described for specimen DWHD-16 exist in each of the other nodules examined. Differences are of a minor character and are related to the nature of the manganese oxide phases. Many of the nodules contain the "10 Å manganite" instead of the "7 Å manganite" and  $\delta$ -MnO<sub>2</sub>, and have correspondingly a lower cobalt concentration. This observation is in accord with thermodynamic calculations (Burns, 1965) which indicate that cobalt is enriched in manganese nodules containing higher oxidation state manganese oxide phases. In the

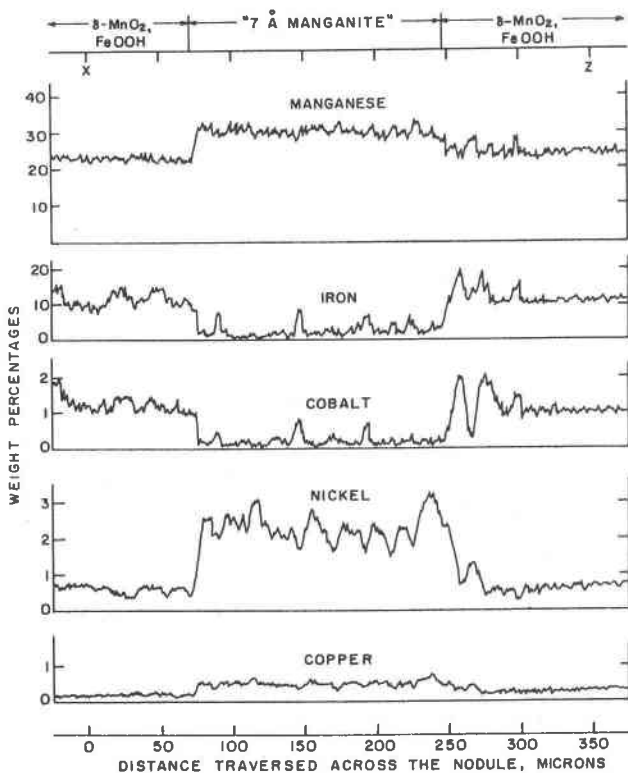


FIG. 2. Analyses made during specimen traverses across section XZ (photograph B.S.E. of Fig. 1) of the manganese nodule DWHD-16. Calibrations were made against pure metal standards.

manganese nodules containing the "10 Å manganite," Ni, Cu, Zn, K and Mg are enriched with manganese in the "10 Å manganite" layers, and Co, Ca and Ti are enriched in regions high in iron concentration.

#### CONCLUSIONS

The results obtained in the present electron-probe investigation of manganese nodules may be summarized as follows:

1. The iron concentration fluctuates whereas the manganese concentration is relatively uniform throughout a manganese nodule, being slightly higher where iron is low.
2. There is a distinct correlation between Fe, Co, Ti, and Ca.
3. There is a pronounced element coherence between Ni, Cu, Zn, and Mg, and between K and Ba. These elements are enriched with Mn and Al in regions of a nodule where the iron concentration is low.

4. The pronounced inter-element relationships suggest that isomorphic substitution is an important factor controlling minor element distribution in manganese nodules. The ions  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Ba}^{2+}$  substitute for  $\text{Mn}^{2+}$  in the "manganite" phases, Co (III) occurs with Fe (III) in hydrated iron oxide phases (Burns, 1965) and Ti (IV) in  $\delta\text{-MnO}_2$ .

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