

## AN OCCURRENCE OF PERMIAN MANGANESE NODULES NEAR DILLON, MONTANA

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*Abstract.*—Concentrically ringed manganese nodules, similar in form to many found on modern ocean and sea floors, occur in a very fine grained argillaceous sandstone bed of the Permian Park City Formation near Dillon, Mont. They are enriched in many rare elements and contain as much as 2.5 percent zinc, 1.3 percent nickel, and 0.22 percent cobalt. The manganese minerals are chalcophanite and todorokite. The nodules probably formed in a shallow marine oxidizing environment on the western side of the Permian sedimentary basin. The occurrence of an appreciable amount of fluorite in the bed suggests that the water was saline.

A review of manganese-iron accumulations in the marine environment by Manheim (1965) shows that they are widely distributed on modern ocean and sea floors, are of great variety in form, and contain unusual amounts of many rare elements in large-abundance ranges. It is the concentrically ringed nodules that have received the most attention, probably due largely to Mero's (1960) stimulating assessment of the economic potential of the nodules and such associated elements as nickel, cobalt, and copper. Present-day abundance of the nodules is a puzzling contrast to their apparent rarity in the geologic column. The only well-documented occurrence is in the Cretaceous rocks of parts of Indonesia (Molengraaff, 1916, 1921; Audley-Charles, 1965). The nodules described here in Permian rock of Montana are considered to represent another ancient occurrence.

The Permian manganese nodules (iron-poor) that occur in the Park City Formation represent a mode of rare-element enrichment in the Permian rocks of the northern Rocky Mountains not previously described. Only one other occurrence of rare-element enrichment associated with manganese (non-nodular) is known. This is in a thin mudstone near the base of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation at Trail Canyon, Idaho (McKelvey and others, 1953, p. 29, bed P-3), shown by X-ray spectrographic analysis

to contain approximately 2 percent manganese, 1 percent zinc, and 0.3 percent nickel. Zinc and nickel, the most abundant rare elements in the manganese nodules, are among those elements enriched in the vanadiferous zone of the Meade Peak in western Wyoming and southeastern Idaho (Love, 1961; McKelvey, 1950; Davidson and Lakin, 1961). The organic-matter- and sulfide-rich vanadiferous mudstone represents a depositional environment, however, that contrasts sharply with the strongly oxidizing one required for the formation of the manganese nodules. Although many rare elements are enriched in both modes of occurrence, some of their magnitudes of enrichment are markedly different.

### GEOLOGIC SETTING

The Permian manganese nodules occur in a very fine grained argillaceous sandstone bed of the Franson Tongue of the Park City Formation at Sheep Creek, about 15 miles southwest of Dillon, Mont. (see index map, fig. 1). The Permian section at Sheep Creek was measured, described, and sampled by members of the U.S. Geological Survey as part of an investigation of the Permian phosphate deposits in the Western States, and a spectrographic analysis of a group of the manganese nodules was reported by Swanson and others (1953, sample ERC-388, p. 18). The Franson Tongue is 100.4 feet thick at Sheep Creek, where it consists of interbedded chert, dolomite, and sandstone (Cressman and Swanson, 1964, p. 434-436). The nodule-bearing bed, 2.3 feet thick, occurs near the top of the Franson (fig. 2). The black nodules are enclosed by a dusky-yellowish-orange sandstone matrix that is similar in appearance to both overlying and underlying sandstone beds. About 3 feet above the nodule-bearing bed lies the base of the Retort Phosphatic Shale Member of the Phosphoria Formation. This unit is not only rich

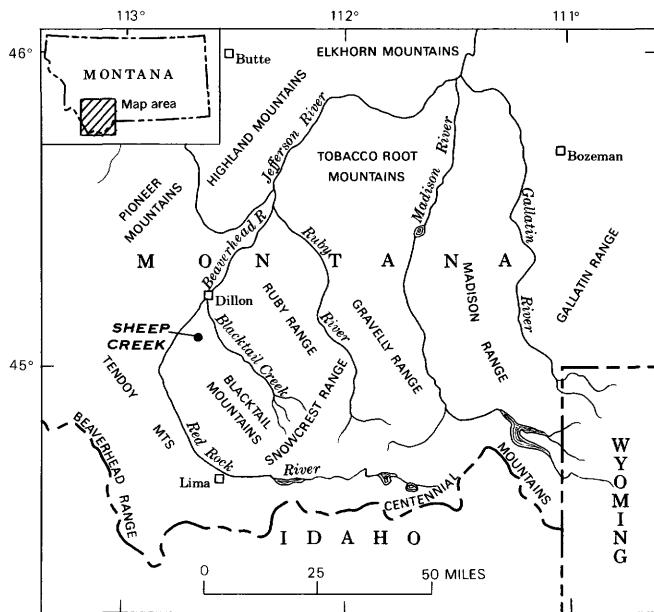


FIGURE 1.—Index map showing location of Sheep Creek manganese nodule occurrence.

in phosphate but contains much oil—one bed as much as 9.7 percent oil (Swanson and others, 1953, p. 23).

The manganese nodules exposed in a bulldozer trench at Sheep Creek have not been recognized at any other locality; the nearest locality containing the interval exposed at Sheep Creek is about 5 miles to the west. Cressman and Swanson (1964), in a detailed study of the origin of the Permian rocks in southwestern Montana, show the Sheep Creek section to be located on the western side of the sedimentation basin but on the eastern edge of the sand facies whose constituents were derived from a northwestern source. They conclude that during deposition of the Franson, which was characterized by the formation of dolomite, the sea was warmer and more saline than normal. The sand of the Franson is considered to have accumulated at depths of less than 50 meters.

Weaver (1955), in a petrographic study of some of the Permian rocks below the Retort Phosphatic Shale Member, including those of the Franson at Sheep Creek, considers the source of the detritus to be chiefly older sediments. He found that kaolinite was the principal clay mineral in the detrital rocks at Sheep Creek, and at another locality about 30 miles to the south, constituting as much as 20 percent of some rocks. At a locality about 25 miles northwest of Sheep Creek, however, illite is more abundant than kaolinite. Weaver found two occurrences of montmorillonite, one in an insoluble residue of carbonate rock at a locality south of Sheep Creek, the other in some small veins in dolomite at Sheep Creek near the base of the Franson Tongue. Three clay layers described by Swanson and

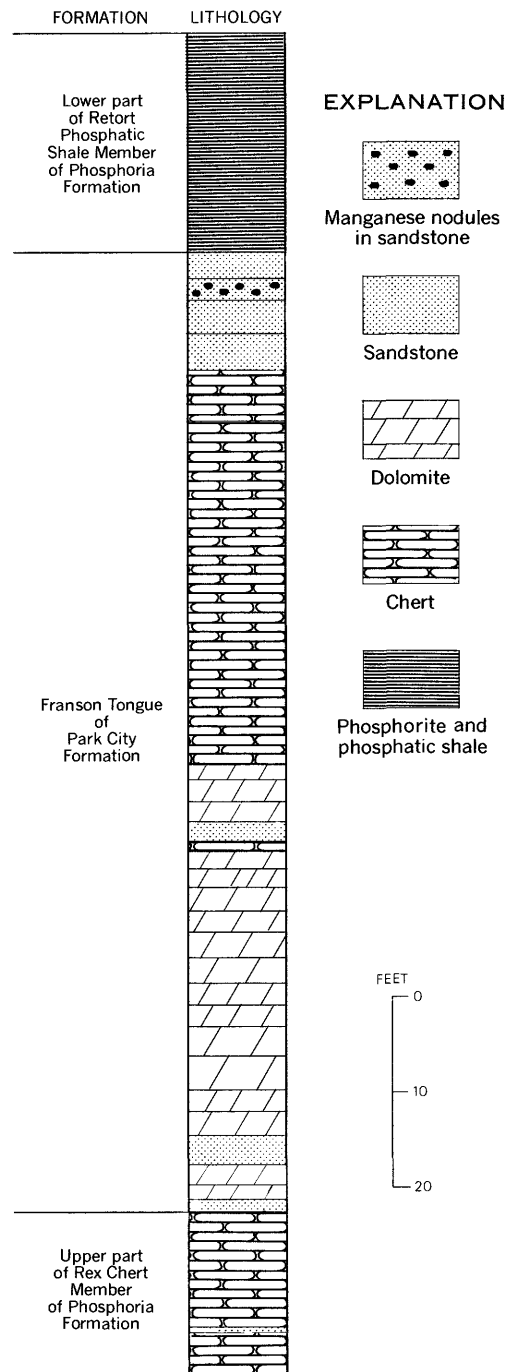


FIGURE 2.—Part of Permian stratigraphic section at Sheep Creek, Mont. Data from Cressman and Swanson (1964, p. 434-436).

others (1953, p. 18) within a chert bed about 50 feet below the top of the Franson at Sheep Creek appear to contain significantly more montmorillonite than kaolinite. Semiquantitative spectrographic analyses (Swanson and others, 1953, p. 21, 22) indicate also that the layers may be enriched in manganese, nickel, and zinc. It is possible that these layers are partly of

bentonitic origin and are an indication of the Permian volcanism that occurred west of here. No montmorillonite is present in the manganese-nodule-bearing bed or adjacent ones, however, and the significance of these layers is not known.

### THE MANGANESE NODULE BED

The manganese nodules are most abundant in the upper part of the very fine grained sandstone bed in which they are found. They occur in a variety of shapes, but tend to be spherical (see fig. 3). The common size is about 2-4 centimeters in diameter, the range about 0.5 to 8 cm. There are compound nodules (see fig. 4) that well illustrate the growth of the nodules outward from a nuclear area. Note in the section of the compound nodule (fig. 4) that the inner growth rings define two discrete nodules and that the outer ones are continuous around both. Nearly all nodules show well-defined growth rings, but in some the rings are diffuse. No nuclear material that is foreign to other parts of the nodules has been discovered, and qualitative X-ray spectrographic analyses of inner and outer parts of the nodules reveal no marked compositional differences. The surfaces of the nodules are irregular, pustulate—some with marked protuberances. Although attention is devoted here to the nodules, all of the manganese is not in this form. Some is lightly and irregularly disseminated in the sandstone and in streaks that parallel the bedding.

#### Mineral composition

The nodules are composed of two manganese minerals, chalcophanite and todorokite, plus quartz, dolomite, fluorite, kaolinite, apatite, goethite, and trace amounts of muscovite-illite. Except for the manganese minerals, the mineral suite is the same as that of the host rock or matrix for the nodules. Quartz appears to be the most abundant mineral, although the combined manganese minerals may be greater in some nodules. Dolomite is a major constituent in some nodules. Fluorite, kaolinite, and apatite are consistently present in small amounts. Goethite, although in small amount, appears to provide the dusky-yellowish-orange coloration of the matrix rock. Fluorite is irregularly distributed as microcrystalline aggregates; its significance is discussed later in the paper.

Because the regular constituents of the matrix rock are incorporated in the manganese nodules, the nodules must have developed either contemporaneously with sedimentation or at some later time. The bedding, which is poorly developed, provides no clue in this regard.

Efforts to separate and concentrate todorokite were not successful, and the mineral is identified solely on the

basis of its principal X-ray peaks of about 9.6 angstroms and 4.8 angstroms. Chalcophanite, however, was found to make up the residue, along with fluorite, after treatment of a portion of a nodule with concentrated HF. X-ray data shown in table 1 were obtained from this sample. The main peaks of chalcophanite are discernible on all X-ray patterns of the nodules but characteristically are of small intensity. The todorokite peaks are barely evident on most patterns but are relatively strong on some. A protuberance on one nodule showed the strongest todorokite peaks. On the basis of X-ray intensities, therefore, chalcophanite is the predominant manganese mineral in the nodules; however, possible differences in crystallinity or ordering of the phases makes any estimate of relative magnitudes somewhat tenuous.

TABLE 1.—X-ray diffraction data of chalcophanite

[ND, not determined]					
Montana <sup>1</sup>		Sterling Hill, Franklin, N.J. <sup>2</sup>			
<i>d</i> (measured)	<i>I</i>	<i>d</i> (measured)	<i>I</i>	<i>d</i> (calculated)	<i>hkl</i>
6.96	100	6.96	10	6.95	001
6.26	15	6.23	1	6.22	010
4.08	25	4.08	5	4.07	011
3.51	35	3.50	6	3.51	112
3.47	25			3.47	002
3.31	15	3.32	1	3.31	121
( <sup>3</sup> )		3.23	½	3.22	221
2.76	15	2.77	2	2.76	222
2.70	5	2.71	½	2.71	012
2.56	15	2.57	4	2.57	021
				2.55	122
2.45	60	2.46	2	2.45	130
2.41	25	2.41	2	2.42	113
2.40	25			2.40	231
2.23	50	2.24	5	2.23	131
2.12	5	2.13	2	2.12	232
ND		1.986	½	1.985	013
( <sup>3</sup> )		1.900	3	1.898	132
ND		1.849	1	1.842	333, 031
1.794	10	1.795	2	1.801	341
				1.790	233
ND		1.750	½		
ND		1.715	½		
( <sup>3</sup> )		1.668	1		
1.593	20	1.597	4		

<sup>1</sup> Cu radiation,  $\lambda=1.5418$  Å. CaF<sub>2</sub> internal standard.

<sup>2</sup> Data from Berry and Thompson (1962, p. 206).

<sup>3</sup> Obscured by CaF<sub>2</sub> peak.

Although Palache and others (1944, p. 739) show chalcophanite to be principally a hydrated oxide of zinc and tetravalent manganese, recent reports (Hewett



FIGURE 3.—Permian manganese nodules. Light spots on nodules are bits of rock matrix.

and Radtke, 1967; Radtke and others, 1967) of new occurrences indicate that many elements may replace zinc. Radtke and others (1967) have named one silver-rich variety, aurorite, that contains only 0.25 percent ZnO. They derived a general formula for aurorite,  $(R)R_3O_7 \cdot 3H_2O$ , that is in agreement with Wadsley's (1953) structural analysis of chalcophanite and the formula  $ZnMn_3O_7 \cdot 3H_2O$ . In the mineral series, therefore, the data indicate that R represents Zn,  $Mn^{+2}$ , Ag, Ba, Ca, Mg, K, Pb, and Cu; and R' includes  $Mn^{+4}$ ,  $Fe^{+3}$ , Al, and Si. Not only is the number of elements that appear to be able to fit in the R position large but the range in ionic radii is unusual—0.69 Å for Mg to 1.34 Å for Ba.

Because chalcophanite probably is the principal manganese mineral of the nodules described here, the chemical analysis of two nodules, table 2, provides some information about the mineral's composition. The elements concentrated in the nodules along with manganese, as contrasted with the matrix rock (analysis 3), are Zn, Ni, Cd, Co, Tl, Cu, and Mo. That they are associated with the chalcophanite was shown by a qualitative X-ray spectrographic analysis of the chalcophanite-fluorite concentrate, referred to above, in which the proportions relative to Mn appear to be approximately the same as in a similar analysis of the whole sample. If all these elements are indeed in chalcophanite, the number and range of ionic sizes of elements in the mineral are both extended beyond the above list. The principal constituents, in addition to  $Mn^{+4}$  and  $H_2O$ , appear to be Zn,  $Mn^{+2}$ , Ni, Cd,

and Co. The other major constituents in the analyses are adequately accounted for by other mineral phases.

Since attempts to concentrate todorokite were unsuccessful, direct evidence of its composition in this occurrence is lacking. Much recent data however, on the composition of todorokite is available. Like chalcophanite, todorokite is basically a hydrated tetravalent manganese oxide. It even appears to have a zinc analog, woodruffite (Fron del, 1953). Todorokite also apparently may contain about the same large and varied suite of elements (Hewett and Fleischer, 1960; Straczek and others, 1960; Fron del and others, 1960; Levinson, 1960; Larson, 1962; Radtke and others, 1967). The difference between the two minerals seems to be in the cation proportions and amounts of  $H_2O$ . At present there is no agreement among the workers on the specific composition and structure of todorokite. The composition of todorokite in the nodules described here, therefore, is probably similar to chalcophanite, the elements available in this occurrence being distributed between two different yet similar structures.

Unlike chalcophanite, which has not previously been identified in marine manganese nodules, todorokite is a widespread component of modern nodules and possibly the principal one (Straczek and others, 1960, p. 1176; Hewett and others, 1963, p. 38; Manheim, 1965, p. 248; Meylan and Goodell, 1967, p. 149). Both minerals appear to be of primary formation in the Permian nodules. They are of secondary formation in occurrences in some manganese deposits of other origins (Hewett and Fleischer, 1960, p. 11, 13).

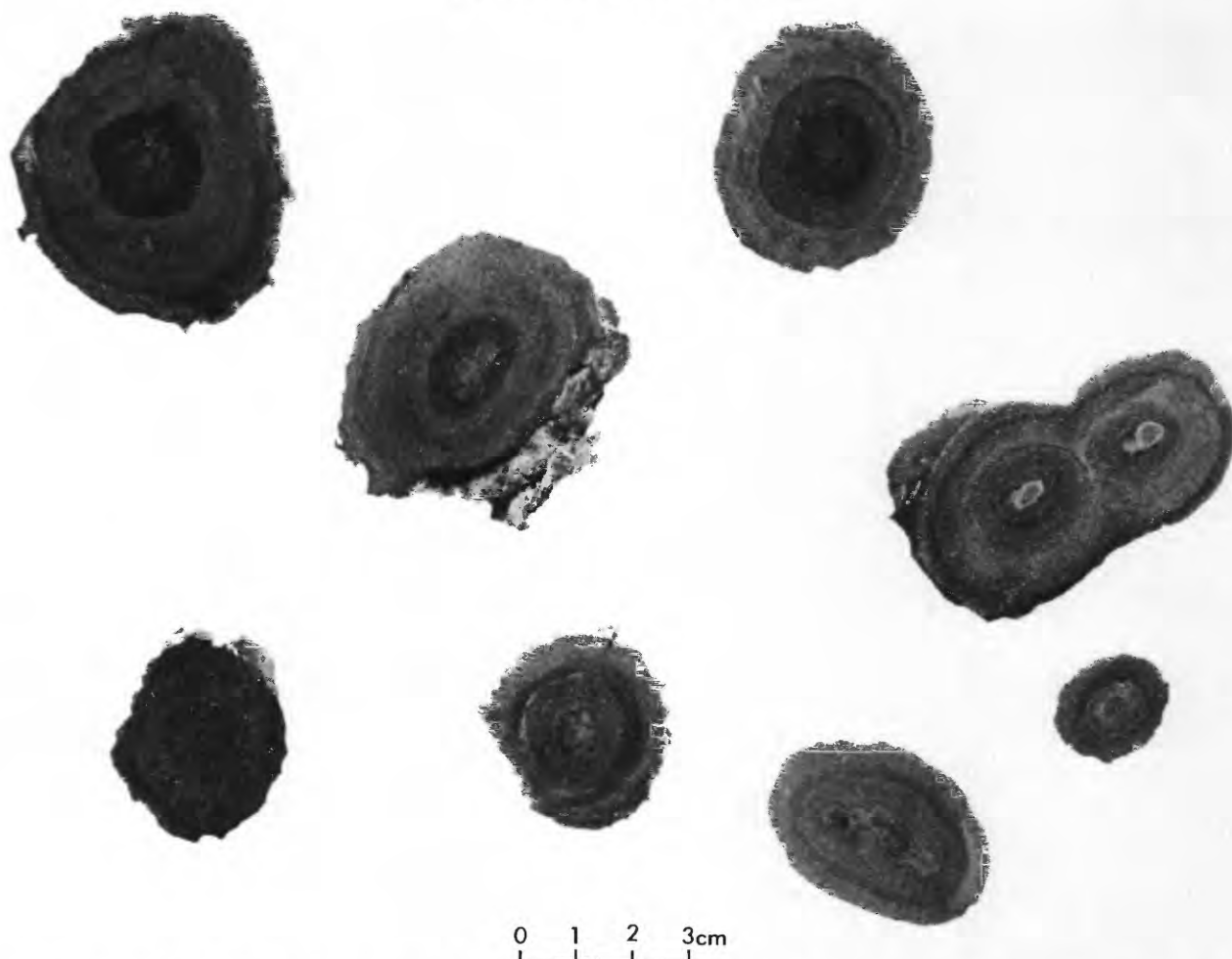


FIGURE 4.—Sawed halves of Permian manganese nodules, showing concentric growth rings. Note compound nodule on right side of photograph.

#### Chemical composition

Manganese nodules are possibly most noted for their contents of nickel, copper, and cobalt. The chemical analyses of the Permian nodules, table 2, reveal this characteristic, although the amount of copper is unusually low relative to the amounts of nickel and cobalt and in comparison with Manheim's estimated averages of the amounts in deep-ocean nodules shown in table 2. Nickel, on the other hand, is unusually high in Permian nodule 1. The individual amounts of these three elements, of nickel especially, tend to characterize the marine manganese nodules, as shown by the data of Hewett and others (1963) in comparison with other geologic environments of manganese deposition—supergene oxides, hypogene vein oxides, hot-spring apron oxides, and stratified oxides.

The amounts of zinc in the Permian nodules are the highest so far reported—about 3 to 4 times greater than the maximum of 0.6 percent Zn found by Riley and Sinhaseni (1958, p. 477) in a Pacific nodule. Cadmium, similar geochemically to zinc, is also high,

and both are above expected amounts in the matrix rock. The reason for this is not known; no other zinc mineral has been recognized, even among the heavy accessory minerals of the matrix rock.

The amount of iron shown in Manheim's average nodule (table 2) is about the same magnitude as manganese, whereas the amounts in the Permian nodules are extremely low, near the minimum of 0.8 reduced weight percent found by Mero (1962, table 2, p. 762) in Pacific nodules. The amounts present are apparently due to background sedimentation as indicated by the amount in the matrix rock (analysis 3 in table 2). This suggests that the separation of iron from manganese in solution occurred elsewhere, owing to the greater ease of oxidizing the ferrous ion than manganese ion (Krauskopf, 1957), and because only manganese was available for oxidation and fixation in the nodules of this locality.

Vanadium and molybdenum are moderately concentrated in the nodules as compared with the matrix

TABLE 2.—Chemical composition, in weight percent, of manganese nodules and matrix rock

	Deep ocean average nodule <sup>1</sup>	Permian nodule 1 <sup>2</sup>	Permian nodule 1 <sup>2</sup>	Permian matrix 3 <sup>3</sup>
<b>Oxides</b>				
SiO <sub>2</sub> -----	16.2	38.5	49.8	-----
Al <sub>2</sub> O <sub>3</sub> -----	4.6	5.6	3.5	5.7
TiO <sub>2</sub> -----	.94	.08	.10	.08
Fe <sub>2</sub> O <sub>3</sub> (total)-----	16.7	.61	.55	1.4
MnO(total)-----	24.5	18.69	7.47	.04
CaO-----	2.2	14.0	13.8	4.2
MgO-----	2.3	.23	4.2	.12
K <sub>2</sub> O-----	.82	-----	-----	-----
Na <sub>2</sub> O-----	2.8	.07	.04	.04
P <sub>2</sub> O <sub>5</sub> -----	.44	2.1	1.9	4.6
CO <sub>2</sub> -----	.61	.93	9.3	-----
H <sub>2</sub> O+-----	-----	5.8	4.1	-----
H <sub>2</sub> O-----	-----	2.6	1.1	-----
O(excess)-----	5.0	3.42	1.20	-----
Ignition loss-----	25	-----	-----	-----
<b>Elements</b>				
F-----	-----	6.4	3.1	-----
Zn-----	0.04-0.4	2.5	1.4	.15
Ni-----	.58	1.3	.68	.007
Co-----	.28	.22	.08	.0015
As-----	-----	.04	.06	-----
B-----	.01	.0015	.0015	.002
Ba-----	.15	.01	.03	.01
Cd-----	.001	.12	.05	.015
Cr-----	.001	.007	.01	.01
Cu-----	.40	.02	.015	.002
Mo-----	.038	.007	.005	.0015
Sc-----	.001	.001	.0007	.0015
Sr-----	.06	.01	.01	.01
Te-----	-----	.0001	.0001	-----
Tl-----	.01	.1	.03	0
V-----	.044	.07	.07	.02
Y-----	.013	.002	.003	.005
Yb-----	.0025	.0003	.0003	.0005
Zr-----	.040	.007	.015	.02

<sup>1</sup> Data from Manheim (1965, p. 245 and 247).

<sup>2</sup> SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO of nodule 2, CaO, H<sub>2</sub>O+, H<sub>2</sub>O-, TiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, CO<sub>2</sub>, F, Ni, As, and Zn analyses by Lois Schlocker, A. C. Bettiga, and W. W. Brannock. MnO and excess O analyses by S. Neil. Cd, Co, and MgO of nodule 1 are quantitative spectrographic analyses by R. E. Mays. Te analyses by H. M. Nakagawa. Other elements are semiquantitative spectrographic analyses by Chris Heropoulos.

<sup>3</sup> Semiquantitative spectrographic analyses by Chris Heropoulos.

rock and are among those elements expected in this mode of occurrence.

Arsenic, for which few data have been reported, is present in the Permian nodules in amounts about 30 to 45 times greater than in average shale (Turekian and Wedepohl, 1961). Sevast'yanov (1967) has reported arsenic contents of manganese-iron concretions, oxidized sediment, and reduced sediment in the Black Sea as 380-910 parts per million, 26-61 ppm, and 3-26 ppm, respectively. The amounts in the Permian nodules (table 2) agree well with Sevast'yanov's values, and his range for reduced sediments includes the value of 13 ppm as given by Turekian and Wedepohl (1961) for average shale. Sevast'yanov attributes the enrichment of arsenic in the oxidized sediment and in the nodules to its polyvalent character, where, like manganese, its higher valent ion is readily formed and fixed in an oxidizing environment.

Thallium is enriched in the Permian nodules about 3 to 11 times more than Manheim's average nodule (table 2), which itself is a significant concentration as compared with the 1.4 ppm of shale (Turekian and Wedepohl, 1961). Little is known about thallium, but because it is readily adsorbed by clays (Krauskopf, 1955, p. 453), its concentration in the nodules may be due to the well-known adsorption capability of manganese.

Rare earths, including yttrium, are frequently enriched in manganese nodules by an order of magnitude over their abundance in marine sediment (Ehrlich, 1968, p. 18, 67) and also show a distribution pattern characterized by an enrichment of cerium. The value Manheim gives for yttrium in table 2 is representative of this total rare-earth enrichment. The values for yttrium in the Permian nodules are well below Manheim's and, in comparison with the amount in the matrix rock, indicate no enrichment. This is substantiated by the complete determination (shown in table 3) of

TABLE 3.—Rare-earth content of a Permian nodule from the Permian Park City Formation near Dillon, Mont.<sup>1</sup>

Element	Content (ppm)
La-----	12.7
Ce-----	11
Pr-----	3.37
Nd-----	11.5
Sm-----	2.52
Eu-----	.58
Tb-----	.38
Dy-----	2.12
Ho-----	.59
Tm-----	.172
Yb-----	.92
Y-----	18.9

<sup>1</sup> Data from Ehrlich (1968, p. 67), who also reported the following (p. 69): Mn (6.4 percent), Ca (9.4 percent), C as CO<sub>2</sub> (17 percent), P (1.1 percent), and Fe (0.30 percent)

the rare earths in one of these Permian nodules (6.4 percent Mn) by Ehrlich (1968, p. 67). Of special interest is Ehrlich's finding that the distribution pattern of the rare earths in the Permian nodule indicates a cerium depletion, rather than enrichment, similar to what he found for phosphorite material and to what is shown for marine apatite by Altschuler and others (1967). It seems likely, therefore, that the rare-earth content of the Permian nodules and matrix rock is mostly due to the apatite common to both, and perhaps the rare earths, as a whole, have been preferentially taken up by the apatite, which makes up a greater part of the total rock than the manganese minerals do.

Tellurium is reported by Lakin and others (1963, p. 1568-1569) to be present in a group of 12 nodules from the Pacific and Indian Oceans in amounts ranging from 5 to 125 ppm. They note the possibility of an association of these unusual amounts of tellurium with volcanic emanations. The determinations of 1 ppm for the Permian nodules fall somewhat below the lowest

value given by Lakin and others, but still represent an appreciable concentration over the 0.01-ppm value given for average clays and shales by Vinogradov (1962).

### SIGNIFICANCE OF FLUORITE

The presence of a significant amount of fluorite in the nodule bed is of particular interest. Hewett and Fleischer (1960, p. 6) note that fluorite is generally considered to be of hydrothermal and hypogene origin in its association with many manganese deposits. Few data of the occurrence here can be interpreted to support this mode of origin. On the other hand, Kazakov and Sokolova (1950) cite many occurrences of sedimentary fluorite in evaporitic sequences of dolomite, dolomitized limestones, and gypsum and anhydrite; and their experimental work supports this mode of origin. Occurrences in the Permian rocks of the northern Rocky Mountain region provide additional examples of sedimentary origins.

Fluorite is widespread in very small amounts in some phosphorites of the Phosphoria Formation, but it is secondary in these occurrences and apparently is the product of a diagenetic reorganization of apatite. Rare occurrences in Permian carbonate rocks of Wyoming have been noted by Sheldon (1963, p. 144) and Gulbrandsen (1960, p. 114). Of most significance, however, is a remarkable occurrence in a Permian carbonate rock sequence in the northern part of the Big Horn Basin of Wyoming that is reported by DeKoster (1960, p. 53-55). He found 12-15 percent fluorite in a dolomitic limestone. Of special importance is the facies change he shows eastward from the carbonate sequence to one within 20 miles that is dominated by gypsum. A possible interpretation of this spatial relationship of fluorite and gypsum is that the fluorite was precipitated from saline waters at a stage of evaporation shortly preceding that at which gypsum is formed. If this were so, the position within an evaporite sequence for the formation of fluorite, as predicted by Kazakov and Sokolova (1950) on the basis of experimental work, is further affirmed. Their data indicate that this could occur at a stage where sea water was concentrated 3 to 4 times. Fluorite could precipitate at an earlier stage of sea-water concentration if an extra supply of fluorine were possible, such as from the dissolution of pyroclastic material in sea water or from volcanic gases. Mansfield (1940), of course, indicated Permian volcanism as an extra source for fluorine as an aid in forming apatite of the Phosphoria Formation. An association of volcanism and phosphorite formation does appear to exist (Gulbrandsen, 1969), but its significance is not yet clear.

A primary sedimentary origin for the fluorite in the nodule bed is considered plausible and is not inconsis-

ent with any other features. It probably indicates, however, a more saline environment for the formation of manganese nodules than any known so far.

### SUMMARY

The manganese nodules described here are considered to have formed virtually syngenetically with their enclosing sediments in a shallow marine environment. The features of this single occurrence in Permian rock in Montana are not identical in all aspects with any known occurrence on the modern sea or ocean floors, but none of the many and broadly ranging characteristics of modern deposits appear to uniquely define a marine origin. An epigenetic hypogene origin in which manganese and associated elements would have been transported by hydrothermal solutions laterally along bedding into this depositional site cannot be disproved, but it is an origin for which positive evidence is meager.

Features of this deposit that appear particularly significant in a concept of marine origin are the following:

1. Both manganese minerals, chalcophanite and todorokite, appear to be of primary formation in this occurrence.
2. The high nickel content of one of these nodules (analysis 1 of table 2) is especially characteristic, although not unique, of many nodules of marine origin.
3. The occurrence of manganese in the form of discrete nodules that tend to a spherical shape and show concentric growth rings is a common feature of marine deposits and not characteristic of deposits of other origins.

The features of this occurrence of manganese nodules do not provide any conclusive information as to the source of the manganese and associated elements. An association with Permian volcanism is possible, but the wide distribution of modern nodules, as shown by Manheim (1965), including areas remote from any possible volcanic effects, indicates that the ocean itself, and the supply of elements from the continents, is a sufficient source. The deposition of manganese, therefore, seems to be principally dependent upon a special environment, one that is strongly oxidizing and can raise  $Mn^{+2}$  to higher valent forms that are precipitated as oxides. Most of the many elements associated with the manganese are probably adsorbed by the manganese oxides by processes that are poorly understood.

The presence of fluorite in the nodule bed places definite restraints upon a marine origin for the nodules as it requires a marked concentration of sea water beyond that indicated by any other characteristics of

the Permian rocks in the region. The presence of dolomite is compatible in this respect, but probably does not require highly saline waters for its formation. If the Permian sea were somehow enriched in fluorine, a lesser degree of concentration would be required for the formation of fluorite. The subsequent formation of large amounts of apatite in this sea is consistent with a condition of fluorine enrichment, though not required.

It is possible, however, that the conditions under which the manganese nodules were formed are barely perceived at our present state of knowledge of the marine environment. This is forcefully illustrated by the recent discoveries of sedimentary iron and heavy-metal deposits in the Red Sea that appear to be derived from existing hot brines of heretofore unknown compositions (Miller and others, 1966).

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