

Cobalt and Nickel Minerals from Nabae Coast, Muroto City, Kochi Prefecture, Japan

By

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Abstract Cobaltite-gersdorffite solid solutions were found as microscopical aggregates composed of very minute grains in dark grey mudstone exposed at Nabae Coast in the western side of Muroto Peninsula, Muroto City, Kochi Prefecture. It is directly accompanied by bitumen layers involved in mudstone and sandstone of early Miocene Tsuru Formation. They are associated with minor millerite, galena, sphalerite, and a tennantite-tetrahedrite series mineral. Also, tiny smear of molybdenite is found nearby the layers. The constituents of mudstone are quartz, potash feldspar, albite and illite with abundant radiolarian remains. Bitumen and mudstone are cut by veinlets of manganoan ferroan dolomite. The solid solutions have ranging Co: Ni ratios from 7: 3 to 1: 9. In analyses with $\text{Co} > \text{Ni}$, As is nearly equal to S in mole ratio, whereas those with $\text{Ni} > \text{Co}$, As is slightly higher than S. X-ray powder study on the dark grey mudstone indicated that the detected sulphide constituents are the solid solutions, millerite and sphalerite. The diffractions due to the solid solutions are indexed by an apparently cubic cell with $a = 5.605 \text{ \AA}$ including (100), suggesting the real symmetry to be orthorhombic. The a -dimension indicates Co: Ni to be about 4: 1, suggesting the extension of the compositional range of orthorhombic cobaltite. Cobalt and nickel sulphides were precipitated around radiolarian remains or siderite chlorite-aggregate probably replacing foraminifera. Closer situation of the dark grey mudstone involving cobaltite-gersdorffite solid solutions and millerite to bitumen suggests the origin of heavy metals to be bitumen, which contained them probably in an absorbed state, and released them during the process of diagenesis.

Introduction

During the geological survey of Nabae Coast in the western side of Muroto Peninsula, Muroto City, Kochi Prefecture (Fig. 1), one of the authors (Y.S.) collected a piece of dark grey mudstone disseminated by visible grains of cobaltite with minor erythrite. The subsequent survey disclosed the occurrence of bitumen in grey mudstone and the accompanying thin layer of dark grey mudstone in the exposure of mudstone with sandstone at the coast, though no exposure as the parental part to the previous material could be found.

The present work is for the description on the chemical compositions of cobaltite-gersdorffite solid solutions, and millerite together with bitumen as the examples of the unique occurrences of these sulphides in sedimentary rock. The X-ray

powder diffraction study on the mudstone with sulphides indicated the solid solution to be orthorhombic form for which the range of substitution of Ni for Co has been now extended up to about 4: 1, thus the formation of such nickeloan cobaltite takes place under such a diagenetic condition.

Also, a comparative study cobalt and nickel sulphides of the different mode of occurrence was attempted, they being from metamorphosed bedded manganese ore deposits in Mesozoic sedimentary rocks and their metamorphic equivalents in Japan. It indicated that gersdorffites have the same compositional characteristics between two, namely, $As > S$ in all of them, meaning that such a material off stoichiometricity is stably formed under a diagenetic condition.

The close association of metallic elements with bitumen or bituminous material is reviewed by PARNELL (1988), who stated the diversity of the contents. In Japan, the present authors have described the different association of metallic elements with bitumen from Unuma, Gifu Prefecture, central Japan, where they include copper and vanadium as the principal members and the mudstone including the bitumen is accompanied by a lot of nodular aggregates of rhodochrosite with amorphous apatite (MATSUBARA *et al.*, 1990).

Occurrence

At Nabae Coast in the western side of Muroto Peninsula, Muroto City, Kochi Prefecture, early Miocene mudstones and sandstones form Tsuru Formation belonging to the southern zone of Shimanto belt (Fig. 1). The former have generally light reddish purple grey colour and moderately bedded in centimeter order. Partially it comprises black lustreous bitumen layers up to 3 cm thick, which are conformable with the surrounding mudstone. Bitumen in the layers is fractured into millimeter order blocks frequently demonstrating the arrangement of cube-like bodies of bitumen. Such fractures are seen in thicker bitumen layers, whereas in thinner ones fractures are less developed. Around bitumen, the colour of mudstone is faded into light grey as seen in bitumen-bearing mudstone from Unuma, Gifu Prefecture (MATSUBARA *et al.*, 1990) obviously due to the reduction of hematite or goethite contained in the light reddish purple grey one during a prolonged diagenesis where bitumen worked as a reducing reagent. The width of light coloured part is variable and reaches a few meters in maximum. At the footwall side of bitumen layers dark grey mudstone layer reaching a centimeter thick is developed. Though invisible even under magnifier, it contains extremely fine aggregates of cobaltite-gersdorffite solid solutions with minor millerite and sphalerite after the microscopic, X-ray powder, and microprobe studies. Mudstones with faded colour are intersected by dolomite veinlets of millimeter order thick or disseminated by minor dolomite grains. Bitumen is entirely amorphous to polarized light and X-ray and devoid of any heavy elements in the detectable quantities of microprobe analyses.

The sulphides in the dark grey mudstone include cobaltite-gersdorffite solid solu-

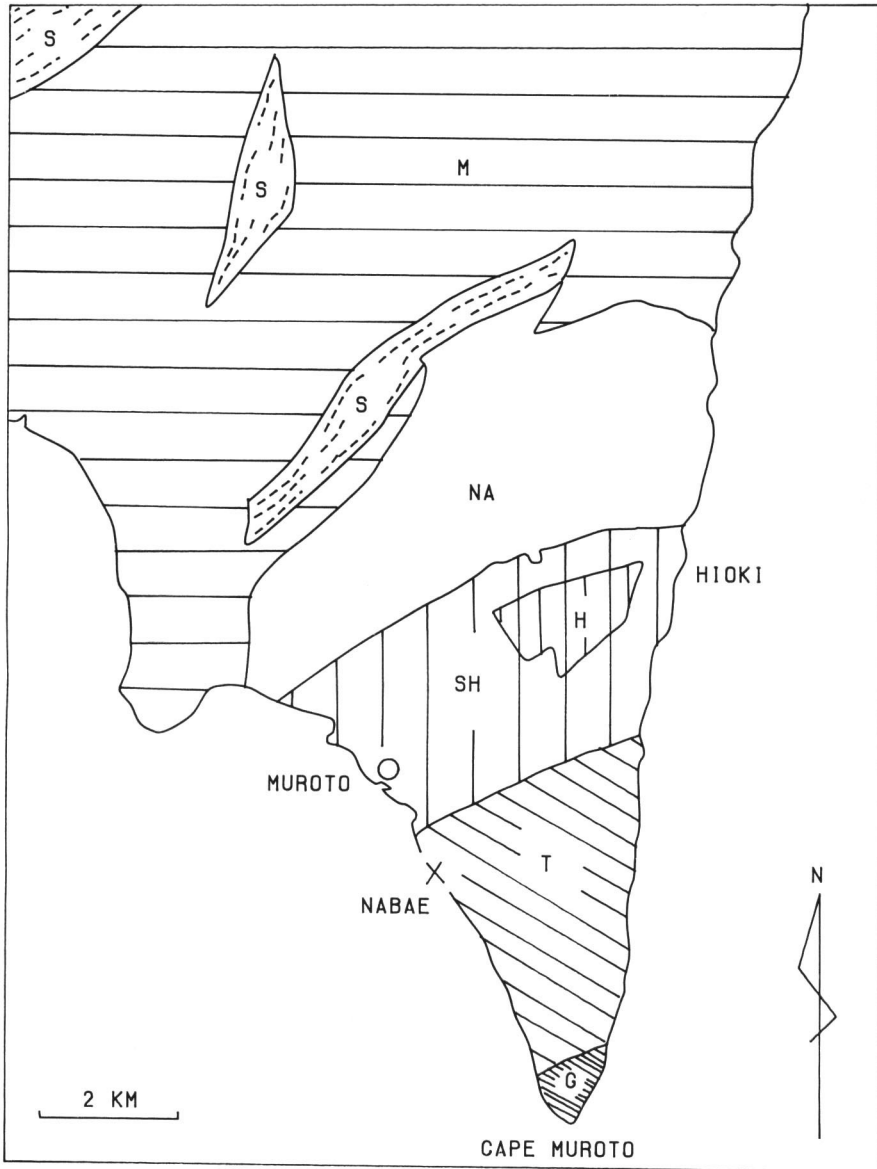


Fig. 1. Index map of the locality of bitumen at Nabae Coast (cross mark), Kochi Prefecture, Japan. The geology is from TAIRA *et al.* (1980) with minor corrections.

Legends: G: gabbroic rocks NA: Nabarigawa Formation S: Sakihama melangé M: Muroto Formation T: Tsuru Formation H: Hioki Formation SH: Shijūjima Formation.

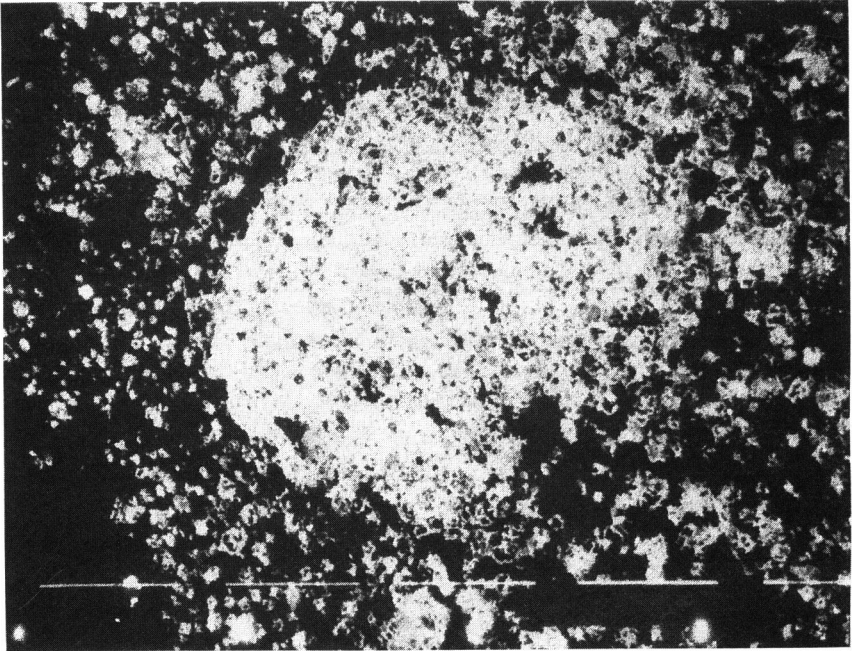


Fig. 2. Back scattered electron image of aggregate of fine grains of cobaltite-gersdorffite solid solutions with minor millerite. Minute dark spots in the aggregate are radiolarian remains. A bar indicates 100 μm .

tions, millerite, galena, sphalerite, and a tennantite-tetrahedrite solid solution. Besides them, a tiny smear of molybdenite is found on fracture walls in mudstone apart from bitumen layers. The minerals forming the colour faded mudstones are quartz, potash feldspar, albite, illite, and dolomite excluding the vein-forming minerals, they being dolomite, aragonite, siderite and chlorite.

Under the electron microscope, cobaltite-gersdorffite solid solutions form spherulitic aggregates up to 300 μm across surrounding radiolarian remains (Fig. 2). Very locally the aggregates reaching visible size interstices clastic materials in the dark grey mudstone. Also, the aggregates embody the aggregate of chlorite and siderite, very probably replacing foraminifera (Fig. 3). Galena occurs as minute discrete grains and accompanies a very small amount of tennantite-tetrahedrite series mineral. Along fractures in mudstones and bitumen, pale pink to nearly white erythrite is formed as crusts or tiny spherules of submillimeter order. Also, a small quantity of annabergite is found in the same mode of occurrence apart from the crust of erythrite, distance between them being a few centimeters. The colour is rather bluish than greenish, probably due to the effect such a minor constituent as Co^{2+} .

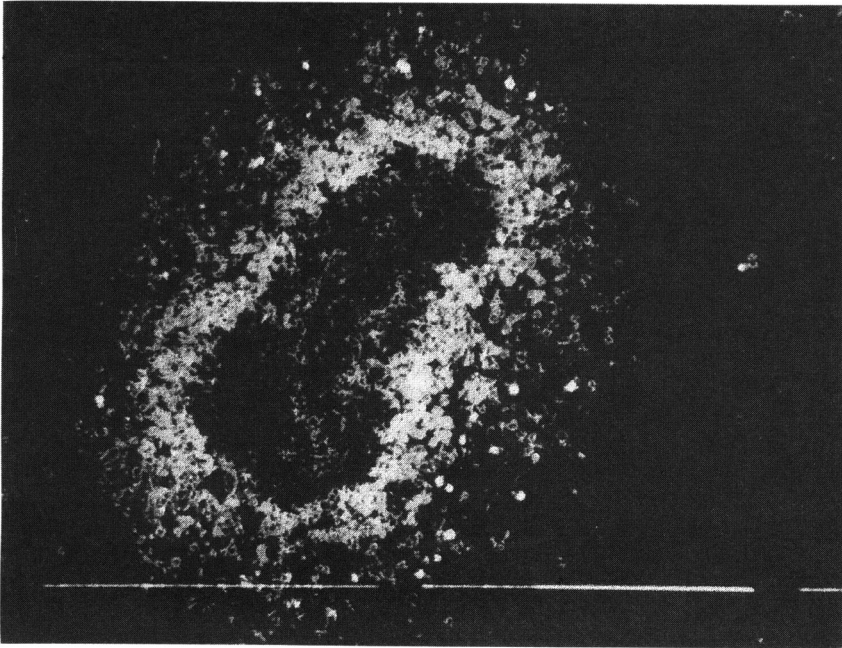


Fig. 3. Back scattered electron image of aggregate of fine grains of cobaltite-gersdorffite solid solutions embodying the aggregate of siderite and chlorite possibly replacing a foraminifera remain. A bar indicates 100 μm .

X-Ray Powder Study of Sulphides

The X-ray powder diffraction study was made on the dark grey mudstone heavily disseminated by sulphides, which were identified as cobaltite with minor millerite and sphalerite (Table 1). Cobaltite is indexed on a cubic cell with $a=5.605 \text{ \AA}$, which is intermediate between those of synthetic CoAsS ($a=5.576 \text{ \AA}$ (BAYLISS, 1969)) and synthetic NiAsS ($a=5.692 \text{ \AA}$ (JCPDS Card No. 12-705)), indicating that the average composition of cobaltite found as microscopical aggregates is a nickeloan cobaltite with $\text{Co: Ni} \cong 3: 1$ if the effects of minor fluctuation of As: S ratio from unity and of the symmetry difference are not considered. The powder pattern has a line indexed as (100) of cobaltite. It is likely that the present cobaltite is crystallographically orthorhombic as indicated by BAYLISS (1982 a), though it is geometrically cubic. The binary system cobaltite-gersdorffite is not crystallographically simple, because in cobaltite at least two different space groups, $\text{Pa}3$ and $\text{Pca}2_1$, are known (BAYLISS, 1982 a) and in gersdorffite at least three, $\text{P}2_13$, $\text{Pca}2_1$, and $\text{Pa}3$, are known (BAYLISS, 1982 b), although $\text{Pca}2_1$ of the latter is considered to be metastable. The present find may extend the range of compositional variation of orthorhombic phase to the nickel richer side.

Table 1. X-ray powder pattern of sulphide mixture composed of cobaltite, millerite, and sphalerite.

1.			2.		h k l		
I	$d_{\text{obs.}}$	$d_{\text{cal.}}$	I	d (Å)	Cob	Mil	Sph
5	5.63	5.61	20	5.56	100		
6	4.80					110	
5	3.967	3.963	10	3.94	110		
			20	3.30	111		
6	3.131						111
5	2.968					101	
60	2.804	2.803	80	2.77	200		
5	2.778					300	
100	2.508	2.507	100	2.49	210	021	
70	2.289	2.288	90	2.27	211		
2	2.233					211	
20	1.981	1.982	60	1.973	220		
2	1.915						220
5	1.863	1.868	10	1.856	221	131	
			5	1.762	310		
1	1.737					401	
40	1.690	1.690	100	1.680	311		
5	1.619	1.618	10	1.608	222		
10	1.556	1.655	40	1.545	320		
20	1.498	1.498	80	1.490	321		
$a=5.605 \text{ \AA}$		$a=5.558 \text{ \AA}$					

1. Mixture of cobaltite, millerite, and sphalerite. Nabae Coast, Kochi Prefecture, Japan. The present study. Diffractometer method. Co/Fe radiation.
2. Cobaltite. Cobalt, Ontario, Canada. JCPDS Card No. 18-431.
(Cob=cobaltite, Mil=millerite, Sph=sphalerite)

Chemical Analyses

Chemical analyses were made by using Link Systems energy dispersive X-ray spectrometer on cobaltite-gersdorffite solid solutions, millerite, dolomite, siderite and chlorite. Also, C, H, and N in bitumen were analysed by microgravimetric method (Tables 2 to 5).

The chemical compositions of cobaltite-gersdorffite solid solutions vary extensively. Co: Ni ratios range from 7:3 to 1:9 even in a single aggregate (Nos. 1 and 6 in Table 2). As seen in this table, there is a marked compositional tendency in them. That is, the materials with $\text{Co} > \text{Ni}$, *i.e.*, cobaltite, have $\text{S} > \text{As}$, whereas those with $\text{Ni} > \text{Co}$, *i.e.*, gersdorffite, have $\text{As} > \text{S}$. No. 1 cobaltite in Table 2 has Co: Ni=7:3 and As: S=49:51, while No. 6 gersdorffite has Co: Ni=1:9 and As: S=52:48, indicating the tendency even in a single aggregate. It depicts a peculiar property of gersdorffite to have such an off stoichiometricity in the materials formed under such a low

Table 2. Chemical analyses of cobaltite-gersdorffite solid solutions and millerite. 1. and 6. are from the same aggregate.

Weight percentages:							
	1.	2.	3.	4.	5.	6.	7.
Co	24.68	24.49	22.40	14.83	3.96	3.78	1.16
Ni	9.68	10.99	12.40	19.34	30.64	31.49	63.74
As	45.20	44.36	45.53	47.11	46.44	46.20	
S	20.19	19.85	19.49	18.43	18.65	18.35	34.63
Sum	99.75	99.69	99.82	99.71	99.69	99.81	99.53

Empirical formulae:

(basis of calculation: As + S = 2 for 1. to 6. and S = 1 for 7)

(1. ~ 3. = cobaltite, 4. ~ 6. = gersdorffite, 7. = millerite)

1. $(\text{Co}_{0.65}\text{Ni}_{0.27})_{\Sigma 0.92}\text{As}_{0.98}\text{S}_{1.02}$
2. $(\text{Co}_{0.65}\text{Ni}_{0.31})_{\Sigma 1.00}\text{As}_{0.98}\text{S}_{1.02}$
3. $(\text{Co}_{0.63}\text{Ni}_{0.35})_{\Sigma 0.98}\text{As}_{1.00}\text{S}_{1.00}$
4. $(\text{Ni}_{0.55}\text{Co}_{0.42})_{\Sigma 0.97}\text{As}_{1.04}\text{S}_{0.96}$
5. $(\text{Ni}_{0.87}\text{Co}_{0.11})_{\Sigma 0.98}\text{As}_{1.03}\text{S}_{0.97}$
6. $(\text{Ni}_{0.90}\text{Co}_{0.11})_{\Sigma 1.01}\text{As}_{1.04}\text{S}_{0.96}$
7. $(\text{Ni}_{0.99}\text{Co}_{0.02})_{\Sigma 1.01}\text{S}_{1.00}$

Table 3. Chemical analyses of dolomite and siderite.

Weight percentages:					
	1.	2.	3.	4.	5.
CaO	28.33	25.44	29.95	27.50	
MgO	11.65	10.95	18.12	14.54	9.71
FeO	9.82	10.22	4.09	7.63	43.17
MnO	6.23	9.02	2.64	5.31	5.61
Sum	56.03	55.63	44.80	54.98	58.49

Cationic counterparts:

(basis of calculation: total cation = 1)

(1. ~ 2. = dolomite forming discrete grain, 3. ~ 4. = dolomite forming veinlet; 5. = siderite)

1. $\text{Ca}_{0.50}(\text{Mg}_{0.28}\text{Fe}_{0.13}\text{Mn}_{0.09})_{\Sigma 0.50}$
2. $\text{Ca}_{0.46}(\text{Mg}_{0.27}\text{Fe}_{0.14}\text{Mn}_{0.13})_{\Sigma 0.54}$
3. $\text{Ca}_{0.49}(\text{Mg}_{0.42}\text{Fe}_{0.05}\text{Mn}_{0.04})_{\Sigma 0.51}$
4. $\text{Ca}_{0.45}(\text{Mg}_{0.35}\text{Fe}_{0.10}\text{Mn}_{0.07})_{\Sigma 0.52}$
5. $(\text{Fe}_{0.65}\text{Mg}_{0.26}\text{Mn}_{0.09})_{\Sigma 1.00}$

temperature condition as within the range of diagenesis. Such off stoichiometricity is also seen in gersdorffite formed under a higher temperature condition. FUKUOKA and HIROWATARI (1980) described gersdorffite in some manganese silicate ores from the contact metamorphosed bedded manganese ore deposits in the eastern part of Yamaguchi Prefecture. All of their materials have the relation $\text{As} > \text{S}$, although some

Table 4. Chemical analysis of chlorite.

Weight percentage:				
SiO ₂	Al ₂ O ₃	FeO	MgO	Sum
22.59	23.22	29.62	8.99	87.42
Empirical formula after addition of H ₂ O: (basis of calculation: total charge = 28) (Fe _{2.66} Mg _{1.44} Al _{1.60}) _{Σ5.70} (Si _{2.75} Al _{1.75}) _{Σ4.00} O ₁₂ (OH) ₈				

Table 5. Chemical analysis of bitumen. (Analyst: I. Nakai)

	wt. %	atom. %
C	88.43	7.363
H	3.08	3.056
O	[7.46]	0.466
N	1.03	0.074
Sum	[100.00]	
(O: by difference. H/C=0.415, O/C=0.063.)		

of their cobaltite analyses have the same tendency as gersdorffite with more remarkable deviation from stoichiometricity along with As/(As+S) ratio. Millerite compositions are less fluctuated as compared with cobaltite-gersdorffite solid solutions. As given in Column 7, Table 2, a part of Ni is replaced by Co. Available analyses of millerite inform the peculiarity of such a cobaltian one. This will be discussed later.

The chemical compositions of dolomite are different due to the occurrence. Vein-forming materials are more magnesian than those occurring as discrete grain aggregates in mudstone. All of them have FeO > MnO. Mg:(Fe+Mn) ratio range from 4:1 to 2:1 in the former, whereas near 1:1 in the latter. The totals of (Mg+Fe+Mn) exceed Ca in all of them. The aggregate of siderite (Table 3) and chlorite (Table 4) is involved as a core of aggregate of very fine-grained cobaltite-gersdorffite solid solutions (Fig. 3). It is very likely that siderite and chlorite replaced a foraminifera remain seeing from the dimensional and morphological relations, although the existence of antecedency between them could not be confirmed. The chemical composition of chlorite is considered to be essentially free from Fe³⁺ due to the close co-existence with siderite and nearby bitumen, inviting a slight cationic deficiency in the octahedral site.

The microgravimetric analysis of bitumen gave H/C=0.415, and the oxygen content was estimated by difference (Table 5). The former value is included within the region of hydrothermal bitumens after PARNELL (1988), who drew the lowest value of diagenetic bitumens at H/C=1.0. The present figure is included in the region of hydrothermal bitumens in his diagram. The later discussion will refer to this result, though the material itself seems to have a diagenetic origin.

Geneses of Cobalt and Nickel Sulphides

It is evident that cobalt and nickel minerals owe their formation to the existence of bitumen, which was also the source of such metallic and semi-metallic elements as zinc, lead and arsenic. According to LEWAN and MAYNARD (1982), such organic materials as tetrapyrrole complexes is capable of preserving some metallic elements and that cobalt, nickel, zinc and manganese occupy the same stable region in Eh-pH diagram.

The metallic and semi-metallic elements contained in the described sulphides had been primarily concentrated in the bitumen while it had preserving capacities to them in certain extent probably before diagenesis during which they had been gradually released and, eventually, the bitumen became essentially free from metallic and semi-metallic elements. The source of manganese in dolomite and siderite could be ascribed to the bitumen. The sulphides found in the dark grey mudstone in direct contact with bitumen have no chemical affinity to manganese, which was precipitated as subordinate constituents of dolomite and siderite. The function of bitumen to invite reducing conditions is also known at Unuma, Gifu Prefecture (MATSUBARA *et al.*, 1990), where hematite- or goethite-bearing mudstones are faded into light grey ones near bitumen obviously due to reduction of iron from the ferric to ferrous state, corresponding to the disappearance of hematite or goethite. The generated ferrous ion became the ingredients of carbonates and chlorite.

Seeing from the heterogeneity of cobaltite-gersdorffite solid solution, the diagenesis had proceeded under a very low temperature condition, where the homogenization of produced sulphides was so severely impeded.

The association of cobaltian millerite with cobaltite-gersdorffite solid solutions is given as the two phases coexistence of (Co, Ni)AsS with (Ni, Co)S, where $\text{Co} > \text{Ni}$ in the former and $\text{Ni} \gg \text{Co}$ in the latter if the result of X-ray powder diffraction study is taken into consideration. This proves the absence of Co analogue of millerite, namely, an upper limit of Co replacing Ni in millerite should be present. The existence of cobalt monosulphide has been suspected. Very probably such a phase is not formed under such a lower temperature condition as the present case. And, if the vapour pressure of sulphur was a bit higher, a mineral of thio spinel series such as siegenite $((\text{Co}, \text{Ni})_3\text{S}_4)$ might have been formed.

The association of siegenite with cobaltite is reported in rhodonite ore from Itaga, Kanuma City, Tochigi Prefecture, as the product of contact metamorphism probably derived from rhodochrosite ore (MATSUBARA & KATO, 1986). Their chemical analyses indicated their compositions as $(\text{Co}_{1.37}\text{Ni}_{1.35}\text{Fe}_{0.30})_{\Sigma 3.02}\text{S}_4$ and $(\text{Co}_{0.77}\text{Ni}_{0.15}\text{Fe}_{0.03})_{\Sigma 0.95}\text{As}_{1.02}\text{S}_{0.95}$, respectively (Matsubara & Kato, unpublished). This association indicates that monosulphide of (Co, Ni) with $\text{Co} > \text{Ni}$ will be absent under such a cobalt-rich circumstance and higher temperature condition, although the occurrence of millerite in rhodonite ores of similar nature has been reported by FUKUOKA (1981). This proves the absence of (Co, Ni)S with $\text{Co} > \text{Ni}$, too.

The Relation of Bitumen to the Concentration of Metallic Elements

PARNELL (1988) demonstrated that solid bitumens are capable of concentrating metallic elements in sedimentary rocks. The present authors have described the occurrence of some vanadium and copper minerals in association with bitumen in mudstone accompanying sandstone and chert from Unuma, Gifu Prefecture (MATSUBARA *et al.*, 1990), where some boulders composed of rhodochrosite and an amorphous Ca phosphate of apatite composition are found in the mudstone of the same horizon as the bitumen-bearing one. Also, in a small bedded manganese ore deposit near this locality called Kurisu mine, thin seam of black mudstone with weak radioactivity is found in the hanging wall side of the ore bed, the ore mineral being rhodochrosite (WATANABE, 1957). At Unuma and the neighbouring area, the co-existence of bitumen with vanadium, copper, manganese, uranium, and phosphorus has been thus confirmed. At the present locality, the association of elements includes cobalt, nickel, zinc, arsenic, molybdenum, and minor manganese and antimony.

These finds serve to create a conclusion that bitumens involved in mudstones accompany variable sets of metallic and semi-metallic elements. There are many bedded manganese ore deposits in Japan and some of them involve radioactive anomaly of black mudstone layers adjacent to manganese ore beds, which are generally developed within or adjacent to chert (WATANABE *et al.*, 1970). It is very likely that the black mudstones are the diagenetic or metamorphic equivalents of bitumens involved in mudstones and that the bitumens have been converted into carbonaceous materials due to diagenesis or metamorphism. If so, the source of metallic elements could be ascribed to a submarine volcanism accompanying flow out of basaltic magma, which had liberated manganese into sea water preferentially, together with some metallic and semi-metallic elements stated above. Anyway, as inferred from the H/C ratio of the present bitumen indicates its hydrothermal origin, or magmatic, if the diagram of PARNELL (1988) is referred to, although the quantity of the accompanied manganese is rather low as compared with the case at Unuma, where bitumen has been still left as a form of organic compound despite the prolonged diagenesis from Jurassic period. Although in most of bedded manganese ore deposits in Japanese Jurassic sedimentary rocks carbonaceous materials are involved in black shales and apparently different from the original bitumens substantially, the content of the accompanying metallic and semi-metallic elements suggests the origin to be same as the present case, or a submarine volcanism.

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