

Geochemical Study of the Sambagawa  
Metamorphic System in the Besshi  
District, Central Shikoku, Japan

Part III-B

Post-metamorphic Hydrothermal Mineralization  
and Alteration of the Schists

By

**Hiroshi TAKUBO**

Geological and Mineralogical Institute, University of Kyoto

(Received October 27, 1965)

**Abstract**

Local and weak hydrothermal mineralizations of younger age are recognized along the post-metamorphic fissures in the Besshi formations. Mineral assemblage in the hydrothermal veins varies with both depth and facies of the wall-rocks. Characteristic alterations near the veins are ankeritization of the basic schists and sericitization of the siliceous and the pelitic schists. The order of increasing stability of the pre-existing metamorphic minerals, except epidote and quartz, of the basic schists, under the influence of the hydrothermal solution enriched with  $\text{CO}_2$  and negative in Eh (reductive), is albite, chlorite, calcite and hornblendes.

Other types of the subordinate local metamorphic phenomena, including the irregularly-shaped segregated veins, are briefly described.

**Preface**

The crystalline schists of the Besshi district are locally affected by the post-metamorphic weak hydrothermal processes. It is easy to differentiate between these effects and the metamorphic phenomena of regional scale. The post-metamorphic hydrothermal processes are generally characterized by such local phenomena as the veining of the fissures and cracks of younger age, the deposition of sulphides replacing calcareous schists and the secondary alteration of crystalline schists bordering the veins. These phenomena had not been noted before the hydrothermal modification of the cupriferous pyritic deposits became locally notable, especially on the deeper levels of the Besshi mine (see sketch K, L, N in Fig. 1).

As an attempt to collect the informations to determine whether or not hydrothermal process took place during both the Sambagawa metamorphism and the mineralization of the conformable pyritic deposits, susceptibility or attitude of the crystalline schists to the post-metamorphic hydrothermal influence has been investigated. The present paper outlines the results of underground survey, microscopic observation, X-ray diffractometric study and chemical analyses which had been carried out before 1964. Samples for laboratory works were collected from the underground of the Besshi and the Yokei mine.

### General Features of the Post Metamorphic Hydrothermal Processes

The hydrothermal veins and the altered schists, though these are only local and of small scale, are found everywhere along the network of drifts in the Besshi, the Yokei and the Ikadazu mine. Their distribution is almost independent of the depth, the rock facies and the distribution of pyritic orebodies. In the Hiura formations, the degrees of mineralization and of wall-rock alteration due to the post-metamorphic hydrothermal processes are seemingly higher in the normal faults striking N50°—60°E, but throughout all formations it seems that they bear no relation to the direction of fissures.

*Mineral assemblage:* Mineral assemblage of the hydrothermal veins, as a whole, varies with depth as shown in Table 1. Arsenopyrite, stannite, biotite and actinolite are rare and their occurrences are limited in the eastern extremity of deeper levels of the Besshi deposit. Most of the veins are poor in ore-minerals and have no economic value, excepting the stibnite-rich veins in the black schists. A massive compact aggregate of fine-grained pyrrhotite is most prominent throughout the deeper levels of the Besshi mine. It occurs in the surrounding schists as well as in the pyritic deposits, showing the various modes of occurrence such as fissure-filling veins, conformable veins replacing the calcareous schists and the authigenic deriva-

Table 1. Mineral association of the hydrothermal veins occurring in the Besshi and the Hiura formations.

Zone	Depth below the present surface	Ore-minerals	Gangue-minerals
shallow	0 —1100 m	absent	calcite, quartz, gypsum
intermediate	900—1500 m	pyrite, stibnite, galena, tetrahedrite, etc.	calcite, quartz, ankerite, sericite, chlorite
deep	1450—2100 m	pyrrhotite, pyrite, arsenopyrite, sphalerite, stannite, etc.	quartz, ankerite, calcite, sericite, albite, chlorite, actinolite, biotite

tives due to the disturbance in massive sulphide ores.

As for the gangue minerals of the hydrothermal veins, carbonate minerals and quartz are predominant throughout the underground. In the shallower depth colloform- and comb-structure of the vein-forming materials are common. The vein-forming quartz on the deeper levels occasionally shows wave extinction. Albite and chlorite are rather rare in the hydrothermal veins, though common in such segregated lenticular veins as mentioned in page.

*Wall-rock alteration:* The schists adjacent to the hydrothermal veins are more or less altered and in many cases bleached. Leading processes of wall-rock alteration are carbonatization for the basic schists and sericitization for the pelitic and the quartz schists. These processes are only local and so selective as varying with the chemical and the mineralogical composition and with the texture of wall-rocks. The width of altered zones bordering the veins is independent of the scale of veins, ranging from a few centimetres to several metres (see the sketches in Fig. 1). Alteration accompanied by bleaching is in general remarkable along the ankerite-bearing veins and is rather rare along the veins carrying quartz, calcite or albite. In the basic schists, the lepidoblastic chlorite and the porphyroblastic albite apparently are most susceptible to attack of the hydrothermal solutions; the former is commonly replaced by ankerite and the latter by ankerite and quartz where the other minerals such as epidote and hornblendes are not so strongly altered as these minerals. Schistose or banded structure of the original schists tends to remain, even in the largely altered schists, in the composite form of thin quartz ankerite veins and more or less schistose ankerite layer which possibly resulted from the selective or differential metasomatism (see sketches C, G in Fig. 1 and Fig. 2). Clay minerals are not common in the alteration zones, but are very rarely found in the siliceous schists intersected by the liparite dykes. Fine-grained sulphide minerals are sparsely disseminated in the bleached part (Fig. 2).

*Physical conditions:* Prominent temperature gradients during the hydrothermal processes are estimated from the remarkable variation in mineral paragenesis depending upon the depth. Temperature of mineralization in the upper limit of actinolite-biotite-pyrrhotite-arsenopyrite-stannite association on the deeper levels of the Besshi mine, is estimated to have been about 600°C, according to the pyrrhotite-sphalerite geothermometer established by Kullerud (1959)<sup>1</sup>. Towards the ground-surface, the temperature must have fallen to several tens degrees, because temperature of the solution

---

1 Chemical analyses of two sphalerites associated with pyrrhotite, from a gash vein adjacent to the cupriferous pyritic ore-body on the 20th-level and from a hydrothermal vein in the Hiura formations on the 22nd-level of the Besshi mine, revealed that the ratios ZnS/FeS are nearly four (analysis Nos. 140 and 141).

which is now precipitating the vein-forming materials and bleaching the wall-rocks in the upper levels is at most of that order.

Considering the depth of burial only, it is assumed that litho-static pressure during the hydrothermal processes might have been at most a few kilobars on the deeper levels.

*Chemistry of the hydrothermal solutions:* From the mineral assemblages of the hydrothermal veins and of the altered schists, the chemical properties of the hydrothermal solutions are presumed to have varied with space and time. As will be described in the later chapter, however, the solutions seem to have been enriched with  $K_2O$  and  $CO_2$  with minor amounts of sulphur and metallic elements at their initial state. Redox potential (Eh) of the solutions is inferred to have been negative, from the notable increase of FeO-content with decrease of  $Fe_2O_3$  in and around the veins. Hydrogen-ion concentration (pH), though informations on this are few, seems to have varied having been controlled mainly by the chemical composition of both wall-rocks and pyritic ores through which the solutions migrated.

*Stage of the hydrothermal processes:* Two different views are possibly given on the origin of the hydrothermal solutions, that is, from the acidic magma having intruded as rhyolite sheets<sup>2</sup> in tertiary period and from the deep buried schists and ores having affected by secondary abyssal auto-metamorphism. Whatever the origin may be, the stage of the hydrothermal processes in question seems to be far younger,—probably from the Miocene to the Recent—, than the main stage of recrystallization of the Sambagawa schists.

*Other types of secondary metamorphism:* Several types of the interesting and locally limited secondary metamorphism other than the hydrothermal processes stated above occasionally blur the general features of the Sambagawa metamorphic rocks. Retrogressive change from hornblende to chlorite is most commonly found in the refolded basic schists. Along the parallel shear faults of younger stage,—but older than the hydrothermal processes stated above—, chlorite- or actinolite chlorite-schist is secondarily formed in the basic schists, and sericite schists in the black- or quartz-schists (see page 66 of Part I). Irregularly-shaped segregated veins of quartz, albite (almost pure albite) and calcite are common in the schists more or less disturbed by weak folding and shearing of younger stage<sup>3</sup>. These veins are of small scale and not conformable to the schistosity of the surrounding rocks, and are free from the ore

---

2 See analysis Nos. 99, 100, 119 and 121.

3 The conformable lenticular small veins in which quartz-grains show the oriented arrangement are not concerned here. Their boundary is sharply defined; their stage seems to be or to be near the main stage of the regional metamorphism,

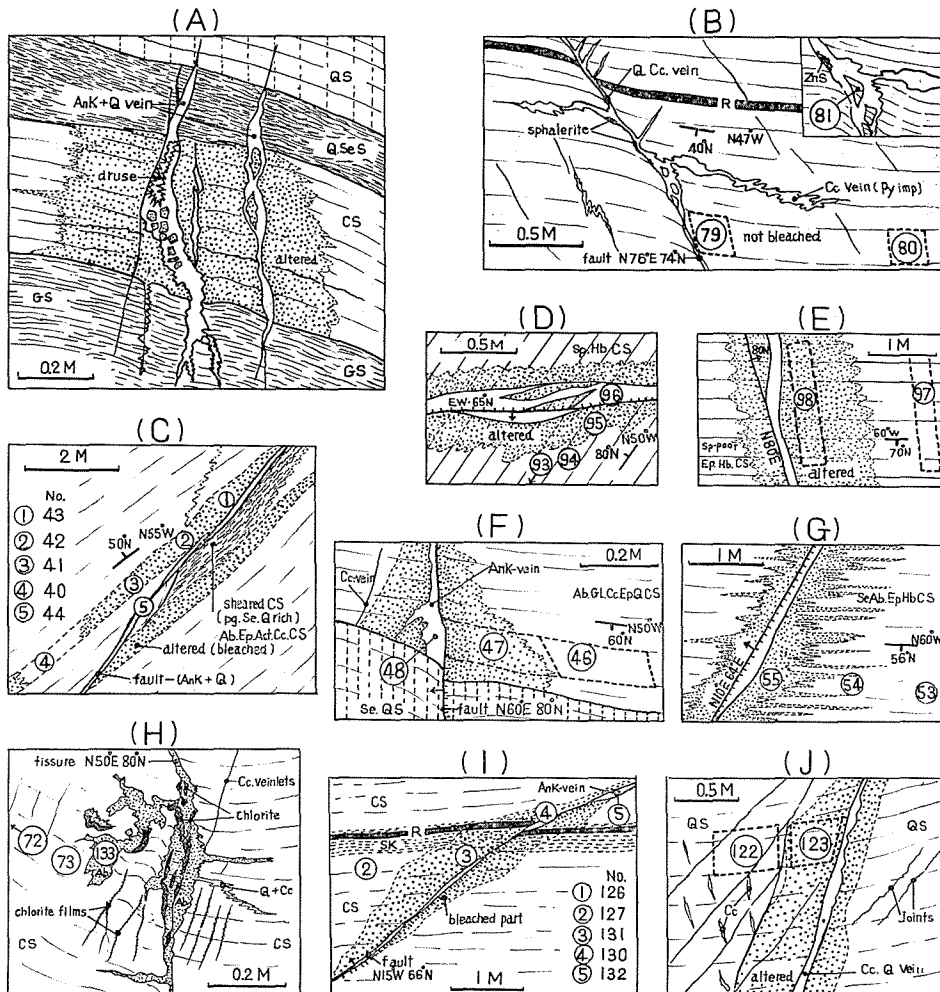


Fig. 1. Sketches showing the location of analysed samples.  
 (A) Post-metamorphic veins crossing the alternation of various schists. Note that the degree of wall-rock alteration depends upon the rock facies. Hiura-F., Fw. cx-cut, 4-L, W2 Besshi Mine.  
 (B) Sphalerite-bearing hydrothermal vein. Wall-rock is not bleached except for horse-stone. Near the western bonanza, 17-L, W1, in the Besshi deposit.  
 (C) Selectively altered layer in the basic schists, Hiura-F., Hw. cx-cut, 8-L, W3, Besshi Mine.  
 (D)-(G), Post-metamorphic veins and altered schists, Hiura-F; (D) Fw. cx-cut, 22-L, E7, (E) Fw. cx-cut, 22-L, E6, (F) Fw. drift, 9-L, E2, (G) Fw. addit, 14-L, E7, Besshi Mine.  
 (H) Post-metamorphic segregated vein, Hiura-F, Hw. cx-cut, 8-L, W2, Besshi Mine.  
 (I) Post-metamorphic alteration in the Yokeyi deposit, 20-L.  
 (J) Hydrothermal alteration of quartz schist, Besshi-F., 20-L, Yokeyi Mine.

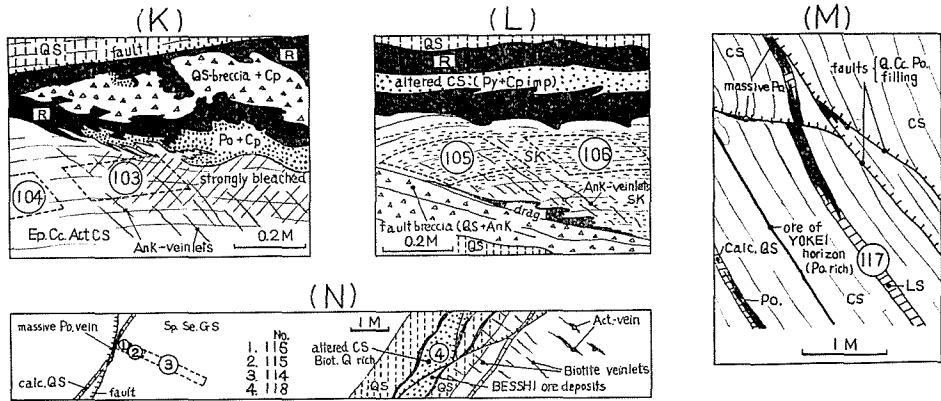
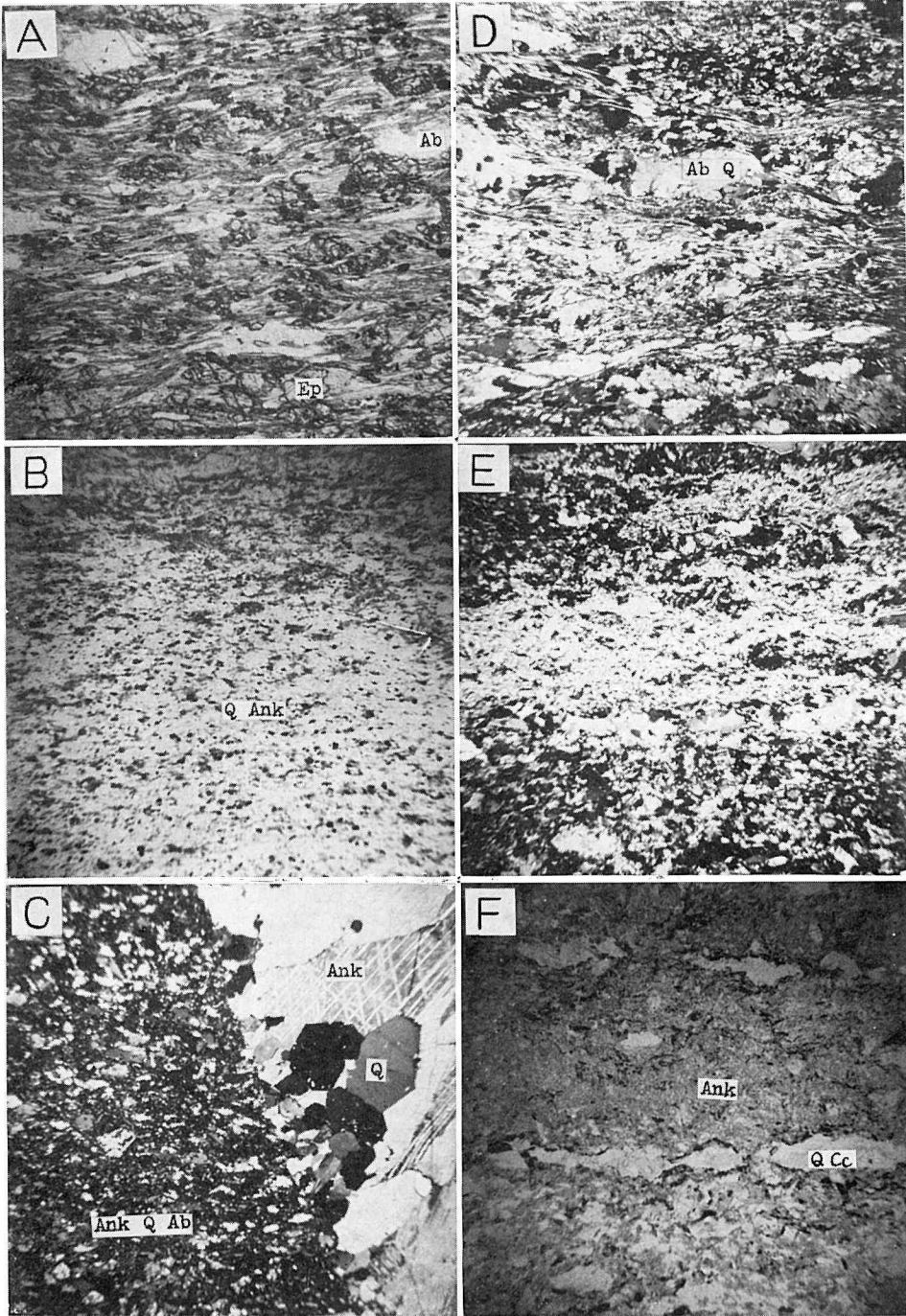


Fig. 1-continued.

- (K) and (L) Abnormal occurrence of the pyritic ore, affected by the faulting and hydrothermal processes of younger stage, in the eastern part on the deeper levels of the Besshi deposit; (K) 23-L, E8, (L) 15m to the southeast of (K).
- (M) Post-metamorphic conformable pyrrhotite veins replacing the highly calcareous schists. Pyrite in the original ores of the ore-horizon is also altered into pyrrhotite. Yokey ore-horizon, Fw. cx-cut, 26-L, E7, Besshi Mine.
- (N) Section, looking SE, showing the post-metamorphic effects in and around the Besshi deposit, on the deeper levels, cx-cut, 26-L, E8, Besshi Mine.

Fig. 2—next page. Thin sections showing the effect of the post-metamorphic hydrothermal alteration on the basic schists.  $\times 20$ 

- (A) Fresh part; main constituent: actinolitic hornblende, epidote and albite, subordinate constituent: chlorite, quartz, sericite and calcite. Albite porphyroblast is less than 0.1 cm in diameter, therefore the specimen is customarily called non-spotted schist. Hiura formations, footwall drift, 9-L, E2, Besshi Mine, ordinary light.
- (B) Moderately altered part, quartz ankerite rock adjacent to (A). Most of chlorite and albite disappear and some of hornblende and epidote are still preserved, ordinary light.
- (C) Altered schist (left) and ankerite vein (right); albite is only relict; Hiura formations, footwall crosscut, 4-L, W2, Besshi Mine (see sketch A of Fig. 1), crossed nicols.
- (D) Fresh part, the right side upper is partly altered, fibrous parts are of actinolite, chlorite and epidote, and other parts are of albite, quartz and calcite. Hiura formations, hanging wall crosscut, 8-L, W3, Besshi Mine (see sketch C of Fig. 1), crossed nicols.
- (E) Completely altered part adjacent to (D). Note that original banded structure is still preserved in the altered schist rich in ankerite, crossed nicols.
- (F) ditto, ordinary light.



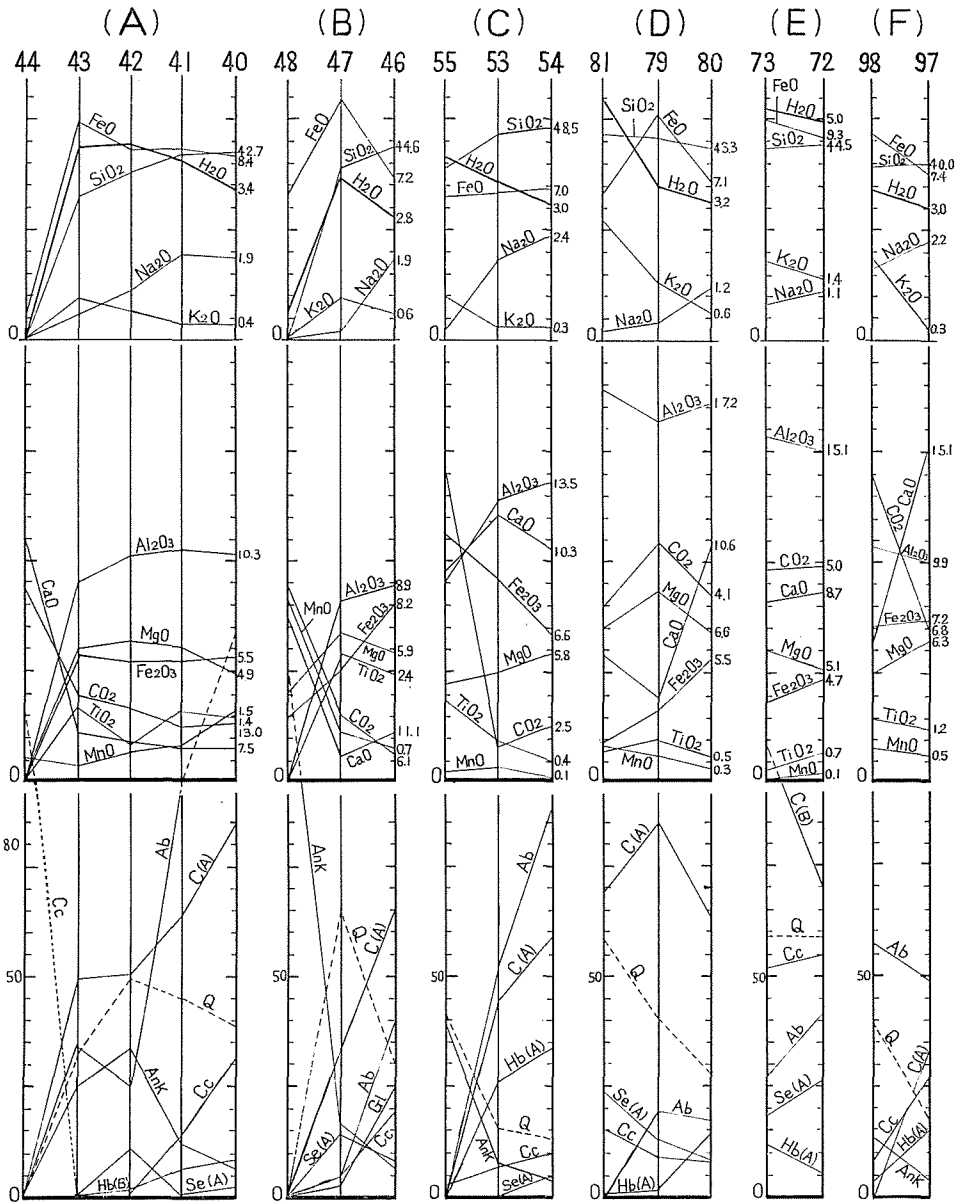


Fig. 3. Diagrams showing the variations in chemical composition (upper) and in relative abundance of minerals, represented by the height of peaks in X-ray powder pattern (lower), for the vein-forming materials and altered schists, in the Besshi Mine.

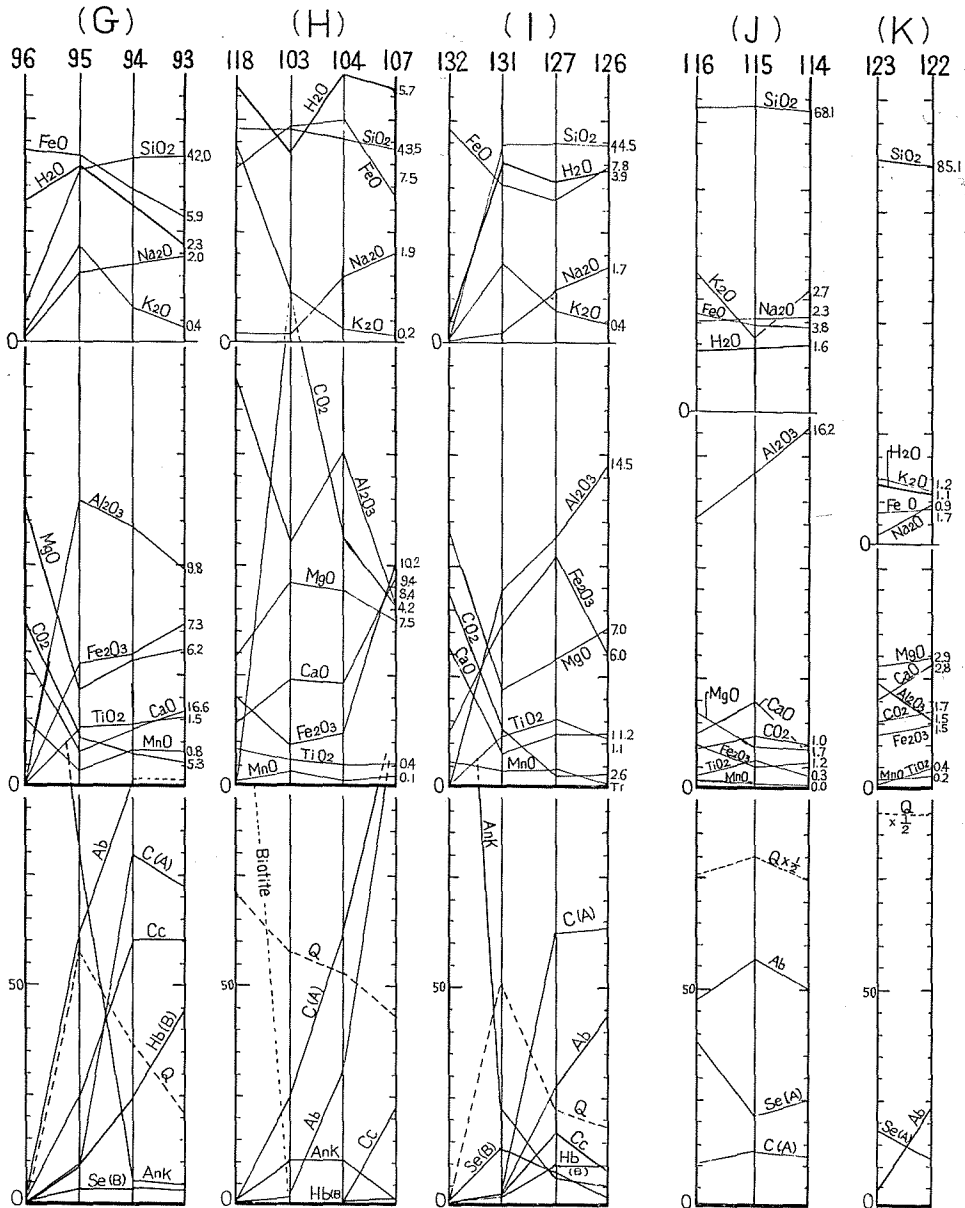
In each case, the samples on left side are the vein-forming materials or the altered schists; towards right, the samples become fresh.

(A) Basic schists, Hiura-F., Hw. cx-cut, 8-L, W3, (see sketch C in Fig. 1).

(B) Basic schists, Fw., drift, 9-L, E2, (sketch F).

(C) Basic schists, altered part more or less stained by weathering, Fw. addit, 14-L, E7, (sketch G).





- (D) Inter-orebody basic schist in the Besshi deposit, 17-L, W1, (sketch B).
- (E) Basic schist adjacent to the segregated chlorite-albite vein, (sketch H).
- (F) Basic schist, Hiura-F, Fw. cx-cut, 22-L, E6, (sketch E).
- (G) Basic schist, Hiura-F, Fw. cx-cut, 22-L, E7, Besshi Mine, (sketch D).
- (H) Inter-orebody basic schists of the Besshi deposit, No. 118: biotite-quartz rock (sketch N), Nos. 103 & 104 (sketch K), No. 107: 23-L, E8.
- (I) Basic schist of the Yokei deposit, 20-L, (sketch I).
- (J) Pelitic schist, adjacent to the pyrrhotite vein, Besshi-F. Hw. cx-cut, 26-L, E8, Besshi Mine, (sketch N).
- (K) Quartz schist, Besshi-F., cx-cut, Yokei Mine, (sketch J).

mineralization and wall-rock bleaching (sketch H in Fig. 1). In addition to these phenomena, carbonatization of eclogitic rocks (see analysis Nos. 217, 218, 219 and 220), actinolitization of diopside-rich rocks (see analysis Nos. 221 and 222) and local higher concentration of phlogopite (see analysis Nos. 223 and 224) are occasionally found in the Tōnaru and the Ōjōin formations. Most of such secondary phenomena as just mentioned bear a close relation to the ultrabasic igneous rocks.

Secondary metamorphic phenomena other than the hydrothermal processes, though these may be only local, can not be neglected, when considering the metamorphic mineral assemblages of the Sambagawa system. In the present paper, however, there is no space to describe the details of these phenomena. The data on the segregated veins only will be cited for reference.

#### Chemical Characteristics of the Hydrothermally Altered Schists

Variation in the bulk chemical composition of the secondarily altered schists has been studied in various cases observed in the Besshi mine. Sketches of the sampling spots are collected in Fig. 1. In most cases, block-sampling method was used. The results are illustrated in Fig. 3, to which the relative abundance of minerals, determined by the X-ray powder method as described in page 40 of Part III-A, are added. Relative increases or decreases in both chemical and mineralogical compositions are summarized in Table 2, being classified according to the mode of alterations and to the type of wall-rocks. More general chemical characteristics of the altered schists of the basic composition are shown in Part II as compared to those of fresh schists., (see CaO-CO<sub>2</sub> diagram in Fig. 1, Nos. 18 and 19 in Table 1, and Fig. 4, of Part II).

From these figures and tables, the following can be picked out as the remarkable and general characteristics for the secondarily altered schists near the post-metamorphic veins:

- (i) The tendencies of variation in chemical and mineralogical compositions are not uniform, but vary case by case being controlled by the types of wall-rock and vein.
- (ii) In all cases of the altered wall-rocks, K<sub>2</sub>O and H<sub>2</sub>O increase and Na<sub>2</sub>O decreases in their content.
- (iii) In the altered basic schists, excepting those of the conformable pyritic deposits and those stained by weathering, FeO-content increases as Fe<sub>2</sub>O<sub>3</sub>-content decreases.
- (iv) Behaviour of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, MnO, CO<sub>2</sub>, TiO<sub>2</sub> is less regular, but most of these, especially CaO, MgO, MnO and CO<sub>2</sub>, tend to vary in their content, being dependent upon the chemical composition of the vein-forming materials, especially of carbonate minerals.

Table 2. Tendencies of variations in the chemical and the mineralogical composition of the schists, related to the hydrothermal alterations of later stage.  
+ : increase and - : decrease in the altered schist. C: almost constant.

Variation diagram from Fig. 3	Common basic schists near the ankerite veins					Basic schists in Besshi deposit			GS	QS	near Ab-Vein
	(A)	(B)	(C)*	(F)	(G)	(D)**	(H)***	(I)	(J)	(K)	(E)
SiO <sub>2</sub>	-	-	-	-	-	+	+	C	C	+	-
Al <sub>2</sub> O <sub>3</sub>	-	-	-	+	+	-	+	-	-	+	+
Fe <sub>2</sub> O <sub>3</sub>	C	-	+	-	-	-	-	?	+	-	-
FeO	+	+	-	+	+	+	+	?	+	-	+
MgO	+	+	-	-	-	+	+	-	+	-	+
CaO	+	-	+	-	-	-	-	-	?	-	-
Na <sub>2</sub> O	-	-	-	-	-	-	-	-	-	-	-
K <sub>2</sub> O	+	+	+	+	+	+	+	+	+	+	+
H <sub>2</sub> O <sup>+</sup>	+	+	+	+	+	+	?	+	?	+	+
CO <sub>2</sub>	+	+	-	+	+	+	+	+	?	-	-
TiO <sub>2</sub>	?	+	+	+	-	+	+	?	?	-	-
MnO	-	+	+	+	-	+	?	+	+	-	-
actinolite	-	-	-	-	-	-	...	-	...	...	+
albite	-	-	-	+	-	+	-	-	-	-	-
ankerite	+	+	+	+	+	...	+	+	...	...	...
biotite	...	...	...	...	...	...	+	...	...	...	...
calcite	-	-	-	-	-	+	-	-	...	...	-
chlorite	-	-	-	-	-	+	-	-	...	...	+
glaucophane	...	...	...	...	...	...	...	...	...	...	...
quartz	+	+	+	+	+	+	+	+	+	+	C
sericite	+	+	-	...	C	+	...	+	+	+	-
Bleaching	+	+	+	+	+		+	+			
Sketch from Fig. 1	(C)	(F)	(G)	(E)	(D)	(B)	(N)	(I)	(N)	(J)	(H)

\* Stained by weathering. \*\* Excepting No. 81. \*\*\* Samples from different places.

(v) In general, variation in content of every chemical component seems to be compatible with variations in the relative abundance of minerals. From the gradient of lines in the variation diagrams, it is assumed that the order of increasing stability of minerals for the hydrothermal influences mostly accords with the result obtained from microscopic study, that is, albite-chlorite-calcite-hornblendes.

(vi) In cases of quartz- and black-schists, addition of K<sub>2</sub>O and accordingly sericitization of albite seem to be the most effective processes under the post-metamorphic hydrothermal conditions.

(vii) Variations in chemical and mineralogical compositions of the basic schists near the segregated veins as shown in sketch (H) of Fig. 1 are different from those in the cases of the hydrothermal veins. The variations recognized as to the segregated veins suggest that the materials forming the segregated veins were supplied from the narrow zone enclosing the vein, though the mechanism of segregation may be unknown.

As a general result, it can be said that the activity of  $H_2O$ ,  $Na_2O$  and  $K_2O$  and the redox-reaction are the important factors having controlled the mineral assemblage of the schists altered by the hydrothermal processes of later stage.

#### Literature

- KULLERUD, G.: Sulfide systems as geological thermometers, in *Researches in geochemistry*, edited by ABELSON, P.H. John Wiley & Sons, New York. pp. 301—335, 1959.
- TAKUBO, H. 1964, 1965, *Geochemical study of the Sambagawa Metamorphic System in the Besshi District, Central Shikoku, Japan*
- Part I Variation of Chemical Compositions of the Schists, Related to the Local Tectonic Phenomena: *Mem. Coll. Sci. Univ. Kyoto, Ser.B, 31* pp. 49—70. (1964)
- Part II General Tendencies in the variation of the Bulk Chemical Composition of the Metamorphic Rocks: *Mem. Coll. Sci. Univ. Kyoto, Ser.B, 31*, pp. 255—277. (1965)
- Part III-A Chemical Characteristics of the Schists in the Conformable Cupriferous Pyritic Ore Deposits: *Mem. Coll. Sci. Univ. Kyoto, Ser.B, 32*, pp. 31—45. (1965)