Melonite and volynskite from the Yokozuru mine, Sannotake, North Kyushu, Japan

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Abstract

A rare assemblage of tellurides has been found in a vein of the Yokozuru mine, Sannotake skarn zone, North Kyushu. The tellurides are melonite, volynskite, hessite, and petzite whose compositions correspond to $\text{Ni}_{0.98}\text{Te}_{2.00}$, $\text{Ag}_{0.99}\text{Bi}_{1.01}\text{Te}_{2.00}$, $\text{Ag}_{1.99}\text{Te}_{1.01}$ and $\text{Ag}_{2.93}\text{Au}_{1.03}\text{Te}_{2.04}$ respectively. Some grains of hessite contain selenium up to 0.68 wt.% replacing tellurium. Optical properties are described for melonite and volynskite. Values of reflectance and microhardness were obtained upon melonite (VHN=67), volynskite (40-80), and siegenite (467-551).

Paragenetic relation suggests that the mineralization of the vein started with deposition of scheelite and quartz, followed by Cu-Bi-Fe sulfides, and ended with the rare mineral assemblage of Ni-Bi-Au-Ag-Te system.

Introduction

During the course of paragenetic investigation of the ores at the Tagawa area in North Kyushu, a vein which has several unique characteristics was studied. The vein, which is called Vein No. 1, a narrow auriferous copper sulfide and scheelite lode of the Yokozuru mine in the Mt. Sannotake contact zone, contains three rare minerals, namely melonite, volynskite, and siegenite. The former two minerals were firstly found in Japan.

Melonite, a rare ditelluride of nickel (NiTe_2), usually occurs associated with other tellurides in such deposits as Kalgoorlie, western Australia (Baker, 1958), Robb-Montbray, Canada (Peacock and Thompson, 1946), and Boulder County, Colorado (Wahlstrom, 1950).

Volynskite, a very rare telluride of silver and bismuth (AgBiTe_2) belonging to miargyrite group, was firstly found in a gold ore from Armenia, USSR (Bezsmertnaya and Soboleva, 1963). The second and third occurrences were also reported from eastern Sayan and Central Asia, USSR (Bezsmertnaya and Soboleva, 1965; Markova, 1967). However, no sufficient data on the chemical composition of the mineral have been presented besides the formula $\text{AgBi}_{1.16}\text{Te}_2$.

Siegenite, a thiospinel of cobalt and nickel ($(\text{Co}, \text{Ni})_3\text{S}_4$), has been known to occur in copper, nickel and iron sulfide ores associated with ultramafic to mafic rocks (Kato and Kobayashi, 1944; Petruk *et al.*, 1969), and frequently in the Mississippi Valley-type ores of southeast Missouri (Craig and Carpenter, 1977). Imai *et al.* (1973) reported siegenite as a later stage alteration product of cobaltian pentlandite in massive copper sulfide ores from the Nippo deposit, Kamaishi mine, Japan.

General description of the deposit

Several pyrometasomatic copper-tungsten deposits develop around the foot of Mt. Sannotake (Fig. 1). All of them, now exhausted, lie within the contact zone between limestone of the Yobuno Paleozoic formations and quartz diorite, a member of the Hirao Granodiorite of Cretaceous age (Matsushita, 1971; Miyahisa, 1952).

Among these deposits, Yokozuru is very famous for an occurrence of scheelite in huge euhedral crystals attaining 15 cm across (Kou, 1900). The Yokozuru mine is located at the north extreme of the mountain (about $130^{\circ}51'E$ long. and $33^{\circ}42'N$ lat.). The mine was firstly exploited for copper ores in 1884, and continued scant production of tungsten and copper ores up to 1955. The deposit of the mine is either scheelite-quartz veins or copper sulfide veins; these veins fill short but abundant fissures trending N-S, developed in andradite-hedenbergite-epidote-vesuvianite-wollastonite skarn. Sulfides and magnetite are present sporadically in the skarn. The vein-forming ore minerals are, in order of decreasing abundance, chalcopyrite, pyrite, magnetite, pyrrhotite, arsenopyrite, bornite, molybdenite, sphalerite, galena, bismuthinite, emplectite, and electrum. Tetradymite was also found and described by Mumeikai Group (1962).

The minerals of the present study occur in Vein No. 1, a narrow vein of 20 cm in width and 20 m long, which intersects steeply the limestone marble about 10 m apart from the skarn zone (Fig. 2). Samples from the massive part of the vein contain chalcopyrite, pyrite, bornite, wittichenite, scheelite, calcite, and quartz, whereas those from the disseminated veinlet involve siegenite and a complex aggregate of melonite, volynskite, hessite, and petzite, together with electrum, bornite, wittichenite, and chalcopyrite.

Experimental procedure

The samples were mounted in the thermoplastic resin (Marumoto, #301) using Struers Prestopress, and polished on cloth laps with graded diamond abrasives down to 1 micron in diameter.

FIG. 1. Geologic map around Mt. Sannotake, North Kyushu.

The microhardness of the minerals was measured with the aid of an Akashi-MVK microhardness tester. An objective 40 $\times$ with a numerical aperture of 0.65 was used.

FIG. 2. Geologic map of the Yokozuru mine.

The apparatus used for measuring reflectance was a Leitz Orthoplan-Pol microscope equipped with a Leitz MPV2 microphotometer. An objective 50 $\times$ with a numerical aperture of 0.85 was used. As standards, tungsten-titanium carbide and silicon carbide supplied by Carl Zeiss were employed.

A JXA-5A electron microprobe analyzer was used to determine the composition of minerals. An accelerating potential of 20 kV and a beam current of 0.02 μ A were charged. Pure metals, chalcopyrite, and galena were used as standards. The measured intensities were necessary to apply the correction procedures of absorption, atomic number, and fluorescence.

Because the here-described phases rich in Ni, Au, Ag, Bi, and Te occur only in microscopic amounts, it was impossible to obtain X-ray data.

Melonite

Lamellar aggregates of melonite form a granular remnant having 0.2 mm in diameter, and are replaced by hessite and volynskite (Fig. 3). The mineral is almost hard to rust. Optical properties, microhardness, and reflectance are shown in Table 1.

Analytical data of the present melonite are shown in Table 2. The average composition obtained from three point analyses gives the formula $\text{Ni}_{0.98}\text{Te}_{2.00}$, which is very close to the theoretical one.

FIG. 3. Sketch showing the textural development of tellurides. M: melonite, Vk: volynskite, H: hessite, P: petzite, E: electrum, Wt: wittichenite, Cp: chalcopyrite with bornite, Cc: calcite.

Volynskite

Volynskite is present as irregular grains, up to 100 microns across, among crystals of melonite, hessite, and chalcopyrite. The mineral generally contains inclusions of electrum. It takes convex surfaces against hessite, suggesting that the former has replaced the latter (Fig. 3). Volynskite rather resembles tetradymite but shows more pale purplish color in reflected light. The optical properties, microhardness, and reflectance of the Yokozuru volynskite are shown in Table 1, which are consistent with those described by Uytenbogaardt and Burke (1971).

The chemical composition of volynskite from Yokozuru is listed in Table 3. The mineral shows homogeneous composition and no significant deviations from the theoretical composition. The averaged value corresponds to $\text{Ag}_{0.99}\text{Bi}_{1.01}\text{Te}_{2.00}$, which is very close to the ideal formula AgBiTe_2 , in contrast to the formula

TABLE 1. Optical and physical properties of melonite and volynskite.

Mineral	melonite			volynskite
Polishing properties	difficult to obtain a good polish			fairly good but pitted surface
Color	yellowish white with a pinkish tint			light grey with a pale purplish tint
Bireflectance	weak (more creamy to faintly pinkish)			very weak
Anisotropy	very strong (straight extinction)			weak
Internal reflections	not present			not present
Cleavage	common // (0001)			not present
Polishing hardness	$\geq$ chalcopyrite > volynskite			> chalcopyrite
Vickers hardness	VHN ₁₀ =67 _{sf} *			VHN ₁₀ =40-80
Reflectance	nm	R_o	R'_e	R
	480	51.8	48.8	50.9
	546	57.3	53.4	51.0
	589	60.9	56.8	51.5
	657	64.2	59.0	52.0

*sf: slightly fractured.

TABLE 2. Chemical composition of melonite.

Wt%	1	2	3	4
Ni	18.64	18.87	18.86	18.79
Te	83.30	83.32	84.94	83.85
Total	101.94	102.19	103.80	102.64

1: Ni_{0.97}Te₂, 2: Ni_{0.98}Te₂, 3: Ni_{0.97}Te₂,
 4(av.): Ni_{0.98}Te₂

TABLE 3. Chemical composition of volynskite.

Wt%	1	2	3	4
Ag	18.89	18.38	18.60	18.62
Bi	36.57	37.54	36.42	36.84
Te	44.41	44.47	44.66	44.51
Total	99.87	100.39	99.68	99.97

1: Ag_{0.98}Bi_{1.01}Te₂, 2: Ag_{0.98}Bi_{1.03}Te₂,
 3: Ag_{0.99}Bi_{1.00}Te₂, 4(av.): Ag_{0.99}Bi_{1.01}Te₂

$\text{AgBi}_{1.16}\text{Te}_2$ presented by Bezsmertnaya and Soboleva (1965).

Hessite, petzite, and electrum

Hessite aggregates take irregular but nearly triangular form attaining 350 microns. Petzite shows vermicular intergrowths at places within hessite and along mutual boundaries. Petzite is also in intimate association with electrum. These texture relations suggest that petzite was formed as a reaction product between hessite and electrum. Another small grain of hessite is found in chalcopyrite as an intergrowth of selenian hessite and hessite.

Hessite is characterized with strong anisotropy and inversion twin lamellae. Petzite is weakly anisotropic but distinctly noticeable under crossed nicols.

Table 4 gives analytical values of hessite, selenian hessite, petzite, and electrum. Hessite coexists with other tellurides, namely volynskite, melonite, and petzite, whereas selenian hessite (Table 4, Nos. 3 and 4) intergrows with chalcopyrite. The name electrum is here referred to gold with 20 percent or more of silver according to Dana's definition.

Siegenite

Siegenite from the Yokozuru mine shows creamy, white color and smooth polished surface under the microscope. Under crossed nicols, the mineral is isotropic. It usually forms rounded grains enclosed in wittichenite, and sometimes takes concavity-form in association with chalcopyrite and bornite. The mineral is rich in cleavages, and is replaced along interstices by chalcopyrite.

The result of microprobe analyses is shown in Table 5. Siegenite from the Buick mine, which is one of the productive mines in the Viburnum Trend,

TABLE 4. Chemical compositions of hessite, petzite and electrum.

Wt%	hessite				petzite		electrum	
	1	2	3	4	5	6	7	8
Ag	62.39	62.34	62.54	65.23	40.85	40.41	13.82	12.25
Au	—	—	—	—	26.11	24.69	86.11	86.72
Te	37.58	37.88	37.17	24.73	33.64	32.79	—	—
Se	—	—	—	6.57	—	—	—	—
S	—	—	0.08	0.68	—	—	—	—
Total	99.97	100.22	99.79	97.21	100.60	97.89	99.93	98.97

Hessite, 1: $\text{Ag}_{1.99}\text{Te}_{1.01}$, 2: $\text{Ag}_{1.98}\text{Te}_{1.02}$, 3: $\text{Ag}_{1.99}(\text{Te}_{1.00}\text{S}_{0.01})$,
 4: $\text{Ag}_{2.01}(\text{Te}_{0.64}\text{Se}_{0.28}\text{S}_{0.07})_{0.99}$; petzite, 5: $\text{Ag}_{2.93}\text{Au}_{1.03}\text{Te}_{2.04}$,
 6: $\text{Ag}_{2.97}\text{Au}_{0.99}\text{Te}_{2.03}$; electrum, 7: $\text{Au}_{0.77}\text{Ag}_{0.23}$, 8: $\text{Au}_{0.79}\text{Ag}_{0.21}$.

southeast Missouri, USA, was also analyzed for comparison. Both are homogeneous within each grain and between grains. The chemical formula of the Yokozuru siegenite is $(\text{Ni}_{1.96}\text{Co}_{1.07}\text{Fe}_{0.02})_{3.05}\text{S}_{4.00}$, and that of the Buick siegenite $(\text{Ni}_{1.72}\text{Co}_{1.18}\text{Fe}_{0.14})_{3.04}\text{S}_{4.00}$. These values correspond to nickel-rich varieties of siegenite, and fall within the compositional range of common siegenites reported by Craig and Carpenter (1977).

The reflectance and microhardness of the siegenite are given in Table 6. Vaughan *et al.* (1971) have shown that the reflectance may decrease along the series Co_3S_4 - Ni_3S_4 from the molecular orbital and band theories of the chemical bond. In comparison with the reflectance of cobalt-rich siegenite from the Langis mine (Petruk *et al.*, 1969), that of the present siegenite well substantiates the noteworthy trend of decreasing reflectance along the linnaeite-polydymite series.

Wittichenite-bornite-chalcopyrite assemblage

Under the microscope, wittichenite is always intergrown or associated with both chalcopyrite and bornite in the ores of the Yokozuru mine (Miyahisa, 1956). Wittichenite occurs as large blebs, lentiforms, and rims along bornite-chalcopyrite-grain boundaries, and in bornite as a network of thin lenticular blades parallel to the bornite (111) directions. Sometimes the wittichenite blades are enlarged where they include small blebs or laths of chalcopyrite.

TABLE 5. Chemical composition of siegenite.

Locality	Yokozuru mine			Buick mine		
	wt%	Atm. Pr.		wt%	Atm. Pr.	
Ni	37.54	1.96	3.05	32.82	1.72	3.04
Co	20.59	1.07		22.61	1.18	
Fe	0.40	0.02		2.63	0.14	
S	41.81	4.00		41.73	4.00	
Total	100.34			99.79		

TABLE 6. Reflectance and microhardness of siegenite

Wavelength nm	Reflectivity		Microhardness VHN 10-gram kg/mm ²
		%	
480		42.2	
546		43.2	467-551
589		44.5	517(av.)
657		47.4	

Sugaki *et al.* (1974) showed that the Yokozuru wittichenite was very close to the theoretical composition Cu_3BiS_3 with electron microprobe analysis.

Discussion

From the mode of occurrence and textural relations, the mineral sequence of Yokozuru has been determined as shown schematically in Fig. 5. Sulfide minerals deposited in the early mineralization stage along the fractures developed in skarn zone, and telluride minerals and electrum formed overlapping and slightly later than sulfides. It probably suggests that decreasing sulfur fugacity and

FIG. 4. Sketch showing the relic texture of siegenite (S) in chalcopyrite (Cp), bornite (Bn) and wittichenite (Wt).

FIG. 5. Schematic representation of mineral sequence in Vein No. 1 of the Yokozuru mine.

temperature downward of the mineralizing solution are important factors to have deposited the telluride minerals here-described.

Although the siegenite and melonite are trace constituents in the vein, the presence of cobalt and nickel components in the ore minerals arouses geochemical interest to the geology and ore deposits in the Sannotake area.

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References

- BAKER, G. (1958) *Austral. Inst. Mining Met. Proc. Stilwell Ann. Volume*, 15-40.
- BEZSMERTNAYA, M.S. & SOBOLEVA, L.N. (1963) *Tr. Inst. Mineral. Geokhim. Kristallokhim. Redkikh, Elementov, Akad. Nauk SSSR*, **18**, 70-84 (abst. in *Amer. Miner.*, **49**, 818).
- BEZSMERTNAYA, M.S. & SOBOLEVA, L.N. (1965) *Akad. Nauk SSSR, Eksperim. Metody Issled. Rudn. Mineral.*, **1965**, 129-141 (abst. in *Amer. Miner.*, **51**, 531).
- CRAIG, J.R. & CARPENTER, A.B. (1977) *Econ. Geol.*, **72**, 480-486.
- IMAI, N., MARIKO, T. & SHIGA, Y. (1973) *Mining Geol. (Japan)*, **24**, 347-354.
- KATO, T. & KOBAYASHI, H. (1944) *Japan. Journ. Geol. Geogr.*, **19**, 181-189.
- KOU, S. (1900) *Journ. Geol. Soc. Tokyo*, **7**, 302-310.
- MARKOVA, E.A. (1967) *Zap. Vses. Miner. Obshestva*, **96**, 324-326 (*Miner. Abstr.*, **20**, 25).
- MATSUSHITA, H. (1971) *Sci. Rept. Dept. Geol., Kyushu Univ.*, **11**, 1-16.
- MIYAHISA, M. (1952) *Journ. Mining Inst. Kyushu*, **20**, 265-269.
- MIYAHISA, M. (1956) *Journ. Mining Inst. Kyushu*, **24**, 346-351.
- MUMEIKAI GROUP (1962) *Journ. Miner. Soc. Japan*, **5**, 324-334.
- PEACOCK, M.A. & THOMPSON, R.M. (1946) *Univ. Toronto, Geol. Ser.*, **50**, 63-73.
- PETRUK, W., HARRIS, D.C. & STEWART, J.M. (1969) *Can. Miner.*, **9**, 597-616.
- SUGAKI, A., SHIMA, H. & KITAKAZE, A. (1974) *Journ. Japan. Assoc. Miner. Petrol. Econ. Geol.*, **69**, 32-43.
- UYTENBOGAARDT, W. & BURKE, E.A.J. (1971) *Tables for Microscopic Identification of Ore Minerals*, Elsevier Pub. Co.
- VAUGHAN, D.J., BURNS, R.G. & BURNS, V.M. (1971) *Geochim. Cosmochim. Acta*, **35**, 365-381.
- WAHLSTROM, E.E. (1950) *Amer. Miner.*, **35**, 948-953.

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