INTRODUCTION

Bismuth and tungsten minerals occur in the copper ores in some of the Miocene hydrothermal vein-type deposits in the Northeast Japan arc (Figure 1, Refs. [1, 2, 3, 4, 5, 6, 7]). The occurrence of these minerals suggests a higher temperature of formation than that of the typical epithermal deposits, and has been regarded as a characteristic of xenothermal deposit (Ref. [8]). Izumino et al. (2016) described the Bi minerals in the deposits hosted by Cretaceous to Paleogene granitoids in the Northeast Japan. They concluded that speciation of Bi mineral is controlled by the redox conditions of the granite magma, not only of redox conditions of the ore forming fluid (Ref. [9]). Ciobanu and Cook (2002), Cook and Ciobanu (2004), and Cepedal et al. (2006) examined the relationship between the oxygen and sulfur activity of the ore forming fluid using Bi/Te( + Se + S) ratio of bismuth-tellurides of the Arakawa deposit are \( \leq 1 \). This composition indicates a relatively high sulfur and tellurium fugacity conditions of the ore forming fluid. It also shows an oxidized environment, close to the hematite-magnetite buffer. Bismuth mineral assemblage of the Arakawa deposit is similar to the other Miocene vein-type copper deposits in the Northeast Japan arc.

GEOLOGY

The Arakawa area is covered by Neogene sedimentary rocks with a gently west-dipping monocline structure (Figure 2). The oldest rock unit exposed in the area is the Cretaceous basement of the Taiheizan plutono-metamorphic rocks. Those rocks consist of amphibolite, biotite schist, and gneissese hornblende- biotite granodiorite (Ref. [14]). The Oligocene Haginari Formation unconformably overlies the Taiheizan plutono-metamorphic

Bismuth and Tellurium Minerals from the Arakawa Deposit in the Northeast Japan Arc

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The Arakawa deposit is a Miocene vein-type copper deposit in the Northeast Japan arc. The ore minerals from the deposit were analyzed by a scanning electron microscope with energy dispersive X-ray spectroscope and/or an electron probe micro analyzer. Bismuth and tellurium minerals we found from the ores are bismuthinite, tetradymite, hessite, tsumoite, pavonite, matildite, and ourayite. Bi/Te( + Se + S) of bismuth-tellurides of the Arakawa deposit are \( \leq 1 \). This composition indicates a relatively high sulfur and tellurium fugacity conditions of the ore forming fluid. It also shows an oxidized environment, close to the hematite-magnetite buffer. Bismuth mineral assemblage of the Arakawa deposit is similar to the other Miocene vein-type copper deposits in the Northeast Japan arc.

Keywords: Vein-type Cu deposit, Arakawa deposit, Bi-minerals, Te-minerals
Figure 2  Geological map of the Arakawa area (Modified from Refs. [14, 15, 16])
rocks, and comprises pyroxene andesite lavas and pyroclastic flow deposits (Refs. [14, 15]). The Hagiinari Formation underlies the units of tuff breccia, lapilli tuff, and tuff of the Middle Miocene Ohkuramata Formation. These units are intercalated with dacite and rhyolite lavas. The Middle Miocene Sunakobuchi Formation, which is composed of mudstone and siltstone and rhyodacitic tuff breccia, overlies the Ohkuramata Formation. A hard mudstone sequence of the Middle Miocene Onnagawa Formation overlies the sedimentary unit of the Sunakobuchi Formation (Figure 2) (Ref. [15]). A stock of micro-granite porphyry intruded in the Ohkuramata Formation (Figure 2). This intrusive rock consists of phenocrysts of quartz, plagioclase, biotite, hornblende, and titanomagnetite in a groundmass of the same mineral assemblage.

The Arakawa deposit consists of northeast-striking 10 major veins in the Miocene sedimentary and volcanic rocks. These veins strike N30°-60° E, and are 0.3-7.0 m thick. These veins exhibit symmetric structure with centimeter-size comb-shaped quartz. These veins are drusy, and rich in breccia, which are fringed directly by chalcopyrite and pyrite and then by quartz. Quartz also occurs in druse. Major primary ore minerals are chalcopyrite, pyrite, sphalerite, and galena, and secondary minerals are native copper, cuprite, azurite, and malachite. Gangue minerals are quartz, calcite, chloride, barite, and apatite. Hydrothermal alteration associated with the veins is characterized by the assemblage of quartz and chloride, and vein wall and vein extension is silicified with disseminated pyrite.

3 METHODOLOGY

The samples observed and analyzed were collected from the Arakawa deposit. Samples collected from the Hikage vein (sample No. 1, sample point A in Figure 2) and waste dump in the Ugaishawa stream, Arakawa orebody (sample No. 2, sample point B) and from the waste dump of the Hisaichi orebody (sample No. 3 and 4, sample point C) were used for the analysis. Macroscopic features of the specimen are as follows. The ore sample from the Hikage vein consists of quartz, chalcopyrite, pyrite, and chamosite. The ore sample of the Arakawa orebody consists of wall rock breccia cemented by quartz, chamosite and hematite and poor in sulfide minerals. The ore sample (sample No. 4) from the Hisaichi orebody consists of quartz, pyrite, chalcopyrite, sphalerite and the ore sample No. 3 consists of quartz, chalcopyrite, and chamosite. Analysis of ore minerals was conducted by a scanning electron microscope with energy dispersive X-ray Spectroscopy (SEM-EDS) and/or an electron probe micro analyzer (EPMA) at Akita University.

The chemical compositions of Bi sulfides were determined at the Faculty of International Resource Science, Akita University, with a JEOL Superprobe JXA-8800R. Acceleration voltage of the focused beam was 20 kV at a beam current of 20 nA. Counting times were 20 seconds (major elements) and 30 seconds (trace elements) for the peak and half of that time for the background, respectively. Natural and synthetic standards were used for calibration: Bi2S3 for Bi, PbS for Pb, FeS2 for Fe, MnS for Mn, FeAl2O4 for FeAl2O4, and native elements for Ag, Cu, Te, and Se. Detection limits (1σ) for each element are 375 ppm for Bi, 74 ppm for S, 120 ppm for Pb, 20 ppm for Fe, 83 ppm for Zn, 73 ppm for Cd, 76 ppm for As, 80 ppm for Pb, 74 ppm for Ag, 69 ppm for Cu, 101 ppm for Te and 62 ppm for Se. Only analysis with totals between 98.5 and 101.5 wt. % were used for further evaluation. Results of representative analysis are given in Tables 1 and 2.

4 OCCURRENCE

The results of microscopic observation are described below for each mineral. Mineral names were determined from the results of mineral chemistry analyzed by EPMA and/or SEM-EDS.

(1) Bismuthinite

Bismuthinite occurs in the Hikage vein (sample No. 1) of the Arakawa orebody. Bismuthinite is associated with chalcopyrite, pyrite, and hematite. Gangue minerals are quartz and chamosite. This mineral occurs with chamosite in an outer part in vein. It is up to 550 μm in size (Figure 3a). This mineral coexists with chamosite, and droplet-form inclusions in chalcopyrite. It exhibits white grey reflection color and lacks in anisotropism and reflection pleochroism.

(2) Tetradymite

Tetradymite occurs in the sample No. 2 from the Arakawa orebody. It is associated with chalcopyrite, pyrite, hessite, tsumoite, and hematite. Gangue minerals are quartz and chamosite. Tetradymite occurs between quartz grains in a quartz vein. Tetradymite is anhedral, up to 750 μm in size, usually less than 20 μm (Figure 3c). It exhibits white color with slightly strong anisotropism and is absent in reflection pleochroism.

(3) Hessite and tsumoite

Hessite and tsumoite occur in the sample No. 2 from the Arakawa deposit. Those minerals are associated with chalcopyrite, pyrite, hessite, tsumoite, and hematite. Gangue minerals are quartz and chamosite. Hessite and tsumoite form a 10 μm size bleb (Figure 3d and e). Those minerals are smaller than 5 μm. Hessite is steel grey in color, and tsumoite is white.

(4) Pavonite and matildite

Pavonite and matildite occur in the sample No. 3 from the Hisaichi orebody. Pavonite is hosted by chamosite in a quartz vein. They are up to 300 μm in size (Figure 3b). It shows white reflection color, weak anisotropism and lacks in reflection pleochroism under the microscope. Matildite is rare and small in size. This mineral occurs as columnar crystals coexisting with chamosite. Matildite is present as a part of a bleb of pavonite.

(5) Ourayite

Ourayite occurs in the sample No. 4 from the Hisaichi orebody. This grain is included by chalcopyrite in a chamosite- quartz vein. This mineral is associated with chalcopyrite, pyrite, and sphalerite. Gangue minerals are quartz and chamosite. This sulfide is about 100 μm in size (Figure 3f), and shows gray reflection color, obscurity of anisotropism and reflection pleochroism under the microscope.

5 DISCUSSION

Chemical compositions of bismuthinite, pavonite, matildite, and ourayite are plotted in the Bi-Ag-Pb ternary diagram (Figure 4). The chemical compositions of bismuthinite, tetradymite, and pavonite are calculated by 10 microprobe analyses. Chemical formula of bismuthinite is (Bi1.25Cu0.2Pb0.3)2(2S2/3Se8/9)3, which contains a small amount of Pb, Cu, and Se. Chemical formula of tetradymite is (Bi1.20Fe0.1Sb0.3)2.1(Te1.10Sb0.8Se0.8)0.1, which is
Bismuth and Tellurium Minerals from the Arakawa Deposit in the Northeast Japan Arc

Table 1  Chemical compositions of Bi and Te minerals from the Arakawa deposit

|                | Ag  | Bi  | Cu  | Fe  | Zn  | Cd  | As  | Sb  | Te  | Se  | S  | Total |
|----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|----|-------|
| Bismuthinite1  | 80.21 | 1.13 | 0.03 | 0.63 | 0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.03 | 1.10 | 17.11 | 100.26 |
| Bismuthinite2  | 80.34 | 1.17 | 0.00 | 0.55 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.03 | 1.14 | 16.78 | 99.83 |
| Average (n=46) | 80.42 | 1.10 | 0.01 | 0.69 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 1.11 | 16.77 | 100.35 |
| Tetradymite1   | 60.47 | 0.00 | 0.01 | 0.03 | 0.07 | 0.00 | 0.00 | 0.00 | 0.26 | 34.16 | 1.17 | 3.22 | 100.46 |
| Tetradymite2   | 59.65 | 0.00 | 0.04 | 0.00 | 0.10 | 0.00 | 0.00 | 0.00 | 0.21 | 33.58 | 1.00 | 4.26 | 99.95 |
| Tetradymite3   | 60.58 | 0.00 | 0.02 | 0.04 | 0.05 | 0.03 | 0.00 | 0.00 | 0.16 | 33.90 | 1.01 | 4.43 | 100.26 |
| Average (n=46) | 60.53 | 0.00 | 0.05 | 0.02 | 0.06 | 0.01 | 0.00 | 0.00 | 0.19 | 33.88 | 0.99 | 4.40 | 100.33 |
| Pavonite1      | 59.41 | 6.27 | 11.45 | 4.92 | 0.08 | 0.01 | 0.00 | 0.00 | 0.21 | 3.36 | 16.86 | 100.55 |
| Pavonite2      | 62.51 | 4.91 | 10.77 | 3.53 | 0.10 | 0.02 | 0.00 | 0.00 | 0.24 | 3.33 | 16.96 | 100.36 |
| Pavonite3      | 62.54 | 5.65 | 11.10 | 3.11 | 0.14 | 0.04 | 0.00 | 0.00 | 0.31 | 3.43 | 16.63 | 100.94 |
| Average (n=46) | 62.50 | 5.60 | 10.83 | 3.12 | 0.07 | 0.02 | 0.00 | 0.00 | 0.31 | 3.41 | 16.68 | 100.49 |
| Monotelite1    | 54.50 | 0.00 | 26.90 | 0.34 | 0.04 | 0.00 | 0.00 | 0.02 | 0.32 | 1.30 | 16.02 | 99.45 |
| Oxytellurite1  | 38.40 | 33.62 | 10.99 | 1.19 | 0.08 | 0.05 | 0.00 | 0.00 | 0.00 | 0.05 | 1.17 | 14.66 | 100.21 |
| Oxytellurite2  | 40.95 | 31.29 | 9.84 | 1.51 | 0.35 | 0.00 | 0.00 | 0.00 | 0.10 | 1.07 | 14.58 | 99.69 |
| Oxytellurite3  | 38.86 | 33.05 | 10.74 | 1.26 | 0.19 | 0.00 | 0.00 | 0.00 | 0.10 | 1.14 | 14.36 | 99.69 |
| Average (n=9)  | 39.28 | 32.58 | 10.95 | 1.34 | 0.16 | 0.01 | 0.00 | 0.00 | 0.07 | 1.13 | 14.61 | 100.14 |

Determined by JEOL Superprobe JXA-8200R

Table 2  Chemical compositions of Bi and Te minerals from the Arakawa deposit (semi-quantitative)

|                | Ag  | Bi  | Pb  | Te  |
|----------------|-----|-----|-----|-----|
| Heuslerite*    | 56.6 | 3.7 | 6.6 | 32.5 |
| Heuslerite**   | 40.0 | 2.6 | 8.7 | 36.9 |
| Tsumoite***    | 0.0  | 0.0 | 9.0 | 90.1 |

* Determined by JEOL JSM-IT300LV with OXFORD X-Max. **JEOL Superprobe JXA-8800R

Figure 3  Photomicrographs of ores from the Arakawa deposit

a. Photomicrograph of bismuthinite (bim), with quartz (qtz) and chalcopyrite (cp), fringed by chamosite (chm) and covellite (cv) at the outer edge. b. Photomicrograph of pavonite (pv) and matildite (mat). Pavonite and matildite are hosted by chamosite. c. Photomicrograph of tetradymite (tdt). Anhedral tetradymite with quartz. d. Photomicrograph of anhedral tetradymite with hessite (hs) and tsumoite (tsu). e. Back scattered electron image of hessite and tsumoite. They form a bleb. f. Photomicrograph of ourayite (our) included by chalcopyrite. Chalcopyrite is cut by sphalerite (sp).
slightly rich in Bi and Se than that of stoichiometric tetradyomite. Chemical formula of pavonite is (Ag_{0.93}Cu_{0.45}Bi_{2.75}Pb_{0.27}Fe_{0.01})_{4.41} (S_{4.81}Se_{0.17}Te_{0.02})_{5.00}, which is rich in Cu, Pb, and Se than that of stoichiometric pavonite. The Cu/(Cu + Ag) atom ratios range from 0.22 to 0.44, which shows pavonite-cupropavonite intermediate compositional range (Figure 4). Chemical formula of matildite is (Ag_{0.96}Cu_{0.02}Bi_{1.01})_{1.99}(S_{1.93}Te_{0.01}Se_{0.06})_{2.00}. Matildite contains slight amounts of Cu and Se. Chemical formula of ourayite is (Ag_{2.80}Cu_{0.58}Pb_{4.35}Zn_{0.01}Fe_{0.08}Bi_{5.19})_{13.01} (S_{12.59}Se_{0.40}Te_{0.02})_{13.00}, which is rich in Cu, Pb, Bi, and Se than that of stoichiometric ourayite (Figure 4). Chemical compositions of the bismuth minerals contained in Cu ore generally are rich in Cu and Se.

The association of Bi sulfides with chalcopyrite and chamosite, and that of Te minerals with quartz in the sample from the Arakawa deposit suggest that the Te mineralization postdated the Bi mineralization. Bismuth sulfides occurs with chalcopyrite. The presence of Te minerals and their mutual relationships is sensitive to changes in physicochemical conditions of ore forming fluid (Ref. [12]). Bi/Te( + Se + S) of bismuth-tellurides of the Arakawa deposit are ≤1, which indicates relatively high sulfur and tellurium fugacity conditions of the ore forming fluid (Ref. [11]). The presence of Bi-Te minerals suggests an oxidized environment, close to the hematite-magnetite buffer (Ref. [10]). This physicochemical condition is consistent with hematite that commonly occurs in the ore veins of the Arakawa deposit. Bismuth mineral assemblage of the Arakawa deposit is similar to that of the other Miocene vein-type copper deposits in the Northeast Japan arc.

6 CONCLUSION

We described bismuthinite, pavonite, matildite, tetradyomite, hessite, isomutite, and ourayite in the ores from the Arakawa deposit. Bismuth-tellurium ratio of Bi-Te(-Se-S) minerals and presence of Bi-Te mineral suggests high tellurium fugacity, high sulfur fugacity, and high oxygen fugacity conditions of the ore forming fluid in the Arakawa deposit.

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183 Bismuth and Tellurium Minerals from the Arakawa Deposit in the Northeast Japan Arc

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