HOKKAIDO UNIVERSITY

Title	Comparison of Smectite-Corrensite-Chlorite Series Minerals in the Todoroki and Hishikari Au-Ag Deposits : Applicability of Mineralogical Properties as Exploration Index for Epithermal Systems
Author(s)	Yoneda, T.; Mokko, H.; Matsumoto, A. et al.
Citation	Natural Resources Research, 30(4), 2889-2908 https://doi.org/10.1007/s11053-020-09672-w
Issue Date	2021-08
Doc URL	https://hdl.handle.net/2115/86480
Type	journal article
File Information	Author Edit for Accepted Manuscript.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Natural Resources Research, DOI 10.1007/s11053-020-09672-w
Journal of the International Association for Mathematical Geosciences, ISSN 1520-7439

Comparison of smectite-corrensite-chlorite series minerals occurring in the Todoroki and Hishikari Au-Ag deposits: Applicability of the mineralogical properties as exploration index for epithermal systems

T. Yoneda[1], H. Mokko[2], A. Matsumoto[2], and T. Sato[3]

1: Hokkaido University, Sapporo, Japan,
2: Graduate School of Engineering, Hokkaido University, Sapporo, Japan,
3: Faculty of Engineering, Hokkaido University, Sapporo, Japan
Corresponding author: yonet@eng.hokudai.ac.jp

Received: 15 November 2019 / Accepted: 26 March 2020

ABSTRACT

The tri-smectite(S)-corrensite(Co)-chlorite(C) series minerals from two epithermal deposits show a discontinuous stepwise sequence of different mixed-layering of chlorite and smectite layers, and there are differences in the mode of occurrence of the two deposits. The Al/Si ratios and Fe/ (Fe + Mg) ratios of the S-Co-C minerals vary closely related to the mixed-layering and the mode of occurrence. The S-Co-C minerals as a product of direct precipitation from the ascending hydrothermal solutions may reflect fluid chemistry originated in the water-rock interaction at deeper strata. The differences in the mixed-layering of the S-Co-C series minerals may be related to the different thermal and redox conditions effected by the fluid mixing and boiling, and also to kinetic factor such as time length of hydrothermal activity that effected vein formation. The corrensite and Co-C minerals as a product of hydrothermal alteration involving dissolution, re-precipitation, and crystallization, may undergo the smectite-to-chlorite transformation in epithermal systems. The transformation and the distribution of the corrensite and Co-C minerals in the host rocks around vein areas may have been controlled by the thermal conditions related to the fluid mixing and the water/rock ratios. In addition, the corrensite and Co-C minerals with high Fe/ (Fe + Mg) ratios may be affected by the host rock.

The factors influencing the conversion of the S-Co-C series minerals may be basically similar in both ore veins and host rocks. However, it is emphasized that the fluid/rock ratios may be a major factor influencing the conversion of the S-Co-S series minerals in host rocks. Additionally, the time length of hydrothermal activity that effected vein formation may be an important factor influencing the conversion of the S-Co-C series minerals in ore veins.

KEYWORDS: Epithermal Au-Ag deposits, Di- and tri-octahedral smectite, Corrensite, Interstratified Chlorite/Corrensite, Chlorite, Epithermal systems.

INTRODUCTION

Various alteration minerals including clay minerals occur as products of hydrothermal alteration in the epithermal system which is known as a shallow hydrothermal system at depths from the surface to ~2 km, closely accompanied with Au-Ag ore deposits and/or geothermal reservoirs (White and Hedenquist 1990; Hedenquist and Lowenstern 1994). The variety of the alteration minerals are understood to result from the different types of alteration with different hydrothermal conditions such as temperature, pressure and chemistry. The alteration types are defined in terms of the alteration mineral assemblages (Meyer and Hemley 1967; Rose and Burt 1979). For example, Shikazono (1988) discriminated the four alteration types from the hydrothermal alteration associated with some epithermal Au-Ag deposits in Japan: propylitic, potassic, intermediate argillic and

advanced argillic alterations. In addition, Utada (1980) classified the hydrothermal alteration into three alteration types related to temperature and chemistry of aqueous solutions: acid-type alteration, intermediate alteration and alkaline type alteration. These classification-categories based on the alteration mineral assemblages are usable as an index in modeling the physical and chemical processes in the hydrothermal systems, and in prospecting the resources accompanied with active/fossil epithermal systems (e.g., Inoue 1995, Hedenquist et al. 1996; Simmons and Browne 2000).

Concurrently, the mineralogical studies on clay minerals from the hydrothermal systems show highly diverse and systematic variations in compositional, structural and morphological properties, depending on the systems and/or on the locations within each system (e.g., Inoue 1995; Kim and Peacor 2002; Bove et al. 2002). These mineralogical properties of the clay minerals are expected to provide useful information to understandings of the epithermal systems as well as the alteration mineral assemblages mentioned above. In this context, noteworthy is the sequential mineral transformations via mixed-layering such as smectite-to-illite and smectite-to-chlorite in hydrothermal environment (e.g., Inoue et al. 2005; Beaufort et al. 2015). The mixed-layering (interstratification) of the clay minerals here is a one-dimensional stacking of unit structural layers of phyllosilicates, and the sequence of layers in the stacking is usually described by the Reichweite parameter which shows random (R0), short distance (R1) and long distance (R>1) orderings (Meunier 2003).

The occurrences and the mixed-layering of smectite-illite and smectite-chlorite series minerals in active and fossil hydrothermal systems have been documented by many investigators (e.g., Inoue and Utada, 1991; Schiffman and Fridleifson, 1991; Shau and Peacor, 1992; Buatier et al. 1995; Patrier et al. 1996; Inoue et al. 2005; G. D. Miron et al. 2012; Yoneda et al. 2016; Kralj, 2016; Forsythe et.al. 2019; and Środoń et al. 2019). These have shown that the mixed-layering of smectite-illite and/or smectite-chlorite series minerals changes characteristically in hydrothermal environments, and that the mineral conversion is controlled by a primary thermal factor and other influencing factors: fluid/rock ratios, chemistry of fluids and/or rocks, and others.

The conversion of trioctahedral smectite (S) to trioctahedral chlorite (C) occurring in the alteration processes is known to be associated with corrensite (Co), a 1:1 regularly interstratified mineral of chlorite and smectite (or vermiculite) layers, as an intermediate stable phase of the mixed layering. The conversion series from trioctahedral smectite, via corrensite, to chlorite (S-Co-C) shows a discontinuous sequence with stepwise different mixed-layering of chlorite and smectite layers in many hydrothermal environments (e.g., Inoue and Utada 1991; Shau and Peacor 1992; Buatier et al. 1995; Beaufort et al. 1997; Murakami et al. 1999; and Kralj 2016). In these cases the mixed-layer structure of chlorite-rich domain in the S-Co-C series is generally described as mixtures of corrensite and chlorite. In some cases, however, the S-Co-C series is described as a continuous series of mixed layering of chlorite and smectite layers (Schiffman and Fridleiffson 1991; Bettison-Varga and Mackinnon 1997).

The transformation mechanisms and the controlling factors implicated in the S-Co-C conversion have been discussed elsewhere (Shau and Peacor 1992; Beaufort et al. 1997; Robinson et al. 2002; Beaufort et al. 2015). Two models of the transformation mechanism are proposed to describe the S-Co-C conversion through corrensite: 1) a continuous transition model based on solid-state transformation mechanisms, valid in rock-dominated systems, and 2) a stepwise transition model based on dissolution-crystallization mechanisms, efficient in fluid-dominated systems (Beaufort et al. 2015). It is further noteworthy that the mineral conversions in geothermal systems are influenced by kinetic effects linked to the fluid/rock ratios or modes of fluid transport (advection or diffusion) related to the rates of dissolution/nucleation/growth, in addition to temperature as the primary factor in the mineral conversion (Robinson et al. 2002).

In addition, the S-Co-C series minerals occur both as the alteration minerals in the host rock of the hydrothermal systems which have been the objects of many studies, as well as with vein minerals in epithermal Au-Ag ore veins (Taguchi and Watanabe 1973; Takeuchi 1984; and Yoneda and Watanabe 1989). Recent study on the occurrence and the mixed layering of C-Co-S minerals from ore veins of the Todoroki epithermal deposit shows the C-Co-S minerals to be saponite, mono-mineralic corrensite, and Co-C minerals with different types of mixed-layering, and the products of direct precipitation from hydrothermal solutions related to the Au-Ag ore formations (Yoneda et al. 2016). These S-Co-C minerals as precipitates in open fractures can be

assumed to have been subject to different environmental conditions of formation from those where they are products of the hydrothermal alteration in host rock.

Better knowledge of the S-Co-C minerals formed under epithermal conditions would help to understand the transformation mechanism and factors controlling the mineral transformation in hydrothermal environments. Further, it may provide a promising index for identification in the exploration of epithermal ore deposits and also geothermal reservoirs at active and fossil hydrothermal systems. In this paper the occurrences and the mineralogical properties of S-Co-C series minerals from the Hishikari epithermal deposits in addition to the Todoroki deposit are described as an extension of the work of Yoneda et al. (2016). In this study a comparative evaluation of the mixed-layering in S-Co-S minerals which have different modes of occurrences in the two epithermal deposits is presented. In addition to the trioctahedral smectite (tri-smectite), dioctahedral smectite (di-smectite) is described because it occurs in close association with the S-Co-C series minerals in the epithermal systems.

ORE DEPOSTS

Todoroki Deposit

The Todoroki ore deposit is located in southwestern Hokkaido, Japan and is composed of epitherma1 Au-Ag bearing quartz veins which are hosted chiefly in rhyolitic pyroclastic rock of middle Miocene age (Fig. 1). Ores of the Chuetsu and Shuetsu veins have been investigated by one of present authors (Yoneda 1994). The K-Ar dating of adularia and illite in hydrothermally altered wall rocks of the Chuetsu and Shuetsu veins indicates a range of 2.08 –3.05 Ma (Sawai et al. 1992). In addition, K-Ar dating of the andesite lava directly over the ore veins gives ages of 3.0 -3.1 Ma (NEDO 1995), suggesting that hydrothermal fluid responsible for the Au-Ag ore veins may be directly related to the Pliocene andesite volcanic activity in this area.

Constituents of the Chuetsu and Shuetsu veins can be divided broadly into three different formation stages: (I) an earlier stage composed of dark grey, massive barren quartz with pyrite, adularia and minor clay mineral, (II) a middle stage characterized by banded and massive quartz with clay minerals (S-Co-C minerals ± di-smectite ± illite ± interstratified illite/smectite ± kaolinite), Au-Ag

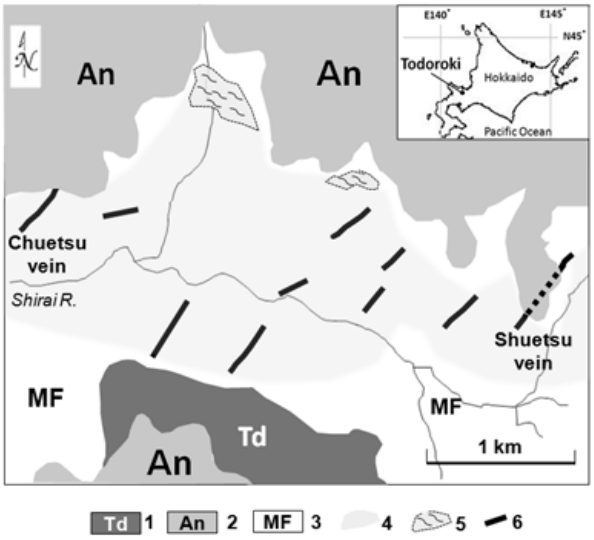


Fig. 1. Geological map of the Todoroki deposit (simplified after Yoneda (1994)). 1: Talus deposit, 2: Andesite lava, 3: Miocene rocks, 4: Alteration zone of illite ± chlorite (NEDO, 1995), 5: Alteration zone of kaolinite ± interstratified illite/smectite, 6: Ore veins.

minerals (electrum + argentite + pearceite ± polybasite +pyrargyrite ± argentian tetrahedrite) and Cu-Pb-Zn-Fe sulfide minerals (sphalerite + chalcopyrite +galena + pyrite ± marcasite), and (III) a later stage composed of large amounts of barren calcite (Yoneda et al. 2016). Different sub-stages can be identified within the stage II veins: for example, a massive white quartz vein is earlier than the other quartz veins, and there is a quartz vein with rhodochrosite in the later sub-stage (Yoneda et al. 2016). Stage II is generally dominated by microcrystalline and fine-grained quartz, occasionally with coarse-grained quartz or comb-like quartz bands (Yoneda et al. 2016).

The electrum and sphalerite observed in the stage II quartz show differences in the chemical compositions of the two ore veins: the Ag contents of electrum (0.62–0.54 atomic ratio, n = 24, mean = 0.58, SD = 0.027) and FeS contents of sphalerite (0.96–0.12 mol.%, n = 113, mean = 0.45, SD = 0.151) from the Shuetsu vein are higher than the Ag contents of the electrum (0.52–0.43 atomic ratio, n = 19, mean = 0.49, SD = 0.016) and the FeS contents of sphalerite (0.16–0.01 mol.%, n = 31, mean = 0.04, SD = 0.03) from the Chuetsu vein (Yoneda et al. 2016).

Based on the fluid inclusion microthermometry of the stage II quartz, the temperature ranges of ore formations are given as 140-270 °C (n=141, mode=200 °C) for the Chuetsu vein and 172–225 °C (n=25, mode = 210 °C) for the Shuetsu vein (Yoneda 1994). The NaCl equivalent salinities of fluid inclusions are examined for the stage II quartz of the Chuetsu vein as 1.65-0.38wt% (N=6,

Mean=0.93 wt %) (Yoneda 1994). In addition, based on the thermometer assuming the equilibrium coexistence of electrum-argentite-sphalerite-pyrite (Shikazono 2003), the approximate temperatures are estimated as a temperature range of 140–242°C for the Chuetsu vein and 171–256°C for the Shuetsu vein. The temperatures of the Shuetsu vein are in a higher range than those of the Chuetsu vein (Yoneda et al. 2016).

The hydrothermal alterations characterized by illite-chlorite assemblage and kaolinite-interstratified illite/smectite assemblage, are developed in the Miocene formations around the ore veins (Fig. 1). The alteration of kaolinite-interstratified illite/smectite is observed in relatively limited areas at higher elevations. In the wall-rock samples collected from mine tunnels nearby the ore veins, quartz, adularia, calcite, chlorite, illite, interstratified illite/smectite, kaolinite and pyrite are observed as alteration products. The wall-rock alteration is characterized by the alteration mineral assemblage of illite-chlorite. Minor interstratified illite/smectite occurring as clay veinlets and minor kaolinite are observed locally in the wall-rocks of the Chuetsu vein. They are interpreted to be products of later-stage alteration compared with the chlorite-illite assemblage. Overall, C-S minerals with mixed-layering are only rarely detected in the wall-rock samples of the two veins.

Hishikari Deposits

The Hishikari deposits are located in southern Kyushu, Japan, and consist of epitherma1 Au-Ag bearing quartz veins which are mined actively at present. The ore deposit has been studied in detail by many researchers (e.g., Izawa et al.1990, 1993; Ibaraki and Suzuki 1990; Nagayama 1993; Imai et al. 1998; Sekine et al. 1998, 2002; Shikazono et al. 2002; Murakami 2007; Sanematsu et al. 2005; Murata et al. 2008; Tohma et al. 2010; Takahashi et al. 2017; Shimizu 2018; Morishita et al. 2018). The mining area is formed by Cretaceous sedimentary rocks of the Shimanto Supergroup (SSG) (dominantly shale and sandstone) and Quaternary volcanic rock (andesite and dacite) (Izawa et al. 1990). The Au-Ag ore veins are hosted in SSG and Pleistocene volcanic rock of the Hishikari Lower Andesites (HLA) overlying the SSG unconformably (Izawa et al. 1990) (Fig. 2). The ore veins are grouped into three ore zones (Main, Sanjin and Yamada deposits). The ore veins in the Main and Sanjin deposits are hosted in both the SSG and the HLA, while the Yamada deposit is in the HLA. The K-Ar dating of hydrothermally altered host rock and vein minerals shows that hydrothermal alteration and mineralization of the Hishikari deposits began at about 1.25 Ma and had ended by about 0.66 Ma, and that the period of mineralization was nearly synchronous with the volcanic activity (1.6 Ma to 0.66 Ma) in the Hishikari area (Izawa et al. 1993). In addition the periods of mineralization for the early and late veins which are classified on the basis of the crosscutting relationships, are shown as 1.11 to 0.86 Ma and 0.84 to 0.73 Ma, respectively (Sekine et al. 2002). A recent Ar/Ar dating for adularia from the Fikusen-1 vein which is located in the southeastern part of the Yamada deposit shows younger ages with a narrow range (from 0.617 Ma to 0.601 Ma) which are thought to be one of the youngest ages in the Hishikari deposits (Tohma et al. 2010).

The quartz veins associate abundant adularia, clay minerals (dominant smectite, and minor amounts of illite, chlorite and kaolinite) and small or minor amounts of carbonates, gypsum, truscottite, xonotlite, wairakite, laumontite and ore minerals such as electrum, chalcopyrite, pyrite, marcasite, naumanite, Ag-sulfosalts, sphalerite, galena and stibnite (Izawa et al. 1990; and Sekine et al. 1998). A banded zonal structure comprised of quartz, adularia and smectite bands is developed within the ore veins (Nagayama 1993). The mineral assemblages, Au grades and Au/Ag ratios of the ore veins are similar in the early and the late veins, but the width of bands at the later veins (> 3 cm) is narrower than that at the early veins (≥10 cm) (Sekine et al. 2002).

The temperature of the ore formation is thought to be around 210°C at lower elevations, and less than 200 °C in volcanic rock at higher elevations, based on fluid inclusion microthermometry (Izawa et al. 1990). Recent study of the fluid inclusion microthermometry of the Hishikari ore veins show the temperature range of 190–220°C for several ore veins in the Zuisen, Keisen, Shosen, and Seisen vein groups (Takahashi et al. 2017) which is similar to the previously determined temperatures. At the Fukusen-1 vein located in the southern margin of the Yamada deposit a lower temperature range of 180–200°C is reported (Tohma et al. 2010).

Four alteration types (IV-I) are reported by Izawa et al. (1990) on the basis of the alteration mineral assemblages as follows: the IV-type (chlorite-illite zone) is defined by

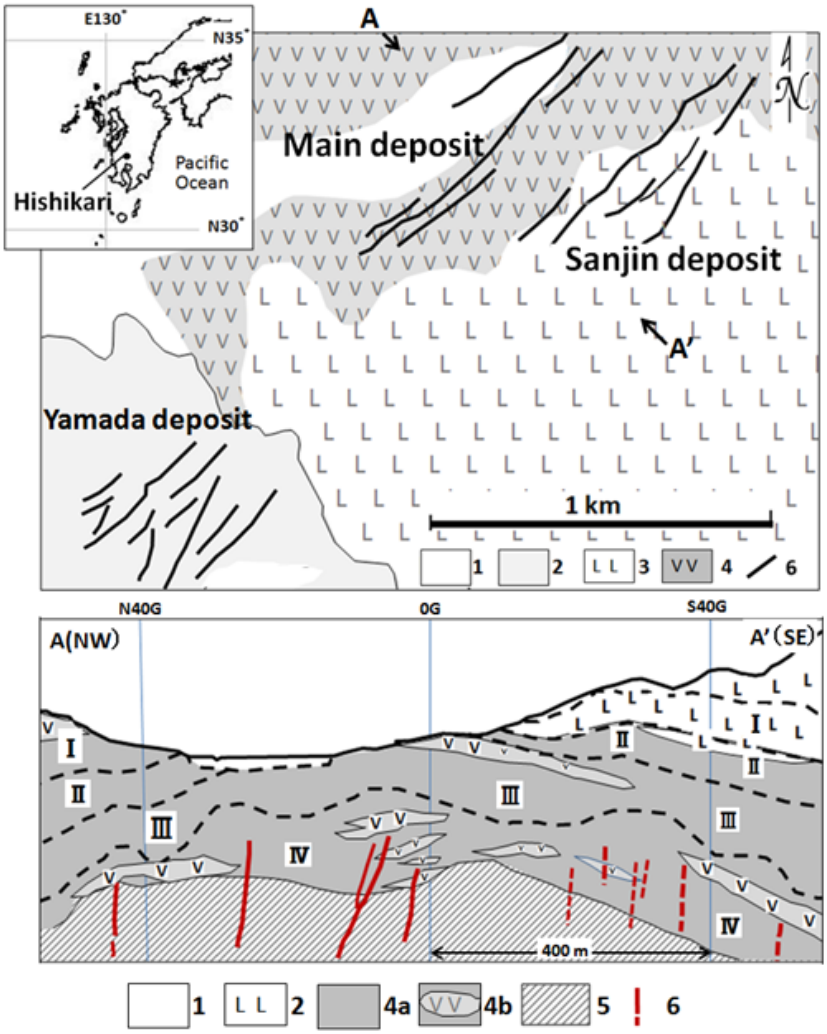


Fig.2. Geological map of the Hishikari deposits (simplified after Ibaraki and Suzuki (1993)). 1: Alluvium, 2: Pyroclastic flow, 3: Shishimano dacites, 4: Hishikari lower andesites (HLA), 4a: HLA tuff breccia, 4b: HLA lava, 5: Shimanto supergroup, 6: Ore veins. I-IV: Alteration zones around the ore veins (see text for details).

presence of chlorite and local illite, and the typical alteration mineral assemblage is quartz-chlorite-adularia-calcite-albite; the type-III (interstratified clay mineral zone) is characterized by presence of C/S and/or interstratified illite/smectite and is commonly accompanied by quartz-adularia-calcite-smectite-laumontite; the type-II (quartz-smectite zone) is defined by quartz with smectite and/or kaolin minerals; and the type-I (cristobalite-smectite zone) is characterized by cristobalite (and/or tridymite) with smectite. The mineral zones characterized by the alteration types show a zonal arrangement in the Hishikari deposits (Izawa et al. 1990: Ibaraki and Suzuki 1990) as follows: the type-IV alteration is the principal alteration directly associated with high grade Au mineralization, the type-III and the type-II alterations envelopes the mineralized center, the type-I alteration and least-altered rocks surround the types of IV-II (Fig. 2). Recent works on the Yamada deposit show that a number of ore veins extend also into the type-III zone (Murata et al. 2008).

SAMPLES AND METHODS

Analytical results of the S-Co-C series minerals from the Todoroki deposit are quoted from Yoneda et al. (2016) to the present study. The studied samples of ore (stage II quartz) and wall-rock are from the eastern area of the Shuetsu vein and from a wide area except the shallow, high-grade mined parts of the Chuetsu vein. Details of the samples and investigation method are given

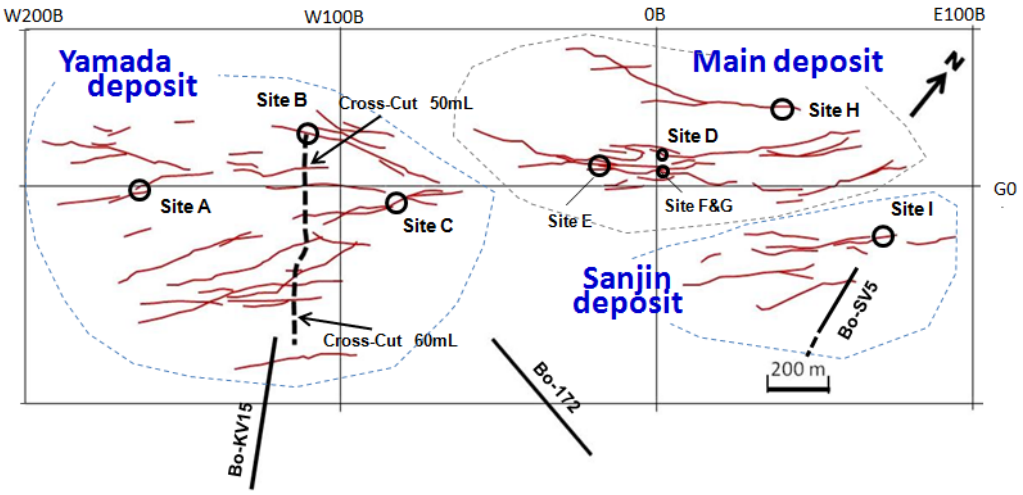


Fig.3. Plan showing distribution of ore veins in the Hishikari deposits. Sampling locations of drill holes (KV15: horizontal drilling at 80mL, SV5: horizontal drilling at 0mL, Bo127: inclined drilling from surface), cross-cuts at 50mL/60mL and vein-sites (A-I) are shown too. Map is modified after Sekine et al. (2002). Site A: Eisen-1-2 at 70mL171W, site B: Seisen-7 at 50mL111W, site C: Yusen-1-2 at 20mL85W, site D: Zuisen-1 at 25mL1E, site E: Hosen-2 at 25mL19W, site F: Hosen-1 at 25mL1E, site G: Hosen-2 at 70mL1E, site H: Daisen-1 at 100mL40E and site I: Keisen-3-1 at 40mL59E.

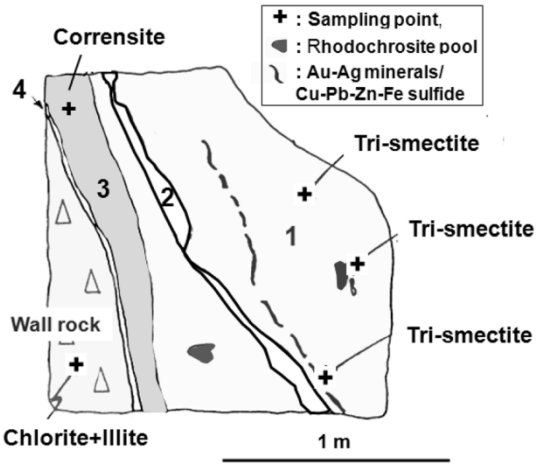


Fig.4. Vein sketch at the upper part of the Chuetsu vein of the Todoroki deposit (see Fig.5 for the location). 1: light grey massive quartz (partly banded) with black streak rich in Au-Ag minerals/Cu-Pb-Zn-Fe sulfide minerals, 2: white quartz, 3: grey clayey quartz, 4: transparent quartz. Corrensite and tri-smectite are detected from ore samples shown in figure.

in Yoneda et al. (2016).

Host-rock and vein-quartz samples of the Hishikari deposits are collected from drilling cores (KV15, SV5 and Bo127), cross-cuts at 50mL and 60mL of the Yamada deposit, and ore veins (Eisen-1 at 70mL, Seisen-7 at 50mL, Yusen-1-2 at 20mL, Zuisen-1 at 25mL, Hosen-2 at 25mL, Hosen-1 at 25mL, Hosen-2 at 70mL, Daisen-1 at 100mL, and Keisen-3-1 at 40mL). Locations of the above samples are shown in Fig. 3. The host-rock samples examined are Quaternary volcanic rocks (HLA and Shishimano dacite). The sampling points of host rocks of the Hishikari deposits range across the alteration zones from IV to I.

Clay minerals in the rock and ore samples of the Hishikari deposits were separated by ultrasonic treatment in distilled water, and then the clay fractions were concentrated by centrifugal sedimentation. Samples of clay fractions were prepared to oriented specimens untreated and solvated by ethylene glycol solution on glass slides, and the oriented specimens were examined by XRD using a Rigaku RINT2100 (radiation: Cu-Kα; accelerating voltage/current: 30 kV/20mA; slit system: divergent 1/2°-scattering 0.3 mm-receiving 1/2°; step scan conditions: step interval = 0.02° 2θ and measurement time per step = 1 sec. In addition, the XRD patterns of tri- and di-smectite were calculated using NEWMOD (Reynolds 1985) for comparison with the observed patterns. Selected ore samples were prepared as polished thin sections for optical microscopic observations and EPMA analyses of clay minerals. The EPMA analyses were performed using a JXA-8900M instrument equipped with wavelength-dispersive X-ray spectrometers (dispersive crystals: TAP, PETJ, LIF and LIFH). Experimental conditions of the EPMA quantitative analysis are as follows: accelerating voltage = 15 kV, probe current = 10 nA, beam diameter = 10 ~ 3 μm, counting time (peak) = 10 s and counting time

(background) = 5 s.

RESULTS

S-Co-C Series Minerals at the Todoroki Deposit

At the Todoroki deposit the S-Co-C series minerals occur as vein mineral which is attributed to the middle-stage Au mineralization. Corrensite and tri-smectite occur in the Chuetsu vein and Co-C minerals in the Shuetsu vein. The S-Co-C minerals in the ore samples aggregate in the form of fine or coarse bands and patches in the microcrystalline and fine-grained quartz, and are closely associated with the Au-Ag and Cu-Pb-Zn-Fe-S minerals. In wall-rock samples usual chlorite without smectite layers is observed frequently accompanying illite.

Corrensite is commonly observed as a mono-mineralic phase in the ore samples from the Chuetsu vein, and tri-smectite is identified also in some ore samples from the upper part of the vein. The occurrence of corrensite and tri-smectite can be interpreted as products of different sub-stages: tri-smectite may be later precipitates than corrensite (Fig. 4). In this context, di-smectite is also identified in an ore sample with manganese oxide from the most upper part of the Chuetsu vein. Distributions of corrensite and smectite plotted on longitudinal sections show that corrensite is distributed widely but smectite is of relatively limited distribution in the ore vein (Fig. 5).

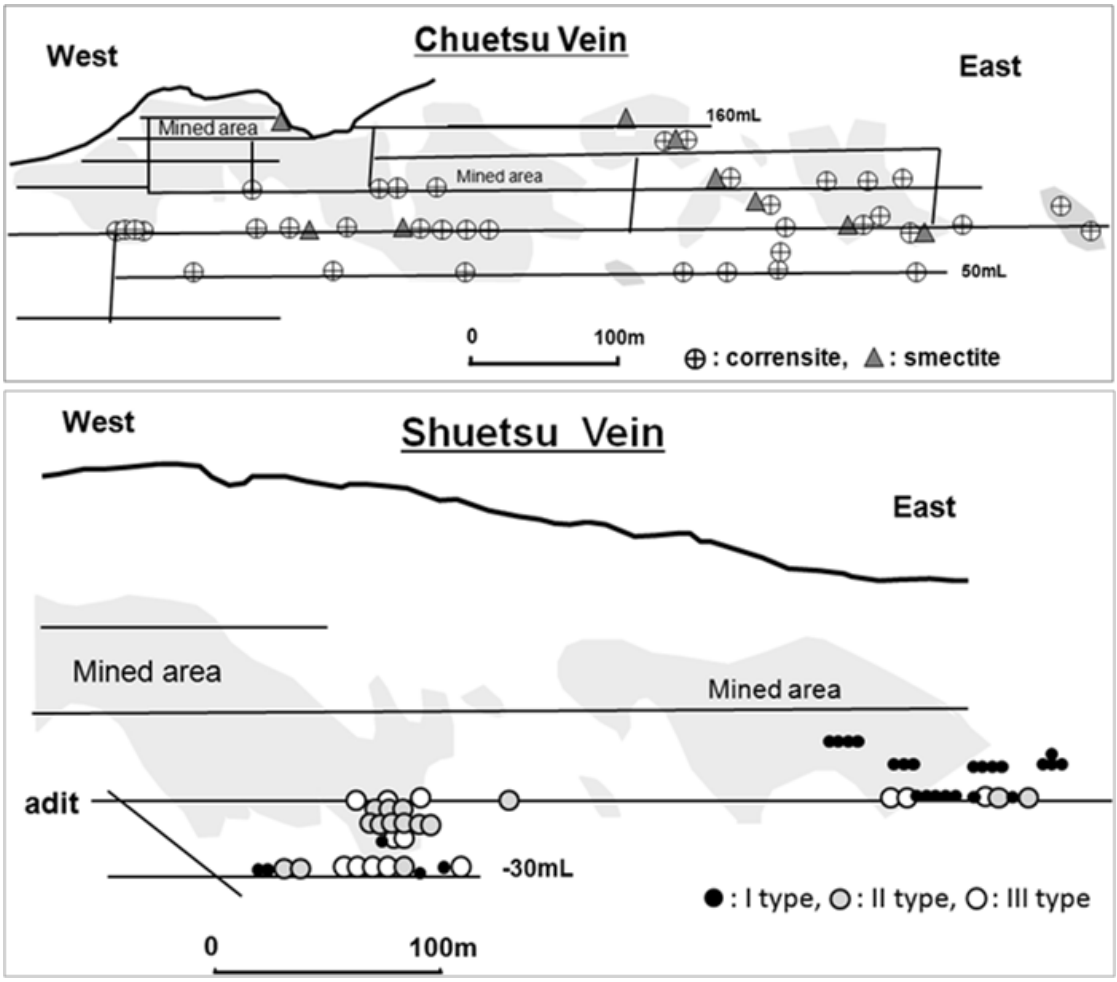


Fig.5. Distribution of corrensite, smectite and Co-C minerals (types of I-III) in the Chuetsu vein (upper) and the Shuetsu vein (lower) of the Todoroki deposit.

Table 1. Mixed-layerings of Co-C series minerals of the I-III types of and corrensite occurring in ore veins of the Todoroki deposit.

Type	Mixed-layere structure	%S	Locality
I	Tri-chlorite ocassinally with smectite or corrensite layers in the chlorite structure	Presumed to be <10%	Shuetsu vein
II	Mixture of interstratified corrensite and chlorite [Co/CC (0.3/0.7, R=1)] and discrete chlorite	Variable over a limited range below 15% with a maximum value in the absence of discrete chlorite	Shuetsu vein
III	Mixture showing segregation structures of corrensite and chlorite layers [Co/C, R=1], of which ratios vary significantly	Variable depending on the ratios of Co and C in the segragation structure, a %S range of 35-15% is determined	Shuetsu vein
Corrensite	Regularly interstratified chhlorite and saponite [(C/S(0.5/0.5), R=1]	Monomineralic corrensite can be estimated %S of 50%	Chuetsu vein

The Co-C minerals occurring in the Shuetsu vein are classified into three different types of mixed-layering on the basis of the XRD modeling: an I type of discrete chlorite frequently with minor amounts of S layers, a II type comprising mixed-layer corrensite and chlorite (Co/CC=0.3/0.7, R=1) and discrete chlorite, and a III type with segregation structures of Co and C layers (Yoneda et al. 2016). The characteristics of the mixed-layering of the Co-C minerals of the Todoroki deposit are detailed in Table 1. The discrete assemblage of the II type and the assemblages of the III type are thought to be packets incorporated in the stacking of clay particles, based on microscopic analyses (EPMA and AEM) (Yoneda et al. 2016). Distributions of the Co-C minerals are shown in longitudinal sections of the Shuetsu vein (Fig. 5). The I type is mainly distributed in the eastern part while the II and III types are dominant in the deep central parts of the vein, but the temporal relationships between the I–III types are not clear. As described, the S-Co-C series minerals from the Todoroki ore veins show a discontinuous sequence with different mixed-layering of chlorite and corrensite layers.

The S-Co-C series minerals from the ore veins and the chlorite from the wall-rock are Mg-rich and Fe-poor with minor amounts of Mn, and show differences in the chemical compositions depending on the types of the series of minerals and locations in the deposit (Yoneda et al. 2016). The Al/Si ratios ranging from 0.1 to 0.9 increase in the order of tri-smectite, corrensite, III-I types and host-rock chlorite. This may be understood to be due to the proportions of smectite layers included in the various samples. In addition, the tri-smectite and corrensite of the Chuetsu vein are very low in Fe (Fe/ (Fe + Mg + Mn) = 0.01–0.03) but abundantly rich in Mg compared with I–III types of the Shuetsu vein which has less Mg and more Fe (Fe/(Fe + Mg + Mn) = 0.06–0.15). The wall-rock chlorite has less Mg and more of Fe compared to III–I types.

S-Co-C Minerals at the Hishikari Deposits

S-Co-C Minerals in theOoreVveins

It is known that smectite occurs widely as a common vein mineral in ore veins of the Hishikari deposits (e.g., Izawa et al. 1990; Nagayama 1993; Sekine et al. 1998). Sekine et al. (1998) reported that smectite is dioctahedral type in most ore veins and trioctahedral smectite occurs in Seisen-2 vein of the Yamada deposit. The smectite is commonly observed in white or greenish clayey bands associated with quartz and adularia bands in the ore veins (Fig. 6a). An ore sample with greenish clayey bands accompanying Au-Ag /Cu-Pb-Zn-Fe-S minerals is exemplified in Figs. 6b and c. The occurrences of smectite bearing clays suggest that the smectite is a precipitate from hydrothermal solutions during the vein formation.

Both di- and tri-smectite are observed as mono-mineralic phase in the ore samples (Fig. 7). For the identification of di- and tri-smectite in this study, the XRD intensity ratios of the basal reflections (I_{003}/I_{002}) of smectite are used in addition to the d(060) spacing of smectite. The I_{003}/I_{002} values of the calculated XRD patterns indicate that the di-smectite with low Fe-content can be distinguished from tri-smectite (Fig. 8). As shown in Fig. 8, the measured values of the I_{003}/I_{002} ratios and Fe-contents of tri-/di-smectite are compatible with those of the calculated XRD patterns. From this, the XRD measurement of the intensity ratios of the basal reflections (I_{003}/I_{002}) is thought to be useful in discriminat-

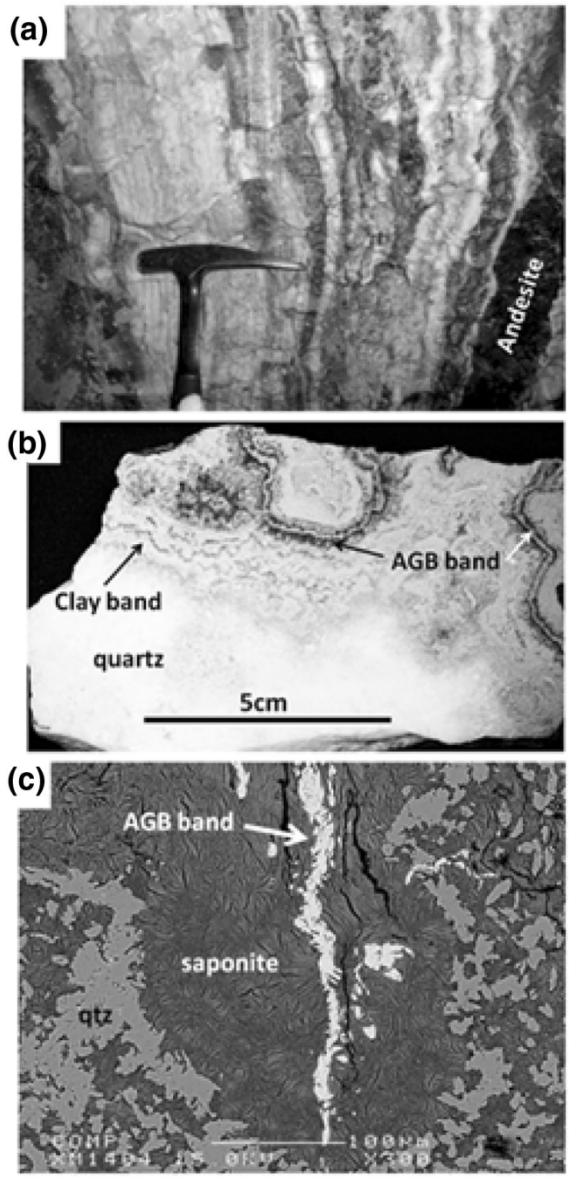


Fig.6. Photographs showing the occurrence of S-Co-C minerals in ore veins of the Hishikari deposits: (a) banded vein-structure with clay bands (Seisen-7 vein at 50mLW111; (b) vein quartz with banded clay and AGB (Au-Ag minerals/Cu-Pb-Zn-Fe sulfide minerals) (Hosen-2 vein at 70mLE1); (c) backscattered electron image showing a co-exsistence of saponite, quartz (qtz), and AGB band (the same sample as (b)).

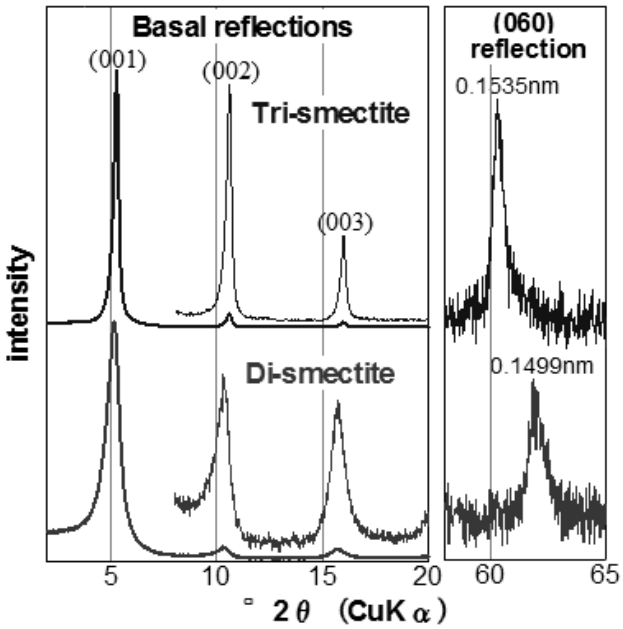


Fig.7. XRD peaks of the basal and (060) reflections of tri-smectite (a) and di-smectite (b) from ore veins of the Hishikari deposits. The basal reflections are obtained from the oriented specimens treated by EG and the (060) reflection is from the randomly oriented specimens. The intensity ratios of basal reflections (I_{003}/I_{002}) for (a) and (b) are 0.46 and 1.00, respectively. (a): green clay associated with massive quartz of the Keisen-3-1 vein (SPN KE3), (b): grey clay associated with banded quartz of the Hosen-2 vein (SPN 880611 01).

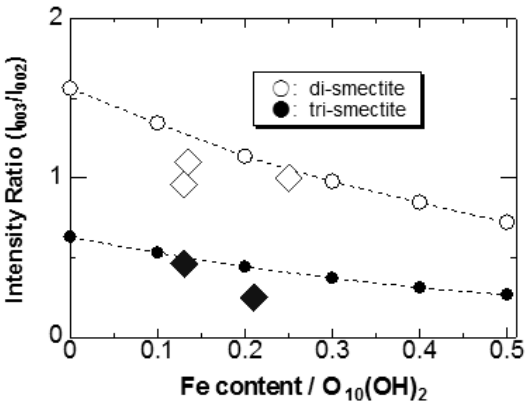


Fig.8. XRD intensity ratios of basal reflections (I003/I002) vs. Fe contents of tri- and di-smectite based on XRD modeling by Newmod (Reynolds, 1985).The measured values of tri-smectite (♦) and di-smectite (◇) from the Hishikari deposits (see Table 2) are plotted.

ing di-smectite with low Fe contents from tri-smectite.

Smectite in greenish clays from the Yusen-1-2 vein (site C), Hosen-2 vein (site G), and Keisen-3-1 vein (site I), is identified as tri-smectite. The smectite in the white/gray/greenish clays from the Eisen-1-2 vein (site A), Seisen-7 vein (site B), Zuisen-1 vein (site D), Hosen-1 vein (site F), Hosen-2 vein (site E) and Daisen-1 vein (site H), is identified as di-smectite. These results show that the tri-smectite, an end-component of the S-Co-C series, may occur more widely in the Hishikari ore veins.

As describes above, no other S-Co-C series minerals without tri-smectite were detected as vein minerals in the ore veins. A minor amount of kaolinite is frequently detected in the ore samples, possibly as a product in later stage or following stage of the vein formations. Acicular

Table 2 Results of the EPMA analyses for smectite and Co-C minerals of the Hishikari deposits. Excess silicon for di-smectite may be due to contamination by co-existing quartz and cristobalite in analyzed samples.

	Mineral in Vein				Alteration mineral in host rock			
Sample No.	K-3-1 V4	ID4	EI-1-2 V26	SE-7 V	Bo12	EI-1-2 23WR	Cross-35WR	SE7-2WR
Location	Keisen-3-1 40E59	Ho-2 25E1	Eisen-1-2 70W171	Seisen-7 50W111	Bo127 299m	Eisen-1-2 70W171	Cross-cuts 50mL nearby Yusen-7	Seisen-7 50W111
Mineral Type	tri-smectite		di-smectite		di-smectite	Co	type III	type I
N	9	9	17	6	1	17	12	12
Si	3.43 (0.13)	3.93 (0.04)	4.06* (0.04)	4.11* (0.03)	4.2*	3.27 (0.07)	3.13 (0.08)	3.30 (0.07)
Al(IV)	0.57 (0.13)	0.07 (0.04)	-	-	-	0.73 (0.07)	0.87 (0.08)	0.70 (0.07)
Al(VI)	0.14 (0.01)	0.67 (0.06)	1.47 (0.04)	1.46 (0.04)	1.3	0.71 (0.11)	0.70 (0.11)	1.47 (0.06)
Mg	2.59 (0.09)	1.72 (0.10)	0.41 (0.02)	0.35 (0.02)	0.2	2.73 (0.20)	2.85 (0.18)	2.14 (0.05)
Fe^{2+}	0.21 (0.05)	0.13 (0.01)	0.14 (0.02)	0.14 (0.00)	0.2	0.97 (0.05)	0.94 (0.05)	1.92 (0.07)
Mn	0.04 (0.01)	0.04 (0.01)	0.00 (0.00)	0.00 (0.00)	0.0	0.03 (0.01)	0.02 (0.01)	0.05 (0.01)
Ca	0.21 (0.05)	0.14 (0.02)	0.12 (0.02)	0.08 (0.01)	0.1	0.07 (0.01)	0.07 (0.01)	0.05 (0.02)
K	0.00 (0.01)	0.01 (0.00)	0.01 (0.00)	0.01 (0.00)	0.1	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)
Na	0.04 (0.05)	0.01 (0.00)	0.03 (0.00)	0.02 (0.01)	0.0	0.01 (0.00)	0.03 (0.02)	0.01 (0.00)
Base	$O_{10}(OH)_2$	$O_{10}(OH)_2$	$O_{10}(OH)_2$	$O_{10}(OH)_2$	$O_{10}(OH)_2$	$O_{10}(OH)_5$	$O_{10}(OH)_5$	$O_{10}(OH)_8$
Al/Si	0.21 (0.06)	0.19 (0.02)	0.36 (0.01)	0.36 (0.01)	0.3*	0.44 (0.03)	0.50 (0.03)	0.66 (0.05)
Fe/(Fe+Mg)	0.07 (0.02)	0.07 (0.01)	0.25 (0.02)	0.29 (0.02)	0.5	0.26 (0.02)	0.25 (0.02)	0.47 (0.01)

*: excess silicon is included, Fe^{2+} is expressed as total Fe.

kaolinite is found associated with a later-stage constituent of banded ore vein (Nagayama 1993).

Analytic results of EPMA for the smectites contained in four ore-samples are shown in Table 2. The Fe-contents of the tri- and di-smectite are low, less than 0.25/ $O_{10}(OH)_2$. The tri-smectite shows lower Al/Si and Fe/ (Fe + Mg) ratios than those of the di-smectite. Mg contents of the di-smectite are understood to show their montmorillonitic character.

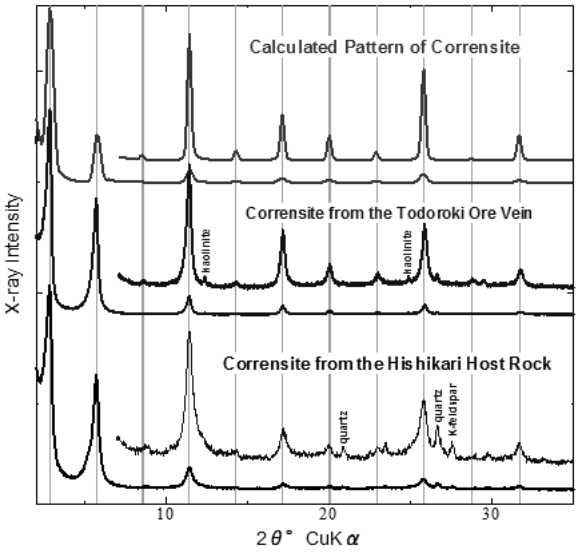


Fig.9. XRD patterns of EG-corrensite. The vertical lines correspond to the basal reflections of calculated corrensite. Values of the CVEG for the proportionality of the higher order reflections are 0.53 and 0.22 for the Hishikari and Todoroki corrensite, respectively.

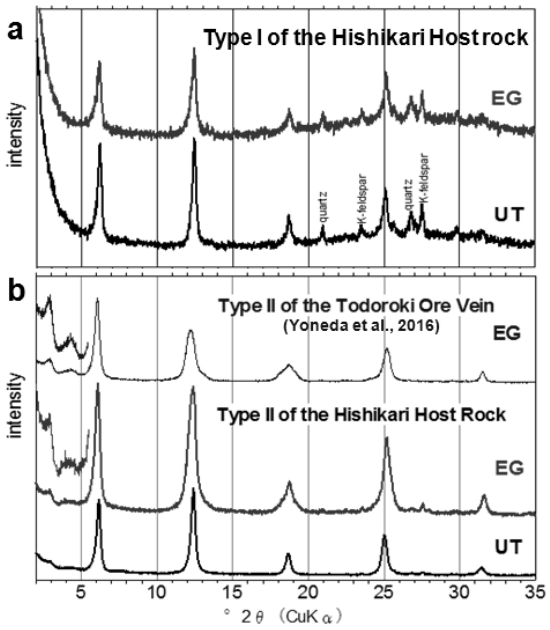


Fig.10. (a) XRD patterns of the I type from the Hishikari host rock. This sample is chlorite without expandable layers. (b) XRD patterns of the II type from the Hishikari host rock and the Todoroki ore vein. Difference between the XRD patterns (EG) of the II type from the two deposits can be mainly due to a difference in the proportion of discrete chlorite mixed with Co/CC in the clay samples. See text for details

S-Co-C Series Minerals in Altered Host Rock

Host rock samples of Hishikari Lower Andesites (HLA) and Shishimano dacite from the Yamada and

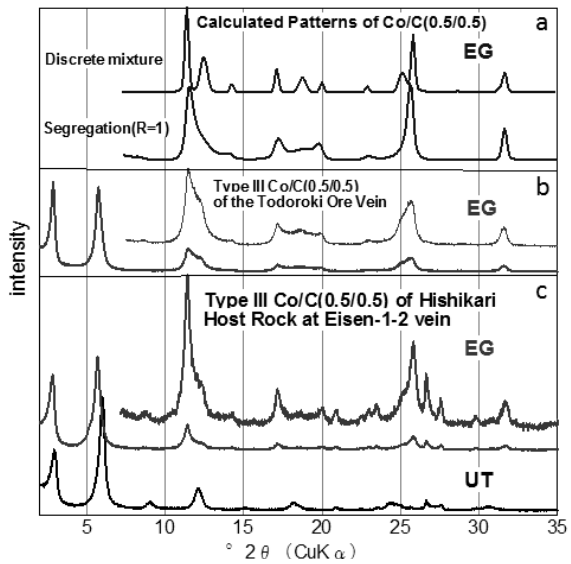


Fig.11. XRD patterns of the III type with Co/C=0.5/0.5 are exemplified. (a) Segregation and discrete mixture of Co and C can be distinguished by degree of peak separation on the calculated XRD patterns, (b) a phase (Co/C=0.5/0.5) of the III type from the Todoroki ore vein, (c) The III type mineral of the Hishikari host rock showing a similar pattern to those of (a)-lower and (b) is interpreted as a segregation with Co/C=0.5/0.5. (a) and (b) are quoted from Yoneda et al.(2016).

Sanjin deposits were examined (Fig. 3). The alterations of the HLA and the Shishimano dacite can be attributed to the alteration types of IV, III and II, and the alteration type-I, respectively. Corrensite and Co-C minerals are observed as the dominant alteration products in the HLA of which alteration types are corresponding to IV and III.

The XRD pattern of corrensite of the Hishikari host rock was compared with that of the Todoroki ore vein and showed the calculated pattern of corrensite in Fig. 9. Corrensite has a superstructure reflection (UT: 2.9 nm, EG: 3.1 nm) and sub-order basal reflections at rational positions. The Hishikari corrensite shows a coefficient of variability (CV_{EG} = 0.53) for the proportionality of the higher order reflections below 0.75, indicating that it may be identified as corrensite (Bailey 1982). The XRD patterns of the Co–C minerals can be distinguished into three types (type I-type III) as well as the I-III types of the Co-C minerals at the Todoroki ore veins. The type I is a discrete normal chlorite without expandable layers (Fig. 10a), and chlorite appearing in minor amounts of smectite layers in the chlorite structure is included in type I. The peak profiles of chlorite basal reflections change by EG treatment due to the containing expandable layers it includes. The ratio of smectite (%S) in type I may be presumed to be <10%. The XRD patterns of type II are characterized by weak reflections at 3.0 nm and 2.0 nm which shift to 3.1 and 2.1 nm, respectively, and by changes in the peak profiles of the reflections at 0.72 and 0.47 nm after EG treatment (Fig. 10b). These characteristics of type II may be interpreted as a mixture of the interstratified Co/CC (0.3/0.7) mineral and discrete chlorite (Yoneda et al. 2016). The %S in type II (Co/CC (0.3/07) + C) may vary over a limited range below 15% with a maximum value in the absence of discrete chlorite. The XRD patterns of type III after EG treatment have the basal reflections peculiar to corrensite and chlorite. The XRD patterns can be interpreted to be due to segregation structures in the Co and C layers, and differences in the XRD patterns in different samples would be related to the ratios of the corrensite and chlorite layers in the segregation structure (Yoneda et al. 2016) (Fig. 11). The layer ratios of type III from the Hishikari deposits are estimated to be in the range of Co/C(0.8/0.2) to Co/C(0.2/0.8), which corresponds to a %S of 40 to 10%.

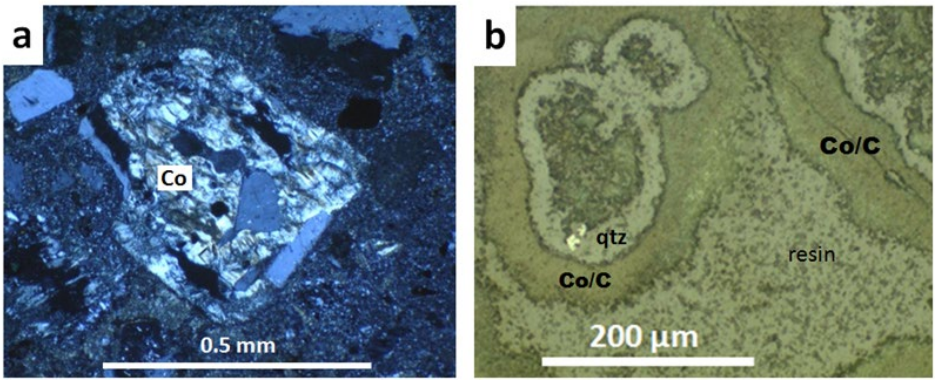


Fig.12. Optical Microscopic occurrences of Co-C minerals in altered host rock of the Hishikari deposits. (a): corrensite (Co) replacing phenocryst plagioclase in altered LHA (wall-rock of the Eisen-1-2 vein at 70mL171W) [cross polar under transmitted light], (b): Co/C mineral (Co/C) occurring as colloform-like band in altered LHA (host rock in Crosscuts at 60mL115W) [parallel polar under reflected light].

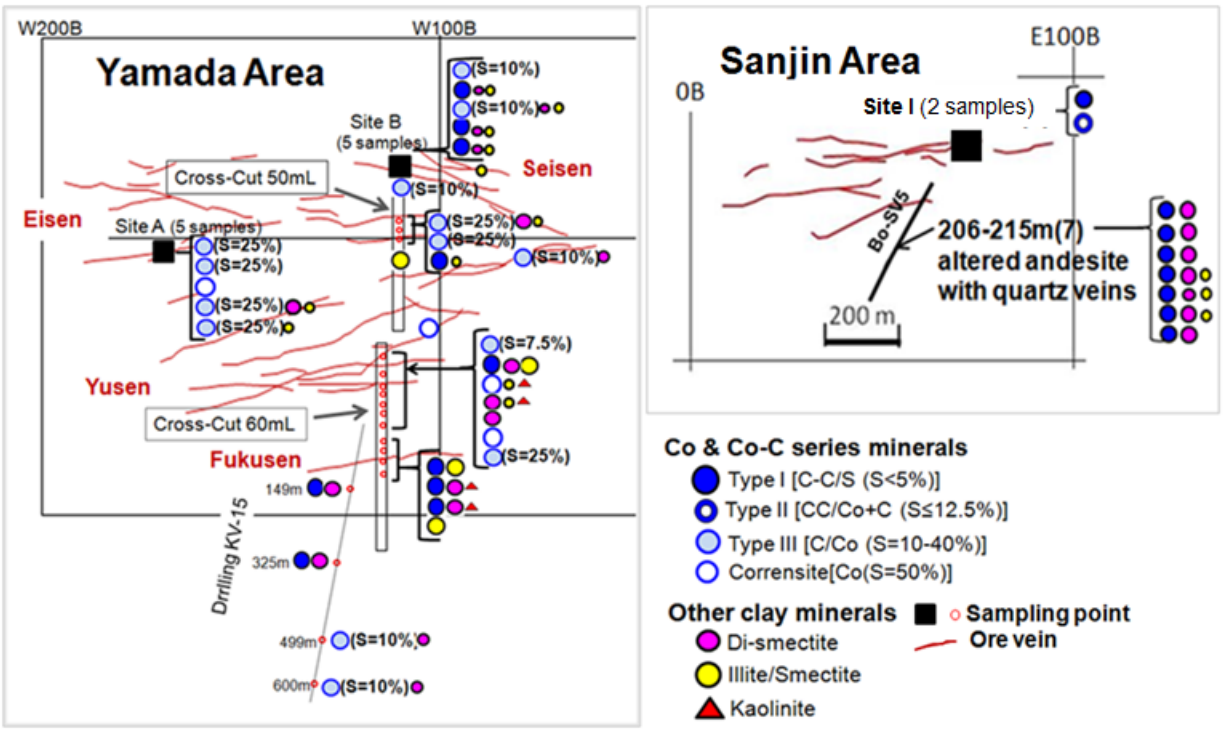


Fig.13. Distribution of corrensite and Co-C minerals at the Yamada and Sanjin deposits of the Hishikari deposits.

The corrensite and Co-C minerals are observed as aggregates of fine-grained clay, partly or perfectly replacing phenocryst, groundmass and matrix in the HLA. Microphotographs of corrensite replacing partly phenocryst of plagioclase in altered andesite and Co-C mineral making colloform-like banding in matrix of tuff are shown in Fig. 12.

Distributions of the corrensite and Co-C minerals at the Yamada and Sanjin deposits are shown in Fig. 13. The S-Co-C series minerals without tri-smectiteis occur dominantly in the HLA. At the Yamada deposit the Co-C minerals of type I and type III and corrensite are distributed, and the Co-C minerals of types I and type II are observed near ore veins of the Sanjin deposit. When comparing the two areas the Co-C minerals of the Sanjin deposit show lower ratios of %S in the mixed-layer structure than those of the Yamada deposit. Consequently, tri-smectite is not identified from the studied host rocks at the Yamada and Sanjin deposits, and the corrensite and Co-C minerals from the altered HLA also show a discontinuous sequence similar to that of the corrensite and Co-C minerals from the Todoroki ore veins. In this context, di-smectite, interstratified illite/smectite and minor kaolinite are frequently observed in the altered HLA. It may be characteristic that the occurrence frequency of di-smectite increase in the southern parts of the Yamada and Sanjin deposits.

Analytical results of EPMA for the Co-C minerals and di-smectite in four host rocks are shown in Table 2. The Co-C minerals from the host rocks show differences in chemical compositions depending on the types of the minerals. The Al/Si ratios wholly range from 0.4 to 0.7 and increase in the order from corrensite, and type III to type I. This increase would be due to a decrease in the proportion of smectite layers of the minerals in the analyzed samples. The Fe/ (Fe + Mg) ratios of the type I (0.47) are higher than those of the type II and corrensite (0.25-0.26). The di-smectite shows abnormal high silicon content probably due to contamination of cristobalite, and rather montmorillonitic character when considering the Mg content.

Mixed-layer Structures and Chemical Compositions of the Two Deposits

The smectite% and Al/Si ratios of the S-Co-C series minerals from the two deposits show a negative-correlation over a wide range (Fig. 14). This compositional correlation of the S-Co-C series minerals can be attributed to the mixed-layering which shows a discontinuous sequence with different mixed-layering of chlorite and corrensite (saponite) layers. The difference in the modes of occurrence of the Co-C minerals of the two epithermal deposits may be summarized as: at the

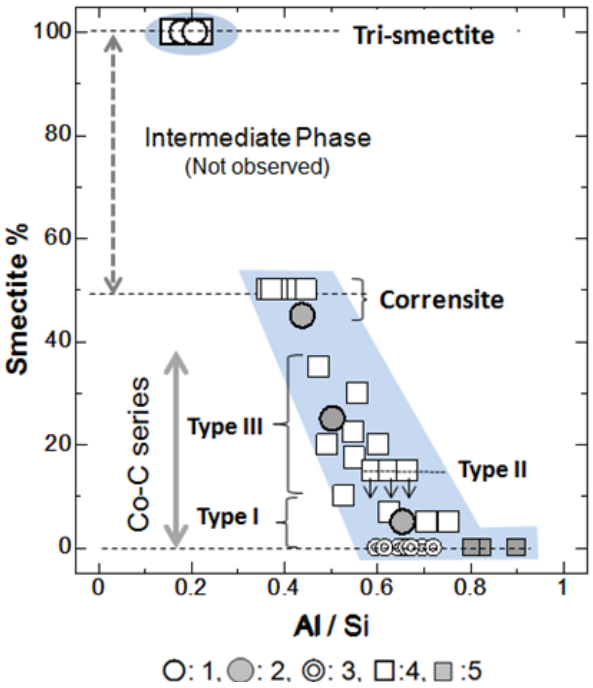


Fig.14. Plot of smectite% and Al/Si ratios of the S-Co-C series minerals from the two deposits. 1: Tri-smectite of the Hishikari ore veins, 2: Corrensite and Co-C minerals in HLA of the Hishikari deposits (this study), 3: Chlorite including C/S mineral in HLA of the Hishikari deposits (Murakami, 2007), 4: Corrensite and Co-C minerals of the Todoroki ore vein, 5: Chlorite in the Todoroki host rock.

Hishikari deposits the Co-C minerals occur as the alteration mineral in the host rock though tri-smectite occurs as the vein mineral. At the Todoroki deposit tri-smectite, corrensite and the Co-C minerals occur as the vein minerals.

The Fe/(Fe + Mg) ratios of the S-Co-C series minerals from the two deposits also show differences related to the modes of occurrence and the types of the series minerals (Fig. 15). It is noteworthy that the C-Co-S minerals which precipitated in the Todoroki and Hishikari veins are systematically Fe-poor, evidencing a geochemical control of clay composition by the chemistry of the hydrothermal fluids. In addition, it is a characteristic of the Hishikari deposits that the S-Co-C minerals have a positive correlation between the Fe/(Fe + Mg) ratios (0.06-0.56) and the Al/Si ratios. Similarly in the Todoroki deposit, the S-Co-C minerals especially from the ore veins show a positive correlation between the Fe/(Fe + Mg) ratios (0.01-0.19) and the Al/Si ratios. These positive correlations of the Fe/(Fe + Mg) ratios with the Al/Si ratios are related to the chlorite percentage in the mixed-layering of the S-Co-C series minerals, and may be due to a crystal chemical

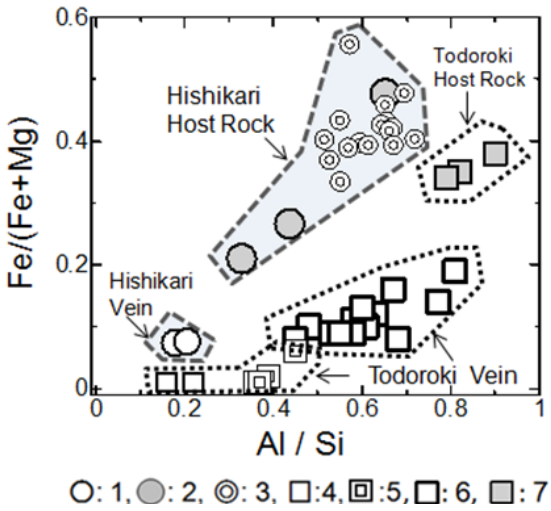


Fig.15. Plot of Fe/(Fe + Mg) ratios and Al/Si ratios of the S-Co-C series minerals from the Hishikari and Todoroki deposits. 1: Tri-smectite of the Hishikari ore veins, 2: Corrensite and Co-C minerals of types I-III in HLA (this study), 3: Chlorite including C/S mineral in HLA (Murakami, 2007), 4: Tri-smectite of the Todoroki Chuetsu vein, 5: Corrensite of the Todoroki Chuetsu vein, 6: Co-C minerals of types I-III in the Todoroki Shuetsu vein, 7: Chlorite in the Todoroki host rock.

adjustment for the misfit of articulated octahedral and tetrahedral sheets of chlorite (Shau and Peacor 1992). Moreover, it is a characteristic of the Todoroki deposit that tri-smectite and corrensite from the Chuetsu vein show low values (0.01-0.06) than the Co-C minerals (types I-III: 0.07-0.19) from the Shuetsu vein.

DISCUSSION

Factors influencing S-Co-S series minerals during vein formations

The occurrence of the S-Co-C series minerals as vein mineral in the Todoroki and the Hishikari ore veins, indicate that they formed by direct precipitation from hydrothermal solutions ascending in open vein-spaces. It is reported that the direct precipitation of these minerals occurs from supersaturated solutions in terms of clay minerals and is a process that requires high activation energy (Simmons and Browne 2000: Beaufort et al. 2015). Especially, Beaufort et al. (2015) describes that the large activation energies in the hydrothermal systems can be attained in conditions where rapid cooling of ascending high-temperature solutions and fracture-controlled mixing of hydrothermal fluids with different compositions and/or temperatures. Additionally, the hydrothermal solutions

responsible for ore formation in the Hishikari ore veins is partly compounded from the water released from hydrous minerals of the sedimentary basement rocks, based on the study of oxygen isotopic ratios ($\delta^{18}O$) of inclusion fluids in vein quartz and adularia (Imai et al. 1998). From these, it appears likely that the precipitates would reflect the chemistry of the ascending solution which may have originated from water-rock interaction at deeper strata, probably providing a source of the Mg contained prominently in the S-Co-C series of minerals occurring in ore veins. The differences in the mineralogical properties of the S-Co-C series minerals depending on the ore veins or deposits are thought to reflect different environmental conditions during the vein formation.

Temperature

The temperature conditions of vein formation can be estimated from the fluid inclusion microthermometry and the mineral assemblage of the vein minerals. At the Todoroki deposit the temperature conditions for the Co-C minerals (types of I-III) from the Shuetsu vein may be in a higher range (171–256°C) than that (140–242°C) for tri-smectite and corrensite from the Chuetsu vein, based on the thermometry of the electrum-argentite-sphalerite-pyrite assemblage. The temperature condition for the tri-smectite formation in the Hishikari veins may be in the range of 175-264 °C when considering to the microthermometry of the fluid inclusions for quartz and adularia: temperature ranges of 177-215°C (mean=202°C, n=28) for the Yusen-1 vein (Yamato et al. 2002), 175-215°C for the Hosen-2vein (Etho et al. 2002a), and 198-264°C (mean=230°C) for the Keisen-3 vein (Sannematsu et al. 2005). Here, the temperatures of the Hosen-2 vein were measured for the columnar adularia containing coexisting liquid-rich and vapor-rich inclusions which indicate hydrothermal boiling (Etho et al. 2002b), and the higher temperatures of the Keisen-3 vein in the Hishikari deposits are thought to suggest that the Keisen veins were the major channels for the ascending hydrothermal fluid (Sannematsu et al. 2005). The thermal ranges of the Mg-rich S-Co-C series minerals occurring in geothermal fields have been summarized as follows (Beaufort et al. 2015): 1) tri-chlorite usually crystallizes as discrete phases at >200 °C, 2) below 200 °C chlorite layers are interstratified with expandable trioctahedral layers (saponite or corrensite) to form interstratified minerals (C/S or C/Co) in which the ratios of the chlorite layers increase as temperatures increase, 3) the appearance of corrensite occurs between 150 and 250°C and the presence of the corrensite may be considered up to ~300°C, and 4) saponite usually occurring at <100 °C has been observed at temperatures up to 300°C.

These thermal ranges of the Mg-rich S-Co-C series minerals are consistent with the temperature ranges of the ore veins which are accompanied by the series minerals in the two epithermal systems. Thus, the S-Co-C series minerals may be understood to be formed in the temperature conditions of vein formation mentioned above. That is, the formations of the C, CC/Co and C/Co in the Shuetsu vein were at higher temperatures than the formation of the Co (presumably at ca. 200°C) in the Chuetsu vein of the Todoroki deposit. In addition, the tri-smectite observed in Todoroki veins was probably at temperatures similar to those forming corrensite (ca. 200°C), and the tri-smectite in Hishikari veins would be formed at the similar temperature condition to the former or at higher temperatures, as tri-smectites show a high-temperature formation in a wide thermal range (<100-300°C) in geothermal fields (e.g., Schiffrnan and Fridleifsson 1991; Patrier et al. 1996; Fulignati et al. 1997; Hulen and Lutz 1999).

The conversion of the S-Co-C series minerals at the Todoroki ore veins is discussed on the basis of petrographic and mineralogical observations (Yoneda et al. 2016). According to it, the corrensite would be consecutively transformed from Mg-rich and Fe-poor amorphous materials (precursor) via smectitic materials, and tri-smectite would have been grown from the same materials which are later-stage precipitates in the Chuetsu vein. On the other hand in the Shuetsu vein, the Co-C minerals may have been consecutively transformed from relatively Mg-poor and Fe-rich amorphous materials (precursor) to corrensitic materials and then to the Co-C minerals at higher temperature condition than in the Chuetsu vein. The different temperature conditions of the two veins would have influenced the conversions of the S-Co-S series minerals which proceeded in each ore veins.

Kinetic Factor

The mixed-layering of the series minerals can be controlled by kinetic factors and not by temperature alone (e.g. Beaufort et al. 2015). Recent hydrothermal

experiments of smectite-chlorite conversion for 9 years at 300°C, show a mineral conversion of discontinuous sequence from inherited smectite, smectite-rich S/C or S/Co, chlorite-rich C/S or Co/C, to product of chlorite-rich C/S or Co/C + discrete chlorite (Mosser‐Ruck et al. 2016). The sequential mineral conversion in the experiments is similar to that of the S-Co-C series minerals in the Todoroki ore vein, while it is shown that the mineral phases transformed in the experiments depend on run times at isothermal condition. This suggests that the conversion of the S-Co-C series minerals may be influenced by kinetic parameters of such as time length of hydrothermal activity that effected vein formation.

Redox and pH

In addition to the above conditions, redox and pH conditions would also be involved in the formation of the S-Co-C series minerals. The differences in redox and pH conditions which are estimated based on the FeS contents of sphalerite and the mineral assemblage of vein minerals (Yoneda et al. 2016), may influence the S-Co-C series minerals at the Todoroki deposit. The possible ranges of oxygen fugacity and pH for the mineral assemblage of pyrite + sphalerite ± potassium mica ± adularia – kaolinite − barite at a temperature of 200°C were shown in Fig. 16. The Chuetsu vein accompanying the mono-mineralic corrensite and tri-smectite may be in an environment with higher oxygen fugacity than that of the Shuetsu vein accompanying the C-Co minerals. Additionally, the low iron contents of corrensite and tri-smectite from the Chuetsu vein can be due to the oxidizing environment of the Chuetsu vein, where ferrous iron is not available for silicate reactions (Beaufort et al. 2015). Barrenechea et al. (2000) shows that the presence of corrensite alone is favored by oxidizing conditions, but the occurrence of corrensite + chlorite is related to more reducing conditions. These suggest that the redox condition plays a role in the conversion of the Co-C minerals.

The pH range of stability fields of potassium mica (illite) and adularia is slightly wide range around neutral (Fig. 16). Taking into account the observed mineral sequence from adularia to illite, though they are minor vein minerals (Yoneda et al. 2016), the pH condition was probably shifted toward the stability field of potassium mica (illite) from that of adularia during vein formations.

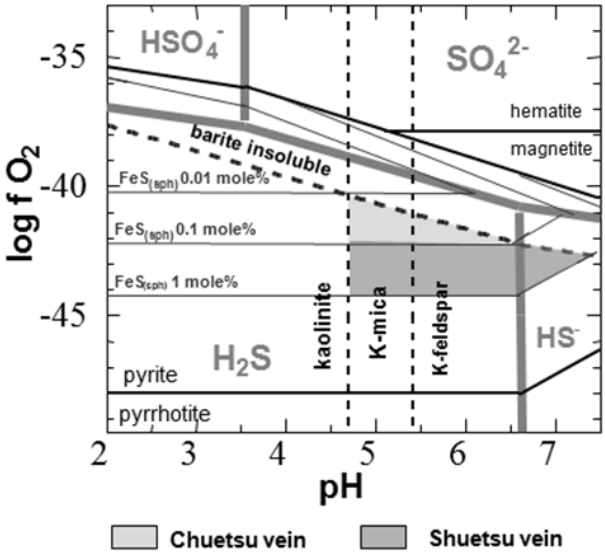


Fig.16. Estimated redox conditions of vein formation for the Todoroki ore veins. Oxidation-reduction conditions at 200°C, total sulfur concentration m=10-3 and total potassium concentration m=10-1, are shown on the pH and oxygen fugacity diagram.

The Hishikari deposits are one of the typical low-sulfidation-style epithermal deposits which are thought to be formed form the reduced and neutral pH hydrothermal solutions (Hedenquist et al. 1996). Recent study on the Fukusen-1 vein shows the pH conditions of neutral to weakly alkaline at the earlier stage which is accompanied by adularia, and of weakly acidic (pH < 5) at the last stage which is accompanied by marcasite and amorphous silica (Tohma et al. 2010). These suggest that pH-lowering of hydrothermal solution occurred at a later stage of vein formation in the epithermal systems.

Effect of Fluid Boiling and Mixing

Boiling of ascending deep fluid and mixing of the fluid with marginal or shallow waters, results in change of fluid chemistry. The boiling removes CO_2, H_2S and other volatiles, increasing pH and K^+/H^+ ratio of solution, which lead to formations of K-feldspar (adularia), calcite, and wairakite or epidote, while condensation of CO_2 -bearing steam into hot water in equilibrium with feldspars and K-mica causes pH-lowering and formations of illite, wairakite, and albite or smectite (Rose and Burt 1979). As in the surficial environment, oxidation of H_2S to H_2SO_4 in steam-heated waters, which are formed from the condensation of steam and H_2S, results in decrease of pH and formations of kaolin minerals, alunite and cristobalite (White and Hedenquist 1990). In addition,

mixing of ascending hydrothermal fluids with marginal/shallow waters in the hydrothermal system is another principal process responsible for a marginal alteration halo of interstratified clay minerals (White and Hedenquist 1990).

This is evidenced in the fluid boiling and subsequent fluid mixing of deeper hydrothermal fluids with oxidizing meteoric waters that has occurred in the Hishikari veins, on the basis of the mineralogy, the fluid inclusion thermometry, the oxygen and hydrogen isotopic analysis and/or the gas analysis of the vein minerals, and thus the precipitation of gold in ore veins is shown to be caused by the boiling and subsequent mixing during vein formation (Izawa et al. 1990; Hayashi et al. 2001; Etoh et al. 2002a; Etoh et al. 2002b; Shikazono 2002; Takahashi et al. 2017). Also, precipitation of the quartz-truscottite-adularia-kaolinite or quartz-truscottite-adularia assemblages in the ore veins are thought to be resulted from cooling due to rapid upflow in addition to the boiling and mixing (Izawa et al. 1990; Takahashi et al. 2017). These hydrothermal events with fluid boiling and subsequent mixing are thought to contribute to the formation of the mono-mineralic, high-temperature tri-smectite of the Hishikari veins, especially the fracture-controlled fluid mixing would have occasioned the supersaturation and cooling of hydrothermal fluids and caused the precipitation of the amorphous materials (precursor) which led to clay formation.

Similarly, the fluid boiling and mixing would have contributed to the formation of the S-Co-S minerals at the Todoroki ore veins, specially the formation of tri-smectite and corrensite under the oxidizing environment can be attributed to fluid mixing of hydrothermal fluids with oxidized meteoric waters, probably in which low solubility of iron may have influenced the very Fe-poor contents of the tri-smectite and corrensite in the Chuetsu vein.

Occurrence of Trioctahedral and Dioctahedral Smectites

For the mono-mineralic di-smectite observed dominantly in the Hishikari veins, it may be supposed to have formed at lower temperatures than the tri-smectite, under environmental conditions affected by the fluid mixing and cooling. This interpretation would agree with experiments which have been conducted under a thermal gradient: the compositions of phyllosilicates change consistently along the thermal gradients, from Al-rich at the cooler end to Mg-rich at the warmer end, and the formation of di-phyllosilicates at the cooler end, followed by di-trioctahedral, and then tri-phyllosilicates at the warmer end of the experiments in a $MgO–Al_2O_3–SiO_2–H_2O$ system (Vidal et al. 2012). Further investigations are necessary to understand between the relationship of di- and tri-smectite at the Hishikari and Todoroki ore veins.

Factors Influencing S-Co-S Series Mineral Formation in Altered Host Rock

The corrensite and Co-C series minerals with a discontinuous stepwise sequence of different mixed-layering of chlorite and corrensite (saponite) layers was identified in the altered host rock (HLA) of the Hishiakari deposit. The microscopic occurrences (Fig. 12) indicate that they are products of alteration processes involving dissolution, re-precipitation and crystallization in which the smectite-to-chlorite transformation would have occurred (Shau and Peacor 1992; Beaufort et al. 1997; Robinson et al. 2002; and Beaufort et al. 2015). In addition the discontinuous sequence in the mixed-layering of the corrensite and Co-C minerals in HLA may indicate that the mineral conversion may have taken place at a high fluid/rock ratio (Schiffman and Staudigel 1995; and Patrier et al. 1996).

According to the stable isotopic study on altered rocks of the Hishikari deposits, the oxygen isotopic zoning of the altered rocks (HLA) enveloping the Hishikari vein systems (from +2‰ in the center to +16‰ at the margin), is due to a temperature decrease from the vein systems towards the peripheral zones corresponding to the alteration zones from the quartz-chlorite (IV) zone to the cristobalite-smectite (I) zone (Naito et al. 1993). In addition, the zoning of the $\delta^{18}O$ and alteration minerals in the host rock (HLA) is thought to be caused by the mixing of two fluids (hydrothermal solution and acidic low-temperature groundwater) on the basis of a kinetics-fluid flow-mixing model (Shikazono et al. 2002) and a compositional variation of the altered volcanic rocks (Shikazono and Takahashi 2010). These findings suggest that the mineral conversion and the distribution of the corrensite and Co-C minerals would be controlled by the temperature, and possibly by pH conditions influenced by the fluid mixing in the hydrothermal system.

As the starting components of the conversion

experiments play an important role (e.g., Vidal et al. 2012), the chemical compositions of host rock may influence the S-Co-C conversion through the alteration processes in the epithermal systems. A difference in Fe/(Fe + Mg) ratios of the S-Co-C series minerals depending on the modes of occurrence (Fig. 15) may be attributed to the influence of the composition of the host rock. The Co-C series minerals from the altered HLA of the the Hishikari deposits and the chlorite from altered rocks of the Todoroki deposit with higher Fe/(Fe + Mg) ratios (>0.2), would be affected by the rock chemistry, whereas saponite from the Hishikari ore veins and S-Co-C series minerals from the Todoroki ore veins with lower Fe/(Fe + Mg) ratios (0.2>), would reflect the chemistry of the hydrothermal solutions responsible for their precipitation.

The di-smectite dominant in the outer zones which correspond to the alteration zones of cristobalite-smectite and quartz–smectite-(kaolinite) assemblages would be formed at lower temperatures (<100°C) and lower pH in condition of lower water/rock ratios. There, the di-smectite may predominantly be influenced by the rock composition but only slightly by the water especially the chemistry of the hydrothermal water involved in the formation of the S-Co-C series minerals. The lack of Mg-rich tri-smectite which is expected to be an initial phase of the S-Co-C series may be attributed to the environmental conditions in the host rock of the outer zones. In addition di-smectite associated with the Co-C minerals in the altered HLA near ore veins may be a product of overprinting caused by other hydrothermal events during or after the vein formation. Further investigations will be necessary to verify this interpretation.

CONCLUSIONS

The tri-smectite(S)-corrensite(Co)-chlorite(C) series minerals occurring in two epithermal Au-Ag deposits, the Hishikari and the Todoroki deposits, show a discontinuous sequence with different mixed-layering of chlorite and smectite layers: mono-mineralic tri-smectite, mono-mineralic corrensite, and C-Co series minerals which can be divided into three different types (a I type including discrete chlorite occasionally with minor amounts of S layers, a II type comprising interstratified CC/Co and discrete chlorite, and a III type characterized by segregation structures of C and Co layers). The S-Co-C series minerals show differences in the mode of occurrence between the two deposits. At the Hishikari deposits the tri-smectite occurs as a vein mineral and the corrensite and Co-C minerals of the I-III types occur as alteration minerals in altered andesites. At the Todoroki deposit tri-smectite, corrensite, and the Co-C minerals occur as vein minerals: S and Co from the Chuetsu vein and the Co-C from the Shuetsu vein, and there is discrete chlorite without smectite layers in altered rhyolitic rocks. In addition the Al/Si ratios and Fe/(Fe + Mg) ratios of the S-Co-C minerals show variations closely related to the mixed-layering and the mode of occurrence.

The S-Co-C minerals occurring in ore veins, which were products of direct precipitation from ascending hydrothermal solutions, may reflect the chemistry of the solutions which would have originated from the water-rock interaction in deeper strata, possibly providing a source of the Mg contained prominently in the series minerals. The differences in mineralogical properties of the S-Co-C series minerals in the ore veins or in the deposits would be related to the different temperature conditions and redox states of the vein formation, and also to the time length of hydrothermal activity that effects vein formation. And these factors controlling the conversion of S-Co-C series minerals may be influenced by the fluid boiling and subsequent mixing of deeper hydrothermal fluids with oxidizing meteoric waters, which occurred during the vein formations.

The S-Co-C minerals formed by hydrothermal alteration that involves dissolution, re-precipitation and crystallization, would have undergone the smectite-to-chlorite transformation in the epithermal systems. The transformation of the S-Co-C minerals and the distributions of the Co-C minerals in host rock around the Hishikari ore veins would have been controlled by the temperature conditions related to the fluid mixing of hydrothermal solution and acidic low-temperature water, and by the water/rock ratios in the hydrothermal system. In addition the Fe/(Fe + Mg) ratios of the corrensite and Co-C minerals in the altered host rocks can be understand to be influenced by the chemical compositions of the host rocks in hydrothermal system.

The di-smectite dominant in the outer zones where kaolinite is present but corrensite and Co-C minerals are absent, may have been formed at lower temperatures (<100°C) and lower pH condition, and in conditions of lower water/rock ratios, and predominantly be influenced by the rock composition but only little by the

compositions of the hydrothermal water especially related to the formation of S-Co-C series minerals. The lack of Mg-rich tri-smectite in the outer zones may be attributed to the environmental conditions in the host rock detailed above.

The factors influencing the formation of the S-Co-S minerals would be basically be similar in both ore veins and host rocks, except for the direct precipitation in ore veins and the replacement in host rocks. However, it is emphasized that the fluid/rock ratios in the hydrothermal systems can be a major factor influencing the conversion of the S-Co-S series minerals occurring as alteration mineral. Additionally, the time length of hydrothermal activity that effected vein formation would be an important factor influencing the conversion of the S-Co-C series minerals occurring as vein mineral. The occurrence and the mineralogical properties of the S-Co-C series minerals may present an exploration index for epithermal systems, in addition to the alteration mineral assemblages.

ACKNOWLEDGMENT

The authors thank Sumitomo Metal Mining for facilitating the underground work, a special thanks goes to Messrs. R. Sekine, K. Morimoto, and H. Shimakura for the help during the field work, and to Mr. T. Seto for useful comments on the manuscript. The authors also thank Prof. E. Izawa for discussions, and are grateful to guest editor and two anonymous referees for their helpful and valuable comments on an earlier version of the manuscript.

REFERENCES

Bailey, S. W. (1982). Nomenclature for regular interstratifications. *American Mineralogist*, 67, 394-398.

Barrenechea, J.F., Rodas, M., Frey, M., Alonso-Azcarate, J., & Mas, J.R. (2000). Chlorite, corrensite, anchlorite-mica in Late Jurassic fluvio-lacustrine sediments of the Cameros basin of Northeastern Spain. *Clays and Clay Minerals*, 48, 256-265.

Beaufort, D., Baronnet, A., Lanson, B., & Meunier, A. (1997). Corrensite: A single phase or a interstratified phyllosilicate in the saponite-to-chlorite conversion series? A case study of Sancerre-Couy deep drill hole (France). *American Mineralogist*, 82, 109–124.

Beaufort, D., Rigault, C., Billon, S., Billault, V., Inoue, A., Inoue, S., et al. (2015). Chlorite and chloritization processes through mixed layer mineral series in low-temperature geological systems -A review. *Clay Minerals*, 50, 497–523.

Bettison-Varga, L., & Mackinnon, I. D. R. (1997). The role of randomly mixed-layered chlorite/smectite in the transformation of smectite to chlorite. *Clays and Clay Minerals*, 45, 506–516.

Bove, D. J., Eberl, D. D., McCarty, D. K., & Meeker, G. P. (2002). Characterization and modeling of illite crystal particles and growth mechanisms in a zoned hydrothermal deposit, Lake City, Colorado. *Ameriican Minneralogist*, 87, 1546-1556.

Buatier, M. D., Früh-Green, G. L., & Karpoff, A. M. (1995). Mechanisms of Mg-phyllosilicate formation in a sedimented ridge (Middle Valley, Juan de Fuca). *Contributions to Mineralogy and Petrology*, 122, 134–151.

Etoh, J., Izawa, E., & Taguchi, S. (2002a). A fluid inclusion study on columnar adularia from the Hishikari low-sulfidation epithermal gold deposit, Japan. *Resource Geology*, 52, 73–78.

Etoh, J., Izawa, E., Watanabe, K., Taguchi, S., & Sekine, R. (2002b). Bladed quartz and its relationship to gold mineralization in the Hishikari low-sulfidation epithermal gold deposit. *Economic. Geology*, 97, 1841–1851.

Forsythe, N. A., Spry, P. G., & Thompson, M. L. (2019) Petrological and mineralogical aspects of epithermal low-sulfidation Au- and porphyry Cu-style mineralization, Navilawa Caldera, Fiji. *Geosciences*, 9(1),42, https:// doi.org/10.3390/geosciences9010042.

Fulignati, P., Malfitano, G., & Sbrana, A. (1997). The Pantelleria caldera geothermal system: data from the hydrothermal minerals. *Journal of Volcanology and Geothermal Research*, *75*(3-4), 251-270.

Hayashi, K., Maruyama, T., & Satoh, H. (2001). Precipitation of gold in a low-sulfidation epithermal gold deposit: insights from a submillimeter scale oxygen isotope analysis of vein quartz. *Economic Geology*, 96, 211–216.

Hedenquist, J.W., & Lowenstern, J. W. (1994). The role of magmas in the formation of hydrothermal ore deposits. *Nature,* 370, 519-527.

Hedenquist, J.W., Izawa, E., Arribas, A., & White, N. C. (1996). *Epithermal gold deposits: Styles, characteristics and exploration.* Tokyo: The Society

of Resource Geology.

Hulen, J. B., & Lutz, S. J. (1999). Altered volcanic rocks as hydrologic seals on the geothermal system of Medicine Lake volcano, California. *Geothermal Resources Council Bulletin*, *28*(7), 217-222.

Ibaraki, K., & Suzuki, R. (1990). Wall rock alteration in the Hishikari gold mine, Kagoshima Prefecture, Japan. *Mining Geology*., 40, 97–106 (in Japanese with English abstract).

Ibaraki, K., & Suzuki, R. (1993). Gold-silver quartz-adularia veins of the Main, Yamada and Sanjin deposits, Hishikari gold mine; a comparative study of their geology and ore deposits. *Resource Geology Special Issue*, 14, 1–11.

Imai, A., Shimazaki, H., & Nishizawa, T. (1998). Hydrogen isotope study of fluid inclusions in vein quartz of the Hishikari gold deposits, Japan. *Resource Geology*, 48, 159–170

Inoue, A., & Utada, M. (1991). Smectite-to-chlorite transformation in thermally metamorphosed volcanoclastic rocks in the Kamikita area, northern Honshu, Japan. *American Mineralogist*, 76, 628–640.

Inoue, A. (1995). Formation of clay minerals in hydrothermal environments. In Velde, B. (Ed.), Origin and mineralogy of clays (268-329). Berlin:Springer.

Inoue, A., Lanson, B., Marques-Fernandes, M., Sakharov, B. A., Murakami, T. Meunier, A., et al. (2005). Illite-Smectite mixed-layer minerals in the hydrothermal alteration of volcanic rocks: I. One-dimensionaL Xrd structure analysis and characterization of component layers, *Clays and Clay Minerals,* 53 (5), 423-439.

Izawa, E., Urashima, Y., Ibaraki, K., Suzuki, R., Yokoyama, T., Kawasaki, K., et al. (1990). The Hishikari gold deposit: high-grade epithermal veins in Quaternary volcanics of southern Kyushu, Japan. *Journal of Geochemical Exploration*, 36, 1-56.

Izawa, E., Kurihara, M., & Itaya, T. (1993). K-Ar ages and initial Ar isotopic ratio of adularia-quartz veins from the Hishikari gold deposit, Japan. *Resource Geology Spec. Issue*, 14, 63–69.

Kim, J. W. & Peacor, D. R. (2002). Crystal-size distributions of clays during episodic diagenesis: the Salton Sea geothermal system. *Clays and Clay Minerals*, 50(3), 371–380.

Kralj, P. (2016). Hydrothermal alteration of chlorite to randomly interstratified corrensite-chlorite: Geological evidence from the Oligocene Smrekovec Volcanic Complex, Slovenia. *Applied Clay Science,* 134(3), 235-245.

Meyer, C. & Hemley, J. (1967). Wall rock alteration. In Barnes, H. L. (Ed.), Geochemistry of hydrothermal ore deposits (166-235). Holt, Rinehart & Winston Inc.

Meunier, A. (2003). Crystal structure–Species–Crystallisation. *In Clays* (pp. 1-60). Berlin: Springer.

Miron, G. D., Neuhoff, P. S., & Amthauer, G. (2012). Low-temperature hydrothermal metamorphic mineralization of island-arc volcanics, south Apuseni mountains. Romania. *Clays and Clay Minerals*, 60 (1), 1-17.

Morishita, Y., Shimada, N., & Shimada, K. (2018). Invisible gold in arsenian pyrite from the high-grade Hishikari gold deposit, Japan: Significance of variation and distribution of Au/As ratios in pyrite. *Ore Geology Reviews,* 95, 79-93.

Mosser-Ruck, R., Pignatelli, I., Bourdelle, F., Abdelmoula, M., Barres, O., Guillaume, D., et al. (2016). Contribution of long.term hydrothermal experiments for understanding the smectite-to-chlorite conversion in geological environments. *Contrib Mineral Petrol, 171(97),* https://DOI 10.1007 /s00410-016-1307-z.

Murakami, H. (2007). Variations in chemical compositions of clay minerals and magnetic susceptibility of hydrothermally altered rocks in the Hishikari epithermal gold deposit, SW Kyushu, Japan. *Resource Geology*, 58, 1–24.

Murakami, T., Sato, T., & Inoue, A. (1999). HRTEM evidence for the process and mechanism of saponite-to-chlorite conversion through corrensite. *American Mineralogist, 84, 1080–1087.*

Murata, K., Koyama, M., & Sekine, R. (2008). Ongoing exploration and development of the newly developed vein groups in the surrounding areas of the Yamada deposit, Hishikari Mine. Shigenchishitsu, 58(2), l11-119 (in Japanese with English abstract).

Nagayama, T. (1993). Precipitation sequence of veins at the Hishikari deposits, Kyushu, Japan. *Resource Geology Special Issue*, 14, 13–27.

Naito, K., Matsuhisa, Y., Izawa, E. & Takaoka, H. (1993). Oxygen isotopic zonation of hydrothermally altered rocks in the Hishikari gold deposit, southern Kyushu, Japan. *Resource Geology Spec. Issue*, 14, 29–36.

NEDO (1995). *Geothermal development promotion survey project N*o. 36 *-the Amemasu-dake area*. Tokyo: New Energy and Industrial Technology

Development Organization (in Japanese).

Patrier, P., Papapanagiotou, P., Beaufort, D., Traineau, H. Bril, H., & Rojas, J. (1996). Role of permeability versus temperature in the distribution of the fine (<0.2 μm) clay fraction in the Chipilapa geothermal system (EI Salvador, Central America). *Journal of Volcanology and Geothermal Research,* 72, 101-120.

Reynolds, R. C. Jr. (1985). NEWMOD*, A Computer Program for the Calculation of the Basal Diffraction Intensities of Mixed-Layered Clay Minerals. HANOVER NH: R. C. Reynolds*.

Robinson, D., Schmidt, S.T., & Santana de Zamora, A. (2002). Reaction pathways and reaction progress for the smectite-to-chlorite transformation: evidence from hydrothermally altered metabasites. *Metamorphic Geology*, 20, 167–174.

Rose, A. W., & Burt, D. M. (1979). Hydrothermal alteration: In Barnes, H. L. (Ed.), Geochemistry of hydrothermal ore deposits (173-235). New York: John Wiley & Sons.

Sanematsu, K., Duncan, R., Imai, A., & Watanabe, K. (2005). Geochronological constraints using 40Ar/39Ar dating on the mineralization of the Hishikari epithermal gold deposit, Japan. *Resource Geology*, 55, 249–266.

Sawai, O., Yoneda, T., & Itaya, T. (1992). K-Ar ages of the Chitose, Todoroki and Teine Au-Ag vein-type deposits, southwest Hokkaido, Japan. *Mining Geology*, 42, 323–330 (in Japanese with English abstract).

Schiffman, P., & Fridleiffson, G. O. (1991). The smectite to chlorite transition in drillhole NJ-15, Hesjavellir geothermal field, Iceland: XRD, BSE and electron microprobe investigations. *Journal of Metamorphic Geology*, 9, 679–696.

Schiffman, P., & Staudigel, H. (1995). The smectite to chlorite transition in a fossil seamount hydrothermal system: the Basement Complex of La Palma, Canary Islands. *Journal of Metamorphic Geology*, 13, 487–498.

Sekine, R., Morimoto, K., & Ushirone, N. (1998). Characteristics of the Yamada vein system, Hishikari mine, Kyusyu, Southwestern Japan. *Resource Geology*, 48, 1–8 (in Japanese with English abstract).

Sekinw, R., Izawa, E., & Watanabe, K. (2002). Timing of fracture formation and duration of mineralization at the Hishikari deposit, southern Kyushu, Japan. *Resource Geology*, 52(4), 395–404.

Simmons, S. F., & Browne, P. R. L. (2000). Hydrothermal minerals and precious metals in the Broadlands-Ohaaki geothermal system: Implications for understanding low-sulfidation epithermal environments. *Economic Geology*, 95, 971-999.

Shau, Y. H., & Peacor, D. R. (1992). Phyllosilicates in hydrothermally altered basalts from DSDP Hole 504B, Leg 83 - a TEM and AEM study. *Contributions to Mineralogy and Petrology*, 112, 119-133.

Shikazono, N., Yonekawa, N., & Karakizawa, T. (2002). Mass transfer, oxygen isotopic variation and gold precipitation in epithermal system: A case study of the Hishikari deposit, southern Kyushu, Japan. *Resource Geology,* 52(3), 211–222.

Shikazono, N. (2003). *Geochemical and tectonic evolution of arc-backarc hydrothermal systems*. Amsterdam: Elsevier.

Shikazono, N., & Takahashi, H. (2010). Compositional variation of hydrothermally altered volcanic rocks in Hishikari gold epithermal system: A useful geochemical indicator of gold–silver epithermal mineralization. *Resource Geology,* 60(2), 117–128.

Shimizu, T. (2018). Fluid inclusion studies of comb quartz and stibnite at the Hishikari Au–Ag epithermal deposit, Japan. *Resource Geology*, 68(3), 326–335.

Środoń, J., Kuzmenkova, O., Stanek, J. J., Petit, S., Beaufort, D., Gilg, H. A., et al. (2019). Hydrothermal alteration of the Ediacaran Volyn-Brest volcanics on the western margin of the East European Craton. *Precambrian Research,* https://doi.org/10.1016/j.precamres.2019.02.015

Taguchi, S., & Watanabe, T. (1973). Clay minerals especially interstratified chlorite/saponite associated with gold ores of the Fuke mine, Kagoshima prefecture. *Science Reports, Department of Geology, Kyushu University*, 11, 243–250 (in Japanese with English abstract).

Takahashi, R., Tagiri, R., Blamey, N. J. F., Imai, A., Watanabe, Y., & Takeuchi, Y. (2017). Characteristics and behavior of hydrothermal fluids for gold mineralization at the Hishikari deposits, Kyushu, Japan. *Resource Geology*, 67(3), 279–299.

Takeuchi, K. (1984). Clay minerals in Arakawa No. 4 vein of the Kushikino mine. *Mining Geology*, 34, 335–342 (in Japanese with English abstract).

Tohma, Y., Imai, A., Sanematsu, K., Yonezu, K., Takahashi, R., Koyama, M., et al. (2010). Characteristics and mineralization age of the Fukusen

No. 1 Vein, Hishikari epithermal gold deposits, southern Kyushu, Japan. *Resource Geology*, 60, 348–358.

Utada, M. (1988). Hydrothermal alterations related to igneous activity in Cretaceous and Neogene formations of Japan. *Mining Geology Special Issue,* 8, 67-83.

Vidal, O., Baldeyrou, A., Beaufort, D., Fritz, B., Geoffroy, N., & Lanson B. (2012). Experimental study of the stability and phase relations of clays at high temperature in a thermal gradient. *Clays and Clay Minerals*, 60, 200-225.

White, N. C., & Hedenquist, J. W. (1990). Epithermal environments and styles of mineralization: Variations and their causes, and guideline for exploration. *Journal of Geochemical Exploration*, 36, 445–474.

Yamato, Y., Ohno, M., & Ushirone, N. (2002). Exploration and development of the Yusen No.1 vein group based on the vein structure, Yamada deposit, Hishikari Mine. *Shigenchishitsu,* 52(1), 11-17 (in Japanese with English abstract).

Yoneda, T., & Watanabe, T. (1989). Chemical composition of regularly interstratified chlorite/smectite in the ores from some Neogene gold-silver vein-type deposits in Japan. *Mining Geology*, 39, 181–190 (in Japanese with English abstract).

Yoneda, T. (1994). *Applied mineralogical study of clays from hydrothermal ore deposits*. PhD thesis: Kyushu University, Japan (in Japanese).

Yoneda, T., Watanabe, T., & Sato, T. (2016). Mineralogical aspects of interstratified chlorite-smectite associated with epithermal ore veins: A case study of the Todoroki Au-Ag ore deposit, Japan. *Clay Minerals,* 51, 653–674.

(The final publication is available at link.springer.com.)