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1 Mineralogical aspects of interstratified chlorite/smectite associated with epithermal 2 ore veins: A case study of the Todoroki Au-Ag ore deposit, Japan

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ABSTRACT: Chlorite (C) – corrensite (Co) – smectite (S) series minerals occur as vein constituents in the two epithermal ore veins, the Chuetsu and Shuetsu veins of the Todoroki Au-Ag deposit. The occurrence characteristics of the C-Co-S series minerals indicate that the clays may be products of direct precipitation from hydrothermal fluids and subsequent mineralogical transformations during and/or after vein formation. The minerals from the Chuetsu vein are characterized by ‘monomineralic’ corrensite showing an extensive distribution throughout the vein, and tri-octahedral smectite occurring locally. The Shuetsu vein minerals are characterized by C-Co series minerals which can be divided into three different types: a I type including discrete chlorite with minor amounts of S layers, a II type comprising interstratified C/Co and discrete chlorite, and a III type characterized by segregation structures of C and Co layers. The types of C-Co series minerals show slightly different spatial distributions in the Shuetsu vein. Different epithermal environments during the vein formations and possible kinetic effects may have played a role in the formation and conversion of Co-C series at the Shuetsu vein and S-Co series at the Chuetsu vein.

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1 KEYWORDS: chlorite-corrensite-smectite series minerals, interstratified chlorite/
2 corrensite mineral, epithermal Au-Ag ore vein, environmental conditions.

3

4 INTRODUCTION

5 It is well known that trioctahedral chlorite (C) – trioctahedral smectite (S) series
6 minerals including corrensite (Co), a 1:1 regularly interstratified mineral of chlorite
7 and smectite (or vermiculite) layers, occur extensively in different geological
8 environments (Sudo & Shimoda, 1977; Velde, 1985; Beaufort et al., 1997; Meunier,
9 2003). Recent studies of minerals of this series from diagenetic, low-grade
10 metamorphic, and hydrothermal environments show that corrensite mostly occurs as a
11 stable single phase, and in many cases the series of minerals occur as a discontinuous
12 sequence with steps of different interstratification of chlorite and smectite layers (e.g.,
13 Inoue & Utada, 1991; Shau & Peacor, 1992; Batier et al., 1995; Beaufort et al., 1997;
14 Fukui & Yoshimura, 1999; Drits et al., 2011; Kogure et al., 2013). In these cases chlorite-
15 rich interstratified chlorite/smectite (C/S) mineral series have been dominantly
16 observed and mostly described as mixtures of corrensite and chlorite, but corrensite
17 mixed with interstratified C/S phase has also been reported (Leoni et al., 2010).
18 However in some cases the corrensite-chlorite series is described as a continuous series
19 of interstratifications of chlorite and smectite layers (Schiffman & Fridleifsson, 1991;
20 Bettison-Varga & Mackinnon, 1997). The transformation mechanism and controlling
21 factors implicated in the smectite to chlorite conversion series have been discussed in
22 recent papers (Shau & Peacor, 1992; Beaufort et al., 1997; Robinson et al., 2002;
23 Kogure et al., 2013). It is noteworthy that the transformation of smectite to chlorite in
24 the case of hydrothermally altered basalts is related to fluid/rock ratios (Shau & Peacor,

1 1992). Moreover the mineral transformation in geothermal systems is controlled by
2 kinetic effects linked to the fluid/rock ratios or modes of fluid transport (advection or
3 diffusion) related to the rates of dissolution/nucleation/growth, in addition to
4 temperatures as the primary factors in the transformation (Robinson et al., 2002).

5 It is also well known that mafic phyllosilicates commonly occur as vein minerals in
6 hydrothermal metallic ore veins (Nagasawa et al., 1976; Shirozu, 1978), and especially
7 interstratified C/S minerals are found as vein minerals in some epithermal Au-Ag ore
8 veins (Taguchi & Watanabe, 1973; Yoneda & Watanabe, 1981, 1989, 1994; Takeuchi,
9 1984) (Fig. 1). However, detailed features of interstratified C/S minerals from
10 epithermal Au-Ag ore veins have not been described like those in other geological
11 environments.

12 In epithermal vein deposits the vein minerals are formed generally by precipitation
13 from hydrothermal solution in open fractures. The fluid/rock ratio during formation of
14 the vein minerals can be presumed to be much higher than that of the secondary
15 minerals in wall rock. In addition, the ore forming processes in epithermal systems
16 (boiling, cooling, oxidation, mixing, and others) may affect the mineralogical features
17 of the C-S series minerals as well as the mineral assemblages and metal contents of the
18 ore deposits (White & Hedenquist, 1990). A better knowledge of the mineralogical
19 sequence of C/S minerals formed as vein constituents under epithermal conditions
20 would help to understand the transformation mechanisms and factors controlling the
21 mineral formation in such geological systems. Further, the relationship between the
22 C/S mineral series in the ore veins and the Au-Ag mineralization would be useful
23 indicators in the exploration of ore deposits. In this study the occurrence and the
24 mineralogical properties of C/S minerals occurring as vein constituents from two
25 epithermal Au-Ag ore veins (the Chuetsu vein and the Shuetsu vein) of the Todoroki

1 deposit are described based on observations of optical and scanning electron
2 microscopy (SEM), X-ray powder diffraction analysis (XRD), XRD modeling of C/S
3 interstratification, and chemical analyses by electron probe micro-analysis (EPMA)
4 and analytical transmission electron microscopy (AEM). The mineralogical changes in
5 minerals of the smectite to chlorite conversion series and their conditions of formation
6 in the epithermal ore veins are discussed with respect to their phase relationships with
7 the coexisting minerals.

8 ORE VEINS AND SAMPLES STUDIED

9 The Todoroki ore deposit is located in southwestern Hokkaido and is comprised of
10 epithermal Au-Ag bearing quartz veins. The Chuetsu and Shuetsu veins, the principal
11 ore veins, are situated at the western and eastern parts of the mining district
12 respectively, and are hosted chiefly in rhyolitic pyroclastic rocks and sandstone/
13 mudstone with tuff of the middle Miocene age (Yoneda, 1994) (Fig. 2). A K-Ar dating
14 for adularia and sericite in hydrothermally altered wall rocks of the Chuetsu and
15 Shuetsu veins indicated respectively 2.09–3.05 Ma and 2.08 Ma, and these K-Ar ages
16 show that the Au-Ag ore veins may be genetically related to the Pliocene volcanic
17 activity which produced the andesite rocks found directly over the ore veins in this area
18 (Sawai et al., 1992).

19 The scale of the veins of the mined parts of the Chuetsu and Shuetsu veins have
20 approximate lengths of 600m along the strike and 140m along the dip with a mean
21 thickness (mined part) of 3m, and 980m (strike), 120m (dip), and 4.5m (mean thickness
22 of mined part), respectively (Japan Mining Industry Association, 1968). The sampling
23 sites at the Shuetsu vein in this study were restricted to the deep central and eastern
24 parts of the vein, because the major parts of the vein have been mined, and those at the
25 Chuetsu vein were more spread out in the vein but not from the shallow high-grade

1 parts which have been mined.

2 The constituents of the Chuetsu and Shuetsu veins can be broadly divided into three
3 different formation stages (Hasegawa et al., 1976; Yoneda, 1994). The earlier stage (I)
4 is characterized by dark gray, massive quartz observable locally as small veins in the
5 Chuetsu vein. In the middle stage (II), quartz occurs as the most common constituent of
6 the two ore veins. Further the stage II quartz may be divided into different sub-stages
7 such as white or gray massive quartz veins and white/grey banded quartz veins with or
8 without rhodochrosite, as shown in Fig. 3. The massive and banded veins of the stage
9 II are dominated by microcrystalline and fine-grained quartz, with occurrences of
10 coarse-gained quartz or comb quartz band. Though a comprehensive chronological
11 relationship among the quartz veins in the different sub-stages is difficult to elucidate,
12 observations of the ore veins show that the white massive quartz vein is earlier than the
13 other quartz veins, and that the quartz vein with rhodochrosite occurred in a later sub-
14 stage. The stage II quartz veins are associated with Au-Ag minerals and Cu-Pb-Zn-Fe
15 sulfide minerals in addition to clays as seen in Fig.4. The Au-Ag/Cu-Pb-Zn-Fe-S
16 minerals are aggregated in the form of black streaks and patches in the stage II quartz,
17 showing a close relationship to formations of clays as seen in some hand specimens of
18 ore samples (Fig. 4). The later stage (III) is composed of calcite and quartz, and
19 without Au-Ag/Cu-Pb-Zn-Fe minerals and clays.

20 The samples of this study were collected from vein quartz, wall rock including rock
21 fragments trapped in the veins, and clay veins cutting through the ore veins or found
22 between the ore veins and the wall rock as follows: stage I quartz (N=2), stage II quartz
23 (N=81: 8 samples from 160 meters mine level (ml is used hereafter), 14 samples from
24 130ml, 13 samples from 110ml, 37 samples from 80ml and 9 samples from 50ml),
25 wall rock (N=18), and veined clay (N=5) from the Chuetsu vein: stage II quartz

1 (N=43: 15 and 28 samples from the eastern part and the deep central part, respectively),
2 wall rock (N=19), and veined clay (N=1) from the Shuetsu vein. Petrographic analyses
3 were performed on the samples from the Chuetsu and Shuetsu veins (Yoneda, 1994).

4 The early stage samples from the Chuetsu vein are barren quartz with minor
5 amounts of pyrite, adularia and clay minerals. Stage II quartz samples from the two ore
6 veins are associated with minor amounts of Au-Ag minerals (electrum + argentite +
7 pearceite ± polybasite + pyrargyrite ± argentian tetrahedrite) and small amounts of
8 Cu-Pb-Zn-Fe sulfides (sphalerite + chalcopyrite + galena + pyrite ± marcasite) in the
9 black streaks and patches. Clay minerals are also common constituents of stage II
10 quartz samples as will be detailed below. Adularia is locally associated with the
11 massive quartz of an early sub-stage in stage II quartz. In the later sub-stage samples of
12 the stage II quartz, rhodochrosite + calcite assemblages are commonly found at the two
13 ore veins.

14 The samples from the Shuetsu vein show higher Cu+Pb+Zn contents (7.49–0.28
15 wt%: N=9) than those from the Chuetsu vein (0.15–0.02 wt%: N=7). In addition, the
16 chemical compositions of electrum and sphalerite in the ore samples show differences
17 between the two ore veins: the Ag contents of electrum (0.62–0.54 atomic ratio, N=24,
18 mean value = 0.58, SD = 0.027) and FeS contents of sphalerite (0.96–0.12 mol%, N =
19 113, mean value = 0.45, SD = 0.151) from the Shuetsu vein are higher than the Ag
20 contents of electrum (0.52–0.43 atomic ratio, N = 19, mean value = 0.49, SD = 0.016)
21 and FeS contents of sphalerite (0.16–0.01 mol%, N = 31, mean value = 0.04, SD =
22 0.03) from the Chuetsu vein.

23 The mineral assemblage of the wall rock samples is quartz + K-feldspar ± calcite +
24 chlorite + illite ± pyrite at the Chuetsu vein, and quartz ± K-feldspar ± calcite + chlorite

1 ± illite ± pyrite at the Shuetsu vein. Interstratified C/S minerals were rarely detected in
2 the wall rock samples of the two mineralized epithermal veins. Illite ± kaolinite ±
3 illite/smectite interstratified mineral were detected in the two veins.

4 METHODS

The clay minerals contained in the ore samples were extracted by hand-picking and separated by ultrasonic treatment in distilled water, and then the clay fractions were concentrated by centrifugal sedimentation as follows: rotation speed 1000r.p.m., distance from axis to surface of the suspension liquid 4.5cm, distance from axis to surface of settling particles 15.5cm, time 60sec, and the concentration taking place at room temperature. Samples of clay fractions, untreated (UT) and solvated by 10% ethylene glycol solution (EG), were mounted on glass slides to prepare oriented-specimens, and the oriented-specimens were examined by XRD using a Rigaku Geigerflex D-6C (radiation: Ni-filtered CuK α ; accelerating voltage/current: 30 kV/10~20 mA; slit systems: divergent 1/6° -scattering 0.3 mm-receiving 1/6° or 1/2° - 0.3mm-1/2° ; scan speed: 1 deg/min). In addition selected samples of clay fractions, saturated in KCl solution (K $^{+}$) and solvated by glycerol vapor after Mg saturation by MgCl₂ solution (MgGly), were prepared similarly to the oriented-specimens. XRD was performed by a Rigaku RU-300 with a graphite monochromator under the conditions of CuK α radiation, accelerating voltage/current: 40kV/200mA; slit systems: divergent 1/6° -scattering 0.3mm-receiving 1/6° or 1/2° -0.3mm-1/2° and step conditions: size 0.01 degree and counting time 1sec.

22 XRD peak deconvolution was performed to explore overlapping peaks from
23 discrete phases, by using “Traces V5” (Diffraction Technology Pty. Ltd. Australia).
24 XRD patterns of C/S interstratifications were modelized using a program coded by

1 Watanabe (1977, 1988), which calculates one dimensional X-ray line profiles based on
2 Kakinoki & Komura (1952), and compared with the observed patterns.

3 AEM analysis were performed on clay particles deposited on copper mesh (150-
4 mesh) covered by collodion foil, and then carbon coated after drying. The clay
5 specimens were analyzed by a Hitachi H-700 equipped with an EDX analytical
6 attachment (Horiba EMAX-2200) under the conditions of an accelerating voltage of
7 200 kV and an X-ray counting time of 100 sec or 200 sec.

8 Selected ore samples were prepared as polished thin sections for optical
9 microscopic observations and EPMA analyses of clay minerals. The EPMA analyses
10 were performed by a JXA-50A under the conditions of an accelerating voltage of 15
11 kV, specimen current of 0.01 μ A, beam diameter of 10 μ m, and counting time of 10sec.
12 Standard samples used are quartz, rutile, synthetic Al_2O_3 , synthetic $MnO-Fe_2O_3$ (1:1),
13 synthetic MgO , wollastonite, synthetic Na-Ca glass, and adularia. Quantitative
14 corrections were performed after Bence & Albee (1968). In addition chips from the
15 selected ore samples were coated by Au and provided for SEM observations of the clay
16 minerals using a JSM25S (accelerating voltage of 15kV).

17

18 **RESULTS AND DISCUSSION**

19 *Petrography*

20 Clays are closely associated with the stage II quartz veins basically showing
21 crustiform quartz texture which is characterized by successive, narrow, subparallel
22 layers of minerals precipitated successively (e.g. Shimizu, 2014) (Fig.4). Banded clay
23 aggregates observed in the stage II quartz are concordant with the crustiform quartz

1 texture (Fig. 4A–C), and patched clay aggregates contained in the ore samples may be
2 also concordant with the crustiform quartz texture, slightly deviated from typical one,
3 where the clay aggregates are accompanied with similar patched aggregates of Au-
4 Ag/Cu-Pb-Zn-Fe minerals in the same thick band of quartz (Fig. 4D).

5 Optical microscopic observations show that clay minerals occur as irregularly
6 patched or finely banded aggregates of particles closely associated with quartz, ore
7 minerals and locally with carbonates (Fig. 5). Clay minerals from the Chuetsu vein are
8 generally composed of very fine-grained particles (Fig.5A) with coarse-grained
9 particles (Fig.5B: tri-smectite). It is noteworthy that band aggregates have apparent
10 concavo-convex surfaces in microcrystalline quartz (Fig.5A). This type of aggregate
11 may be interpreted as a colloform texture of which form is retained even after re-
12 crystallization to fine-grained clay particles. Clay minerals from the Shuetsu vein occur
13 as similar aggregates (Fig. 5C, D) with coarser grained-particles (Fig. 5E). In addition,
14 clay minerals observed in the black streaks and patches of the ore samples show
15 evidence of simultaneous formation with sphalerite (Fig. 5D) and electrum-argentite
16 (Fig. 5F).

17 Macroscopic and microscopic observations of clays/clay minerals mentioned above
18 suggest that they may be products of direct precipitation from hydrothermal fluids in
19 the middle stage of vein formation, and that initial precipitates from the hydrothermal
20 fluids may have been amorphous materials based on the colloform texture that is
21 generally interpreted to originate from gel deposition (e.g., Shimizu, 2014). The latter
22 may be supported by the presence of amorphous materials precipitating as clay scales
23 in geothermal wells (e.g., Reyes & Cardile, 1989). In addition, the microscopic
24 occurrences suggest that the initial clay precipitates could be precursors which would
25 be changed to fine-grained and/or coarser-grained clay particles in subsequent

1 dissolution/re-crystallization process.

2 The dominant clay minerals in the ore samples from the two veins are C/S mixed-

3 layer minerals. These C/S minerals show differences in XRD basal reflections as

4 illustrated in Fig. 6A, where XRD patterns of UT and EG specimens of the selected ore

5 samples (C1, S1, S2, and S3) are shown. Accordingly, the C/S minerals can be

6 distinguished into four types of mineralogical association (named I to IV type

7 hereafter). It must be noted that the I–III types occur in the ore samples from the

8 Shuetsu vein, whereas the IV type occur only in the ore samples from the Chuetsu vein.

9 Optical microscopic images of the I-IV types are shown in Fig 5 (A: IV type, C: III

10 type, D: II type and E: I type).

11 The I and II types show XRD basal reflections of chlorite, however the II type is

12 also characterized by weak reflections at 30Å and 20Å which respectively shift to 31Å

13 and 21Å, and by change in peak profile of the reflections at about 7.2 Å and 4.7 Å by

14 EG treatment, (Fig. 6A). Some samples grouped into the I type show also slight

15 changes in peak profile of the basal reflections after the EG treatment as seen in Fig.

16 6A. The reflections with a superstructure reflection at about 29Å (UT) observed in the

17 types III and IV agree with those of corrensite, however the III type shows

18 significant changes in the shape of the higher order basal reflections after the EG

19 treatment. Additionally, the tri-octahedral smectite is observed locally in the ore

20 samples from the Chuetsu vein. The tri-octahedral smectite (d (060) = ~1.53Å) shows

21 basal reflections with d -values deviating somewhat from those of typical saponite to

22 vermiculite (Fig. 6B). In many cases the smectite can be observed as ‘monomineralic

23 phase’ in the ore samples. Di-octahedral smectite coexisting with quartz and Mn oxides

24 has been only reported in an ore sample from the upper oxidized zone (160ml) of the

25 Chuetsu vein (Yoneda & Watanabe, 1981).

1 The IV type is distributed widely but the tri-smectite is of relatively limited
2 distribution in the Chuetsu vein. This may be attributed to the temporal difference of
3 clay formations: smectite may be associated with later sub-stage quartz, while the IV
4 type is associated with earlier and major sub-stages in the vein formation. In the
5 Shuetsu vein, the I type is dominantly distributed in the eastern part while the II and III
6 types are dominant in the deep central part of the vein, but their temporal relationships
7 between the I–III types are not clear. In some hand specimens with crustiform texture,
8 different types of C/S minerals are observed separately in different clay bands of a
9 hand specimen, but the banded clays show no specific trend of formation sequences for
10 the I–III types. These characteristics in distribution of the clay minerals in each vein
11 may be related to the hydrothermal environmental conditions and mineralogical
12 conversion for the clay minerals which will be discussed later, in addition to the
13 geological conditions (e.g., distributions of open spaces for mineral deposition and
14 pathways for upwelling hydrothermal fluid).

15 The SEM observations were performed for selected samples of the I–IV types and
16 smectite. The IV type of fine-grained and irregularly-curved particles (Fig. 7A) shows
17 a different morphology from tri-smectite with coarser particles gathering like flower
18 petals (Fig. 7B). The III type appears to be composed roughly of lathe-shaped particles
19 less curved than the IV type (Fig. 7C). The II type is characterized by bundle-like
20 aggregates of elongated particles (Fig. 7D), which may correspond to aggregates of the
21 acicular or reed shaped particles observed in the optical microscopic observations of
22 the II type. Other particles with different appearances are not distinctly recognized in
23 the SEM observations of the II and III types. In the I type there are platy or flaky
24 particles with slight curvatures (Fig. 7E).

25 In addition to the above, trace amounts of illite minerals including interstratified

1 illite/smectite and kaolin minerals are found mixed in the C/S minerals in the ore
2 samples of the two veins. Illite minerals or kaolin mineral are also detected in infillings
3 of druses of the ore samples. These minerals can be interpreted to result from a later
4 event which post-dated the middle stage of the vein formation.

5 *XRD characterization and C/S modeling*

6 The parameters in calculating XRD patterns for C/S interstratifications are
7 described as follows. A normal distribution function is incorporated in the program,
8 and the calculation was performed with \bar{N} (the mean number of layers) = 10 and $\sigma=2.0$
9 in this study. The calculated line profiles are comparable to the profiles obtained using
10 the slit system (1/2° -0.3mm-1/2°) of the RAD-II diffractometer (RIGAKU Co. Ltd.
11 Japan) (Watanabe, 1988). The atomic parameters of the fundamental layers used in the
12 calculations for the XRD patterns are shown in Table 1. The tetrahedral and octahedral
13 compositions used in the fundamental layers are comparable to those obtained by
14 EPMA analysis for the I–IV types. The probability parameters for the calculations of
15 the XRD patterns for the C/S interstratified structures including completely segregated
16 structures (i.e. mixtures of two discrete phases), are shown in Fig. 8.

17 The IV type C/S mineral (sample: C1) has a superstructure reflection (UT: 29Å,
18 EG: 31Å, K⁺: 27Å, MgGly: 32.5Å), sub-order basal reflections at rational positions,
19 and d (060) spacing at 1.543Å. The basal reflection after the MgGly-treatment shows
20 that the expandable layer of the IV type mineral may be smectitic and not vermiculitic.
21 The coefficients of variability (CV) for the proportionality of the higher-order
22 reflections (CV_{EG}=0.22 for 10 reflections, CV_K=0.33 for 8 reflections, CV_{MgGly}=0.34
23 for 11 reflections) are <0.75 (Bailey, 1982), indicating that the IV type may be
24 identified as corrensite. The observed XRD pattern of the EG-specimen (C1) shows

1 that corrensite occurs as a pure mineral phase in the clay fractions of the sample,
2 containing minute amounts of kaolinite as impurities (Fig. 9A). The IV type can be
3 characterized as a ‘monomineralic phase’ in the ore samples. The calculated XRD
4 pattern of EG-corrensite (Fig. 9B), shows a slight difference in intensity ratios of peaks
5 possibly due to the difference of Mg contents.

6 XRD patterns of the I type of C/S minerals deviate from that of a true chlorite
7 structure by a broadening of peaks corresponding to basal reflections and the
8 occurrence of a reflection due to a superstructure after EG-treatment (Fig. 10). These
9 changes can be due to minor amounts of swelling layers interstratified with the chlorite
10 layers. The I type can be grouped as a tri-octahedral chlorite with occasional smectite
11 layers and a ratio in the chlorite structure which may be presumed to be <10%.

12 The XRD pattern of the II type is characterized by weak 30Å- and 20Å-reflections
13 which shift respectively to 31Å and 21Å after the EG-treatment. After K⁺ saturation,
14 the XRD pattern of the II type shows peaks at 11Å, 9.3Å, and 7.7Å in addition to
15 broadened peaks of the basal reflections corresponding to chlorite at 14.2Å, 7Å, 4.7Å,
16 3.55Å, and 2.84Å (Fig. 11A). Such XRD pattern is similar to that due to the C/S
17 interstratification of the chlorite mineral occurring in the hydrothermal alteration zone
18 of the Wanibuchi deposit, a Kuroko-type ore deposit in Japan (Watanabe et al., 1974).
19 The XRD pattern of the II type can be explained as interstratifications of chlorite and
20 corrensite layers (Yoneda & Watanabe, 1994).

21 Calculations of XRD patterns of the II type were performed for three different
22 models of interstratified structures: 1) interstratifications (Reichweite g=3) of chlorite
23 and tri-smectite, 2) interstratifications (Reichweite g=2) of chlorite and corrensite, and
24 3) interstratifications (Reichweite g=1) of chlorite (double layers) and corrensite. As a

1 result the structural model of the interstratifications ($g=1$) of chlorite (double layers)
2 (0.7) and corrensite (0.3) with the probability point corresponding to 8 in Fig. 8
3 explains the characteristic XRD peaks of the II type. In this study this type of
4 interstratified chlorite/corrensite is abbreviated as CC/Co. In addition the observed
5 peaks corresponding to those of chlorite indicate that the II types can be interpreted as
6 a mixture of the interstratified CC/Co mineral and discrete chlorite. A superimposed
7 pattern (Fig. 11B d) of the calculated interstratified CC/Co (Fig. 11B b) onto chlorite
8 (Fig. 11B c) fits the observed pattern of the II type (Fig. 11B a), and provides an
9 approximate ratio of chlorite (0.5) and CC/Co (0.5) in the II type sample. Peak
10 deconvolution of the same observed pattern was performed by non-linear least squares
11 fitting using the Pseudo-Voigt profile function, after subtraction of a background by
12 cubic curve fitting. Deconvolution with 7 and 3 elementary peaks respectively
13 observed within $2\theta = 5\text{--}15$ and $2\theta = 23\text{--}27$ are shown in Fig. 12, suggesting that the
14 overlapping peaks of the II type can be interpreted clearly to be resulting from a
15 mixture of interstratified CC (0.7)/Co (0.3) mineral and discrete chlorite possibly
16 having a low crystal-thickness distribution and/or randomly interstratified structure
17 with small amounts of smectite.

18 The XRD pattern of the III type is characterized by changes in the basal reflections
19 at $2\theta=10^\circ\text{--}28^\circ$, where the peak profiles at about 7–8 \AA , 4.4–5.2 \AA and 3.4–3.6 \AA changed
20 after EG-treatment (Fig. 13A). A comparison of the XRD patterns with simulated
21 patterns shows that the EG-S3 can be better understood as a segregation structure of
22 chlorite (0.5) and corrensite (0.5) (Fig. 13A-c) rather than a mixture of the two discrete
23 phases (Fig. 13A-b). The XRD patterns of K⁺ and MgGly-S3 are similar to the C/Co
24 segregation structure. Other EG-samples of the III type, showing somewhat different
25 variations of peak profiles at about 7–8 \AA , 4.4–5.2 \AA and 3.4–3.6 \AA , can be interpreted

1 to result from a C/Co segregation structure between C(0.3)/Co(0.7) and C(0.7)/Co(0.3),
2 though the observed peak at about $2\theta=25-26^\circ$ of the sample #S80511B shows a larger
3 segregation tendency as compared with others (Fig. 13B). Interstratified
4 chlorite/saponite minerals showing a XRD pattern similar to the III type has previously
5 been documented in the Kuroko ore deposits (Shirozu et al., 1975).

6 *Chemical compositions of the chlorite-corrensite-smectite series minerals*

7 Quantitative point analyses by EPMA of the interstratified C/Co minerals from 18
8 ore samples, tri-octahedral smectite from 2 ore samples, and tri-octahedral chlorite
9 from 4 wall rock samples in contact with the ore veins, were performed and 321
10 analytical data-sets were obtained (Yoneda & Watanabe, 1989; Yoneda, 1994). For
11 each selected samples, the analytical values in oxide wt% and in atomic% were
12 averaged (Table 2).

13 The chlorite-corrensite-smectite (C-S) series minerals from the ore veins are Mg-
14 rich and Fe-poor ones with small amounts of manganese, and show compositional
15 features related to the types of C-S minerals and distinct differences from wall-rock
16 chlorite. From the tri-octahedral smectite to IV type, III type, II type, I type and wall-
17 rock chlorite, the Al/Si ratios, the tetrahedral negative-charges and the octahedral
18 charges increase, while the interlayer charges decrease from IV type, III type, II type,
19 I type and to wall-rock chlorite. These compositional variations relating to the types of
20 C-S minerals can be understood to be due to the proportions of smectite layers
21 comprising the various samples. In addition, the octahedral compositions of the C-S
22 series minerals show a characteristic differences related to the types of C-S minerals as
23 shown in the Mg-Fe-Al (VI) plots (Fig. 14). It is discriminative that the IV type and tri-
24 smectite are very poor in Fe but abundantly rich in Mg as compared with the I-III
25 types which are less Mg and more Fe. The wall-rock chlorites are poorer in Mg and

1 richer in Fe as compared to the I–III types. These differences in the octahedral
2 compositions especially in Mg and Fe contents of the vein minerals can be explained
3 by the compositions of hydrothermal fluids: Mg-rich & Fe-poor fluids in the Chuetsu
4 vein and comparatively Mg-poor & Fe-rich fluids in the Shuetsu vein, based on the
5 relationships between the precipitated clay compositions and the fluid compositions in
6 geothermal wells (Reyes & Cardile, 1989).

7 An AEM analysis of the particles of C/S minerals from 11 ore samples has also
8 been performed (Yoneda, 1994). EDX analyses were performed on both particles
9 showing single-crystal and poly-crystal patterns in selected-area electron diffraction.
10 Analytical results are represented in averaged structural formulae (Table 3). Compared
11 with the EPMA analyses of the same samples, the standard deviations of each averaged
12 values are large, and the values of Si and Na are high but Mg is low, suggesting that
13 the analytical values may be affected by contamination in AEM analyses of this study.
14 Averaged Al/Si ratios obtained by AEM and EPMA analyses are plotted together
15 in Fig. 15. Despite a slight overestimation of Si content in the AEM analyses, the
16 averaged Al/Si ratio obtained by EPMA and AEM analyses can be considered
17 comparable. This would suggest that the variations in the Al/Si ratios observed in
18 C-Co series minerals may arise due to differences within the scales of the clay
19 particles, and that the discrete assemblage of chlorite and CC/Co of the II type and
20 the assemblage showing a segregated structure of chlorite and corrensite of the III
21 type can be understood to be packets incorporated in the stacking of clay particles.

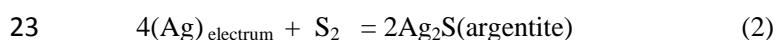
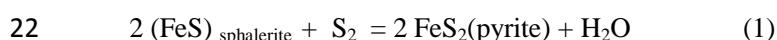
22 *Mineralogical changes and environmental conditions of formation*

23 The I type mineral is chlorite with occasional smectite layers (10% \geq). The
24 percentage of smectite layers (S%) in the II type (C + CC(0.7)/Co(0.3)) varies in a

1 limited range below 15% with a maximum value in absence of discrete chlorite. In the
2 III type (C+Co) the smectite% can be estimated by using the XRD modeling of the C/S
3 interstratifications as described above. The III type has a S% range of between 35%–
4 15% and that of the IV type, monomineralic corrensite, can be estimated near 50%.
5 Considering the percentage of smectite layers and the compositional variations of the
6 chlorite-corrensite-smectite series minerals, the mineralogical differences in this
7 mineral series in the two ore veins can be summarized as in Fig. 16. The Chuetsu and
8 Shuetsu veins are characterized by different mineral series within the C-Co-S series
9 minerals: a smectite-corrensite series at the Chuetsu vein and a corrensite-chlorite
10 series at the Shuetsu vein. It is noteworthy that the former (Chuetsu) series of minerals
11 ($\text{Fe}/(\text{Fe}+\text{Mg}+\text{Mn}) = 0.01\text{--}0.03$) shows much lower Fe contents than that of the Shuetsu
12 series of minerals ($\text{Fe}/(\text{Fe}+\text{Mg}+\text{Mn}) = 0.06\text{--}0.15$), and that an interstratified phase of
13 CC/Co is observed as a discrete phase in the C-Co series.

14 The interstratified C/S minerals being closely associated with Au-Ag and sulfide
15 minerals in the ore samples which formed during the middle stage mineralization of the
16 Chuetsu and Shuetsu veins, their conditions of formation can be approach from the
17 condition of stability of the ore minerals.

18 The equilibrium temperature and S_2 fugacity of the electrum-sphalerite-pyrite-
19 argentite assemblage may be expressed as a function of $\text{FeS}\%$ in sphalerite and the Ag
20 mole ratio in electrum as the following sulfidation reactions (Barton & Toulmin, 1964,
21 1966; Vaughan & Craig, 1997).



1 The intersection of two equilibrium curves of (1) and (2) here gives an invariant point
2 of temperature and S₂ fugacity for an electrum-sphalerite-pyrite-argentite assemblage.
3 If equilibrium is assumed during ore formation in each vein-type deposit, the
4 compositions of sphalerite and electrum may permit to approximate temperature
5 (electrum-sphalerite temperature) and S₂ fugacity (Shikazono, 1985). (140–242°C and
6 171–256°C for the Chuetsu and Shuetsu veins respectively). Based on the electrum-
7 sphalerite-pyrite-argentite assemblages it may be suggested that ore deposition took
8 place at higher temperature (171 to 256°C) in the Shuetsu vein than the Chuetsu vein
9 (140 to 242°C), but at similar values of S₂ fugacity ($\log f_{S_2} = -12.9 + 0.05/-0.76$ for the
10 Chuetsu vein and $\log f_{S_2} = -12.7 + 0.29/-0.31$ for the Shuetsu vein). Moreover,
11 homogenization temperatures of primary and pseudo-secondary fluid inclusions of
12 quartz from the middle stage ores of the two veins range from 140 to 270°C for the
13 Chuetsu vein, and from 172 to 225°C for the Shuetsu vein (Yoneda, 1994).

14 In addition, the oxidation-reduction state of sulfur-containing aqueous solution co-
15 existing with sphalerite and pyrite can be expressed as in the following reactions
16 (Shikazono, 2003).



19 Equation (3) is for a reduced sulfur predominant region, and equation (4) is for an
20 oxidized sulfur predominant region. Accordingly, the FeS content of sphalerite may be
21 linked to the physicochemical conditions of the hydrothermal solution such as
22 temperature, concentration of dissolved sulfur species, pH, and oxygen fugacity
23 (Barnes & Kullerud, 1961). The possible ranges of pH and oxygen fugacity for the
24 mineral assemblage of pyrite + sphalerite – kaolinite ± potassium mica ± adularia –

1 kaolinite – barite were calculated at a temperature of 200°C, a total potassium
2 concentration of 10^{-1} mol/kg H₂O and a total sulfur concentration of 10^{-3} mol/kg H₂O,
3 by using the thermodynamic data of Helgeson (1969), Helgeson & Kirkham (1974) and
4 Helgeson et al. (1978), and the maximum/minimum FeS contents of sphalerite in the
5 two veins. On the basis of the thermodynamic stability of the mineral assemblage
6 mentioned above, the physicochemical parameters of pH and oxygen fugacity indicate
7 that the hydrothermal environments of the II stage ore formations in the two veins
8 could be in the reduced sulfur species predominant conditions and in pH conditions
9 around neutral, but with different redox conditions between the Chuetsu and Shuetsu
10 veins: the calculated log f_{O₂} (atm) ranges of $-38 \sim -40$ presumable for the Chuetsu
11 vein and of $-40 \sim -42$ presumable for the Shuetsu vein show a higher oxidation state in
12 the Chuetsu vein. This tendency of the redox conditions in the reduced sulfur
13 predominant region is the same at other temperatures close to 200°C, because the
14 oxygen fugacity of the mineral assemblage depends on the FeS contents of the
15 sphalerite included in the assemblage.

16 On the basis of the occurrences of chlorite-corrensite-smectite series minerals, it is
17 possible that the minerals may have been formed by precipitation from upwelling
18 hydrothermal fluids, which may have reacted with rocks in the deeper strata, during the
19 middle stage of the epithermal systems. If the periods and water/rock ratios of the vein
20 formation can be assumed to be similar in the Chuetsu and Shuetsu veins, it may be
21 inferred that the difference in the electrum-sphalerite formation temperatures and/or in
22 chemical compositions of the hydrothermal fluids may have played a role in the
23 formation of the Co-C series at the Shuetsu vein and of the S-Co series at the Chuetsu
24 vein. Additionally difference in redox conditions of the ore formation could have
25 affected the crystal chemistry of the smectite-corrensite-chlorite series minerals.

1 Further investigations will be necessary to verify such hypothesis. Moreover,
2 hydrothermal events such as boiling, mixing and cooling of upwelling fluids, which
3 have large influences on the hydrothermal condition for mineral deposition in the
4 epithermal systems (e.g., White & Hedenquist, 1990; Lonker et al., 1993), could be a
5 factor to affect the formation of S-Co and Co-C series minerals. Especially the
6 variation of boiling conditions, of which intensity may be linked to the formation of
7 banded quartz with the crustiform, colloform, microcrystalline and comb textures in
8 epithermal veins (Shimizu, 2014), may be likely to influence on the middle stage
9 mineral formation in the Chuetsu and Shuetsu ore veins.

10 The formations of S-Co and Co-C series in the two ore veins can be attributed to
11 the difference of temperatures and/or chemical composition of solutions involved in the
12 formation process of the two epithermal veins. In addition the spatial and/or temporal
13 mineralogical changes of trioctahedral clay minerals can be a product of a
14 transformation process including dissolution, re-precipitation, and crystal growth
15 similar to that described in both diagenetic or hydrothermal environments (Beaufort et
16 al., 2015 and references therein) during and subsequent to the vein formation. These
17 kinetic effects may have implicated in the mineralogical conversion for the $S \rightarrow Co$
18 series at the Chuetsu vein and for $Co \rightarrow C$ series at the Shuetsu vein in addition to the
19 predominant hydrothermal conditions during the vein formation mentioned above.

20 A chronology for the formation of clay minerals in two ore veins may be
21 considered as follows. In the Chuetsu vein, Mg-rich & Fe-poor amorphous materials
22 (precursor) may have been precipitated from hydrothermal fluids through the middle
23 stage of ore formation, and consecutively transformed to smectitic materials and then
24 to corrensite. However at later sub-stage of the middle stage, the smectitic materials

1 may have been grown to well-crystallized tri-smectite possibly in a lower temperature
2 as compared with the temperature that the conversion to corrensite was dominated. On
3 the other hand, comparatively Mg-poor & Fe-rich amorphous materials (precursor)
4 may have been precipitated from hydrothermal fluids through the middle stage of ore
5 formation, and consecutively transformed to corrensitic materials and then to chlorite
6 in the Shuetsu vein. Though the transformation of precursor to corrensitic materials is
7 uncertainty, the higher temperatures during ore formation in the Shuetsu vein may have
8 influenced the mineralogical conversion which is different from that in the Chuetsu
9 vein. In addition, the spatial and temporal variations in the occurrence of the I-III
10 type minerals may be understood that the transformation of the $\text{Co} \rightarrow \text{C}$ had been
11 affected by the variation of environmental conditions possibly due to the hydrothermal
12 events occurred in the epithermal systems.

13

14 CONCLUSIONS

15 Chlorite-corrensite-smectite series minerals occur as vein constituents in the two
16 epithermal Au-Ag ore veins, the Chuetsu vein and the Shuetsu vein of the Todoroki
17 Au-Ag ore deposit. The occurrence characteristics of the minerals indicate that the
18 clay minerals may be products of direct precipitation from hydrothermal fluids and
19 subsequent mineralogical changes during and after vein formation. The series of
20 minerals from the Chuetsu vein are characterized by ‘monomineralic’ corrensite
21 showing an extensive distribution throughout the vein, and tri-octahedral smectite
22 occurring locally. The occurrence of smectite may be due to a product of relatively later
23 sub-stages of the vein formation as compared with corrensite. The Shuetsu vein series
24 minerals are characterized by chlorite/smectite minerals which can be divided into

1 three different types: I type including chlorite with minor amounts of smectite layers, II
2 type comprising chlorite/corrensite mixed-layers and discrete chlorite, and III type
3 characterized by segregation of corrensite and chlorite layers.

4 Based on the occurrences of the series of minerals and the chemistry of the co-
5 existing minerals in the ore samples, the differences in the temperature and/or
6 compositions of the hydrothermal fluids may be related to the formation of the IV type
7 and tri-smectite at the Chuetsu vein, and of the I–III types at the Shuetsu vein. Finally
8 the difference and variation of the epithermal environments during the vein formations
9 and possible kinetic effects may have played a role in both the formation of corrensite,
10 then its conversion to chlorite in the Shuetsu vein and the formation of smectite, then
11 its conversion to corrensite in the Chuetsu vein.

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16 REFERENCES

- 17 Barnes H. L. & Kullerud G. (1961) Equilibria in sulfur-containing aqueous solutions
18 in the system Fe-S-O, and their correlation during ore deposition. *Economic
Geology*, **56**, 648-685.
- 20 Barton P. B. Jr. & Toulmin P. (1964) The electrum-tarnish method for the
21 determination of fugacity of sulfur in laboratory sulfide systems. *Geochimica et
Cosmochimica Acta*, **28**, 619-640.
- 23 Barton P. B. Jr. & Toulmin P. (1966) Phase relations involving sphalerite in Fe-Zn-S
24 system. *Economic geology*, **61**, 815-849.
- 25 Beaufort D., Baronnet A., Lanson B. & Meunier A. (1997) Corrensite: A single phse or

- 1 a mixed-layer phyllosilicate in the saponite-to-chlorite conversion series? A case
2 study of Sancerre-Couy deep drill hole (France). *American Mineralogist*, **82**, 109-
3 124.
- 4 Beaufort D., Rigault C., Billon S., Billault V., Inoue, A. Inoue S., and Patrier P. (2015)
5 Chlorite and chloritization processes through mixed layer mineral series in low-
6 temperature geological systems - A review. *Clay Minerals*, **50**, 497-523.
- 7 Bence A.E. & Albee, A.L. (1968) Empirical correction factors for the electron
8 microanalysis of silicates and oxides. *The Journal of Geology*, **76**, 382-403.
- 9 Bettison-Varga L. & Mackinnon I.D.R. (1997) The role of randomly mixed-layered
10 chlorite/smectite in the transformation of smectite to chlorite. *Clays and Clay
11 Minerals*, **45**, 506-516.
- 12 Buatier M. D., Früh-Green G. L. & Karpoff A. M. (1995) Mechanisms of Mg-
13 phyllosilicate formation in a sedimented ridge (Middle Valley, Juan de Fuca).
14 *Contribution of Mineralogy and Petrology*, **122**, 134-151.
- 15 Drits V.A., Ivanovskaya T.A., Sakharov B.A., Zviagina B.B., Gor'kova N.V.,
16 Pokrovskaya E.V. & Savichev A.T. (2011) Mixed-layer corrensite—chloites and
17 their formation mechanism in the glauconitic sandstone — clayey rocks (Riphean,
18 AnabaruUplift), *Lithology and Mineral Resources*, **46**, 566-593.
- 19 Fukui M. & Yoshimura T. (1999) Chlorite/Smectite mixed-layer minerals in Aosawa
20 basalts distributed in the Dewa hill, Yamagata Prefecture. *Journal of the Clay
21 Science Society of Japan*, **39**, 19-36 (in Japanese with English abstract).
- 22 Hasegawa K., Mitani K., Sugimoto R., Futamae K. & Hayakawa F. (1976) Geology
23 and ore deposits of the Todoroki and Meiji district in Shikaribetsu province,
24 Hokkaido. *Reports of Geological Survey of Hokkaido*, **48**, 33-60 (in Japanese with
25 English abstract).
- 26 Helgeson H. C. (1969) Thermodynamics of hydrothermal systems at elevated
27 temperatures and pressures. *American Journal of Science*, **267**, 729-804.
- 28 Helgeson H.C. & Kirkham D.H. (1974):Theoretical prediction of the thermodynamic
29 behavior of aqueous electrolytes at high pressures and temperatures. I. Summary of

- 1 the thermodynamic/electrostatic properties of the solvent. *American Journal of*
2 *Science*, **274**, 1089-1198.
- 3 Helgeson H. C., Delany J. M., Nesbitt H.W. & Bird D. K. (1978) Summary and
4 critique of the thermodynamic properties of rock-forming minerals. *American*
5 *Journal of Science*, **278-A**, 1–229.
- 6 Inoue A. & Utada M. (1991) Smectite-to-chlorite transformation in thermally
7 metamorphosed volcanoclastic rocks in the Kamikita area, northern Honshu, Japan.
8 *American Mineralogist*, **76**, 628-640.
- 9 Japan Mining Industry Association (1968) Todoroki mine. Pp. 2150-153 in: *List of Ore*
10 *deposits of Japan*. Japan Mining Industry Association, Tokyo, Japan (in Japanese).
- 11 Kakinoki J. & Komura Y. (1952) Intensity of X-ray by an one-dimensionally
12 disordered crystal. *Journal of Physical Society of Japan*, **7**, 30-35.
- 13 Kogure T., Drits V.A. & Inoue S. (2013) Structure of mixed-layer corrensite-chlorite
14 revealed by high-resolution transmission electron microscopy (HRTEM). *American*
15 *Mineralogist*, **98**, 1253-1260.
- 16 Leoni L., Lezzerini M., Battaglia S. & Cavalcante F. (2010) Corrensite and chlorite-
17 rich Chl-S mixed layers in sandstones from the 'Macigno' Formation (northwestern
18 Tuscany, Italy). *Clay Minerals*, **45**, 87-106.
- 19 Lonker S.W., Franzson, H. & Kristmannsdottir, H. (1993) Mineral-fluid interaction in
20 the Reykjanes and Svartsengi geothermal systems, Iceland. *American Journal of*
21 *Science*, **293**, 605-670.
- 22 Meunier A. (2003) Clays, pp. 329-415. Springer, Berlin.
- 23 Nagasawa K., Shirozu H. & Nakamura T. (1976) Clay minerals as constituents of
24 hydrothermal metallic vein-type deposits. *Mining Geology Special Issue*, **7**, 75-84
25 (in Japanese with English abstract).
- 26 Reyes, A.G. & Cardile C.M. (1989) Characterization of clay scales forming in
27 Philippine geothermal wells. *Geothermics*, **18**, 429-446.
- 28 Reynolds, R.C. (1980) Interstratified clay minerals, Pp. 249-303 in: Crystal structures
29 of clay minerals and their X-ray identification (G.W. Brindley & G. Brown, editor),

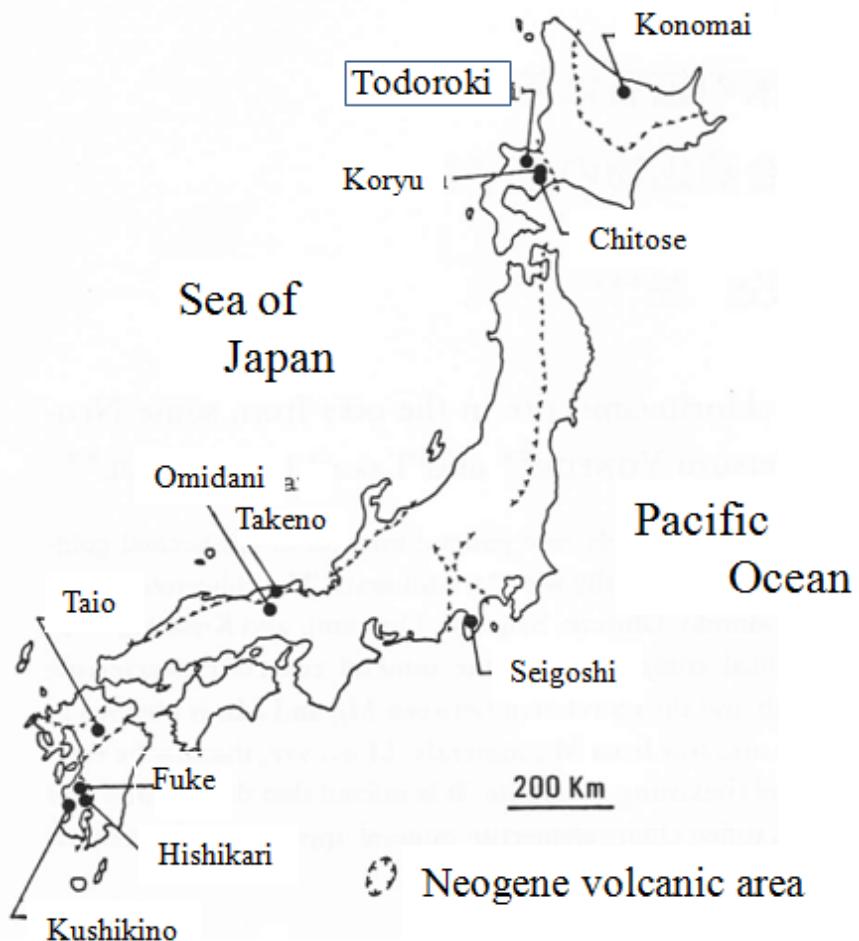
- 1 Min. Soc., London.
- 2 Robinson D., Schmidt S.T. & Santana de Zamora A. (2002) Reaction pathways and
3 reaction progress for the smectite-to-chlorite transformation: evidence from
4 hydrothermally altered metabasites. *Metamorphic Geology*, **20**, 167-174.
- 5 Sato, M. (1965) Structure of interstratified (mixed-layer) minerals. *Nature*, **208**, 70-71.
- 6 Sato, M. (1987) Interstratified (mixed layer) structures and their theoretical X-ray
7 powder patterns I. theoretical aspects. *Clay Science*, **7**, 41-48.
- 8 Sawai O., Yoneda T. & Itaya T. (1992) K-Ar ages of the Chitose, Todoroki and Teine
9 Au-Ag vein-type deposits, Southwest Hokkaido, Japan. *Mining Geology*, **42**, 323-
10 330 (in Japanese with English abstract).
- 11 Schiffman P. & Fridleifsson, G.O. (1991) The smectite to chlorite transition in drillhole
12 NJ-15, Hesjavellir geothermalfield, Iceland: XRD, BSE and electron microprobe
13 investigations. *Journal of Metamorphic Geology*, **9**, 679-696.
- 14 Shau Y.H. & Peacor D.R. (1992) Phyllosilicates in hydrothermally altered basalts from
15 DSDP Hole 504B, Leg 83 — a TEM and AEM study. *Contributions to Mineralogy
and Petrology*, **112**, 119-133.
- 17 Shikazono N. (2003) Geochemical and tectonic evolution of arc-backarc hydrothermal
18 systems.pp. 83-201. Elsevier, Amsterdam.
- 19 Shimizu T. (2014) Reinterpretation of quartz textures in terms of hydrothermal fluid
20 evolution at the Koryu Au-Ag deposit, Japan. *Economic Geology*, **109**, 2051-2065
- 21 Shirozu H., Sakasegawa T., Katsumoto N. & Ozaki M. (1975) Mg-chlorite and
22 interstratified Mg-chlorite/saponite associated with kuroko deposits. *Clay Science*,
23 **4**, 305-321.
- 24 Shirozu H. (1978) Chlorite minerals. Pp. 243-264 in: *Clays and Clay Minerals of
Japan* (T. Sudo & S. Shimoda, editors). Developments in Sedimentology 26,
26 Elsevier, US.
- 27 Sudo T. & Shimoda S. (1977) Interstratified clay minerals – mode of occurrence and
28 origin. *Minerals Science and Engineering*, **9**, 3-24.

- 1 Takeuchi K. (1984) Clay minerals in Arakawa No.4 vein of the Kushikino mine.
2 *Mining Geology*, **34**, 335-342 (in Japanese with English abstract).
- 3 Taguchi S. & Watanabe T. (1973) Clay minerals especially interstratified
4 chlorite/saponite associated with gold ores of the Fuke mine, Kagoshima prefecture.
5 *Science Reports, Department of geology, Kyushu University*, **11**, 243-250 (in
6 Japanese with English abstract).
- 7 Vaughan D. J. & Craig J. R. (1997) Sulfide ore mineral stabilities, morphologies, and
8 intergrowth textures. Pp. 367-434 in: *Geochemistry of hydrothermal ore deposits*
9 Third edition (H. L. Barnes, editor), John Wiley & Sons, Inc., New York.
- 10 Velde B. (1985) Clay minerals, pp.104-191. Elsevier, Amsterdam.
- 11 Watanabe T., Nakamura Y. & Shirozu H. (1974) An interstratified mineral of chlorite
12 and saponite from the Wanibuchi mine. *Journal of the Mineralogical Society of*
13 *Japan*, **11**, Special Issue No.1, 123-130 (in Japanese with English abstract).
- 14 Watanabe T. (1977) X-ray line profile of interstratified chlorite/saponite. *Science*
15 *Reports, Department of geology, Kyushu University*, **12**, 303-309 (in Japanese with
16 English abstract).
- 17 Watanabe T. (1988) The structural model of illite/smectite interstratified mineral and
18 the diagram for its identification. *Clay Science*, **7**, 97-117.
- 19 White N. C. & Hedenquist J. W. (1990) Epithemal environments and styles of
20 mineralization: variations and their causes, and guideline for exploration. *Journal*
21 *of Geochemical Exploration*, **36**, 445-474.
- 22 Yoneda T. & Watanabe T. (1981) Clay minerals in the gold-silver ore of the Chuetsu-
23 hi vein of the Todoroki mine, Hokkaido, Japan. *Mining geology Special Issue*, **10**,
24 143-149 (in Japanese with English abstract).
- 25 Yoneda T. & Watanabe T. (1989) Chemical composition of regularly interstratified
26 chlorite/smectite in the ores from some Neogene gold-silver vein-type deposits in
27 Japan. *Mining geology*, **39**, 181-190 (in Japanese with English abstract).
- 28 Yoneda T. (1994) *Applied mineralogical study of clays from hydrothermal ore deposits*.

- 1 PhD thesis, Kyushu University, Japan (in Japanese).
- 2 Yoneda T. & Watanabe T. (1994) Chlorite/smectite mixed-layer mineral having a 20
- 3 A-reflection from the Todoroki epithermal gold-silver ore-vein. *Journal of Clay*
- 4 *Scociety of Japan*, **34**, 71-79 (in Japanese with English abstract).
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1

2 **FIGURES**



3

4 Fig. 1 Epithermal Au-Ag vein-type ore deposits where productions of
5 interstratified C/S minerals have been described as vein minerals (Taguchi
6 & Watanabe, 1973; Yoneda & Watanabe, 1981; Takeuchi, 1984; Yoneda &
7 Watanabe, 1989).

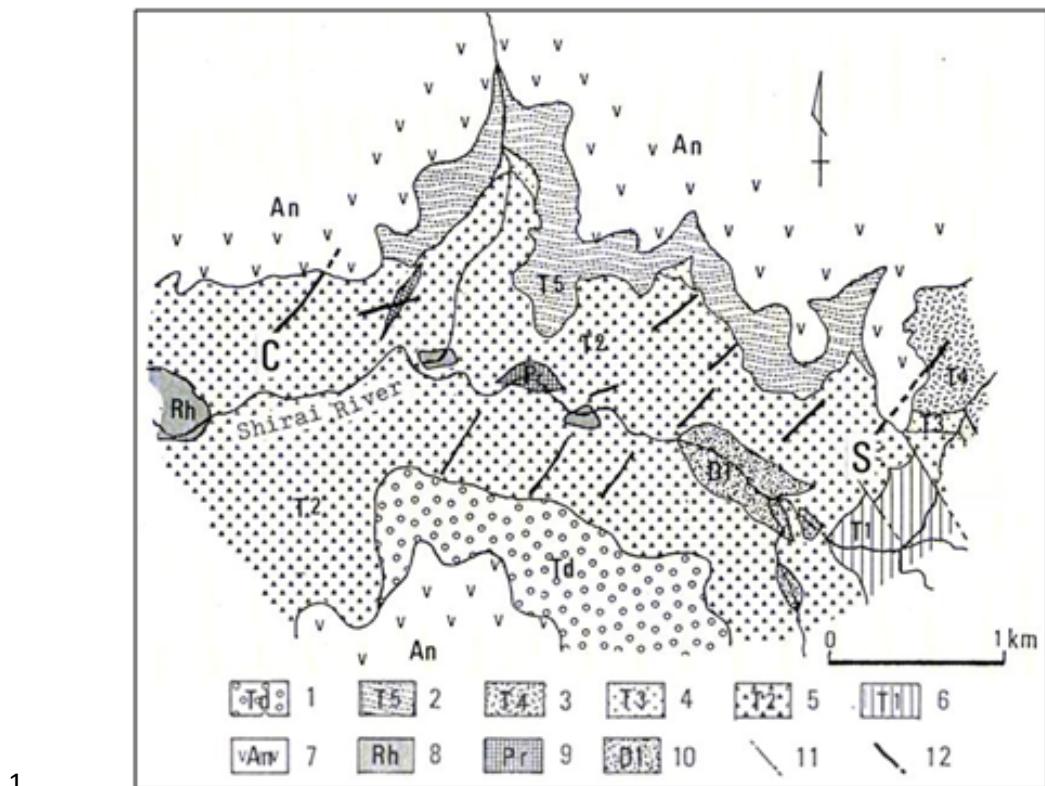


Fig. 2 Geological map of the Todoroki Au-Ag ore deposits (Hasegawa et al., 1976; Yoneda, 1994).

1: Talus deposit, 2: Tuff/sandstone with coal seam, 3: Andesitic tuff, 4: Sandstone/mudstone, 5: Rhyolitic tuff and tuff breccia, 6: Conglomerate/mudstone/tuff, 7: Andesite lava, 8: Rhyolite, 9: Propylite, 10: Dolerite, 11: Fault, 12: Ore veins (C: Chuetsu vein, S: Shuetsu vein)

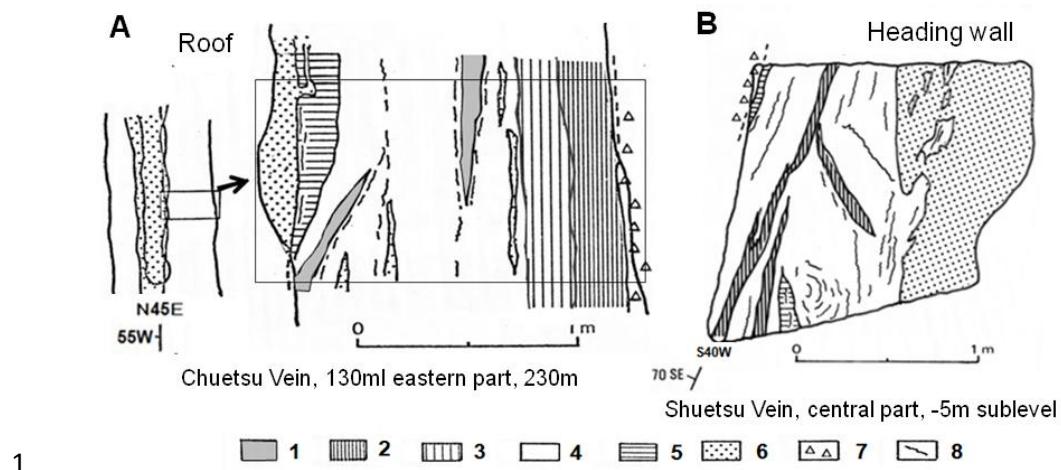


Fig. 3 Vein sketches showing the constituents and structures of the Chuetsu and Shuetsu veins. See in the text for details.

1: dark gray massive quartz (the I stage), 2: white/gray banded quartz with Au-Ag minerals/Cu-Pb-Zn-Fe-S sulfides (the II stage), 3: white/gray banded quartz with rhodochrosite and Au-Ag minerals/Cu-Pb-Zn-Fe sulfide minerals (the II stage), 4: gray quartz (partly banded) (the II stage), 5: white massive quartz (the II stage), 6: calcite (the III stage), 7: wall rock, 8: black streak rich in Au-Ag minerals/Cu-Pb-Zn-Fe sulfide minerals (AgB).

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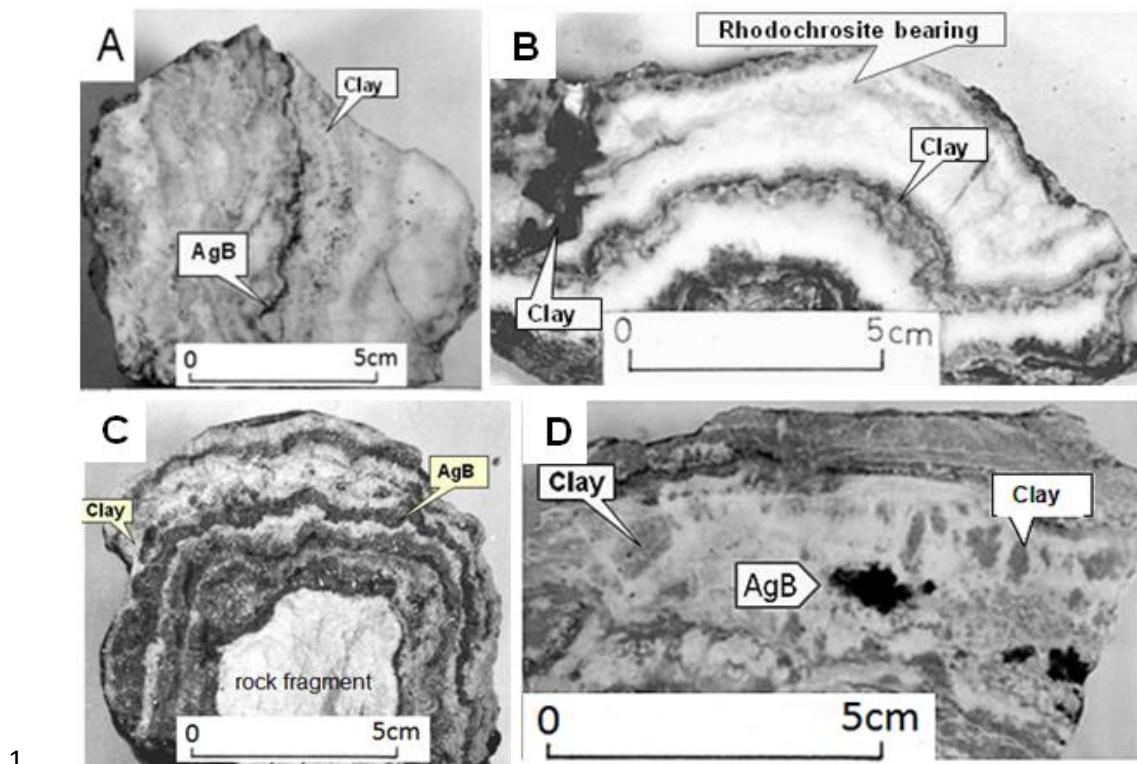
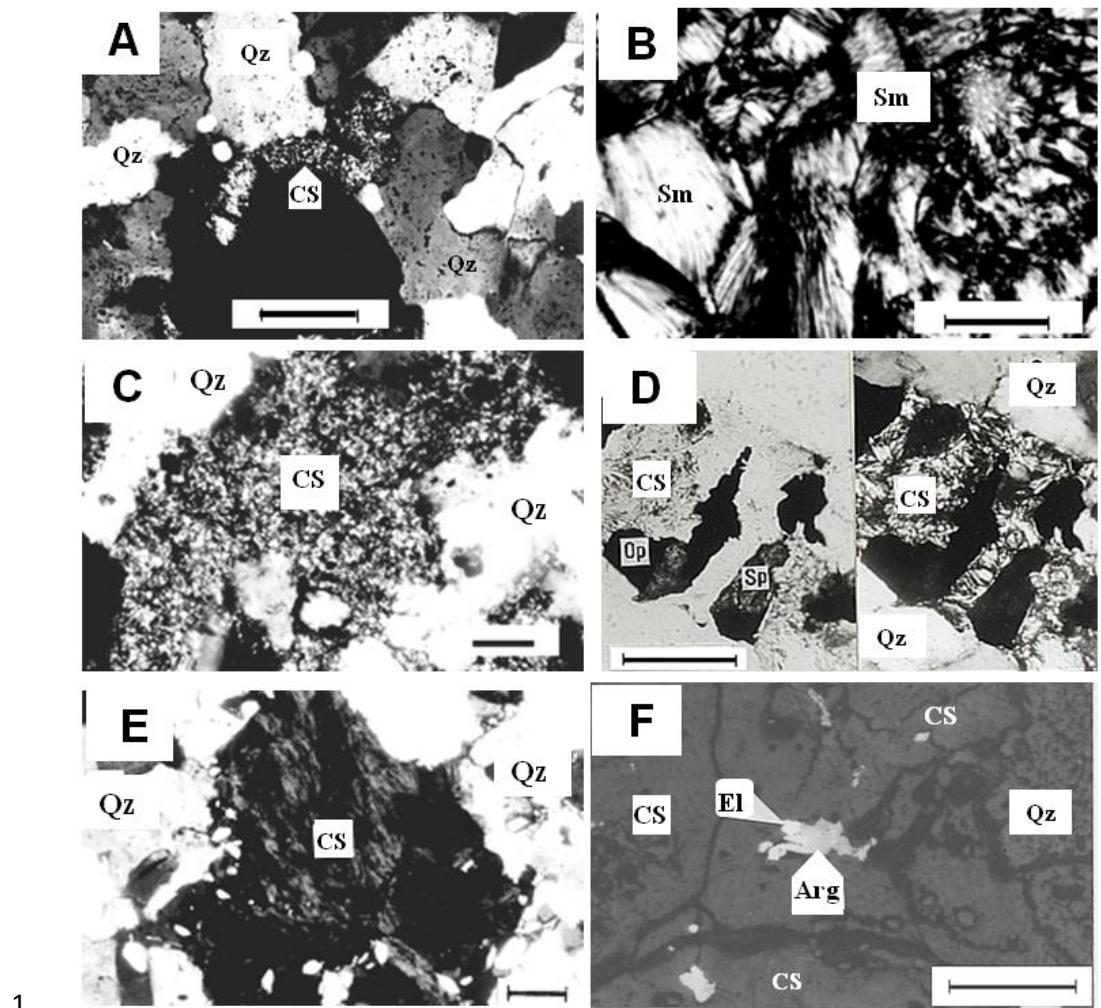


Fig. 4 Ore samples with ore minerals and clays from the middle stage quartz veins.

A: Banded quartz with Au-Ag minerals/Cu-Pb-Zn-Fe sulfide minerals (AgB) and clays (Chuetsau 130ml, #C80304), B: Banded quartz with rhodochrosite and clays (Chuetsau 50ml, #C71408), C: Banded quartz with AgB rich in Cu-Pb-Zn sulfides and clays crusting a rock fragment (Shuetsu central lower part, #S80509), D: quartz with patchy AgB and patchy ~ banded clays (Shuetsu eastern part, #S80601).



1
 2 Fig. 5 Microphotographs of the clay minerals observed in the ore samples.
 3 A-C & E: transmitted light (cross polar), D: transmitted light (left half-
 4 parallel, right half-cross), F: reflected light (parallel polar). Bar scale:
 5 100µm, Qz: quartz, CS: chlorite-smectite series mineral, Sm: smectite, Op:
 6 opaque ore mineral, Sp: sphalerite, El: electrum, Arg: argentite.
 7 A: C1 (#C50507) – IV type, B: C10 (#C80304) – tri-smectite, C: #S80508C
 8 – III type, D: #S80508A – II type, E: #S80607 – I type, F: #C11204 – IV
 9 type. See in the text for details.
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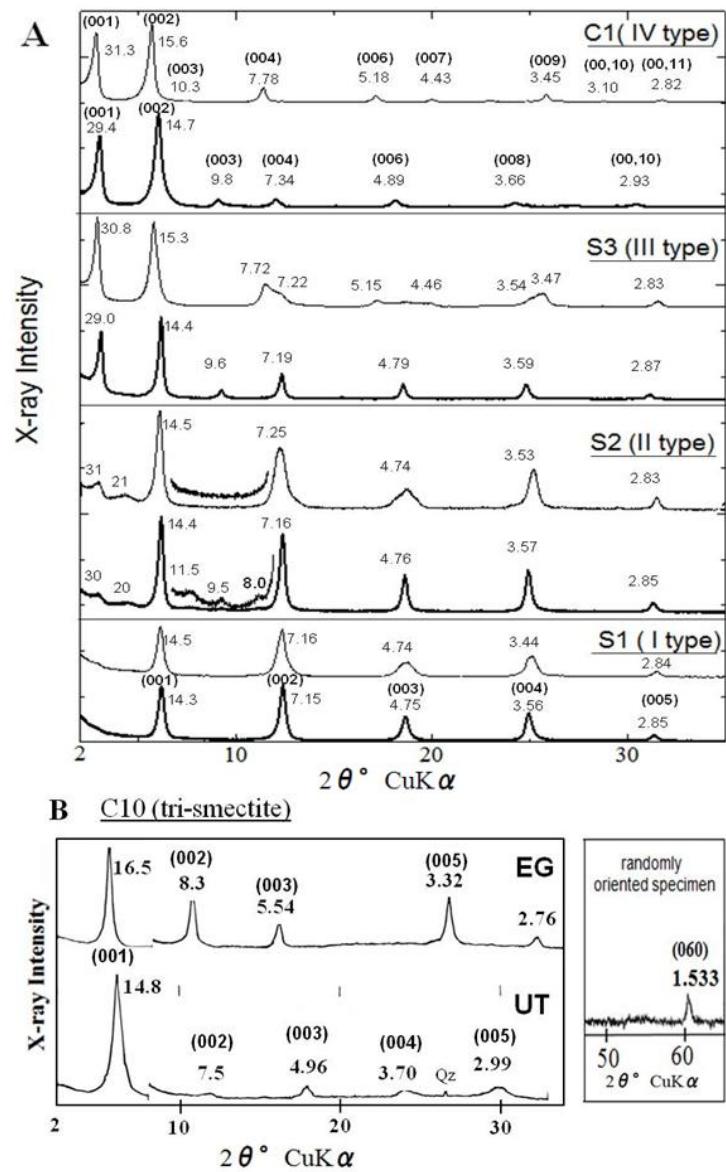
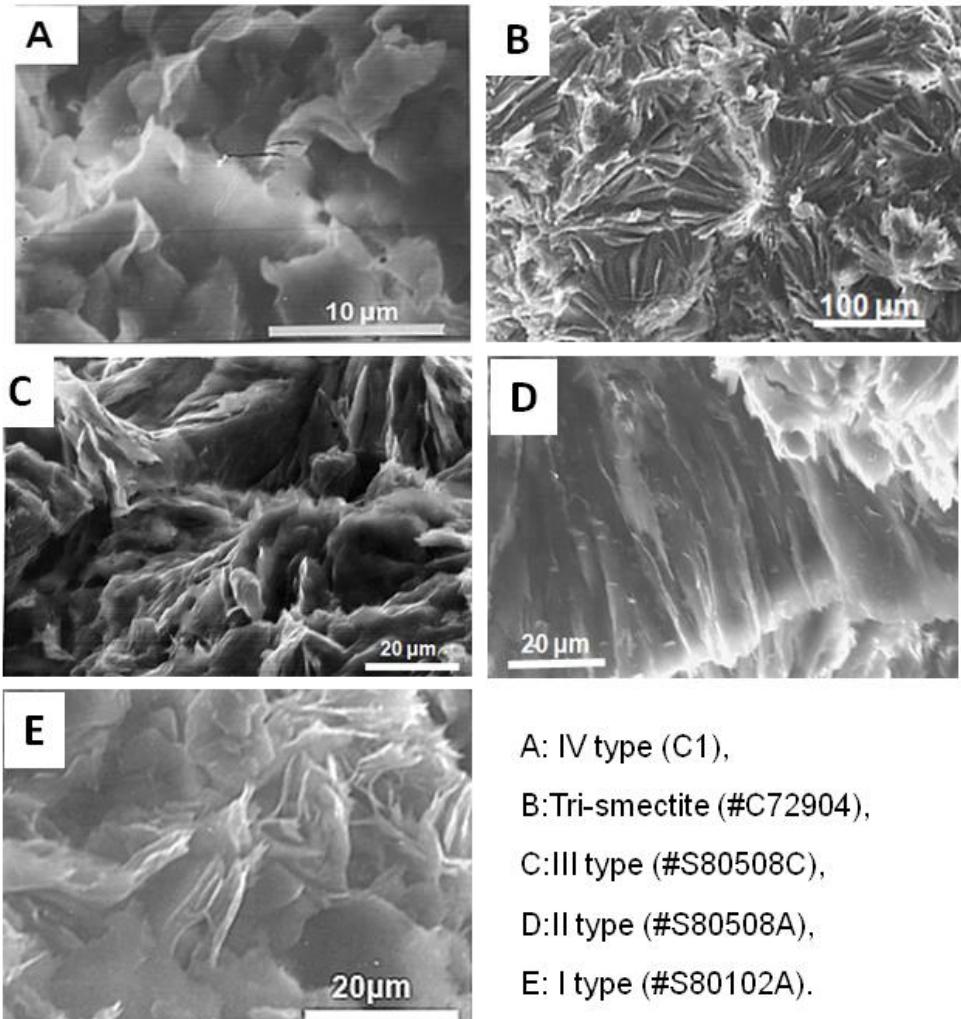


Fig. 6 XRD patterns of chlorite-corrensite-smectite series minerals of the selected ore samples (C1: #C50507, S1: #S80601, S2: #S72912, S3: #S80508B and C10: #C80304).

The d-spacings (Å) and indexes in parentheses are given near the XRD peaks (the same in the following illustrations). A: patterns (thick line: UT, thin line: EG) of chlorite-corrensite series minerals can be divided into four types (I-IV). Vertical lines are positions of basal reflections (14.2 Å and its higher order reflections) corresponding to normal chlorite. B: Randomly oriented and oriented patterns of tri-octahedral smectite.

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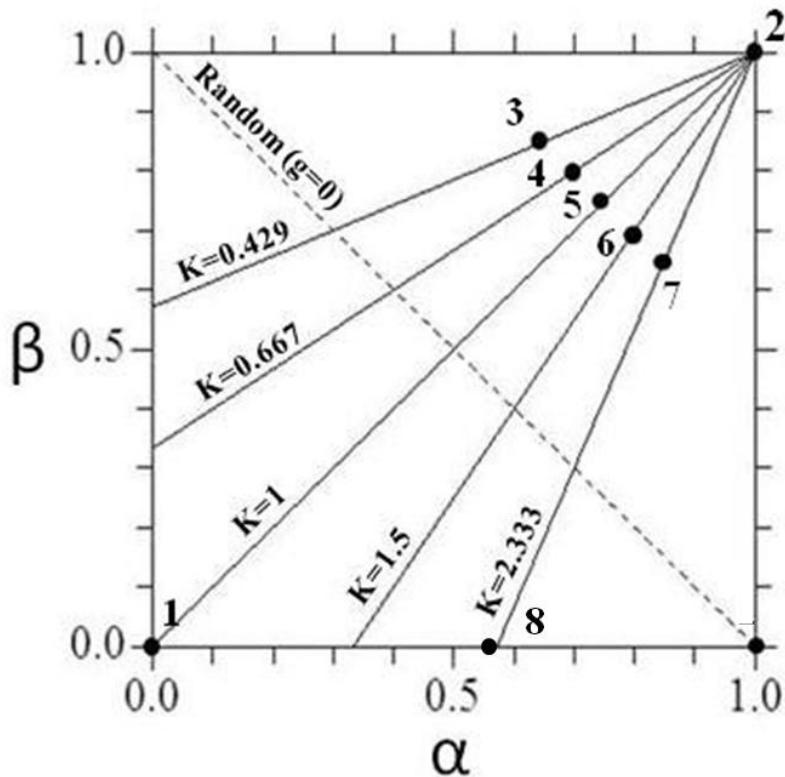
A: IV type (C1),
B:Tri-smectite (#C72904),
C:III type (#S80508C),
D:II type (#S80508A),
E: I type (#S80102A).

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4 Fig. 7 Secondary electron images of chlorite-corrensite-smectite series
5 minerals in selected samples.

6



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2 Fig. 8 Probability parameters used in this study for the calculations of the
 3 XRD patterns for the C/S interstratified structures. The location in the
 4 diagram is defined in terms of its own independent parameters of both
 5 existing layer probabilities (W_A and W_B) and transition probabilities (α and
 6 β). The relationship can be expressed as $\beta = K\alpha + (1-K)$ and $K = W_A/W_B$,
 7 where α is the probability from the layer A to the B and β is the probability
 8 from the layer B to the A. The points shown in numerals are used in this
 9 study. Points 1 and 8 are interstratifications (Reichweite $g=1$) respectively
 10 of regular and irregular type, points on the diagonal line (broken line) are
 11 random structure (Reichweite $g=0$), points from 3 to 7 are in the area of the
 12 segregation structure (the right above area to the diagonal dotted line), and
 13 point 2 is a completely segregated structure (Sato, 1965 & 1987).

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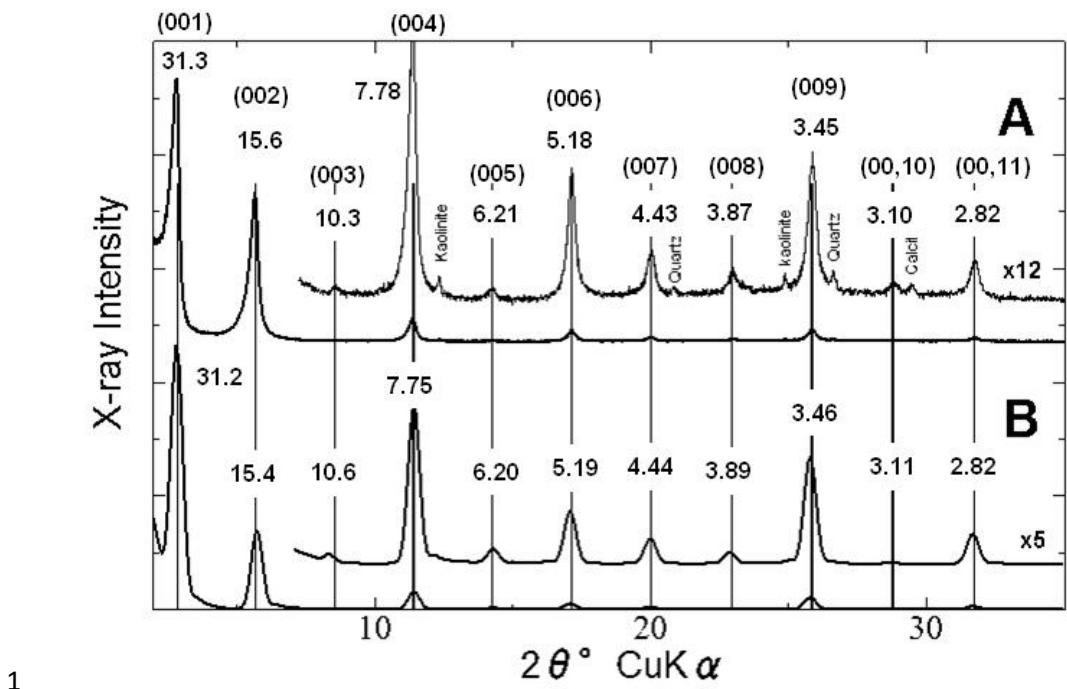


Fig. 9 (A) Observed XRD patterns of the EG-specimen (C1) of IV type, and (B) calculated XRD pattern of EG-corrensite, with probability parameters shown as point 1 (Reichweite $g=1$, regular interstratification) in Fig. 8. Vertical lines are corresponding to the basal reflections calculated for corrensite.

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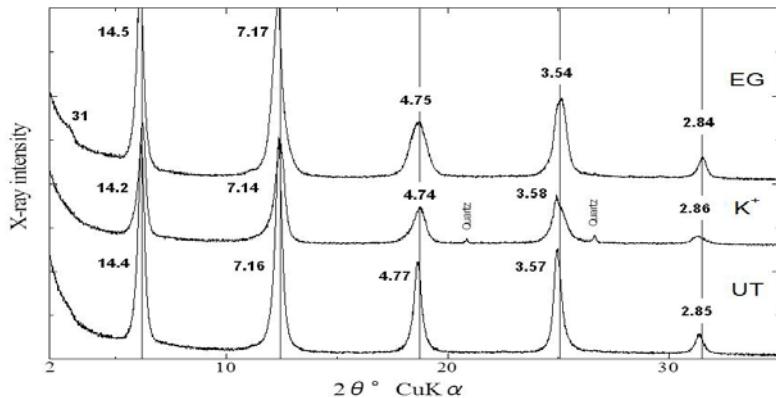
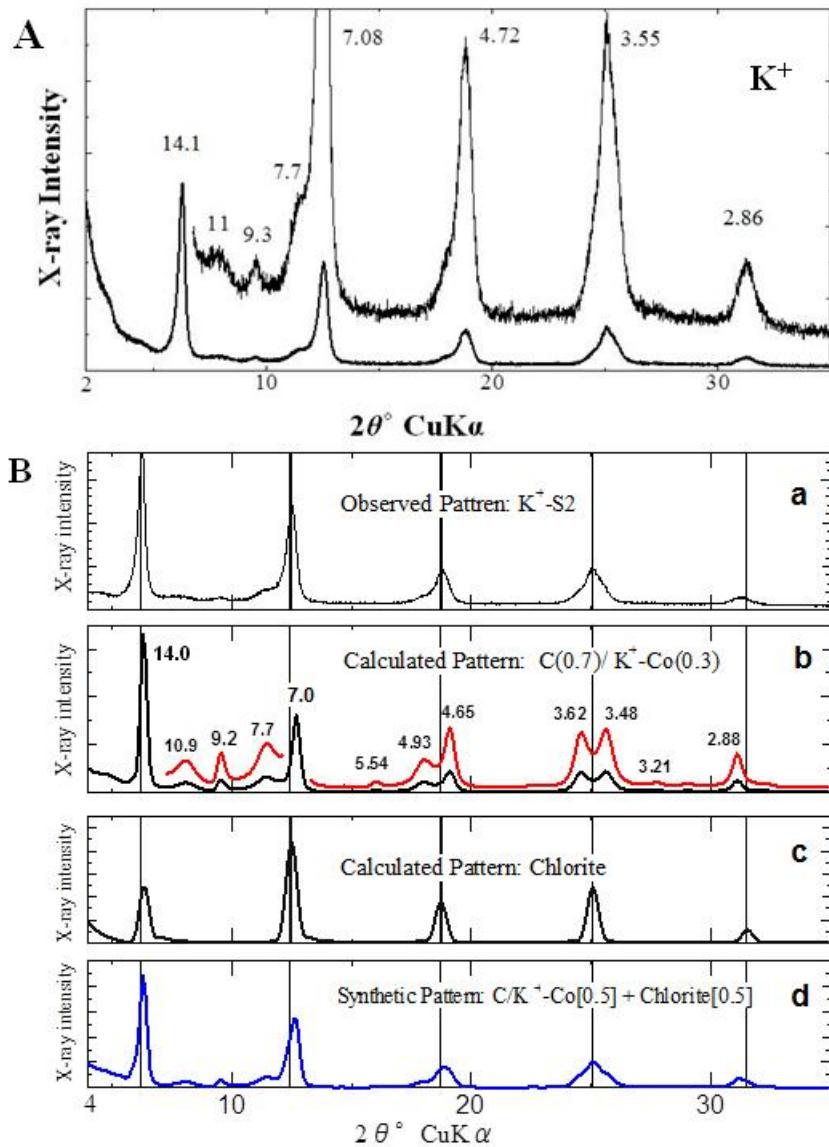
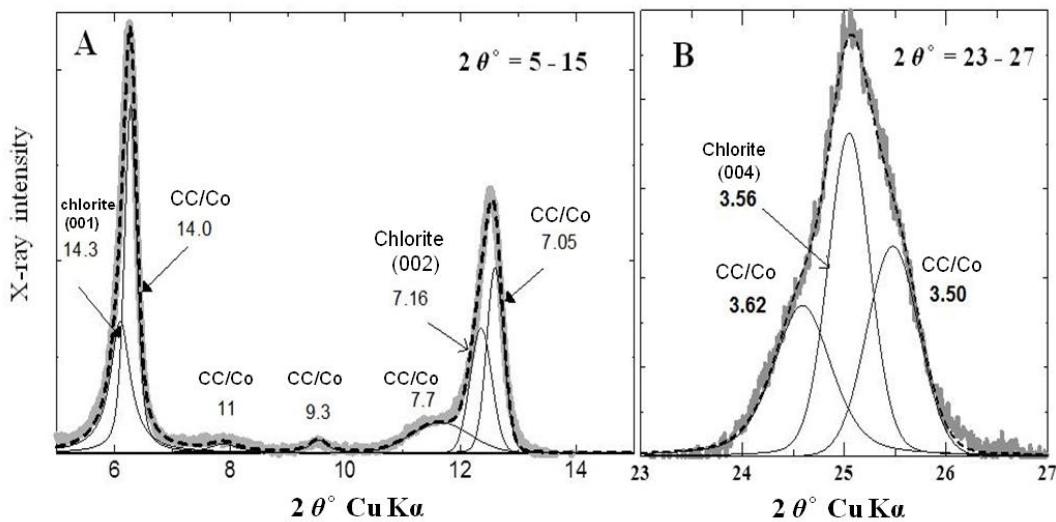


Fig. 10 Observed XRD patterns of EG-, K^+ - and UT-specimens (S1: #S80601) of I type. Vertical lines are the positions of the basal reflections of chlorite.

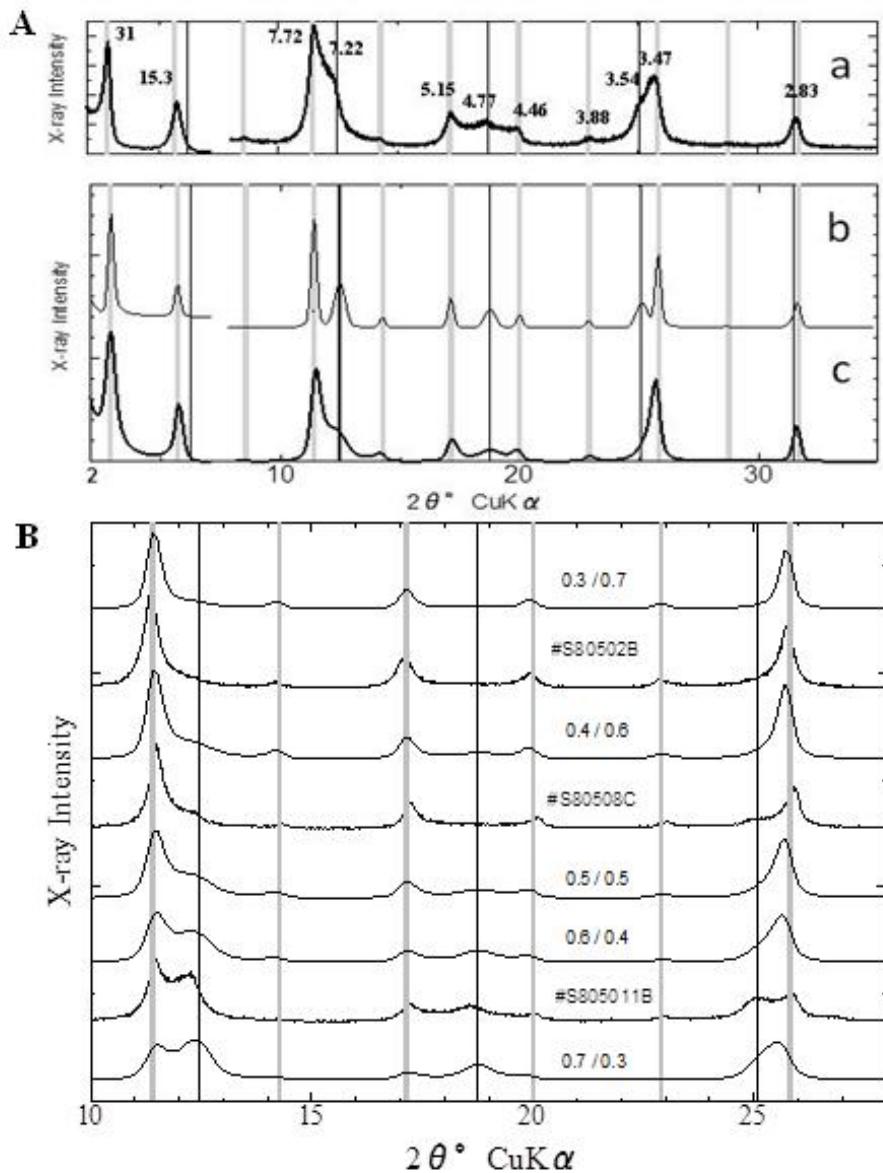


1
 2 Fig. 11 (A) Observed XRD pattern of the K^+ -specimens (S2) of the II type,
 3 and (B) a comparison between the observed pattern and the calculated
 4 patterns; a: observed pattern of the II type, b: calculated pattern of C/Co, c:
 5 calculated pattern of chlorite, d: synthetic pattern of C/Co and chlorite
 6 where the ratio can be estimated to be 0.5:0.5. Vertical lines are the
 7 positions of the basal reflections of chlorite.
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1
2 Fig. 12 XRD peak deconvolution for the observed pattern (K^+ -specimen of
3 sample S2) of II type. Thick gray curves are observed XRD patterns, and
4 fine curves are decomposed peaks and broken curves are composed ones.
5 Seven elementary peaks in (A) and three elementary peaks in (B) can be
6 attributed to interstratified chlorite (0.7)/corrensite (0.3) mineral (14.0 Å, 11
7 Å, 9.3 Å, 7.7 Å, 7.05 Å, 3.62 Å, and 3.50 Å), and to chlorite (14.3 Å, 7.16 Å,
8 and 3.56 Å).

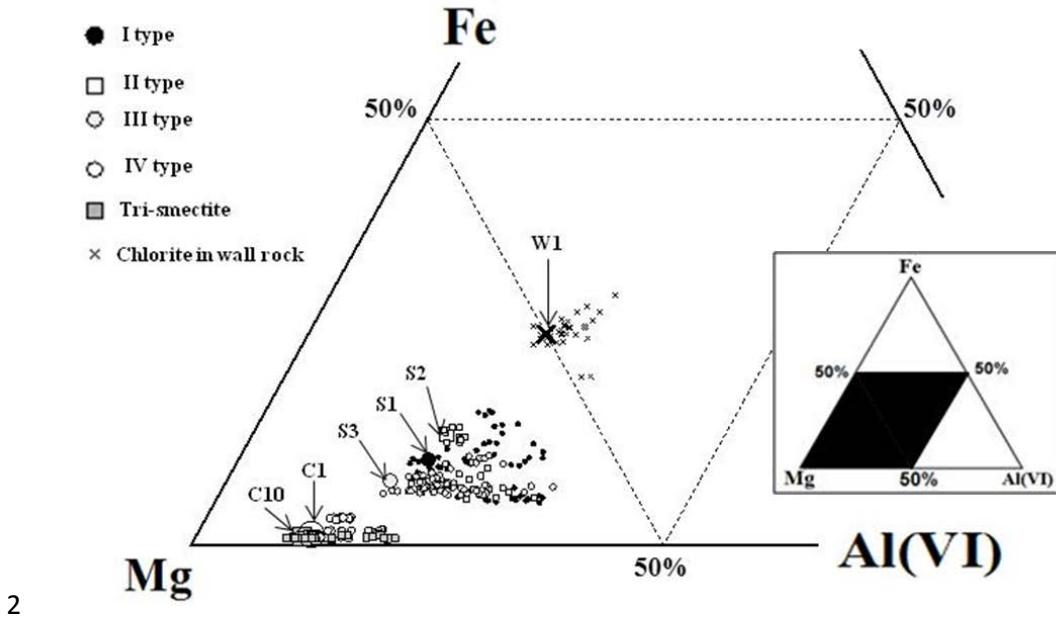
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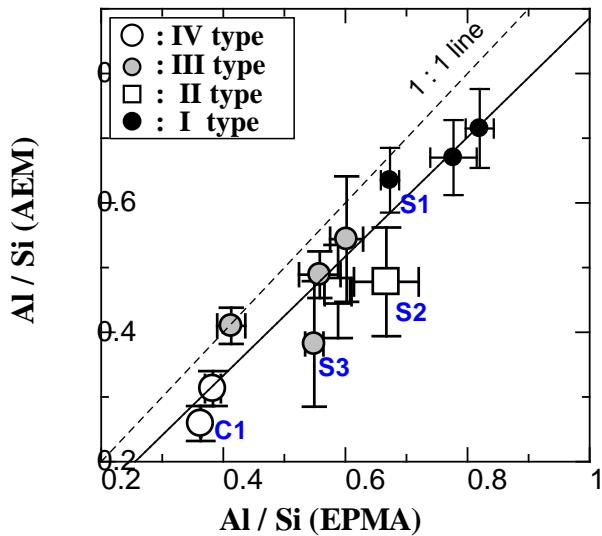
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 3 calculated patterns of the discrete mixture and the segregation of chlorite
 4 and corrensite. Vertical fine and thick lines are the positions of the basal
 5 reflections of chlorite and calculated EG-corrensite, respectively. (B) Other
 6 EG-samples of the III type can be interpreted to be due to the C/S
 7 segregation structures with the ratios of the two layers between
 8 approximately 0.3(C)/0.7(Co) and 0.7(C)/0.3(Co).

10

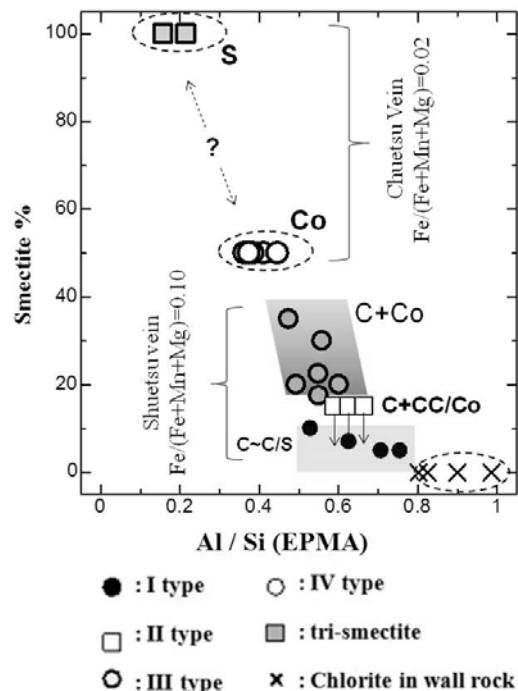
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4 Fig. 14 Plot of Mg-Fe-Al^{VI} ratios of chlorite-corrensite-smectite series
 5 minerals from ore samples and chlorite from the wall rocks. 321 analyses
 6 (EPMA) are plotted. The Fe ratios increase in order from tri-smectite (0.1%
 7 ≥) and IV type (0.2% ≥) to III type (5–8%), II type (5–13%) and I type
 8 (4–15%) and to wall-rock chlorite (19–29%), and the Al (VI) ratios of the
 9 tri-smectite (9–20%) and IV type (9–18%) are plotted in a lower area on the
 10 diagram as compared with those of I, II and III types (16–31%, 17–31%
 11 and 15–33%, respectively) and wall-rock chlorite (23–31%).



1
2 Fig. 15 Plot of analytical values of EPMA vs. AEM analyses for I-IV type
3 minerals of selected ore samples.



4
5 Fig. 16 Two mineralogical conversion series of chlorite-corrensite-smectite
6 in the Todoroki epithermal ore veins: a corrensite-smectite series at the
7 Chuetsu vein and a chlorite-corrensite series at the Shuetsu vein. Smectite %
8 was estimated by the XRD modeling of C/S interstratification (see text).

1 **TABLES**

2
3 Table 1 Atomic parameters of the fundamental layers by reference to
4 Reynolds (1980). Identical ratios of tetrahedral and octahedral
5 compositions are used in all fundamental layers.

Chlorite (14.2 Å)		Double layer chlorite (28.4 Å)		K⁺-corrensite (26.6 Å)		EG-corrensite (31.1 Å)	
Atom	Z	Atom	Z	Atom	Z	Atom	Z
1.75 Mg, 0.65 Fe, 0.6 Al	1.000	1.75 Mg, 0.65 Fe, 0.6 Al	1.000	1.75 Mg, 0.65 Fe, 0.6 Al	1.000	1.75 Mg, 0.65 Fe, 0.6 Al	1.000
4 O, 2 OH	0.925	6 OH	0.964	6 OH	0.962	6 OH	0.967
3.2 Si, 0.8 Al	0.806	6 O	0.865	6 O	0.856	6 O	0.877
6 O	0.770	3.2 Si, 0.8 Al	0.847	3.2 Si, 0.8 Al	0.837	3.2 Si, 0.8 Al	0.860
6 OH	0.572	4 O, 2 OH	0.787	4 O, 2 OH	0.773	4 O, 2 OH	0.806
3.5 Mg, 1.3 Fe, 1.2 Al	0.500	3.5 Mg, 1.3 Fe, 1.2 Al	0.750	3.5 Mg, 1.3 Fe, 1.2 Al	0.733	3.5 Mg, 1.3 Fe, 1.2 Al	0.772
6 OH	0.428	4 O, 2 OH	0.713	4 O, 2 OH	0.693	4 O, 2 OH	0.738
6 O	0.230	3.2 Si, 0.8 Al	0.653	3.2 Si, 0.8 Al	0.630	3.2 Si, 0.8 Al	0.683
3.2 Si, 0.8 Al	0.194	6 O	0.635	6 O	0.610	6 O	0.667
4 O, 2 OH	0.075	6 OH	0.536	0.33 K, 2 H ₂ O	0.500	1.7 CH ₂ O	0.575
1.75 Mg, 0.65 Fe, 0.6 Al	0.000	3.5 Mg, 1.3 Fe, 1.2 Al	0.500	6 O	0.390	1.7 CH ₂ O	0.544
			0.464	3.2 Si, 0.8 Al	0.370	1.2 H ₂ O	0.516
EG-Smectite (16.9 Å)		6 O	0.365	4 O, 2 OH	0.307	1.2 H ₂ O	0.484
Atom	Z	3.2 Si, 0.8 Al	0.347	3.5 Mg, 1.3 Fe, 1.2 Al	0.267	1.7 CH ₂ O	0.456
1.75 Mg, 0.65 Fe, 0.6 Al	1.000	4 O, 2 OH	0.287	4 O, 2 OH	0.227	1.7 CH ₂ O	0.425
4 O, 2 OH	0.937	3.5 Mg, 1.3 Fe, 1.2 Al	0.250	3.2 Si, 0.8 Al	0.164	6 O	0.333
3.2 Si, 0.8 Al	0.837	4 O, 2 OH	0.213	6 O	0.144	3.2 Si, 0.8 Al	0.317
6 O	0.807	3.2 Si, 0.8 Al	0.153	6 OH	0.038	4 O, 2 OH	0.262
1.7 CH ₂ O	0.638	6 O,	0.135	1.75 Mg, 0.65 Fe, 0.6 Al	0.000	3.5 Mg, 1.3 Fe, 1.2 Al	0.228
1.7 CH ₂ O	0.582	6 OH	0.036			4 O, 2 OH	0.194
1.2 H ₂ O	0.530	1.75 Mg, 0.65 Fe, 0.6 Al	0.000			3.2 Si, 0.8 Al	0.14
1.2 H ₂ O	0.470					6 O	0.123
1.7 CH ₂ O	0.418					6 OH	0.033
1.7 CH ₂ O	0.362					1.75 Mg, 0.65 Fe, 0.6 Al	0.000
6 O	0.194						
3.2 Si, 0.8 Al	0.163						
4 O, 2 OH	0.063						
1.75 Mg, 0.65 Fe, 0.6 Al	0.000						

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1 Table 2 Results of the EPMA analysis for the selected samples. Averaged
 2 oxide wt% (upper) and the structural formulae (lower) with standard
 3 deviations in parentheses are shown. N: the number of analyses.

Sample No.	S1	S2	S3	C1	C10	W1
	C-S minerals in ore samples					Chlorite
N	I	II	III	IV	Smectite	
SiO ₂	29.4	30.2(1.70)	34.8(0.73)	40.1(0.96)	48.1(0.78)	25.0(2.11)
TiO ₂	0.0	0.0(0.01)	0.0(0.01)	0.0(0.01)	0.0(0.01)	0.0(0.01)
Al ₂ O ₃	16.8	17.0(0.40)	16.2(0.31)	12.3(0.26)	6.5(0.31)	16.9(1.17)
FeO*	6.0	8.2(0.39)	4.5(0.28)	0.7(0.06)	0.3(0.02)	13.6(1.38)
MnO	6.3	3.6(0.62)	7.0(0.37)	4.2(0.50)	2.9(0.20)	2.3(0.20)
MgO	24.7	23.4(0.48)	25.5(0.69)	29.4(0.52)	20.4(0.57)	15.3(1.25)
CaO	0.2	0.3(0.06)	0.7(0.11)	1.3(0.20)	1.0(0.05)	0.2(0.05)
Na ₂ O	0.0	0.0(0.03)	0.0(0.02)	0.0(0.02)	0.1(0.06)	0.0(0.02)
K ₂ O	0.2	0.0(0.01)	0.0(0.01)	0.0(0.03)	0.1(0.03)	0.0(0.07)
Total	83.6	82.7	88.7	88.0	79.4	73.3
Si	6.05	6.23(0.22)	6.64(0.09)	6.63(0.08)	7.45(0.10)	6.01(0.13)
Al(IV)	1.95	1.77(0.22)	1.36(0.09)	1.37(0.08)	0.55(0.10)	1.99(0.13)
Al(VI)	2.12	2.38(0.07)	2.29(0.08)	1.03(0.07)	0.64(0.08)	2.83(0.10)
Fe	1.03	1.41(0.10)	0.72(0.05)	0.10(0.01)	0.04(0.00)	2.74(0.10)
Mn	1.10	0.62(0.10)	1.13(0.06)	0.57(0.09)	0.38(0.03)	0.46(0.05)
Mg	7.57	7.21(0.19)	7.24(0.13)	7.21(0.12)	4.71(0.14)	5.49(0.19)
Σ	11.82	11.62(0.12)	11.38(0.08)	8.93(0.08)	5.77(0.09)	11.53(0.09)
Ca	0.04	0.06(0.01)	0.15(0.02)	0.23(0.04)	0.16(0.01)	0.04(0.01)
Na	0.04	0.01(0.01)	0.01(0.01)	0.01(0.01)	0.03(0.02)	0.01(0.01)
K	0.06	0.00(0.00)	0.00(0.00)	0.01(0.01)	0.01(0.01)	0.01(0.02)
Base	O ₂₀ (OH) ₁₆	O ₂₀ (OH) ₁₆	O ₂₀ (OH) ₁₆	O ₂₀ (OH) ₁₀	O ₂₀ (OH) ₄	O ₂₀ (OH) ₁₆
Layer charge						
tetrahedral	-1.95	-1.77(0.22)	-1.36(0.09)	-1.37(0.08)	-0.55(0.10)	-1.99(0.13)
octahedral	1.79	1.63(0.20)	1.05(0.10)	0.90(0.11)	0.18(0.11)	1.89(0.15)
interlayer	0.18	0.14(0.03)	0.30(0.05)	0.47(0.07)	0.37(0.02)	0.09(0.03)
Al/Si	0.67	0.67(0.05)	0.55(0.02)	0.36(0.01)	0.16(0.01)	0.80(0.04)
Fe/(Fe+Mn+Mg)	0.11	0.15(0.01)	0.08(0.01)	0.01(0.00)	0.01(0.00)	0.32(0.01)

4 *FeO is expressed as total Fe.

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1 Table 3 Results of the AEM analysis for the selected samples. Structural
2 formulae based on averaged values with standard deviations in parentheses
3 are shown. N: the number of analyzed particles.

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Sample Name	S1	S2	S3	C1
Type	I	II	III	IV
N	7	15	19	8
Si	6.66(0.31)	7.00(0.53)	7.32(0.34)	7.88(0.23)
Al(IV)	1.34(0.31)	1.00(0.53)	0.68(0.34)	0.12(0.23)
Al(VI)	2.88(0.54)	2.30(0.33)	2.09(0.52)	1.92(0.17)
Fe	1.02(0.18)	1.83(0.24)	1.10(0.16)	0.15(0.04)
Mn	1.11(0.28)	0.51(0.08)	0.85(0.14)	0.36(0.08)
Mg	5.41(0.66)	6.15(0.81)	6.60(0.49)	5.47(0.28)
Ca	0.21(0.12)	0.06(0.08)	0.16(0.12)	0.11(0.09)
Na	1.06(0.69)	0.92(0.70)	0.89(0.78)	0.11(0.20)
K	0.13(0.12)	0.08(0.06)	0.11(0.11)	0.04(0.05)
Base	O ₂₀ (OH) ₁₆	O ₂₀ (OH) ₁₆	O ₂₀ (OH) ₁₆	O ₂₀ (OH) ₁₀
Al/Si	0.64(0.05)	0.48(0.08)	0.38(0.10)	0.26(0.03)
Fe/(Fe+Mn+Mg)	0.14(0.02)	0.22(0.03)	0.13(0.01)	0.04(0.02)

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2 **CAPTIONS**

3

4 Fig. 1 Epithermal Au-Ag vein-type ore deposits where productions of
5 interstratified C/S minerals have been described as vein minerals (Taguchi
6 & Watanabe, 1973; Yoneda & Watanabe, 1981; Takeuchi, 1984; Yoneda &
7 Watanabe, 1989).

8

9 Fig. 2 Geological map of the Todoroki Au-Ag ore deposits (Yoneda, 1994).

10 1: Talus deposit, 2: Tuff/sandstone with coal seam, 3: Andesitic tuff, 4:
11 Sandstone/mudstone, 5: Rhyolitic tuff and tuff breccia, 6: Conglomerate/
12 mudstone/tuff, 7: Andesite lava, 8: Rhyolite, 9: Propylite, 10: Dolerite, 11:
13 Fault, 12: Ore veins (C: Chuetsu vein, S: Shuetsu vein)

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15 Fig. 3 Vein sketches showing the constituents and structures of the Chuetsu
16 and Shuetsu veins. See in the text for details.

17 1: dark gray massive quartz (the I stage), 2: white/gray banded quartz with
18 Au-Ag minerals/Cu-Pb-Zn-Fe-S sulfides (the II stage), 3: white/gray banded
19 quartz with rhodochrosite and Au-Ag minerals/Cu-Pb-Zn-Fe sulfide
20 minerals (the II stage), 4: gray quartz (partly banded) (the II stage), 5: white
21 massive quartz (the II stage), 6: calcite (the III stage), 7: wall rock, 8: black
22 streak rich in Au-Ag minerals/Cu-Pb-Zn-Fe sulfide minerals (AgB).

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24 Fig. 4 Ore samples with ore minerals and clays from the middle stage quartz
25 veins.

26 A: Banded quartz with Au-Ag minerals/Cu-Pb-Zn-Fe sulfide minerals
27 (AgB) and clays (Chuetsau 130ml, #C80304), B: Banded quartz with
28 rhodochrosite and clays (Chuetsau 50ml, #C71408), C: Banded quartz with
29 AgB rich in Cu-Pb-Zn sulfides and clays crusting a rock fragment (Shuetsu
30 central lower part, #S80509), D: quartz with patchy AgB and patchy ~
31 banded clays (Shuetsu eastern part, #S80601).

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1 Fig. 5 Microphotographs of the clay minerals observed in the ore samples.
2 A-C & E: transmitted light (cross polar), D: transmitted light (left half-
3 parallel, right half-cross), F: reflected light (parallel polar). Bar scale:
4 100µm, Qz: quartz, CS: chlorite-smectite series mineral, Sm: smectite, Op:
5 opaque ore mineral, Sp: sphalerite, El: electrum, Arg: argentite.

6 A: C1 (#C50507) – IV type, B: C10 (#C80304) – tri-smectite, C: #S80508C
7 – III type, D: #S80508A – II type, E: #S80607 – I type, F: #C11204 – IV
8 type. See in the text for details.

9

10 Fig. 6 XRD patterns of chlorite-corrensite-smectite series minerals of the
11 selected ore samples (C1: #C50507, S1: #S80601, S2: #S72912, S3:
12 #S80508B and C10: #C80304). The d-spacings (Å) and indexes in
13 parentheses are given near the XRD peaks (the same in the following
14 illustrations). A: patterns (thick line: UT, thin line: EG) of chlorite-
15 corrensite series minerals can be divided into four types (I–IV). Vertical
16 lines are positions of basal reflections (14.2Å and its higher order
17 reflections) corresponding to normal chlorite. B: Randomly oriented and
18 oriented patterns of tri-octahedral smectite.

19

20 Fig. 7 Secondary electron images of chlorite-corrensite-smectite series
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23 Fig. 8 Probability parameters used in this study for the calculations of the
24 XRD patterns for the C/S interstratified structures. The location in the
25 diagram is defined in terms of its own independent parameters of both
26 existing layer probabilities (W_A and W_B) and transition probabilities (α and
27 β). The relationship can be expressed as $\beta = K\alpha + (1 - K)$ and $K = W_A/W_B$,
28 where α is the probability from the layer A to the A and β is the probability
29 from the layer B to the B. The points shown in numerals are used in this
30 study. Points 1 and 8 are interstratifications (Reichweite $g=1$) respectively
31 of regular and irregular type, points on the diagonal line (broken line) are
32 random structure (Reichweite $g=0$), points from 3 to 7 are in the area of the
33 segregation structure (the right above area to the diagonal dotted line), and
34 point 2 is a completely segregated structure (Sato, 1965 & 1987).

1

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3 and (B) calculated XRD pattern of EG-corrensite, with probability
4 parameters shown as point 1 (Reichweite g=1, regular interstratification) in
5 Fig. 8. Vertical lines are corresponding to the basal reflections calculated for
6 corrensite.

7

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9 #S80601) of I type. Vertical lines are the positions of the basal reflections of
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11

12 Fig. 11 (A) Observed XRD pattern of the K⁺-specimens (S2) of the II type,
13 and (B) a comparison between the observed pattern and the calculated
14 patterns; a: observed pattern of the II type, b: calculated pattern of C/Co, c:
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17 positions of the basal reflections of chlorite.

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20 sample S2) of II type. Thick gray curves are observed XRD patterns, and
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23 attributed to interstratified chlorite (0.7)/corrensite (0.3) mineral (14.0 Å, 11
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28 calculated patterns of the discrete mixture and the segregation of chlorite
29 and corrensite. Vertical fine and thick lines are the positions of the basal
30 reflections of chlorite and calculated EG-corrensite, respectively. (B) Other
31 EG-samples of the III type can be interpreted to be due to the C/S
32 segregation structures with the ratios of the two layers between
33 approximately 0.3(C)/0.7(Co) and 0.7(C)/0.3(Co).

34

1 Fig. 14 Plot of Mg-Fe-Al^{VI} ratios of chlorite-corrensite-smectite series
2 minerals from ore samples and chlorite from the wall rocks. 321 analyses
3 (EPMA) are plotted. The Fe ratios increase in order from tri-smectite (0.1%
4 ≥) and IV type (0.2% ≥) to III type (5–8%), II type (5–13%) and I type
5 (4–15%) and to wall-rock chlorite (19–29%), and the Al (VI) ratios of the
6 tri-smectite (9–20%) and IV type (9–18%) are plotted in a lower area on the
7 diagram as compared with those of I, II and III types (16–31%, 17–31%
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9

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12

13 Fig. 16 Two mineralogical conversion series of chlorite-corrensite-smectite
14 in the Todoroki epithermal ore veins: a corrensite-smectite series at the
15 Chuetsu vein and a chlorite-corrensite series at the Shuetsu vein. Smectite %
16 was estimated by the XRD modeling of C/S interstratification (see text).

17

18 Table 1 Atomic parameters of the fundamental layers by reference to
19 Reynolds (1980). Identical ratios of tetrahedral and octahedral
20 compositions are used in all fundamental layers.

21

22 Table 2 Result of the EPMA analysis for selected samples. Averaged oxide
23 wt% (upper) and the structural formulae (lower) with standard deviations in
24 parentheses are shown. N: the number of analyses.

25

26 Table 3 Result of the AEM analysis for selected samples. Structural
27 formulae based on averaged values with standard deviations in parentheses
28 are shown. N: the number of analyzed particles.

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