Significance of the mineralogical properties of phyllosilicate as an indicator in the exploration of ore deposits

T. Yoneda1 and H. Mokko1

1Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Japan

e-mail: yonet@eng.hokudai.ac.jp

ABSTRACT:
The mineralogical properties of phyllosilicate, such as mineral association, particle size, mineral chemistry, etc. show highly diverse and systematic variations closely related to their occurrences in hydrothermal systems. The mineral chemistry and particle size of hydrothermal chlorites were examined to explore their applicability as indicators during ore prospecting. A comparison of fluid inclusion thermometry indicates that the two thermodynamic chlorite geothermometers are usable for a wide compositional range of trioctahedral chlorites from hydrothermal systems, and that the chlorite solid solution model including thermodynamic properties employed in the two thermometers may only have small differences in the temperature estimation. The particle size properties of hydrothermal chlorites can be related to their crystal-growth mechanisms and to the environmental conditions of mineral formations in the hydrothermal systems as well as those of the alteration. Further detailed and integrative studies on the mineral properties of phyllosilicate in hydrothermal systems are expected to develop useful indicators for exploration of ore deposits.

KEY WORDS: Phyllosilicate / Mineralogical properties / Hydrothermal systems / Chlorite compositions / Particle size / Ore prospecting

1. INTRODUCTION
It is well known that phyllosilicate occur extensively as a product of water-rock interaction in hydrothermal ore deposits and geothermal areas, and shows highly diverse and systematic variations in mineralogical properties, such as mineral species and assemblage, mineral chemistry, crystal structure, and morphology, depending on the localities and the modes of occurrence [1, 2, 3, 4]. The mineral properties of phyllosilicates reflect geological and physicochemical conditions by which minerals form in hydrothermal systems as shown by a number of published works. Therefore, their mineral properties have been investigated to develop indicators/susceptible in ore prospecting. For example, mineral species and assemblage of the phyllosilicate, which characterize the alteration zones surrounding ore bodies, have been used for an effective index in different stages of the practical ore prospecting as reconnaissance survey (e.g., remote sensing) and detailed investigation (e.g., drilling core analysis). In addition, the mineral properties of phyllosilicates such as chemical composition, particle size and size distribution, and mixed-layer structure are being studied in recent years, with the aim of using them as indicators of the formation conditions of phyllosilicate and then to ore formation in hydrothermal systems [5, 6, 7, 8].

In this study the chemical composition, the particle size, and particle size distribution of chlorite, which is one of the phyllosilicate closely associated with hydrothermal ore deposits, are described and discussed to explore their applicability as indicators of the physicochemical conditions during its formation in hydrothermal systems.

2. CHEMICAL COMPOSITION OF CHLORITE
Chlorite is an ubiquitous alteration or gangue mineral in hydrothermal ore deposits, as well as secondary mineral in diagenetic and metamorphic rocks. The general composition formula of chlorite can be written as

\[(\text{R}^{2+}^{2.5}, \text{R}^{3+}^{3}, \square)^{\text{oct}}\text{Si}_{4+x}^{\text{tet}(x-1)}\text{O}_{10}^{\text{oct}}(\text{OH})_{8}\]

where, \(\text{R}^{2+}\) is a divalent cation (e.g., Mg, Fe\(^{2+}\), Mn, etc.), \(\text{R}^{3+}\) is a trivalent cation (mainly Al, occasionally Fe\(^{3+}\), etc.), \(\square\) represents a vacancy, \(\text{tet}\) represents tetrahedral site, and \(\text{oct}\) represents octahedral site. Chlorite shows a wide range of compositional variations due to substitutions like Fe\(^{3+}\)$→$Mg exchange, Tschermak substitution Al$^{3+}\text{Mg}^{2+}\leftrightarrow\text{Si}^{4+}\text{Al}^{3+}$, and di-/tri-octahedral substitution $3($Fe\(^{3+}\)Fe$^{2+}$)\text{Mg}^{2+}\leftrightarrow\square^{10}\text{2Mg}^{2+}$. The compositional variations of hydrothermal chlorite are known to be sensitive to physicochemical features of the fluids (temperature, pH, activities of dissolved species, etc.), and chemical and physical properties of the original rocks (e.g., bulk composition, permeability) in the hydrothermal systems [10, 11, 12, 13, 14, 15, 16, 17, 18]. In this section the chemical geothermometers that link chlorite compositions to the temperatures of chlorite formation in hydrothermal systems are reviewed. Moreover, temperature values from some chlorite geothermometers are compared with those from fluid inclusion thermometers using data from some hydrothermal vein-type deposits in Japan [19].

2.1 Chlorite geothermometers
The chemical thermometer of chlorite can be classified into two different approaches: empirical and thermodynamic. An empirical thermometer and two thermodynamic thermometers using different solid solution models with multiple chlorite components are compared in this study.
The Cathelineau’s geothermometer [10] is well known as an empirical chlorite geothermometer, which was formulated using Fe-Mg & Mg-chlorites from active geothermal fields, Los Azufres and Salton Sea. This thermometer is based on correlation of the number of tetrahedral Al or octahedral vacancy in chlorites with the temperature values obtained from direct measurement of wall rocks, geochemical thermometer for geothermal water, and fluid inclusion thermometer for minerals from the geothermal wells. The Cathelineau’s thermometer based on the correlation of the temperatures and the number of tetrahedral Al (Al IV) of the chlorites is given as

$$T(℃) = -61.92 + 321.98 \text{ (Al IV)}.$$  

The Walshe’s thermometer [11] represents the chlorite compositions using six chlorite components listed as follows:

$$C1: [Mg_{6}][Si_{4}]O_{10}(OH)_{8} \quad C2: [Mg_{4}Al][Si_{2}Al]O_{10}(OH)_{6} \quad \text{ (clinochlore)}$$
$$C3: [Fe^{2+3}_{4}Al]^{2+}[Si_{2}Al]O_{10}(OH)_{8} \quad C4: [Fe^{2+3}_{2}Fe^{2+3}_{6}]^{2+}[Si_{4}]O_{10}(OH)_{8}$$
$$C5: [2Al]^{2+}[Si_{2}O_{10}(OH)_{8}] \quad C6: [Fe^{2+3}_{4}Fe^{2+3}_{6}]^{2+}[Si_{2}Fe^{2+3}]O_{10}(OH)_{2}$$

where, C1, C4, C5 and C6 are presumed thermodynamic components. This thermometer uses two intra-crystalline exchange reactions as shown eqs (1) and (2) for a set of chlorite compositions, which could obtain an equilibrium temperature after simultaneously satisfying both equations at a given pressure (e.g., equilibrium vapor pressure).

$$2[C2]+14/3SiO_{2}+8/3H_{2}O = 10/[C1]+[C5] \quad (1)$$
$$[C2]+3/[C3]+5/[C4]+25/2SiO_{2} = 5/[C1]+10/[C6]+5/2H_{2}O \quad (2).$$

In addition to the equilibrium components, the derived by doing convergence calculation from the initial chlorite compositions in which total iron is assumed to be ferrous. In this Walshe’s thermometer, the ferric iron contents derived are distributed to tetrahedral and octahedral sites corresponding to the equilibrium activities of chlorite components C4 and C6.

The thermodynamic thermometers with four chlorite end-components were developed by Vidal et al. (2001)[15] and Inoue et al. (2009)[16] for chlorites in diagenetic and low-grade metamorphic rocks. The latter authors have applied their thermometer to low-temperature chlorites from hydrothermal systems [16,17]. Inoue’s chlorite thermometer employs the following components:

$$C1: [Mg_{6}][Si_{4}]O_{10}(OH)_{8} \quad \text{(Al-free chlorite)}$$
$$C2: [Mg_{4}Al][Si_{2}Al]O_{10}(OH)_{6} \quad \text{(corundophilitic)}$$
$$C3: [Fe^{2+3}_{4}Al][Si_{2}Al]O_{10}(OH)_{8} \quad \text{(chamosite)}$$
$$C4: [Mg_{2}Al][Si_{2}Al]O_{10}(OH)_{8}$$

where, C1 and C3 are the same as those of Walshe[11]. Inoue et al. [16] have shown that the chlorite compositions of low temperature formation can be explained fairly well by the four components model, and proposed the following exchange reaction (3) involving quartz as a chlorite thermometer applicable to hydrothermal chlorite formed at low-temperature.

$$3[C4]+[C1]=3[C2]+7SiO_{2}+4H_{2}O \quad (3),$$

and gave the expressions:

$$x = \log K_{(3)} = 3\log a_{C2} - 3\log a_{C1} - \log a_{C1},$$

$$T(℃) = [1/(0.00293-5.13×10^{-5}x+3.904×10^{-3}x^{2}]-273,\text{ where } a_{ij} \text{ represents the ideal activity of } i-th \text{ chlorite component. Although no chlorite component with ferric iron is contained in this solid solution model, this thermometer, Inoue et al. used the structure formulas of chlorites recalculated on the basis of the Fe^{2+3} contents determined by Mössbauer and X-ray photoelectron spectroscopies [16,17]. They distributed the whole ferric iron into the octahedral sites of chlorite structure, and made a point that the Fe^{2+3} in chlorite should be taken into account when estimating formation temperature, especially for low-T chlorite, because ferric iron contents influence the number of vacancy in the chlorite structure [16].}$$

The activity-composition relations of chlorite solid solution models of the two thermometers mentioned above are shown in Table 1.

| Activity-composition relations of the two chlorite thermometers. | a_i = the activity of i-th component = k_i Π_j x_{j,p,i}^{p_i}, k_i = the normalization constant for i-th component, X_{j,p} = the mole fraction of the j atom on the p site. Random mixing of atoms is assumed in the six octahedral sites and two tetrahedral sites. The ideal activities are used for a_i, a_k. |
|-------------------------------------------------------------|
| **Model of Walshe (1986)** | a_1 = k_1 (X_{A1})^0 (X_{O1})^2 |
| a_2 = k_2 (X_{A1})^0 (X_{A1})^0 X_{A2} X_{ALT} X_{ALT} |
| a_3 = k_3 (X_{A2})^0 (X_{A2})^0 X_{A2} X_{ALT} X_{ALT} |
| a_4 = k_4 (X_{A1})^0 (X_{A2})^0 X_{ALT} X_{ALT} |
| a_5 = k_5 (X_{A2})^0 (X_{A1})^0 X_{ALT} X_{ALT} |
| **Model of Inoue et al. (2009)** | same as a_i of Walshe (1986) |
| a_1 = k_1 (X_{A1})^0 (X_{A1})^0 (X_{O2})^2 |
| same as a_i of Walshe (1986) |
| **Model of Inoue et al. (2009)** | same as a_i of Walshe (1986) |
| a_1 = k_1 (X_{A1})^0 (X_{A1})^0 (X_{O2})^2 X_{ALT} X_{ALT} |
| (k_1 = 45.563; k_2 = 729) |

Table 1 Activity-composition relations of the two chlorite thermometers.

2.3 Chlorite samples and chemical compositions

Chlorite samples used in this study are listed in Table 2, which occur as gangue in the hydrothermal ore veins. These chlorites are associated mostly with quartz, and frequently with iron and base metal sulfides, Au-Ag minerals or illite (Fig. 1).

| Mineral Exploration & Mining Technology 2 |
Chlorite analyses by EPMA show that chlorites from Toyoha, Ohe, Sado and Yatani were rich in iron ([Fe/(Fe+Mn+Mg)]>0.5) and the number of Al$^{IV}$ was larger than 1.0 whereas those from Chitose and Todoroki were rich in Mg ([Fe/(Fe+Mn+Mg)]<0.3) and the number of Al$^{IV}$ was less than 1.0 (Fig. 2). The chlorite analyses also show that all of them have tri-octahedral structures. In general, it is characteristic that the number of tetrahedral Al$^{IV}$ positively correlates with Fe-Mg ratios of chlorites, depending on the ore veins.

### 2.3 Comparison of thermodynamic thermometers with homogenized temperature of fluid inclusions

The homogenization temperature of fluid inclusions in quartz or sphalerite were measured in the same samples in which chlorites were analyzed (Table 2). The temperature ranges of fluid inclusions are 225-235°C (n=3) for TY3, 255-285°C (n=7) for OE1, 205-245°C (n=6) for OE22, 255-295°C (n=8) for OE5, 225-245°C (8) for YT3A, 215-255°C (n=13) for SD1, 205-295°C (n=11) for SD2, 165-205°C (n=8) for TD9, 225-275°C (n=5) for CT6, and 235-275°C (n=10) for CT16. These homogenization temperature ranges were concordant with the ranges of ore formation temperature in each ore veins [19].

![Fig. 1 An occurrence of chlorite as gangue in an ore vein. Left: Chlorite(chl) in galena(gl)-rich ore (TY3), right: radial aggregate of chlorite coexisting with illite(il) (OE22).](image)

Table 2 Chlorite samples used [19].

<table>
<thead>
<tr>
<th>Mine-Vein/Sample</th>
<th>Brief Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOYOHAB-Soye Vein</td>
<td>Pb-Zn polymetallic deposit</td>
</tr>
<tr>
<td>ORE-Senai Vein</td>
<td>Mn-Ca-Pb-zn deposit</td>
</tr>
<tr>
<td>ORE32</td>
<td>Sphalerite-galena-vein</td>
</tr>
<tr>
<td>ORE5</td>
<td>Sphalerite with sphalerite</td>
</tr>
<tr>
<td>SADO-Osite Vein</td>
<td>Au-Ag base metal deposit</td>
</tr>
<tr>
<td>Todoroki-SHATTU</td>
<td>Au-Ag deposit</td>
</tr>
<tr>
<td>CHIT SE Daiisuka</td>
<td>Au-Ag deposit</td>
</tr>
<tr>
<td>CT16</td>
<td>Coarsely banded quartz with spotted and banded sulfides with Au-Ag</td>
</tr>
</tbody>
</table>

![Fig. 2 Tetrahedral Al vs. Fe/(Fe+Mn+Mg) of chlorites.](image)

![Fig. 3 A comparison of chlorite geothermometers with fluid inclusion thermometer. For each sample average temperatures of chlorites are represented by plots while average homogenization temperatures are given as lines. The length of lines corresponds to the superposed temperature range of the four calibrations in each sample.](image)
For Mg-chlorites, Cathelineau's thermometer was nearly equivalent to the homogenization temperatures, but those of Fe- and Fe-Mg-chlorites had much higher temperatures than the homogenization temperatures (Fig. 3). The good fitting of the Mg-chlorites may be due to the similarity of mineral chemistry of the chlorite incorporated in this empirical calibration [19].

Regarding the thermodynamic thermometers for Mg- and Fe- & Fe-Mg-chlorites, Inoue's thermometer assuming that ferric iron is 20% of total Fe gives coincident temperatures with the homogenization temperatures, except sample TD9 (Fig. 3). However, Inoue's thermometer with assumption that the total Fe is ferrous showed extremely higher temperatures over the ore formation temperatures. On the other hand, the Walshe's thermometer, which incorporates the Fe-chlorite components with ferric iron, also showed good agreement with the homogenization temperatures (Fig. 3). These indicate that the amount of ferric iron in the chlorite structure have to be taken into account to estimate realistic temperature values for iron-bearing chlorites from hydrothermal systems.

A comparison of the homogenization temperatures of fluid inclusions in minerals co-existing with analyzed chlorites suggests that the two thermodynamic geothermometers are usable for a wide compositional range of trioctahedral chlorites from geothermal fields and hydrothermal ore deposits. It also shows that including thermodynamic properties of chlorites (chlorite end-components, distribution of ferric iron, etc.) in the solid solution model used in the two thermometers may have significant effects on the temperature estimation.

From a practical point of view, the Walshe's thermometer may be a more costless approach than Inoue's thermometer at present stage. As mentioned before, the former calculated the amount of ferric iron with the chlorite component through the convergent calculation while the latter did not. Incorporating the ferric component in Inoue's thermometer needed additional quantitative analysis of ferric iron by XPS or Mössbauer analysis in addition to WDS or EDS microanalysis for chlorite.

### 3. PARTICLE SIZE DISTRIBUTION

Analyses of particle size distribution for clays in rocks can be related to geological information of ancient environments (sedimentation, diagenesis, metamorphism, weathering, etc.) [20]. XRD analytical technique for the determination of particle size and distribution of clay minerals, BWA (Bertaut-Warren-Averbach) technique, has been developed by Eberl et al. (1996) [21] and Drits et al. (1997) [22]. In this study, a preliminary examination was performed to test the capability and applicability of XRD-BWA analysis to chlorites from hydrothermal systems.

The XRD-BWA analysis allows us to evaluate crystalline thicknesses (X-ray scattering domain sizes) and their distributions in phyllosilicates having periodic layer-stacking of 2 nm to 100 nm in thickness [22]. That is, the particle size (thickness) and particle size distribution of phyllosilicate (clay minerals) can be measured by evaluating XRD peak broadening of 002 reflections. This particle size analysis has been applied to illite, smectite, and kaolinite of diagenetic, weathering or hydrothermal environments [e.g., 7, 23, 24], but its application for chlorite is probably rare.

The calculated XRD patterns of chlorite were analyzed in the first step. Two computer programs, 'Mudmaster' [21] for particle size analysis and 'NEWMOD' for calculation of XRD pattern, were used. As shown in Fig. 4 the thickness distributions of the model used in calculation of XRD pattern and the analytical results for chlorite peaks of the calculated pattern shows a good accordance, indicating that the particle size analysis was valid for the calibrated XRD pattern of chlorite.

![Fig. 4 Particle size analysis for calculated XRD pattern of chlorite](image)

As for its application to natural phyllosilicates, many researchers have expressed some problems in this approach, such as superposition of other mineral peaks especially within low-tails of reflections, variations of crystal chemistry (extensive compositional variation of chlorite as shown in the...
section above), removal of instrumental broadening, sample preparation damage, etc. [25]. These factors were presumed not to have large effects in estimating particle size properties of chlorites in hydrothermal ore deposits used in this study. The XRD-BWA analysis was applied to chlorite and co-existing illite in core samples (Th-6 drilling) of hydrothermal alteration zones around the Toyoha Pb-Zn deposits, Japan.

The negative correlation between mean thickness and FWHM values of the 002 peaks (Fig. 5) may be an evidence showing that the mean thicknesses, which were obtained by the XRD-BWA analysis, were suitably estimated for the natural chlorites in hydrothermally altered rocks.

![Fig. 5 Mean thickness and FWHM of the 002 peaks of chlorite.](image)

The mean thicknesses between chlorites and co-existing illites show a positive correlation (Fig. 6). In addition, as exemplified in Fig. 7, the thickness distributions of the chlorite and illite showed shapes similar to lognormal distribution that is observable in many crystalline substances [20]. These features may suggest that the particle size properties of the hydrothermal chlorites can be related to their crystal-growth mechanisms, as shown for illites and other minerals [26]. In addition the features of the particle size properties of chlorite may be useful as an indicator of environmental condition, as shown for illite of which particle sizes are related with intense wall rock alteration and fracturing in hydrothermal activity [7]. Further detailed studies on the particle size properties of chlorites from hydrothermal environments are necessary to develop a useful indicator in the exploration of ore deposits.

4. CONCLUSIONS

The mineralogical properties of phyllosilicates, such as mineral association, particle size, mineral chemistry, etc. show highly diverse and systematic variations closely related to their occurrences in hydrothermal systems. The mineral chemistry and the particle size of hydrothermal chlorites were examined to explore applicability of those mineral properties as an indicator during ore prospecting. On the basis of a comparison of fluid inclusion thermometry, it is concluded that the two thermodynamic chlorite geothermometers are usable for a wide compositional range of trioctahedral chlorites from geothermal fields and hydrothermal ore deposits, and that the solid solution model including thermodynamic properties of chlorites employed in the two thermometers may only have little difference in the temperature estimation.

The features of the particle size properties of hydrothermal chlorites can be related to their crystal-growth mechanisms and to the environmental conditions of mineral formations in hydrothermal systems.

Further detailed and integrated studies on the mineral properties of phyllosilicate in hydrothermal systems are expected to develop a useful indicator in the exploration of ore deposits.

ACKNOWLEDGEMENTS

This research was financially supported partly by the Hokkaido Development Engineering Center Fund, project no. PK250707.
REFERENCES


