Chemistry of Chlorite and Its Genetic Significance in the Talc Deposits in the Yesan-Gongju-Cheongyang Area, Chungnam, Korea

충남 예산−공주−청양지역의 활석 광산에서 산출되는
녹니석의 화학적 특징과 광상 성인과의 관계

Geon-Young Kim(김건영) · Soo Jin Kim(김수진)

Department of Geological Sciences, Seoul National University, Seoul 151-742, Korea
(서울대학교 지질과학과)

ABSTRACT : Chlorite from the talc deposits of Daeheung, Pyeongan, and Shinyang (Cheongdang) mines in the Yesan-Gongju-Cheongyang area has been studied on the chemical and genetic view points. Talc ores are hydrothermal alteration products of serpentinite which was originated from ultramafic rocks. The major constituent minerals of the talc ores are talc, chlorite, and phlogopite with minor amphibole, antigorite, carbonates, olivine, pyroxene, chromite, smectite, and some other expandable clay minerals such as regularly interstratified chlorite/smectite. Among these minerals, olivine and chromite are indicative of ultramafic origin.

Chlorite is the most abundant impurity mineral of the talc ores. There are two distinct types of chlorites in genesis, that is, the talc-related chlorites and the talc-unrelated chlorites, both having different chemistry. The former has very high $Mg/(Mg+Fe)$ ratio with extremely narrow variation in $Mg/(Mg+Fe)$ (0.784~0.951/14 oxygens), significant octahedral substitution range of 0.892 (−0.200~0.692/14 oxygens, an ideal clinochlore/chamosite composition), wide range in Al contents (2.975 (1.085~3.160)/14 oxygens), and high Cr and Ni contents. It was formed under a very limited and high $Mg/(Mg+Fe)$ condition. Therefore, the formation of the talc-related chlorites was mainly affected by serpentinite. The latter has higher Fe content with wide range in $Mg/(Mg+Fe)$ ratio (0.378~0.852/14 oxygens), narrower octahedral substitution range of 0.560 (−0.035~0.525/14 oxygens, an ideal clinochlore/chamosite composition), higher values with narrower range in Al contents (1.491 (1.468~2.959)/14 oxygens), and lower Cr and Ni contents than the former. It was formed under a low $Mg/(Mg+Fe)$ and relatively Al-rich condition. Its composition was getting close to the former, so that the formation of the talc-unrelated chlorites was mainly affected by country rock (granitic gneiss) in contact with the talc ore bodies. The chemistry of the coexisting minerals such as mica and amphibole also shows two different chemical behaviors similar to those of chlorite. Two different chemical behaviors of chlorite and coexisting minerals definitely indicate two different origin for two different chlorites. Therefore, the talc ore and associated chlorite were formed by hydrothermal alteration of serpentinite, and the chlorites within the talc ores and blackwall zones are not the remnants of steatitization of chlorite schist or chlorite gneiss, but the products formed mainly by metasomatic reaction of the hydrothermal solution with the serpentinite during steatitization. This study shows that the talc deposits have been formed by two different processes, that is, serpentinization and steatitization, at two different stages.

요약 : 충남 예산-공주-청양지역의 대홍, 평안, 신양 (청당)광산에서 산출되는 녹니석에 관

하여 화학적 및 성인적 연구를 하였다. 이들 광상은 초염기성암기원의 사문암이 열수변질작용을 받아 생성되었다. 활석 광석의 주 구성 광물은 활석, 녹니석, 금운모, 각섬석류, 사문석, 탄산염광물 등이고 이밖에 감람석, 휘석류, 크롬철석, 스멕타이트, 녹니석/스멕타이트의 혼합층상광물들과 같은 팽윤성 광물들이 소량 산출된다. 이 중 감람석과 크롬철석은 광상의 초염기성암기원을 지시하는 중요한 광물이다.

녹니석은 활석 광석의 불순 광물 중 가장 많은 양을 차지하는 광물이다. 이들 녹니석은 성인적으로 활석과 밀접하게 연관된 녹니석과 그렇지 않은 녹니석의 두 가지 뚜렷한 타입으로 나뉘어지며 이들은 화학적으로도 명확한 차이를 보인다. 전자의 녹니석은 $Mg/(Mg+Fe)$비가 높으며 매우 일정한 범위의 $Mg/(Mg+Fe)$비 (0.784~0.951/산소수 14 기준)를 보여주고, 높은 8면체 치환양 (0.892 (-0.200~0.692)/산소수 14, 이상적인 클리노클로어/차모사이트 성분 기준)과 넓은 범위의 Al 함량 변화 (2.975 (1.085~3.160)/산소수 14 기준), 높은 Cr, Ni 함량을 갖는다. 이들은 매우 제한되고 높은 $Mg/(Mg+Fe)$비를 갖는 환경에서 생성되었으며 따라서, 활석과 밀접하게 연관된 녹니석은 생성시, 주변암에 둘러싸여 있는, 초염기성암 기원의 사문암에 의해 주로 영향을 받았다. 후자의 녹니석은 전자의 녹니석에 비하여 Fe 함량이 더 높으며 광범한 범위의 $Mg/(Mg+Fe)$비 (0.378~0.852/산소수 14 기준)를 보여주고, 더 적은 범위의 8면체 치환양 (0.560 (-0.035~0.525)/산소수 14, 이상적인 클리노클로어/차모사이트 성분 기준)과, 전반적으로는 더 높은 값을 가지면서 더 좁은 범위의 Al 함량 변화 (1.491 (1.468~2.959)/산소수 14 기준)를 보여주며, 낮은 Cr, Ni 함량을 갖는다. 이들은 낮은 $Mg/(Mg+Fe)$비를 갖고 전자에 비해 Al이 풍부한 환경에서 생성되었으며, 따라서 활석과 연관되지 않은 녹니석은 생성시 광체와 인접한 화강암질 편마암에 의해 주로 영향을 받았을 것으로 생각된다. 녹니석의 이러한 2가지 화학조성상의 경향은 녹니석과 공존하는 운모류나 각섬석류들의 화학분석결과와도 잘 일치한다. 이러한 결과는 이 지역의 활석 광상이 초염기성암 기원의 사문암이 열수변질작용을 받아 생성되었음을 명확하게 지시하며, 따라서 활석 광석내에 존재하는 녹니석은 활석의 근원 광물로서 녹니석 편암 및 녹니석 편마암 내의 녹니석이 활석화되고 남은 잔존광물이 아니라, 주변암에 의해 성분상의 영향을 받은 열수와 사문암과의 변질교대작용에 의한 활석화과정 중에 주로 생성된 것으로 추정된다. 이러한 결과는 연구지역의 활석광상이 초염기성암의 사문암화 작용과 활석화 작용의 두 가지 변질작용에 의해 형성되어졌음을 알려준다.

INTRODUCTION

The large talc deposits in Korea are originated from either the alteration of ultramafic rocks or magnesian carbonates. The talc deposits in the Yesan–Gongju–Cheongyang area are known as products of hydrothermal alteration of serpentinite originated from ultramafic rocks (Chi and Kim, 1977; Woo et al., 1991; Yun et al., 1994). The talc deposits originated from ultramafics and serpentinites are produced through alteration involving only slight chemical transfer since the chemical composition of the primary rocks is relatively similar to that of talc or talc–chlorite mixtures (Moine et al., 1989). The alteration of serpentine into talc involves the addition of silica, and talc–magnesite assemblages can be produced by the addition of CO_2 (Turner, 1948). Tremolite or dolomite may crystallize when calcium is present in the primary rocks or introduced into the primary rocks. The talc ores of ultramafic origin are thus characterized by the assemblage talc ± serpentine ± chlorite ± tremolite ± carbonates (Moine et al., 1989). Table 1 shows mineralogy of the talc ores and their characteristics of three representative talc mines (Daeheung, Pyeongan, Shinyang). As shown in Table 1, the talc ores contain a lot of impurity minerals such as chlorite, phlogopite, amphiboles, carbonates, and antigorite, so that they show very low whiteness values. Chlorite is the major impurity mineral in talc ores. The close association of chlorite with talc suggests that both have a close relation in their genesis. Therefore, Lee (1994) suggests that the major precursor material of talc and serpentine in the Daeheung mine is chlorite from chlorite schist or chlorite gneiss intercalated in the granitic gneiss. Although the possible formation from

Table 1. Characteristics of the talc ores from the three representative talc mines in Yesan-Gongju-Cheongyang area.

	Daeheung	Pyeongan	Shinyang
Ore form	massive schistose nodular	massive schistose nodular	banded massive
Talc	++++++	++++++	++++++
Chlorite	++++	++++	+++
Phlogopite	++	+++	+
Amphibole	++	+	+
Serpentine	+	+	++
Dolomite	++	++	+
Magnesite	+	+	++
Calcite	+	+	+
Minor minerals	Olivine, Pyroxene, Smectite Chlorite/Smectite, Spine (Fe-Cr, Fe-Ni, Fe-Ti minerals)		

chlorite was suggested by other previous workers (Woo et al., 1991 and Yun et al., 1994), the present study shows that talc has been formed by other process.

Chlorite occurs over a wide range of temperature, pressure, and activity of H_2O, from diagenesis to granulite and eclogite facies (Laird, 1988). It also usually occurs as a common constituent of deuteric or hydrothermal alteration zones around ore bodies as well as a common mineral in low-to -medium grade regional metamorphic rocks (Bailey, 1988). In addition, it is known that the chemistry of chlorite is generally controlled by host rock composition, parent mineralogy, or metamorphic grade. Especially Laird (1988) reports that the Fe/(Fe+Mg) ratios of chlorites from various protoliths are sensitive to the rock composition, and Bevins et al. (1991) shows that Fe/(Fe+Mg) ratios of chlorite are controlled by initial bulk-rock chemistry of metabasites affected by low-grade regional metamorphism. Therefore, the potential use of chlorite in ore genesis studies is particularly attractive, and many workers used the chemistry of chlorite as the indicator of the

extent of metasomatic alteration (Zhong et al., 1985; Shikazono and Kawahata, 1987).

In this paper we will describe the chemistry of chlorite and its mineralogical and textural relation to other coexisting minerals, giving the data suggesting two different origins for chlorite. Eventually, we will attempt to apply these results to deciphering the history of the talc ore formation.

GEOLOGY AND ORE DEPOSITS

The Yesan-Gongju-Cheongyang talc mining area consists nearly entirely of Precambrian granitic gneiss (Woo et al., 1991) with minor hornblende gneiss, tremolite schist, serpentinite, talc-chlorite schist, and dike rocks in the restricted mining area (Figs. 1 and 2). The granitic rocks were formed by regional metamorphism of both epidote-amphibolite and later greenschist facies and granitization (Lee and Choi, 1994).

Talc mineralized zones are developed generally as elongate or lens-shaped bodies in the Precambrian granitic gneiss. The Daeheung, Pyeongan, and Shinyang talc mines are three representative mines in the northeast trending mineralized zone developed over the area of about 6 to 7 km in length and 10 to 100 m in width.

Detailed geologic maps of the Shinyang and Daeheung mines are shown in Fig. 2. Some tremolite schist and hornblende gneiss occur along the margins of the talc ore bodies consisting of talc-chlorite schist. The occurrence of fresh serpentinite in the talc-chlorite schist is a good evidence for the ultramafic origin of the talc deposits. Serpentinite bodies showing alteration to talc are often observed (Fig. 3A). Under the microscope, olivine is also found as relicts in serpentinite (Fig. 4A). Unaltered serpentinite blocks as relicts of steatitization are also present within the talc ore bodies. Many acidic and basic dikes, which seem to be not directly related to steatitization, are found in the area.
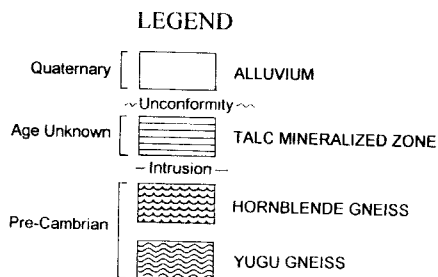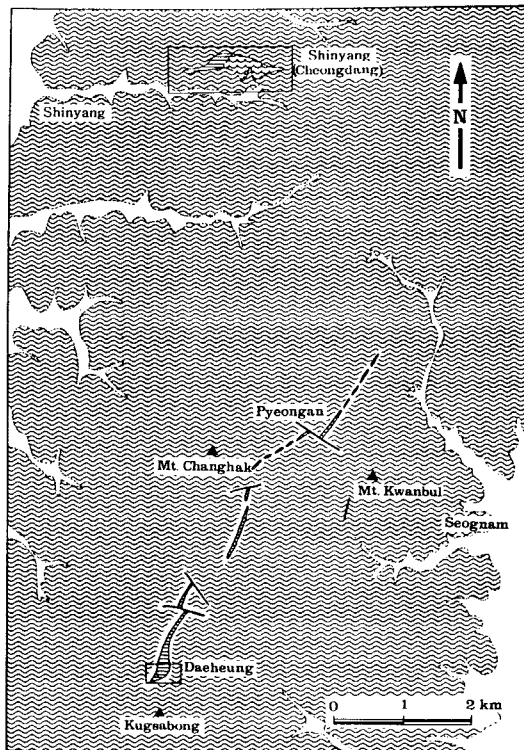
Abundant joints and small faults are deve-

LEGEND

Quaternary [☐] ALLUVIUM

--Unconformity--

Age Unknown [▤] TALC MINERALIZED ZONE

— Intrusion —

Pre-Cambrian [▨ HORNBLENDE GNEISS

▨ YUGU GNEISS]

Fig. 1. Geologic map of the Yesan-Gongju-Cheongyang area.

LEGEND

Quaternary [☐] ALLUVIUM

--Unconformity--

Age Unknown [▦] ACIDIC DIKE ROCK

[▦] BASIC DIKE ROCK

— Intrusion —

[▦] TALC-CHLORITE SCHIST

[■] SERPENTINITE

— Intrusion —

Pre-Cambrian [▥] TREMOLITE SCHIST

[▨] HORNBLENDE GNEISS

[▨] YUGU GNEISS

Fig. 2. Geologic map. A. Shinyang mine. B. Open pit of the Daeheung mine.

loped in the rocks and the talc ore bodies. Such high stress condition might promote open-system conditions. These joint and fault surfaces are typically coated with thin selvages of black mineral aggregate usually consisting of chlorite and/or talc. Occasionally in the contact zone between talc-chlorite schist and granitic gneiss, blackwall-type zones (Sanford, 1982) occur and especially nodular type of ore bodies are widely distributed (Fig. 3B). Such black-colored parts consisting mainly of chlorite are widely distributed in the
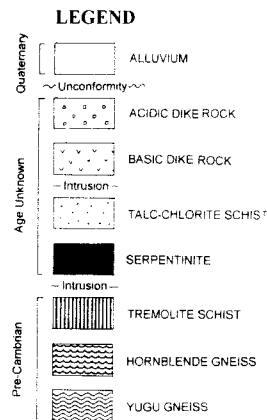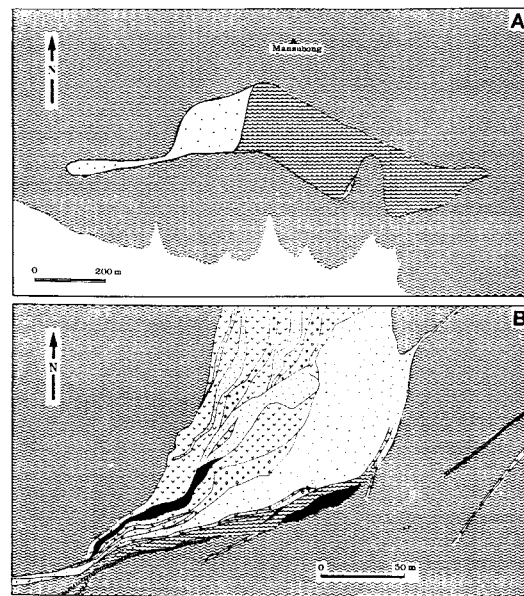
mining area and it will be designated blackwall hereafter. Several centimeter- to 10s centimeter-scaled xenoliths of gneiss often occur in the nodular bodies. From these facts, it can be supposed that the steatitization might have occurred mainly along the fracture zones in the serpentinite. Smectite, corrensite, and other expandable clay minerals also often occur in the fracture zones.

The characteristics of the talc ores from the study area are summarized in Table 1. There are
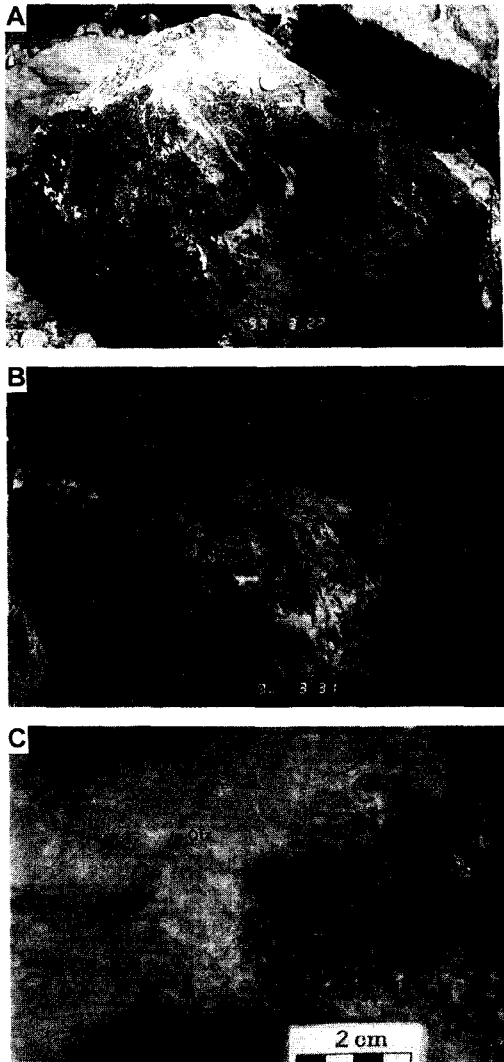
Fig. 3. Photographs. A. The less-altered serpentinite showing steatitization from serpentinite (dark) to talc ore (light). B. The nodular talc ore. C. Chlorite in quartz vein.

little differences in mineralogy and occurrence of the talc ores among three talc mines. The major constituent minerals of the talc ores are talc, chlorite, phlogopite, amphibole, antigorite, and carbonates and the minor minerals are olivine, pyroxene, chromite, smectite, and some other expandable clay minerals such as regularly interstratified smectite/chlorite. Among these, olivine

and chromite are indicative of ultramafic origin (Figs. 4A and B). Chlorite is widely and abundantly distributed in the deposits. Radiating acicular crystals of tremolite-actinolite in talc ore bodies are found near the contacts between the talc-chlorite schist and granitic gneiss. The color of the talc ores is generally dark gray to greenish gray due to the high chlorite content of the ores. Talc ores are mined in the open pits in the Daeheung mine, and in underground for the relatively pure talc ore bodies in the Pyeongan and Shinyang mines.

EXPERIMENTAL METHODS

The samples were collected systematically by their color, texture, and the degree of alteration. In order to get general mineralogical information, optical microscopic studies were performed and X-ray powder diffraction (XRD) patterns of all samples were obtained using a Rigaku Geigerflex with Ni-filtered CuKα radiation. Samples were examined on the random or oriented mounts at 40kV/30mA in a continuous scan mode. Slits were selected so that the X-ray beam divergence was less than the sample length and scanning speed was adjusted to the purpose. For accurate measurement of d-spacing for the clay samples, XRD patterns were recorded by step scan mode. Step interval and counting time were $0.02°(2\theta)$ and 2 seconds, respectively.

Polished thin sections for electron microprobe analysis were prepared and carbon-coated. Backscattered electron images (BEI) were obtained with a JEOL JXA 733, fitted with a Link energy-dispersive X-ray (EDS) detector, and quantitative chemical analyses were performed using the wave dispersive X-ray spectrometer (WDS) controlled by a Link Specta System. Quantitative mineral analyses were done using standard ZAF correction procedures within the Specta software supplied by Link Systems. An operating voltage of 15 kV with a current of 10 nA was used for
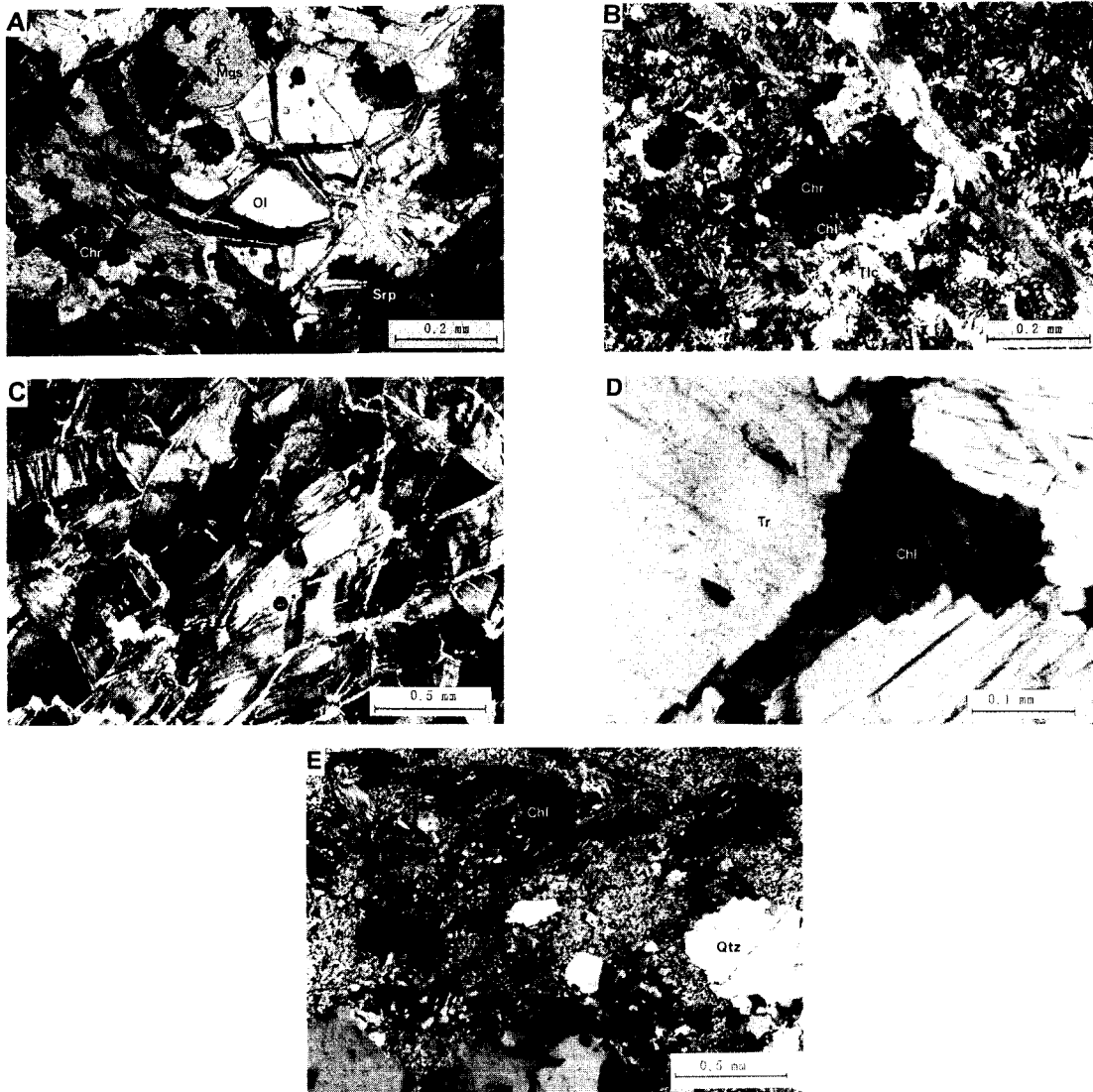
Fig. 4. Photomicrographs of thin sections. A. Serpentinization of olivine with carbonatization. B. Chromite rimmed with chlorite in serpentinite. C. Coarse-grained chlorite. D. Chlorite in association with amphibole. E. Chlorite in altered gneiss (Tlc: talc, Chl: chlorite, Srp: serpentine, Chr: chromite, Ol: olivine, Qtz quartz, Mgs: magnesite, Tr: tremolite).

both the back-scattered imaging and the microprobe analyses. The beam diameter of 3~4μm was employed.

RESULTS

Occurrence of Chlorite

Chlorite can be divided into two types by its associated minerals, occurrence, and chemistry; that is, talc-related chlorite and talc-unrelated
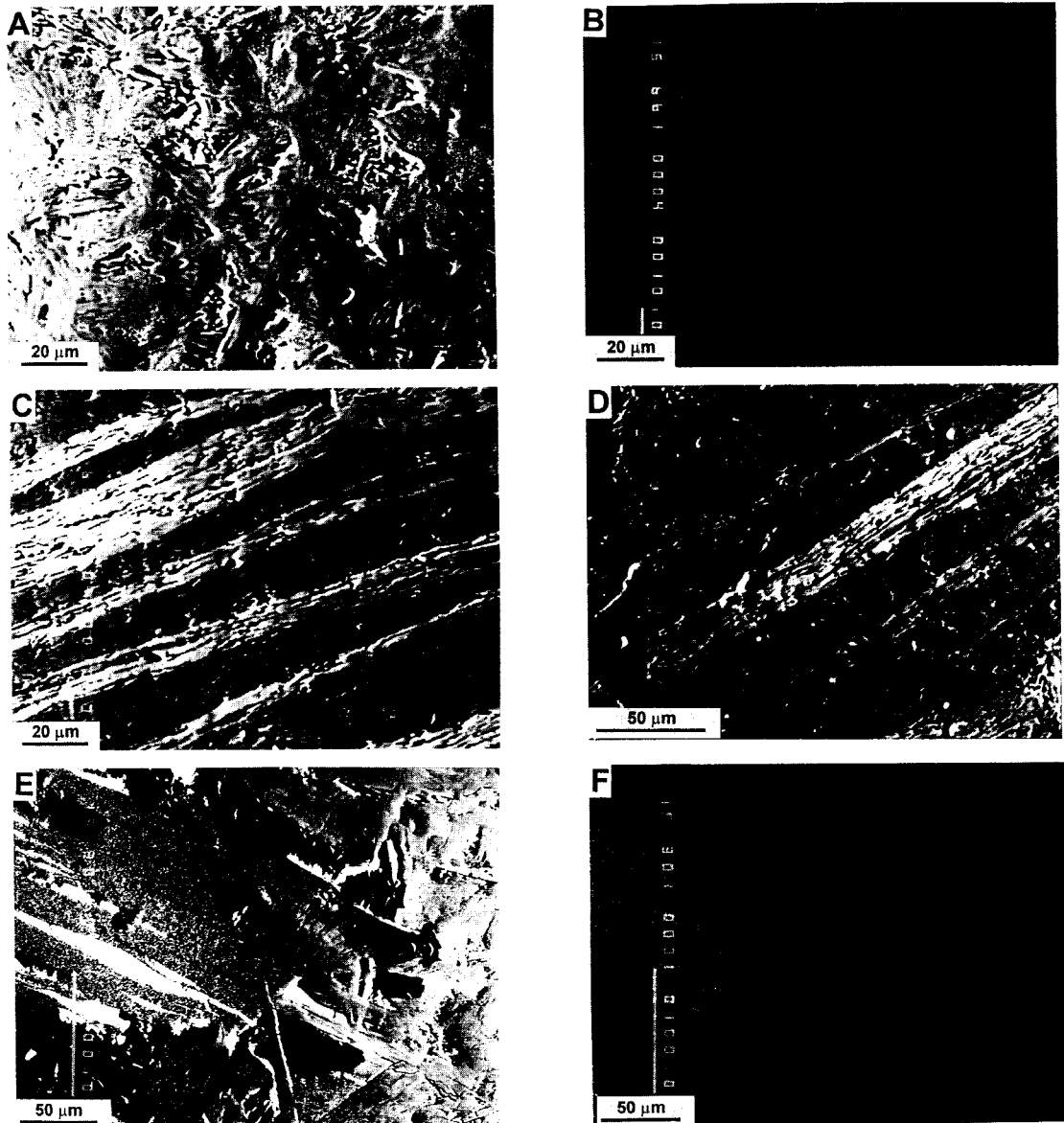
Fig. 5. Back-scattered electron micrographs showing closely coexisting talc and chlorite. A. Fine-grained chlorite within talc grains. B. X-ray image of A for Al. C. and D. Fine-scale interleavings of talc (light) and chlorite (dark). E. Chlorite (white-dotted phase) with serpentine and talc (intermediate toning in the right part of photograph), together with magnesite (darkest toning) and calcic dolomite (bright toning). F. X-ray image of E for Al showing the distribution of chlorite clearly. In the back-scattered electron image, it is not easy to distinguish between serpentine and talc because of their similar chemistry.

chlorite.

Chlorite related to talc ores

Chlorite from the talc ore or blackwall: All talc ores contain chlorite in close association with
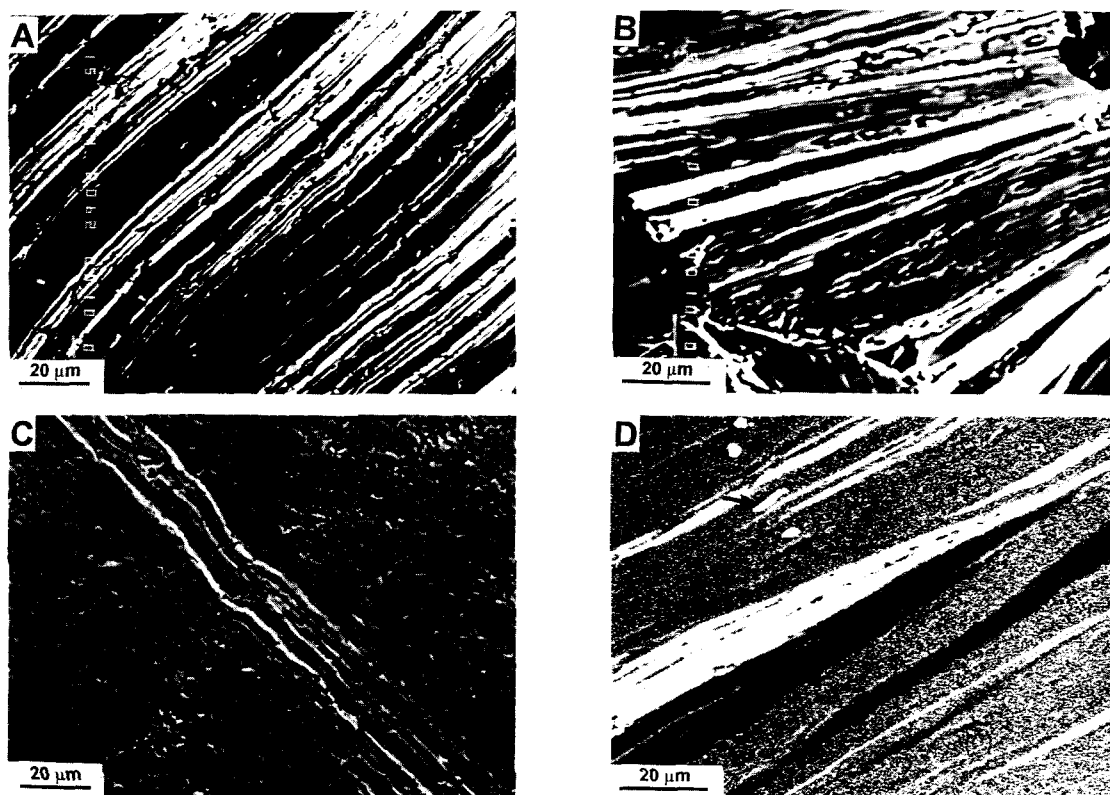
Fig. 6. Back-scattered electron micrographs. A. and B. Fine scale interleavings of chlorite (dark) and phlogopite (light). C. The interleaving of phlogopite (light) in the talc. D. Photomicrograph of back-scattered electron image plus X-ray image for Al showing the incoherent fine-scale intergrowths of talc (darker phase), phlogopite (light phase), and chlorite (white-dotted phase). The most bright phases arrowed are Fe-Ti minerals.

talc. In some cases, it is difficult to find chlorite with an ordinary optical microscope because of its fine-grained nature, but XRD analysis show the presence of small amount of chlorite in this case. However, fine-grained chlorite can be easily detected under the electron microscope (Figs. 5A and B). Talc ore samples from the border zone usually contain aggregate of coarse-grained chlorite, phlogopite, and/or amphibole. Especially samples from the blackwall zone are composed mainly of coarse-grained chlorite (Fig. 4C). Both coarse- or fine-grained chlorite mentioned above is often finely interleaved with talc. Such a texture is easily observed under the optical and electron microscopes (Figs. 5C and D).

Chlorite in serpentinite : Chlorite is also associated with serpentine in rare case. It is also observed that carbonate and talc are included in serpentinite (Figs. 5E and F). Magnesite is dominant carbonate mineral in the fresh serpentinite, whereas dolomite is in the altered serpentinite and talc ores.

Chlorite in association with mica : Many talc ores contain intergrowth of chlorite and mica within the fine-grained talc matrix (Figs. 6A and B).

Chlorite associated with chromite : High Ni and Cr concentrations in the primary ultramafics are mostly preserved in the talc ores. Chromite and Fe-Ni minerals are formed in the talc ores.

Such chromites are usually surrounded by chlorite (Fig. 4B).

Chlorite not related to talc ores

Chlorite in the altered gneiss: Granitic gneiss in contact with talc ore bodies is highly altered and disturbed by steatitization. Chlorite in the altered gneiss is usually associated with the altered feldspar and mica (Fig. 4E).

Chlorite associated with amphibole: Amphiboles of acicular, fibrous, or flake form are found near the border zone of talc ore bodies and often transformed into chlorite (Fig. 4D).

Chlorite in dike rocks: Chlorite is also found in various dike rocks intruding talc ore bodies. It is an alteration product of mafic minerals of dike rocks. It is considered that the dike rocks are not affected by steatitization.

Chlorite in quartz vein: Chlorite also occurs in quartz veins within talc ore bodies (Fig. 3C), which are considered to be related to hydrothermal alteration process resulting in steatitization. This type of chlorite is not directly associated with talc.

Chemistry of Chlorite

Chemical analyses of chlorites have been normalized to 14 oxygens assuming all iron is ferrous. The chemistry of octahedral substitution suggests an ideal clinochlore/chamosite composition. They were plotted on the Hey's classification diagram (1954). It shows that chemical analyses fall into the wide range from delessite to thuringite (Fig. 7A). The talc-related chlorites mostly fall into the clinochlore and penninite fields, whereas the talc-unrelated chlorite into the wide range over diabantite, pycnochlorite, and ripidolite fields. A few of the latter are also plotted in clinochlore and penninite fields (Fig. 7B). Several chlorite data plotted in the talc-chlorite field in Fig. 7B are excluded, because it is considered that
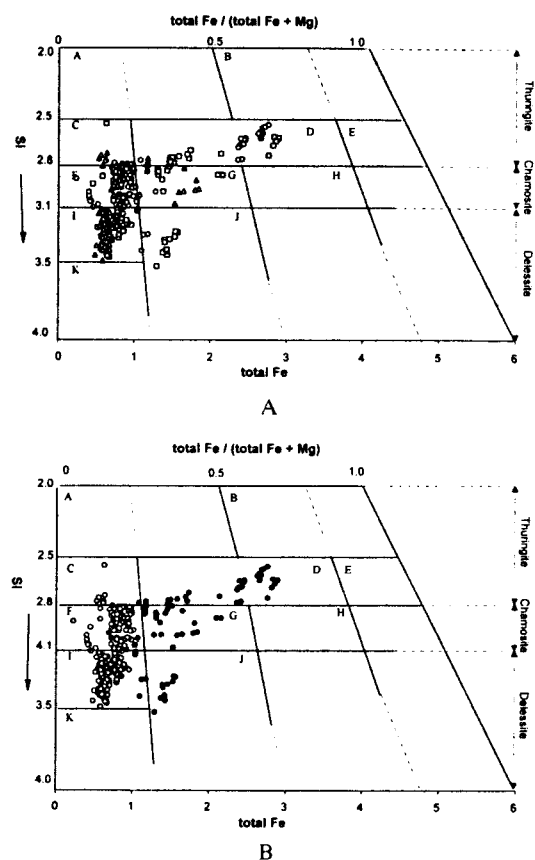

A

B

Fig. 7. Total Fe vs. Si compositional variation of chlorites (after Hey, 1954). A. Chlorite from the representative three mines (open square: Daeheung mine, open circle: Pyeongan mine, open triangle: Shinyang mine). B. Talc-related chlorite (open circle) and Talc-unrelated chlorite (closed circle). Cations were calculated on the basis of 14 oxygens. A: corundophilite, B: pseudothuringite, C: sheridanite, D: ripidolite, E: daphnite, F: clinochlore, G: pycnochlorite, H: brunsvigite, I: penninite, J: diabantite, K: talc-chlorite.

the chlorite is interleaved with talc. Though the nomenclature of Hey (1954) is used in many petrologic papers and presented in many mineralogy textbooks, because the boundaries between "varieties" have little structural meaning (Brown and Bailey, 1962), chlorite composition discussed below follows the simplified classification scheme
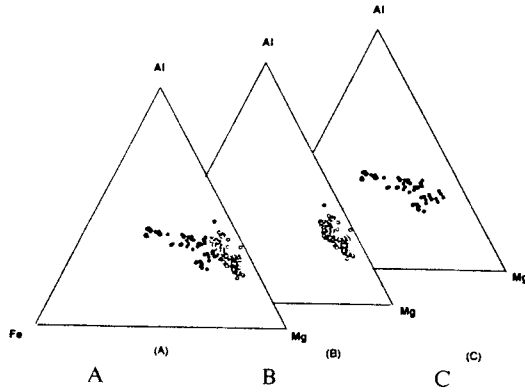
Fig. 8. Plots of chemical compositions of chlorites of various types in the Al-Fe-Mg diagram. A. Plots of all chlorite data. B. Plots of talc-related chlorite. C. Plots of talc-unrelated chlorite. Symbols are the same as in Fig. 7B.

recommended by the Nomenclature Committee of AIPEA (Bailey, 1980). Therefore, chlorite composition of the study area is between clinochlore (Mg-dominant species) and chamosite (Fe^{2+} -dominant species) according to the dominant divalent octahedral cation present. The talc-related chlorites belong to clinochlore, whereas the talc-unrelated chlorites to clinochlore-chamosite. Such tendencies are clearly found in the Al-Fe-Mg diagram (Fig. 8). Although all the data of chlorites are plotted over a wide range in the Al-Fe-Mg diagram (Fig. 8A), the talc-related chlorites show large variation in Al content with a very narrow range in Fe/(Fe+Mg) (Fig. 8B), whereas the talc-unrelated chlorites show a wide range in Fe/(Fe+ Mg) from chamosite to clinochlore (Fig. 8C). Even though the values are not presented as a different figure, the talc-unrelated chlorites have narrower range of Al contents (1.491 (1.468~2. 959)) but generally higher Al content than the talc -related chlorites (2.075 (1.085~3.160)). Fig. 9 shows the plots of Al(VI)+2Ti+Cr+1 vs. Mg/ (Mg+Fe). The talc-related chlorites have very high and narrow range in Mg/(Mg + Fe) ratios (0.784~0.951) with significant octahedral substitu-
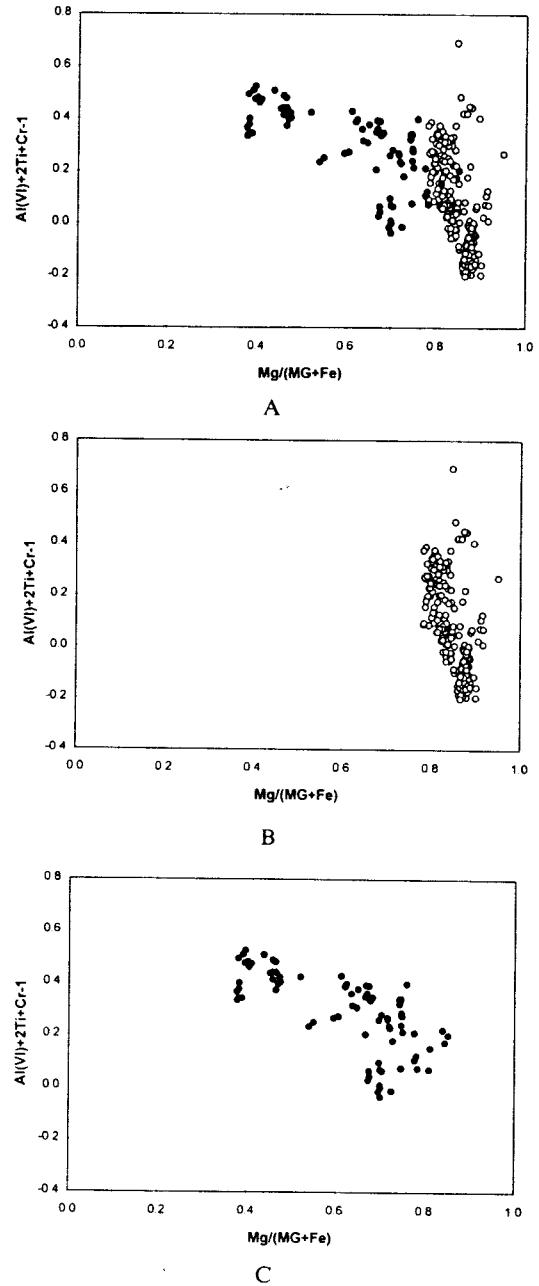

Fig. 9. Plots of chlorite compositions in Al(VI)+ 2Ti+Cr+1 vs. Mg/(Mg+Fe). A. Chlorites of all types. B. Talc-related chlorite. C. Talc-unrelated chlorite. Vertical axis exhibits the dioctahedral substitution. (After Laird, 1988). Symbols are the same as in Fig. 7B.
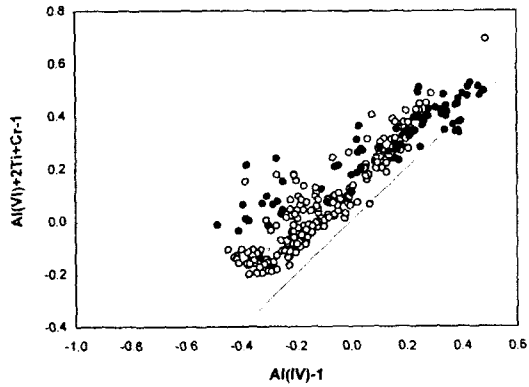
Fig. 10. Plots of chlorite compositions in Al(VI)+ 2Ti+Cr−1 vs. Al(IV)−1. The origin is end member clinochlore/chamosite. Compositional variation along the 1:1 line represents Tschermak substitution. (After Laird, 1988). Symbols are the same as in Fig. 7B.
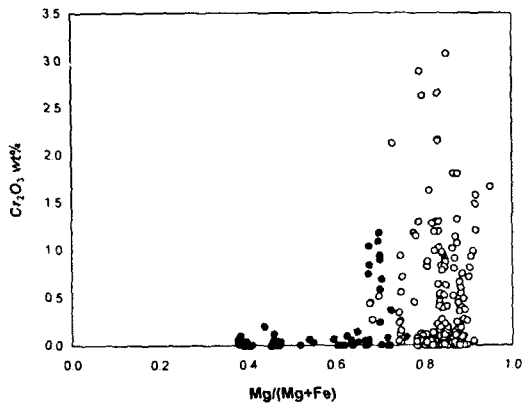

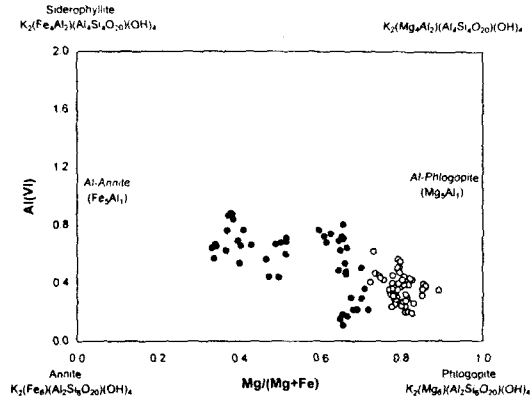Fig. 11. Plots of chlorite compositions in Mg/(Mg +Fe) vs. CrO₃ (wt%). Symbols are the same as in Fig. 7B.

Fig. 12. Mica compositions in Mg/(Mg+Fe) vs. Al(VI). Cations of mica were calculated on the basis of 22 oxygens. open circle : talc-related mica, closed circle : talc-unrelated mica.

than the talc-unrelated chlorites. Cr and Ni contents also appear to be higher in the talc-related chlorites. Fig. 11 shows the plots of chlorite compositions in Mg/(Mg+Fe) vs. CrO₃ (wt%). Especially, chlorites from the altered gneiss have less CrO₃ (wt%) contents than other type.

Occurrences and Chemistry of Other Coexisting Minerals

Mica and chlorite are important minerals coexisting with talc, and most micas from the talc ores have phlogopite compositions (Fig. 12). In the contact zone between talc ore body and granitic gneiss, the mica is more Fe-rich. Although micas also occur in the hornblende gneiss, altered gneiss, and dike rocks, they are not related to talc. Especially muscovite occurs only in the granitic gneiss, and not in talc ores. In plots of octahedral cations on Mg/(Mg+Fe) vs Al(VI) diagram (Guidotti, 1984), all compositions of trioctahedral mica show a series of variation in Mg/(Mg+Fe). However, they are divided into two groups by Mg /(Mg+Fe) ratio (Fig. 12). The talc-related micas have phlogopite compositions, and the talc-unrelated micas have biotite compositions. Under the

tion range of 0.892 (−0.200~0.692) (Fig. 9B), whereas the talc-unrelated chlorites show wide variation in Mg/(Mg+Fe) ratio (0.378~0.852) and some octahedral substitution range of 0.560 (−0.035~0.525) (Fig. 9C). It is an important result that Mg/(Mg+Fe) values of the talc-related chlorites are markedly higher than the talc-unrelated chlorites. Fig. 10 shows the positive correlation between Al(VI)+2Ti+Cr−1 vs. Al−1. The talc-related chlorites show less Tschermak substitutions, less Al contents, and more Mg, Si contents
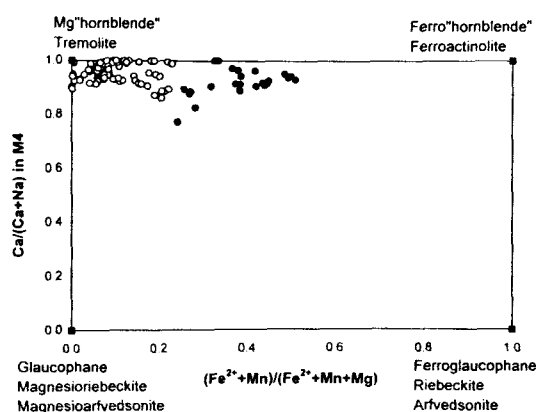
Fig. 13. The chemical variations of the calcium-rich amphiboles. Amphibole formulae were calculated on the basis of 13eCNK (Robinson et al., 1982). Plot of $(Fe^{2+}+Mn)/(Fe^{2+}+Mn+Mg)$ vs. $Ca/(Ca+Na)$ in M4 site. Various end members are indicated. open circle: talc-related amphibole, closed circle: talc-unrelated amphibole.

electron microscope, mica from the talc ores often shows interleaving with chlorite or talc (Fig. 6).

Under the microscope, amphiboles show various occurrences such as acicular, fibrous and flake forms. Tremolite-actinolite amphiboles from talc ores and some tremolite schist show a close relation to talc. The compositions of calcium-rich amphiboles from the study area are divided into two groups by $(Fe^{2+}+Mn)/(Fe^{2+}+Mn+Mg)$ (Fig. 13). The talc-related amphiboles show higher Mg contents than the talc-unrelated amphiboles. It is important fact that the chemical behaviors of mica and amphibole are similar to those of chlorite.

The serpentine mineral is identified as antigorite on the basis of its X-ray diffraction pattern. In several serpentinite samples, antigorite has replaced olivine resulting in some pseudomorphs of antigorite after olivine and relicts of olivine (Fig. 4A). Antigorite sometimes occurs in the talc ores as remnants of steatitization as well as in serpentinite. Fe contents of talc and antigorite from fresh serpentinites are lower than those from the

talc ores or altered serpentinites suggesting that some Fe was introduced into serpentinite by hydrothermal solution during the steatitization.

DISCUSSION

Chlorite, due to its extensive solid solution, is a sensitive indicator of the extent of metasomatic alteration (Zhong et al., 1985). Maruyama et al. (1986) suggested that the Fe/(Fe+Mg) ratio in chlorite from mafic rock can be used to monitor bulk rock Fe/(Fe+Mg). Zhong et al. (1985) proposed that the Fe/(Fe+Mg) and Al/(Al+Si) ratios of chlorite, as determined by electron microprobe analysis and X-ray diffractometry, seem to monitor the metasomatic exchange of Al, Fe and Mg between the metamorphosed ultramafic rocks and the country rock. The Mg/(Mg+Fe) ratio and the Al variation of octahedral or tetrahedral sites of chlorite from the study area are variable and sensitive to the coexisting minerals (Figs. 7, 8, 9, 10, and 11). Chemical data show that there are two distinct types of chlorites : that is, the talc-related chlorite and talc-unrelated chlorite. Both types of chlorites have different occurrences and chemical compositions.

The field occurrences of talc and chlorite suggest that they have formed by hydrothermal alteration. The presence of two types of chlorites having different chemistry suggests the two different protoliths of different Mg/(Mg+Fe) ratios and Al contents, namely, serpentinite and granitic gneiss. The talc-related chlorite has very high Mg /(Mg+Fe) ratio with extremely narrow variation in Mg/(Mg+Fe), significant octahedral substitution range, wide range of Al contents, and high Cr and Ni contents, suggesting that it was originated from serpentinites which was formed from ultramafic rocks. It was formed under a very limited and high Mg/(Mg+Fe) conditions receiving various amount of Al from granitic gneiss. The talc-unrelated chlorite has higher Fe content with wide range in Mg/(Mg+Fe) ratio, narrower
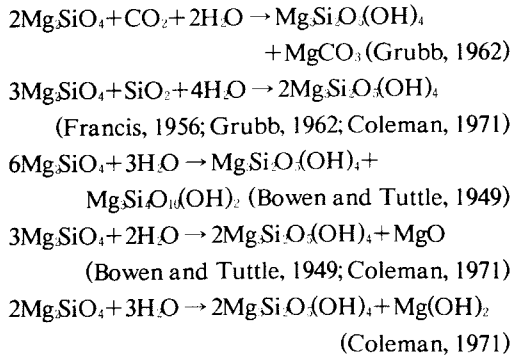
octahedral substitution, high Al values with nar-row range, and lower Cr and Ni contents than the talc-related chlorite, suggesting that its composi-tion might have been affected by granitic gneiss surrounding the talc ore bodies. It was formed under a low $Mg/(Mg+Fe)$ and relatively Al-rich conditions receiving various amount of Mg from serpentinite getting close to the composition of talc-related chlorite.

The chemistry of the coexisting minerals such as mica and amphibole shows two different chem-ical behaviors similar to those of chlorite, sup-porting this interpretation most probable. The altered gneiss containing large amount of chlorite is limited to the border zone. The chlorite in the altered gneiss is of Fe- and Al-rich type. Howev-er, muscovite and quartz which are generally the major constituents of schist or gneiss, never exist in the talc ores, and the compositions of the talc-related chlorites are close to Mg end-member chlorite, clinochlore having very narrow range of $Mg/(Mg+Fe)$ ratio. Therefore, the altered gneiss containing large amount of chlorite is not the rel-icts of chlorite schist or chlorite gneiss. In addition, the chemistry of this chlorite suggests that the precursor of talc ores are not chlorite schist or chlorite gneiss but serpentinite originat-ed from ultramafic rocks. Muscovite and quartz were not present originally in the precursor rock of talc ores. Sanford (1982) showed that in north-ern Appalachian occurrences $AlMgSi$ and $FeMg$ diffused into the country rock and that this metasomatism is manifested in the chlorite composition. Al and Fe are distinctly abundant in chlorite from country rock, whereas Mg, Cr, and Ni are less in chlorite from the country rock. These observations are consistent with data pre-sented by Zhong et al. (1985) who show increasing Al and Fe contents in chlorite with increasing metasomatism of ultramafic rocks. Present study is in good accordance with their works.
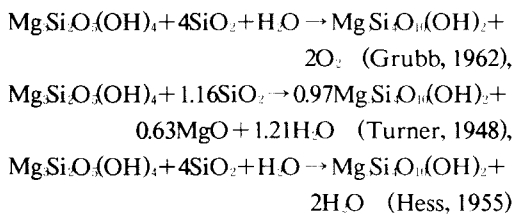
Therefore, two different chemical behaviors of chlorite and coexisting minerals definitely indi-cate that the talc ore deposits have been formed by hydrothermal alteration of serpentinite origi-nated from ultramafic rock, and that the chlorites within the talc ores and blackwall zones are not the remnants of steatitization of chlorite schist or chlorite gneiss, but the products formed mainly by metasomatic reaction of hydrothermal solu-tion with serpentinite during the steatitization. The chlorite aggregates within the altered gneiss at the border zone of talc ore bodies are also not the relicts of steatitization of chlorite schist or chlorite gneiss but the products affected by meta-somatic reaction of hydrothermal solution with granitic gneiss.

The occurrences and chemistry of chlorite and other coexisting minerals allow an interpreta-tion of the crystallization history. The talc miner-alized zones in the study area have undergone two principal stages of alteration, that is, ser-pentinization of ultramafic portolith and stea-titization of serpentinite. Both processes are often found together in the same rock. The serpen-tinization might begin from the ultramafic protolith, an assemblage of olivine and some other mafic minerals such as enstatite which was replaced by serpentine and to a lesser extent by talc, magnesite, and chlorite. Woo et al. (1991) demonstrated that the serpentinites were derived from the ultramafic protoliths, most probably an dunite, peridotite, or olivine gabbro. The ul-tramafic protolith is not preserved but the least altered serpentinite from the study area contain olivine which has been partially replaced by antigorite and magnesite along the grain bound-aries and microcracks (Fig. 4A). Most probably, the ultramafic bodies with a small concentration of enstatite was tectonically emplaced, and the first reaction was retrograde hydration of this originally high temperature pressure assemblage in response to the lower grade environment of re-gional metamorphism. The related reactions can be expressed in the equation as follows :

$2Mg_2SiO_4 + CO_2 + 2H_2O \rightarrow Mg_3Si_2O_5(OH)_4$
$+ MgCO_3$ (Grubb, 1962)

$3Mg_2SiO_4 + SiO_2 + 4H_2O \rightarrow 2Mg_3Si_2O_5(OH)_4$
(Francis, 1956; Grubb, 1962; Coleman, 1971)

$6Mg_2SiO_4 + 3H_2O \rightarrow Mg_3Si_2O_5(OH)_4 +$
$Mg_6Si_4O_{10}(OH)_2$ (Bowen and Tuttle, 1949)

$3Mg_2SiO_4 + 2H_2O \rightarrow 2Mg_3Si_2O_5(OH)_4 + MgO$
(Bowen and Tuttle, 1949; Coleman, 1971)

$2Mg_2SiO_4 + 3H_2O \rightarrow 2Mg_3Si_2O_5(OH)_4 + Mg(OH)_2$
(Coleman, 1971)

The second event was the steatitization of the serpentinite by the hydrothermal solution related to the probably deep seated igneous body, and it is evidenced by the mineralogical observation that talc and chlorite have replaced serpentine (Fig. 5E). Steatitization may be defined as the process of hydrothermal alteration of ultrabasic rocks that results in the formation of a talcose rock (Bates and Jackson, 1987). It may be applied either to the process by which in its final stages soapstones (steatite) or relatively pure concentrations of talc are formed. Thus, whether the serpentine, talc, and chlorite were formed simultaneously or sequentially, the crystallization of serpentine which replaced olivine might occur at least in part before the formation of major talc ore bodies. The reactions can be expressed in the equation as follows:

$Mg_3Si_2O_5(OH)_4 + 4SiO_2 + H_2O \rightarrow Mg_3Si_4O_{10}(OH)_2 +$
$2O_2$ (Grubb, 1962),

$Mg_3Si_2O_5(OH)_4 + 1.16SiO_2 \rightarrow 0.97Mg_3Si_4O_{10}(OH)_2 +$
$0.63MgO + 1.21H_2O$ (Turner, 1948),

$Mg_3Si_2O_5(OH)_4 + 4SiO_2 + H_2O \rightarrow Mg_3Si_4O_{10}(OH)_2 +$
$2H_2O$ (Hess, 1955)

It is obvious that talc-forming fluids migrated at least in part along joints, compositional layering, fault surfaces, and lithologic contacts, as evidenced by thin selvages of chlorite and/or talc along these surfaces and blackwall zones usually occurring at the contact of talc ore bodies and granitic gneiss. During steatitization and/or ser-
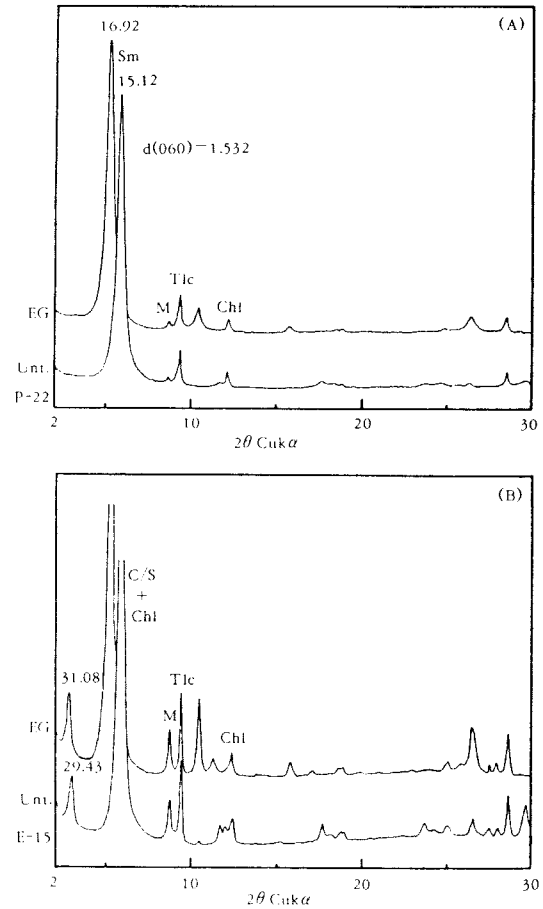

Fig. 14. X-ray diffraction patterns. A. Smectite (Sm) from sample P-22, B. Interstratified chlorite/smectite (C/S) from sample E-15. These samples also contain chlorite (Chl), talc (Tlc), and mica (M). EG : ethylene glycol solvated, Unt. : untreated (air-dried).

pentinization, excess MgO (extracted from reaction) is reacted with the Si- and Al-rich solution resulting in the formation of chlorite and/or some smectite minerals. At the same time these processes were assisted by corresponding metasomatic addition of Al_2O_3, CaO, K_2O, CO_2, and iron to the parent rocks, thereby forming chlorite, tremolite-actinolite, phlogopite, carbonate minerals along the margins of the talc ore body. These chloritization and carbonatization usually occur following the addition of other components
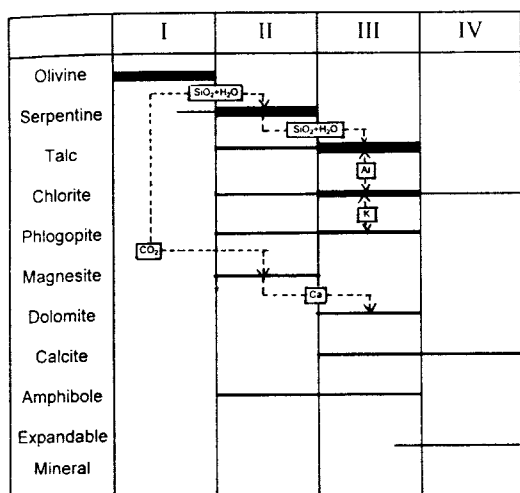
Fig. 15. Mineral paragenesis for the talc ore bodies in the study area.

(Grubb, 1962). Through chloritization and carbonatization accompanied with the steatitization of serpentinites, the extraneous hydrothermal solutions often become partially more siliceous, thereby promoting steatitization, and where temporarily dammed, some chlorites and phlogopite are formed together with talc during the late stage of steatitization.

X-ray diffraction studies of smectite show that the d(060) spacing is 1.532 and the d(001) spacing shift from 15.1 Å to 16.9 Å with ethylene glycol solvation. Therefore, the smectite is trioctahedral saponite (Fig. 14A). Because X-ray diffraction study of the interstratified chlorite/smectite shows that the distinct 29.4-Å (001) superlattice spacing shifts to 31.1 Å with ethylene glycol solvation (Fig. 14B), it is considered that it is regularly interstratified 'corrensite' (Hauff, 1981). It is considered that these expandable minerals have been formed by supergene alteration of other earlier clay minerals such as chlorite, phlogopite, and talc. Further detailed study for these expandable clay minerals are needed.

Mineral paragenesis of minerals discussed above is summarized in Fig. 15. The alteration history mentioned above is undoubtedly complex,

involving retrogressive recrystallization from the original ultramafic assemblage plus chemical mass transfer between the granitic gneiss and the ultramafic intrusive. However, the chemistry and occurrences of chlorites were very useful to understand the general process of ore formation of the study area.

CONCLUSIONS

The chlorites of the study area are classified into two types by chemical behaviors, that is, they are the talc-related chlorite and talc-unrelated chlorite. The chemistry of the talc-related chlorite has been affected by serpentinites which was originated from ultramafic rocks, therefore, its chemistry shows very high Mg/(Mg+Fe) ratio with a extremely narrow variation in Mg/(Mg+Fe), significant octahedral substitution range, and high Cr and Ni contents. The chemistry of talc-unrelated chlorite has been affected by granitic gneiss surrounding the talc ore bodies, therefore its chemistry is higher Fe content with a wide range in Mg/(Mg+Fe) ratio, higher Al content, and lower Cr and Ni contents than the talc-related chlorite. The chemical data of the coexisting minerals such as mica and amphibole also show two different chemical behaviors similar to those of chlorites, supporting the above interpretation.

Therefore, the two different chemical behaviors of chlorite and coexisting minerals definitely indicate two different origins for two different chlorites and associated minerals. The talc ore and associated chlorite have been formed by hydrothermal alteration of serpentinite, and the chlorites within the talc ores and blackwall zones are not the remnants of steatitization of chlorite schist or chlorite gneiss, but the products mainly formed by metasomatic reaction of hydrothermal solution with serpentinite during steatitization.

The talc mineralized zones in the study area have undergone two principal stages of alteration, that is, serpentinization of ultramafic portolith

and steatitization of serpentinite. Whether the serpentine, talc, and chlorite were formed simultaneously or sequentially, it is quite evident that the serpentinization occurred at least in part before the steatitization.

REFERENCES

Bailey, S. W. (1980) Summary of the AIPEA nomenclature committee. Can. Mineral., 18, 143 -150.

Bailey, S. W. (1988) Chlorites: structures and crystal chemistry. In: Hydrous Phyllosili-cates, Reviews in Mineralogy, Vol. 19 (eds Bailey, S. W.), 347-403. Mineralogical Society of America.

Bates, R. L., and Jackson, J. A. eds. (1987) Glossary of Geology. 3rd. ed. 642.

Bevins, R. E., Robinson, D., and Rowbotham, G. (1991) Compositional variations in mafic phyllosilicates from regional low-grade metabasites and application of the chlorite geothermometer. Jour. Metamorphic Geol., 9, 711-721.

Bowen, N. L., and Tuttle, O. F. (1949) The system $MgO-SiO_2-H_2O$. Geol. Soc. Am. Bull., 60, 439- 460.

Brown, B. E., and Bailey, S. W. (1962) Chlorite polytypism: I. Regular and semi-random one -layer structures. Am. Mineral., 47, 819-850.

Chi, J. M., and Kim, K. B. (1977) A study of talc mineralization of serpentine. Jour. Korean Inst. Mining Geol., 10, 67-74. (in Korean).

Coleman, R. G. (1971) Petrologic and geophysical nature of serpentinites. Geol. Soc. Am. Bull., 82, 897-918.

Francis, G. H. (1956) The serpentinite mass in Glen Uruquhart, Invernesshire, Scotland. Am. Jour. Sci., 254, 201-226.

Grubb, P. L. C. (1962) Serpentinization and chrysotile formation in the Matheson ultrabasic belt, northern Ontario. Econ. Geol., 57, 1228- 1246.

Guidotti, C. V. (1984) Micas in metamorphic rocks. I: Micas, Reviews in Mineralogy, Vol. 13 (eds Bailey, S. W.), pp. 357-468. Mineralogical Society of America.

Hauf, P. L. (1981) Corrensite: Mineralogical ambiguities and geologic significance. U.S. Geological Survey Open File Report 81-85.

Hess, H. H. (1954) Serpentines, orogeny, epeirogeny. Geol. Soc. Am. Bull., Spec. Paper, 62, 391- 409.

Hey, M. H. (1954) A new review of the chlorites. Mineral. Mag., 30. 277-292.

Laird, J. (1988) Chlorites: metamorphic petrology. In: Hydrous Phyllosilicates, Reviews in Mineralogy, Vol. 19 (eds Bailey, S. W.), 405-453. Mineralogical Society of America.

Lee, S. H. (1994) Phase equilibria between coexisting minerals in the talc ores and process of talc formation in the Daeheung Talc Deposits, Korea. Jour. Petrol. Soc. Korea, 3, 156- 170. (in Korean).

Lee, S. H., and Choi, G. J. (1994) Geochemistry and chemical equilibria of coexisting minerals in the gneisses around the Daeheung Talc Deposits, Korea, Jour. Petrol. Soc. Korea, 3, 138-155. (in Korean).

Maruyama, S., Cho, M., and Liou, J. G. (1986) Experimental investigations of blueschist-greenschist transition equilibria: pressure dependence of Al_2O_3 contents in sodic amphiboles-A new geobarometer. In: Blueschists and Eclogites (eds Evans, B. W. and Brown, E. H.), Geol. Soc. Am. Memoir 164, 1-16.

Moine, B., Fortune, J. P., Moreau, P., and Viguier, F. (1989) Comparative mineralogy, geochemistry, and conditions of formation of two metasomatic talc and chlorite deposits: Trimouns (Pyrenees, France) and Rabenwald (Eastern Alps, Austria). Econ. Geol., 84, 1398- 1416.

Robinson, P., Spear, F. S., Schumacher, J. C., Laird, J., Klein, C., Evans, B. W., and Doolan, B. L. (1982) Phase relations of metamorphic am-

phiboles: natural occurrence and theory. In: Amphiboles: Petrology and Experimental Phase Relations, Reviews in Mineralogy, Vol. 9B (eds Veblen, D.R. and Ribbe, P. H.), 1-227, Mineralogical Society of America.

Sanford, R. F. (1982) Growth of ultramafic reaction zones in greenschist to amphibolite facies metamorphism. Am. Jour. Sci., 282, 543-616.

Shikazono, N., and Kawahata, H. (1987) Compositional differences in chlorite from hydrothermally altered rocks and hydrothermal ore deposits. Can. Mineral., 25, 465-474.

Turner, F. J. (1948) Mineralogical and structural evolution of the metamorphic rocks. Geol. Soc. Am. Memoir., 30, 132.

Woo, Y-K., Choi, S-W., and Park, K-H. (1991) Genesis of talc ore deposits in the Yesan area of Chungnam, Korea. Jour. Korean Inst. Mining Geol., 24, 363-378 (in Korean).

Yun, S. P., Moon, H-S., and Song, Y. (1994) Mineralogy and genesis of the Pyeongan and Daeheung talc deposits in ultramafic rocks, the Yoogoo area. Econ. Environ. Geol., 27, 131-145. (in Korean).

Zhong, W. J. S., Hughes, J. M., and Scotford, D. M. (1985) The response of chlorite to metasomatic alteration in Appalachian ultramafic rocks. Can. Mineral., 23, 443-446.