

# The Mineralogical and Geochemical Study on Korean Scheelites and its Application to the Ore Prospecting

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**Abstract:** Twenty five samples of the scheelite-powellite series from twelve Korean tungsten deposits of various geologic settings were studied mineralogically and geochemically. Variations in the trace-element contents of the scheelite minerals are considered in relation to geologic settings and mineralogic properties. Scheelites from ore deposits developed in similar geologic settings and under similar physicochemical conditions are characterized by specific combinations of trace elements.

## 1. Introduction

Tungsten minerals have been reported from about one hundred forty localities in Korea, of which only a few have been developed for production. Little research on the mineralogical and geochemical properties of tungsten minerals and deposits has been undertaken in Korea.

Apart from scheelite and wolframite, which are hypogene minerals, almost all other tungsten mineral species from Korea are supergene, and occur as weathering products of the former. Therefore scheelite and wolframite are the significant minerals for considering the geology and genesis of tungsten deposits in Korea. The scope of this study is to determine systematically the chemistry of scheelite collected from various geologic settings and to correlate it with geologic occurrence and colour characteristics. For this study scheelite minerals from various geologic settings were selected: San Nae, Il Gwang and Dal Seong deposits pertaining to the Cretaceous-early Tertiary epoch; Dae Wha, Weol Ag and Bog Su deposits pertaining to the Jurassic-early Cretaceous epoch; Sang Dong deposit pertaining to the Cambrian epoch; Og Bang and Ssang Jeon deposits pertaining to the Pre-

cambrian epoch; and Hong Seong, Sam Bong and Cheong Yang deposits of unknown age. These epochs are represented by tungsten-bearing deposits in five tungsten metallogenic provinces, depicted on Figure 1.

The tetragonal tungsten mineral, scheelite ( $\text{CaWO}_4$ ), is the most important source of tungsten in Korea. It is capable of incorporating variable amounts of the powellite ( $\text{CaMoO}_4$ ) end-member to form a solid-solution series. This is readily recognized in the field by a distinctive change in fluorescence colour, from white when the scheelite is pure, to yellow when it contains more than a few weight percent of molybdenum.

## 2. Sampling and analytical techniques

The distribution of twenty five specimens collected from twelve mines is shown in Figure 1. Genetically they include six hydrothermal vein deposits, two pegmatite veins, two contact-metasomatic deposits, one metamorphosed exhalative-sedimentary deposit, and one of unknown origin. As far as conditions allowed, more than one specimen were collected from different sites in the same mine or prospect. This was done according to depth in hydrothermal and pegmatite deposits (as at Dae Wha, Og

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Bang and Weol Ag mines), and according to colour in all the deposits examined. With a few exceptions these samples represent the five tungsten provinces. These provinces have been the most productive economically and contain a number of important mines, such as the Sang Dong, Dae Wha, Weol Ag, Bog Su, Og Bang and San Nae deposits.

The modes of occurrence, pertinent geologic and mineralogic features, and localities of individual scheelite-bearing samples studied are briefly described in Table 3. More detailed geologic information is given below.

All specimens were examined petrographi-

cally. Samples were broken to sand-size grains in a jaw-crusher prior to being powdered in a shatter box with a tungsten carbide grinding container (100ml). Grains of -80+120 mesh were then sieved and cleaned, because a complete scheelite separation was thought possible at this grain size from observations of polished and thin sections of ore samples. The lighter-grains were removed by means of super panning, followed by successive heavy-liquid treatments, first using tetrabromoethene with a density of 2.964 g/ml and then methylene iodide with a density of 3.325 g/ml, at 20°C. The heavy-mineral grains thus separated were subjected to

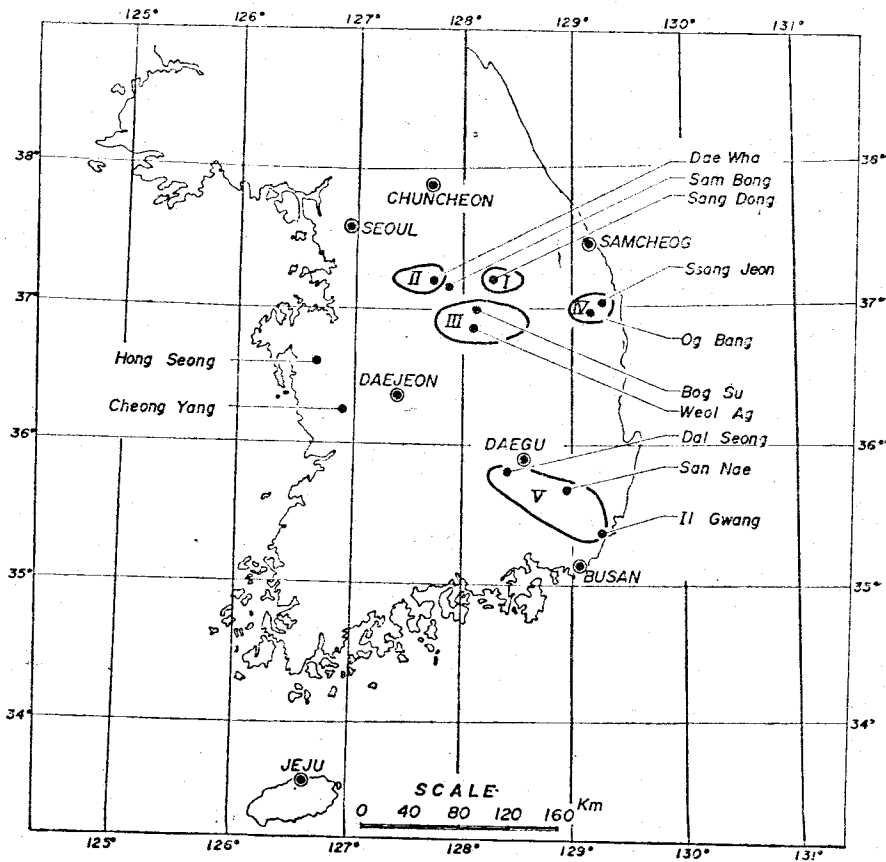


Fig. 1 Locality map of tungsten deposits including the five major tungsten provinces of the Republic of Korea. I = Sang Dong province; II = Dae Wha province; III = Dan Yang province; IV = Og Bang province; V = Gyeong Sang province (modified after Kim, 1971).

magnetic separation, first by a permanent magnet to remove magnetite and pyrrhotite, then by a Frantz isodynamic magnetic separator with variable magnetic flux. Final purification was accomplished by hand-picking under a high-power binocular microscope with the aid of an ultraviolet lamp. When the mineral series yielded two different fluorescence colours, the separation of the two was possible only with the aid of an ultraviolet lamp.

Since in comparative studies of trace elements only completely separated mineral grains can be successfully analyzed, portions of the prepared samples were mounted in araldite, and the polished and thin-sections were studied for any impurities. Microscopic observation confirmed that some unusually high Si contents (above 1%, in the case of two samples from the Weol Ag and Cheong Yang mines) were due solely to incomplete separation of quartz, which forms fine-grained intergrowths with the scheelite minerals.

### 2.1. Sample preparation

Quantitative trace analyses of all the treated samples were made for 18 elements by Grating Spectrography using the following procedures:

In order to get better burning conditions so called buffer was mixed for 30 minutes in an agate mortar and Wig-L-Bug for each pulverized sample in a weight ratio of 1:1. The buffer was composed of specpure carbon powder SP-3 and specpure NaCl in a weight ratio of 1:1. An internal standard was added to the buffer. For this the compound  $\text{La}_2\text{O}_3$  was found to be suitable. A test of the samples for the element La was negative. Therefore specpure  $\text{La}_2\text{O}_3$  (0.2 wt. % La) was added to the buffer as an internal standard.

30mg of each sample mixed with buffer (+internal standard) was loaded into sample electrodes and covered with graphite powder SP-2. To avoid spattering during burning each loaded

sample electrode was ignited in an electric furnace at 800°C.

Three analyses were made of each sample. If these results varied, more analyses were done.

### 2.2. Standards

The base substance of the standards consisted of specpure  $\text{CaCO}_3$  and  $\text{WO}_3$ . This was then mixed with the relevant specpure elements (such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{MnCO}_3$ ,  $\text{PbO}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{MoO}_3$ ,  $\text{SnO}$ ,  $\text{As}_2\text{O}_3$ ,  $\text{Ag}_2\text{O}$ ,  $\text{SrCO}_3$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$ , and  $\text{Bi}_2\text{O}_3$ ) in a concentration of 5,000ppm each. Further addition of the base substance resulted in a lowering of the concentration of the interesting elements.

Each standard was also mixed with buffer in a ratio of 1:1 and burned at least 10 times (with a 7 step neutral filter). From the intensity ratios obtained for each standards the mean values were determined and the working curves were drawn up.

This base substance was added to the standard until the analytical elements could just barely be recognized photometrically and supplied "blind values". The detection limit could then be determined.

### 2.3. Experimental apparatus and conditions

Excitation system:

Source unit	Jarrell-Ash Standard Varisource
Sample electrode	National SPK L-3703 (anode)
Counter electrode	National SPK L-3751
Analytical gap	$\pm 4\text{mm}$
Input voltage	220 Volt
Arc current	11A (DC)
Preburn time	2 sec.
Exposure time	45 sec.
Atmosphere	25ft <sup>3</sup> /hr of 1:4 $\text{O}_2$ -Ar mixed gas

Optical system:

Spectrograph	Jarrell-Ash 1.5 meter Wadsworth Grating Spectrograph
Grating	15,000 grooves/inch; reciprocal linear dispersion 5.4 Å per min. in second order
Slit width	25 microns

Filter	Seven step neutral filter
Analysis film	35mm Eastman Kodak SA-1 film
Developing conditions:	
Development	Eastman Kodak D-19 at $\pm 24^\circ\text{C}$ for 2 min.
Stop	Kodak step bath for 30 sec.
Fixing	Eastman Kodak Rapid Fixer at $\pm 24^\circ\text{C}$ for 10 min.
Washing	Running Water for 10min. and distilled water for 1 min.
Drying	Warm air for 4 min. Cold air for 5 min.

#### 2.4. Photometry, calibration and calculation

The spectral plates were evaluated photometrically with the Jarrell-Ash console microphotometer (slit width  $15\mu$ , slit height 0.5 mm, scanning rate  $2.5\text{\AA}/\text{min.}$ , 15 times enlargement of the film plate). In the most favorable blackness area and filter step the densities of the

Tab. 1 Analytical lines used (after Harrison 1939, and Meggers, Corliss and Scribner 1961)

Element	Analytical lines ( $\text{\AA}$ )	Detection limit (ppm)
Al I	3092.713	1
Bi I	3067.716	1
Fe I	3020.640	1
Si I	2506.899	1
Mg II	2802.695	1
Sn I	3262.328	1
Pb	2802.003	1
Mn	2801.064	1
Mo	3132.594	1
Cu I	3273.962	1
	2824.369	1
Sr II	3464.570	1
Cr I	4254.346	1
Y II	3600.734	1
Ag I	3280.683	1
Ti II	3234.516	1
Ni I	3003.629	10(*1)
As I	2349.840	50(*1)
Yb	3987.994	
La II	3245.120	int. standard

\* Analyzed by A. A. method and colorimetry.

analytical lines and the internal standard lines, as well as the background, were read.

The logarithmic intensity ratios ( $I_{\text{elem.}}/I_{\text{La}}$ ) from the blackness values were computed in the conventional manner (with background correction) on a Jarrell-Ash calculating board using emulsion calibration curves obtained by 7-step sector method. The concentration could be determined from the working curves drawn up for each element.

Each plate was supplied with a narrow Fe-spectrum. The relative standard deviations ( $s/\bar{x}$ ) were 0.25 for Al, Bi, Fe, Si, Mg, Sn, Pb, Mn, Mo, Cu, Sr, Cr, Y and Ag, and 0.35 for Ti, Ni and As.

The ppm-values shown in the Table 3 are mean values of 3 or 5 analyses each, which were read in the 1st., 2nd., 3rd., 4th., 5th., or 6th. step. The percentages refer to the weight of each sample.

Because Ni and As show higher detection limit 10 and 50 ppm respectively, they were analyzed again by atomic absorption spectrophotometric method (Perkin-Elmer 303 model) and by colorimetry.

### 3. Parageneses of the scheelite-bearing deposits

The scheelite-powellite series in Korea occurs in various kinds of mineral deposits, including hydrothermal veins, pegmatites and contact-metasomatic bodies. The paragenetic relations in these deposits in the light of mineral associations are discussed below.

#### 3.1. Hydrothermal vein deposits

Hydrothermal vein deposits are found in granitic intrusives and some extends into host metamorphic rocks. The veins vary from a few cm to 2m in thickness and up to about 1km in length. Mineralogy is simple: quartz and K-feldspar are the essential associates irrespective of the nature of the wall rock, and may be

accompanied by one or more of muscovite, biotite, plagioclase, sericite, tourmaline, pyrrhotite, apatite, calcite, chalcopyrite, sphalerite, wolframite, cassiterite, zircon, bornite, bournonite, magnetite and pyrite, in order of decreasing abundance.

Scheelite is generally subhedral and coarse-grained, although in some cases it may be only a fraction of a mm in size. The fluorescence colour of scheelite from the hydrothermal veins is very variable, ranging from white to willow-green. Occasionally in these deposits, the scheelite occurs in two different fluorescence colours within a single specimen, indicative of compositional differences and at least of a two-stage process of mineralization—in which the later formed mineral is richer in molybdenum than the earlier one. The scheelites with different fluorescence colours occur either as separate grains or as overgrowths. In many tungsten deposits of this type, scheelite and wolframite are found together, but there are no features to show whether or not they crystallized contemporaneously. In the case of the Il Gwang breccia pipe and the San Nae vein deposit, scheelite is clearly replaced by wolframite along its (111) cleavage plane. The scheelite occurs at the Weol Ag and Cheong Yang mines in weakly greisenized granitic rock. The scheelite minerals were probably disseminated in the granitic rock at the deuteric stage. At the Dae Wha and San Nae mines, the amount of scheelite increases with depth. The types of wall-rock alteration in the hydrothermal tungsten deposits include: greisenization, sericitization, carbonitization, chloritization, kaolinitization and skarnitization.

### 3.2. Pegmatite veins

The scheelite-bearing pegmatite of the Ssang Jeon mine is a quartz-rich dike of variable thickness (2 to 15 m) in Precambrian gneiss. Scheelite content increases with depth in the

ore body. The scheelite is associated with quartz, coarse-grained wolframite (1 to 5 cm), sodic plagioclase, K-feldspar, muscovite, and minor accessories. The rock is nearly devoid of sulfides.

The scheelite-bearing pegmatites of the Og Bang mine are always enclosed in schistose amphibolites which form a belt 2 to 3 km in length and about 1 km wide. The individual amphibolite bodies are usually several hundred m long and up to 50 m thick, and within these the pegmatite has a wide range of thickness, from a few cm up to 2 m. The pegmatites are mainly composed of albite, with some oligoclase, biotite, hornblende and quartz, and local development of orthoclase and tourmaline. No scheelite-bearing pegmatite veins have been found in the Precambrian gneisses which surround the amphibolite. According to Lee (1967), higher concentrations of scheelite commonly occur in lenticular form and also as pockets or stringers within the middle parts of thicker pegmatites. Lower concentrations or a complete absence of scheelite is characteristic of the marginal zones of the veins. Disseminated scheelite can also be recognized in the pegmatite and in the marginal zones close to the amphibolite/pegmatite contact. This disseminated material is not economically significant. The scheelite content tends to increase where coarse-grained biotite, hornblende and fluorite are abundant. Bismuthinite is present only when scheelite is abundant. According to So and Kim (1975), all the chemical features of the amphibolites indicate that they are formed from igneous progenitors.

### 3.3. Contact-metasomatic deposits

The tungsten deposits of this type are the pyrometasomatic scheelite deposits. They are characterized by tactite of complex mineralogy formed by contact-metasomatism of carbonate rocks. The major minerals in the tactites which

contain members of the scheelite series are garnet group minerals, pyroxene of the diopside-hedenbergite series, and epidote group minerals, in addition to quartz. These minerals vary in relative abundance even from site to site within the same mine.

The scheelite from tactites varies in grain size from a few  $\mu$  to a few cm, and in crystal habit from euhedral to anhedral. The scheelite is particularly enriched in contact areas, which consist of quartz, calcite and metal sulfides. In contact-metasomatic deposits scheelite minerals are not associated with wolframite.

The ore deposits of the Sang Dong mine, which occur in six laterally extensive but relatively thin beds within the Lower Paleozoic Myobong Formation, are stratabound and genetically related to basic metavolcanic layers interbedded with metapelitic strata (So, 1968). The ore-bearing beds differ from the normal metapelitic strata of the Myobong Formation in that they contain abundant amphibole whose content varies with the abundance of scheelite and titanium minerals, and have high cobalt, nickel and beryllium contents. The ore-bearing units also contain small amounts of pyrrhotite, pyrite, bismuthinite, native bismuth, ilmenite (mostly altered to titanite and rutile), magnetite, joseite ( $\text{Bi}_4\text{Te}_2\text{S}$ ), chalcocopyrite, molybdenite, sphalerite, wolframite and, more rarely, arsenopyrite, galena, hematite, siderite and hauchecornite. The genesis of the Sang Dong tungsten ores is still controversial.

The mineral associations of hydrothermal veins, pegmatites and contact-metasomatic deposits containing scheelite are listed in Table 2.

#### 4. Factors controlling trace-element content of scheelites

In this paper variations in the contents of trace impurities in scheelite are taken as a basis for considering the factors influencing the che-

Tab. 2 Mineral associations in various scheelite-bearing deposits

Mineral	Major (>20%)		Minor (20~5%)		Accessory (5~1%)		Trace (<1%)	
	○	●	○	●	○	●	○	●
Amphibole	—	—	—	1	—	—	—	—
Apatite	—	—	—	—	2	—	2	—
Biotite	1	—	1	—	1	—	—	1
Calcite	—	1	—	—	2	1	—	—
Chlorite	—	—	1	—	—	1	2	—
Epidote	—	—	—	1	—	1	—	—
Fluorite	—	—	—	—	2	—	—	—
Garnet	—	—	—	2	2	—	—	—
K-feldspar	4	—	1	—	2	1	—	—
Monazite	—	—	—	—	—	1	1	—
Muscovite	2	—	3	—	—	1	—	—
Plagioclase	1	—	3	—	—	1	—	—
Pyroxene	—	—	—	2	—	—	—	—
Quartz	7	—	1	2	—	—	—	—
Sericite	2	—	2	—	3	—	—	—
Titanite	—	—	—	—	—	1	—	—
Tourmaline	—	—	1	—	—	—	2	—
Zircon	—	—	—	—	—	—	2	—
Arsenopyrite	—	—	—	—	—	—	1	1
Native-bismuth	—	—	—	—	—	—	—	—
Bismuthinite	—	—	—	—	—	—	—	—
Bornite	—	—	—	—	—	—	1	—
Bournonite	—	—	—	—	—	—	1	—
Cassiterite	—	—	—	—	—	—	1	—
Chalcocopyrite	—	—	—	—	2	—	2	2
Galena	—	—	—	—	—	—	1	—
Geothite	—	—	—	—	—	—	1	—
Hematite	—	—	—	—	—	—	—	—
Ilmenite	—	—	—	—	—	1	—	—
Joseite	—	—	—	—	—	—	—	—
Magnetite	—	—	—	—	—	—	—	1
Marcasite	—	—	—	—	—	—	—	—
Molybdenite	—	—	—	—	1	—	1	—
Pyrite	—	—	—	—	3	1	1	—
Pyrrhotite	—	—	1	1	—	1	—	1
Rutile	—	—	—	—	—	—	—	1
Siderite	—	—	—	—	—	—	—	—
Sphalerite	—	—	—	—	1	—	1	—
Wolframite	—	—	—	—	2	—	2	—

○=in hydrothermal veins and pegmatites; ●=in contact-metasomatic deposits. The numbers in the Table signify the number of deposits in which the mineral was found.

mical composition of the mineral series.







The quantitative analyses show that the scheelites are rich in trace impurities. As shown in Table 3, large amounts of Si, Sr, Mg, Fe, Al, Y and Mn constantly occur, in addition to small amounts of Mo, Cr, Pb, Cu and Yb, frequent concentrations of Bi, Ag, Ti and Sn, and scattered occurrences of Ni and As; As was only found at two localities and Ni at five localities. None of the elements shows a systematic variation in concentration with the modes of occurrence of the scheelite series.

#### 4.1. Relation between genetic type, host rock composition and trace impurities in scheelite

Figure 2 presents the median values and variation ranges of each element in scheelites of different genetic types. The variation range of most elements in scheelites from hydrothermal vein deposits is the greatest (in ppm, Al: 11-680, Bi: 0-530, Fe: 15-620, Si: 2-17000, Mn: 13-420, Pb: <1-600, Sn: 0-400, Mo: <1-25000, Sr: 320-4200, Y: 11-280), followed by

pegmatite veins (in ppm, Al: 125-580, Bi: <1-350, Fe: 94-540, Mn: 46-220, Pb: <1-14, Sn: 0-27, Sr: 40-2600); contact-metasomatic deposits have the smallest range (in ppm, Al: 84-190, Bi: 0-16, Fe: 190-280, Mn: 10-70, Pb:  $\leq 1$ , Sn: 0, Sr: 1100-1350). Silver, titanium, nickel and arsenic occurred in such small amounts or so sporadically that it was hard to recognize ranges. Nickel and arsenic were detected only in scheelites from hydrothermal and pegmatite deposits. The tendency to have a larger amount of Y (0.1 to 0.3%) in the scheelite-powellite series from hydrothermal deposits than in these from deposits of other origins (Hsu and Galli, 1973) is not clear in the studied scheelites; they have much smaller amounts of Y, always <280ppm.

The quantitative relationships of the trace elements in the scheelite minerals were represented in the form of triangular diagrams. In order to show the contrasts between the relationships obtained, the very small amounts of

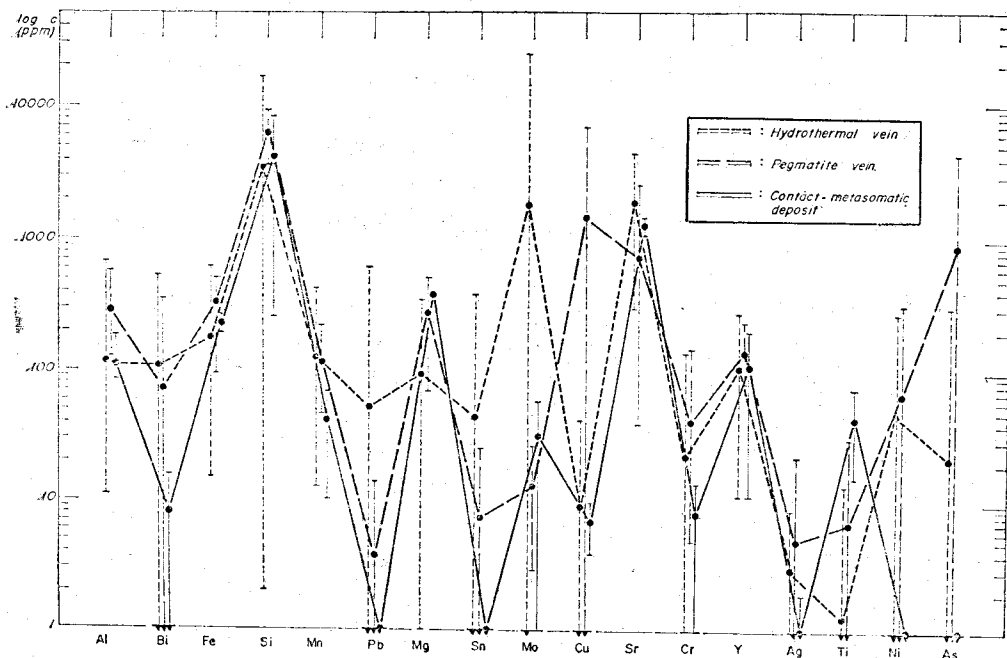


Fig. 2 Proportions and variation ranges of elements in scheelites from hydrothermal, pegmatitic and contact-metasomatic deposits (A black triangle above the element symbol signifies the detection limit).

copper and lead were multiplied by 10 and the values obtained were added to the amounts of the remaining elements in the triad and converted to 100. This gave coordinates of the points on the three component diagrams (Fig. 3): Mn-Y-Mg and Mg-10Cu-10Pb.

The element combinations of the samples from pegmatite veins and contact-metasomatic deposits remain within a limited area shown in the diagrams, whereas samples from hydrothermal veins have a much wider compositional variation. In Figure 3a (Mn-Y-Mg) the values for samples from pegmatite and contact-metasomatic

deposits are concentrated in the Mg corner (Mn: 10-220ppm, median of seven analyses 98ppm; Y: 11-240ppm, median 126ppm; Mg: 72-530ppm, median 310ppm). In Figure 3b (Mg-10Cu-10Pb) they occupy the Mg corner with one exception (Mg: 72-530ppm, median of six analyses 326ppm; Cu: <1-10ppm, median 5ppm; Pb: <1-14ppm, median 4ppm). All the other combinations of the trace elements detected in the studied samples show no numerical relationships with the type of geologic occurrence.

For a definite chemical characterization in terms of metallogenic epoch and ore province,

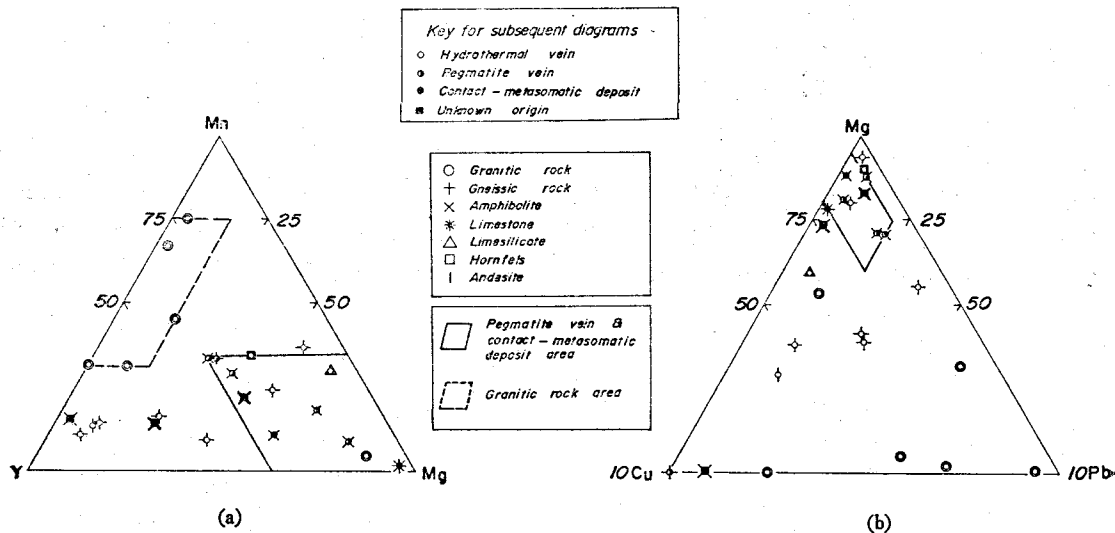


Fig. 3 Trace-element combination of the studied scheelite specimens of different geneses and with different host rocks.

the number of specimens studied is probably too small, but all that were available were collected.

Scheelites from similar geologic conditions show a characteristic combination of the elements plotted in the triangular diagrams, but because of the small number of samples, it was difficult to evaluate the genetic significance of individual trace-element combinations.

The effects, if any, of the country rocks on the trace impurities of scheelites are not clearly detected, except that scheelite minerals in granitic rocks seem to have a characteristic

combination of trace elements. (Fig. 3a, Mg: 1-96ppm, median of five analyses 35ppm; Mn: 65-420ppm, median 214ppm; Y: 100-280ppm, median 167ppm). The grain size of the scheelite minerals appears to be unrelated to trace-element content.

#### 4.2. Relation between fluorescence colour of scheelites and genetic types

The scheelite minerals from the hydrothermal deposits have a wide variation of molybdenum content (<1-25000ppm) and generate nearly all of the fluorescence colours shown by the speci-

mens studied. Those from pegmatite veins are white to pale-yellow (Mo=3-25ppm), except for the Ssang Jeon mine, and those of contact-metasomatic origin are pale-yellow (Mo=1-62ppm) (Fig. 4).

**4.3. Effect of trace impurities on fluorescence and natural colour of scheelite**

Under normal lighting conditions, scheelite is difficult to distinguish from its host rock. Its fluorescence permits immediate recognition and practically positive identification. The fluorescence of scheelite has been an important aid in the exploration for, and development of, schee-

lite deposits. Widespread use of the ultraviolet lamp for scheelite prospecting has aroused interest in the variations in fluorescence colours displayed by the mineral. Fluorescence colours of the specimens studied were obtained with a UVS-11 short-wave ultraviolet lamp which produces 220 microwatts/cm<sup>2</sup> of 2537Å radiation at a distance of 6 inches. The classification of colours was made by simultaneously viewing and comparing of all the finely prepared samples with the same lamp in total darkness.

The factors of determining whether or not a substance will fluoresce have not been satisfact-

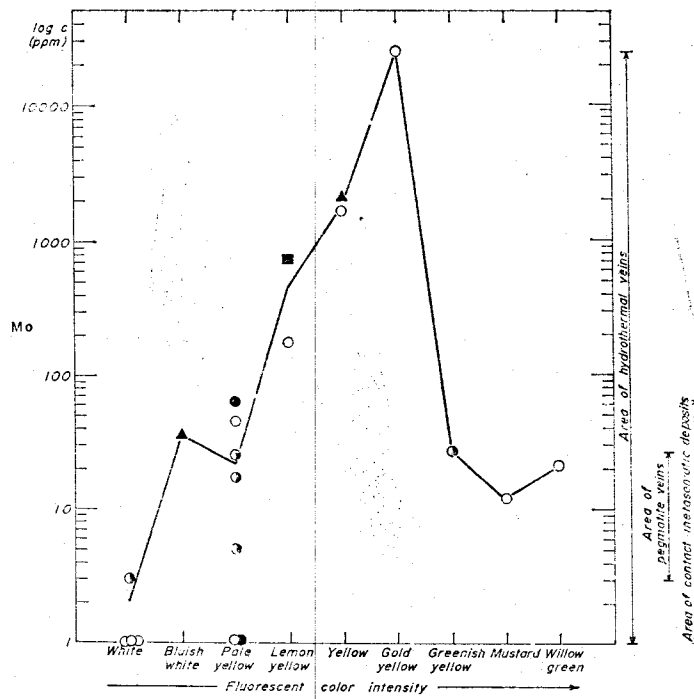


Fig. 4 Relation between molybdenum content and fluorescence colour of scheelite.

orily established, but prevailing opinion is that fluorescence is due to the type and quantity of trace elements. Studies with artificial compounds have shown that certain elements in minute quantities induce fluorescence, but equal quantities of other elements may be detrimental to fluorescence (Vanderwilt, 1946).

A wide range of fluorescence colours, from white through yellow to green, for the twenty five scheelite specimens studied were correlated with their chemical composition in order to afford some quantitative basis for estimating the effects of the trace impurities on fluorescence colour. In Figures 4 and 5, the measured

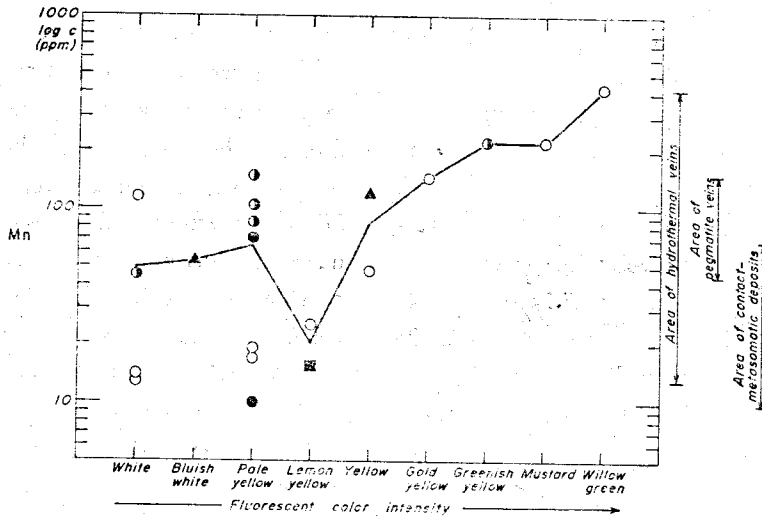


Fig. 5 Relation between manganese content and fluorescence colour of scheelite.

amounts of molybdenum and manganese are plotted against the fluorescence colours of the samples studied, and the resulting curve is based on the weighted average intensity for each fluorescence colour. The increase in the molybdenum content of the scheelite as fluorescence changes from white to golden yellow is striking and apparently significant, except for pale-yellow and greenish colours. The minerals with pale-yellow fluorescence colour show a large range in molybdenum content, and in all but one of the white samples molybdenum is completely absent. The manganese content (Fig. 5) shows

a general trend paralleling that of molybdenum, but here no exceptions for greenish colour were noted. The change in fluorescence colour caused by <math><1\text{ to }25000\text{ ppm}</math> molybdenum and by 13 to 420 ppm manganese is quite marked, whereas under ordinary light the materials usually look identical. The presence of all other elements apparently does not affect the fluorescence. The approximate molybdenum and manganese contents of scheelite can be determined by matching its fluorescence colour with the above results. The effect caused by copper content, suggested by Greenwood (1943), was not apparent.

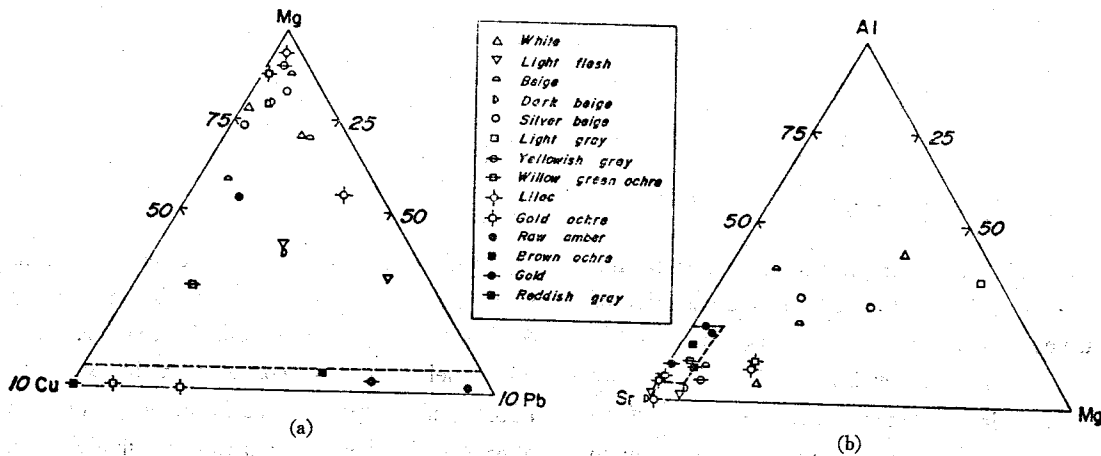


Fig. 6 Correlation between colour and trace-element combination of the studied scheelite specimens.

The diagrams of combinations of Mg-10Cu-10Pb (Fig. 6a) and Al-Sr-Mg (Fig. 6b) show the effects of trace elements on natural colours of scheelite minerals. In Figure 6a the values of the element combination of the specimens that have deeper intensity than lilac are on the Cu-Pb side, with two exceptions (Mg: 1-210 ppm, median of six analyses 57ppm; Cu: 12-7200 ppm, median 1221 ppm; Pb: 1-600 ppm, median 112 ppm). In Figure 6b they are concentrated on the Al-Sr side in the Sr corner, with one exception (Al: 18-680ppn, median of seven analyses 193 ppm; Sr: 360-2650 ppm, median 1177 ppm; Mg: 1-210 ppm, median 56 ppm).

#### 4.4. Relation of trace elements in scheelites with depth

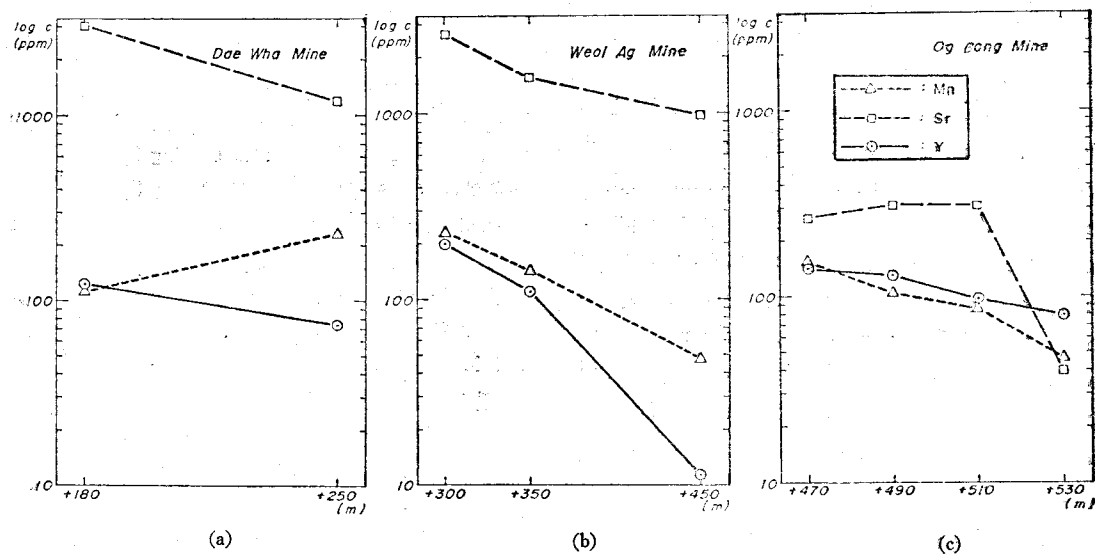


Fig. 7 Relation of selected trace-element contents in scheelites to depth, in m above sea level.

#### 5. Conclusions

Twenty five samples containing members of the scheelite-powellite series from twelve Korean tungsten deposits of various geological settings were collected for mineralogical and geochemical studies. The scheelite series occurs predomi-

Goldschmidt and Peters(1933) have suggested that the germanium content of sphalerite is related to the depth of vein formation. Among all the trace elements detected in Korean scheelites, three elements, manganese, strontium and yttrium, show a general tendency to decrease upwards in ore bodies from different geologic settings, defined in terms of their metallogenic epochs and provinces—the Weol Ag and Dae Wha hydrothermal veins and the Og Bang pegmatite. However, in two cases, the Og Bang and Dae Wha deposits, strontium and manganese show a slight upwards increase (Fig. 7). More study on the depth control of these trace-element contents is required before firm conclusions can be reached.

nantly in hydrothermal veins in Korea, but is also found in contact-metasomatic deposits and in pegmatites.

Spectrochemical analyses (elements in order of abundance: Si, Sr, Al, Mg, Fe, Y, Mn, Mo, Cr, Pb, Cu, Bi, Ag, Ti, Sn, Ni, As and Yb) showed that scheelite is very rich in trace

impurities. Large amounts of Si, Sr, Mg, Fe, Al, Y and Mn constantly occur, in addition to small amounts of Mo, Cr, Pd, Cu and Yb and frequent concentrations of Bi, Ag, Ti and Sn, and scattered occurrences of Ni and As. The chemical behavior of the trace impurities during the crystallization of scheelite minerals under various geologic conditions is shown by their concentration and the varying ratios of the characteristic impurity elements.

The variation ranges of the trace elements in scheelite from hydrothermal vein deposits is the greatest, and is followed by those in pegmatite veins, with contact-metasomatic deposits having the smallest range.

Scheelites from deposits of the same genetic type and, to some extent, with the same host rocks show a characteristic combination of the trace elements, as shown on triangular diagrams (Fig. 3).

The molybdenum contents of the scheelites increase from a trace ( $<1\text{ppm}$ ) in those specimens fluorescing white to a maximum (2.5%) in material with golden yellow fluorescence. Manganese acted in a similar manner without exception; the other elements showed no systematic variation. There are some clear relations between fluorescence colour of scheelites and genetic type. The trace elements in scheelites can also affect their natural colour.

Among the trace elements in the scheelites studied, manganese, strontium and yttrium show a characteristic tendency to decrease upwards at shallower levels in hydrothermal and pegmatite veins from different geologic settings. This depth control of trace elements should be closely examined for use in prospecting.

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### 한국산 灰重石鑛의 광물학적, 지화학적 연구 및 그의 探査에의 이용

#### 요 약

한반도 내에 부존되고 있는 중석광상들은 세 주요한 Metallousenetic Epoch (Pre-Cambrian E., Jurassic-early Cretaceous E., 및 late Cretaceous-early Tertiary E.)에 생성되었고 성인적으로 열수작용과 접촉교대작용에 기인된다고 보고되었다. 이중 12개 광상(달성, 산내, 일평, 상동, 대화, 월악, 복수, 옥방, 정전, 홍성, 삼봉, 청양)을 본 연구의 대상으로 택하고 각 지역에서 채취한 표품중 모두 25개 시료에 대하여 지화학적 실험을 수행하였다.

즉 각 분쇄된 시료(-80 + 120mesh)는 super panner, 증액, isodynamic separator, UV lamp를 이용한 물리적인 처리과정을 거쳐 최종으로 입체현미경 하에서 단체분리된 후 Jarrell-Ash 1.5m Grating Spectrometer를 이용하여 본 연구대상 시료로 개발한 Spectrochemical method (Carrier: NaCl, Internal standard:  $\text{La}_2\text{O}_3$ )로 정량 분석되었다.

본 연구에서 밝혀낸 국내 회중석 광내에 함유되는 희유 원소의 종류는 모두 Al, Bi, Fe, Si, Mn, Pb, Mg, Sn, Mo, Cu, Sr, Cr, Y, Ag, Ti, Ni, As, Yb의 18개 원소이며, 이들은 각각의 절대적 및 상대적인 함량과 각 광화작용의 시기, 광상의 성인, 모암, 각 원소의 mobility 그리고 회중석광의 형광색 및 육안색과 비교 검토되었다.

본 연구의 결과로 회중석광이 정출되는 과정에서 유사한 지질환경의 물리화학적인 여건이 이루어지면 그 내에 함유되는 몇 성분원소들의 화학적인 특성은 매우 유사성을 보여주는 typochemical habit를 가짐을 알 수 있었다.

본 연구에서 밝혀진 한국산 회중석 광내의 稀有成分으로서 Y, Mn, Sr 원소들의 Geochemical mobility의 特性은 앞으로 회중석광의 심도탐광을 위하여 고려되어야 하고, 더욱 연구개발되어야 할 것이다. 또한 상기 회중석 광내의 물리적 및 화학적으로 결합되어 있는 불순물의 희유성분들은 선광 제련 과정에서 금속성분

의 추출농집工程에 유용한 자료가 될 것이다.

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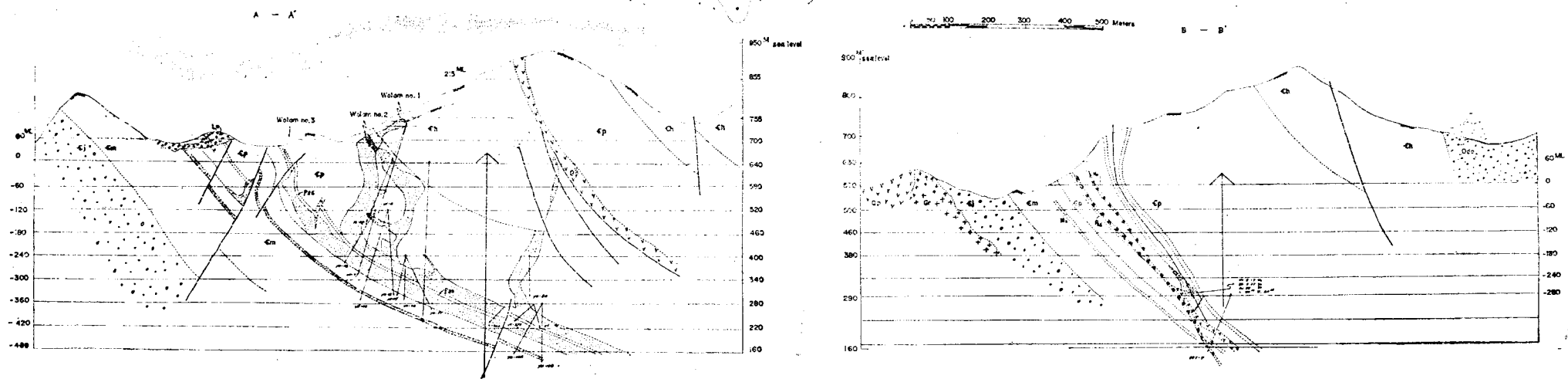
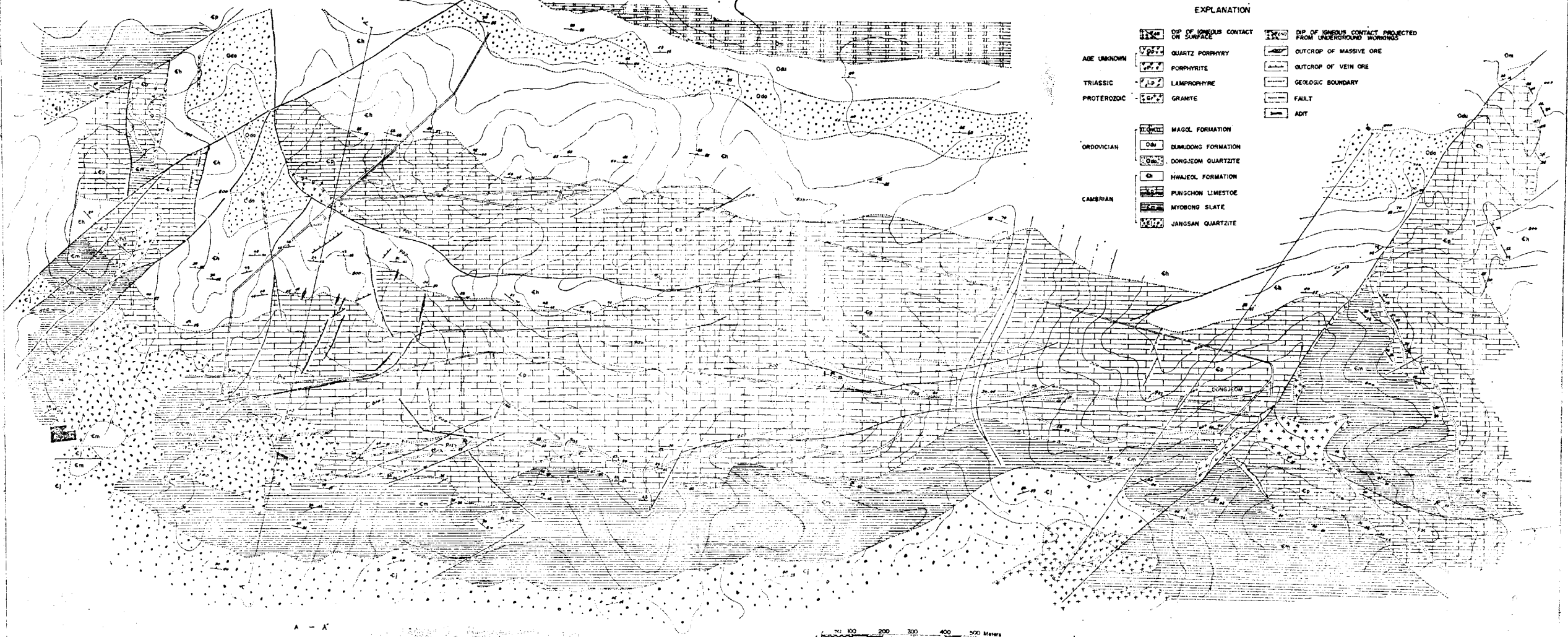
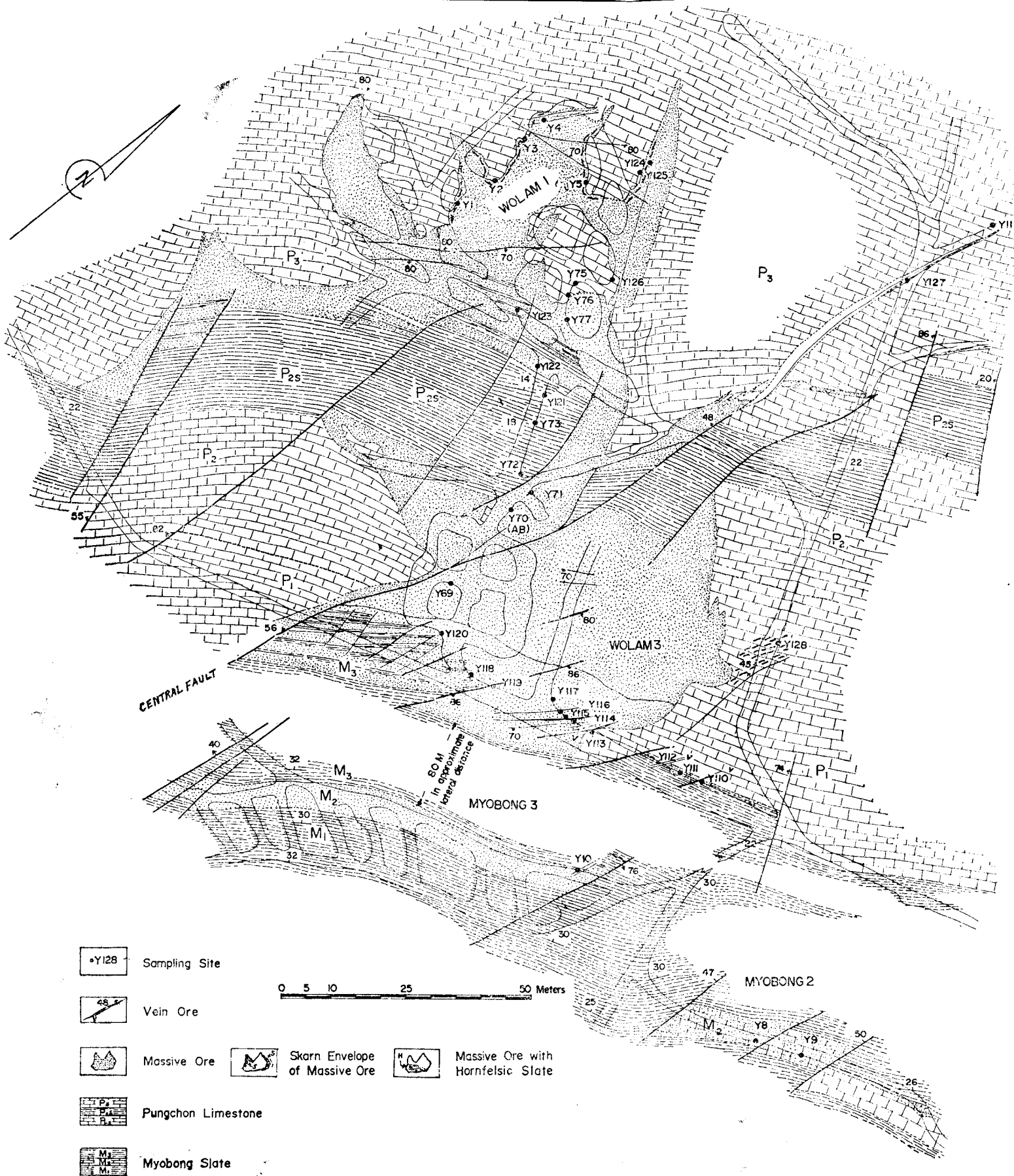


Plate. 3 Geologic map and sections of the Yeonhwa I mine area














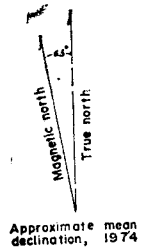
-  Sampling Site
  -  Vein Ore
  -  Massive Ore
  -  Skarn Envelope of Massive Ore
  -  Massive Ore with Hornfelsic Slate
  -  Pungchon Limestone
  -  Myobong Slate
- 0 5 10 25 50 Meters

Plate. 5 Plan map. Wolam 1 and 3 orebodies, Yeonhwa I mine



- |  |                         |
|--|-------------------------|
|  | ASL                     |
|  | 165 <sup>L</sup> (805M) |
|  | 115 (755)               |
|  | 60 (700)                |
|  | 0 (640)                 |
|  | -60 (580)               |
|  | -120 (520)              |
|  | -180 (460)              |
|  | -240 (400)              |
|  | -300 (340)              |
|  | -360 (280)              |
|  | Banwol Ore Body         |
|  | Eesec Ore Body          |
|  | West No 1,2-Ore Body    |
|  | East No 1,2-Ore Body    |
|  | Hangang No 1,2-Ore Body |
|  | Walam No 1,2-Ore Body   |
|  | Namsan No 1,2-Ore Body  |

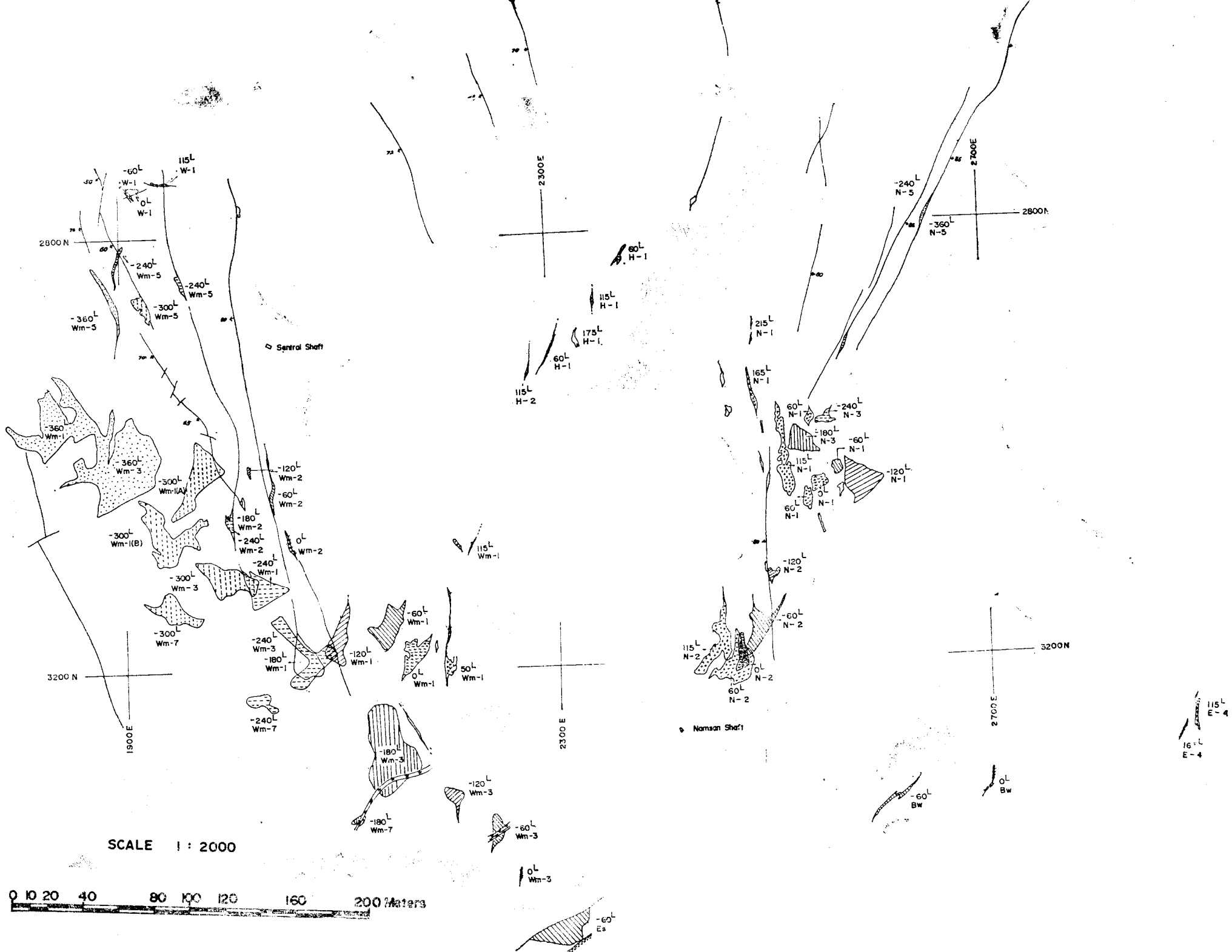


Plate. 4 Composite plan view of the Yeonhwa I mine orebodies

Tab. 3 Age and characteristics of major tungsten deposits studied and trace-element contents in scheelites from these deposits

Metallogenic epoch	Metallogenic province	Genetic type	W-deposits <sup>1)</sup>	Country rock	Wall rock <sup>2)</sup> alteration	Colours		Grain size (cm)	Al		
						Fluorescence	Natural				
Late Cretaceous to early Tertiary epoch	Gyeong Sang province	Hydrothermal vein (stockwork)	Dal Seong	Altered andesite	ser.	lemon yellow	willow green ochre	1.0—2.0			
		Hydrothermal vein (fissure filling)	San Nae	Biotite granite	kao., ser.	gold yellow	raw amber	0.3—0.5	1		
		Hydrothermal vein (breccia filling)	Il Gwang (1) (2) (3)	Granodiorite	"	"	willow green	brown ochre	0.1—0.3	1	
							white+dark yellow	gold ochre	0.5—2.0		
							mustard	gold	0.5—1.0	9	
							yellow	silver beige	0.01—0.5	17	
Jurassic to early Cretaceous epoch	Sang Dong province	Controversial	Sang Dong	Amphibolite		bluish white	silver beige	"	13		
	Dae Hwa province	Hydrothermal vein (fissure filling)	Dae Hwa (1) (2)    "	Granitic gneiss	"	white	dark beige	2.0—2.5	14		
						white+gold yellow	liiac	"	14		
						white	dark beige	"	1		
						"	white+raw amber	"	1		
						pale yellow	light flesh	"	2		
						white	lilac	"	1		
						white+yellow	raw amber	<0.1	68		
	Dan Yang province	Hydrothermal vein (fissure filling)	Weol Ag (1) (2) (3)	Granite Hornfels Limesilicate	"	white+dark yellow	yellowish gray	<0.1	9		
						yellow	beige	0.1—0.3	9		
						white	raw amber	<0.1	68		
	Precambrian epoch	Og Bang province	Contact-metasomatic deposit	Bog Su	Limestone	ska.	pale yellow	white	0.3—1.0	8	
			Pegmatite vein	Og Bang (1) (2) (3) (4)	Amphibolite	"	"	pale yellow	white	1.0—3.0	58
								pale yellow	beige	"	12
pale yellow								beige	"	22	
white								light gray	"	25	
Pegmatite vein			Ssang Jeon	Gneiss	ser.	greenish yellow	reddish gray	<0.1	28		
Unknown epoch				Contact-metasomatic deposit	Sam Bong	Amphibolite	cab., ska.	pale yellow	gold ochre	0.2—0.5	19
				Hydrothermal vein (fissure filling)	Cheong Yang	Granite	gre., ser.	white+dark yellow	light flesh	0.2—0.5	9
	U nknown	Hong Seong		Amphibolite		lemon yellow	gold ochre	0.1—0.3	2		

1) In column four—Specimens denoted thus: 1, 2, 3, 4 are collected at different depths (4→1 deepest). All other specimens are collected according to color.

2) Wall rock alteration: cab.=carbonitization, chl.=chloritization, gre.=greisenization, kao.=kaolinitization, ser.=sericitization, ska.=skarnization.

3) Yb: only relative determination (+<+<+<+<+).

4) Main associated minerals: (shown in order of abundance) Ar=arsenopyrite, Bi=native bismuth, Bis=bismuthinite, Bo=bornite, Bou=bournonite, Ch=chalcopyrite, Ga=galena, Ge=geothite, Il=ilmenite, Jo=joseite, Ma=magnetite, Mo=molybdenite, Py=pyrite, Pyr=pyrrhotite, Ru=rutile, Sp=sphalerite, Wo=wolframite.

Grain size (cm)	Minor and trace elements (ppm)																			Main associated minerals <sup>4)</sup>	By-product
	Al	Bi	Fe	Si	Mn	Pb	Mg	Sn	Mo	Cu	Sr	Cr	Y	Ag	Ti	Ni	As	Yb <sup>5)</sup>			
1.0-2.0	38	—	140	60	25	<1	20	—	170	4	320	12	145	2	—	—	—	++	Ch, Py, Bo	Au, Ag, Cu, Fe	
0.3-0.5	145	—	91	2,300	145	1	46	—	25,000	3	600	28	280	3	—	—	—	++	Ch, Py, Ma, Il	Ag, Au, Pb, Zn	
0.1-0.3	110	80	370	4,100	420	26	24	10	21	17	610	140	118	3	—	—	320+	+	Pyr, Py, Ch, Sp, Ge, Ga, Bou	Mo, Cu, Pb, Zn	
0.5-2.0	18	3	230	2,050	65	14	1	—	<1	42	360	4	138	4	—	—	—	+	"	"	
0.5-1.0	94	28	250	2,900	210	30	9	—	12	12	1,000	22	100	7	—	—	—	+	"	"	
0.01-0.5	170	130	340	6,600	120	1	240	—	1,800	8	220	14	180	3	41	—	—	++	Pyr, Py, Bis, Bi, Il, Mg, Jo, Ch, Mo, Sp, Wo, Ar, Ga,	Mo, Bi	
"	135	105	150	2,700	54	1	100	3	35	1	235	12	230	2	—	—	—	+++	"	"	
2.0-2.5	140	1	160	170	115	2	240	400	<1	4	3,100	1	118	2	—	—	—	+++	Ch, Py, Mo, Bi	Au, Ag, Cu, Pb, Mo	
"	145	—	185	1,500	230	<1	340	250	10	<1	1,200	22	74	1	12	—	—	++	"	"	
"	16	1	17	4	14	1	13	6	<1	<1	3,500	2	75	2	—	—	—	+++	"	"	
"	11	—	15	6	19	1	30	—	42	4	2,900	1	67	5	—	—	—	++	"	"	
"	20	—	120	68	17	<1	14	—	<1	<1	2,150	25	125	2	—	—	—	+++	"	"	
"	15	66	30	2	13	4	58	4	<1	1	4,100	9	72	3	—	—	—	+++	"	"	
<0.1	680	480	620	14,000	230	600	96	—	2	36	2,650	4	200	9	—	—	—	+++	"	"	
<0.1	94	410	210	5,000	145	<1	190	—	3	<1	1,550	5	110	2	3	—	270	+++	Wo, Ch, Py, Sp, Mo, Ma	Au, Ag, Mo	
0.1-0.3	92	1	135	2,200	48	1	100	8	1,600	6	970	37	11	3	4	290	—	+++	Ch, Py, Ga		
0.3-1.0	84	16	190	250	10	1	380	—	62	10	1,100	1	11	2	78	—	—	+	Ch, Py		
1.0-3.0	580	3	500	9,000	150	14	530	—	17	8	260	12	125	—	—	—	—	—	Pyr, Ch, Py, Sp, Ar, Ma, Il, Ru	Zn	
"	125	<1	94	4,100	105	<1	145	6	25	<1	310	40	130	—	—	—	—	+	Ch, Py, Ar, Fl, Wo	F	
"	220	1	115	3,500	86	2	72	—	5	1	310	9	97	—	—	—	—	+++	"	"	
"	250	1	260	5,000	46	4	450	5	3	7	40	5	80	3	—	—	—	+	"	"	
<0.1	280	350	540	8,800	220	1	210	27	28	7,200	2,600	150	240	23	33	—	4,500	+++	Mo	Mo	
0.2-0.5	190	—	280	8,000	70	<1	380	—	1	4	1,350	14	200	—	16	—	—	+++	Ch, Py		
0.2-0.5	95	530	50	17,000	16	57	300	—	1	10	4,200	25	35	2	—	130	—	++	Wo, Py, Sp, Mo	Ag, Au, Pb, Zn, Fe	
0.1-0.3	26	290	91	24	15	2	3	—	780	20	420	14	76	3	—	68	—	+	Pyr, Py		