

# Mineral Chemistry of Cassiterite, Columbite, Tantalite and Associated Minerals from Soonkyoung Tin-bearing Pegmatite

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**Abstracts:** Cassiterite, tantalite, columbite and tantalite rutile are found as accessory minerals in Soonkyoung tin-bearing pegmatites. These minerals occur as finely disseminated specks of up to micro-size in diameter and coarse grain size varying from 0.5–50mm in albite, muscovite and quartz assemblage.

Cassiterite generally shows a moderate to intense pleochroism, having a color brownish yellow to deep reddish brown. The substitution of  $Ta^{+5}$ ,  $Nb^{+5}$ ,  $Ti^{+4}$  and  $Fe^{+2}$  for  $Sn^{+4}$  in cassiterite ranges 0.01–0.10 mol%. The zoned cassiterite give a higher Ta/Nb ratios in margin than the ratios in core. This is due to the preferential  $Ta^{+5}$  affinity to lower temperature during the crystallization of cassiterite.

Tantalite–columbite and tantalite rutile occur in cassiterite with exsolution texture and/or infiltrate into the micro-fissures of cassiterite with micro quartz vein. The compositions of tantalite–columbite show the wide ranges of  $Ta_2O_5$ : 14–46 wt.%,  $Nb_2O_5$ : 60–28 wt. % and  $FeO$ : 10.15 wt.%. The variation of chemical composition in tantalite–columbite exhibits the decreasing trends of  $Mn^{+2}/M^{+2}+Fe^{+2}$  with  $Ta^{+5}/Ta^{+5}+Nb^{+5}$  increasing. These trends of variations indicate that the Ta/Nb fractionation are enhanced by higher Ta-complex activity in late stage of pegmatite consolidation and lower activity of F in agreements with the F- and Li-micas not to be developed in Soonkyoung tin-bearing pegmatite.

## INTRODUCTION

The primary tin-bearing pegmatites such as those of Soonkyoung, Seongdeog, Gackhi mine in Sangdong area and Wangpiri, Samdeog, Jangjae mine in Ulchin area are spatially related to the Pre-Cambrian granite. In Sangdong area, pegmatites are widely distributed in the metasedimentary rocks of Yuli Series. Most of all the pegmatites are barren of tin but the pegmatites which are spatially close to the Nonggeori Granites and Naedeogni Granite of Pre-cambrian period are productive of tin.

Soonkyoung tin mine is located between the Naedeogni granite and Nonggeori Granite. Seongdeog tin mine is laid on the eastern extension part of Naedeogni Granite. Tin mineralization of the pegmatite in this area is closely related with Naedeogni Granite and/or its originated source rock.

Systematical geologic survey on this area was carried out drilling exploration on tin productive pegmatites to estimate of the ore reserves. Ore reserves are estimated about on e million tons containing 0.35 wt.%  $SnO_2$  and 300 ppm Ta+Nb (Kim and Park, 1986).

Tin and Ta–Nb minerals are developed within Soonkyoung Pegmatite, associating with the albitization and greisenization of the pegmatite. Though surface geology, occurrence and tenor of ore is clear, detailed mineral chemistry and the mechanism of ore formation are in doubt. The primary purpose of this paper is to describe the characteristic occurrences, chemical composition of tin and associated Ta–Nb minerals and is to infer the possible role of the chemical fractionation of Ta–Nb minerals to the mineralization of tin from Soonkyoung tin-bearing pegmatites.

## GEOLOGICAL SETTING

The geology of the area consists of Pre-Cambrian metasediments and unconformably overlying Choseon Super Group of Cambro-Ordovician age (Fig. 1). The metasediments consist of biotite–muscovite–garnet schist, biotite–muscovite–andalusite schist, mica schist, phyllite and quartzite with thin limestone bed embedded and was called Yuli Series.

Pre-cambrian Nonggeori and Naedeogni Granites in this area are intruded into the metasediments of Yuli Series. Pegmatites are widely distributed in Yuli Series with the form of lit par lit, veins, lenses, sill, and stringers. The K/Ar ages of muscovite from Naedeogni Granite is  $1,673 \pm 20$ – $1,787 \pm 19$  ma of Middle-Proterozoic Eon. The K/Ar age of muscovite from barren

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pegmatite is shows  $1,792 \pm 18$  ma of Middle proterozoic Eon. The K/Ar ages of muscovite in the tin-bearing pegmatite at eastern part of Naedeogni Granite exhibit  $1,773 \pm 18$ – $1,792 \pm 18$  ma of also Middle Proterozoic Eon. Nonggeori Granite shows the similar ages of  $1,767 \pm 36$ – $1,802 \pm 18$  ma with Naedeogni Granite by dating the K/Ar ages of muscovite. (Ueda, 1969., Farrar, 1978., Yun, 1985., Lee, 1987)

The Naedeogni Granite is coarse grained, equigranular textured with the exposure of 3 Km<sup>2</sup>. Tin productive pegmaties of same age with Naedeogni Granite are developed around this stock. The Naedeogni Granite contains plagioclase, orthoclase, quartz, muscovite, tourmaline, biotite, apatite, zircon, beryl, cassiterite in order of abundance with increasing size of the minerals from granite to pegmatite.

The Nonggeori Granite with dimension of 8 Km<sup>2</sup> crops out 4 Km to the east of the Naedeogni Granite. it has similar mineralogy as the naedeogni Granite except for higher amounts of biotite and lower amounts of tourmaline than those of Neadeogni Granite.

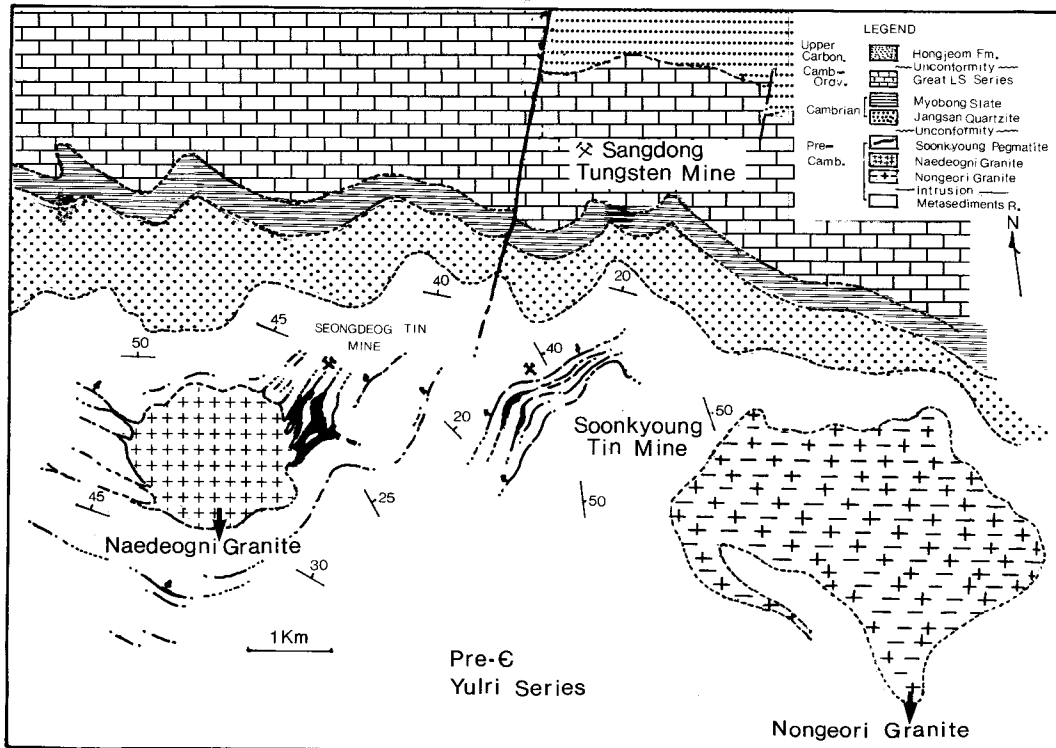
The pegmatites in variables shape such as swelling, pinching dikes, lenticular, sill, stringer

and vein types occur in the metasediments rocks by the cutting the rocks or with the concordant bounded bodies. The pegmatite and Naedeogni Granite is bounded gradationally. Those pegmatites are named Soonkyoung Pegmatites. The pegmatites bodies vary in thier dimensions, with the ranges in length from less than 20M to 500M and in thickness from 0.2M to 50M. The mineral assemmlages of pegmatites are plagioclase, K-feldspar, perthite, muscovite, quartz, tourmaline in common minerals. A minor amounts of apatite, zircon, cassiterite, sphene, granet and beryl are found in the pegmatites.

### CHEMISTRY OF SOONKYOUNG PEGMATITE

Soonkyoung tin mine has been cited as one of the best known examples of a primary tin pegmatite deposits in Korea. Tin mineralization of Soonkyoung Pegmatite is related with greisenization and albitization of pegmatite (Fig. 2, B, C) and with structural control for the latest pegmatite fluids to infiltrate early stage pegmatites (Fig. 2, A, C, D).

The variations of chemical composition in ma-



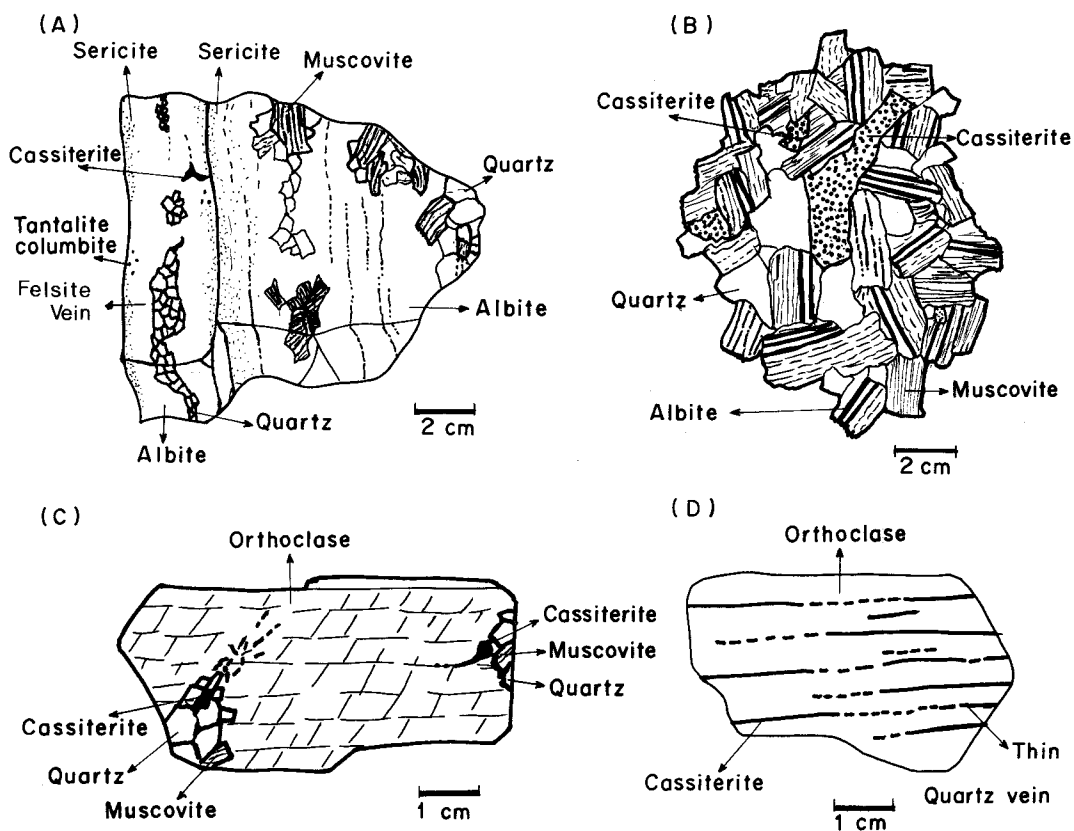


Fig. 2. Occurrences of cassiterite and its associated Ta-Nb mineral from the pegmatite in Sang-dong tin mineralized area. (A) Cassiterite and tantalite-columbite bearing felsite vein. (B) Cassiterite associated with greisenization of pegmatite. (C) Tin bearing greisen vein developed into the cleavage of orthoclase. (D) Thin cassiterite veins infiltrated into the cleavage of K-feldspar.

for elements from granites to barren pegmatites show the magmatic differentiation patterns with increasing of D.I values, whereas the productive pegmatite manifest the outstanding differences of geochemical abundance compared with barren pegmatites, i.e. higher CaO, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> in productive pegmatite than those of barren fresh pegmatite. These phenomena are due to the fractionation of apatite associating with greisenization and albitization of pegmatite in productive pegmatite (Kim, 1988).

$\Sigma$ REE abundances patterns of the intrusives decrease gradually from the Naedeogni and Nonggeori Granites to pegmatites. The REE concentrated patterns show the negative Eu anomaly except one of the productive pegmatites. The patterns show higher LREE, lower HREE in granites and barren pegmatite while productive pegmatite have V-shape pattern or smooth concave-shape. This fact is in part

due to the fractionation of zircon, garnets containing the heavy REE in productive pegmatites. High depletion in Eu of the above mentioned two granites and barren pegmatite indicates that the magma has undergone relatively complete differentiation whereas low depletion of Eu in productive pegmatite is due to the fact that the rocks contain the feldspar in early differentiated stages. These facts indicate that the productive pegmatite form from the latest pegmatitic fluids which are more calcic, sodic and a higher REE contents than the barren pegmatite fluids (Kim, 1988).

Two main types of pegmatites are distinguished in Soonkyoung tin mine area in terms of its occurrences; massive body type occurring around Naedeogni Granite and lenticular, vein types which predominate around Soonkyoung tin mine. The massive type is changed gradually to vein or lenticular type from Naedeogni Gra-

nite to eastward. Cassiterite has been found marginal extension part of massive pegmatite but is not found in massive pegmatite by the naked eyes. The massive pegmatite extended from Neadeogni Granite are classified as the tin barren pegmatite.

## OCCURRENCE OF TIN PRODUCTIVE PEGMATITE

The lenticular, vein type pegmatite are potential source rocks for cassiterite in Soonkyoung mine area. These pegmatites are divided into three internal units group as follow :

### Zoned Pegmatite

These pegmatites are composed of fourfold subdivision of sericite-quartz assemblage in boarder zone, muscovite-albite-tantalite-columbite-needle like tourmaline-quartz in wall zone, muscovite-albite-quartz-cassiterite(Fig. 2, B) in intermediate zone, and quartz-muscovite in core zone with symmetrical patterns. The grain size of the crystals increase from boarder toward core zone. These cassiterite bearing pegmatites which vary in width from 0.2 to 2.0.M. are dipping 40 to 55°NW. Ta/Nb ratios of tantalite-columbite in zoned pegmatites decrease toward core zone. These pegmatites are the major body of productive tin pegmatites.

### Lenticular Unzoned Pegmatites

The mediu to coarse-grained pegmatite, with albite and quartz as principal minerals, is the other main host rock containing the cassiterite.

The zoned textures are not found in these pegmatites, ranging in thickness form 1.5 to 10M and in length from 10 to 500 M. In these prgmatites, three mineral assemblages can be distinguished into albite-muscovite-quartz-cassiterite, quartz-muscovite-alkail feldsfar-cassiterite and plagioclase-microcline-muscovite-quartz-tourmaline. The latest mineral assemblages among them is not productive of tin.

### Fracture Fill Pegmatites.

The mineralogical characteristics of these pegmatite show the equigranular fine grained aplitic rock infiltrated into the pre-existing pegmatites(Fig.2,A). They have vein features in common ranging in thickness from 0.1 to 1.0 M which consist of plagioclase, muscovite, microcline, quartz, tourmaline and the accessory minerals of higher amounts of apatite, zircon, garnet and lower amounts of cassiterite than those of the zoned pegmatite.

## MINERAL CHEMISTRY OF ORE

Cassiterite, columbite, tantalite, and tantalian

rutile are produced from Soonkyoung Pegmatites. Cassiterite grains of variable size from cryptocrystalline to coarse crystals are disseminated in the part of greisenization and albitization of pegmatite. Tantalite and columbite are exsolved and/or dispersed in cassiterite crystals generally associating with quartz. In zoned pegmatite, the minerals occurs in wall zone with the shape of independant crystals. Tantalian rutiles are ordinarily infiltrated into the micro-fissure of pre-existing cassiterite and columbite-tantalite with thin quartz vein.

Generally the paragenetic and geochemical characteristics of the ore minerals from the cogenetic granitic to pegmatite suites are in short of information. The variational relationship between the composition of Ta-Nb minerals and crystal structure was reported by Foord(1982), Laurent et al.(1985) and Cerny(1985). However gechemical features of their evolution in differentiating residual granite magmas and geochemical characters of thier phases in fractionating the different pegmatite are obscure. Recent studies are dealt with the paragenetic and geochemical evolution of Ta-Nb bearing minerals in geochemically defined and petrologically well known pegmatite sequences-(Cerny et al., 1988). From those point of view, detailed mineral chemistries of cassiterite, tantalite-columbite and tantalian rutile from Sookyoung pegmatite carried out and results are decribed follows.

Chemical analysis were done by EPMA(JEOL, JXA 733) in wavelength disperse(WD) mode at geology department of Yonsei Univ. Standard used were metals of Sn, Ta, Nb, Fe, Mn, Ti and then recalculated oxide forms. Conditions of analysis were accelarating potentials of 15KV and samples current of 40nA.

### Cassiterite

The cassiterite occurs as finely disseminated specks of up to micro size in diameter and as coarse grained size ranging 0.5-50mm in albite, muscovite and quartz assemblage. Cassiterite generally shows the moderate to intense pleochroism, having a color brownish yellow to deep reddish brown. The zoned cassiterite has the color of pale brown or yellow in core zone and in margin zone dark brown to deep red. These color patterns occationally is alternative and generally the intensity of color is increased from core to margin zone.

The Table 1 shows that the cassiterite has a variable composition ranging of SnO<sub>2</sub> : 91.22-95.95 wt. %, Ta<sub>2</sub>O<sub>5</sub> ; 0.21-2.97wt. % and Nb<sub>2</sub>O<sub>5</sub> ; 0.09-0.48 wt.%. The amounts of TiO<sub>2</sub> in cassiterite is 0.09-0.48 wt. %, FeO(total) is

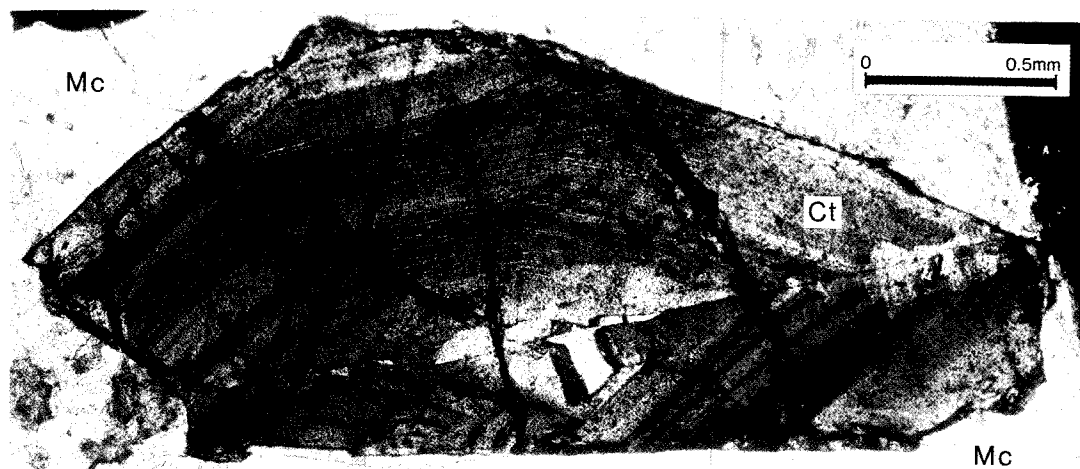


Fig. 3. Zoned cassiterite from Soonkyoung tin pegmatites, (Sample, TI-1), Sangdong area. Polarized photo., (+), Abb.; Mc: muscovite, Ct: cassiterite.

Table 1. Microprobe analysis of cassiterite from Soonkyoung tin-bearing pegmatites, Sangdong area.

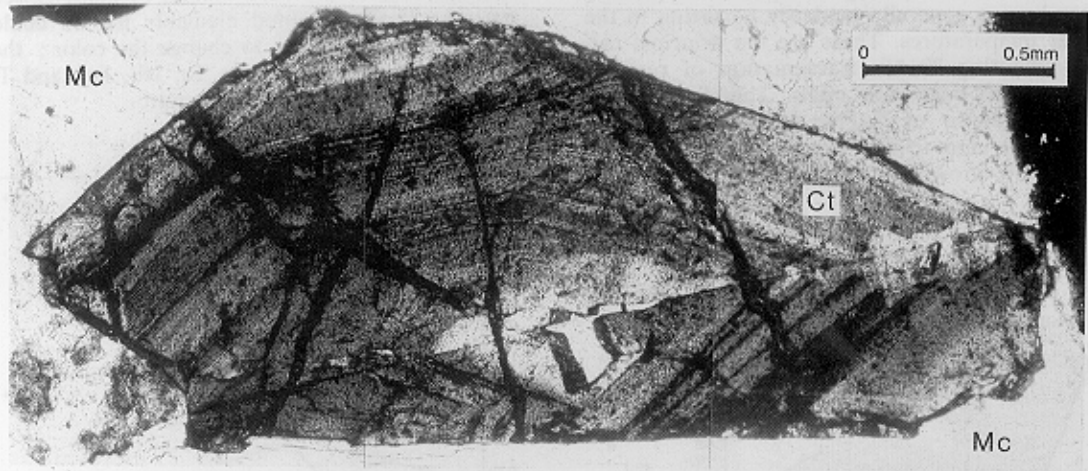
	7405	5D-5	5D-2	SK-1	MSD-1	MSD-4	TI-1	TI-2	D8511	D8732	D8746	D8747	C2-8
SnO <sub>2</sub>	93.13	92.42	92.75	95.14	93.17	95.51	95.52	92.49	94.19	92.44	95.09	93.92	95.95
TiO <sub>2</sub>	0.32	0.48	0.32	0.36	0.35	0.32	0.18	0.44	0.18	0.31	0.31	0.39	0.09
Ta <sub>2</sub> O <sub>5</sub>	1.90	1.42	2.97	1.12	1.16	0.21	0.23	1.32	0.56	1.24	1.88	1.88	0.38
Nb <sub>2</sub> O <sub>5</sub>	0.55	1.79	0.49	0.41	0.25	0.52	0.41	0.64	0.21	0.41	0.44	0.58	0.09
MnO	0.02	0.30	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.04	0.00
FeO*	0.35	0.59	0.61	0.30	0.29	0.12	0.08	0.37	0.15	0.26	0.36	0.31	0.08
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	96.27	97.00	97.16	97.33	95.22	96.68	96.44	95.26	95.29	95.67	98.08	91.12	96.59
Numbers of cations based on 4 oxygens													
Sn <sup>+4</sup>	1.930	1.886	1.908	1.948	1.952	1.966	1.975	1.932	1.947	1.935	1.928	1.985	
Ti <sup>+4</sup>	0.013	0.018	0.012	0.014	0.014	0.012	0.007	0.017	0.012	0.012	0.015	0.004	
Ta <sup>+5</sup>	0.027	0.020	0.042	0.016	0.017	0.003	0.003	0.019	0.018	0.026	0.026	0.005	
Nb <sup>+5</sup>	0.013	0.041	0.011	0.010	0.006	0.012	0.010	0.015	0.010	0.010	0.013	0.002	
Nn <sup>+2</sup>	0.001	0.013	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	
Fe*	0.015	0.025	0.026	0.013	0.013	0.005	0.003	0.016	0.011	0.015	0.013	0.003	
Mg <sup>+2</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Total	1.998	2.004	2.000	2.000	2.001	1.999	1.999	2.000	2.000	1.999	1.999	1.998	2.000

Total Fe as Fe<sup>+2</sup>. MgO not determined.

0.08–0.61 wt. % and those of MnO<sub>2</sub> has the composition ranging of trace up to 0.30 wt. %. The chemical compositions of the minor elements in cassiterite indicate that TiO<sub>2</sub> and FeO\* (total Fe, as FeO) is in proportion to Ta<sub>2</sub>O<sub>5</sub> but MnO<sub>2</sub> is in proportion to Nb<sub>2</sub>O<sub>5</sub>, the pat-

terns of which is due to the fact originated from the chemical affinity.

Fig. 4 is the contour map which shows the symmetrical substituted patterns of Ta and Nb for Sn in cassiterite. The ratios of Ta/Nb in the crystal is increasing from core to margin. The



thermal stability of F-based and Ta-Nb complexes is different (Wang, 1982). The Ta bearing ones have a generally tendency persisting to the lower temperatures. These are the principal factors affecting Ta/Nb fractionation of residual granitic and pegmatitic melts. Therefore the increasing factor of Ta/Nb ratio from core to margin is due to the decreasing temperature during the growth of cassiterite.

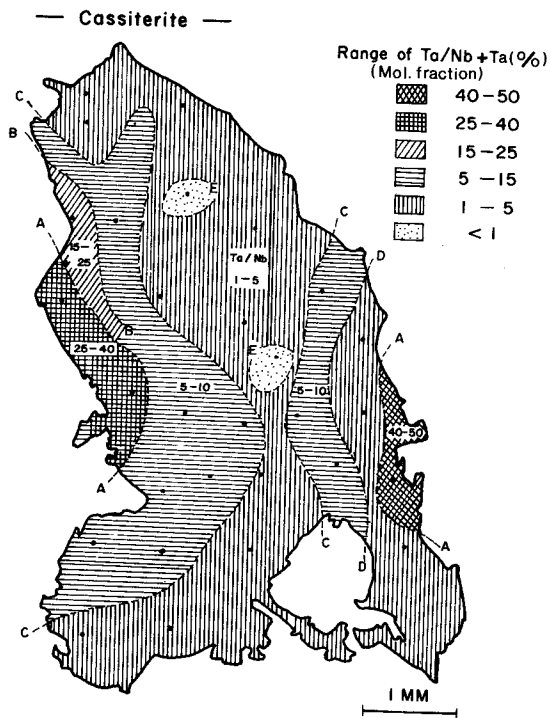


Fig. 4. Symmetrical patterns of substitutional concentration of chemical composition in cassiterite crystal from the Soonkyoung tin mine area. Ta/Ta+Nb ratios (atom mol. fraction). Black circle: Point to analyze by EPMA.

Fig. 5 is the compositional section of zonal cassiterite from the core to the margin. The size of the crystal is about 10 mm, the color is pale brown in core and dark brown to dark red in margin. The color intensity is changing to deeper from core to margin. The compositional variations of zonal cassiterite from the core to the margin show the generally increasing pattern of Ta, Nb, Ti, Fe and Mn, and decreasing of Sn. Sn and the substituted elements for Sn such as Ta, Nb, Ti, Mn, Fe\* (\* means total Fe as FeO) are compensated each other completely. These are due to the fact that the equilibrated

temperature is decreasing from the core to the rim and due to the environment of quasi-closed system. The substituted elements for Sn could be the principal factor to change the color; the dark zones are enriched in Ta, Nb, Fe\* and Ti and pale zones are relatively pure.

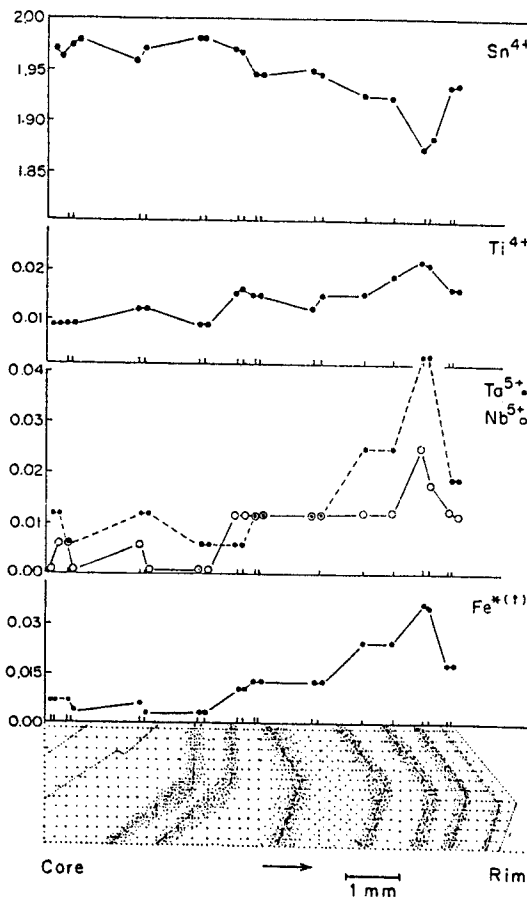


Fig. 5. Variation of chemical composition of zoned cassiterite from Soonkung Pegmatite.

Fig. 6 is the diagram to show the chemically substituted pattern of cassiterite. The substituted elements for Sn are Ti, Ta, Nb, Fe\*, Mn with the correlation coefficient of -1. The chemical composition of cassiterite exhibits that the ranges of substitution of (Ta<sup>5+</sup>, Nb<sup>5+</sup>, Ti<sup>4+</sup>, Fe\*) for Sn<sup>4+</sup> is 0.01-0.01 Mol. fraction % (Table 1).

The partitioning of Ti<sup>4+</sup> against Fe\* + Ta + Nb + Ti in cassiterite is 0.25, which indicates Ti<sup>4+</sup> partitioning about 25% among all the substituted elements (Fig. 7). Fig. 8 exhibits the coupled-substitution between Fe\* and (Ta, Nb)<sup>5+</sup>

with correlation coefficient 0.5. Laurent et al. (1985) studied the crystallochemical characteristics of cassiterite by means of ESR spectra. This research showed that the ferric ion mainly substituted for tin in highly distorted co-ordination polyhedra but occasionally could be found in interstitial sites in the rutile type structure.

Fig. 9 represents the correlation between  $\text{Sn}^{4+}$  and  $\text{Ti}^{4+}$  in cassiterite. The diagram shows the limit for  $\text{Ti}^{4+}$  in cassiterite.  $\text{Sn}^{4+}$  up to 0.01 mol.% and then  $\text{Ti}^{4+}$  could not substitute  $\text{Sn}^{4+}$  each other.

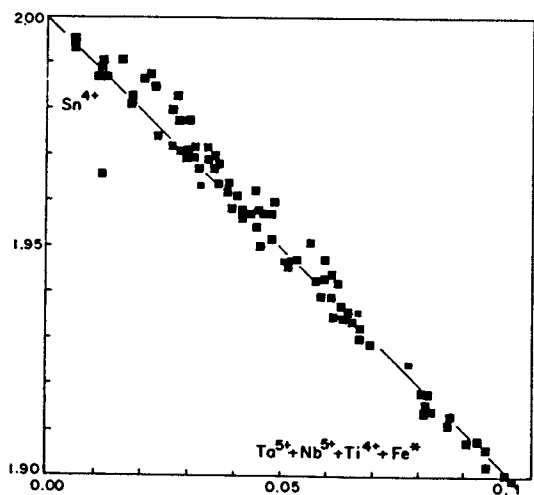


Fig. 6. Relationship between  $\text{Sn}^{4+}$  and  $\text{Ta}^{5+} + \text{Nb}^{5+} + \text{Ti}^{4+} + \text{Fe}^*$  in cassiterite from Soonkyoung tin-bearing pegmatite.

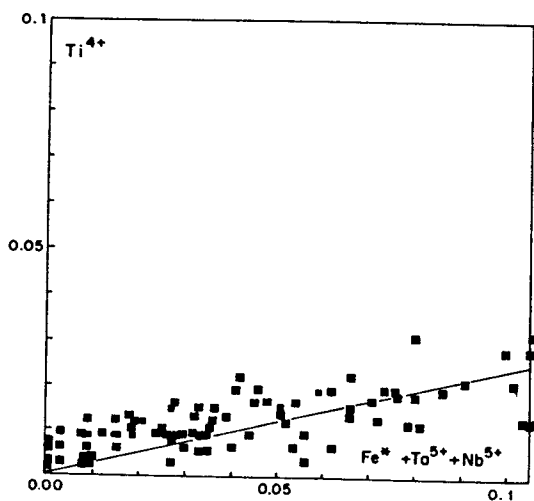


Fig. 7. Relationship between  $\text{Ti}^{4+}$  and  $\text{Fe}^* + \text{Ta}^{5+} + \text{Nb}^{5+}$  in cassiterites from Soonkyoung tin-bearing pegmatite.

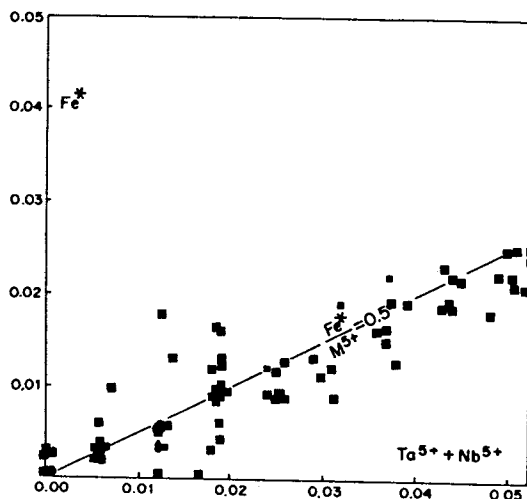


Fig. 8. Relationship between  $\text{Fe}^*$  and  $\text{Ta}^{5+} + \text{Nb}^{5+}$  in cassiterites from Soonkyoung tin-bearing pegmatite.

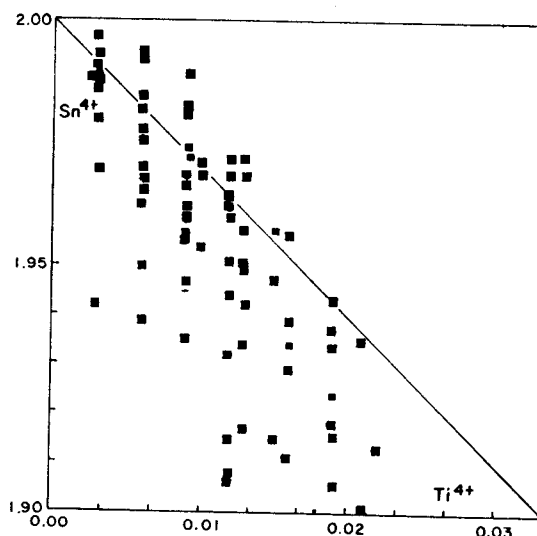


Fig. 9. Substitution of  $\text{Ti}^{4+}$  for  $\text{Sn}^{4+}$  in cassiterite from Soonkyoung tin-bearing Pegmatites.

#### Tantalite-Columbite

Tantalite-columbite generally are distributed in the cassiterite with form of exsolution texture and micro-fissures infiltrated into the pre-existing structure. The paragenetic sequence of tantalite-columbite is divided into 2 stages: the one is euhedral, lath-shape independant crystals and/or exsolution texture in cassiterite which represent early stage, the other is mostly mic-



ro-veins associated with quartz, which shows the paragenesis of late stage. The size of crystals is about 10  $\mu\text{m}$ –1mm (Fig. 10).

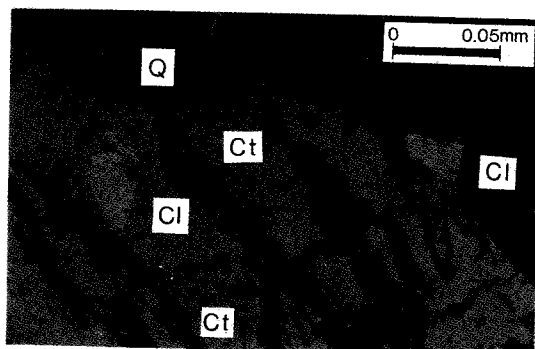


Fig. 10. Columbite exsolution in cassiterite and columbite island in quartz from Sookyoung tin-bearing pegmatite. (Abb.; Cl: columbite, Ct: cassiterite, Q: quartz)

X-ray  $K\alpha$  images of tantalite-columbite demonstrate that the Ta-Nb complexes are closely associated with quartz of late stage (Fig. 11–SEM) and the tantalite replaced the columbite (Fig. 11–Ta, Nb). Titanium have a tendency to concentrate in tantalum rather than in niobium (Fig. 11–Ta, Ti), whereas total iron both concentrate tantalum and niobium (Fig.

11–Fe<sup>\*</sup>). This is due to the chemical affinity between Ta<sup>4+</sup> and Ti<sup>4+</sup>, and due to the tantalum persisting to low temperature.

In the view of paragenetic sequence of tin mineralization, the cassiterite of early stage is crystallized in the late stage of pegmatite and then columbite is exsolved in cassiterite and crystallized with quartz during the decreasing temperature of melt. After that, tantalite replaces the columbite and infiltrates into the micro-fissure of pre-existing cassiterite.

The chemical composition of tantalite-columbite have a variable range of Ta<sub>2</sub>O<sub>5</sub>: 14–46 wt. %, Nb<sub>2</sub>O<sub>5</sub>: 60–28 wt. %. The substitution of FeO<sup>\*</sup>, TiO<sub>2</sub> and SnO<sub>2</sub> in tantalite-columbite amounts to 10–15 wt. %, and the most of all Fe<sup>\*</sup>O (Table. 2). Fig. 12 shows the Ta-Nb complexes with relation of limited solid solution. Columbite-tantalite, tantalian rutile and cassiterite plot along the (Sn, Ti)+(Fe<sup>\*</sup>, Mn)(Ta, Nb)<sub>2</sub> join, which indicates the dominance of the substitution (Mn, Fe)+2(Ta, Nb)=(Sn, Ti) (Fig. 13).

Cassiterite have a compensatory substitution patterns between Ti<sup>4+</sup> and Sn<sup>4+</sup> (Fig. 9). Consequently, Sn<sup>4+</sup> does decrease with increase in substitution of Ti<sup>4+</sup> for Sn<sup>4+</sup> in cassiterite. But Sn content increase with increase Ti content in tantalite-columbite (Fig. 14).

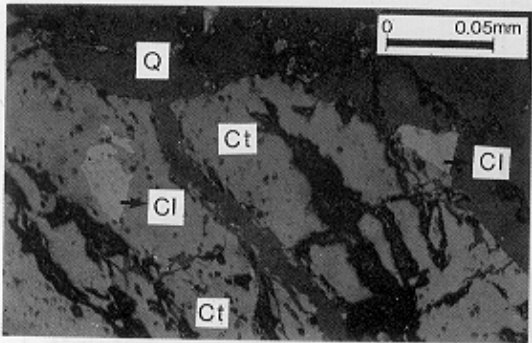
#### Tantalian Rutile

Tantalian rutile is associated with generally cassiterite with the forms of quartz bearing micro-fissures (Fig. 15) of the latest stage. The width

Table 2. Microprobe analysis of tantalite-columbite from Sookyoung tin-bearing pegmatite, Sangdong area.

	7405	D8746	D8747	D8732	TI-1	TI-2	SK143
SnO <sub>2</sub>	1.27	1.03	1.43	0.81	1.57	0.31	0.92
TiO <sub>2</sub>	2.11	2.44	4.04	1.78	4.40	1.09	2.28
Ta <sub>2</sub> O <sub>5</sub>	40.20	36.97	46.03	38.38	35.13	13.99	33.61
Nb <sub>2</sub> O <sub>5</sub>	36.39	39.94	27.87	38.12	33.36	59.71	42.64
MnO	2.02	2.76	2.48	2.95	1.87	5.76	3.52
FeO <sup>*</sup>	12.00	11.94	11.30	12.00	12.85	10.23	11.61
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	94.80	95.08	93.15	94.04	89.18	91.09	94.58
Cations number on basis of 24 oxygens							
Sn <sup>4+</sup>	0.144	0.113	0.168	0.091	0.184	0.032	0.100
Ti <sup>4+</sup>	0.451	0.506	0.894	0.378	0.971	0.213	0.468
Ta <sup>+5</sup>	3.109	2.771	3.683	2.946	2.803	0.989	2.496
Nb <sup>+5</sup>	4.679	4.976	3.708	4.864	4.426	7.018	5.264
Mn <sup>+2</sup>	0.487	0.644	0.618	0.705	0.465	1.268	0.814
Fe <sup>*</sup>	2.854	2.752	2.781	2.832	3.153	2.224	2.651
Mg <sup>+2</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	11.72	11.76	11.85	11.82	12.00	11.34	11.79

Total FeO<sup>\*</sup> as Fe<sup>+3</sup>. MgO not determined.



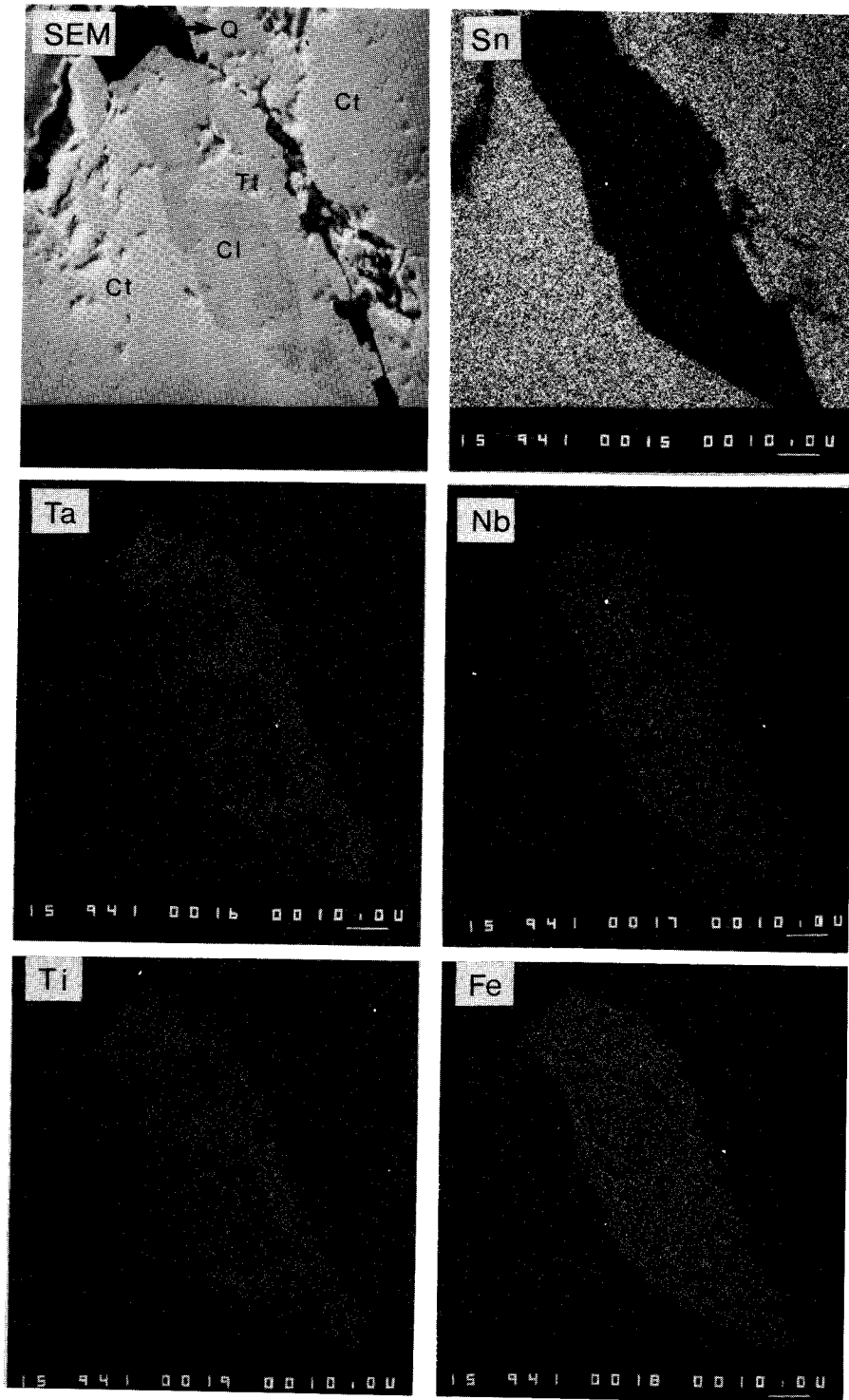
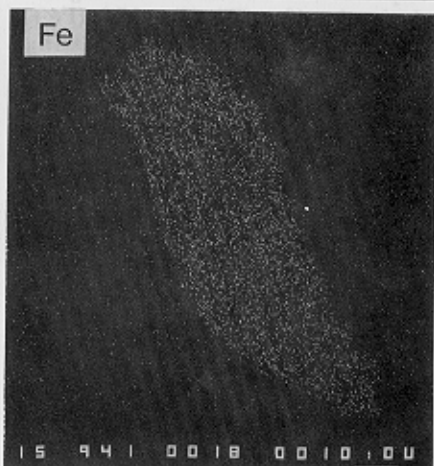
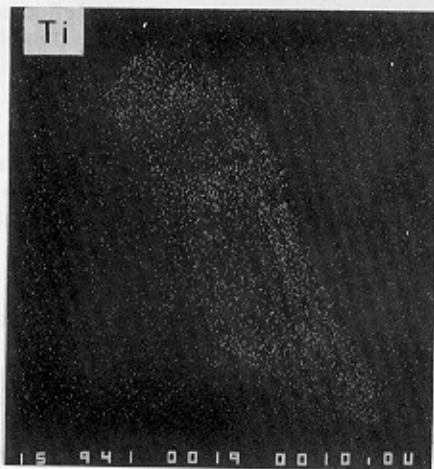
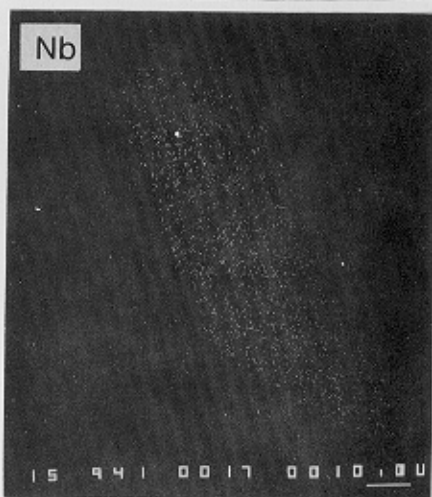
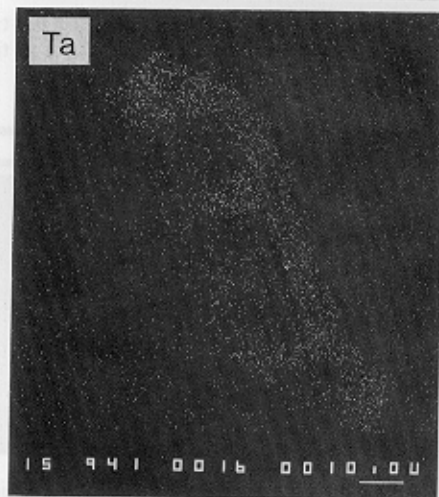
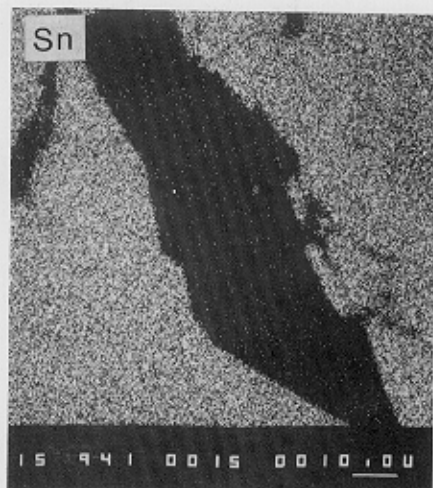
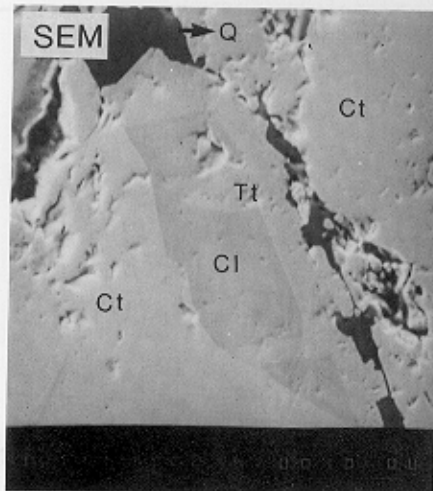


Fig. 11. The SEM and X-ray K $\alpha$  images of Sn, Ta, Nb, Ti, Fe\* of cassiterite and tantalite columbite from Sookyoung tin mine area (Abb.; Ct: cassiterite, Tt: Tantalite, Cl: columbite, Q: quartz).



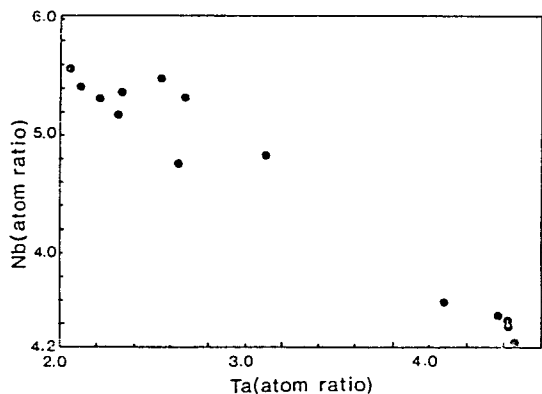


Fig. 12. Interrelation between Ta and Nb of columbite-tantalite from Soonkyoung tin-bearing Pegmatite.

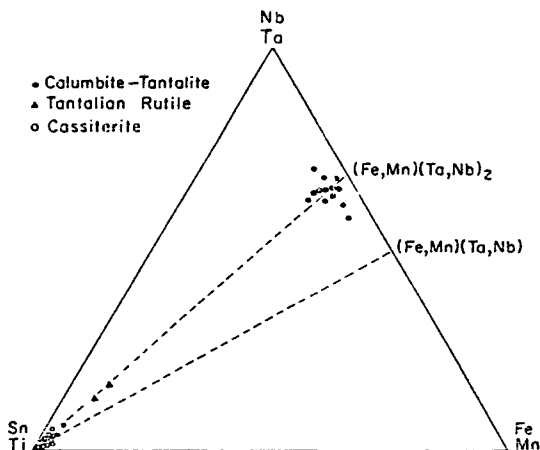


Fig. 13. Composition of Ta and Nb bearing oxides minerals in the (Sn+Ti)-(Ta+Nb)-(Fe+Mn) diagram from Soonkyoung tin-bearing Pegmatite. Atomic ratios with all Fe as FeO.

of the fissures is relatively wider than those of tantalite-columbite.

The Table. 3 is the result of chemical analysis of the rutile to tantalian rutile. The chemical compositions of the tantalian rutile show the wide ranges of the compositions of  $TiO_2$ : 57.41–78.28 wt. %,  $Ta_2O_5$ : 5.08–21.52 wt. %,  $Nb_2O_5$ : 3.02–6.81 wt. %,  $FeO^*$ : 2.06–5.58 wt. %,  $MnO$ : 0.00–0.01 wt. %, and  $SnO_2$ : 1.70–10.35 wt. %.

The Ta/Nb ratios of the tantalian rutile are the higher than of tantalite-columbite, which indicate  $Ti^{4+}$  having the closely chemical affinity with  $Ta^{+5}$  and  $Ta^{+5}$  persisting to the tantalian rutile of the low temperature phases. Fig. 16 exhibits the ratios of Ta/Ta+Nb and Mn/Mn+

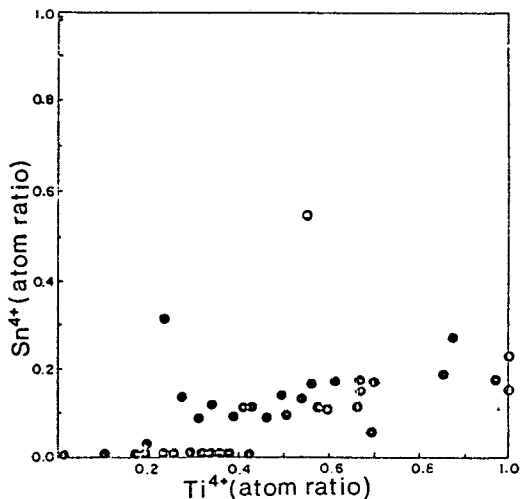


Fig. 14. The Sn and Ti contents of columbite-tantalite from Soonkyoung tin-bearing Pegmatite.

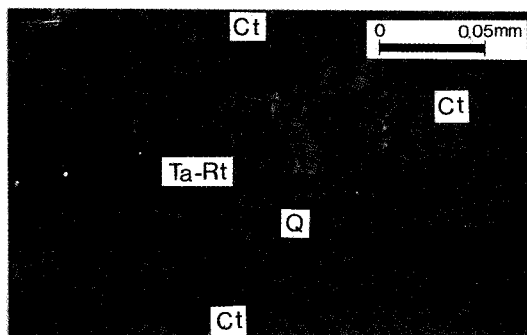
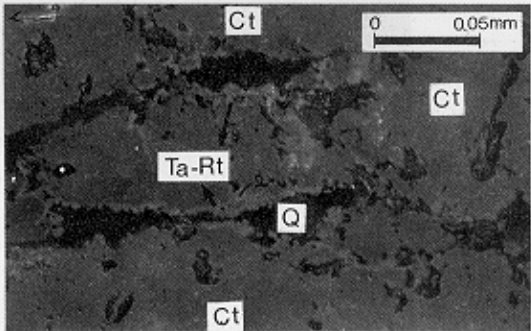


Fig. 15. Tantalian rutile bearing micro-quartz veins in cassiterite crystal (Reflected photo). Abb.; Ct: cassiterite, Ta-Rt: tantalian rutile, Q: quartz.

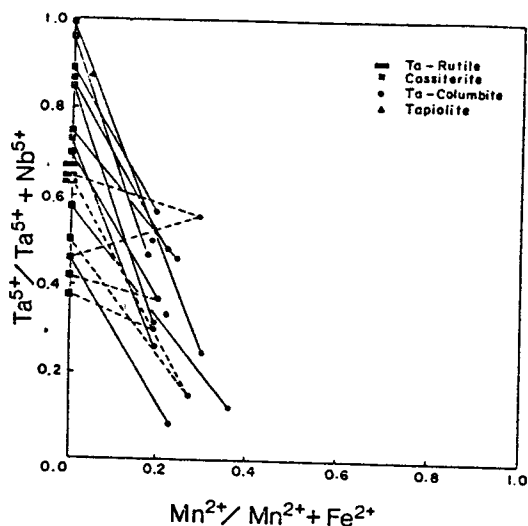
$Fe^*$  of the coexisting tantalian rutile, tantalite-columbite and cassiterite assemblage in views of the compositional differences of parent ore fluids.

The compositions of tantalian rutile and coexisting tantalite-columbite suggest a distinctly symmetric shape on Ta/Ta+Nb and Mn/Mn+ $Fe^*$  ratios in comparison with the tantalite-columbite and cassiterite pairs. Namely cassiterite and columbite-tantalite pairs exhibit relatively definite slopes of the minerals pairs that may be to equilibrium. However tantalian rutile and tantalite-columbite pairs have a gentle slope to account for the sudden changes in condition of parent fluids compared to the condition of previously mentioned pairs.



**Table 3.** Microprobe analysis of tantalian rutile from Soonkyoung tin-bearing Pegmatite, Sang-dong area.

MSD1-1	MSD1-2	MSD1-3	MSD1-4	D851-1	D851-2	S143-1	T11-51	T11-52	
SnO <sub>2</sub>	1.70	1.97	2.39	10.35	6.29	1.80	1.74	0.14	0.19
TiO <sub>2</sub>	78.28	95.81	86.00	71.79	60.55	57.41	57.85	90.04	90.92
Ta <sub>2</sub> O <sub>5</sub>	8.39	1.29	5.08	6.53	14.89	21.52	20.15	0.04	0.10
Nb <sub>2</sub> O <sub>5</sub>	3.02	0.26	1.60	2.26	6.01	6.55	6.81	1.02	0.83
MnO	0.00	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.00
FeO*	2.47	0.50	2.06	2.71	4.58	5.61	5.85	1.14	0.86
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	93.86	99.83	97.14	93.64	92.33	92.89	92.41	92.39	92.90
Cations number on basis of 4 oxygens.									
Sn <sup>+4</sup>	0.021	0.021	0.028	0.132	0.086	0.025	0.024	0.002	0.002
Ti <sup>+4</sup>	1.808	1.957	1.871	1.721	1.559	1.508	1.517	1.967	1.973
Ta <sup>+5</sup>	0.070	0.010	0.040	0.057	0.139	0.204	0.191	0.000	0.001
Nb <sup>+5</sup>	0.042	0.003	0.021	0.033	0.093	0.103	0.107	0.013	0.011
Mn <sup>+2</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Fe	0.063	0.011	0.050	0.072	0.131	0.164	0.171	0.028	0.021
Mg <sup>+2</sup>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Total	2.004	2.002	2.010	2.014	2.008	2.005	2.011	2.011	2.007

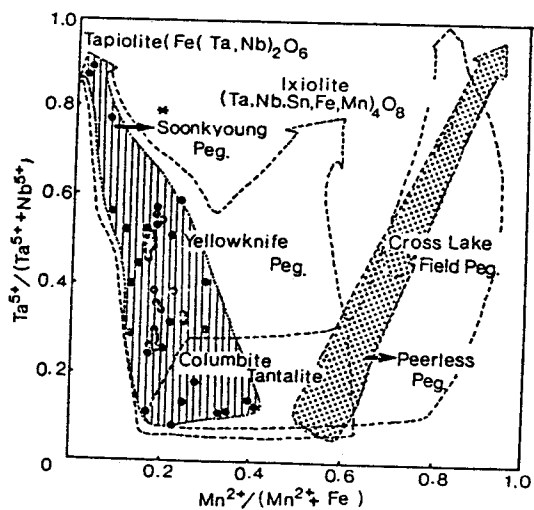

**Fig. 16.** Compositions of coexisting minerals in the columbite-tantalite, cassiterite, and tantalian rutile from Soonkyoung tin-bearing Pegmatite.

### FRACTIONATION TRENDS OF TANTALITE-COLUMBITE

As shown in Fig. 17, the compositionally variational trends of Ta/Ta+Nb and Mn/Mn+Fe\* in tantalite-columbite show the negative correlation coefficient each other. The variational trends of tantalite-columbite exhibit extreme-

ly Ta/Nb dominated fractionation trend in comparison with the restricted Mn/Mn+Fe\* fractionation.

Fluorides and other complexes of Ta and Nb minerals have different thermal stability, the Ta-bearing one generally preferring to lower temperatures. This could be the principal factor


**Fig. 17.** Fractionation trends of columbite-tantalite in Soonkyoung tin-bearing pegmatite in comparison with Yellow knife pegmatite, Cross lake Pegmatite and Peerless Pegmatite in atomic ratios. (After Cerny et al., 1988)

affecting Ta/Nb fractionation in residual granitic and pegmatitic melts (Wang et al., 1982, Cerny et al., 1986).

Mn/Mn+Fe\* fractionation of tantalite and columbite is not well understood. Shawe (1974) and Hiedreth (1979, 1981) demonstrated that Mn is transferred by volatile in granitic magma. Shawe (1968) and Baily (1977) proposed preferential complexing Mn with F to explain its separation from Fe and late precipitation. Cerny et al. (1968) postulated that the environments of fractionation of Ta/Nb and Mn/Fe could be divided into two categories such as Li, Rb, Cs, F-poor environment and Li, Rb, Cs, F-rich parageneses. The former, limited Mn enrichment accompanies the fractionation of Ta, which extremely fractionates in ixiolite and subordinate microlite and the later, extensive Mn enrichment precedes the main Ta fractionation, which subsequently generates near end-member manganotantalite, wodginite and microlite.

Soonkyoung Pegmatite in Sangdong area show the extensive and extreme Ta/Nb+Ta fractionation but limited Mn/Fe+Mn fractionation (Fig. 17). This pegmatite categorizes the beryl-columbite type that lack significant amounts of Li- and F-enriched micas in agreement with Yellowknife Pegmatite field and the Moose pegmatite (Cerny et al., 1986).

### CONCLUDING REMARKS

The substitutional elements for Sn<sup>4+</sup> in cassiterite are Ta<sup>+5</sup>, Nb<sup>+5</sup>, Ti<sup>+4</sup> and Fe\*, which range from 0.01 mol.% to 0.15 mol.%. The substitutional relationship between Ta, Nb and Fe\* shows the coupled substitution in cassiterite. Ta/Nb ratios in the crystals is increasing from core to rim keeping abreast with changing color to deeper. The amounts of substitutional elements for Sn are increasing from core to margin, which could be the principal factor to change the color.

The paragenetic sequence of tantalite-columbite is divided into 2 stages: the one is euhedral, lath-shape independent crystals and/or exsolution texture in cassiterite which represent early stage, the other is mostly micro-veins associated with quartz, which shows the paragenesis of late stage. The chemical composition of tantalite-columbite have a variable range of Ta<sub>2</sub>O<sub>5</sub>: 14-46 wt.%, Nb<sub>2</sub>O<sub>5</sub>: 60-28 wt.%. The content of Fe\*O, TiO<sub>2</sub>, SnO<sub>2</sub> in tantalite-columbite amounts to 10-15 wt.% and the most of all Fe\*O (Table 2). The substitutions between Ta and Nb in tantalite-columbite show the limited solid solution.

The Ta/Nb ratios of the tantalian rutile are the higher than of tantalite-columbite, which in-

dicates Ti<sup>4+</sup> having the closely chemical affinity with Ta<sup>+5</sup> and Ta<sup>+5</sup> preferring to the tantalian rutile of low temperature phases.

The cassiterite is crystallized in the late stage of pegmatite and then columbite rich phases is exsolved in cassiterite and crystallized with quartz during the decreasing temperature of melt. After that, tantalite rich phases replaces the columbite and infiltrates into generally micro-fissure of cassiterite and then tantalian rutile of latest stage fills the micro textures of pre-existing minerals.

The fractionational variations of tantalite-columbite exhibits the increasing trends of Ta/Ta+Nb. In contrast, that of Mn/Mn+Fe\* shows the restrict fractionation. These phenomena represent the Li-, F- poor environments, and Be-, Ta- rich environment in agreements with the lacking of significant Li- and F enriched micas, with the relatively abundance of beryl and extreme Fe-tantalite end member in Soonkyoung pegmatite. According to the substitutional characteristics of ore minerals, the fractionation trends of tantalite-columbite suggest that the Soonkyoung pegmatite is belong to the Ta-Be complex pegmatite associated with the fractionation of beryl and tantalite rich phase.

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## 順鏡 페그마타이트에서 産出되는 錫石, 콜롬바이트, 탄탈라이트 및 隋伴鑛物에 대한 鑛物化學

金壽永·文熙壽·朴魯榮

요약 : 上東地域, 順鏡 含鑛石 페그마타이트에서는 錫石을 비롯하여 탄탈라이트-콜롬바이트, 그리고 含Ta-金紅石 등이 産出된다. 錫石은 散布狀의 微晶質에서부터 巨晶質에 이르기까지 多樣하며, 一般的으로 탄탈라이트-콜롬바이트, 含Ta-金紅石과 共存하고 있다. 탄탈라이트-콜롬바이트는 微細脈 혹은 溶離狀能로서 錫石結晶에 胚胎되며 간혹 獨立鑛物로서 石英에 隨伴되는 경우가 있다. 含Ta-金紅石은 上記한 鑛物 중 最後期相으로서 石英을 隨伴하는 細脈狀으로 産出된다.

錫石에서  $\Sigma Ta^{+5}$ ,  $Nb^{+5}$ ,  $Ti^{+4}$  및  $Fe^{*}$ 은  $Sn^{+4}$ 과 負의 相關關係로 置換에 全적으로 關係하고 있으며, 0.01–0.15mol. % 까지 置換하고 있다.  $Ta^{+5}$ 와  $Nb^{+5}$ 는  $Fe^{*}$ 雙置換關係이며  $Ta^{+5}$ 는  $Ti^{+4}$ 와 化學的 親化關係로서 密接히 隨伴된다. 異常構造가 發達된 錫石은 結晶의 內核에서부터, 外殼으로 갈수록 Ta/Nb 比가 增加하며, 이는 溫度의 下降에 따른 Ta의 參與 效果가 높아지는데 起因된다.

含Ta金紅石은  $TiO_2$  : 57.41–86.00wt%,  $Ta_2O_5$  : 5.08–21.51 wt%,  $Nb_2O_5$  : 1.60–6.81 wt%,  $FeO^{*}$  : 2.06–5.85 wt% 그리고  $SnO_2$  : 1.74–10.35 wt%의 化學造成으로 構成되어 있다. 본 鑛物은 탄탈라이트-콜롬바이트에 比하여 Ta / Ta+Nb의 比가 높다.

탄탈라이트-콜롬바이트의 化學造成에 의하면, Ta / Ta+Nb가 增加하고, Mn / Mn+ $Fe^{*}$ 은 減少하는 分結傾向을 보여 주고 있다. 이것은 分結作用이 進行되는 동안 Ta의 活動도가 增加되는 것으로 Li과 F가 枯渴되고, Be과 P가 豊富한 環境을 指示하는 것이다. 이와같은 環境은 順鏡 페그마타이트에 Li과 F 雲母의 存在와 탄탈라이트와 綠柱石이 錫石 鑛化作用과 密接히 隨伴되는 것과 一致하는 것이다.

본 페그마타이트는 Ta-Be 複合型的의 페그마타이트로서 錫石은 탄탈라이트-콜롬바이트, 綠柱石 등의 分結作用을 隨伴하며 形成되었다.