Geochemistry of the Country Rock of Eosangcheon Manganese Deposit

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Abstract: The Ordovician limestone and dolomite was mineralized by the intrusion of quartz porphyry to form hydrothermal ore deposit along the fault shear zone, which trends N30°–40°W dipping 60°–70° SW. The primary manganese carbonates in the upper part of the deposit were oxidized to form supergene manganese ore deposits.

The quartz porphyry is plotted mainly in granite region of the triangular diagram of normative composition. The granite phase contains more copper and lead, but less zinc, nickel and chromium than the granodiorite phase which occupies the northwestern part of the quartz porphyry.

The content of copper, lead, zinc, nickel and chromium in the quartz porphyry is lower compared with the granitic rocks from the copper province in the Gyeongsang basin. But the granitic rocks from the lead–zinc province has lower content of copper and nickel than the quartz porphyry.

The primary distribution pattern of trace elements in the country rock of limestone and dolomite has close relation with the hydrothermal mineralization, showing anomalous or high content near the fault shear zone.

The secondary distribution pattern of trace elements in soils shows close relation with the solubility of the carbonates of the elements under weathering condition.

INTRODUCTION

Eosangcheon mine is located at 128 21′–128 22′E′, 37°05′ 30′′–37°06′ 30′′ in Imhyeon-ri, Eosangcheon-myun, Danyang-gun, Chungcheongbugdo, Korea.

The topography of the mine is related to the geology: quartz porphyry area is less steep while limestone-dolomite area is steep, forming mountaineous district.

Manganese oxide ores are embedded in the fault shear zone, which trends N30°–40°W dipping 60°–70° SW in the sedimentary rocks, Four holes were drilled, each 100m deep, by Geological and Mineral Institute of Korea in 1979.

Present work was undertaken to study geochemistry of the country rock of limestone and dolomite, quartz porphyry and soil in relation with man-

ganese ore deposit on the basis of geochemical data. For this study 18 rock samples were taken; 8 from the quartz porphyry and 10 from the country rock. 11 soil samples were taken from the limestone-dolomite area. In addition, 21 core samples were taken from drillcores, 8 rock samples from outcrops, and 22 ore samples from main level of the mine.

Major elements were determined by wet analysis methods and X-ray fluorescence, and trace elements were analysed by atomic absorption spectrometry, emission spectrometry and X-ray fluorescence.

Whole analytical results were plotted in some diagrams. Niggli values of fm, c, alk, and al were plotted against that of si to find the compositional differences between the marginal part and the rest parts of the quartz porphyry.

To determine the nature of the source magma which the quartz porphyry was derived from,

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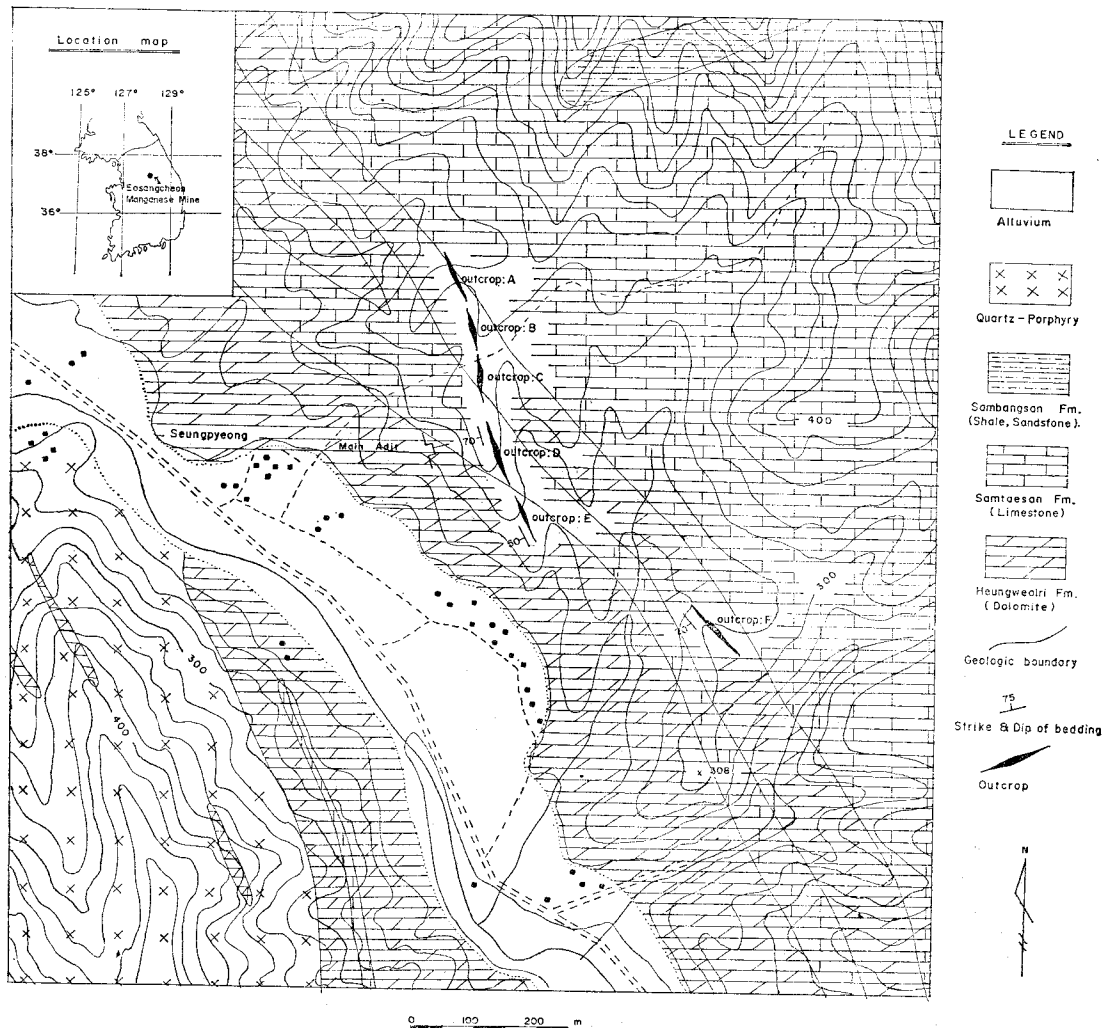** Korea Institute of Energy and Resources

Fig. 1   Geologic map of Eosangcheon mine

those values of fm and c were also plotted against that of al.

Variation diagrams of trace elements in the country rock and soil were also prepared to display the relative abundances. The abundance values were useful to find whether the limestone and dolomite contained synsedimentary manganese materials or not.

GENERAL GEOLOGY

The study area is occupied mostly by the Ordovician limestone (Samtaesan Formation), dolomite (Heungweolri Formation) and partly by the age-unknown shale-sandstone (Sambangsan Formation). These sedimentary formations are intruded by the Cretaceous quartz porphyry, which occupies the southwestern part of the area. Quaternary alluvium deposit lies on the border zone between the sedimentary rocks and the quartz porphyry. Supergene manganese oxide deposits occur in the upper part of the fault shear zone, which trends N30°–40° W dipping 60°–70° SW

Table 1. Chemical analysis of outcrop ore samples

outcrop	ore	grade (%)			length/ width(m)	direction	remarks
		Mn	SiO$_2$	CaO			
A	Mn–oxide	1.20		1.70	30/3		openpit
B	〃	2.40	4.33	30.80	40/1.5–3		
C	〃 +MnCO$_3$	6.88			10/2		
D	Mn–oxide	14.28	18.56	8.03	25/2	N45°W, 70°SW	main level
E	〃	2.06	2.68	34.7	20/2–3	N30°W, 70°SW	openpit
F	〃	2.13			15/2–3	N55°W, 70°SW	〃

in the limestone-dolomite area (Fig. 1).

Samtaesan Formation occupies the eastern half of the study area. This formation consists of limestone and dolomite, which strike N30°–40°W and dip 40°–85° SW, and has some minor isoclinal folds.

The Heungwoelri Formation occupies diagonally the central part of the study area. This formation consists mainly of white-grey dolomite with some thin limestone layers, which strike N20°–30°W and dip 50°–80°SW.

The Sambangsan Formation, which lies uncomformably on the Samtaesan Formation, which consists of dark grey-green shale and white brown quartzose sandstone with some thin limestone layers. The general strike and dip of the formation are N30°–50°W, 30°–40°NE and N10°–15°W, 30°–40° NE. The age of the formation has been unknown, but it was suggested to be of the period from late Chosun System to Upper Pyongyang System (Son, 1974).

The quartz porphyry trends approximately in N30° W direction and contains xenolithes of the dolomite and limestone, which remain in the original direction. The quartz porphyry contacts with the Heungwoelri Formation at its eastern margin.

MANGANESE ORE DEPOSIT

Supergene manganese ore deposit was formed by superficial oxidation of the primary man-ganese carbonates which occupied the upper parts of the hydrothermal sulphide deposit in the fault shear zones.

Manganese oxide ores are embeded irregularly, but vertically in parallel lense shapes in the fault shear zone. Along the zone many outcrops have been found and 6 outcrops were investigated for this study (table 1).

The lower limit of the supergene oxidation is expected to be quite deep from the surface, because the supergene manganese oxides were found at the depth of 100–140m from the surface by drilling the fault shear zone (Fig. 2, table 2). Therefore, it may be suggested that the primaryrhodochrosite was not completely oxidized at the depth and still in the superficial oxidation process.

In the country rock of the limestone and dolomite near the fault shear zone, not only the supergene manganese oxides but also rhodochrosite and galena occur in parallel to the fault according to the obtained data from the drilled cores. Therefore, it seems that they are zonally arranged in the sequence of manganese, lead-zinc, copper in the upper parts of the fault shear zone, and this corresponds with the general zonal arrangement which has been observed in many manganese ore deposits in the limestone-dolomite areas in Korea (Hwang, 1981).

Primary rhodochrosite occurs mainly in the limestone which was not disseminated by pyrite. This may suggest that pyrite played an important
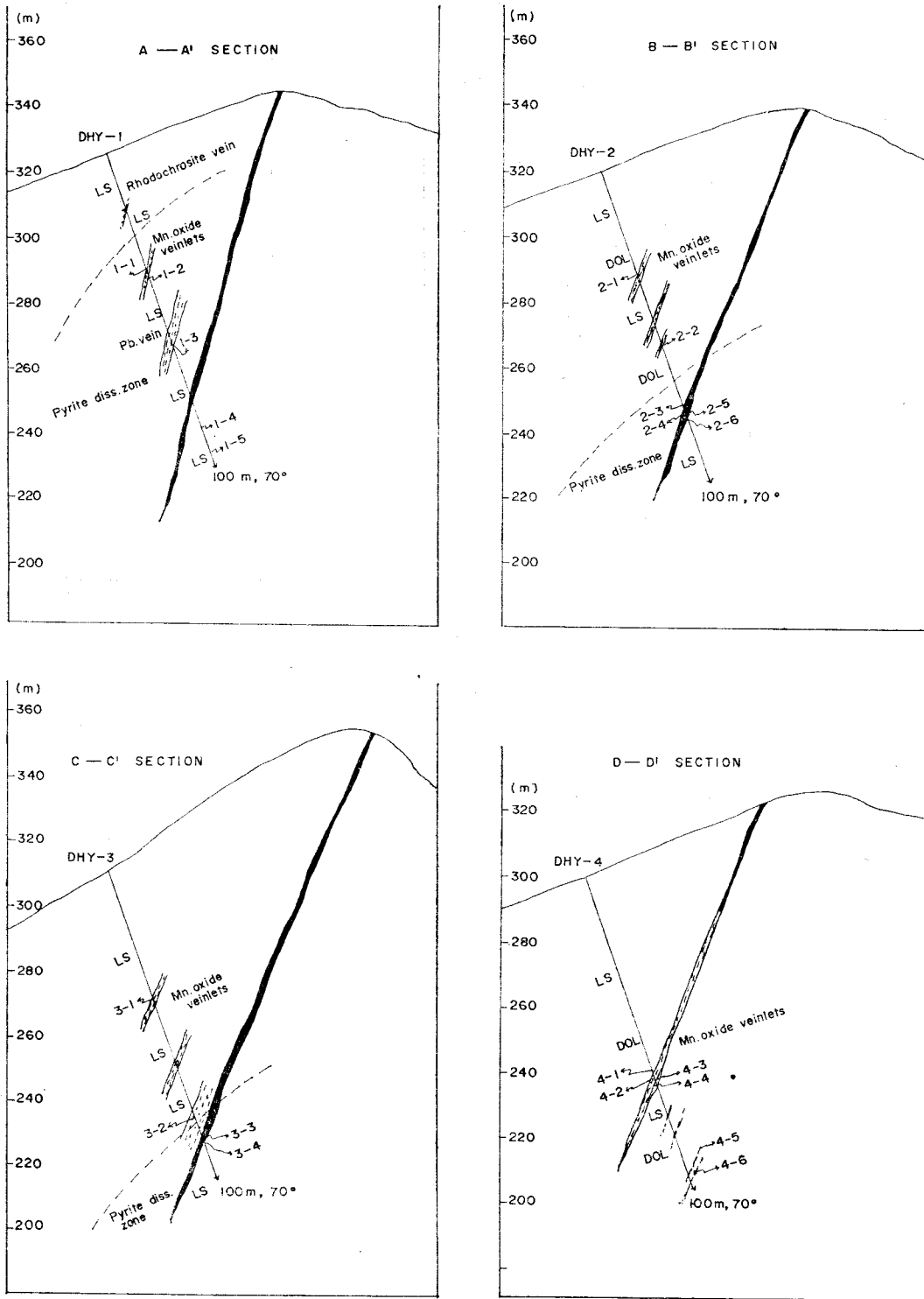
Fig. 2   Drilling section at Eosangcheon mine

Table 2. Manganese content (%) of cores

DHY-1	DHY-2	DHY-3	DHY-4	remarks
1: 0.11	1: 0.10	1: 1.13	1: 8.76	depth=100m, drill-angle=70°
2: 0.09	2: 0.07	2: 15.70	2: 5.17	direction, vein dip
3: 0.01	3: 7.10	3: 16.50	3: 10.40	DHY-1=N75° E, 75°
4: 0.12*	4: 14.00	4: 21.50	4: 9.89	DHY-2=N75° E, 70° *=copper%
5: 0.04*	5: 13.40		5: 0.02	DHY-3=N65°E, 70° figure=sample No.
	6: 1.13		6: 0.04	DHY-4=N35°E, 70°

role in the superficial oxidation, because pyrite produces strong oxidizing ferric/ferrous sulphate in the oxidation zone and dissolves other sulphide minerals in ore veins.

Thus, considering the mineralogical composition of the outcrops and drilled cores, the manganese ore deposits are thought to be composed mainly of supergene manganese oxides, but accompanied by other primary manganese and sulphides of lead-zinc and copper.

The formation trend of manganese oxides of the Eosangcheon mine was studied by Kim and Kim (1982): rhodochrosite→todorokite→birnessite, rancieite→nsutite, pyrolusite, chalcophanite.

Microscopic studies on the polished and thin sections indicate that the supergene manganese oxides were formed by replacing hypogene manganese carbonates and oxides in situ. Supergene manganese oxides are commonly filled in cavities, forming multiple fine collorform bands or layers.

According to Garrel and Dryer (1952) the major control of replacement depends upon the pH of the mineralizing fluid, which in turn controls the solubility of the carbonate host rocks. Limestone, on dissolving, changes ore forming solution causing ores to be precipitated. It was futher proposed by Ames (1961) that principal factor is the solubility of the replacement products relative to the solubility of the host rocks in the same solution, rather than merely the solubility of the host rocks.

The general trend of solubility order of the dominent minerals of the mine is calcite⟩ rhodo-

chrosite⟩ manganese oxide. Accordingly, manganese oxides remain as replacement products which are more stable than rhodochrosite in the supergene environment. Similarly, rhodochrosite was formed by replacing limestone with manganese ions in the hypogene conditions.

After iron is precipitated, manganese precipitates as oxides in the supergene oxidizing condition when the solution becomes still more alkaline. But in supergene reducing condition, mangnese precipitates as carbonate such as secondary rhodochrosite.

Manganese, which was taken into solution as sulphate in existence of sulphide, breaks down upon neutralization and yields the higher oxides of manganese in the supergene oxidizing condition. For instance, pyrolusite is common in the Eosangcheon mine and sulphides occur in the fault shear zone. Pyrolusite is the most stable and common higher oxide.

GEOCHEMISTY OF QUARTZ PORPHYRY, COUNTRY ROCK AND SOIL

Quartz Porphyry

To study the relation of the quarzt porphyry with the manganese deposit in the study area, 8 relatively fresh rock samples were taken from outcrops of the quartz porphyry (Fig. 3) and analysed by atomic absorption spectrometry for major chemical composition. This analytical result of the major chemical composition was treated by computer to obtain Niggli values and CIPW norms (table 3) and was plotted in various
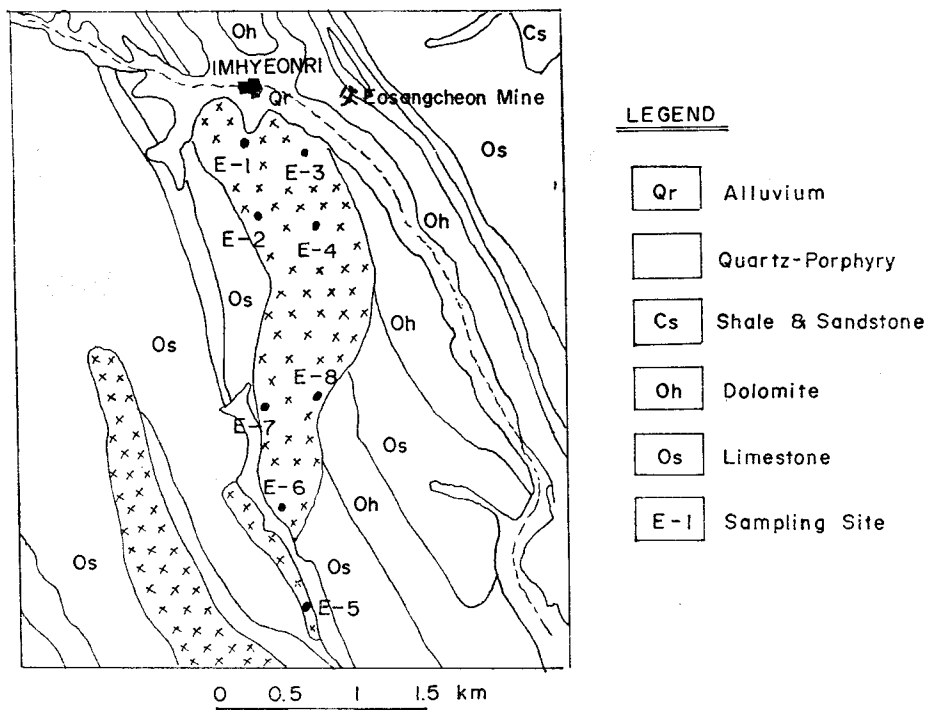
Fig. 3 Map showing sampling points of Eosangcheon mine

diagrams in order to investigate the chemical roles of the quartz porphyry in relation to its manganese ore deposit.

A) Major Chemical Composition

There is compositional difference between the northwestern margin and rest parts of the quartz porphyry; the margin (E–1 & E–2) shows lower values of SiO_2 and K_2O contents but higher values of Al_2O_3, FeO, MgO, CaO, Na_2O and Ti_2O contents than the rest parts (E–3∼E–8), There are no significant differences in the values of Fe_2O_3, MnO and P_2O_5 contents.

The chemical compositional differences can be much clearly demonst rated by plotting them in various triangular diagrams (Fig. 4).

The major chemical composition is largerly analogous to the mineralogical composition observed under microscope, and its analogy is well reflected in the normative mineral proportion of albite>orthoclase>anorthite which was calculated from the major chemical composition.

Niggli Value

Niggli values against that of si trends to increase in alk and al, but decrease in fm and c from the northwestern margin to the rest parts of the quartz porphyry. This reflects a formation sequence of the margin and the rest parts of the quartz porphyry. The early crystallization at the marginal part removed Fe, Mg, Ca and Na from the original magma and increased si and K in the residual magma, which solidified later.

The relatively alkali-rich and c-poor magma was subfemic at the stage when the northwestern margin formed, and changed into salic at the later stage when the rest parts formed (Fig. 5).

Normative Mineral

The quartz porphyry is plotted mainly in the granite region of the triangular diagram of normative composition of quartz-plasio clase-K-feldspar except its northwestern margin, which is plotted in the granodiorite and other region (Fig. 6). The D. I. (normative Or + Ab +An)
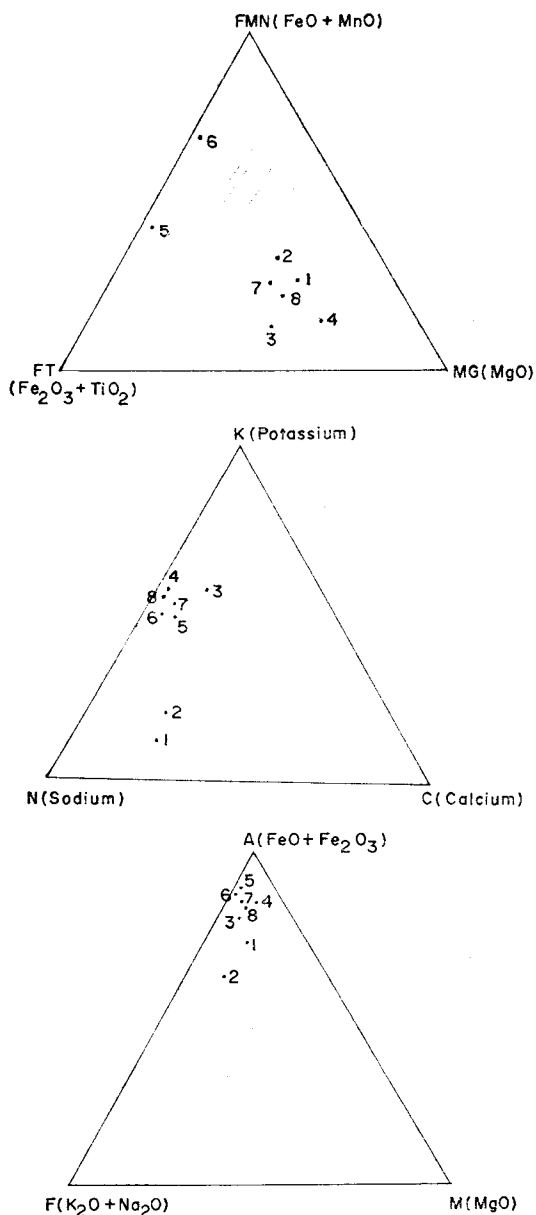
FMN(FeO + MnO)

•6

•5

•2
7• •1
•8
•4
3

FT
(Fe₂O₃+TiO₂)   MG(MgO)

K (Potassium)

4
8• •7 •3
6• •5

•2
•1

N(Sodium)   C(Calcium)

A(FeO+Fe₂O₃)

5
6•7•4
3 •8
•1

•2

F(K₂O +Na₂O)   M(MgO)

Fig. 4 Triangular diagrams of major oxides

is low in the northwestern margin, but increases toward the rest parts of the quartz porphry. This transfer from the granodiorite to granite phases may be due to magmatic differenciation.

B) Trace Element

There are some differences in the variation of metal contents between the granite and granodiorite phases: the contents of copper and lead are higher in the granite whilst the content of zinc, nickel, chromium and molybdenum are higher in the granodiorite. The variation trends of lead, zinc, nickel and chromium are in accordance with the general variation trends between felsic rocks and mafic rocks. Only copper and molybdenum are in oppositional trends. Other elements do not show comparable variations (table 4–a).

In comparison of certain trace elements with the granitic rocks from the Gyeongsang basin (Lee, 1981), the quartz porphyry is lower than copper province in the content of copper, lead, zinc, cobalt, etc. and still lower than lead-zinc province in the content of copper and molybdenum, but higher than lead-zinc province in the content of copper and nickel (table 4–b).

To the variations of ore metals in the quartz porphyry, Goldschmidt's rule is applicable as an useful guide with Ringwood's electronegativity (Mason, 1958). Thus, it is expected that ore metals such as copper, lead, zinc, etc. exchanged major elements of silicates by camouflage, capture or admission during crystallization of the quartz porphyry, being slightly modified by electronega-
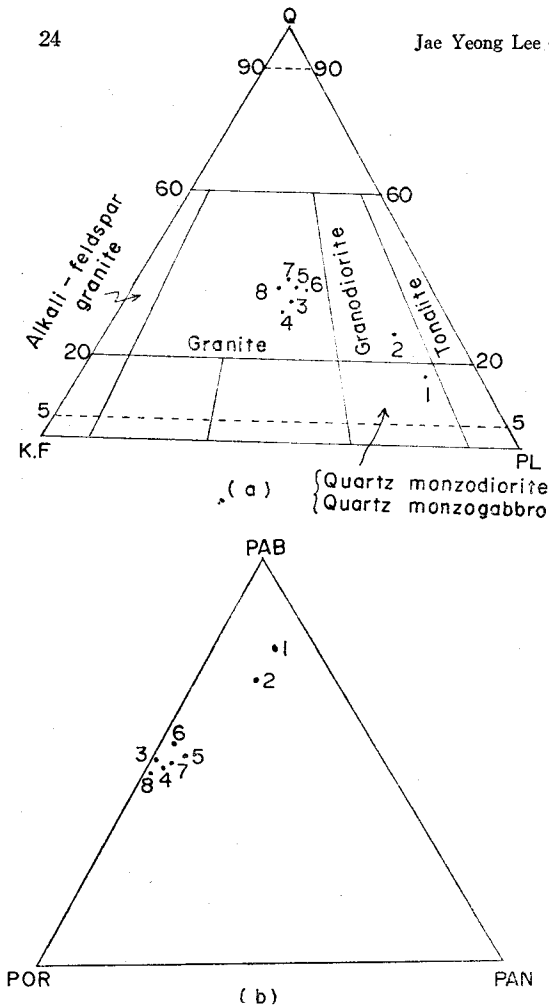
60
40
fm
20
0
10 30 50 70
al
Subfemic   • • Salic

60
40
alk
20
0
10 30 50 70
al
Relatively alkali-rich

60
40
c
20
0
10 30 50 70
al
C-poor

Fig. 5 Variation diagrams of Niggli values for the quartz porphyry from Eosangcheon mine

Fig. 6 Triangular diagrams of normative minerals:
(a) Q–K–F–Pl   (b) Ab–Qr–An

tivity. When the difference of electronegativity is more than 0.1, metal elements with lower electronegativity are preferentially corporated in silicate crystals which are diadochic between major elements and metal elements.

In addition, absorption of the ore metals to the surface of the silicates should be considered during the final crystallization of the quartz porphyry, because it plays an important role in increasing the ore metal contents. The copper content, higher in the granite phase than in the granodiorite phase, seems to be related with this absorption. The absorbed metal elements are removable by leaching with dilute acids. Most ore metals, which show opposite relation in their contents to the Goldschmidt's rule in the study area, seem to be due to the absorption.

Limestone and Dolomite

40 rock samples were taken; 10 from the country rock, 8 from the outcrops and 22 from the main level (Fig. 7).

A) Dispersion Pattern of Trace Element

It is characteristic in the study area that the background values of lead and zinc are high whilst manganese is very low, compared with those of carbonate rocks from other areas.

Table 3. Chemical analysis of the quartz porphyry   (a) Major composition (wt. %)

component	E-1	E-2	E-3	E-4	E-5	E-6	E-7	E-8
SiO_2	65.12	67.16	74.06	75(20	74.90	73.68	74.46	74.02
Al_2O_3	16.76	16.55	13.24	12.52	13.68	15.27	14.44	14.42
Fe_2O_3	0.63	1.67	1.28	0.62	0.75	0.42	0.67	0.73
FeO	1.20	1.83	0.28	0.28	0.28	0.56	0.35	0.35
MnO	0.05	0.05	0.01	0.04	0.07	0.12	0.03	0.05
MgO	1.23	1.26	0.60	0.75	0.01	0.01	0.35	0.47
CaO	2.39	1.99	0.25	0.25	0.74	0.45	0.45	0.25
NaO	6.85	5.60	3.64	3.80	3.77	3.80	3.46	3.36
K_2O	1.22	1.95	4.99	5.25	4.41	4.31	4.58	4.85
Ti_2O	0.97	0.83	0.29	0.31	0.12	0.10	0.19	0.26
P_2O_5	0.20	0.07	0.07	0.08	0.03	0.07	0.04	0.06
H_2O_0	0.29	0.36	0.34		0.16	0.32	0.14	0.32
S	0.02	0.01	0.02	0.01	0.01	0.01	0.07	0.02
Ig. loss	3.16	0.96	0.96	0.59	1.20	1.07	0.84	1.11
total	100.11	100.29	100.03	100.00	100.13	100.19	99.93	100.26
D. I.	79.34	79.79	92.84	94.75	29.54	91.59	91.78	91.91

(b) Niggli values

component	E-1	E-2	E-3	E-4	E-5	E-6	E-7	E-8
al	42.58	41.96	46.22	44.64	49.79	53.54	51.24	50.89
fm	14.40	20.16	12.42	11.19	5.37	5.32	8.07	9.47
c	11.04	47.17	1.59	1.62	4.90	2.87	2.90	1.60
alk	31.99	28.71	39.77	42.55	39.95	39.27	37.79	38.04
si	80.83	288.93	438.77	454.98	462.58	438.35	448.36	443.30
k	0.10	0.19	0.47	0.48	0.43	0.43	0.47	0.49
mg	0.55	0.40	0.43	0.60	0.02	0.02	0.39	0.44
w	0.32	0.45	0.81	0.67	0.71	0.41	0.64	0.66
p	0.35	0.12	0.17	0.20	0.08	0.17	0.10	0.12
qz	52.89	74.10	179.71	184.78	202.80	185.25	197.19	191.15

(c) C. I. P. W. Norms(mol. wt. %)

component	E-1	E-2	E-3	E-4	E-5	E-6	E-7	E-8
q	14.16	20.88	32.55	31.57		33.96	35.43	34.82
or	7.21	11.52	29.49	31.03	26.06	25.47	27.07	28.66
ab	57.97	47.39	30.80	32.16	31.90	32.16	29.28	28.43
an	10.57	9.42	0.79	0.73	3.48	1.78	1.97	0.93
c	0.30	1.77	1.56	0.32	1.43	3.70	3.07	3.31
hy	3.21	3.80	—	—	—	0.75	—	—
mt	0.91	2.42	0.08	0.12	0.77	0.61	0.66	0.52
hm	—	—	1.22	0.52	0.22	0.22	0.21	0.37
il	1.84	1.58	0.55	0.59	0.23	0.19	0.36	0.49
ap	0.46	0.16	0.16	0.18	0.07	0.16	0.69	0.12
en	—	—	1.49	1.87	0.02	0.02	0.87	1.17
salic	90.20	90.98	95.19	95.80	97.45	97.07	96.82	96.12
femic	6.42	7.95	3.51	3.30	1.31	1.95	2.20	2.67
total	96.62	98.93	98.70	99.10	98.76	99.02	99.02	98.80

Table 4. Contents of trace elements (ppm)

(a) quartz porphyry

No.	Cu	Pb	Zn	Ni	Cr	Co	Mo	Mn	As	W	Bi	Be	Ag	phase
E-1	15	10	50	25	65	10	5	800	20	5	10	5	1	gd
E-2	20	10	42	18	70	10	2	750	20	5	10	4	1	gd
E-3	30	30	24	10	55	10	4	600	20	5	10	3	1	qp
E-4	15	13	62	10	50	10	1	1,800	20	5	10	5	1	qp
av.	20	15.8	44.5	15.8	60	10	3	987.5	20	5	10	4.3	1	

(b) granitic rocks in the Gyeongsang basin

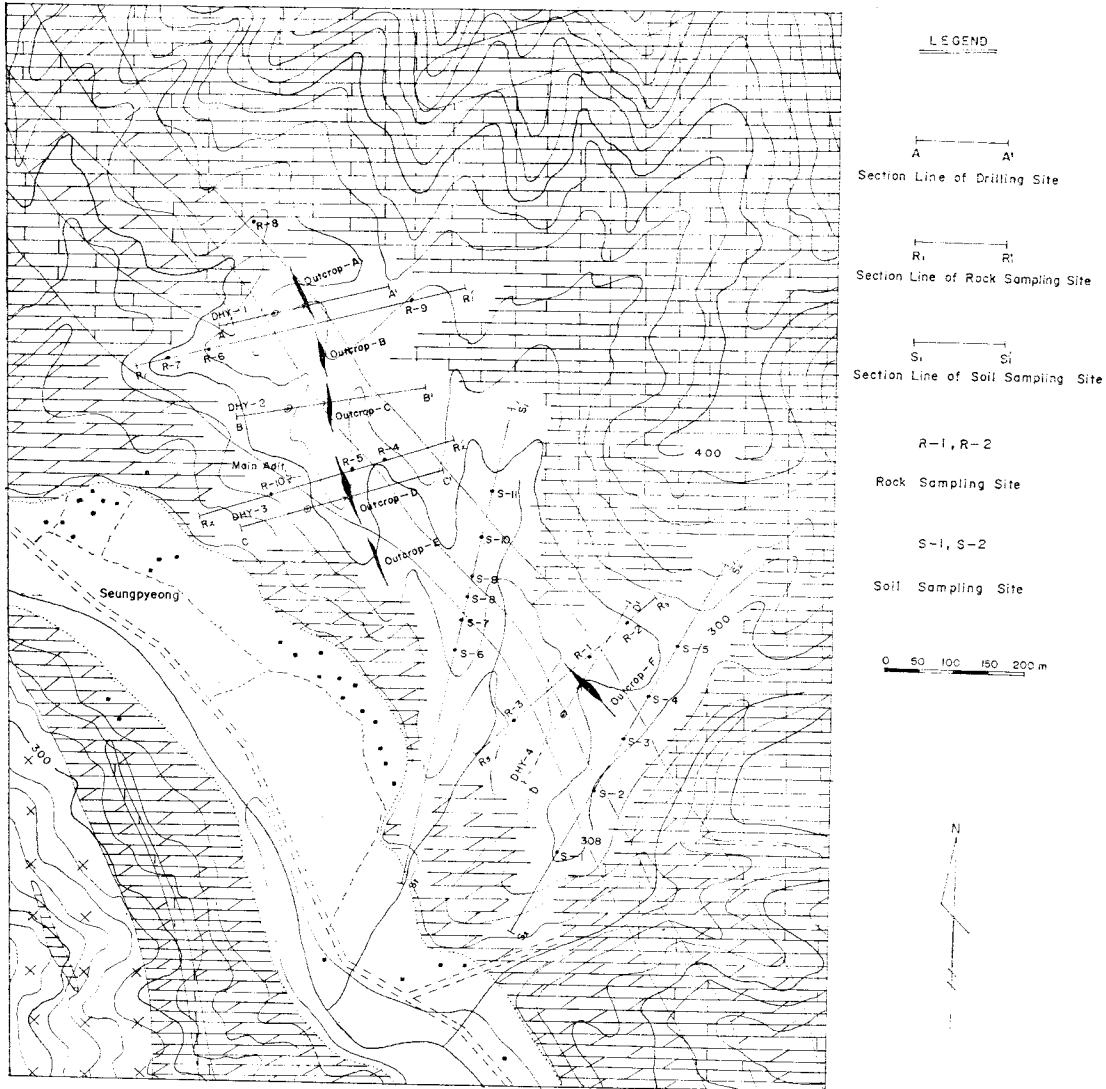| province	Cu	Pb	Zn	Ni	Co	Mo	W
copper	66	34	139	25	27	3	10
lead-zinc	5.5	150.5		6.5	13.5	13.5	

Fig. 7 Map showing sampling points of country rock, cores and soils at Eosangcheon mine

The contents of manganese, lead, zinc, copper, strontium and barium are high or anomalously high near the mineralized fault shear zone and decrease away from the zone (table 5). The anomaly reflects to certain degree the mineralogical composition of the ores of the Eosangcheon manganese ore deposit.

Manganese content is 183 ppm on the average, but anomalously high (6,800 ppm) or at least higher than 300 ppm near the zone, where lead, zinc and copper also show close genetic relation with the hydrothermal mineralization. The averages of lead and zinc are very high in comparison with those (Pb=6 ppm, Zn=15 ppm) of

Table 5. Trace elements in the country rock

traverse	No.	Mn	Sr	Ba	Pb	Zn	Cu	Ni	Co	Mo	remark
R_1–R'_1	R–8	380	350	80	40	1,050	3	8	10	5	near fault
	R–7	150	25	40	50	1,400	4	7	10	5	
	R–6	180	35	40	45	2,400	3	5	10	5	
	R–9	580	120	360	600	770	3	8	10	5	near veinlet
R_2–R_2'	R–10	150	11	10	40	1,950	5	15	10	5	
	R–5	300	250	50	80	350	800	4	10	5	near fault
	R–4	270	55	10	100	620	9	2	10	5	
R_3–R_3'	R–3	100	17	15	140	770	9	2	10	5	
	R–1	6,800	110	30	100	39,000	2	5	10	5	near fault
	R–2	250	12	2	140	2,100	3	3	10	5	
average		183	26	20	82	628	5	5	10	5	
av(Dongnam)		1,172			15	35	13			5	unmineralized
av(world)		1,300	26	100	8	25	15	12			

the carbonate rocks from Dongnam magnetite mine (Soe and Lee, 1983) and the world's averages (Pb=8 ppm, Zn=25 ppm). Strontium and barium have different variation trends because they have no ore genetic relation with those base metals (Fig. 8).

The essential factors, which control the amounts of trace elements in the carbonates at the Eosangcheon mine, are substitution of trace elements for calcium and magnesium and solubility of the carbonates of the trace elements. Thus the contents of strontium (130 ppm) and barium (88 ppm) in the limestone are higher than those (Sr=26 ppm, Ba=7 ppm) in the dolomite, and manganese is only slightly higher in the limestone (281 ppm) than in the dolomite (223 ppm). Strontium has higher content than barium in the limestone, forming probably less soluble mixed crystals. The manganese content, 2 times higher than strontium, may be related to the manganese mineralization by the hydrothermal solution.

The background of manganese in the country rock is too low to be remigrated and to contribute to the hydrothermal mineralization of manganese. Futhermore, there is no synsedimentary manganese ores in the country rocks at the study area. The

anomalous values of lead and zinc seem to be related with the primary epigenetic dispersion by the hydrothermal mineralization along the fault shear zone. If the anomalous values had been of synsedimentary origin, they might have been dissolved at least partly by the hydrothermal solution and remigrated to form galena ore. But this kind of galena was not found in the study area.

B) Mn-rich Outcrops

Manganese content is highest (24.2%) at the outcrop near the main level of the mine and trends to decrease away from the outcrop along the fault shear zone; 1.2% at the northmost outcrop "A" and 2.06% at the southmost outcrop "E". Manganese content is 22.21% and ranges from 5.53% to 40.51% at the main level (table 6).

Limestone and dolomite are partly silicified, showing highest SiO_2 content (69%) and lowest manganese content (1.2%) at the outcrop "A". This inverse proportion in content of manganese to silicate is also observed at the outcrop "D". This seems to be due to the different sequence of mineral formation between rhodochrosite and quartz during the hydrothermal mineralization. The limestone and dolomite might be replaced by
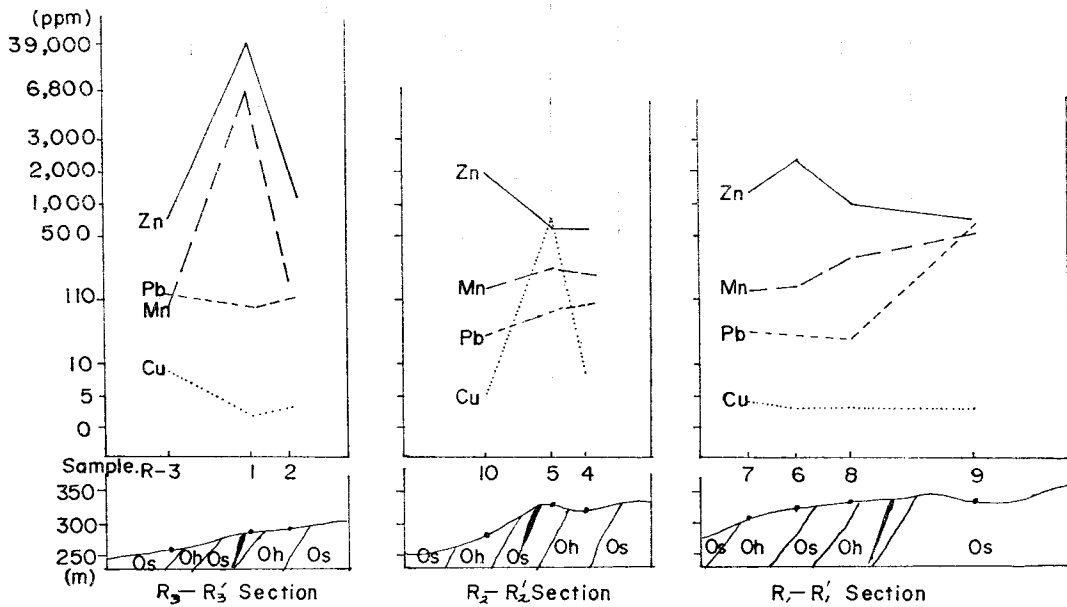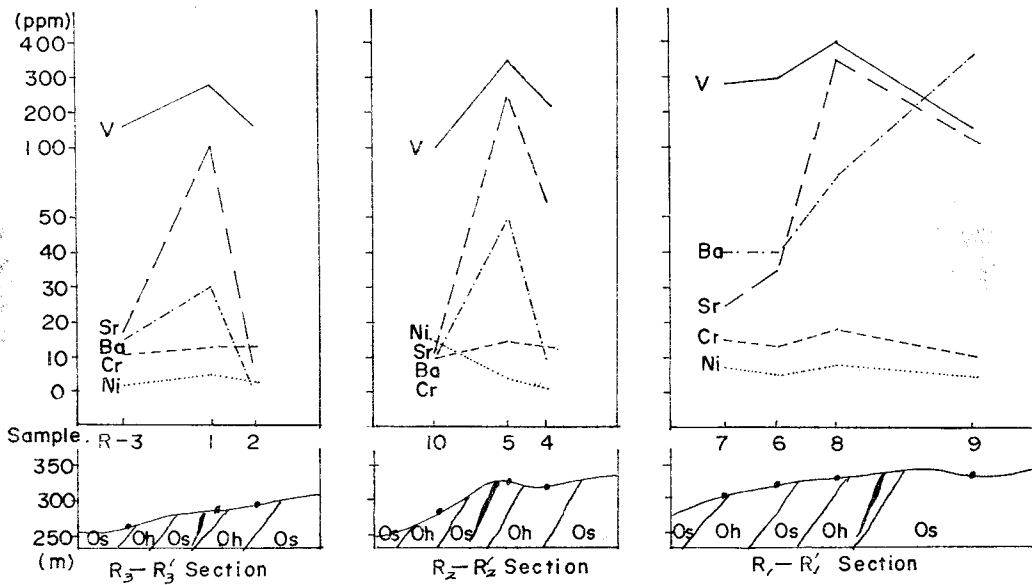
Fig. 8 Primary dispersion patterns in limestone (Os) and dolomite (Oh):
  (a) Mn, Cu, Zn   (b) Sr, Ba, Cr, Ni, V

manganese at the earlier stage and then by quartz at the later stage.

Some veinlets of galena, rhodochrosite and

manganese oxides are found in the drilled cores near the fault shear zone and on the surface where anomalies were found (see Fig. 2).

Table 6. Chemical analysis of ores

(a) Outcrops

outcrop	Mn	SiO$_2$	CaO	variation of Mn	silicification
A	1.20	69.0	1.70	low	high
B	2.40	4.33	30.80	↓	
C	6.88				
	8.43	31.40	14.70	high	moderate
D	10.20				
	24.20	5.73	2.36	↓	
E	2.06	2.63	34.70		slight
F	2.13			low	

(b) Main level

No.	Mn(%)	No.	Mn(%)	No.	Mn(%)	No.	Mn(%)	No.	Mn(%)	remark
1	31.05	2	15.92	3	16.10	4	15.04	5	22.56	Sampling
6	14.60	7	19.55	8	40.51	9	11.94	10	11.76	width=1.5m
11	19.02	12	36.00	13	6.90	14	21.23	15	5.35	
16	31.36	17	19.73	18	14.33	19	33.17	20	31.49	
21	33.48	22	38.66								aw=22.26

Table 7. Trace elements in soils at the Eosangcheon mine

sample No.	Mn	Ag	Ba	Be	Co	Cr	Cu	Mo	Ni	Pb	Sr	V	Zn
S– 1	400	<1	170	1.2	10	15	4	<5	40	40	70	280	770
S– 2	700	<1	140	1.0	<10	20	100	5	50	40	75	200	770
S– 3	750	<1	180	1.5	10	25	200	5	80	500	5	180	2,550
S– 4	680	1	300	1.2	40	30	160	5	150	800	7	120	5,000
S– 5	300	<1	40	1.0	<10	25	70	15	35	80	5	60	620
S– 6	1,800	1.5	600	1.8	60	30	180	7	120	2,500	7	160	22,000
S– 7	650	<1	500	1.0	40	30	80	<5	130	120	10	90	2,400
S– 8	900	1	480	1.3	35	35	120	10	180	150	15	150	3,000
S– 9	750	1	480	1.2	30	30	180	6	200	3,00	7	100	2,100
S–10	600	<1	450	1.0	30	30	130	15	130	100	6	130	1,400
S–11	650	1	500	1.2	75	50	100	9	150	150		200	1,200

C) Soil

Various trace elements dissolved from the limestone and dolomite of the Eosangcheon mine have been accumulated in the alkaline and calcareous soils which were developed on the limestone and dolomite, while some others were leached from the soils depending on the soil-forming conditions, chemical, biological, mechanical, etc.. Thus, the amounts of trace elements in soils are largerly influenced by the original concentration of trace elements in the country rock and then soil development. The soils at the mine are shallow and contains much fragmental materials because of rapid erosion and run-off of the surface soils owing to steep slopes. Therefore, it may be expected that trace elements wereless concentrated in soils due to the lack of time necessary for their accumulation. The amounts of trace elements are presented in
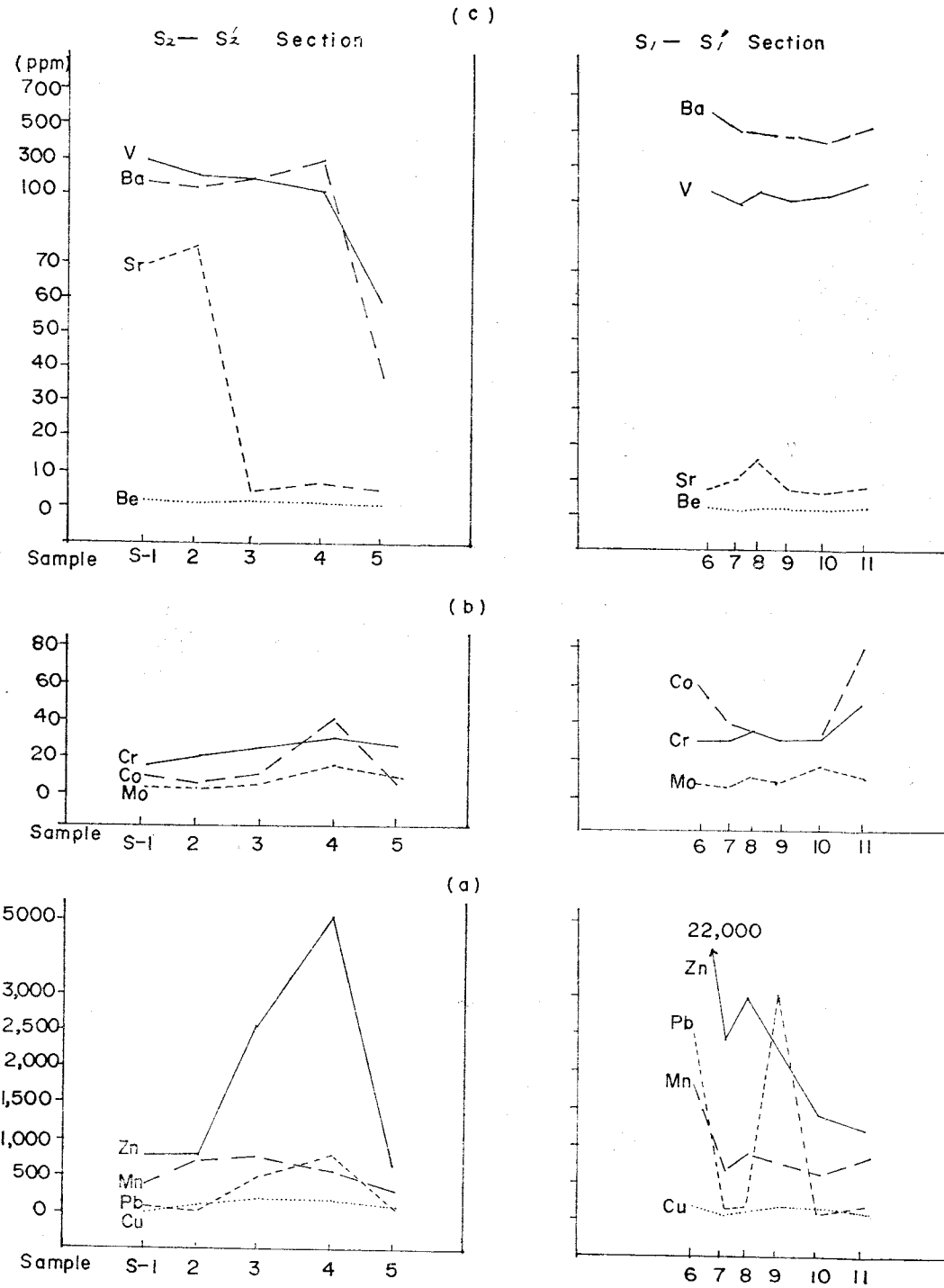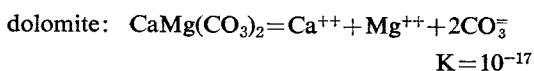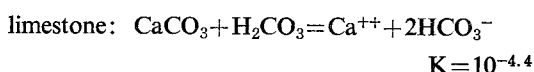
Fig. 9   Secondary dispersion patterns in soils at Eosangcheon mine
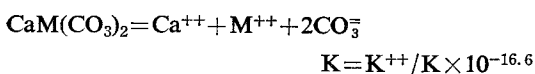(a) Mn, Pb, Cu, Pb, Zn   (b) Mo, Co, Cr   (c) Sr, Ba, V, Be

table 7.

In order to interpret this secondary dispersion pattern of trace elements in soils (Fig. 9) in relation to the primary dispersion pattern and the mineralization in the country rock, it is necessary to understand some geochemistry of carbonates before considering the chemical property of trace elements under clay-rich, alkaline and calcareous soils.

CO_2 dissolves in natural water and makes water acid. This carbonic acid is important in controlling the solubility of $CaCO_3$ in most environments. The overall processes, when limestone dissolves in carbonic acid, may be summerized by equations according to kinds of salts (Krauskopf, 1967)

limestone: $CaCO_3 + H_2CO_3 = Ca^{++} + 2HCO_3^-$

$$K = 10^{-4.4}$$

dolomite: $CaMg(CO_3)_2 = Ca^{++} + Mg^{++} + 2CO_3^=$

$$K = 10^{-17}$$

limestone containing other metals:

$CaM(CO_3)_2 = Ca^{++} + M^{++} + 2CO_3^=$

$$K = K^{++}/K \times 10^{-16.6}$$

The incongruent reaction was excluded because dolomite dissolves congruently at ordinary temperature according to Garrel et al. (1960), and it is expected that limestone containing other metals has similar property to dolomite in dissolving process. The M^{++} stands for $Mn^{++}(K = 10^{10.2})$, $Sr^{++}(K = 10^{-9.6})$, Ba^{++} $(K = 10^{-8.8})$, $Cu^{++}(K = 10^{-33.8}$ for malachite), Zn^{++} $(K = 10^{-10.8}$ at 20C), Pb^{++} $(K = 10^{-13.1})$, etc..

The forward reaction shows how limestone and dolomite dissolve, and the reverse reaction represents the precipitation of carbonate when CO_2 evaporates from solution.

Calcite is somewhat soluble even in water containing no CO_2:

$CaCO_3 \rightleftharpoons Ca^{++} + CO_3^=$ $K = 10^{-8.3}$
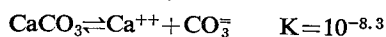
and the hydrolysis reaction would be:

$CaCO_3 + H_2O = Ca^{++} + OH^- + HCO_3^-$
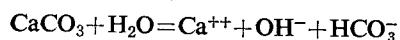
In the limestone area at the mine, surface water and ground water are approximately saturated with $CaCO_3$, and such waters can either dissolve or precipitate the carbonates depending on the amounts of dissolved CO_2. Thus, in soils in contact with solutions containing various metal ions the precipitated carbonates are easily replaced to some extent by other less soluble carbonates of manganese, strontium, barium, copper, lead, zinc, etc.

The elements of ore metals seem to be derived from those disseminated in limestone and dolomite during the manganese mineralization. The metals might form mixed crystals of carbonates, or be absorbed by clays, organic materials, etc. in soils at the mine.

Manganese

According to Vinogradov (1959), it is well known that manganese occurs in soils at least in two forms, the mobile form and the immobile form. The mobile includes Mn^{++} compounds and exists in the soil solutions as carbonates, bicarbonates, sulphates, and other soluble in the acid environments with pH up to 6. This Mn^{++} precipitates as MnO_2 by being oxidized at surface or changes into $Mn(OH)_2$ at pH=8 as following:

$Mn(OH)_2 + 2H_2O + 2CO_2 = Mn(OH)_2 + 2H_2CO_3$
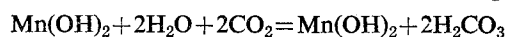
Though the Mn^{++} ion in solution is not easily oxidized, the hydroxide Mn $(OH)_2$ oxidizes to be manganic hydroxide Mn $(OH)_3$ and then by futher oxidation forms MnO. nH_2O, finally crystallizing pyrolusite Mn_2O, which is the most stable oxide form. Neither the Mn^{3+} compound nor Mn_2O are soluble in soil solutions.

According to the Eh-pH diagarm of manganese minerals, MnO_2 may also form directly from rhodochrosite by replacement or by futher oxidation of lower oxide forms.

Manganese, mostly derived from rhodochrosite through these processes, is more highly concentrated in soils than in rocks compared with other trace elements. Thus, Eosangcheon mine has very high average of manganese in soils (638 ppm),

3.5 times higher than in the country rocks (183 ppm), and its anomalies are very high due to this high background of manganese in soils. An manganese anomaly (1,800 ppm) is 3 times higher than its average, and 10 times higher than that in the country rock. This anomaly seems to be due to the oxidation of rhodochrosite in the limestone and dolomite.

Strontium and Barium

Strontium and barium occur mainly as carbonates and sulphates in soils, because they are relatively resistant to weathering. Strontium is more stable as strontianite ($SrCO_3$) than as celesite ($SrSO_4$), while barium is more stable as barite ($BaSO_4$) than as witherite ($BaCO_3$). If chlorine ion is abundant in the soils, barium and strontium leave the soils gradually as chloride. But this is not expected because no chlorine is supplied from sea wind, which usually supply it to soils near sea. Therefore, barium occurs in residual lumps and residual clay as barite, and to a minor extent as witherite. On the contrary, strontium is expected to occur as strontianite and to minor extent as celesite in soils. In nature strontianite forms a secondary alteration product of primary celesite and replacement of limestone.

Thus, barium is concentrated more in the soils than in the carbonate rocks, but to less extent than manganese due to originally low amount in the rocks. Accordingly, the average of barium (349 ppm) in soils at the mine is very high, about 20 times higher than the original value in the limestone and dolomite.

Strontium, on the contrary, is rather lower in soils (19 ppm) than in rocks because of its lower solubility as strontianite in the rocks. Strontianite may remain in limestone forming mixed crystal with $CaCO_3$ whilst barium may be dissolved from limestone and concentrated in soils. Rhodochrosite is also rather less soluble than strontianite, but it is main ores at the mine and most manganese contents were derived from the min-

eralized manganese carbonates in the country rocks of limestone and dolomite.

Copper, Lead, Zinc and Others

Copper and zinc are very mobile in acid condition ($pH < = 5$), where sulphides are weathered in the superficial environment, but are restricted in alkaline and calcareous soils as stable carbonates. The solubility products of the carbonates are $10^{-33.8}$ for malachite $Cu_2(OH)_2CO_3$ and $10^{-10.8}$ for smithonite $ZnCO_3$. Therefore, Cu is more concentrated in soils than Zn. Copper and zinc ions also exist in the forms absorbed in limonite, iron-rich clay, manganese oxide or organic materials.

High contents of Ca^{++} and HCO_3^- characteristic of the soils at the mine can also effectively restrict the secondary dispersion of molybdenum by precipitating $CaMoO_4$. Molybdenum tends to be precipitated in the presence of iron and be preferentially retained in the iron-rich soils of the mine. The average of molybdenum in soils is 8 ppm, slightly higher than that (5 ppm) in rocks.

Lead is immobile and cerrusite has lower solubility product ($K = 10^{-13.1}$) than smithonite ($K = 10^{-10.8}$). Therefore, cerrusite is more stable in limestone than smithonite and may be concentrated even as residual minerals as well as secondary cerrusite, increasing lead contents in soils.

Accordingly, copper has much higher average (120 ppm) in soils than in rocks (5.6 ppm) while the average of zinc is not so higher in soils (1,981 ppm) than in rocks (1,212 ppm) and the average of lead in soils (218 ppm) is approximately two times higher than in rocks (97 ppm).

Thus, very high and anomalous values in soils seem to be related to the hydrothermal mineralization, which formed manganese ore deposits at the Eosangcheon mine. Therefore, an anomaly of lead (2,500 ppm) and zinc (22,000 ppm), and another one of lead (3,000 ppm) may be due to the oxidation of lead-zinc sulphides embedded

in the country rocks of limestone and dolomite.

Cobalt and chromium are also slightly concentrated in soils in the amount of 33 ppm (Co) and 28 ppm (Cr) relative to 10 ppm (Co) and 12 ppm (Cr) in rocks.

The secondary dispersion patterns of above trace elements in soils at the mine are helpful to interpret the anomalous values in reation with the mineralization.

Summerization and Conclusion

Quartz porphyry is plotted mainly in the granite region of the triangular diagram of normative composition (Qtz-Pl-Or), and shows a trend of magmatic differentiation from the granodiorite to granite phases. This is traced from the northwestern margin toward the rest parts of the quartz porphyry.

The difference of the phase in the quartz porphyry is reflected to some degree in the contents of certain ore metals: the granite phase contains on the average 23 ppm Cu, 22 ppm Pb, 43 ppm Zn, 10 ppm Ni and 53 ppm Cr compared with 18 ppm Cu, 10 ppm Pb, 46 ppm Zn, 22 ppm Ni and 68 ppm Cr in the granodiorite phase. The former two elements are higher in the granite phase and the later three elements are higher in the granodiorite phase. This variation, which is dependant on phase difference, coinsides with the general primary syngenetic pattern that differ depending on mafic or felsic rocks.

The quartz porphyry has lower content of copper, lead, zinc, nickel and chromium compared with the granitic rocks from the copper province in the Gyeongsang basin, but the content of copper and nickel is higher than that in the granitic rocks from the lead-zinc province in the Gyeongsang basin.

The content of ore metals in the country rock is high or anomalously high near the mineralized fault shear zone and trends to decrease away from the zone. Anomalies of manganese, copper,

lead and zinc seem to be related with the hydrothermal mineralization.

The secondary dispersion pattern of ore metals in soils shows close relation with the solubility of carbonates of the metals under weathering condition. This pattern is useful to interpret the anomalous values in relation with the mineralization in the study area.

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어상천망간광산 모암의 지구화학

이 재 영·황 덕 환

요약：어상천 망간광상은 조선계 홍월리층의 돌로마이트와 삼태산층의 석회암내에 발달한 단층 파쇄대를 따라 형성된 표성산화망간광상이다. 본 산화망간광상의 하부에는 백악기 석영반암에 의하여 형성된 열수교대 내지 충진광상이 본 단층파쇄대를 따라 발달한다.

석영반암은 주성분으로 부터 계산한 노음치를 Q-K-F-Pl 삼각도에 점시하면 북서단은 화강섬록암의 영역에 그리고 주암체는 화강암의 영역에 점시되고 D. I. 치는 상기 북서단에서 부터 주암체쪽으로 증가한다. 따라서 이것은 마그마의 분화작용과 관계되는 것으로 보인다.

본 석영반암내 암질의 차이는 미량성분에도 반영이 되어 나타나고 있는 데 북서단에서 아연, 닉켈, 크롬, 몰리브덴의 함량이 높고 주암체에서는 동, 연의 함량이 높은 현상은 산성암과 염기성암에서 일반적으로 볼 수 있는 함량의 변화와 일치한다.

경상분지내 백악기 화강암류와 비교해 보면 동, 연, 아연, 닉켈, 크롬의 함량은 석영반암쪽이 분지내 동광상구의 화강암류보다 낮으나 동과 닉켈의 함량은 연·아연 광상구의 화강암류보다도 높은 경향을 보인다.

석회암 및 돌로마이트로 구성된 모암은 석영반암에 의한 광화작용으로 단층파쇄대에서는 망간, 연, 아연, 동등의 함량이 현저히 높고 멀어짐에 따라 감소되는 일차후생분산형태를 보인다.

토양중 미량원소의 함량은 토양의 생성조건 및 물리화학적조건과 밀접한 관계를 보이며 모암에서의 그들이 형성하는 탄산염의 용해도와도 주목할만한 관계를 보인다. 즉 난용성의 탄산염을 형성하는 미량원소는 토양중의 함량도 낮은 경향을 보인다.