Geochemical characteristics of halogen-bearing hastingsite, scapolite and phlogopite from the Sangan iron skarn deposits, northeastern Iran

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Mesozoic shale, siltstone, sandstone and carbonate rocks and Eocene volcanic, volcanoclastic and pyroclastic rocks are intruded by late Eocene granitic batholith and related acidic dikes. As a result of hydrothermal activity associated with the granitoid, two distinct skarn zones of calcic skarn zone and magnesian skarn zone were formed in the carbonate rocks.

Cl-bearing amphiboles of ferroactinolite to potassium-rich ferrohastingsite composition are restricted to the calcic skarn zone and associating with salite, grandite, magnetite, calcite and sometimes with scapolite. The Cl content of amphiboles shows positive relationships with $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ and $\text{K}/(\text{K} + \text{Na})$ and a negative relation with $\text{Si}/(\text{Si} + \text{Al}^{\text{IV}})$. In contrast, F-bearing phlogopite is a major mineral in the magnesian skarn. F content exhibits positive relationship with wt% of SiO_2 and MgO . The estimated $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ equilibrating with the phlogopite ranges from 4.6 to 5.5 at 400°C. Cl-rich scapolite is widespread in both calcic and magnesian skarn zones. The scapolite has a compositional range of 23 to 40 mole% meionite in marialite-meionite solid solution series. X_{Cl} of the scapolite ranges from 0.44 to 0.98 (mostly more than 0.75). Scapolite of $X_{\text{Cl}} = 0.98$ from the hornfels is the most Cl-rich scapolite ever reported. Cl content of the scapolite positively correlate with $\text{Na}/(\text{Na} + \text{Ca} + \text{K})$. Calculated X_{NaCl} values for fluid in equilibrium with scapolite from the Sangan deposits reach up to more than 55 wt% equivalent NaCl.

The Cl-rich hastingsite, Cl-rich scapolite, F-rich phlogopite, and fluid inclusions with high salinity (up to 70 wt% eq. NaCl) in granitic rocks and in skarn zones suggest that hydrothermal fluids were derived from the granitoid magma. The ore elements such as Fe and Cu could be transported by solutions as metal-chloride complexes. Large amounts of cations such as Al, Si, and Ca incorporated in the fluids should be derived from the country rocks and from the breakdown products of early skarn minerals.

Keywords: Halogen, Hastingsite, Scapolite, Phlogopite, Fluid inclusions, Iron skarn deposit, Granite, Sangan, Iran

I. Introduction

The Sangan iron ore deposit is located about 300 km southeast of Mashhad, northeastern Iran (Fig 1). The iron mineralization is observed in vast area and shows close proximity with associated intrusive and carbonate rocks. The high grade iron ore deposits are

extending for more than 20 km along granitic intrusions and are divided into Western, Central and Eastern ore deposits. This study is mainly concentrated on the Western ore deposit which is subdivided into orebodies of A', A, B, South C and North C (Fig. 1). The iron ores and halogen-rich minerals of hastingsite, scapolite and phlogopite are associated with skarn min-

Fig. 1. A simplified geological map of western orebodies of the Sangam iron ore deposits. Ore bodies are shown as A', A, B and C. White parts are zones that are mainly consisting of skarns and carbonates. Enclosed areas will be shown for geological mapping. Symbols of star, cross and small square are sampling locations of scapolite, hastingsite and phlogopite, respectively.

erals such as garnet and clinopyroxene.

Cl and F are important volatile elements in the various geological environments. They play important roles in the hydrothermal transport of metal components through the formation of halide-complexes and in the metasomatism through ionization of HCl and HF (Chou and Eugster, 1977, Burnham and Ohmoto, 1980). Amphiboles and micas are good indicators of fluid composition and halogen activity (Munoz and Ludington, 1974, 1977; Valley *et al.*, 1982; Munoz 1984; Vanko, 1986; Sisson, 1987; Mora and Valley, 1989; Zhu and Sverjensky, 1991, 1992; Enami *et al.*, 1992; Nijland *et al.*, 1993; Leger *et al.*, 1996; Sato *et al.*, 1997). Cl-scapolite has been experimentally investigated as a good indicator of NaCl concentration in the fluid (Orville, 1975; Ellis, 1978; Rebbert and Rice, 1997). Cl and F contents in amphiboles, scapolite and

phlogopite from the Sangam deposit are analyzed to discuss the origin and role of halogens during mineralization. The relationships among F and Cl-bearing minerals, anhydrous minerals and country rocks especially in the skarn zones are also discussed in this study.

II. Geology of ore deposit

Lower Jurassic contact metamorphosed and metasomatized shale, siltstone and sandstone with thickness of more than 500 m are the oldest formations in the mining area. They are exposed in many outcrops in the northern part of orebodies (Boomeri, 1992), and are extending with the strike of approximately east-west (Fig. 1).

Middle Jurassic calcite and dolomite marbles which host the iron ore bodies and skarn minerals overlie the Lower Jurassic metamorphosed and metasomatized shale, siltstone and

sandstone (Boomeri, 1992). Marbles are strongly replaced by skarn in A' and South C ore bodies. In contrast, thick massive marbles (>50 m) are exposed in A and B orebodies. Magnetite among the marble in B orebody is topographically the highest cliffs over the Sang-an ore deposit. The beds dip toward the south with an angle of approximately 85° around orebody B. Fauvelet and Eftekhari-Nezhad (1990) believe that the shale, sandstone siltstone and carbonates have a Late Proterozoic age. However, from the paleobotanical studies of fossils, their age range from Jurassic to Cretaceous (Kermani and Forster, 1991; Boomeri, 1992; B.H.P. Exploration, 1993).

The carbonate rocks are unconformably overlain to the south by a thick pile (3,000 m.) of volcanic rocks composed of dacitic and rhyodacitic volcanic, andesitic pyroclastic and volcanoclastic rocks (Fig. 1). The lavas are mainly dacite porphyry, interlayered with various porphyritic, andesitic and rhyodacitic pyroclastics and volcanoclastics of Eocene age (41.1 ± 3.5 Ma) (Fauvelet and Eftekhari-Nezhad, 1990). There is a transitional unit between the carbonate rocks and Eocene pyroclastic rocks. This unit is composed of agglomeratic and volcanoclastic rocks with rounded to sub-angular lithoclasts of limestone, shale, siltstone and sandstone. The fragments of volcanic rocks are scattered within the sedimentary lithoclasts. The large volume of transitional unit is Eocene volcanoclastic rocks which locally mixed with conglomeratic rocks consisting of pebbles of Mesozoic formation (pebbles of limestone, siltstone, sandstone and shale). All of the formation in the area are extensively folded, faulted, tilted, metamorphosed and metasomatized.

In the north of Western ore deposit, the formations are intruded by Sarnowsar granite intrusion (Fig. 1) with late Eocene age (Fauvelet and Eftekhari-Nezhad, 1990). There are some

skarn zones directly in contact with the granite, however, the main ore bodies are far from the granite. The B orebody (the most prominent ore body) is 1 km away from the Sarnowsar granite (Fig. 1). The granite apophyses are intruding into the A' ore body. The A' and North C ore bodies are also intruded by a dacite porphyry which is in contact with the granite. All the formations of Mesozoic to Oligocene age are also intruded by granitoid-related felsic subvolcanic dikes (Fauvelet and Eftekhari-Nezhad, 1990), which cut the formations along the NE-SW direction.

Fauvelet and Eftekhari-Nezhad (1990) mentioned that pre-Neogene faults and structures generally trend to the WNW-ESE and a few trend to the NE-SW. A major fault defines the contact zone between the Eocene pyroclastic rocks and Mesozoic carbonate rocks (Fauvelet and Eftekhari-Nezhad, 1990). This fault was off-set by many faults with approximately N-S trending. The felsic dikes are apparently parallel to these N-S faults.

III. Petrography and chemistry of intrusive rocks

The granite is medium grained with granular and porphyritic (partially myrmekitic and graphic) textures. It is composed of perthitic orthoclase, zoned plagioclase, quartz, biotite, hornblende, sphene, magnetite and apatite. Feldspar is partially altered to sericite and kaolinite. Hornblende is partially replaced by sphene, magnetite, and biotite. The granitic rocks contain xenoliths with microgranular and porphyritic texture. The xenoliths are composed of plagioclase, biotite, amphibole, magnetite, sphene, apatite, K-feldspar and diopside. The granitic rocks are classified into granite, monzo-granite, syeno-granite and granodiorite (Boomeri *et al.*, 1997), based on modal classification scheme of Streckeisen (1973).

The dacite porphyry (more than 10 m in thickness) is usually found adjacent to the granite and is exposed in the garnet-magnetite and the magnesian zones. The dacite porphyry should be apophyses of granite, and partly show graphic, granophyric and glomeroporphyritic textures. The dominant phenocryst is oligoclase-andesine plagioclase. The groundmass shows microcrystalline texture, where quartz underwent secondary growth. Amphiboles are usually altered and corroded by groundmass. Other minerals are augite, sanidine, biotite, chlorite, sphene, apatite, magnetite and epidote. The rhyodacitic and dacitic dikes are also porphyritic in texture and most of them are extensively altered to sericite and calcite in ore mineralization zones. In contrast to dacite porphyry, the dikes (less than 10 m in thickness) extend for several km contain no pyroxene.

The chemical compositions of Sangan igneous rocks show that the igneous rocks belong to high-K calc-alkaline series. (Boomeri, 1992; Boomeri *et al.*, 1997). High-K series are more common in active continental margins, particularly at the acid end of the magmatism spectrum (Wilson, 1989). These high-K characteristics may reflect increasing degrees of crustal contamination by magma in the active margins or by K-metasomatism (Wilson, 1989).

IV. Contact Metamorphism and skarns

Effects of contact metamorphism and metasomatism are observed in the rock formations along the contact zone of the granitic rocks. The shale, siltstone and sandstone are gradually transformed into dark quartzite and hornfels from B and C orebodies toward the granite. The hornfels is composed of quartz, biotite, plagioclase, K-feldspar, scapolite, diopside, sphene, magnetite, zircon and amphibole. Biotite is widespread in all assemblages, however, appearance of the other minerals depends on the chemical nature of the original rocks.

The biotite usually occurs along fractures with a texture of hydrothermal origin. Therefore, original contact metamorphic effects may be overprinted by late hydrothermal activities. However, there are no common metamorphic minerals such as cordierite and andalusite in the samples studied. The rocks are extensively fractured, commonly sericitized and consist of numerous quartz and calcite veinlets especially adjacent to orebodies.

The skarns and orebodies are mainly formed in carbonate rocks. The magnetite ores are massive and lenticular in shape extending along this carbonate unit. The skarn and orebodies have moderate to steep dips and are controlled by the stratigraphy and faults. Shale and pyroclastic rocks are also partially replaced by magnetite and skarn minerals. Based on mineralogy, chemical composition and alteration assemblages, the metasomatized zones in the western orebody are divided into two distinct zones of calcic skarn and magnesian skarn zones.

The calcic skarn zone continues from A' orebody to A, B, and South C orebodies, with a trend of SSE. The total distance is approximately 4.5 km. The calcic skarn zone is further divided into garnet-scapolite-pyroxene, magnetite and garnet-pyroxene skarn zones (Fig. 1).

The magnesian skarn zone in western orebodies is only restricted to the North C orebody (Fig. 2-b). However, it extends in a SSE direction toward the middle orebodies with a total distance of approximately 2.5 km.

1. Garnet-scapolite-pyroxene skarn zone

The garnet-scapolite-pyroxene skarn zone is formed with NS direction along A' and northern part of A orebodies. The carbonate rocks in this zone are, as mentioned before, mainly replaced by skarns (Fig. 2-a). A swarm of rhyodacitic dikes and granitic apophyses are intruding into the A' orebody (Fig. 2-a). More

Fig. 2. (a) Geologic map and schematic A-A' cross section of enclosed area 1 in Fig. 1. (b) Geologic map and schematic B-B' cross section of enclosed area 2 in Fig. 1.

than 90% of the skarn minerals are garnet and magnetite, accompanied by Cl-rich scapolite, calcite, clinopyroxene and amphiboles of actinolite-ferroactinolite series and Cl-rich ferrohastingsite. They contain clinopyroxenes in diopside-hedenbergite solid solution series and garnet in andradite-grossular solid solution series (Boomeri, 1992; Boomeri *et al.*, 1996a). Common occurrence of clinopyroxene inclusions in garnet and the related textural relationships suggest an earlier generation of clinopyroxene relative to garnet and magnetite. Clinopyroxene and garnet are also partially replaced by amphibole, chlorite, biotite, iron oxides, sulfides, carbonates and quartz. Assemblages and chemistry of the minerals suggest the following mineral assemblages; diopsidic pyroxene $\rightarrow$ grandite $\pm$ salite $\pm$ magnetite $\rightarrow$ calcite $\pm$ hastingsite $\pm$ scapolite $\pm$ magnetite $\pm$ sulfide minerals $\rightarrow$ chlorite $\pm$ actinolite $\pm$ calcite $\pm$ quartz $\pm$ feldspar $\pm$ pyrite and $\rightarrow$ iron

hydroxide $\pm$ copper carbonates $\pm$ quartz $\pm$ calcite.

2. Magnetite skarn zone

The magnetite skarn zone is defined as a zone containing the orebodies of A' and B (Fig. 1), where scapolite, hastingsite and olivine are not present in this zone. Limestone is extensively replaced by magnetite and is slightly replaced by amphibole, chlorite, pyroxene, tourmaline, mica and talc. Siderite and ankerite are common in this zone. Volcaniclastic rocks are commonly altered to chlorite and carbonate clasts are replaced by feldspar, amphibole, biotite and tourmaline. Mineralized limestones are varied in iron grade from 10% to 70% (B.H.P. Exploration, 1993). The most characteristic feature in this zone is replacement of huge bodies of magnetite in the limestone and marble. However, diopside is also locally replaced by magnetite. Diopside is found in small amount (<5%) in barren lime-

Table 1. Summary of some characteristics of skarn zones from the Sangon deposit

skarn zones	Magnesian skarn	Calcic skarn		
	orebody North C	orebody South C	orebodies B and A	orebody A'
host rocks	dolomite	limestone	limestone	limestone
main minerals	magnetite, tremolite, phlogopite, olivine diopside, scapolite	magnetite, garnet, clinopyroxene, hastingsite	amphiboles magnetite, diopside	magnetite garnet, clinopyroxene, hastingsite, scapolite
alteration minerals	clinocllore, serpentine, calcite, dolomite	actinolite, chlorite, calcite	actinolite, chlorite, calcite, siderite, ankerite, mica	actinolite, chlorite, calcite
associated igneous rocks	rhyodacitic dykes granitic apophyses	rhyodacitic dykes	rhyodacitic dykes	rhyodacitic dykes granitic apophyses
composition of gangues	Mg- rich	Fe-rich	Ca-rich	Fe-rich

stone and marble. In some locations of this zone, primary hematite was also precipitated and magnetite was replaced by martite and calcite. These ores associate with much calcite, scattered quartz and pyrite veins in a brecciated zone. The magnetite zone indicates the following mineral assemblages; diopside $\rightarrow$ magnetite $\pm$ pyrrhotite $\pm$ pyrite $\rightarrow$ amphiboles $\pm$ magnetite $\pm$ pyrite $\pm$ chalcopyrite $\pm$ calcite $\rightarrow$ amphiboles $\pm$ chlorite $\pm$ talc $\pm$ calcite $\pm$ quartz $\pm$ ankerite $\pm$ siderite $\pm$ pyrite $\pm$ hematite $\rightarrow$ iron hydroxide $\pm$ copper carbonate $\pm$ native copper $\pm$ calcite $\pm$ quartz.

3. Magnesian skarn zone

The magnesian skarn zone (in North C orebody) is mainly characterized by dolomitic marbles and contains minerals of magnetite, Fe-rich phlogopite, tremolite, clinocllore, and calcite. Other minerals are olivine, serpentine, clinopyroxene, scapolite, epidote, calcite and sulfide minerals. The dolomite marbles without overprint of metasomatism contain fresh forsterite (about 5 to 10 vol.%). The forsterite is usually altered to serpentine and disappears in strongly altered zones. The olivine crystals can be rarely observed in massive magnetite ore zones. The following sequences are obser-

ved in a section from olivine marble to massive magnetite (in borehole number 214), olivine-bearing marble, felsic igneous dike, monomineral diopside. The diopsidic rocks are partially replaced by phlogopite and tremolite that exhibit contemporaneous textures and are developed along pyroxene cleavages, fractures and grain boundaries. As the diopsidic rocks diminish, Cl-rich scapolitic rocks which have a few diopside, tremolite, phlogopite, epidote, quartz and pyrite are encountered. The next assemblage is epidote, phlogopite, clinocllore and tremolite. These associations suggest the following paragenetic sequence: forsterite $\rightarrow$ diopside $\rightarrow$ scapolite $\pm$ epidote $\pm$ phlogopite $\pm$ magnetite $\pm$ pyrrhotite $\pm$ pyrite $\pm$ dolomite $\pm$ calcite $\rightarrow$ magnetite $\pm$ tremolite $\pm$ pyrite $\pm$ chalcopyrite $\pm$ sphalerite $\pm$ clinocllore $\pm$ serpentine $\pm$ dolomite $\pm$ calcite $\rightarrow$ Iron hydroxide $\pm$ copper carbonate $\pm$ dolomite $\pm$ calcite. Some of the major differences in skarn zones of the Sangon deposit are given in Table 1.

V. Halogen-bearing minerals

Electron microprobe analyses were conducted by an automated JEOL JXA-8600 Superprobe of Yamagata University with accelera-

ting voltage of 15 KV and a beam current of 2×10^{-8} amp. The following standards were used for X-ray analysis: apatite, SiO_2 , TiO_2 , Al_2O_3 , Cr_2O_3 , Fe_2O_3 , MnO , MgO , wollastonite, albite, adularia, CaF_2 and NaCl . The diameter of focused electron beam is $5 \mu\text{m}$. Data were processed by on-line computer using Oxide ZAF in the XM-86 PAC program composed by JEOL.

1. Amphiboles

Cl-bearing amphiboles in the Sangan deposit are calcic amphiboles of tremolite-actinolite series in magnesian skarn zone and ferroactinolite to K-rich ferrohastingsite in the garnet-bearing skarn zones according to Leake's nomenclature (1978) and Hawthorne (1985) (Fig. 3). The tremolite-actinolite series minerals contain only small amounts of fluorine and ferrohastingsite contains considerable amount of chlorine (Table 2). The ferroamphiboles and crystalline calcite are developed as small envelops or veins in garnetitic rocks. They grew in an assemblage usually composed of clinopyroxene and garnet or clinopyroxene and scapolite. In hand specimens, the ferroamphiboles are dark green and fibrous in shape. Under plain polarized light, the ferrohastingsite show very strong green pleochroism and well-developed cleavages.

Table 2 shows electron microprobe analyses of the Cl-bearing-amphiboles. The amphibole formula is based on the 23 oxygens. Fe^{3+} in amphiboles from the calcic skarn zone was calculated from charge balance and cations were renormalized to sum $(\text{Si} + \text{Al} + \text{Ti} + \text{Fe} + \text{Mn} + \text{Mg} + \text{Ca}) = 15$ (Leake *et al.*, 1997). H_2O was calculated assuming $\text{Cl} + \text{F} + \text{OH} = 2$.

The hastingsite is characterized by high Fe, K, Al and Cl contents. Cl content ranges from 0.9 to 2.5 wt%. The correlations between Cl and cation contents are shown in Fig. 4. The Cl contents show positive correlation with $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ and $\text{K}/(\text{K} + \text{Na})$ and a nega-

Fig. 3. Compositions of calcic amphiboles from the Sangan deposits. Field boundaries modified from Leake (1978) and Hawthorne (1985).

Abbreviations are Am, amphibole; Ga, garnet; Scp, scapolite; Cpx, clinopyroxene.

tive relation with $\text{Si}/(\text{Si} + \text{Al}^{\text{IV}})$.

2. Scapolite

Scapolitic rocks occur widely in these skarn zones and hornfels. The scapolite is optically colorless, having well-developed cleavages, and euhedral to subhedral shape. Euhedral crystals are commonly large in size (up to 5 mm in length) and sometimes show complete form of ditetragonal dipyrmaid. In hornfels, scapolite occurs in microscopic scale sublayers with quartz and K-feldspar or biotite. The scapolite-rich parts are mainly composed of granoblastic scapolite usually containing diopside inclusions. The scapolite is generally associated with biotite, diopside, quartz, K-feldspar, plagioclase, magnetite, sphene and amphibole. It appears that argillaceous and calcareous shale and siltstone near the granite contact were replaced by scapolite. Within the calcic skarn zone, scapolite occurs locally in garnet-scapolite-clinopyroxene skarn zone and is commonly accompanied by salite and analcime, sometimes with hastingsite, albite, K-feldspar and accessory minerals such as zircon, apatite, calcite, quartz, amphibole and chlorite. Scapolite in rocks of pyroclastic rock origin often contains analcime, albite and K-feldspar

Table 2. Representative electron microprobe analyses of amphiboles from the Sangani deposit

Zones	Calcic zones*										Mgnesian zone	
Samples	A'13-1	A'14-2	A'53-3	2182-1	2182-2	514	1244	421	SC	D1	91813	91821
SiO ₂	39.43	43.67	38.15	42.88	38.18	44.11	35.42	40.55	37.75	37.62	57.09	57.39
Al ₂ O ₃	8.00	5.63	10.07	7.07	10.85	7.71	12.55	9.88	12.80	13.35	1.55	0.95
TiO ₂	0.07	0.07	0.09	0.09	0.30	0.05	0.49	0.23	0.26	0.39	0.04	0.01
Fe ₂ O ₃ **	1.81	2.94	3.22	2.99	2.65	2.36	7.74	2.25	4.63	5.48	0.00	0.00
FeO	29.72	30.32	28.49	28.88	28.05	30.47	24.96	28.69	23.66	23.38	5.42	8.03
MnO	0.44	0.51	0.43	0.80	0.65	0.36	0.50	0.07	0.20	0.18	0.14	0.09
MgO	1.23	1.68	1.44	2.33	1.25	2.26	1.61	2.38	3.50	3.70	20.56	19.16
CaO	10.62	11.48	11.16	11.30	11.20	11.54	11.23	11.31	11.77	11.65	12.87	12.79
Na ₂ O	1.21	0.86	1.59	1.18	1.21	1.13	1.35	1.39	1.28	1.41	0.37	0.18
K ₂ O	1.98	1.11	2.38	1.13	2.49	1.27	2.72	2.00	2.86	2.68	0.08	0.08
Cl	1.84	0.78	2.19	0.89	2.53	0.89	2.54	1.42	2.17	1.65	0.10	0.08
F	0.00	0.02	0.14	0.00	0.05	0.23	0.00	0.09	0.06	0.13	0.31	0.16
- O	0.42	0.19	0.55	0.21	0.59	0.33	0.58	0.36	0.51	0.43	0.15	0.09
H ₂ O***	1.32	1.65	1.20	1.65	1.17	1.59	1.19	1.47	1.22	1.42	1.76	1.92
Total	97.25	100.55	99.99	100.95	99.98	103.65	101.72	101.36	101.65	102.61	100.13	100.76
Numbers of cations on O=23												
Si	6.666	7.030	6.303	6.848	6.289	6.854	5.766	6.486	6.004	5.910	7.887	7.963
Al ^{IV}	1.334	0.970	1.697	1.152	1.711	1.146	2.234	1.514	1.996	2.090	0.113	0.037
Sum T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al ^{VI}	0.262	0.099	0.264	0.178	0.397	0.266	0.175	0.349	0.404	0.383	0.141	0.119
Ti	0.009	0.009	0.011	0.010	0.037	0.006	0.060	0.028	0.031	0.046	0.004	0.001
Fe ³⁺	0.230	0.357	0.400	0.359	0.328	0.277	0.948	0.270	0.554	0.648	0.000	0.000
Fe ²⁺	4.127	4.062	3.913	3.791	3.842	3.881	3.357	3.776	3.154	3.033	0.606	0.907
Mn	0.063	0.070	0.060	0.108	0.090	0.047	0.069	0.009	0.027	0.024	0.016	0.011
Mg	0.309	0.404	0.353	0.553	0.306	0.523	0.391	0.567	0.830	0.866	4.233	3.963
Sum T	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000	5.000
Fe ²⁺	0.077	0.020	0.024	0.066	0.023	0.079	0.041	0.062	0.000	0.039	0.020	0.025
Ca	1.923	1.980	1.976	1.934	1.977	1.921	1.959	1.938	2.006	1.961	1.905	1.902
Sum B	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.006	2.000	1.925	1.927
Na	0.397	0.269	0.510	0.364	0.387	0.340	0.426	0.431	0.395	0.430	0.099	0.047
K	0.426	0.228	0.501	0.230	0.524	0.252	0.565	0.408	0.580	0.537	0.013	0.014
Sum A	0.823	0.497	1.011	0.594	0.912	0.592	0.991	0.839	0.975	0.967	0.113	0.061
Cl	0.523	0.214	0.609	0.242	0.701	0.230	0.710	0.380	0.590	0.440	0.023	0.019
F	0.000	0.012	0.073	0.000	0.026	0.110	0.000	0.040	0.030	0.070	0.134	0.070
OH	1.477	1.775	1.318	1.758	1.273	1.650	1.290	1.570	1.390	1.490	1.843	1.911
XFe ²⁺	0.930	0.910	0.917	0.873	0.926	0.881	0.896	0.869	0.792	0.778	0.125	0.186

Note: * Cations are normalized to sum (Si+Al+Ti+Fe+Mn+Mg+Ca) = 15 XFe²⁺ = Fe²⁺/(Fe²⁺ + Mg).

Fe₂O₃ calculated from charge balance. *H₂O calculated assuming OH = 2 - (Cl + F).

inclusions in its cleavages. Within the magnesian zone (borehole 214), scapolitic rock (10 m in thickness) is following an altered dacitic dike and a diopsidic rock and is accompanying by small amounts of phlogopite, tremolite, chlorite, quartz, pyrite, apatite,

pyroxene and epidote. The host rocks are probably dolomitic rock origin.

Electron microprobe analyses for scapolite were recalculated on (Al+Si)=12 based on the methods of Evans *et al.* (1969). The CO₃ was estimated assuming 1-Cl=CO₃ and mole% of

Fig. 4. Relationships of Cl atom per formula unit (pfu) and mole ratio of $X_{Fe^{2+}}$, X_{Si} and X_K , respectively, in ferroamphiboles from the Sangon deposits. Cl atoms pfu shows a negative relation with X_{Si} (Fig. 4a) and positive relation with $X_{Fe^{2+}}$, (Fig. 4b) and X_K (Fig. 4c). Symbols are the same as in Fig. 3. Fig. 4-d is plots of Cl atoms pfu versus $Fe^{2+}/(Fe^{2+} + Mg)$ of amphibole from the Sangon, Adirondack, Black Rock Forest and Salton sea (for references and explanations see text). $Fe^{2+}/(Fe^{2+} + Mg)$ ratios are very different area by area whereas the range of Cl content is similar.

marialite-meionite solid solution was obtained from $Mei = Ca/(Ca + Na + K)$. Eq_{An} and X_{Na} in scapolite are obtained by $Eq_{An} = 100(Al - 3)/3$ and $X_{Na} = Na/(Na + Ca + K)$.

Scapolite contains 23 to 40 mole% meionite in marialite-meionite solid solution series and contains considerable amounts of Cl and K (Table 3). The Cl content ranges from 44 to 98 mole% (mostly more than 75 mole%) (Fig. 5). The scapolite with Cl atom per formula unit = 0.98 from the hornfels is the most Cl-rich scapolite ever reported.

Evans *et al.* (1969) indicated an linear correlation within the range of $Ca/(Ca + Na)$ (or $Eq_{An} = 100(Al - 3)/3$) from 0 to 0.75 in the $Na_4Al_3Si_9O_{24}Cl$ and $NaCa_3Al_5Si_7O_{24}CO_3$ join. Scapolite from the Sangon deposit is less than

0.45 Eq_{An} and show a linear trend (Fig. 5). And also, the Cl content of the scapolite are well positively correlated with X_{Na} (Fig. 6). As Fig. 5 shows, the Cl- Eq_{An} trend is, however, not consistent with stoichiometry lines of Evans *et al.* (1969). The trend of Sangon scapolites is similar to those from other areas (Fig. 5). The composition is similar to those from hydrothermal type of Vanko and Bishop (1982).

3. Phlogopite

Phlogopite is a major mineral in the magnesian skarn zone. Phlogopite is found in this zone with assemblages of magnetite-phlogopite, phlogopite-tremolite, scapolite-phlogopite-tremolite-epidote, assemblage of phlogopite-epidote and assemblage of olivine-serpentine-phlogopite. Generally, either for-

Table 3. Representative electron microprobe analyses of scapolite from the Sangan deposit

Location	Garnet-scapolite-pyroxene zone								HFZ	MGZ
Samples	11	12	13	14	5	1PR11-2	9	2181	NBI12-1	214451
SiO ₂	56.20	58.34	55.27	58.23	60.30	55.65	59.69	56.66	57.17	54.28
Al ₂ O ₃	23.37	22.04	23.28	22.83	22.75	23.20	22.44	22.05	22.38	23.05
FeO	0.18	0.16	0.09	0.29	0.14	0.00	0.19	0.56	0.20	0.11
CaO	8.73	7.53	8.51	6.97	6.07	8.81	6.39	6.32	6.09	8.41
Na ₂ O	7.49	8.40	8.16	8.90	8.52	7.90	9.16	7.81	9.45	8.53
K ₂ O	1.35	1.24	1.22	1.21	1.45	1.01	1.19	2.76	1.22	0.89
Cl	3.14	3.34	2.95	3.36	3.94	3.02	3.75	2.85	4.04	3.21
CO ₂ *	1.21	1.01	1.38	1.02	0.43	1.32	0.60	1.51	0.09	0.99
-O	0.71	0.75	0.67	0.76	0.89	0.68	0.85	0.64	0.91	0.72
total	101.0	101.3	100.2	102.1	102.7	100.2	102.6	99.87	99.72	98.75
Numbers of cations on Si + Al = 12										
Si	8.052	8.302	8.019	8.207	8.306	8.046	8.314	8.226	8.210	7.997
Al	3.948	3.698	3.981	3.793	3.694	3.954	3.686	3.774	3.790	4.003
Fe	0.021	0.019	0.010	0.034	0.016	0.000	0.022	0.068	0.024	0.014
Ca	1.341	1.149	1.323	1.052	0.896	1.364	0.954	0.983	0.937	1.328
Na	2.081	2.318	2.295	2.433	2.276	2.213	2.475	2.199	2.631	2.438
K	0.246	0.225	0.226	0.218	0.254	0.186	0.211	0.512	0.223	0.168
Cl	0.763	0.805	0.726	0.803	0.919	0.740	0.885	0.701	0.983	0.800
CO ₃	0.237	0.195	0.274	0.197	0.081	0.260	0.115	0.299	0.017	0.200
W	3.69	3.71	3.85	3.74	3.44	3.76	3.66	3.76	3.81	3.95
Eq _{An}	31.59	23.25	32.71	26.44	23.14	31.79	22.85	25.79	26.32	33.44
X _{Al}	0.33	0.31	0.33	0.32	0.31	0.33	0.31	0.31	0.32	0.33
ln _K	-1.35	-1.94	-1.29	-1.70	-1.97	-1.35	-1.97	-1.75	-1.70	-1.26
Mei	0.37	0.31	0.34	0.28	0.26	0.36	0.26	0.27	0.25	0.34
X _{Na}	0.57	0.63	0.60	0.66	0.66	0.59	0.68	0.60	0.69	0.62
m NaCl _F	0.40	0.29	0.48	0.42	0.35	0.42	0.36	0.39	0.51	0.52
wt% NaCl	68.70	57.10	74.70	70.60	64.10	70.40	65.00	67.60	77.40	78.00

Note: W = (Fe + Ca + K + Na), Mei = Ca/(Ca + Na + K), X_{Al} = Al/(Si + Al), X_{Na} = Na/(Ca + Na + K), lnK = -0.0028(X_{Al})^{-5.5580} (Ellis, 1978), m NaCl_F is moles of NaCl in fluid (see text), HFZ=hornfels zone, MGZ=Magnesian zone, Eq_{An}=100(Al-3)/3, * CO₂ is calculated on Cl+ CO₃ = 1.

sterite or diopside-bearing marbles in contact with magnetite zones are altered to association of phlogopite, tremolite clinocllore and serpentine. Phlogopite is usually intergrown with magnetite as a primary mineral in the ore zones. There are typical examples from alteration of phlogopite to clinocllore and serpentine in the magnesian zone. Phlogopite is green in color and phlogopite crystals intergrown with magnetite are large in size and

sometimes more than 10 cm in diameter.

Total iron in phlogopite is assumed as Fe²⁺ and OH is calculated on OH=4-(Cl+F). Phlogopite shows a large compositional variation, and can be divided into Al-rich and Al-poor phlogopites (Table 4 and Fig. 7). The Al-rich phlogopite grains are observed as inclusions in Al-poor phlogopite. The Al-rich phlogopite contains relatively low amount of F in comparison with the Al-poor phlogopite.

Fig. 5. Comparison of scapolite composition in terms of Cl and Eq_{An} from the Sangam deposits with some other areas. $Eq_{An} = 100(AI - 3)/3$. Explanations for scapolite from every area are given in the text. Data for the other areas are from Jiang *et al.* (1994), Vanko and Bishop (1982), Buick and Cartwright (1994), Mora and Valley (1989), Rebbert and Rice (1997).

Fig. 6. Relationship of mole ratio of X_{Na} and X_{Cl} atoms per formula unit in scapolite from the Sangam deposits. $X_{Na} = Na/(Na + Ca + K + Fe)$.

Fig. 7. $Mg/(Mg + Fe)$ vs. Al^{IV} of phlogopite from the Sangam deposits. These plots show considerable variations among chemical composition of the phlogopite as: I: Al-Fe-poor, II: Al-poor, Fe-rich, III: Al-rich, Fe-poor and IV: Al-Fe-rich phlogopites. Fields modified from Deer *et al.* (1962).

Back-scattering electron scanning images show that Al-poor phlogopite is partially replaced by Al-rich phlogopite. Fe content in phlogopites is also variable from grain to grain.

Table 4. Representative electron microprobe analyses of phlogopite from the magnesian zone

Samples	911011	911012	91712	91722	BK121	BK143	91822	91912	9151	214452	214372
SiO ₂	39.03	44.23	41.05	45.84	44.86	45.51	43.58	40.10	42.79	43.50	37.02
Al ₂ O ₃	18.74	12.95	17.51	12.16	11.66	11.63	13.18	15.29	13.58	11.25	17.99
TiO ₂	0.09	0.14	0.08	0.04	0.06	0.00	0.21	0.01	0.00	0.40	0.19
FeO	1.39	1.23	0.77	0.81	0.90	0.88	4.45	2.09	1.71	5.78	4.37
MnO	0.00	0.00	0.02	0.03	0.00	0.00	0.09	0.05	0.01	0.05	0.07
MgO	24.82	27.41	25.86	27.64	27.49	27.81	25.07	25.94	26.64	23.82	22.34
CaO	0.00	0.05	0.04	0.04	0.02	0.00	0.10	0.00	0.00	0.00	0.01
Na ₂ O	0.42	0.40	0.14	0.11	0.09	0.11	0.07	0.24	0.40	0.07	0.20
K ₂ O	7.74	8.53	8.72	7.96	9.20	9.26	8.06	10.35	10.04	9.46	9.86
Cl	0.01	0.01	0.03	0.01	0.03	0.00	0.07	0.05	0.04	0.11	0.03
F	1.51	2.70	1.95	2.79	2.62	2.27	2.32	2.36	1.62	2.44	0.46
- O	0.64	1.14	0.83	1.18	1.11	0.96	0.99	1.01	0.69	1.06	0.20
H ₂ O	3.57	3.18	3.46	3.16	3.17	3.38	3.27	3.02	3.18	3.12	3.87
Total	96.69	99.69	98.78	99.40	98.99	99.88	99.48	98.50	99.31	98.95	96.19
Numbers of cations on O = 22											
Si	5.546	6.106	5.712	6.289	6.241	6.266	6.097	5.708	5.976	6.215	5.443
Al ^{IV}	2.454	1.894	2.288	1.711	1.759	1.734	1.903	2.292	2.024	1.785	2.557
Sum T	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Al ^{VI}	0.685	0.215	0.584	0.255	0.154	0.155	0.270	0.274	0.211	0.111	0.561
Ti	0.010	0.015	0.008	0.004	0.006	0.000	0.022	0.001	0.000	0.043	0.021
Fe ²⁺	0.165	0.142	0.090	0.093	0.104	0.101	0.520	0.249	0.200	0.691	0.538
Mn	0.000	0.000	0.002	0.003	0.000	0.000	0.011	0.006	0.001	0.006	0.008
Mg	5.255	5.640	5.362	5.651	5.700	5.706	5.227	5.504	5.546	5.071	4.895
Sum O	6.115	6.013	6.046	6.006	5.964	5.962	6.050	6.034	5.958	5.922	6.023
Ca	0.000	0.008	0.005	0.006	0.003	0.000	0.015	0.000	0.000	0.000	0.001
Na	0.117	0.106	0.038	0.028	0.024	0.028	0.020	0.067	0.108	0.019	0.056
K	1.403	1.502	1.548	1.394	1.632	1.626	1.438	1.880	1.788	1.725	1.849
Sum A	1.520	1.616	1.590	1.428	1.660	1.654	1.473	1.947	1.896	1.744	1.906
Cl	0.003	0.003	0.006	0.002	0.006	0.000	0.015	0.013	0.009	0.027	0.007
F	0.669	1.149	0.840	1.179	1.124	0.966	1.001	1.037	0.703	1.077	0.212
OH	3.327	2.849	3.154	2.819	2.870	3.034	2.984	2.950	3.289	2.897	3.780
X _{Mg}	0.969	0.975	0.983	0.983	0.982	0.983	0.908	0.956	0.965	0.879	0.900
f	4.930	4.630	4.810	4.610	4.640	4.730	4.580	4.910	4.670	4.640	5.490

Note: Abbreviations are X_{Mg} = Mg/(Mg+Fe²⁺). Total Fe as FeO. OH = 4 - (F+Cl).
 $f = \log(fH_2O)/(fHF)$.

Most of the grains are iron-poor (Table 4 and Fig. 7). TiO₂ is generally minor. Fe-rich grains have relatively higher TiO₂ contents. The F content ranges from 1.50 to 2.90 wt% (for one analysis F = 0.50 wt%). In contrast with F, Cl content is less than 0.1, except one sample in which phlogopite is associated with Cl-rich scapolite and with some grains of F rich apatite. Cl content of phlogopite in this sam-

ple ranges from 0.11 to 0.15 wt% and F from 2.32 to 2.52. Figure 8 exhibits positive relationships of SiO₂ wt% and MgO wt% with F contents. Phlogopite with low F content shows textural feature of retrograde generation.

Fig. 8. Figures a and b show relationships between wt% F and wt% SiO₂ and MgO in phlogopite, respectively, from the Sangam deposits. These plots show two types of F-poor and F-rich phlogopites. Both of the two types show positive correlation for wt% F vs. wt% SiO₂ and MgO. Figure c is the plot of Mg/(Mg + Fe²⁺) vs. log(X_F/X_{OH}) for phlogopite from the Sangam deposit. Parallel lines (contours) show values of log(f_{H₂O}/f_{H_F}) that were calculated for fluid in equilibrium with the phlogopite (see symbols) at 400°C (see text).

VI. Discussion

1. P-T conditions

The upper limit of the contact metamorphic grade of the Sangam deposit are characterized by forsterite and diopside in the magnesian zone and diopsidic pyroxene in the calcic skarn (following reactions 1 and 2). Talc is associated with ankerite, calcite and dolomite. This assemblage defines the lower limit of contact metamorphism in the calcic skarn zone (reaction 3). The mineral parageneses are considered to have formed through the following reactions.

(A) in magnesian zone :

(B) in magnetite zone :

Assemblages of these minerals without cordierite and andalusite are interpreted as due to very low pressure condition of the contact metamorphism (Tracy and Frost, 1991). The highly fractured state and high oxygen fugacity, and other significant features of the Sangam deposit (for example, presence of primary hematite), are also interpreted to reflect low pressure condition of the contact metamorphism (Einaudi *et al.* 1981). Application of hornblende barometry on its Al content (Schmidt, 1992) for the Sarnowsar granite yields an equilibration pressure of <2.5 (±0.6) kb (Boomeri, in preparation). This is equivalent to hydrostatic pressure of less than 1 kb from $P_{\text{hydrostatic}} = P_{\text{lithostatic}}/2.7$ of Shepherd *et al.* (1986).

In siliceous dolomites, diopside, forsterite and wollastonite appear progressively at 475°, 575° and 660°C, respectively, at a pressure of 1 kb (Tracy and Frost, 1991). Absence of wollastonite can indicate the upper limit of temperature of the contact metamorphism in the area. The presence of F-rich and hydrous minerals in

Fig. 9. Photomicrographs of fluid inclusions in quartz and calcite from the Sangam deposit. (a) Dense distribution of liquid-rich fluid inclusions with or without halite in calcite from the calcic skarn zone. (b) Polyphase fluid inclusion in quartz in the Sarnowsar granite with daughter minerals of halite and sylvite. (c), (d), (e) and (f) are fluid inclusions in quartz vein intruded in scapolitic rocks adjacent to a lenticular magnetite ore near the granite. Halite, sylvite and hematite are observed in the most of the polyphase fluid inclusions. The other solid phases are unidentified. Scales for the Figs. 9b, 9c, 9d and 9f are same as Fig. 9a.

the magnesian zone indicates a low X_{CO_2} condition (Meinert, 1982). Meinert (1982) inferred that X_{CO_2} during skarn formation is <0.1 . Reduction in X_{CO_2} to 0.1 will reduce the temperature of diopside to 400° and of wollastonite to 520°C (Tracy and Frost, 1991). Therefore, absence of wollastonite suggests that the formation of early anhydrous minerals occurred at $<520^\circ\text{C}$ in the Sangam deposit. Serpentinization of forsterite-bearing magnesian skarn under low pressure condition (500 bar) implies equilibration conditions of $X_{\text{CO}_2} < 0.05$ and temperatures $<420^\circ\text{C}$ (Einaudi *et al.*, 1981). Maximum temperature a $X_{\text{CO}_2}=0.05$ for the stability of siderite implies about 325°C for the condition of late stages of retrograde alteration (Meinert,

1982).

Calcite from the Sangam deposits occasionally contains Ca-Na-rich fluid inclusions (Fig. 9-a). Homogenization temperature with dissolution of halite in the fluid inclusions are in the range of 140° to 150°C and 230° to 245°C , indicating that the range of salinities are from 29.3 to 29.7 and from 33.5 to 34.4 wt% of NaCl eq. (Boomeri *et al.*, 1996b). With pressure correction, filling temperatures are estimated ranging from 180° to 320°C at 1 kb. Quartz in the granite also hosts fluid inclusions with several generations from high temperature to low temperature stages. They are one-phase and two-phase fluid inclusions (Fig. 9b) associated with polyphase and vapor-rich fluid inclusions.

Upon heating, the solid phases dissolved into a liquid phase at 140° to 250°C, 300° to 330°C, 450° to 510°C, and above 510°C, while some solid phases did not change. However, based on homogenization of fluid inclusions in the granite and pressure correction (Boomeri, in preparation), filling temperatures rise close to granite solidus. The temperatures for the Sangan deposit are estimated to be above 520° C for the hornfels, 520°–450°C for anhydrous skarns (association of clinopyroxene, garnet and forsterite), 450–320°C for hydrous skarns (association of phlogopite and amphiboles) and less than 320°C for retrograde alteration (association of chlorite, ferroactinolite).

2. Cl-rich hastingsite

Cl-rich hastingsite is commonly found in skarns, hydrothermal and metamorphic environments that are accompanied by significant metasomatism, for example in magnetite bearing skarn deposit (Krutov, 1936, Krutov and Vinogradova, 1966), in magnetite bearing metamorphic assemblages (Leger *et al.*, 1996), in skarns (Matsumoto and Miyahisa 1960; Matsumoto, 1968, 1969; Dick and Robinson, 1979; Gulyaeva *et al.*, 1986; Suwa *et al.*, 1987), and in hydrothermally altered rocks (Vanko, 1986; Enami *et al.*, 1992, Sato *et al.*, 1997). Hastingsite in most of these environments were formed in high salinity fluids. In the Salton Sea geothermal system, for example, hastingsite occurs in metasandstones, metabasites and veins at temperatures over 350°C (drilling depths between 3,100 and 3,180 m) by reactions involving high-salinity geothermal fluids, with 15.4 to 19.7 wt% total dissolved Cl (Enami *et al.*, 1992). Thomas (1982) mentioned that Cl-bearing amphiboles may be unstable at magmatic temperatures from his experiments on Na-bearing hastingsite and observation of natural occurrences of hastingsite. Presence of chlorine in hastingsite should be the result of their lower temperature of formation or a very

specific chemical environment (Thomas, 1982; Malinovsky, 1966, 1967; Dick and Robinson, 1979).

Crystal-chemical effects have been discussed for many Cl-rich amphiboles. Cl-rich amphiboles generally has high Fe/Mg, and the octahedral site (Volfinger *et al.*, 1985; Kamineni, 1986), the tetrahedral site (Morrison, 1991) and the A-site (Morrison, 1991; Enami *et al.*, 1992) have important control on the incorporation of Cl. Oberti *et al.* (1993) considered the mechanism of Cl incorporation in amphibole and indicated a significant bonding interaction between K in the A site and Cl in O3' site and concluded that increasing Cl content in amphibole requires increasing Fe²⁺, K and Al. As shown in Fig. 4, Cl-bearing amphiboles from the Sangan deposit have the positive relationships of Cl with $X_{Fe^{2+}}$ and X_K and negative relationship of Cl with X_{Si} , similar to those of previous description such as from Adirondack Mountains, New York (Morrison, 1991), Black Rock Forest, Cornwall, New York (Leger *et al.*, 1996) and the Salton Sea geothermal system, California (Enami *et al.*, 1992). However, Fe/(Mg+Fe²⁺) ratios in hastingsite are very different area by area whereas the ranges of Cl contents are similar (Fig. 4-d). Munoz and Swenson (1981), Munoz (1990), Morrison (1991) and Zhu and Sverjensky (1992) discussed for mica-amphibole pairs, where the two minerals are formed under the same T, P and exchanged with the fluids of the same composition, and they interpreted that these minerals will delineate a linear trend on the log (X_{Cl}/X_{OH}) or (X_F/X_{OH}) versus the X_{Fe} or X_{Mg} diagrams, respectively. Incorporation of Cl in hastingsite may be considerably affected by the chemical composition of the fluid. Shiraishi *et al.* (1994) described a high K hastingsite (K₂O range from 3.07 to 4.55 wt.%) with low (Cl+F) content (about 0.35 wt% with F>Cl and total Fe/Mg=2). Both the crystal structure constraints and

the chemical composition of fluid play important roles in the formation of Cl-bearing amphiboles. The presence of fluid inclusions with high salinity (30 wt% NaCl eq.) and low filling temperatures (180° to 320°C) in calcite (Boomeri *et al.*, 1996b) are associated with hastingsite indicates that high salinity and low temperature solutions were responsible for formation of hastingsite in the Sangam deposit.

3. Cl-rich scapolite

Extensive formation of Cl-rich scapolite are also attributed to a Na and Cl rich condition. For example, Ramsay and Davidson (1970) discussed the origin of scapolite in Mary Kathleen, Australia, and suggested that scapolite in the metasediments formed by isochemical metamorphism of marls and shales containing variable amounts of evaporitic halite. They also mentioned that scapolite was metasomatically formed in metadolerites and metavolcanics by recrystallization processes of the igneous rocks in the presence of volatile-rich pore-fluids derived from the adjacent sedimentary rocks. Vanko and Bishop (1982) discussed the origin of marialitic scapolite in the Humboldt lopolith, N.W. Nevada, and concluded that the source of Na and Cl transported by hydrothermal fluids were either pre-existing evaporates or evaporitic brine derived from country rocks. Mora and Valley (1989) suggested that scapolite in the northwest of the Idaho batholith was formed during regional metamorphism by the reaction of plagioclase with calcite and halite. Buick and Cartwright (1994) mentioned that scapolitization in the Reynolds Range Group, central Australia, could have been caused by pre-regional contact metamorphism around early granites. Jiang *et al.* (1994) suggested that scapolite-biotite rocks in Tongmugou Pb-Zn deposits, north-western China, are the products of Cl-rich alteration of volcanoclastic sedimentary rocks by saline submarine hydrothermal

fluids. It was also experimentally indicated by Orville (1975), Ellis (1978), Vanko and Bishop (1982), Rebbert and Rice (1997), that Cl-rich scapolite is an indicator of Cl compositions and high concentration of NaCl in the fluids.

Ellis (1978) investigated the following reaction:

$\text{NaCl}_{\text{scapolite}} + \text{CaCO}_{3\text{calcite}} = \text{CaCO}_{3\text{scapolite}} + \text{NaCl}_{\text{fluid}}$
at 750°C and 4 kbar. The expression derived from this experiments is:

$$\ln K_D = -0.0028(X_{\text{Al}})^{-5.5580}$$

where $K_D = (X_{\text{CaCO}_{3\text{scp}}} X_{\text{NaClfl}}) / (X_{\text{NaClscp}} X_{\text{CaCO}_{3\text{cc}}})$ and X_{Al} is an atomic ratio of Al/(Si+Al) in scapolite. Mora and Valley (1989) also applied it to calculate the NaCl content of fluid responsible for the formation of scapolite northwest of the Idaho batholith. Although experimental condition is very different with natural scapolite, it is useful for a qualitative estimation of formation processes (Mora and Valley, 1989). The expression used to estimate NaCl contents of fluid responsible for the formation of scapolite in the Sangam deposit assumes ideal mixing. Calculated X_{NaCl} for fluid in equilibrium with the Sangam scapolite using the equation by Ellis (1978) ranges from 55 to 78 wt% equivalent NaCl (Table 3). These salinities are almost consistent with those obtained from fluid inclusions in quartz from the Sangam granitic rocks (Boomeri *et al.*, 1996b).

Vanko and Bishop (1982) indicated that in several runs (750°C, 2.8 Kb) with excess calcite and NaCl/(NaCl+H₂O) between 0.5 and 0.7, only carbonate rich-scapolite can be obtained. With little or no CaCO₃, experiments were run in high fluid salinity and produced marialitic scapolite. They suggested that a minimum salinity for the production of marialitic scapolite in the absence of calcite is about 50 mole% NaCl at 700 to 750°C and concluded that salinities necessary to cause extensive scapolitization are even higher. This hypothesis can be

well documented by high saline fluid inclusions in quartz veins that intruded scapolitic rocks in the Sangán deposit (Fig. 9).

4. F-bearing phlogopite

It is experimentally indicated that the substitution of F or Cl in the hydroxyl site of mica is controlled by the activity of F or Cl, composition of mica and temperature (Munoz and Ludington, 1974; Munoz 1984). They suggested that Mg-rich micas incorporate more F than Fe-rich micas under similar condition. Such relations have been termed Fe-F avoidance principle (Ramberg, 1952; Ekstrom, 1972). This principle has been documented in natural micas (Zaw and Clark, 1978, Munoz, 1984; Mora and Valley, 1989; Zhu and Sverjensky, 1992). In the Sangán deposit, although positive relation of MgO wt% with F wt% in phlogopite are seen in Fig. 8-b, moles of Mg in octahedral site is very weakly correlated with X_F/X_{OH} (Fig. 8-c). Because of its small X_{Mg} range, clear correlation is not possibly present for the Sangán phlogopites. Role of Fe-F avoidance principle are better shown by coexisting phlogopite and amphibole in the magnesian zone where amphibole only contains negligible amounts of F (Table 4).

With respect to the presence of Fe in the chemical composition of phlogopite from the Sangán deposits, the simultaneous mixing of (Mg, Fe^{2+}) and (F, OH) in a homogeneous biotite solution in terms of the exchange reaction:

where $\log K = \log K_{ph} - \log K_{An} = 1.107$ (Munoz, 1984), can be considered.

Using experimental and thermodynamic data, Munoz (1984) derived the following equation of

$$\begin{aligned} \log K = &2100/T + 1.523X_{Mg} \\ &+ 0.416X_{An} + 0.02X_{Sid} \end{aligned}$$

$$= \log(f_{H_2O}/f_{HX}) + \log(X_F/X_{OH}).$$

Gunow *et al.* (1980) defined the mole fraction of siderophyllite (X_{Sid}) and mole fraction of annite (X_{An}) in biotite as follows:

$$\begin{aligned} X_{Sid} &= ((3 - Si/Al)/1.75) \times (1 - X_{Mg}) \text{ and} \\ X_{An} &= 1 - (X_{Mg} + X_{Sid}). \end{aligned}$$

By assuming a formation temperature of 400°C (the estimated temperature for hydrous skarn from phase equilibrium), we used Munoz's equations to calculate $\log(f_{H_2O}/f_{HF})$ for F-bearing phlogopite in the Sangán deposit. Values of the $\log(f_{H_2O}/f_{HF})$ range from 4.61 to 4.90 (Table 4). In one sample, it is 5.49 (sample 214372, Table 4). Textures show that the diopside was altered to form the phlogopite and tremolite in the retrograde stage. X_{Mg} (mole fraction of phlogopite) was plotted versus the $\log(X_F/X_{OH})$ and values of the $\log(f_{H_2O}/f_{HF})$ are shown by the parallel lines (Fig. 8-c). The lines representing $\log(f_{H_2O}/f_{HF})$ values are slightly cut by the phlogopite composition. This is probably due to variations in the composition of fluid in equilibrium with the phlogopite. However, the small slope of X_{Mg} of the phlogopite vs. $\log(X_F/X_{OH})$ with $\log(f_{H_2O}/f_{HF})$ values indicate that most of them were formed at almost similar conditions. Phlogopite in sample 214372 may have been formed under a condition where another fluid mixed with the original fluid.

5. Implications for environment of formation of the Sangán deposit

Above discussions confirmed that the Cl-rich amphiboles and scapolite are in equilibrium with highly saline fluids. Here, we discuss the origin of the halogens and highly saline solutions in the Sangán ore deposits.

The magnetite ores and skarn zones are, as pointed out, in close proximity with granitic rocks in the Sangán mining area. In addition, most of the scapolitic rocks are just in contact with granitic rocks. The granitic rocks also contain F-rich biotite (up to more than 4 wt%

F) and fluorapatite, (Boomeri, in preparation). This evidence indicates that highly saline fluids were derived from magma during hydrothermal activity associated with the granitic rocks in the area. Experimental work by Chou and Eugster (1977) on the solubility of magnetite in supercritical chloride solutions shows that the solutions can transport large amounts of dissolved cations as chloride complexes. These solutions infiltrated in the permeable zones along fissures, faults, dikes and contact boundaries. The channeled high-temperature fluids in the first stage of metasomatism formed anhydrous silicates such as clinopyroxene, garnet and forsterite and some magnetite in the skarn zones. In the hydrous stage of metasomatism, circulation of highly saline and halogen-rich hydrothermal fluids, which are reacting with early silicate minerals and aluminosilicate rocks, should be responsible for the formation some halogen minerals such as Cl-rich hastingsite, Cl-rich scapolite and F-bearing phlogopite. Distribution of these minerals in the skarn zones and of fluid inclusions in the granite and skarn zones suggests that the solutions infiltrated throughout the ore deposits should be in a similar origin (Boomeri *et al.*, 1996b).

Different mineral assemblages in the skarn zones were formed due to the control of stratigraphic lithology on the solutions and decreasing temperature with time and distance. Large amount of cations, such as Al, Si, and Ca incorporated in the fluids, might be derived from country rocks and breakdown products of early stage calc-silicate. In calcic skarns, chemical environments with abundant iron-rich calc-silicates in reaction with highly saline fluids appear to be susceptible to the formation of the Cl-hastingsite. Whereas, in the magnesian skarn zone, Mg-rich minerals such as forsterite, diopside, tremolite and phlogopite are dominantly formed. In this case, remain-

ing iron in the solutions tended to form magnetite.

VII. Conclusions

1) Major difference in mineral associations of the skarn zones is due to different chemistry of host rocks. In the calcic skarn, iron-rich hydrothermal solution interacted with limestone, salite and garnet to form hastingsite and magnetite. In the magnesian zone, the solution interacted with dolomite, diopside and forsterite to form phlogopite and then magnetite.

2) Occurrence of Cl-rich hastingsite and Cl-rich scapolite indicates the presence of high saline fluids in the Sangan ore-forming system. The high saline fluids derived from magma are associated with intrusion of the country granitic rocks. These fluids were able to transport large amounts of cations as halide complexes.

3) In addition to octahedral sites, substitution of Al for tetrahedral sites and K for A sites plays an important role in the incorporation of Cl in amphibole structure. The substitution of Si for tetrahedral sites plays an important role in the incorporation of F in the atomic structure of phlogopite.

Acknowledgements: We would like to thank the geologists and staff of the Sangan mines for providing the facilities and kindly helping us during our field study and two anonymous reviewers for their constructive and useful criticism and comment. The senior author would like to express his thanks to Mr. Victor Maglambayan and Mr. Kaul Gena who were his helpful friends in the laboratory. Also the senior author would like to acknowledge the Ministry of Education for the scholarship during his studies at Akita University. Finally, the graduate and undergraduate students of Economic Geology course at Akita University

who helped out in various stages of the study.

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イラン東北部サンガン鉄スカルン鉱床に産する含ハロゲンヘースティングス閃石、柱石および金雲母の地球化学的特徴

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サンガン鉄スカルン鉱床地域は、中性代の頁岩、シルト岩、砂岩、炭酸塩岩、および始新世の火山岩類、火山砕屑岩類が、後期始新世の花崗岩類および関連する酸性岩脈により貫入されている。花崗岩類に伴う熱水活動の結果、炭酸塩岩中に石灰質および苦灰質の2種類のスカルンが形成された。鉄アクチノ閃石〜高カリウム鉄ヘースティングス閃石の組成を有する含塩素角閃石は石灰質スカルンに限られ、サーラ輝石、ザクロ石、磁鉄鉱、方解石、そして稀には柱石とともに産する。角閃石中の塩素含有量は $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ および $\text{K}/(\text{K} + \text{Na})$ と正の相関を、また、 $\text{Si}/(\text{Si} + \text{Al}^{\text{IV}})$ とは負の相関を示す。一方、含フッ素金雲母は苦灰質スカルンの主要な鉱物であり、そのフッ素含有量は SiO_2 および MgO wt% と正の相関を示す。金雲母と平衡にある流体の $\log(f_{\text{H}_2\text{O}}/f_{\text{HF}})$ は 400°C で $4.6 \sim 5.5$ と見積もられる。また、塩素に富む柱石は石灰質スカルン、苦灰質スカルンの両方に広く分布する。柱石中の塩素含有量は正の $\text{Na}/(\text{Na} + \text{Ca} + \text{K})$ の相関を示す。柱石は $23 \sim 40 \text{ mol}\%$ のメイオナイト成分を有し、 X_{Cl} 値はほとんどの試料であり、 0.75 を越え、世界中でこれまで報告されたものの X_{Cl} 値よりも高い 0.98 を示すものである。この X_{Cl} 値から、柱石と平衡な流体は、 $55 \text{ wt}\%$ もしくはそれ以上の NaCl 相当塩濃度を有すると算出される。

花崗岩類やスカルン中に産する塩素に富むヘースティングス閃石、塩素に富む柱石およびフッ素に富む金雲母、さらに高塩濃度の流体包有物は、花崗岩質マグマからもたらされ、鉱化に関連した金属は塩素錯体で運ばれたと考えられる。流体中に取り込まれた大量のアルミニウム、珪素、カルシウム等は、母岩や初期のスカルン鉱物の分解によりもたらされたであろう。