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Potassian Hastingsitic Hornblende from the Sampo Mine, Okayama Prefecture, Japan

By

Akira KATO and Satoshi MATSUBARA

Department of Geology, National Science Museum, 3–23–1 Hyakunin-cho, Shinjuku-ku, Tokyo, 169

Abstract The microprobe analyses of potassian hastingsitic hornblende from the pyrometasomatic ore deposit of the Sampo mine indicate the wider compositional variation range covering the compositional fields of hastingsitic hornblende and ferro-edenitic hornblende. The most SiO_2-poor and SiO_2-rich analyses are: SiO_2 38.54, 39.58; Al_2O_3 10.04, 8.85; Fe_2O_3 6.26, 6.04; FeO 26.70, 26.16; MgO 1.11, 1.36; MnO 0.53, 0.41, CaO 11.46, 11.73, Na_2O 1.04, 1.01; K_2O 1.64, 1.87; Cl 1.60, 1.71; H_2O (calc.) 1.45, 1.04; $-O{=}Cl_2$ 0.36, 0.39; totals 100.01%, 99.37%, respectively. These yield empirical formulae, respectively; $(K_{0.34}Na_{0.33})_{\Sigma 0.67}Ca_{2.01}(Fe^{2+}{}_{3.65}Mg_{0.27}Mn_{0.07})_{\Sigma 3.99}(Fe^{3+}{}_{0.77}Al_{0.23})_{\Sigma 1.00}(Si_{6.30}Al_{1.70})_{\Sigma 8.00}O_{21.98}((OH)_{1.58}Cl_{0.44})_{\Sigma 2.02}$ and $(K_{0.39}Na_{0.32})_{\Sigma 0.71}Ca_{2.07}(Fe^{2+}{}_{3.61}Mg_{0.33}Mn_{0.06})_{\Sigma 4.00}(Fe^{3+}{}_{0.75}Al_{0.25})_{\Sigma 1.00}(Si_{6.53}Al_{1.47})_{\Sigma 8.00}O_{22.00}(O_{0.38}(OH)_{1.14}Cl_{0.48})_{\Sigma 2.00}$. These are for the core and rim of a single prismatic crystal, respectively, and prove the existence of wider compositional variation range from a skarn accompanied by a granitic intrusion, which produced the pyrometasomatic ore deposit worked for iron and copper. The comparative study with similar clinoamphiboles from various skarns accomanying metallic mineralization informs that the higher contents of potassium and chlorine are characteristic to them, although a few analyses present lower potassium contents. The skarns involving such clinoamphiboles are accompanied by the mineralization of copper, zinc, arsenic, gold, etc. besides iron, and no specific relationship seems to exist. Clinoamphiboles of similar composition in igneous rocks are generally devoid of chlorine. It is very likely that chlorine in these minerals will be from ore-forming fluids together with sodium contained therein.

Introduction

The occurrence of hastingsite in skarns from Japan was initiated by MATSUMOTO and MIYAHISA (1960) from the pyrometasomatic ore deposit of the Obira Mine, Oita Prefecture, where zinc, lead, copper, and tin were mined. They presented two wet chemical analyses of the mineral with slightly different SiO_2 contents, and these cover the compositional ranges of hastingsite and hastingsitic hornblende after the nomenclature of amphibole (LEAKE, 1978). While, the compositional ranges covered by the present analyses correspond to those of hastingsitic hornblende and ferroedenitic hornblende (LEAKE, 1978). The former is rather common in skarns of pyrometasomatic origin, whereas the report on the latter is rarer than the former. One of the few examples is known in southern Yukon (DICK & ROBINSON, 1979), where ferroedenitic hornblende is found in a set of chlorine-bearing potassian hastingsite and hastingsitic hornblende analyses and the skarn involving them is accompanied by iron-rich sphalerite. The present work is the comparison with compositionally similar clinoamphiboles of skarn origin concluding that they are characterized by higher potassium and moderate to high chlorine contents, while these minerals from igneous rocks contain no or very low chlorine. Thus, it is very likely that chlorine in them was a fraction of ore-forming fluids, which are frequently trapped within gangue minerals of metallic ores as alkali halides.

Description of the Examined Material

The ore deposits of the Sampo mine located about 40 km WNW of Okayama are of pyrometasomatic origin developed by the intrusion of late Cretaceous biotite granite into Permian limestone and were worked for copper and iron. Besides them a weak radioactive anomaly was found along a vein within the granite, but it met with no mining activity. They were studied in detail by MATSUEDA (1980), where such rare skarn minerals as malayaite (TAKENOUCHI & SHOJI, 1969), cuspidine (KATO *et al.*, 1970), iron-wollastonite (MATSUEDA, 1973), zeophyllite (MATSUEDA, 1975), and a new mineral natroapophyllite (MATSUEDA *et al.*, 1981) are found. The pyrometasomatic ore deposits consist of two discrete orebodies, Yoshiki ore deposit in the south and Niiyama ore deposit in the north, the distance between two being about 300 meters. The former was worked for copper and iron, and the latter for iron, the principal ore minerals being chalcopyrite and magnetite in both of them.

The examined material (NSM-M19630) was collected from the dump probably derived from Yoshiki ore deposit by the second author about 25 years ago just after the termination of mining works. It consists of dark yellow green fine grained aggregate composed of magnetite and chamosite in which subparallel aggregated dark dull green prisms of clinoamphibole (such longer names as hastingsitic hornblende and ferroedenitic hornblende aggregates will not be used hereafter) exceeding 2 cm long accompanied by coarse-grained calcite are involved with rather sharp boundaries. The dimension of clinoamphibole-calcite aggregate reaches 10 cm across. Besides these aggregates, minor discrete prisms of clinoamphibole are embedded within calcite, and one of them was subjected to chemical analyses, where the compositional zoning is developed so well. Besides clinoamphibole and calcite, submillimeter order pyrite cubes forming aggregates is involved within calcite pieces. Although the number of observed materials is not so large, no peculiar regularity was noticed in the mode of distribution of the any minerals and their aggregates.

Under the microscope, both of discrete and aggregated grains of clinoamphibole are prismatic within calcite (Fig. 1). The other form than prism was not be specified owing to the tapering terminations. No trace of alteration is found even in case of direct contact with chamosite. A simple twin with the trace parallel to the elongation is observed between crossed polars in a few grains forming subparallel aggregates. It is strongly pleochroic with axial colours changing from brownish green to deep bluish

Fig. 1. Photomicrograph of isolated prismatic forms of hastingsitic hornblende embedded within larger calcite grains. One polar. Field view: 0.53×0.76 mm.

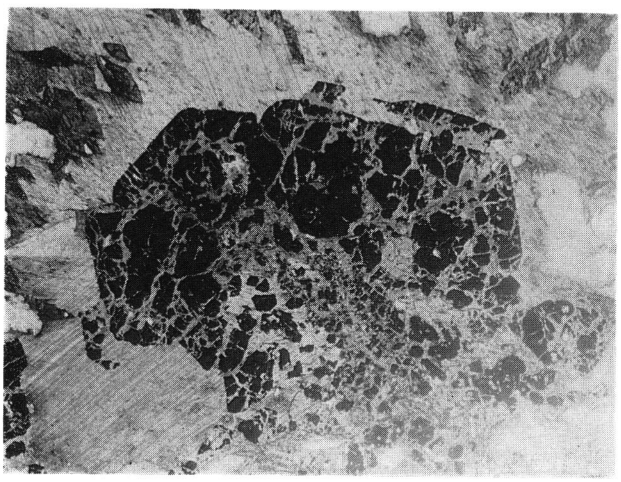

Fig. 2. Photomicrograph of a magnetite grain embedded in calcite. It is partially pseudomorphed by minutely developed network of chamosite. One polar. Field view 3.3×4.75 mm.

green through olive green. It is optically biaxial with very small 2V. Apart from the aggregates of clinoamphibole and calcite, larger grains of dodecahedral magnetite are pseudomorphed by network veinlets of chamosite composed of extremely minute flakes (Fig. 2). Also, chamosite aggregates fill the interstices of clinoamphibole prisms and intersect them. Pyrite grains are of submillimeter order size and form minor aggregates along the boundary of clinoamphibole aggregates and magnetite-chamosite

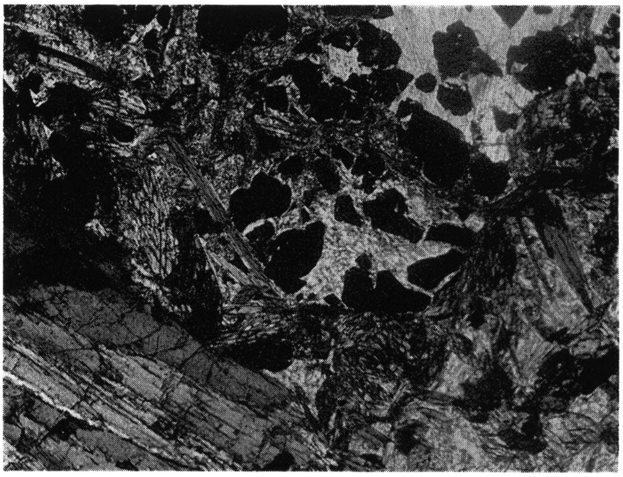

Fig. 3. Photomicrograph of pyrite grains surrounded by chamosite and calcite. One polar. Field view 1.3×1.9 mm.

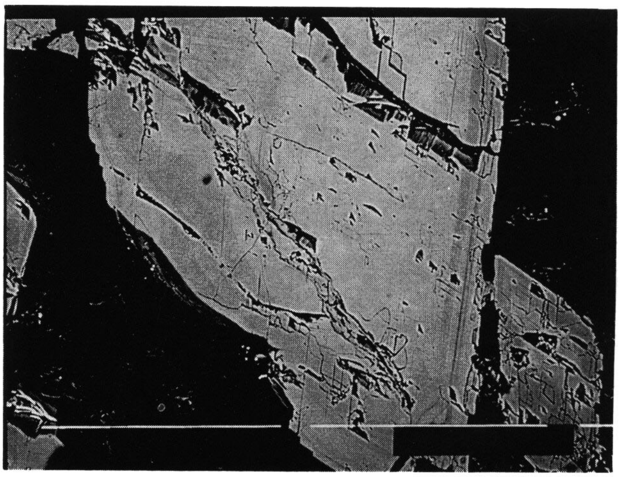

Fig. 4. Backscattering electron image of the analysed grain of hastingsitic hornblende. Note the zoning surrounding the grain. Analysis 1. in Table 1 for the core and 2. for the rim. Field view 0.14×0.2 mm.

aggregates (Fig. 3).

The backscattered electron images demonstrate the compositional zoning, which could not be noticed under the microscope. Darker margins in Fig. 4 are ascribed to the higher silica contents. Closer observation of figure informs the recurrent zoning along the rim.

Chemical Analyses and Comparative Study with Clinoamphiboles of Similar Compositions

The chemical analyses of a non-aggregated single grain were made by using Links Systems energy dispersive X-ray spectrometer. In Table 1, those with minimum and maximum SiO_2 contents are demonstrated to indicate the range of most significant compositional variation. The allotment of FeO and Fe_2O_3 was due to the following way. At first, the total number of cations is calculated to 13, and, secondly, one fifth of octahedral cations is regarded as trivalent. Namely, the trivalent cations are to be composed exclusively of Fe^{3+} and Al, the latter being the residual of the total Al minus tetrahedral Al. H_2O contents were derived from the charge balance to obtain the total of anionic valency $= -48$ where H_2O is regarded as OH only. The reason taking this manner is the emergence of unexpectedly lower figure of Fe_2O_3 if the basis composed of the total of octahedral and tetrahedral cations $=13$ and total of cationic valency $=48$ is taken, though the reason is unknown. The material with the lowest SiO_2 figure (1. in Table 1) corresponds to hastingsitic hornblende according to the nomenclature of amphibole (LEAKE, 1978), and that with the highest SiO_2 figure (2. in Table 1) has $Mg/(Mg+Fe^{2+})$ and $Si/(Si+Al)$ ratios is plotted within the field covered by ferroedenitic hornblende. The former name was used in the title due to the dominance to the latter in the examined material. Although the range covers those of two, there are such compositional characteristics as higher Cl and K contents, the latter exceeding Na. Also, the SiO_2 contents seem to reciprocate with Al_2O_3 contents. These characteristics are also seen in Yukon materials (DICK & ROBINSON, 1979), relating that in skarns of pyrometasomatic origin such calcic clinoamphibole rich in iron is to have wider compositional variation ranges. The dominance of potassium over sodium and the higher Cl content are not seen in the material from the Obira mine, where it was formed in a skarn of pyrometasomatic origin accompanying metallic mineralization of Cu, Zn, Pb, As, Sb, and Sn together with non-metallic one including B and F, datolite and fluorite, respectively (MATSUMOTO & MIYAHISA, 1960).

MATSUEDA (1980) provides five microprobe analyses of hastingsite in mafic horn-

Table 1. Chemical analyses of hastingsitic hornblende (1.) and ferroedenitic hornblende (2.) from the Sampo mine, Okayama Prefecture.

	SiO_2	Al_2O_3	Fe_2O_3*	FeO*	MnO	MgO	CaO	K_2O	Na_2O	Cl	H_2O*	$-O=Cl_2$	Total
Weight percentages:													
1.	38.54	10.04	6.26	26.70	0.53	1.11	11.46	1.64	1.04	1.60	1.45	−0.36	100.01
2.	39.58	8.85	6.04	26.16	0.41	1.36	11.73	1.87	1.01	1.71	1.04	−0.39	99.40

Empirical formulae:

1. $(K_{0.34}Na_{0.33})_{\Sigma 0.67}Ca_{2.01}(Fe^{2+}{}_{3.65}Mg_{0.27}Mn_{0.07})_{\Sigma 3.99}(Fe^{3+}{}_{0.77}Al_{0.23})_{\Sigma 1.00}(Si_{6.30}Al_{1.70})_{\Sigma 8.00}O_{21.98}$ $((OH)_{1.58}Cl_{0.44})_{\Sigma 2.02}$
2. $(K_{0.39}Na_{0.32})_{\Sigma 0.71}Ca_{2.07}(Fe^{2+}{}_{3.61}Mg_{0.32}Mn_{0.06})_{\Sigma 4.00}(Fe^{3+}{}_{0.75}Al_{0.25})_{\Sigma 1.00}(Si_{6.53}Al_{1.47})_{\Sigma 8.00}O_{22}$ $((OH)_{1.14}Cl_{0.48}O_{0.38})_{\Sigma 2.00}$

* calculated

fels from Yoshiki ore deposit. If the nomenclature of LEAKE (1978) is strictly adopted, one of them with the lowest SiO_2 content is hastingsite, three of them are magnesian hastingsite, and one is hastingsitic hornblende with lower Al_2O_3 content. But all of them have higher K_2O contents though $Na \geq K$ in mole ratio.

Hastingstic clinoamphiboles are found in various skarns accompanying metallic mineralization, and some of them contain moderate to high chlorine contents up to 7.24 wt.% as seen in the material from Dashkesan, Transcaucasia (KRUTOV, 1936), although the material from Kon-i-Zak ore district, Uzbekistan contains no chlorine despite its accompaniment with the mineralization of gold and arsenic (TIMOFEEVA, 1964). While, most of them have higher K_2O contents frequently exceeding that of Na_2O in mole ratio admitting the usage of adjective 'potassian' or 'potassium'. This tendency prevails in all the clinoamphiboles here considered. The K/(Na+K) mole ratio seen in the material from the Obira mine, Japan, 0.18 after MATSUMOTO and MIYAHISA (1960) is the lowest figure among those examined here.

X-ray Powder Study

The X-ray powder study using Cu/Ni radiation was made after the employment of the diffractometer. The pattern is compared with that of material from Dashkesan,

Table 2. X-ray powder pattern of hastingsitic hornblende from the Sampo mine, Okayama Prefecture and hastingsite from Dashkestan, Transcaucasia.

1.		2.		1.		2.	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
9.15	1	9.13	10	2.625	5		
8.52	100	8.52	100	2.573	3	2.587	40
		5.01	15			2.546	5
4.81	7	4.81	10	2.407	5		
4.57	3	4.57	20	2.367	5	2.374	30
4.27	1	4.27	10	2.310	1	2.316	15
		3.89	5			2.291	20
3.419	3	3.40	10			2.257	10
3.314	10	3.32	25	2.185	5	2.196	35
3.155	55	3.16	60			2.169	15
2.972	3	2.983	30	2.066	2		
2.838	13	2.817	5	2.038	4	2.050	25
2.768	1					2.029	10
2.754	10	2.753	30	1.911	2b		
		2.718	5			1.875	25
2.626	5			1.831	2	1.836	15

1. Hastingsitic hornblende. Sampo mine, Okayama Prefecture, Japan. b=broad. Cu/Ni radiation. Diffractometer method. The present study.
2. Hastingsite. Dashkesan, Transcaucasia. Co/Fe radiation. Camera method. JCPDS Card No. 20-378.

Transcaucasia appeared in JCPDS Card No. 20–378 (Table 2). Some diffraction peaks are rather broad probably due to the fluctuating cell parameters reflective of compositional variation, making it difficult to derive the cell parameters from the obtained pattern. A slight discrepancy between two patterns exists.

Genetical Implications

The examined material consists of aggregates of two sets of different associations. One is the aggregates of magnetite and chamosite, and the other is those of clinoamphiboles and calcite with minor pyrite and microscopical chamosite. These textural relationships are deciphered as follows. The earliest mineral is magnetite forming aggregates essentially devoid of gangue minerals meaning the incorporation of iron into marble, though the components of media transporting iron are not clear, except for the expectation that it was capable of dissolving limestone. Then, the aggregates of clinoamphiboles and calcite were formed partially reaplacing magnetite aggregates. Very probably, the incorporated material included sodium, potassium, silica, chlorine, sulphur, and water vapour at least, and the iron in clinoamphiboles and pyrite might have been derived from the surrounding magnetite mass at least in part. The existence of minor pyrite in the aggregates composed of clinoamphiboles and calcite corresponds to the interpretation of MATSUEDA (1980), who states the later formation of sulphides than the mineralization of magnetite. Finally, a preferential invasion of chamosite to magnetite took place, where a part of iron involved as the components of chamosite must have owed the origin to the invaded magnetite. A part of chamosite-forming material entered the aggregates of clinoamphiboles and calcite, and intersected the former. Calcite of such mode of occurence as observed in the present material is not seen in any other cases here referred to. This is interpreted as the scanty or the expiration of the skarn-forming materials other than that forming clinoamphiboles, or inert nature of the material to calcite.

Hastingsitic clinoamphiboles in skarns of pyrometasomatic origin are now found to be compositionally ranged to cover wider fields. The metallic mineralization accompanied by such clinoamphibole-bearing skarns seems to have no specific metallic elements or their combinations. Namely, metallic elements accompanied by the chemical ingredients responsible for the formation of such clinoamphiboles are not definite but diverse.

It is well-known fact that liquid inclusions in gangue minerals of various kinds of ores represented by quartz contain higher concentration of sodium, potassium, and chlorine as such solid forms as halite and sylvine, and that these phases has no specific partner elements. From these evidences it is plausible that these elements in hastingsitic clinoamphibles owe the origin to fractions of ore-forming fluids, or the existence of these halides is another form to retain them. If so, the retention is to be favoured under circumstances where the other ingredients of hastingsitic clinoamphiboles are available.

Hastingsitic amphiboles of magmatic origin are generally rich in alkalis but some of them have rather high SiO_2 contents such as the material in nepheline syenite from Orissa, India (BOSE, 1964), SiO_2 content being 38.84 wt.%, corresponding to $Si_{6.34}$ and having $Fe^{3+}>Al$ in the octahedral site if the chemical analysis is calculated on the basis of total $O=24$, thus it is ferropargasitic hornblende rather than hastingsitic hornblende after the nomenclature of LEAKE (1978). While, in the mineral associations with hastingsite from Yukon, quartz is present (DICK & ROBINSON, 1979), and the SiO_2 content of the representative analysis is 37.36 wt.%, corresponding to $Si_{6.09}$ if the chemical analysis is calculated on the basis of $O+Cl=24$. Thus, it is evident that in hastingsitic clinoamphiboles the SiO_2 contents are not always reflective of the degree of the saturation of SiO_2 of their associated rock-forming silicates.

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