

Potassian pargasite and aluminian diopside from Hôkizawa,
Yamakita-machi, Kanagawa Prefecture, Japan.

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神奈川県山北町箒沢産含カリウムパルガス閃石および含アルミニウム透輝石

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箒沢産の石榴石スカルン中に産する単斜角閃石は、化学分析の結果含カリウムパルガス閃石で比較的SiO₂含有量の低いものである。また、共存する透輝石はAl₂O₃に富んでいる。これらは丹沢山地の中心に露出する石英閃緑岩の貫入に伴うドロマイト質石灰岩の交代作用の産物で、比較的珪酸分に乏しい高温条件下での産物である。また、丹沢山地ではこの岩体に伴われる金属の鉍化作用の痕跡がない。パルガス閃石のFe²⁺Fe³⁺置換体にあたるヘイスティング閃石は、スカルン中に産するものはしばしば著しい金属鉍化作用を伴っている。従って、含カリウムパルガス閃石は金属鉍化作用を伴わない証拠ともなり得る。また、インド産のパルガス閃石に富み含アルミニウム透輝石を含む岩石では、パルガス閃石は今回のものよりもSiO₂に富みAl₂O₃に乏しいが、含アルミニウム透輝石は逆で今回のものよりSiO₂に乏しくAl₂O₃に富んでいる。

Abstract. The average of four microprobe analyses of potassian pargasite in a garnet skarn from Hôkizawa, Yamakita-machi, Kanagawa Prefecture, is : SiO₂ 38.33, Al₂O₃ 16.69, TiO₂ 0.57, Fe₂O₃ 4.01, MgO 12.65, FeO 11.68, MnO 0.19, CaO 12.82, Na₂O 1.88, K₂O 2.20, Cl 0.09, -O=Cl₂ 0.02, total 98.01%, after the allotment of Fe into FeO and Fe₂O₃ using the basis of total of octahedral+tetrahedral cations=13 and positive charge=46. The anhydrous formula after this base is : (Na_{0.54}K_{0.42}Ca_{0.05})_{Σ1.01}Ca_{2.00}(Mg_{2.81}Fe²⁺_{1.01}Al_{0.64}Fe³⁺_{0.45}Ti_{0.06}Mn_{0.02})_{Σ4.99}Al_{2.00}(Si_{5.71}Al_{0.29})_{Σ6.00}O₂₃, or precisely a subsilicic potassian pargasite. The X-ray powder pattern is indexed on a monoclinic cell with \underline{a} =9.929Å, \underline{b} =18.080Å, \underline{c} =5.330Å, β =105.9°. The chemical analysis of aluminian diopside in association with potassian pargasite is : SiO₂ 47.44, Al₂O₃ 7.03, TiO₂ 0.30, Fe₂O₃ 3.90, MgO 11.77, FeO 4.15, CaO 25.02, total 99.61%, after the same allotment of Fe on the basis of total cations=4 and positive charge=12, giving Ca_{1.00}(Mg_{0.66}Fe²⁺_{0.13}Fe³⁺_{0.11}Al_{0.99}

$\text{Ti}_{0.01}\Sigma 1.00(\text{Si}_{1.78}\text{Al}_{0.22})\Sigma 2.00\text{O}_6$. The Al_2O_3 contents in diopside range from 2 to 10 wt.%. That of grossular is: SiO_2 37.64, Al_2O_3 11.15, Fe_2O_3 14.95, TiO_2 0.63, FeO 1.20, MnO 0.61, CaO 33.62, total 99.80%, after the same allotment of Fe on the basis of total cations=8 and positive charge=24, giving $(\text{Ca}_{2.88}\text{Fe}^{2+}_{0.08}\text{Mn}^{2+}_{0.04})\Sigma 3.00(\text{Al}_{1.05}\text{Fe}^{3+}_{0.90}\text{Ti}_{0.04})\Sigma 1.99\text{Si}_{3.00}\text{O}_{12}$, or a ferrian grossular. The skarn was derived from dolomitic limestone due to the intrusion of a quartz-diorite mass exposed in Tanzawa Mountains.

INTRODUCTION

Hôkizawa is one of the most famous localities of skarn minerals not only in Kanagawa Prefecture but also in Japan due to the occurrences of vesuvianite (Yoshiki and Watanabe, 1932), diopside (Kamiyama, 1934a), monticellite (Kamiyama, 1934b), wollastonite (Kamiyama and Katayama, 1934), tobermorite and plombierite (Matsubara, 1980). Most of them are found in dumps derived from unspecified exposures probably developed long the contact of a quartz-diorite mass occupying an extensive area in Tanzawa Mountains with limestone, which is partially dolomitic. As seen in the natures of described minerals, most of skarn-forming minerals were produced under higher temperature and silica-poorer conditions, where the effects of retrograde stages might have existed. The studied material was collected by the first author in a dump accumulated along the river course of the River Naka, which has the drainage involving exposures of quartz-diorite, skarns and metamorphic rocks.

After the microprobe analyses, the essential constituents of the examined materials are found to be potassian pargasite, aluminium diopside, and ferrian grossular. The first one is characterized by its lower SiO_2 and rather high K_2O contents worthy of description under the name potassian pargasite, or precisely subsilicic potassian pargasite (Leake, 1978). The X-ray powder pattern is compared with that of potassium pargasite from Einstödingen, East Antarctica (Matsubara and Motoyoshi, 1985), which has a similar but slightly smaller cell, the difference being ascribed to the lodging of smaller octahedral and tetrahedral cations.

Although the locality is so prolific in skarn minerals, no remarkable metallic ore deposits are developed around the contact aureole of the quartz-diorite body. Clinoamphiboles in skarns accompanying metallic mineralization contain more $\text{FeO}+\text{Fe}_2\text{O}_3$ than the present material, or they correspond to hastingsite, the $\text{Fe}^{2+}\text{Fe}^{3+}$ analogue of pargasite. It seems that the content of $\text{FeO}+\text{Fe}_2\text{O}_3$ in the present pargasite is too low to accompany metallic mineralization, which was not accompanied by the quartz-diorite plutonism.

OCCURRENCE

The studied material is a piece of skarn dominated by reddish brown massive grossular with many greenish grey specks composed of two minerals, or less dark to light

grey and darker grey ones. The former is observed to be rather granular, and the latter is tabular to fibrous under the magnifier, the maximum dimensions being a millimeter across and a few millimeter long, respectively. These correspond to aluminian diopside and potassian pargasite, respectively. The grossular masses involve minor composites of latter two, but the aggregates of latter two involve no grossular grains.

In thin section grossular forms aggregates apparently composed of rather equigranular grains, all of which are devoid of birefringence. Potassian pargasite forms nearly monomineralic aggregates composed of prisms or intergrowths with prismatic aluminian diopside grains, which forms larger rectangular grains, too. Also, minute grains of potassian pargasite are included within grossular grains (Fig. 1a and 1b). Potassian pargasite is moderately pleochroic with axial colours changing from very pale grey to bluish grey.

CHEMICAL ANALYSES

Chemical analyses of potassian pargasite, aluminian diopside and grossular were made by employing Link Systems energy dispersive X-ray spectrometer as given in Table 1.

Three chemical analyses of potassian pargasite are tabulated. All of them have K₂O contents high enough to be attached with the adjective "potassian". Among pargasite analyses, the present ones, especially No.2, belong to those with lower SiO₂ content, which allows the usage of adjective "subsiliic" (Leake, 1978) as well as the figure of average, and suggest the existence of compositional continuity to magnesio-sadanagaite (Shimazaki *et al.*, 1984), this being unusually potassium dominant and silica poor clinoamphibole together with its Fe²⁺ analogue, in these no Na dominant analogues being known to date. The allotment of Fe²⁺ and Fe³⁺ in the present analyses is based on the total of the octahedral and tetrahedral cations to be 13 and of the total of cationic valency to be 46. Pargasite with similar SiO₂ content is known in eclogite, though this contains more Al₂O₃ and Na₂O and less CaO and K₂O (Bocchio, 1977). As to K₂O content in pargasite, Matsubara and Motoyoshi (1985) described potassium pargasite with $K/(K+Na)=0.63$ in granulite from Einstödingen, East Antarctica. They drew $Fe^{2+}/(Mg+Fe^{2+})-K/(K+Na)$ diagram on which the chemical compositions of their pargasitic hornblende and potassium pargasite of the same genesis are on a near linear line with a positive gradient. If the chemical composition of the present pargasite is plotted on their diagram, the point is so remote from the line, probably reflective of the fundamental difference in geologic condition.

The chemical analysis of diopside intergrown with potassian pargasite is given in column No.4. While diopside grains with rather rectangular outline in thin section have wider range of Al₂O₃ content as given in column Nos. 5 and 6. The basis of calculation of empirical formula is the total of cations to be 4 and that of positive charge to be 12. It is worth mentioning that the analysis Nos. 5 and 6 has the relation $Fe^{3+} > Al$ in the octahedral site, indicating the capability of taking up Fe³⁺ in place of Al. All the analyses

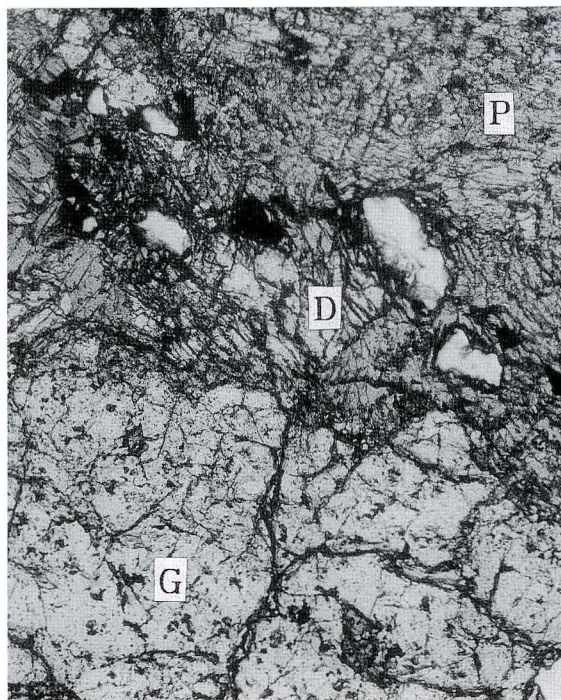


Fig. 1a. Potassium pargasite(P)(upper half) with aluminian diopside (D)(near rectangular grain in the center) and ferrian grossular(G)(down half). One polar. Field view: 1.33 x 1.75mm.

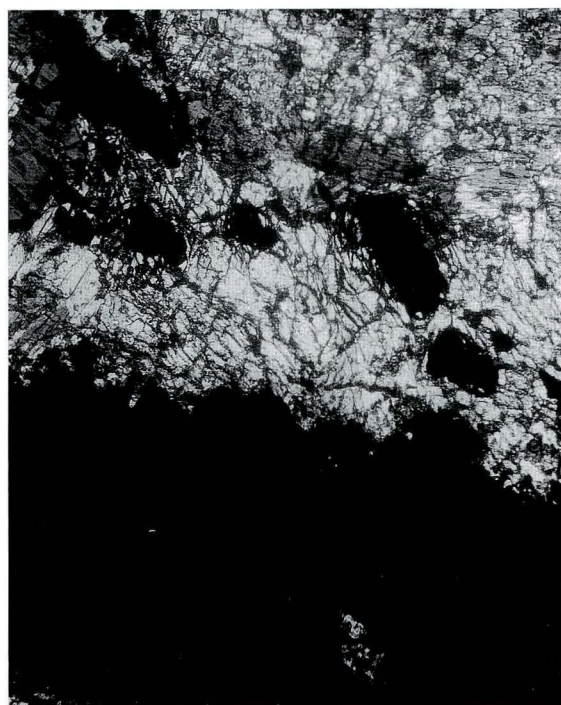


Fig. 1b. Ditto. Crossed polars.

Table 1. Chemical analyses of potassian pargasite, aluminian diopside, and ferrian grossular.

Weight percentages: (*: calculated)

	1.	2.	3.	4.	5.	6.	7.
SiO ₂	38.33	37.69	39.21	47.44	52.55	44.31	37.64
Al ₂ O ₃	16.69	17.63	15.10	7.03	2.15	9.92	11.15
TiO ₂	0.57	0.55	0.43	0.30	0.26	0.80	0.63
Fe ₂ O ₃	4.01	3.81	3.74	3.90	1.81	7.10	14.95
FeO	8.10	8.61	7.85	4.15	0.65	1.92	1.20
MgO	12.65	11.89	13.68	11.77	16.34	11.01	
MnO	0.19				0.44		0.61
CaO	12.82	12.62	12.94	25.02	26.11	25.08	33.62
Na ₂ O	1.88	1.92	1.98				
K ₂ O	2.20	2.16	2.14				
Cl	0.09	0.17					
Sum	98.03	97.09	97.07	99.61	100.31	100.14	99.80
-O=Cl ₂	0.02	0.04					
Total	98.01	97.05					

Empirical formulae: (1.~3.: anhydrous basis neglecting Cl)

1. Potassian pargasite. Mean of 4 analyses. (Na_{0.54}K_{0.42}Ca_{0.05})_{Σ1.01}Ca_{2.00}(Mg_{2.81}Fe²⁺_{1.01}Al_{0.64}Fe³⁺_{0.45}Ti_{0.06}Mn_{0.02})_{Σ4.99}Al_{2.00}(Si_{5.71}Al_{0.29})_{Σ6.00}O₂₃.
2. Ditto. The SiO₂ lowest analysis. (Na_{0.56}K_{0.41}Ca_{0.03})_{Σ1.00}Ca_{2.00}(Mg_{2.66}Fe²⁺_{1.08}Al_{0.77}Fe³⁺_{0.43}Ti_{0.06})_{Σ5.00}Al_{2.00}(Si_{5.65}Al_{0.35})_{Σ6.00}O₂₃.
3. Ditto. The SiO₂ highest analysis. (Na_{0.57}K_{0.41}Ca_{0.02})_{Σ1.00}Ca_{2.05}(Mg_{3.04}Fe²⁺_{0.98}Al_{0.51}Fe³⁺_{0.42}Ti_{0.05})_{Σ5.00}Al_{2.00}(Si_{5.85}Al_{0.15})_{Σ6.00}O₂₃.
4. Aluminian diopside. Prisms in direct contact with potassian pargasite. Ca_{1.00}(Mg_{0.66}Fe²⁺_{0.13}Fe³⁺_{0.11}Al_{0.09}Ti_{0.01})_{Σ1.00}(Si_{1.78}Al_{0.22})_{Σ2.00}O₆.
5. Ditto. A rectangular grain. The Al₂O₃ lowest analysis. Ca_{1.02}(Mg_{0.89}Fe³⁺_{0.05}Fe²⁺_{0.02}Mn_{0.01}Ti_{0.01})_{Σ0.98}(Si_{1.92}Al_{0.08})_{Σ2.00}O₆.
6. Ditto. The same grain as 5. The Al₂O₃ highest analysis. Ca_{1.01}(Mg_{0.61}Fe³⁺_{0.20}Al_{0.10}Fe²⁺_{0.06}Ti_{0.02})_{Σ0.99}(Si_{1.66}Al_{0.34})_{Σ2.00}O₆.
7. Ferrian grossular. (Ca_{2.88}Fe²⁺_{0.08}Mn_{0.04})_{Σ3.00}(Al_{1.05}Fe³⁺_{0.90}Ti_{0.04})_{Σ1.99}Si_{3.00}O₁₂.

demonstrate the coupled substitution of Al(Al,Fe³⁺) for (Mg,Fe)Si very clearly, although minor Ti may require the excess of tetrahedral Al for charge balance in such a monovalent cation free case.

Grossular is to contain higher Fe₂O₃ content, indicating that the formation of the present skarn was made under rather oxidizing condition. The microprobe survey informs the chemical inhomogeneity to be very small if present. The calculation of empirical

Table 2. X-ray powder pattern of potassian pargasite and potassium pargasite.

1.			2.			1.			2.		
I	d _{obs.}	d _{cal.}	I	d _{obs.}	hkl	I	d _{obs.}	d _{cal.}	I	d _{obs.}	hkl
10	9.02	9.02	5	9.04	020				2	1.960	190
100	8.47	8.47	60	8.47	110	1	1.937	1.937			281
			2	5.10	130	8	1.906	1.906	1	1.901	510
2	4.93	4.93	2	4.94	111	1	1.869	1.869	2	1.865	191
9	4.52	4.51	5	4.52	040	1	1.864	1.863			242
5	4.23	4.23	4	4.23	220	2	1.827	1.826	5	1.822	530
			1	3.90	131				2	1.802	0.10.0
15	3.381	3.388			041	1	1.776	1.775			2.10.0
		3.384	30	3.38	131			1.774			312
		3.381			150	1	1.733	1.733			223
45	3.288	3.284	30	3.280	240			1.733			551
85	3.155	3.145	100	3.138	310	3	1.694	1.695			082
25	2.949	2.952	12	2.949	151			1.693	5	1.689	550
		2.944			221			1.693			262
45	2.820	2.822	45	2.815	330	14	1.653	1.654			481
10	2.763	2.760	8	2.759	331			1.654			601
25	2.707	2.709	10	2.706	151			1.654			461
8	2.597	2.596	7	2.593	061	3	1.642	1.643			333
12	2.566	2.566	6	2.564	002			1.643			480
		2.563			241	4	1.617	1.618			1.11.0
		2.562			202	6	1.597	1.598			531
12	2.395	2.395	19	2.389	400			1.597			600
16	2.356	2.355	10	2.352	351	2	1.572	1.572			620
			12	2.345	421	5	1.562	1.563			1.11.1
			5	2.301	171	4	1.525	1.526			243
5	2.260	2.259	2	2.255	331			1.524			173
		2.258			080			1.524			1.11.1
2	2.234	2.230	2	2.228	042	1	1.521	1.520			192
					242	5	1.505	1.506			551
12	2.165	2.167	8	2.161	261			1.505			640
		2.164			332			1.505			0.12.0
			5	2.111	440	3	1.484	1.485			513
8	2.047	2.047	4	2.046	202	2	1.474	1.472			153
			8	2.039	402			1.472			442
					280	1	1.451	1.450			4.10.1
9	2.020	2.021	6	2.016	351			1.449			661
2	2.006	2.007	5	2.002	370	3	1.409	1.411			660

a = 9.929Å	a = 9.917Å
b = 18.080Å	b = 18.020Å
c = 5.330Å	c = 5.321Å
β = 105.9°	β = 105.49°

1. Potassian pargasite. Hōkizawa, Kanagawa Prefecture. Cu/Ni radiation. Diffractometer method. The present study.
2. Potassium pargasite. Einstödingen, East Antarctica. Cu/Ni radiation. Diffractometer method. After Matsubara and Motoyoshi (1985).

formula is based on the total cation=8 and the total cationic valency=24. Seeing from the ratio of total metallic cations to Si is close to 5:3, the substitution of H_4 for Si is unlikely.

The degrees of inhomogeneity of three examined silicates vary significantly despite the close co-existence. They are to increase in the order of grossular, potassian pargasite, and aluminian diopside if the ranges of mole percents of end member formulae are taken into consideration.

X-RAY POWDER STUDY

A few fractions of potassian pargasite were examined by X-ray powder diffractometer. All them are essentially identical, the pattern of best quality is given in Table 2 in which it is compared with that of potassium pargasite from Einstödingen, East Antarctica (Matsubara and Motoyoshi, 1985). From the indexing the cell parameters are calculated as: $a=9.929\text{\AA}$, $b=18.080\text{\AA}$, $c=5.330\text{\AA}$, $\beta=105.9^\circ$. The slightly larger unit cell edges than those of the latter will be due to the higher contents of tetrahedral Al relative to Si and of octahedral Fe^{2+} relative to Mg and the other cations.

The powder patterns of aluminian diopside forming visible aggregates are close to that given in JCPDS Card No.11-654.

The powder pattern of ferrian grossular consists of rather sharp peaks even in the higher angle region. The coincidence of calculated d -values using a cubic cell with $a=11.942\text{\AA}$ with observed ones (Table 3) will be due to the less inhomogeneous nature and to the lesser degree of deviation from the cubic symmetry, if present.

DISCUSSION

Here, two matters are considered. One is the comparison with skarns accompanying metallic mineralization represented by the existence of hastingsite, which has higher FeO and Fe_2O_3 contents, concluding that pargasite is to be involved in skarns without accompanying metallic mineralization. The other is the consideration on pargasite–diopside association, which is also found in higher grade metamorphic rocks.

Despite the frequent and extensive occurrence of skarn minerals around the acidic plutonic body located in the center of Tanzawa Mountains, the development of metallic ore deposits is very poor or essentially null. The obtained results enable to compare the mineral with hastingsite, which corresponds to the $Fe^{2+}Fe^{3+}$ analogue of pargasite and is found in skarns accompanied by metallic mineralization due to activities of acid intrusive. As far as our literature survey informs, pargasite and its potassium-bearing derivatives do not accompany any significant metallic mineralization, serving as a proof of barren skarn. The comparison of hastingsite in skarns accompanying metallic mineralization with the present potassian pargasite informs that the higher FeO, Fe_2O_3 and SiO_2 contents in the former may be responsible for metallic mineralization.

Table 3. X-ray powder pattern of ferrian grossular.

I	d _{obs.}	d _{cal.}	hkl	I	d _{obs.}	d _{cal.}	hkl
3	4.233	4.222	220	6	1.723	1.724	444
55	2.987	2.987	400	22	1.656	1.656	640
2	2.824	2.815	330	2	1.625	1.625	633, 552
100	2.670	2.670	420	37	1.596	1.596	642
8	2.547	2.546	332	9	1.493	1.493	800
30	2.437	2.438	422	2	1.470	1.470	811, 554
14	2.342	2.342	510, 431	1	1.408	1.407	660
13	2.180	2.180	531	8	1.335	1.335	840
1	2.112	2.111	440	3	1.303	1.303	842
18	1.936	1.937	611	3	1.273	1.273	664
4	1.888	1.888	620	1	1.259	1.259	851

$$a = 11.942\text{\AA}$$

Table 4. Chemical analyses of pargasite and fassaite from India and of potassian pargasite and aluminian diopside from Hôkizawa.

	1.	2.	3.	4.
SiO ₂	42.05	38.33	46.52	47.44
Al ₂ O ₃	15.86	16.59	10.07	7.03
TiO ₂	0.76	0.57	0.32	0.30
Cr ₂ O ₃	0.12		0.06	
Fe ₂ O ₃	2.36	4.01	2.22	3.90
FeO	8.35	8.10	5.26	4.15
MgO	14.18	12.65	11.45	11.77
MnO	0.21	0.19	0.31	
CaO	10.98	12.82	22.58	25.02
Na ₂ O	2.52	1.88	0.27	
K ₂ O	0.83	2.20	0.15	
H ₂ O ⁺	1.28		0.28	
H ₂ O ⁻	0.12		0.12	
F	0.08			
Cl		0.09		
-O=F ₂ , Cl ₂	0.035	0.02		
	99.665	98.01	99.61	99.61

1. Pargasite. Aganampudi, India. After Rao and Rao (1981).
2. Potassian pargasite. Hôkizawa, Kanagawa Prefecture. Same as column 1, Table 1.
3. Fassaite (=aluminian diopside). Aganampudi, India. After Rao and Rao (1981).
4. Aluminian diopside. Hôkizawa, Kanagawa Prefecture. Same as column 4, Table 1.

The association of pargasite and diopside is also found in metamorphic rocks of higher grades. After Rao and Rao (1981), a pargasite-rich rock from Aganampudi, India, contains 60% pargasite, 39% fassaite (=aluminian diopside), and 1% spinel. The rock is from a charnockite region and its metamorphic origin is very likely. In Table 4 the chemical analyses of pargasite and fassaite are compared with the present materials, column Nos. 1 and 4, Table 1 being selected. The most notable differences in pargasite analyses are the lower SiO_2 and higher Al_2O_3 contents than the Indian material, whereas the present diopside has higher SiO_2 and lower Al_2O_3 contents than the Indian material. Therefore, a cross-cutting relation of joins connecting the $\text{Al}/(\text{Si}+\text{Al})$ ratios of two minerals between two pairs comes out. In the present material, the variable Al_2O_3 contents in the examined diopside grain reveal the inhomogeneity, which has been reserved even after the subsequent formation of potassian pargasite. The multi-staged formation of diopside with different Al_2O_3 contents is very likely and a part of the products co-existed with potassian pargasite. At the present stage, the discussion on the cross-cutting relation seen in the two pargasite-diopside pairs seems meaningless.

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