ON MINERALS ASSOCIATED WITE ULTRABASIC ROCKS, FOUND IN THE VICINITY OF COMMON BOUNDARIES OF SHIMANE, TOTTORI,OKAYAMA AND HIROSHIMA PREFECTURES   (I)

—HYDROGROSSULAR AND CHROMITES FROM THE TAKASE MINE, OKAYAMA PREFECTURE—

By

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Outline of Geology

The geology in the district consists of Sangun metamorphic rocks of Upper Palaeozoic system, granitic rocks, and sandstone, breccia rock layers of Early Tertiary formation. (Geological map is omitted in the paper.)

1. *Sangun metamorphic rocks*

The Sangun metamorphic rocks are metamorphosed in low grade, and constructed of green and black phyllites. The original metamorphosed sedimentary rocks belong to Sangun metamorphic rock in a narrow sense, and the associated serpentinites and gabbros are contained in the Sangun metamorphic rocks in a broad sense. Peridotite is almost serpentinized with olivine relics. The serpentinite mass of Tari and Inazumi, Tottori prefecture, and the one of Takase, Okayama prefecture are continuous each other or generated at same age. Gabbroic rocks are found as xenolithic and dyke forms in the chromite deposits in the region.

2. *Granitic rocks* .

Granitic rocks in the district include quartz porphyry and granite porphyry besides granite, but the quartz porphyry is early generated than the granite. The granitic rocks are intruded into the Sangun metamorphic rock in Late Cretaceous or Early Tertiary period. The contact metamorphic evidences of the Sangun metamorphic rock effected by the granitic rock are quite marked at many places. The chemical analysis of a specimen of the granite was denoted in the previous paper (Kitahara, 1964).

3. *Tertiary system*

In the district, sandstone and brecciated rock are deposited sparsely in a small scale.

The sediments are composed of brecciated and sandy layers contained abundantly sandstone and brecciated rock of older age.
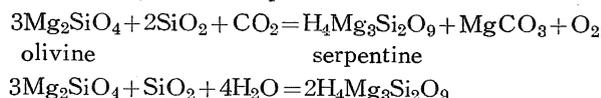
Ultrabasic Complexes

The ultrabasic rock body of Takase mine is elongated in some degree to nearly E-W direction. The body is an elliptical mass 2 kilometers long and 1.25 kilometers wide, with a total area of about 33 square kilometers. The ultrabasic complexes are mainly composed of serpentinized harzburgite, pyroxenite and gabbro. Granite porphyry and quartz porphyry was intruded into the ultrabasic rock. Serpentinites are constituted of massive, schistose and brecciated rocks. Gabbro and pyroxenite occur as xenolithic or dyke forms in the serpentinite. A part of gabbro layer in the earth crust of lower level had been caught up by a peridotitic magma, and the gabbro xenoliths in the serpentinite was altered to gabbro of meta-state. On the other hand, the gabbro dykes are transformed from an eclogite magma generated by concentration of heat or by pressure depression from an eclogite pocket in the mantle (Kitahara, 1963). It is inferred that the pyroxenite xenoliths in the serpentinite are also originated from a pyroxenite layer or pocket in the mantle, but there is the question of pyroxenite dykes in ultrabasic body. It is resolved that the gabbro dykes and some of pyroxenite dykes are not differentiated from an ultrabasic magma. In the earlier papers, various investigators have reported that the formation of ultrabasic bodies found in the vicinity of common boundaries of Shimane, Tottori, Okayama and Hiroshima prefectures is generated by fractional crystallization of a basic magma in situ. The writer (1962) has described from his mining geological survey that the ultrabasic complexes of the region were formed by the intrusion of ultrabasic and gabbroic magmas. The variations of successive dunitic, pyroxenitic and gabbroic magmas in the rock types may be explained as due to intrusion. It is appreciated that all the ultrabasic complexes have not been formed by similar processes or from similar magmas. Portions of the overlying gabbroic rock were caught up and included in the ultrabasic rock as described above. On the other hand, the intrusion of ultrabasic rock magma was either accompanied, or closely followed by the intrusion of gabbroic rock. Loewinson-Lessing (1900) viewed the ultrabasic and basic rocks of the platinum–bearing belt of the Urals as products of the separation of the original gabbro magma which occurred as the result of magmatic differentiation, but Vorobyeva (1961) mentioned that the magmatic nature of the rocks of the gabbro–pyroxenite–dunite belt of the Urals has been in large measure obscured by postmagmatic processes. Thus the origin of the gabbro–pyroxenite–dunite of the Urals is ambiguity, but the origin of the ultrabasic complexes in the Tari mine district is suggested as described above.

Harzburgite is described as composed of olivine, enstatite, and aluminian chromite ; and in general it is strongly serpentinized. Harzburgite or saxonite containing enstatite probably forms 4/5 of the ultrabasic mass and pyroxene–rich peridotite perhaps constitutes 1/30 or less in the region. The chemical analysis of a massive serpentinized harzburgite from the Shinguchi level of the mine is as shown the following ; SiO_2 38.98, TiO_2 0.02, Al_2O_3 3.58, Cr_2O_3 0.28, Fe_2O_3 4.57, FeO 1.10, MnO 0.06, MgO 40.05, CaO 0.12, H_2O+ 10.61, H_2O- 0.80 (Wt.%).

Like many other ultrabasic masses, the Takase ultrabasic rock shows little or no contact metamorphic effect on the wall rocks ; namely, there is no indication of high temperature metamorphism. Bowen and Tuttle made a detailed study of the system $MgO-SiO_2-H_2O$ and reached the following conclusions. Under certain conditions of crustal deformation, apparently involving strong overthrusting, dunitic and related materials, coming at times perhaps from a peridotite shell of the earth, at other times from a peridotite mass that has formed as a differentiate of gabbroic magma, can be intruded in a completely crystalline state into substratum. In this way all this fits imperfectly with Bowen and Tuttle's theory. It is said that peridotite or serpentinite always occurs in an orogenetic zones and has usually cataclastic structure.

Some limited serpentinization can be attributed to autometasomatism, a more important factor must be sought for the large-scale serpentinization. It may be assumed that the chief serpentinizing solutions were siliceous solutions with dissolved CO_2. On reaching the ultrabasic bodies, intense serpentinization resulted according on the following reactions :

$$3Mg_2SiO_4+2SiO_2+CO_2=H_4Mg_3Si_2O_9+MgCO_3+O_2$$
$$\text{olivine} \qquad\qquad\qquad \text{serpentine}$$
$$3Mg_2SiO_4+SiO_2+4H_2O=2H_4Mg_3Si_2O_9$$

Ore Deposits of Takase Mine

The chromite deposits of Takase mine are contained in the ultrabasic body which constructs the Takase mountain mass. The boundary between the ore body and its country rock is sharp, and the ore body often includes country rock mass with xeno-lithic form and also ore body blocks are seen in the mother rock. The ore body and the country rock are together sheared and show cataclastic structure.

The ore bodies of the mine are classified into east, middle and west deposits. The bodies are folded, sheared and overturned by Sangun metamorphism. It is suggested that normal fault was originated by the later block movement.

The serpentinization of the ultrabasic rock progresses tremendously in the east 1st level and on the contrary is not distinct in the Shinguchi level. The chromite deposits are generally developed in the position gotten greatly serpentinization. The ore body has comparatively a gentle slope, but shows a steep slop in the lower level of the deposits.

a) *East deposits of the mine*

The deposits run N-S with dip of 30°W.

East 1st level

The strike of the ore body is E-W with dip of 0°−10°S. The elongated direction of the ore body is N30°E with shoot of 5°−10°S. The length of the direction is 60 m with width of 40 m. The ore body is cut by two faults of E-W system.

b) *Central deposits* (New 3rd level)

1) *Middle upper deposits*

The ore body is the largest deposit in the mine. The strike of the body is N30°W with dip of 10°−20°S, and the length is 40 m and the width is 15 m.

2) *Middle north deposits*

The strike of the body is NS—N20°W with dip of 0°—10°W. The elongated direction is N45°W with shoot of 5°N. The body is developed as long as 110 m to elongated side.

3) *Middle south deposits*

The deposits are classified 2nd, 3rd and 4th ore bodies : the 2nd body, striking N75°W and dipping to 5°—10°S ; the 3rd body, striking E-W and dipping to 5—10°N ; and the 4th body, striking N60°W and dipping to 5°—10°S.

(The detailed description of the ore deposit map will be given in a separate paper.)

Occurrence and Origin of Hydrogrossular

The curious mass included in serpentinite was found in the Shinguchi level near the south western boundary of the chromite deposits. The mass is irregular rounded lenticular in sharp, and in size 2 m measured along the long diameter of the lens. Hydrogrossular forms a part of the curious xenolithic pyroxenite. It would then represent portion of the overlying pyroxenite pocket caught up by the very viscid ultrabasic magma. A portion of the xenolithic pyroxenite is composed of so-called rodingite. The definitions of rodingite was given by Marshall (1911) for the original rock in New Zealand. In general rodingite is chiefly constructed of a fine grained mosaic of grossular grains with a small amounts of diopside. Hutton (1943) first described hydrogrossular from rodingite in New Zealand, and it has since been recorded in altered gabbroic rocks and rodingite from other localities where its occurrence is due to redistribution or metasomatism involving the addition of calcium (Miles, 1950 ; Bilgrami and Howie, 1960).

Serpentinized harzburgite (1)

The harzburgite caught up the pyroxenite as mentioned above, in thin section, is mainly constituted of serpentinized olivine and chloritized enstatite with diopside grains 0.2—0.5 mm in diameter.

The chemical analysis of the rock is as shown in Table 1.

Pyroxenite (2)

It seems that the xenolithic form pyroxenite mentioned above is original rock of the hydrogrossular. The rock is compact and black in color.

Under the microscope, enstatite is ordinary 0.07—0.50 mm and found sometimes 2—3 mm in diameter. Diopside (Al-augite) ($\gamma=1.713$, a little altered one) is generally 0.1 mm and sometimes 2 mm in diameter. Diopside is frequently included in enstatite. The pyroxenes are more or less altered to chlorite. Some diopside is altered to epidote. The quantity ratio of diopside to enstatite is almost 7/3. Magnetite 0.1—0.3 mm in diameter is also observed. The chemical analysis of the rock is as shown in Table 1. As the rock is abundant in Al_2O_3 content, it is realized that the rock is chloritized Al-pyroxenite with Al-augite and Al-enstatite.

Pyroxenite (3)

It is inferred that this green pyroxenite is generated from the pyroxenite (2) by Ca-metasomatism. In thin section, augite ($\gamma=1.706$) 0.1—0.4 mm in diameter includes enstatite ($\gamma=1.609$) and also cuts enstatite. Enstatite with parting is rarely found. The two kind of pyroxenes are altered to chlorite. Magnetite 0.01—0.10 mm in diameter

Table 1. Chemical analyses of basic, ultrabasic rocks

	Wt. %					Atom. ratios when O=160				
	(1)	(2)	(3)	(5)		(1)	(2)	(3)	(4)	(5)
SiO_2	38.13	34.34	36.06	48.16	Si	33.6	31.5	33.3	37.3	47.0
TiO_2	0.04	0.47	0.42	1.84	Ti	0.1	0.3	0.3	0.01	1.4
Al_2O_3	7.52	16.01	15.59	13.78	Al	7.6	17.3	17.0	26.5	15.8
Cr_2O_3	0.23	0.04	0.03	—	Cr	0.2	0.03	0.02	—	—
Fe_2O_3	1.99	2.69	0.70	3.77	Fe^3	1.2	1.9	0.4	2.6	2.8
FeO	1.59	4.39	5.50	10.94	Fe^2	1.1	3.4	4.2	0.7	8.8
MnO	0.07	0.13	0.06	0.20	Mn	0.1	0.1	0.1	0.1	0.2
MgO	39.22	25.10	18.48	6.51	Mg	50.0	34.5	25.6	1.3	9.6
CaO	0.44	9.22	14.29	12.55	Ca	0.4	9.0	12.5	38.1	13.1
Na_2O	0.30	0.63	0.45	1.51	Na	0.5	1.1	0.8	—	2.8
K_2O	0.06	0.17	0.12	0.16	K	0.1	0.2	0.1	—	0.2
P_2O_5	n.d	n.d	n.d	0.22	P	—	—	—	—	0.2
H_2O+	9.98	6.52	7.19	0.51	H_+	57.0	39.8	44.2	3.3	3.2
H_2O-	0.38	0.40	1.11	0.04						
	99.95	100.11	100.00	100.19		(Analyst : J. Kitahara)				

(1) : Harzburgite (serpentinized),   (2) : Al–pyroxenite (chloritized),   (3) : Al–pyroxenite (chloritized),   (4) : Hydrogrossular (analysis : Table 2),   (5) : Gabbro (relatively fresh)
(1), (2), (3), (4) : Shinguchi level of Takase mine, Okayama pref.
(5) : New 3rd level of Takase mine, Okayama pref.

presents as spotted or curved forms. Judging from the chemical analysis of Table 1, the pyroxenes are Al_2O_3 containing kind somewhat altered to chlorite, and the rock composed of the pyroxenes is chloritized Al–pyroxenite.

The hydrogrossular is a metamorphic–metasomatic product resulting from intensive alteration of an original calcareous aluminous rock (Al–pyroxenite) brought into the present position as xenolith within the harzburgite body.

Alteration into massive lime garnet from an original Al–pyroxenite implies an increase in silica, alumina and lime, and removal of magnesia. It is suggested that the addition of elements could be due to a metasomatic replacement caused by magmatic infiltration.

Rock type	Pyrop	Alman	Spess	Gross	And
Garnet from peridotite	71	16	½	2	4½
_____ metagabbro	31	45½	2	12	5½
_____ calc silicate rock	2	3	1½	47½	25½
_____ pyroxenite	0	30½	0	45½	24
_____ skarn rock	2	3	1	12	82
_____ serpentine schist	½	3	1	42½	53
Garnet from Ca–Al–silicate rock (Al–pyroxenite from Takase mine) (Kitahara)	3	1½	½	86	9

The dominant cations in the original two pyroxens were Al, Ca and Mg with some Fe^2. Addition lime and a small amount of water could diplace magnesia and silica. A source of additional lime would still be necessary for the production of hydrogrossular from pyroxenite. It seems that the some chloritization of orthopyroxene and clinopyroxene is caused by hydrothermal acting at the period of garnetization of the two pyroxenes.

Grossularite is typically formed by the contact or regional metamorphism of impure limestones. A portion of the relation between chemical composition and mother rock (occurrence) in the garnet is as shown in the before description (Tiger, 1958).
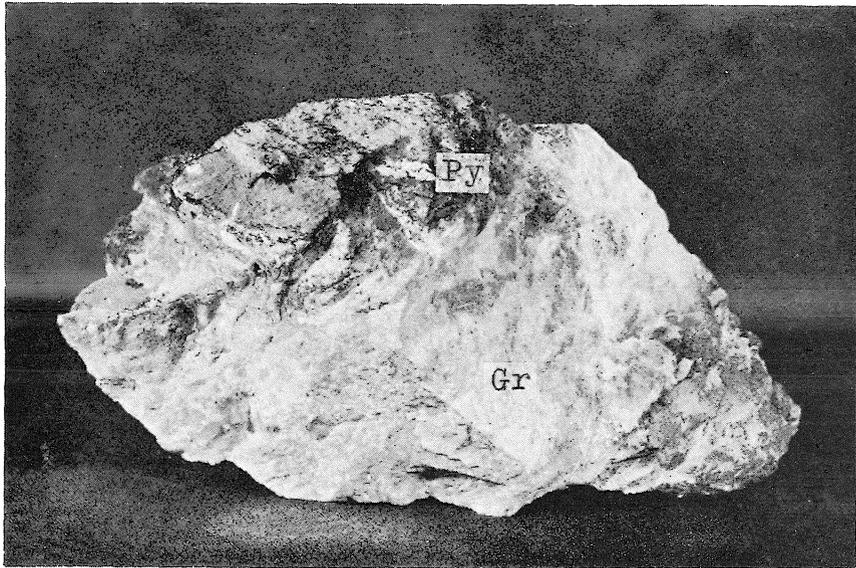

Fig. 1. Hydrogrossular (Gr) (rodingite in part) from Al–pyroxenite (Py)
by metasomatism.   Scale : ¾
Shinguchi level of Takase mine, Okayama pref.

The hydrogrossular is formed from the Al–pyroxenite (3) mentioned above by Ca–Al metasomatism (Fig. 1). Clinopyroxene and enstatite were completely replaced by isotropic hydrogrossular ; the remaining pyroxene is fairly fresh. The structure of pyroxene is decomposed ; SiO_2, Al_2O_3 and CaO components are added it ; MgO is fallen down from it, and then the grossular is generated. Peridotite magma was generated by concentration of heat or by decrease of pressure of a position of peridotite shell which constitutes upper mantle. Pyroxenite in the mantle was caught up in peridotite magma ; the magma was intruded into earth crust ; the pyroxenite was metasomatized by the magma, and the grossular was formed in a part of the pyroxenite. Rodingite is ordinary produced from gabbro by metasomatism, but a part of the green Al–pyroxenite (3) in the mine was metasomatized to the hydrogrossular. The complex of the Al–pyroxenite and the hydrogrossular can be called a rodingite. As described before, rodingite is always formed from gabbro, but the chemical composition of Al–pyroxenite is similar to it of gabbro (Table 1, (5), unaltered one) and then rodingite may be formed from Al–pyroxenite too. Rodingite was due to the action of concentrated magmatic water under high pressure,

and that lime-silicate rocks were transformed by calcium rich aqueous solutions which came from a cooling peridotite mass ; monoclinic pyroxene was suggested as the source of the calcium. It is considered, therefore, that the hydrogrossular is due to a metasomatic replacement of pyroxenite. It must be by reconstructive transformation ; that is, a tearing down of the various structures and a rebuilding on the basis of the hydrogrossular unit cell.

Hydrogrossular

The crystal structure of garnets was first investigated by Menzer (1926, 1928) who showed that the unit cell contains eight formula units. The silicon oxygen tetrahedra exist as independent groups linked to octahedra of the trivalent ions, while the divalent metal ions are situated in the interstices within the Si–Al network, each divalent ion being surrounded by eight oxygens.

The crystal structure of hydrogrossular has been shown to be fundamentally simillar to that of grossular : hibschite, $Ca_3Al_2Si_2(OH)_4O_8$, has a cell side of 12.16 Å (Pabst, 1937) and eight molecules to the unit cell ; space group Ia3d. Hydrogrossular corresponds to the partial substitntion of $(OH)_4^{-4}$ for $(SiO_4)^{-4}$ in the structure : i. e. there is replacement of SiO_2 by $2H_2O$, with vacant Si spaces in the structure.

An interesting point reviewed by Wickman is that six-coordinated aluminum usually occurs only in those silicates formed under high pressure or in connection with hydroxyl groups. In progressing toward the hydrous end of the series, there are fewer silicons, and the structure terminates with (OH) groups in place of the oxygen which coordinated the silica. When the structure is completely devoid of silicons, the aluminums and calciums become completly surrounded with hydroxyl groups. The deficiency of silica should not be termed replacement of silica by water.

Menzer found that grossular has eight molecules to the unit cell, is built on a body-centered lattice, and has the space group O_h^{10}. The atomic positions are given as follows :

16 Al in 16 (a)	0	0	0
24 Ca in 24 (c)	1/4	1 4	0
24 Si in 24 (d)	1/4	3/8	0
96 O in 96 (h)	x	y	z

The name hydrogrossular is applied to members of the series 3CaO. Al_2O_3 $3SiO_2$ – 3CaO. Al_2O_3. $6H_2O$ with a composition between grossular and hibschite (plazolite), 3CaO. Al_2O_3. $2SiO_2$. $2H_2O$ (Hutton,1943). Minerals in this compositional range have also been called hydrogarnet, the latter being more broadly defined to conform with the general formula $X_3 Y_2 (ZO_4)_{3-m} (OH)_{4m}$ (McConnell, 1942). The compositional range between hibschite and the silica – free form 3CaO. Al_2O_3. $6H_2O$ is not yet known to occur naturally. Hydrogrossular is considered as a phase in the two-component system $Ca_3Al_2Si_3O_{12}$ – $Ca_3Al_2(OH)_{12}$ as described before. This indicates a compositional range from 25% to 65% of the $Ca_3Al_2 (OH)_{12}$ component, according to Yoder's data (1950). A satisfactory formula is suggested by Hutton – $Ca_3Al_2(SiO_4)_{3-m}(OH)_{4m}$. Although Hutton introduced the name hydrogrossular for composition intermediate between grossular and hibschite (and plazolite), it seems reasonable to extend the name to include the latter minerals also.

Members of the hydrogrossular series are probably more common than has been

realized ; it has been suggested (Hutton and Yoder, 1950) that the majority of garnets described as grossular belong in fact to this series. Hutton says that the usual constituent of altered gabbros and related basic intrusive rocks is a member of the garnet-hydrogarnet series near the grossular end. The variations of specific gravity and refractive index with combined water of grossular are as follows.

	1	2	3	4
%H_2O_+(samples dried at 105°C.)	0.48	0.83	1.02	1.16
R. I.	1.741	1.731	1.730	1.728
S. G.	3.591	3.523	3.505	3.488
% SiO_2	36.84	—	—	36.55

1. Hydrogrossular from Takase mine, Okayama pref. (by Kitahara)
2. 3. 4. Hydrogrossular from South Africa.

Flint and Wells arrived at the conclusion that a complete series of solid solution, the hydrogarnet series, exists between these two end members of $3CaO. Al_2O_3. 3SiO_2$ and $3CaO. Al_2O_3. 6H_2O$. It is seen that there is experimental evidence for a complete series of solid solutions between grossular and $Ca_3Al_2(OH)_{12}$ and field evidence for a series of solid solutions between grossular and plazolite. It is believed that the dry end member of grossular – $Ca_3Al_2(OH)_{12}$ series does exist, but it is suspected that the majority of naturally occuring garnets described as grossular do contain some hydroxyl groups.

Optical and Physical Properties of Hydrogrossular

The grossular shows reddish brown appearance. In thin section, garnet grains from 0.1 mm up to 5 mm diameter are pale brownish gray and some garnet grains are intimately associated with colorless diopside. The garnet grains are fully isotropic and replace both pyroxenes which are cloudy near the garnet. Some diopside show undulatory extinction and the cleavage is curved.

In the $3CaO. R_2O_3. 6H_2O - 3CaO. R_2O_3. 3SiO_2$ system, the density of $3CaO. R_2O_3. 6H_2O$ may be calculated from the value of lattice parameter of it. Lattice parameters a_0, refractive indices n, and densities d of $3CaO. R_2O_3. 6H_2O$ and $3CaO. R_2O_3. 3SiO_2$ are tabulated respectively as follows ;

	a_0(Å)	n	d
$3CaO. Al_2O_3. 6H_2O$	12.56	1.605	2.54
$3CaO. Fe_2O_3. 6H_2O$	12.74	1.710	2.78
$3CaO. Al_2O_3. 3SiO_2$	11.84	1.735	3.53
$3CaO. Fe_2O_3. 3SiO_2$	12.06	1.895	3.83

The physical constants of the hydrogrossular in the mine are described as follows. Lattice parameter is $a_0 = 11.867$ Å, density is $d_4 = 3.591$, refractive index is $n = 1.741$, mol. weight is $M = 451.4$, packing index ($\frac{\text{volume of ions} \times 10}{\text{volume of unit cell}}$) is P. I. $= 6.2$, and mol. refraction ($\frac{M(n^2-1)}{d(n^2+2)}$) is $R_0 = 50.75$.
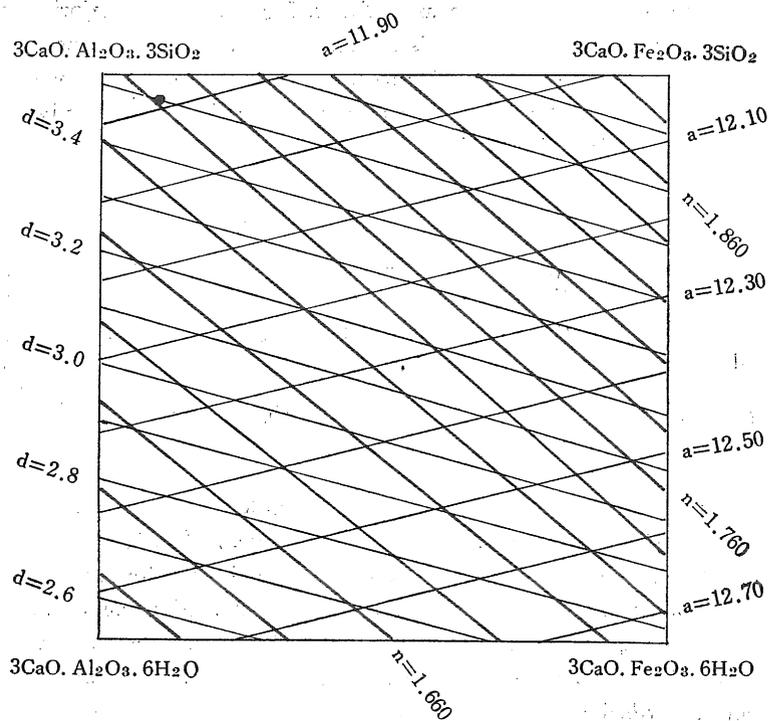
Fig. 2. Variations in physical constants with composition in the series
   $3CaO. R_2O_3. 6H_2O - 3CaO. R_2O_3. 3SiO_2$.
   • : hydrogrossular from Shinguchi level of Takase mine, Okayama
   prefecture   (Calc. and draw. : Kitahara)

The relation between the physical constants of lattice parameter, refractive index and density, and the chemical composition in $3CaO. R_2O_3. 6H_2O - 3CaO. R_2O_3. 3SiO_2$ system can be diagrammatized (Fig. 2). The hydrogrossular in the mine displays

$$\frac{3CaO. (Al_2O_3 + Fe_2O_3). 3SiO_2}{3CaO. (Al_2O_3 + Fe_2O_3). 6H_2O} = \frac{95.8}{4.2} \text{ and } \frac{3CaO. Al_2O_3. (3SiO_2 + 6H_2O)}{3CaO. Fe_2O_3. (3SiO_2 + 6H_2O)} = \frac{91.2}{8.8} \text{ as shown}$$

in the figure.

For members of the hydrogrossular series the presence of $(OH)_4$ replacing SiO_4 results in their having a lower density and refractive index, and a larger cell edge than grossular.

Chemical Composition of Hydrogrossular

The chemical composition and its atomic ratios of the pure hydrogrossular which constructs a portion of pyroxenite (or rodingite) are as shown in Table 2. The chemical formula of the hydrogrossular is expressed as $(Ca_{2.86}, Mg_{0.10}, Fe^2_{0.05}, Mn_{0.01})_{3.02} (Al_{1.99}, Fe^3_{0.19}, Ti_{0.003})_{2.18} Si_{1.86}O_8 (SlO_4)_{0.94} (OH)_{0.25}$. The m value in the general formula of the garnet $Ca_3Al_2Si_2O_8(SiO_4)_{1-m} (OH)_{4m}$ is calculated as 0.0615. The mol.% of end member of the garnet is given as follows.

From the result, it is understood that the garnet is rich in Gr (+Hydro-Gr) component and somewhat higher in An component compared with Alm, Py and Sp components.

Table 2.　Chemical analysis of hydrogrossular

	Wt. %	Mols		Atom. ratios		Atom. ratios when O=24
SiO_2	36.84	613	Si	613		5.588
TiO_2	0.04	0.5	Ti	0.5		0.005
Al_2O_3	22.26	218	Al	436		3.974
Fe_2O_3	3.44	21	Fe^3	42		0.383
FeO	0.84	12	Fe^2	12		0.109
MnO	0.16	2	Mn	2		0.018
MgO	0.85	21	Mg	21		0.191
CaO	35.12	627	Ca	627		5.715
H_2O+	0.48	27	$H_+(OH)$	54		0.492
H_2O-	0.08		O	2633		
	100.11					

Numbers of ions on basis of 24 (O)

$$\left.\begin{array}{ll} Si & 5.588 \\ OH/4 & 0.123 \end{array}\right\} 5.711$$

$$\left.\begin{array}{ll} Al & 3.974 \\ Fe^3 & 0.383 \\ Ti & 0.005 \end{array}\right\} 4.362$$

$$\left.\begin{array}{ll} Mg & 0.191 \\ Fe^2 & 0.109 \\ Mn & 0.018 \\ Ca & 5.715 \end{array}\right\} 6.033$$

(Analyst : J. Kitahara)

	Mol. %	
Alm	1.67	
And	8.79	
Gr	80.59	} 86.19 (Hydr-Gr 6.5%)
Hydro-Gr	5.60	
Py	2.93	
Sp	0.42	

The hydrogrossular is not formed from limestone by metamorphism (Gr only rich) and not skarn (And rich). The garnet is commonly generated from Ca–silicate rock (Gr + (And)), but is formed from Ca–Al–silicate rock rather than Ca–silicate rock by metasomatism.

X–ray Powder Photograph of Hydrogrossular

Debye–Scherrer photograph of the grossular was taken in a camera of 90.04 mm diameter, using CuK (1.5418) radiation. Exposure times were approximately 1.5 hours. The voltages used in X–ray diffraction are 30 to 35 kvp at 12–15 ma. The characteristic radiation is superposed on a background of general radiation, which contains all wavelengths above some minimum value, which is a function of the voltage across the x–ray tube. Wavelength of useful x–ray Cu target is $K_\alpha = 1/3$ ($K_{\alpha_2} + 2K_{\alpha_1}$) $= 1.5418$, and Ni filter

is used as element which highly absorb K_β.

The powder method is to record the x–ray diffraction on photographic film, using a powder camera as described above. A back–reflection record is available for determination by the method of Bradley and Jay. The distance is S = 12.4 (θ expressed in radian).

$$\theta = \frac{1}{4R} \cdot S \text{ radians}$$

$$\theta = \frac{180}{\pi} \cdot \frac{1}{4R} \cdot S \text{ degrees.}$$

S and R are normally measured in millimeters. ($\frac{180}{\pi} = 57.3$: the conversion factor from radians to degrees) It is evidently an easy matter to determine θ for each cone by measuring S after the film is opened out. The actual powder photograph of the specimen
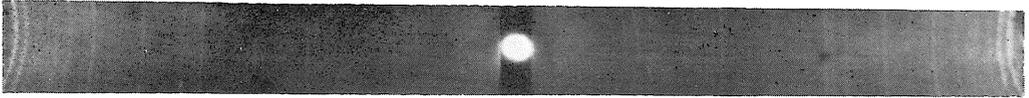

Fig. 3. X–ray powder photograph for hydrogrossular from Shinguchi level of Takase mine, Okayama pref. (Photo. : Kitahara)

is shown in Fig. 3. After the angles θ are found, Bragg's equation $\theta = \sin^{-1}(\frac{\lambda}{2} \cdot \frac{n}{d_{hkl}})$ can be used to calculate the interplaner spacings d of the sets of planes giving rise to arcs. The lattice planes of the sample are written the following.

420, 422, 431–510, 521, 433, 541, 444, 730, 800, 660–822, 851–754, 763–932,844, 10. 2.2, 10.4.2, 963–11.2.1, 875, 10.7.3–11.6.1, 10.8.2, 12.6.2, 13.4.1–11.8.1–11.7.4, 888, 996–10.7.7–13.5.2–14.1.1, 10.10.2, 13.6.3–14.3.3, 10.10.4–12.6.6–14.4.2, 12. 7.5–11.9.4

Some difficulty was also experienced from a given film to the several phases present. In the presence of a center of symmetry the structure factor may be expressed as

$$F_{hkl} = \sum_{1}^{N} f_n e^2 \pi i (hu_n + kv_n + lw_n),$$

$$|F|^2 = [f_1\cos2\tau (hu_1 + kv_1 + lw_1) + f_2\cos2\tau (hu_2 + kv_2 + lw_2) + \cdots]^2$$
$$+ [f_1\sin2\tau (hu_1 + kv_1 + lw_1) + f_2\sin2\tau (hu_2 + kv_2 + lw_2) + \cdots]^2,$$

where F_{hkl} is a structure factor, which depends on the atomic arrangement in a unit cell and

u_n, v_n, w_n are the coodinates of the n_{th} atom in the cell expressed as fractions of the cell edge lengths.

The intensity (1) of a diffracted beam can be written

$$I = \frac{p}{\sin^2\theta} \cdot \frac{1+\cos^2 2\theta}{2\cos\theta} \cdot \{\sum f\cos2\pi (h_m + k_n + l_p)\}^2,$$

where p is a multiplicity factor of the reflecting planes, that is, the number of planes in a crystal having identical interplanar spacings and $\frac{1+\cos^2 2\theta}{\sin^2\theta. \cos\theta}$ is the Lorentz polarization factor.

The measured spacing d_{hkl} value on large θ (example, 72°69') of the sample is computed as 0.80547 Å from the Bragg's equation. Since the $\sum h_i^2$ value of the lattice

plane is 216, the indices of the net planes (hkl) are denoted as 10.10.4, 12.6.6 and 14.4.2. The observed intensity of reflection on the lattice planes is very strong and the intensity on the planes calculated from the intensity equation of a diffracted beam as mentioned before is resolved as 8.8.

The relation between the interplanar spacing d and the indices hkl for isometric crystal is

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}.$$

The lattice parameter of the hydrogrossular is obtained as 11.867 Å by the equation in the form

$$a_0 = \frac{1}{2} \frac{\lambda}{\sqrt{\dfrac{\sin^2\theta}{h^2 + k^2 + l^2}}} \quad \text{or} \quad a_0 = d_{hkl} \sqrt{h^2 + k^2 + l^2},$$

where $\sqrt{\dfrac{\sin^2\theta}{h^2 + k^2 + l^2}} = 0.0422.$

Origin of Chromites

The chromite deposits have a general N 30°–60° E trend and dip 30° to 40° to the W or NW. Chromites occur in peridotite and other ultrabasic rocks. Some of the chromite is probably chromian spinel or aluminian spinel rather than chromite itself.

Thayer (1946) in a general investigation had concluded that there is a relationship between the composition of chromite and that of the containing rock, but a reverse relationship between the chromite composition and its country rock has been often discovered by Kitahara (1959).

The chromites from the mine are relatively rich in magnesia and alumina and are believed to have crystallized from Al–harzburgitic or troctolitic magma. The writer considers that the main chromite concentration is best explained by magmatic segregation and the ultramafic and chromite complex —chromitite is intruded into Palaeozoic sediments in the Takase mine deposits.

The main ultrabasic zone is characterized by the minerals enstatite and forsterite, an environment of high magnesia and low iron, alumina contents. It appears that this distinct chemical environment in which small amounts of alumina occur with chromium and magnesia is most favourable for the formation of chromite concentrations.

Bowen (1928) implied that chromium would readily enter the spinel structure to form chromite and thus explain the small amounts of accessory chromite common in ultrabasic rocks. This has been confirmed by the work of Wilde and Ress (1943) on the system $MgO-Al_2O_3-Cr_2O_3$. They showed that there is complete solid solution between $MgO.Cr_2O_3$ and $MgO.Al_2O_3$. The writer (1958) has been independently mentioned that any chromium present in magma will enter the spinel structure to form chromite. As chromium will not enter the olivine or enstatite structure in appreciable amounts, the crystallization of spinel allows chromium to enter the crystal phase during the cooling of the ultrabasic rocks. Chromium bearing spinels enclose olivine, but are themselves enclosed by enstatite grains. An explanation on the origin of the chromite concentrations must be based on the fact that the chromite is a primary mineral, formed during crystallization of the ultrabasic rocks.

Structure of Chromite

The structure of the spinel group was first investigated by Bragg (1915) and Nishikawa (1915) who showed that there are 32 oxygen ions and 24 cations in the unit cell ; 8 of the latter are in 4-fold coordination (the A position), and 16 in 6-fold coordination (the B position).

Barth and Posnjak (1932) reinterpreted the X-ray data and demonstrated that the spinels occur in two structural types. The two types are known as normal and inverse, and differ in their distribution of cations among the A and B positions. A further study variety of structure within the spinel group is demonstrated by the ability of the spinels to take up in solid solution the oxides Al_2O_3 and Fe_2O_3, the end-members being represented γ-Al_2O_3 and γ-Fe_2O_3. The γ-Fe_2O_3 and ulvöspinel (Fe_2TiO_4) have the spinel structure, the former having a cation deficiency while in the latter the replacement $2Fe^{+3} \rightleftharpoons Fe^{+2} + Ti^{+4}$ occurs. The writer (Kitahara, 1963) showed that the unbalanced chromite containing γ-Al_2O_3 and γ-Fe_2O_3 as solid solution is commonly described as the following structural formula,

$$(Fe^2_a, Mg^2_b, Mn^2_c, Al^3_u, Fe^3_{d-u} \square_{\frac{1}{2}d}) (Cr^3, Al^3_{p+v}, Fe^3_{q+\frac{3}{2}d-V})_2O_4,$$
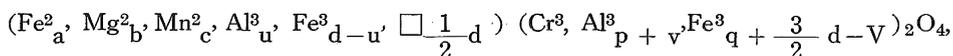
where symbol $\square$ is a lattice vacancy, $d = \frac{2}{3} v$ and $m+n = p+q+2d$.

A general formula giving the cell edge a_0 of members of the spinel group as a function of the ionic radii of the divalent ions r^{+2} and of the trivalent ions r^{+3} has been given by Mikheev (1955) as $a_0 = 5.778+0.95r^{+2}+2.79r^{+3}$. It has been mentioned by Kitahara (1963) that the difference between calculated and measured cell eges of chromitte is expressed as $\frac{0.206X + 0.059Y}{100}$, where X and Y are mol. percents of γ-Al_2O_3 and γ-Fe_2O_3 respectively.

Chemical Analyses of Chromites

The main chromite are massive, and the porphyritic ores are rarely found in the marginal positions of the ore deposits. The chromite ores are distinctly sheared, and has numerous cracks. The component is almost magnesiochromite with small quantities of gangue minerals.

The usual methods of chemical analysis are not particularly suitable for chromite and various schemes of analysis for determing FeO in chromite have been suggested by Konopicky and Caesar (1939), Ross, et al. (1954), Malhota and Prasada Rao (1956), Saradi (1958) and Bilgrami and Inganells (1960) ; a rapid method of analysis for chromite has been described in detail by Dinnin (1959), and modified analytical method has been mentioned by Kitahara (1962).

Two new chemical analyses of chromites from the levels of the Takase mine, Okayama pref. are given in Table 3 . The analyses were carried out on cleaned chromites obtained by the heavy solution separation. The writer has described that chromites from various localities show some characteristic features (Kitahara, 1962) ; thus chromites from the Tari district is charaterized by high Al_2O_3, MgO and low Cr_2O_3. The chromites from the

Table 3. Chemical analyses of chromites

	Wt. %		Mols			Atom. ratios		Atom. ratios when O=16	
	8	26	8	26		8	26	8	26
Cr_2O_3	42.73	41.87	281	275	Cr	562	550	4.07	4.03
Al_2O_3	25.25	24.13	248	236	Al	496	472	3.60	3.46
Fe_2O_3	3.02	4.42	19	28	Fe^3	38	56	0.28	0.41
TiO_2	0.17	0.37	2	5	Ti	2	5	0.01	0.04
FeO	13.45	14.29	187	199	Fe^2	187	199	1.36	1.46
MgO	14.77	14.16	369	354	Mg	369	354	2.68	2.59
MnO	0.14	0.19	2	3	Mn	2	3	0.01	0.02
CaO	0.08	0.03	1	1	Ca	1	1	0.01	0.01
H_2O_+	(−)	(−)			O	2207	2184		
SiO_2	0.36	0.47							
	99.97	99.93							

(−) : Weight increase

(Analyst : J. Kitahara)

	8	26	
(Cr, Al, Fe^3, Ti)	7.96	7.94	(structural formula)
(Fe^2, Mg, Mn, Ca)	4.06	4.08	
RO/R_2O_3	1.016	1.024	
Cr/Fe	2.48	2.16	
MgO/RO	1.94	1.74	

8 : East 1st level of Takase mine, Okayama pref.

26 : Shinguchi level of Takase mine, Okayama pref.

mine are richer in Cr_2O_3, and 2 – 4% poorer in MgO compared with the chromite components from the Hirose and Wakamatsu mines. The structural formulae of the Takase mine chromites calculated on the basis of 16 (O) are given in Table 3. The calculating method of the structural formulae was followed the procedure recommended by Stevens (1944), although correction was made for ulvöspinel (Fe_2TiO_4) by taking out from the molecular proportion 2FeO equivalent to TiO_2.

It will be seen from the structural formulae given in Table 3 that the summation of the trivalent group is lower than the ideal value of 8, and the summing of the bivalent group is higher than the ideal value of 4. The ratio R^{+2}/R^{+3} is usually fairly close to 1/2 in the natural members of the spinel and chromite series ; the ratios of the Takase mine chromite specimens are $\frac{1}{1.96}$ (No. 8) and $\frac{1}{1.95}$ (No.26). This variation may be due to analytical error or defect formula.

Kitahara (1958) has discussed in detail the various factors that might influence the chemical composition of chromites. The Tari environ chromites are mainly chromian spinel, but the Takase mine chromites are aluminian chromite. The Takase mine chromites are mostly found in harzburgite (saxonite). The chromites are rich in Al_2O_3, and this may be due to a general high Al_2O_3 content of the host rock containing aluminian enstatite.

There is a continuous replacement series from spinel to chromite. Small amounts of

Ti may also enter the spinel structure. The Al ion may be replaced by Cr, grading continuously to magnesiochromite. Although the ideal composition of the end–member of magnesiochromite is $MgCr_2O_4$, all natural magnesiochromites contain a considerable amount of Fe^{+2} replacing Mg, and there is a continuous variation from $MgCr_2O_4$ to $FeCr_2O_4$. The analyses of the magnesiochromite from the mine show that the variation in Mg/Fe ratios are 2.68/1.36 (No. 8) and 2.59/1.46 (No. 26). It is considerable replacement of Cr by Al and some amounts of Fe^{+3} may also replace Cr.

The chemical analyses of the Takase mine chromites expressed in the form of end–member formula are given in Table 4.

Table 4. End member formula % of Takase mine chromites

	No. 8	No. 26
Spinel ($MgO. Al_2O_3$)	45.2	43.7
Magnesiochromite ($MgO. Cr_2O_3$)	22.1	21.7
Ferrochromite ($FeO. Cr_2O_3$)	29.2	29.3
Magnetite ($FeO. Fe_2O_3$)	3.5	5.3

The end–member formula percentage is obtained by the formula given by Stevens (1944). It will be seen from Table 5 that the mine chromites are aluminian chromite ((Mg, Fe). Cr_2O_3 high) rather than chromian spinel ($MgO. Al_2O_3$ high) as described before.

Physical Properties

The chromites are constituted in the massive type. The minerals are black color in hand specimen and give a brown streak.
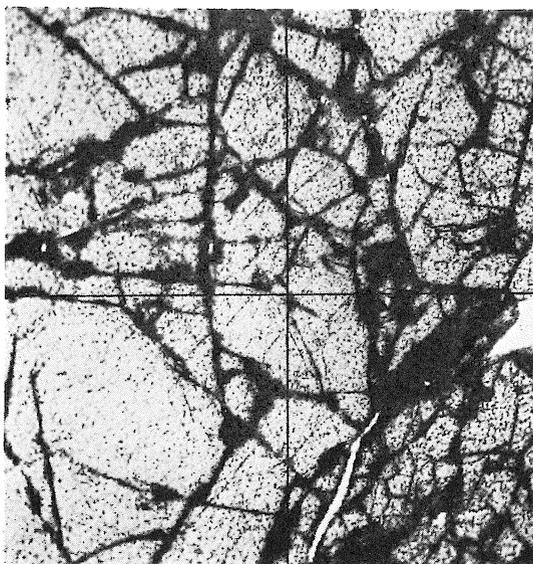

Fig. 4. Photomicrograph of chromite
(No. 8).   Open nicol, x 60
East 1st level of Takase mine,
Okayama pref.

The physical constants of the two chromites are given in the following Table 5.

Table 5.

Sample	d_4	n	a_0	mol. wt
No. 8	4.23	1.92 (calc.)	8.218	177.41 (calc.)
No. 26	4.25	1.93 (calc.)	8.227	179.25 (calc.)

The polished No. 8 sample (Fig. 4) under polarized light exhibits orange color and has cross cutting lines showing brownish black. Chlorite with diopside relics is seen. The polished No. 26 specimen (Fig. 5) shows orange or light red color and contains cross–cutting lines and fissures.
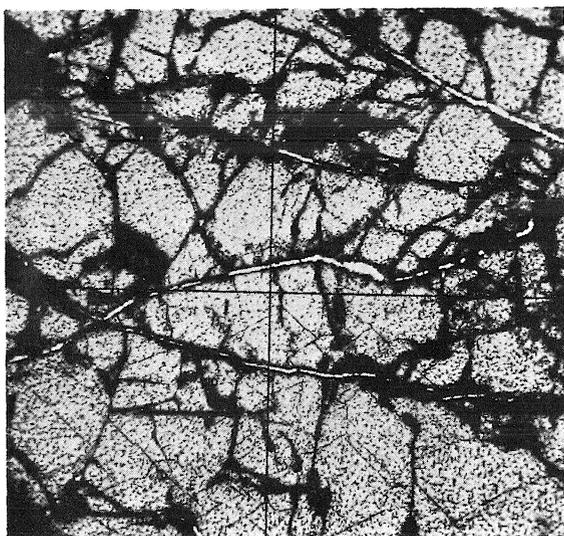

Fig. 5. Photomicrograph of chromite (No. 26). Open nicol, x 60 Shinguchi level of Takase mine, Okayama pref.

X–ray Powder Data for Chromites

X–ray photographs of chromite samples (No. 8, No. 26) was taken in a camera of 90.04 mm diameter, using CuK radiation. The voltages used are 35 kvp at 15 ma , and the exposure times were nearly 1.2 hours. The record of the X–ray diffraction on photogrphic film was attempted by the method of Bradley and Jay. The x–ray powder lines for the samples were indexed and are given in Table 6.

The lengths of the edge of the unit cube (lattice perameters) a_0 for the chromites calculated as d_{844} from the equation of X–ray spectroscopy are as given in a paragraph of the physical properties.

Table 6. X–ray powder data of specimens

hkl	No. 8			No. 26		
	d (calc.)	d (obs.)	I.	d (calc.)	d (obs.)	I.
220	2.902	2.875	w	2.905	2.89	w
311	2.474	2.439	s	2.474	2.45	s
400	2.052	2.027	m	2.054	2.04	m
511 333	1.579	1.565	m	1.581	1.58	m
440	1.451	1.427	s	1.453	1.44	s
533	1.255	1.250	f			
622	1.238	1.230	vw	1.240	1.235	vw
444	1.183	1.186	vvw	1.185	1.188	vw
642	1.098	1.097	f			
731 553	1.068	1.062	wm	1.071	1.067	w
800	1.026	1.023	vw	1.029	1.031	vvw
662	0.941	0.940	vw	0.944	0.941	vw
931	0.861	0.859	w	0.863	0.862	w
844	0.838	0.839	m	0.840	0.840	m

Structure (Hl_1 type) : 8(Mg, Fe, Mn) in (a) O, O, O ; 16(Cr, Al, Fe) in (d) $5/8, 5/\bar{8}, 5/8$; 320 in (e) x, x. x (x=3/8)

Production and Use

The Takase chromite mining was started in 1923 and has continued since. The yearly production in 1960 has been 17,340 tons.

Chromite generated by magmatic segregations may form important economic deposits as a source of chromium. The chromite mines located in the vicinity of common boun-daries of Shimane, Tottori, Okayama and Hiroshima prefectures are at present Japan's largest producer of chromite ore.

The chromites in the Takase mine are comparativaly higher than them in the Tari environs in Cr_2O_3 content and also is rich in MgO content, so the chromites in the mine are used as industrial raw materials than fire–proof materials.

Summary

A new hydrogrossular generated in aluminum pyroxenite which have undergone metasomatic metamorphism involving the addition of alumina and lime and the subtraction of magnesia is found from the Shinguchi level of the Takase mine, Okayama pref. It is considered that the aluminum pyroxenite originated from pyroxenite pocket in peridotite mantle was derived as xenolith in ultrabasic rock – harzburgite. Optical, chemical and powder x–ray data of the hydrogrossular are given and the formula is described.

Two kind of chromites was investigated by chemical and x–ray powder photograph method. These data are given in table. The chromites is said as aluminian chromite rather than chromian spinel. The origin of the chromites are mentioned in the paper.

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