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Yamaguchi, Masaru
Faculty of Sciences, Kyushu University

<https://doi.org/10.5109/1526111>

出版情報 : 九州大学理学部紀要 : Series D, Geology. 10 (2), pp.233-245, 1961-03-10. Faculty of Science, Kyushu University

バージョン :

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Chrome-diopsides in the Horoman and Higashi-Akaishi Peridotites, Japan*

By

Masaru YAMAGUCHI

Abstract

Green clino-pyroxene in the Horoman peridotite, Hokkaido, has been identified as chrome-diopside by optical, chemical, X-ray and infra-red absorption studies. For comparison, additional measurement was made on vein chrome-diopside in the dunite from Higashi-Akaishi, Shikoku. Cell dimensions for the Horoman chrome-diopside are $a=9.720 \text{ \AA}$, $b=8.891 \text{ \AA}$, $c=5.252 \text{ \AA}$, $\beta=73^\circ 51'$, cell volume= 435.9 \AA^3 and for the Higashi-Akaishi chrome-diopside are $a=9.734 \text{ \AA}$, $b=8.915 \text{ \AA}$, $c=5.274 \text{ \AA}$, $\beta=74^\circ 04'$, cell volume= 440.1 \AA^3 . High alumina content and small cell volume of the Horoman chrome-diopside are worthy of notice in that there is a possibility of the presence of a small amount of OH ions substituting for O ions in the structure of chrome-diopside.

Introduction

In the course of studies of ultramafic rocks and the inclusions in basaltic rocks, the writer has identified the green clino-pyroxene in the Horoman peridotite, Hokkaido, as a chrome-diopside with comparatively high alumina and chrome content.

Many chemical data on chromian diopsides from various localities in the world have been given by ROSS and others (1954), and those on Japanese chrome-diopsides, though very scanty, are also at hand; as crystals occurring in chromite vein running through the dunite from Higashi-Akaishi, Shikoku (HARADA, 1943), as a constituent in olivine rich inclusion in the basalt from Ichinome-gata (ROSS and others, 1954) and as phenocryst in the basalt from Sano (KUNO, 1957). In this paper new data on the minerals of the Horoman peridotite and the Higashi-Akaishi dunite are given with the hope to give more accurate information of chrome-diopsides. Some petrographic and crystal-chemical significances of this mineral are also discussed.

Mode of Occurrence

1. Horoman peridotite

The Horoman peridotite has been described in detail by IGI (1953). It occurs along the migmatite zone of the Hidaka metamorphic complex, Hokkaido. The mass is composed of various banded facies of dunite, peridotite, plagioclase-

* Received September 24, 1960.

bearing periodotite in contact each other with sharp boundaries or gradual transition. Flow banding as revealed by the directional arrangement of each constituent minerals indicates that a large dome structure is developed in the central part of the mass. The periodotite in question is greyish green, coarse grained, with many rock cleavages. The mode of the rock is given in Table 1. Spots of green chrome-diopsides and dull bronzites are unevenly scattered among abundant olivine grains, all of these minerals being subparallel to the rock cleavages.

Table 1. Mode of peridotite from Horoman, Hokkaido.

Olivine	74%
Serpentine	10%
Bronzite+Picotite	9%
Chrome-diopside	7%

Under the microscope, olivine grains, both fine and coarse are arranged to show banded texture, the coarse grains also present in the lenticular form among the fine grained matrix.

Large grains of olivine in particular are strongly strained to show wavy extinction, and not a few individual large olivine crystals have banded, the slip planes of each band being nearly normal to the *a* axis of the original crystals. All of these features exhibited in the olivines are regarded as of deformational origin, and the fine olivines are to be derived from the large ones through the process of shearing.

Bronzite is of the Bushveld type; namely, subhedral large grains with a fine exsolution lamellae of diopside.

Anhedral pale bluish-green chrome-diopside occurs in the interstices between olivine grains.

Picotite is red brown interstitial mineral, often separated to smaller fragments.

Small mosaic grains of plagioclase associated with irregular small grains of picotite and olivine also occur in patches or in lenticular forms among the large olivine grains.

2. Higashi-Akaishi dunite

The Higashi-Akaishi dunite (5 km in length) is one of the largest lenticular masses of the several ultramafic intrusions which occur along the spotted schist zone of the Sambagawa crystalline schist. Detailed study by HIDE and others (1956) of the geologic structure of the area revealed that the dunite was intruded syntectonically into the anticlinal core of the recumbent fold of spotted schists (biotite schist and chlorite schist with albite spots), the crest of the fold being shoved about 4 km toward the south.

The dunite mass is composed mainly of massive dunite, often schistose in places and serpentized marginally. Thin pyroxenite layers occur in some places alternating with dunite, where pyroxene-garnet rocks ("eclogites") in the

forms of lenses or pools of various scales are enclosed in dunites or in pyroxenites.

Chromite veins composed of coarse aggregate of chrome-diopside, chromite, kaemmererite and calcite occur in several places in the dunite.

Separation of Samples

The samples were crushed, silk screened (150-200 mesh) and passed through the Frantz isodynamic separator. Serpentine minerals present in small amount were removed with methylene iodide. The residue was treated for several minutes with warm dilute hydrochloric acid, washed with alcohol and hot water, and dried. Concentrates obtained are of pure chrome-diopside of beautiful emerald-green in colour. Thin exsolution lamellae (probably bronzite), which are hardly recognized in thin section, are very rarely observed in the separated samples both from Horoman and from Higashi-Akaishi. Several rock samples were omitted in the separation, as they contain chrome-diopsides with fairly large amount of exsolution lamellae recognizable easily in thin section.

Chemical Compositions and Optical Properties

Table 2 gives chemical compositions and optical properties of the chrome-diopsides newly investigated, together with some existing data on such kind of minerals.

Table 2. Chemical compositions and optical properties of chrome-diopsides.

Wt. per cent	1	2	3	4	5
SiO ₂	50.97	51.41	52.12	53.32	53.42
TiO ₂	0.49	0.33	0.80	n.d.	0.12
Al ₂ O ₃	4.86	4.69	4.08	3.70	0.68
Fe ₂ O ₃	0.92	0.69	0.82	1.15	1.36
Cr ₂ O ₃	1.47	1.03	1.44	1.06	0.56
FeO	1.41	2.64	2.24	0.23	2.01
MnO	0.10	0.11	0.09	n.d.	0.07
MgO	17.89	16.32	16.48	15.40	15.99
CaO	21.28	21.63	19.34	25.00	25.75
Na ₂ O	0.83	0.72	2.14	n.d.	0.12
K ₂ O	tr	0.04	0.08	n.d.	0.06
H ₂ O(+)	0.23	0.11	n.d.	—	0.16
H ₂ O(—)	0.07	n.d.	n.d.	—	0.01
P ₂ O ₅	n.d.	n.d.	n.d.	n.d.	0.03
NiO	n.d.	0.040	0.041	0.14	0.016
V ₂ O ₅	n.d.	0.05	0.03	n.d.	0.004
Total	100.52	99.81	99.70	100.00	100.36
Anal.	T. Katsura	M. D. Foster	M. D. Foster	Calculated	H. Haramura

Table 2 (Continued)

	1	2	3	4	5
α	1.678-1.684	n.d.	n.d.	1.671-1.674	1.672-1.676
β	1.687-1.693 (β mean 1.690)	n.d.	n.d.	1.681-1.685	1.679-1.683
γ	1.697-1.703	n.d.	n.d.	1.704-1.706	1.699-1.703
+2V ^	58°-54° (avg 56°)	n.d.	n.d.	58°-56° (avg 57°)	58°-54° (avg 56°)
C Z	38°(avg)	n.d.	n.d.	40°(avg)	39°(avg)

1. Chrome-diopside of the Horoman peridotite, Hokkaido, Japan.
Collected by Takeo Bamba, No. 86 (Yamaguchi, this paper).
2. Chrome-diopside from inclusions in basalt, Ichinome-gata, Akita Prefecture, Japan (Ross, Foster, Myers, 1954).
3. Chrome-diopside from inclusions in basalt, Salt Lake Crater, Oahu, Hawaiian Islands (Ross, Foster, Myers, 1954).
4. Chrome-diopside of chromite-vein in dunite, pit No. 5 (dead), chromite mine of the Meiji Mining Company, Higashi-Akaishi, Shikoku (Harada, 1943). Recalculated free of serpentine impurities, to 100 per cent.
5. Chromian diopside in basalt from Sano, Yamanashi Prefecture, Japan (Kuno, 1957).

Crystal Chemistry

1. X-ray examination

Fine powders of the diopside samples mixed with powdered silicon as an internal standard were mounted in a slightly depressed circular area on a glass slide and measured with Norelco, Geigerflex and Shimadzu X-ray diffractometers. Peaks for 2θ in the range of angles from 96° to 19° were measured several times under the following experimental conditions: copper radiation with a nickel filter at 35 kV and 10-15 mA, scanning speed $\frac{1}{2}^\circ$ per minute, chart speed 10 mm per minute, time constant 4-5, slit 1-1-0.2 mm.

Trials were made for indexing on reflection planes in comparison with the known data. The observed and calculated spacings for each plane are in close agreement with each other as shown in Table 3.

The unit cell dimensions a , b and c , and β were determined using diffraction angles 2θ from the following reflection planes: $\{750\}$, $\{260\}$, $\{53\bar{1}\}$, $\{060\}$, $\{350\}$, $\{600\}$, $\{531\}$, $\{150\}$, $\{510\}$, $\{041\}$, $\{331\}$, $\{330\}$, $\{31\bar{1}\}$, $\{131\}$, $\{311\}$. The results are shown in Table 4, which also lists unit cell volumes, and specific gravities observed and calculated. Specific gravities were on the one hand determined with a pycnometer filled with carbon tetrachloride and a rapid balance, and on the other hand calculated from the unit cell volume and molecular weight, the latter having been calculated from the general chemical formula of pyroxene corresponding to the chemical composition of the chrome-diopside. The Avogadro's number used is $N=6.02486 \times 10^{23}$. It is shown that the specific gravities calculated are in fairly close agreement with the observed specific gravities.

Table 3. Reflection angles and observed and calculated spacings of chrome-diopside in peridotite, Horoman, Hokkaido.

 $a=9.7196\text{\AA}$, $b=8.8908\text{\AA}$, $c=5.2515\text{\AA}$, $\beta=73^\circ 51'$

 (Cu $K\alpha$, $\lambda=1.5418\text{\AA}$, Cu $K\alpha_1$, $\lambda=1.54050\text{\AA}$)

C_{22}^6 h k l	2θ Observed	Relative Intensity	d (\AA) Observed	d (\AA) Calculated	$d_{obs.} - d_{calc.}$
1 1 0	n.o.			6.4384	
2 0 0	n.o.			4.6680	
0 2 0	19.98 α	10	4.4439	4.4454	-0.0015
1 1 1	n.o.			4.4018	
. . .	24.98 α	4	3.5645		
0 2 1	26.71 α	9	3.3346	3.3351	-0.0005
2 2 0	27.71 α	70	3.2191	3.2192	-0.0001
2 2 1	29.92 α	100	2.9862	2.9858	+0.0004
3 1 0	30.43 α	65	2.9374	2.9373	+0.0001
3 1 1	30.94 α	45	2.8900	2.8895	+0.0005
1 3 0	n.o.			2.8247	
1 3 1	35.08 α	30	2.5579	2.5581	-0.0002
2 0 2	n.o.			2.5331	
1 1 2	n.o.			2.5182	
0 0 2	35.59 α	30	2.5224	2.5222	+0.0002
2 2 $\bar{1}$	35.83 α	45	2.5040	2.5045	-0.0005
1 3 $\bar{1}$	37.75 α_1	3	2.3807	2.3807	0.0000
4 0 0	n.o.			2.3340	
3 1 $\bar{1}$	39.31 \downarrow	20	2.2900	2.2903	-0.0003
3 1 2	40.54	2	2.2233	2.2237	-0.0004
0 4 0	n.o.			2.2227	
1 1 $\bar{2}$	40.82	14	2.2087	2.2089	-0.0002
2 2 2	n.o.			2.2009	
0 2 2	41.11	10	2.1938	2.1937	+0.0001
3 3 0	42.06	20	2.1464	2.1461	+0.0003
3 3 1	42.45	38	2.1276	2.1273	+0.0003
4 2 1	42.98	16	2.1026	2.1025	+0.0001
4 2 0	43.77	3	2.0664	2.0664	0.0000
0 4 1	44.51	22	2.0338	2.0340	-0.0002
4 0 2	44.93	12	2.0157	2.0151	+0.0006
2 4 0	n.o.			2.0068	
2 0 $\bar{2}$	n.o.			1.9986	
1 3 2	46.15	5	1.9652	1.9653	-0.0001
2 4 1	n.o.			1.9463	
5 1 1	n.o.			1.8908	
3 3 $\bar{1}$	n.o.			1.8510	
4 2 2	n.o.			1.8353	
5 1 0	49.89	15	1.8270	1.8273	-0.0003
2 2 $\bar{2}$	n.o.			1.8229	
3 3 2	n.o.			1.8154	

Table 3 (Continued)

C_{2h}^6 h k l	2θ Observed	Relative Intensity	d (Å) Observed	d (Å) Calculated	$d_{obs.} - d_{calc.}$
1 3 $\bar{2}$	n.o.			1.8073	
2 4 $\bar{1}$	n.o.			1.7925	
4 2 $\bar{1}$	n.o.			1.7658	
1 5 0	52.33	20	1.7468	1.7468	0.0000
1 1 3	n.o.			1.7090	
3 1 $\bar{2}$	n.o.			1.7050	
1 5 1	n.o.			1.6778	
0 4 2	55.02	5	1.6676	1.6676	0.0000
3 1 3	n.o.			1.6591	
4 4 1	n.o.			1.6264	
1 5 $\bar{1}$	n.o.			1.6247	
2 2 3	n.o.			1.6237	
5 3 1	56.77	25	1.6202	1.6203	-0.0001
4 4 0	57.18	10	1.6096	1.6096	0.0000
5 1 $\bar{1}$	n.o.			1.5854	
5 3 0	58.35	4	1.5801	1.5798	+0.0003
0 2 3	n.o.			1.5727	
6 0 0	59.34	7	1.5560	1.5560	0.0000
3 5 0	59.87	8	1.5436	1.5439	-0.0003
6 0 2	60.55	6	1.5278	1.5277	+0.0001
4 0 $\bar{2}$	61.08	5	1.5158	1.5157	+0.0001
4 4 2	n.o.			1.4929	
0 6 0	62.64	10	1.4818	1.4818	0.0000
5 1 3	n.o.			1.4494	
5 3 $\bar{1}$	65.93	25	1.4156	1.4156	0.0000
2 6 0	66.10	20	1.4123	1.4123	0.0000
. . .	66.42	8	1.4063		
. . .	71.49	8	1.3186		
0 6 2	74.15	5	1.2777	1.2776	+0.0001
8 0 0	82.63	2	1.1667	1.1670	-0.0003
5 1 $\bar{3}$	present			1.0974	
6 6 0	n.o.			1.0731	
. . .	91.90	10	1.0717		
7 5 0	92.42	15	1.0670	1.0669	+0.0001
8 4 0	n.o.			1.0332	

n.o.=not observed.

Table 4. Cell dimensions and observed and calculated specific gravities of chrome-diopsides in ultramafic rocks, Japan.

	1	4
a	9.720 Å	9.734 Å
b	8.891 Å	8.915 Å
c	5.252 Å	5.274 Å
β	73°51'	74°04'
Unit Cell Volume	435.9 Å ³	440.1 Å ³
SG _{obs.}	3.309	3.268
SG _{calc.}	3.323 (3.311)*	3.280

1. Chrome-diopside of Horoman peridotite, Hokkaido, Japan (Sample No. 86).

4. Chrome-diopside of chromite-vein in dunite from pit No. 5 (dead), chromite mine of the Meiji Mining Company, Higashi-Akaishi, Shikoku, Japan (Sample No. AK46).

* Calculated from the recalculated ionic content (Table 7) on the basis of 6 (O+OH) ions.

2. Infra-red absorption

Infra-red absorptions of chrome-diopsides were measured with the Hitachi double-beam infra-red spectrometer. Some preliminary tests were made by the Kbr disk method on powdered samples of chrome-diopside, augite, olivine and spinel. Broad absorption bands were observed in the region of 3μ for chrome-diopside, while no absorption occurs in the same region for spinel, augite (in nodule) and most olivines. According to KELLER and PICKETT (1949), LYON and KINSEY (1942), MARA and SUTHERLAND (1953) and many others, absorption bands in the 3μ region indicate the presence of OH ions in crystals.

In order to ascertain the existence of OH ions in diopsides, finely powdered samples of two skarn diopsides and two chrome-diopsides in question were heated at 110°C for about 24 hours, and that the Horoman chrome-diopside was again heated at 1000°C for about 4 hours. To these heated samples, few drops of hexachlorobutadiene ($\text{CCl}_2=\text{CCl}-\text{CCl}=\text{CCl}_2$) were added and this mixture (paste) was placed between NaCl disks and measured by single beam. The results being shown in Fig. 1. In the case of samples heated at 110°C, broad absorption band still appears in the region of 2.9μ . It is noteworthy, on examining the absorption in more detail, that both Horoman and Higashi-Akaishi chrome-diopsides have at least two absorption peaks at about 2.95μ and 2.86μ , though the resolutions are not good, and that upon heating them at 1000°C, the 2.95μ absorption has become weaker, while the 2.86μ absorption stronger.

The Horoman chrome-diopside heated at 1000°C 4 hours has also been measured by the X-ray diffractometer in the same way as already mentioned, which the diffraction pattern obtained has been exactly the same with the unheated sample, indicating no recognizable change in the structure between heated and unheated samples so far as the X-ray is concerned.

Although WARREN and BISCOE (1931) have expressed the general formula for the pyroxenes as $X_m Y_{2-m} (Si, Al)_2 (O, OH, F)_6$, most investigators have not recognized of the presence of OH ions in the pyroxenes because no criteria had been found to prove the presence of OH ions. But, the result mentioned above may indicate that chrome-diopside contains at least two types of OH in the crystal: the one is probably the water impurities or the absorbed water which can be removed by strong heating, the other is OH incorporated in the pyroxene structure which can not easily be removed. To confirm the problem, further

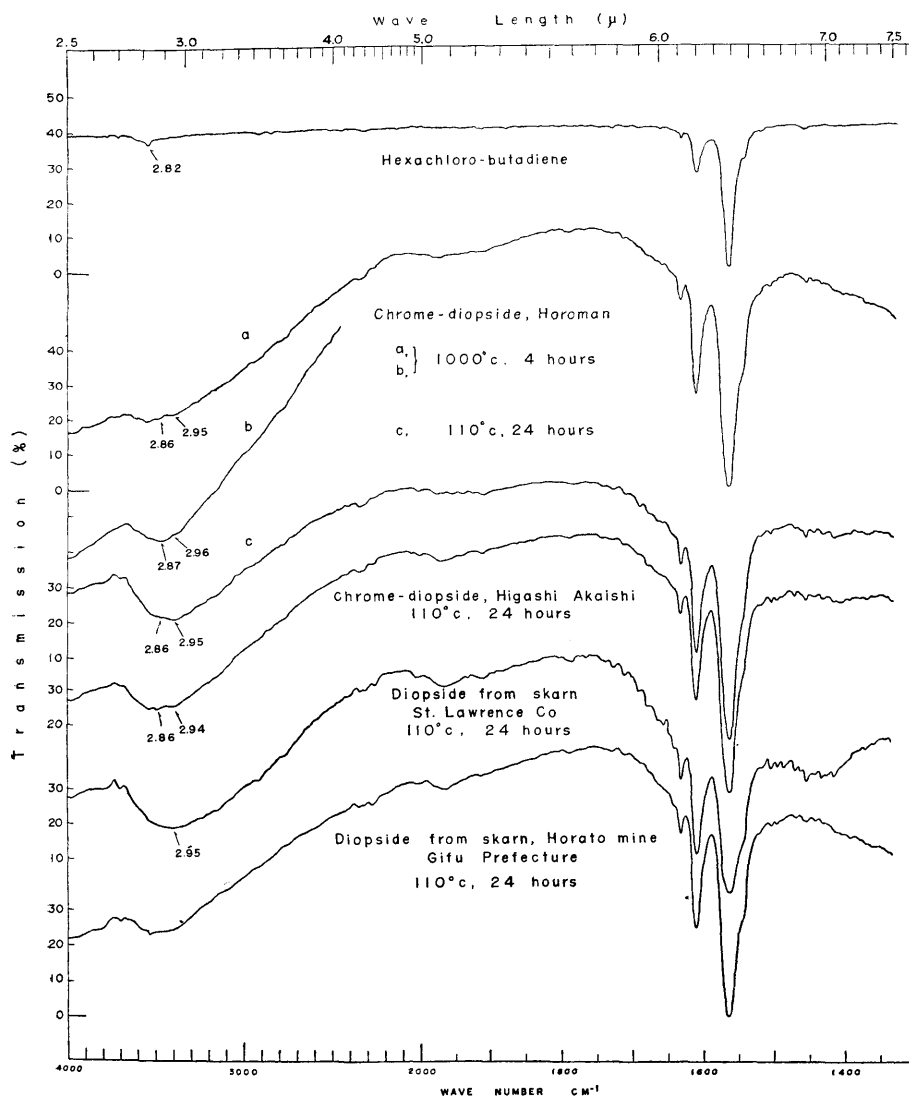


Fig. 1. Infrared absorption spectrograms of chrome-diopside and diopside. The difference of absorption between a and b is due to the difference in the amount of sample used for the measurements.

measurement on a single crystal is in preparation.

3. Ionic contents in the unit cell

The chemical analysis of the Horoman chrome-diopside has been recalculated into the standard formula (Table 5): as described by HESS (1949), cations are allotted for several groups in which the balance between charges on cations and cation basis is maintained. In this calculation Si ions are almost used up for the allotment for Ca, Mg and Fe^{+2} (+Mn) ions, and the other minor ions such as Na, Fe^{+3} and Cr in 8 and 6 fold coordinations, which should be combined with Al in 4 fold coordination replacing Si ions, cannot balance in charge with the cation basis (Table 5a). On the contrary, when Na, and other cations with 3 valency are calculated so as to balance in charge with Si ions, Mg, Fe and Ca ions cannot balance in charge with Al ions in the tetrahedral positions (Table 5b).

As the sample in question is pure and the unbalance of charges on these cations on the basis of 6 oxygens exceed the error of chemical analysis, the contradictory result of the calculation just described may be due to the combined effect of the large amounts of Al in 4 fold coordination replacing Si in the tetrahedral positions and the amount of cations of +3 charges.

For the requirement of electrical stability which means the sum of positive and negative charges on the ions balances, small amounts of OH ion substituting O ions should be introduced into the pyroxene structure. The possibility of this substitution has already been pointed out in the section of "Infra-red absorption."

On the assumption that the Horoman chrome-diopside contains small amounts of OH ion in the structure, the chemical formula was so recalculated as to give 6 anions including OH ions. Thus, the OH ions equal in amount to the deficiency of positive charges on the basis of 6 anions were introduced and allotted to cation groups in the ratio of available cations so as to balance their charges, the result being shown in Table 6. Again, satisfactory results were obtained for recalculated chemical composition and ionic contents (Table 7), both of which lies within the error of the original analysis. The recalculated specific gravity (3.311) closely accord with the observed specific gravity (3.309)*.

Petrographic Significance

As previously described, the Horoman chrome-diopside is noted by its high Cr_2O_3 and Al_2O_3 contents. As far as the literature at hand is concerned, the highest content ever described ($\text{Cr}_2\text{O}_3=2.43$, $\text{Al}_2\text{O}_3=6.58$ per cent) is known in chrome-diopsides which occur as ultramafic inclusions in basaltic rocks (ROSS et al., 1954, p. 716, Table 15, No. 9 and p. 709, Table 6, No. 3), while these oxides in the chrome-diopsides of most dunites are lower in amount than those of the Horoman peridotite.

* Recalculation was not made for the Higashi-Akaishi chrome-diopside, for its analysis is not superior.

Tabl 5. Calculation of the ionic contents in the unit cell of the Horoman chrome-diopside on the basis of 6 oxygens.

Number of atoms		a									b																									
Si ⁺⁺	1.847	2.015	26	1552	74	189	9	23	23	26	44	49	26	46	26	44	1552	74	100	5	4	49														
Al ⁺⁺	0.208																						.168,	.040												
Ti ⁺⁺	0.013																																			
Fe ⁺⁺	0.025																																			
Cr ⁺⁺	0.042	2.015	13					23	13			12	13	23	13	22					12															
Fe ⁺⁺	0.043																					37	189	9	23	13	22	776	776	37	189	9	776	37	189	9
Mn ⁺⁺	0.003																																			
Mg ⁺⁺	0.965																																			
Ca ⁺⁺	0.826	2.015	13	776	37								13	23	13	22	776	776	37		189	9														
Na ⁺	0.058																						23	13	22	776	776	37	189	9						
K ⁺	tr																																			
O ⁻²	6.000																																			
W		Ca	Ca	Ca			Na	Na	Na	(Cr Fe ⁺⁺)	Ca	Na	Na	Na	Ca	Ca																				
X, Y		Ti	Mg	Fe ⁺⁺	Mg	Fe ⁺⁺	Cr	Fe ⁺⁺	Al	(Cr Fe ⁺⁺)	Ti	Cr	Fe ⁺⁺	Al	Mg	Fe ⁺⁺	Mg	Fe ⁺⁺	Mg	Fe ⁺⁺	(Cr Fe ⁺⁺)															
Z		2Al	2Si	2Si	Si	Si	SiAl	2Al	2Al	Al	2Al	2Si	2Si	2Si	2Si	2Si	2Si	SiAl	SiAl	Al	Al															
							*	*	*									*	*																	

* Charges are not balanced. The deficiency of the positive charges in total to the negative charges on the basis of 6 oxygens is 0.093.

Table 6. Calculation of the ionic contents in the unit cell of the Horoman chrome-diopside on the basis of 6 oxygens. The deficiency of the positive charges to the basis of 6 oxygens are balanced by substituting OH ions for O ions.

Number of atoms											
Si ⁺⁴	1.847	} 2.015	23	13	22	33	2	1486	70	189	9
Al ⁺³	0.208		26	23	22	33	2				49
	{ .168				22						18
	{ .040										
Ti ⁺⁴	0.013	} 2.015	13								
Fe ⁺³	0.025			13							12
Cr ⁺³	0.042			23							19
Fe ⁺²	0.043										
Mn ⁺²	0.003						2		35		9
Mg ⁺²	0.965					33		743		189	
Ca ⁺²	0.826		13			33	2	743	35		
Na ⁺¹	0.058			23	13	22					
K ⁺¹	tr										
O ⁻²	6.000										
W		Ca	Na	Na	Na	Ca	Ca	Ca	Ca		
X, Y		Ti	Cr	Fe ⁺³	Al ⁺³	Mg	Fe ⁺²	Mg	Fe ⁺²	Mg	Fe ⁺²
Z		2Al	SiAl	SiAl	SiAl	SiAl	SiAl	2Si	2Si	Si	Si
OH		—	OH	OH	OH	OH	OH	—	—	—	—
(OH ⁻¹ 0.093)			23	13	22	33	2				

As discussed by KUNO (1957) there is a general tendency that Cr₂O₃ is enriched in the early formed clinopyroxene crystallized out from basalt magma. Al₂O₃ seems also to have the same general tendency. The effect on cell dimensions of the entrance of Al and Cr ions in the pyroxene structure has not yet been clearly known (BROWN, 1960). But the entrance of Al and Cr ions seems to reduce the cell volume of plutonic pyroxene (YAMAGUCHI, in preparation). The Horoman and Higashi-Akaishi chrome-diopsides, which have very small cell volumes offer good examples of the above conclusion.

It is suggested that the Horoman chrome-diopside seem to have a small amount of OH ions incorporated in the pyroxene structure. The higher Cr₂O₃ and Al₂O₃ content, the smaller cell volume, the presence of OH ions in the structure and the occurrence of the mineral in strongly deformed peridotite, all these features of the Horoman chrome-diopside may be preferable to consider that the mineral has crystallized under wet condition of high pressure.

Table 7. Recalculated chemical composition of the Horoman chrome-diopside and the ionic contents in the unit cell on the basis of 6 (O+OH) ions.

Wt per cent		Number of atoms												
SiO ₂	50.67	Si ⁺⁴ 1.833	} 2.000		23	13	21	33	2	1466	78	192	5	
Al ₂ O ₃	4.84	Al ⁺³ 0.206 { .167		26	23	13	21	33	2					49
		.039					21							18
TiO ₂	0.48	Ti ⁺⁴ 0.013		13										
Fe ₂ O ₃	0.91	Fe ⁺³ 0.025	} 2.000			13								12
Cr ₂ O ₃	1.46	Cr ⁺³ 0.042			23									19
FeO	1.41	Fe ⁺² 0.043												
MnO	0.10	Mn ⁺² 0.003							2		39		5	
MgO	17.77	Mg ⁺² 0.958	} 6.000					33		733		192		
CaO	21.16	Ca ⁺² 0.820		13				33	2	733	39			
Na ₂ O	0.82	Na ⁺¹ 0.057			23	13	21							
K ₂ O	tr	K ⁺¹ tr												
H ₂ O	0.38	OH ⁻¹ 0.092	} 6.000		23	13	21	33	2					
Total	100.00	O ⁻² 5.908		78	115	65	105	165	10	4398	234	576	15	147
W				Ca	Na	Na	Na	Ca	Ca	Ca	Ca			
X, Y				Ti	Cr	Fe ⁺³	Al	Mg	Fe ⁺²	Mg	Fe	Mg	Fe	(Cr Fe ⁺³)
Z				2Al	SiAl	SiAl	SiAl	SiAl	SiAl	2Si	2Si	Si	Si	Al
OH				—	OH	OH	OH	OH	OH	—	—	—	—	—
O				60	50	50	50	50	50	60	60	30	30	30

Acknowledgement

I wish to express my sincere thanks to Professor Tôru TOMITA, of our Department, for his generosity of providing a sample of the Horoman peridotite collected by Dr. Takeo BAMBA, reading the manuscript with constructive criticism and correcting my English writing. My hearty thanks are due to Mr. Tsunehiko ÔSHIMA for offering some other samples of the Horoman peridotite, to Dr. Takashi KATSURA of the Tokyo Institute of Technology for his kind help with chemical analysis, to Professor Hisashi KUNO of Tokyo University for giving pyroxene samples studied by him which made possible to compare his result with the present study. Grateful thanks are due to Dr. Yoshiya KANDA of the Department of Chemistry, Kyushu University for taking the infra-red absorption spectrum.

This study was partly financed by the Grant in Aid for Scientific Researches from the Ministry of Education, Japan.

References

- BROWN, G. M. (1960): The effect of ion substitution on the unit cell dimensions of the common clinopyroxenes. *Am. Mineral.*, **45**, 15-38.
- HARADA, Zyumpei (1943): On the chrome minerals of Japan (II) (in Japanese). *Jour. Jap. Assoc. Mineral. Petrol. Econ. Geol.*, **29**, (1), 12-23.
- HESS, H. H. (1949): Chemical composition and optical properties of common clinopyroxenes, I. *Am. Mineral.*, **34**, 621-666.
- HIDE, Kei, YOSHINO, Gensei, and KOJIMA, George (1956): Preliminary report on the geologic structure of the Besshi spotted schist zone (in Japanese with English abstract). *Jour. Geol. Soc. Japan*, **62**, (733), 574-584.
- IGI, Sachio (1953): Petrographical studies on the peridotite in the Horoman region at the southern end of the Hidaka Mountain Range, Hokkaido (in Japanese with English abstract). *Jour. Geol. Soc. Japan*, **59**, (691), 111-121.
- KELLER, W. D., and PICKETT, E. E. (1949): Absorption of infra-red radiation by powdered silica minerals. *Am. Mineral.*, **34**, 855-868.
- KUNO, Hisashi (1957): Chromian diopside from Sano, Yamanashi Prefecture. *Jour. Geol. Soc. Japan*, **63**, (744), 523-526.
- LYON, W., and KINSEY, E. L. (1942): Infra-red absorption spectra of water molecule in crystals. *Phys. Rev.*, **61**, 482-489.
- MARA, R. T., and SUTHERLAND, G.B.B.M. (1953): The infra-red spectrum of brucite $\text{Mg}(\text{OH})_2$. *Jour. Opt. Soc. Amer.*, **43**, 1100-1102.
- ROSS, C. S., FOSTER, M. D., and MYER, A. T. (1954): Origin of dunites, and of olivine-rich inclusions in basaltic rocks. *Am. Mineral.*, **39**, 693-737.
- WARREN, B. E., and BISCOE, J. (1931): The crystal structure of the monoclinic pyroxenes. *Zeitschr. Kristallographie*, Band **80**, 391-401.