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Note on rock-forming minerals in the Joetsu district, Niigata Prefecture, Japan. (11) Chromian andradite from the Kotaki district.

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ABSTRACT

The chromian andradite garnet occurs as green, fine-grained, round crystals of aggregate in the diopside skarn in serpentinite, Hisui-kyo (jadeite valley), Kotaki, Niigata prefecture. The chromian andradite occurs as a fine vein in the diopside skarn. The chromian andradite coexists with serpentinite, chlorite and chromite. The chromian andradite varies in composition from $Alm_{2.5}And_{54.6}Gro_{26.6}Pyr_{0.4}Sch_{1.5}Uva_{14.4}$ to $Alm_{3.0}And_{43.1}Gro_{30.0}Pyr_{0.1}Sch_{1.2}Uva_{22.7}$. The sum of andradite (And), grossular (Gro) and uvalovite (Uva) molecules of garnets is more than about 95 mol. %, with small amounts of almandine (Alm), schlomite (Sch) and pyrope (Ptr) molecules. They are ugrandite garnets. The space group is Ia3d, and the unit cell dimension is a = 12.022(8) Å. The chromian andradite is isotropic, not anomalous birefringence.

KEY WORDS
Andradite, Chromian andradite, Garnet, Grossular, Kotaki, Uvarovite

Introduction

The garnet solid solution series of uvarovite (Uva)-grossular (Gro)-andradite (And) (ugrandite) are common minerals in skarns, calc-silicate rocks and marbles (Knorring 1951, Huckenholz and Yoder 1971). Ugrandite froms over a very wide range of P-T conditions of any metamorphic and magmatic events. The occurrences of Cr-rich ugrandite are known in mafic and ultramafic rocks and serpentinites (Kitahara 1959, Seki 1965). Although ugrandite shows solid solusion series among uvarovite-grossularite-andradite, the majority of ugrandite are near grossular-andradite and uvarovite-grossular joins. The chromian garnet in this study has intermadiate composition among grossular, andradite and uvarovite. The chromian andradite in this composition is rare. Therefore, I give the chemical composition and the description on the occurence and the physical properties of the chromian andradite.

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Occurrence

The green chromian andradite occurs as fine vein of fine-grained crystals of aggregate in the small xenolith of the diopside skarn (6 cm in the length) in serpentinite. Fig. 1 a-1 shows the photographs of the chromian andradite bearing rock. The chromian andradite vein is found along serpentinite with chromite in the diopside skarn (Fig. 1 a-2). Diopside in the skarn is large-grained crystal. The boundary of diopside and the vein of the green chromian andradite is sharp (Fig.1b). After diopside skarn is enclaved in serpentine, the chromian andradite forms as a reaction vein of diopside and serpentine. Serpentine and chlorite are needle-shaped crystals in the vein. Chromite forms as fine-grained granular crystal. The chromian andradite coexists with serpentinite, chlorite and chromite (Fig. 1 c). The photograph (Fig.1d) shows a number of euhedral and subhedral garnet crystals (0.03mm in length). The hexagonal crystal is often found.

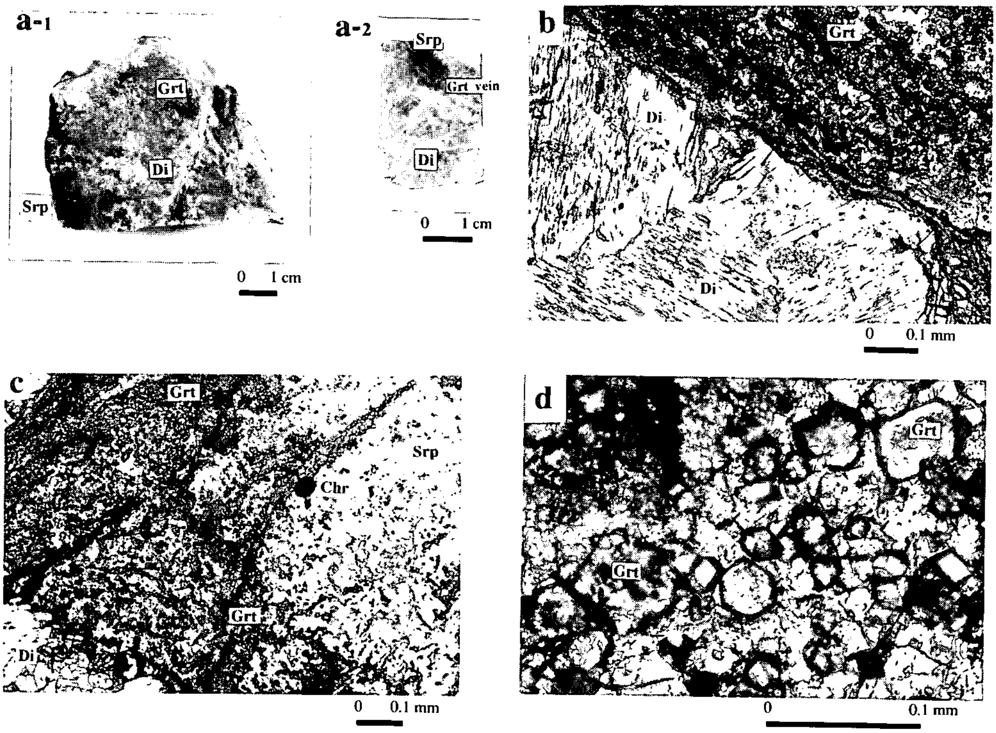

Fig 1. a-1, a-2: Photograph of chromian andradite garnet in the diopside skarn. b and c: Photomicrographs of the chromian andradite vein in the diopside surrounding of serpentine. d: High magnification photomicrograph of the euhedral chromian andradite. Hexagonal crystal is observed. Chr: chromite, Grt: garnet, Srp: serpentine

Mineralogical data and discussion

Chemical composition : Electron microprobe analyses of the garnets, clinopyroxenes and chromite were performed using JEOL 733 superprob at the National institute of Polar Research. The analyses of two garnets, chromite and diopside are given in Table 1 together with their structural formulae. Clinopyroxene is diopside ($Di_{94.1}$ $HD_{3.1}$ $CaTs_{2.3}$ $Jd_{0.5}$). The composition of chromite is $(Ca_{0.02}\ Mg_{0.07}\ Mn_{0.07}\ Fe^{2+}{}_{0.94})_{1.05}$ $(Ti_{0.04}\ Fe^{3+}{}_{0.56}\ Cr_{1.28})_{1.88}\ O_4$. Ferric iron for garnet is estimated by using stoichiometric calculation on the basis of 12 oxygen atoms and 8 cations. Two analyses of garnets represent the maximum and minimum determined Cr content. The end members used here are almandine (Alm: $Fe^{2+}{}_3\ Al_2\ Si_3\ O_{12}$), andradite (And : $Ca_3\ Fe^{3+}{}_2\ Si_3\ O_{12}$), grossular (Gro : $Ca_3\ Al_2\ Si_3\ O_{12}$), pyrope (Pyr : $Mg_3\ Al_2\ Si_3\ O_{12}$), schrlomite (Sch : $Ca_3\ Fe^{3+}{}_2\ Ti_3\ O_{12}$), spessartine (Spr : $Mn_3\ Al_2\ Si_3\ O_{12}$) and uvarovite (Uva : $Ca_3\ Cr_2\ Si_3\ O_{12}$).

The sum of andradite, grossular and uvarovite molecules of garnets in the present study is more than about 95 mol.%, with small amounts of almandine, schlomite and pyrope molecules. They were plotted in the center of the andradite field in the Fe^{3+}-Cr-Al diagram (Fig.2). Their chemical compositions are similar to garnets reported by Kitahara (1951) and Regault (1961). These garnets occur in skarn contacted with ultramafic rocks and serpentinite. Kitahara (1951) reported that black melanite containing 3.11 % $Cr_2\ O_3$ was formed by contact metamorphism between ultra-basic rock and chromite vein. The chemical composition of Cr-rich garnet is strongly influenced by the bulk chemistry. Natural occurrences of chromian andradite require a host rock with a restricted composition of CaO and Cr_2O_3-Al_2O_3-Fe_2O_3 rich bulk chemistry. In the present study, serpentine is found along the chromian andradite vein in the diopside skarn. The observation indicates that Cr is supplied from serpentinite. Pyrope and knorringite are not stable at lower pressure than 1.5 GPa and 1000℃ (Boyd and England 1962, Ringwood 1977). The chromian andradite in the present study has very low pyrope and knorringite contents. When oxygen fugacity increases, $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ ratio of the chromain andradite increases. The almandine molecule is also low. These facts suggest that the chromain garnet crystallizes at low pressure and high oxygen fugacity.

Fig. 2 is constructed using analyses taken from the literatures (Deer et al. 1982) and the present study. Fig 2. shows that there is a complete solid solution along the uvarovite-grossular join. Huckenholz and Knittel (1975) reported that uvarovite froms a complete solid solution with grossular below 855℃ at 1 atm. The natural occurrences in Fig. 2 are agreement with their experimental results in the uvarovite-grossular join. However, garnet on the uvarovite-andradite join is not observed. Solid lines in Fig. 2 are thermodynamically calculated spinodals by Ganguly (1976). The broken curve is the approximate position of the solvus at 800℃. Fig. 2 shows that complete miscibility exists between uvarovite and andradite. These relationships are compatible with the analytical

Tablel. Chemical compositions of garnets, chromite and clinopyroxene.

	1	2	3*	4	5
	Ganet	Ganet	Ganet	Chr	Cpx
SiO_2	36.73	36.67	35.97	0.19	53.34
TiO_2	0.56	0.73	0.89	1.49	0.09
Al_2O_2	6.59	5.83	5.82	1.26	1.19
Cr_2O_3	6.74	4.22	3.11	41.48	0.14
Fe_2O_3	15.21	18.46	19.90		
FeO			1.36	46.09	1.90
Mno	0	0.04	0	2.25	0.01
Mgo	0.04	0.09	0.31	0.33	16.99
Cao	33.64	33.79	32.49	0.42	25.76
Na2O	0	0	-	0	0.88
Total	99.51	99.73	93.51	99.62	
Strunctural fromulae on the basis of 12 oxygens				O=4	O=6
Si	3.004	3.004	2.954	0.007	1.954
Al^{IV}			0.046	0.058	0.046
Al^{VI}	0.562	0.636	0.157		0.005
Ti	0.044	0.034	0.055	0.044	0.003
Cr	0.274	0.436		1.278	0.004
Fe^{3+}	1.068	0.850	1.230	0.562	
Fe^{2+}	0.070	0.086	0.093	0.940	0.058
Mn	0.002	0	0	0.074	0.003
Mg	0.010	0.004	0.038	0.019	0.928
Ca	2.966	2.948	2.859	0.018	1.011
Na	0	0		0	0.005
Total	8.000	7.998		3.000	4.017
Almandine	2.5	3.0	3.1		
Andradite	54.6	43.1	64.1		
Grossular	26.6	30.0	25.2		
Pyrope	0.4	0.1	1.3		
Schormite	1.5	1.2	1.2		
Spessartine	tr.	0	0		
Uvarovite	14.4	22.7	10.1		

Kitahara (1959)

data for natural garnets. The miscibility gap becomes narrower with increasing temperature. Huckenholz and Knittel (1976) described that there is a complete solid solution series between uvarovite and andradite below 1137℃ at 1 atm. Although they did not carry out experiment below 1050℃, the solvus closed already at 1050℃ The relationship of the solvus is not clear. The chromain andradites in the present study are plotted on solvus at 800℃ (dashed line). The temperature is higher than that suggested by serepentine as host rock.

X-ray powder study: The X-ray power data for the chromain andradites in the present study are given in Table 2 together with uvarovite, grossular and andradite. The unit-cell parameters obtained from the 11 sharp reflections with asterisk by using silicon as an external standard. They were refined by a least-squares method (Sakurai, 1968). The results were

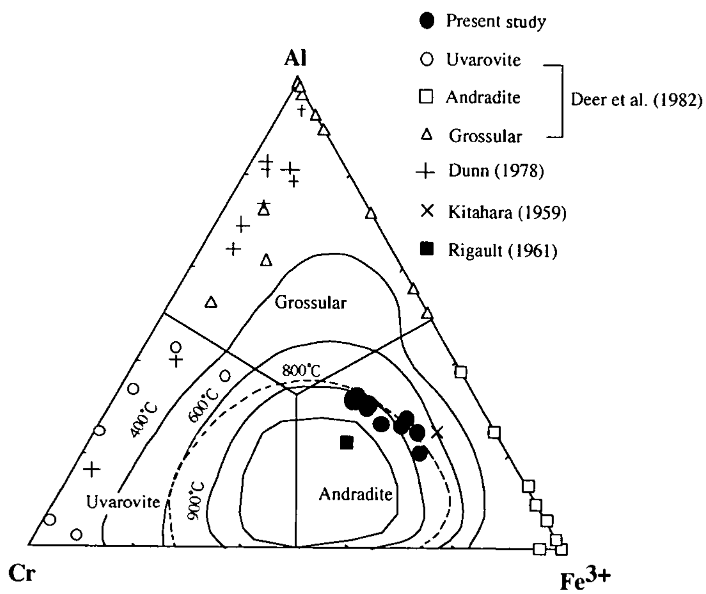

Fig.2. Plots of urandite garnets from skarn, chromite ore, serpentinite, ultramafic and mafic rocks in the Cr-Fe^{3+}-Al triangle (Sources of data, Kitahara 1959, Rigault 1961, Dunn 1978, Deer et al. 1982). Solid lines are calculated spinodals by Ganguly (1976). Broken curve is the approximate position of the solvus at 800℃.

Table2. X-ray powder data of andradite, chromian andradite and uvarovite.

	1			2		3		4	
HKL	d Å (obs)	d Å (cal)	I/Io	d Å (obs)	I/Io	d Å (obs)	I/Io	d Å (obs)	I/Io
220	4.25*	4.2	30	4.263	14	4.24	16		
321						3.205	6		
400	2.986*	3.005	100	3.013	60	2.999	70	2.959	25
420	2.679*	2.688	37	2.684	100			2.647	100
332	2.559*	2.563	34	2.571	14	2.557	20	2.524	11
422	2.445*	2.454	16	2.462	45	2.499	55	2.417	20
431						2.352	25	2.321	18
510	2.358*	2.357	13	2.365	18				
521	2.194*	2.194	17	2.202	18	2.191	16	2.162	17
611	.			1.9564	25	1.946	20	1.921	25
620				1.9068	12	1.896	10	1.872	2
541						1.854	8		
444	1.739*	1.735	33	1.7406	10	1.732	8	1.710	17
640	1.660	1.667	12	1.6728	25	1.664	25	1.643	25
721				1.6412	4			1.612	2
642	1.610*	1.606	17	1.6112	60	1.603	60	1.581	50
800	1.502*	1.502	12	1.5073	14	1.500	10	1.481	10
741	1.486	1.749	15			1.477	6	1.458	2
653						1.432	8	1.417	1
822	1.418*	1.416	21	1.4213	4	1.414	6	1.324	10
a Å	12.022(8)			12.059		11.999		11.855	

1 : This study
2 : Andradite (Huckenholz and Knittel 1976)
3 : Uvarovite (Huckenholz and Knittel 1975)
4 : Grossular (Huckenholz and Knittel 1975)

given in Table 2, together with other data for comparison. The cell dimension a = 12.022(8) Å of the chromain andradite in the present study is between the cell dimensions of andradite (12.059 Å) and uvarovite (11.999 Å). The cell dimension calculated on the basis of each molecule for garnet is about 11.98 Å. This value is not agreement with the cell dimension 12.022(8) Å calculated by a least- squares method.

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