Experimental study on ion exchange of Ca^{2+} , Fe^{2+} and Mn^{2+} between garnet solid solution and 2N aqueous chloride solution at 600°C and 1 kb

Etsuo UCHIDA, Masataka GIMA and Naoya IMAI

Department of Mineral Resources Engineering, School of Science and Engineering, Waseda University, Shinjuku, Tokyo 169, Japan

Experiments on ion exchange of Ca^{2+} , Fe^{2+} and Mn^{2+} between grossular–almandine–spessartine garnet solid solution and 2N aqueous chloride solution were conducted at 600°C and 1 kb under relatively reducing conditions in order to determine the stability relation and mixing property of the garnet solid solution. The experimental results revealed that calcium ion is slightly preferentially partitioned into aqueous chloride solution compared with ferrous and manganese ions. Grossular, almandine and spessartine form an almost continuous solid solution except for the semicircular region along the grossular–almandine join, where mineral assemblages of fayalite + anorthite and hedenbergite + anorthite + wustite appear instead of the garnet solid solution. Mixing properties of the garnet solid solution were evaluated from the experimental results by considering the formation of $\text{FeCl}_3^-_{\text{aq}}$ and $\text{MnCl}_3^-_{\text{aq}}$ in the aqueous phase. Almandine–spessartine solid solution shows slightly negative deviation from ideality. On the other hand, grossular–spessartine solid solution shows slightly positive deviation. Mixing property of grossular–almandine solid solution was not well determined due to the large unstable region.

Keywords: Garnet, Aqueous chloride solution, Ion exchange, Mixing property, Stability relation

I. Introduction

Two series of garnet solid solutions, pyrope and grossular, are common in metamorphic, metasomatic and igneous rocks. It is well known that pyrope, almandine and spessartine, and grossular and andradite form complete solid solutions in nature, respectively. The pyrope and grossular series garnet solid solutions were originally defined based on their miscibility relations. However, garnet solid solutions with intermediate compositions between pyrope and grossular have been reported from metamorphic rocks and skarns (Fron del and Ito, 1965; Nemec, 1967; Brown, 1969; Ackermann *et al.*, 1972; Shimazaki, 1977; Hsu, 1980). Experimental studies have

also revealed that grossular and spessartine (Ito and Fron del, 1968; Shoji *et al.*, 1995), and grossular and almandine (Hariya and Nakano, 1972) form continuous solid solutions, respectively.

Although the extensive solid solution of garnet is widely known, its mixing properties are less well constrained. Therefore, we have conducted ion exchange experiments of Ca^{2+} , Fe^{2+} and Mn^{2+} between garnet solid solution and 2N aqueous chloride solution in order to clarify the stability relation and mixing property of the garnet solid solution, and to obtain the chemical composition of the aqueous chloride solution in equilibrium with the garnet solid solution of variable composition. Experiments were carried out for the following binary and ternary systems:

Table 1. Experimental data for the ion exchange in the system $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Fe, Mn) Cl_2 - H_2O at 600°C and 1 kb

Run No.	Duration days	Starting Materials				Run Products					
		Solid	mg	Solution	μl	Garnet		Solution			
						Alm	Spe	ΣmFe	ΣmMn	mFeCl ₂ *	mMnCl ₂ *
202	7	Spe	28.5	FeCl ₂	30	0.131	0.869	0.132	0.868	0.132	0.868
203	7	Spe	24.3	FeCl ₂	40	0.186	0.814	0.150	0.850	0.150	0.850
204	7	Spe	19.4	FeCl ₂	50	0.382	0.618	0.435	0.565	0.435	0.565
211	7	Alm	15.4	MnCl ₂	50	0.728	0.272	0.776	0.224	0.776	0.224
212	7	Alm	18.2	MnCl ₂	30	0.868	0.132	0.911	0.089	0.911	0.089
214	7	Alm	30.3	MnCl ₂	30	0.951	0.049	0.969	0.031	0.969	0.031
215	7	Alm ₅₀ Spe ₅₀	31.1	FeCl ₂	20	0.756	0.244	0.816	0.184	0.816	0.184
216	7	Alm ₅₀ Spe ₅₀	20.7	FeCl ₂	40	0.712	0.288	0.768	0.232	0.768	0.232
217	7	Alm ₅₀ Spe ₅₀	31.9	MnCl ₂	20	0.720	0.280	0.789	0.211	0.789	0.211
218	7	Alm ₅₀ Spe ₅₀	20.4	MnCl ₂	40	0.517	0.483	0.603	0.397	0.603	0.397
243	7	Alm ₅₀ Spe ₅₀	20.2	MnCl ₂	30	0.501	0.499	0.550	0.450	0.550	0.450
244	7	Alm ₄₀ Spe ₆₀	27.0	MnCl ₂	20	0.412	0.588	0.435	0.565	0.435	0.565
245	7	Alm ₄₀ Spe ₆₀	19.1	MnCl ₂	30	0.342	0.658	0.390	0.610	0.390	0.610
246	7	Alm ₄₀ Spe ₆₀	14.2	MnCl ₂	40	0.365	0.635	0.398	0.602	0.398	0.602

* Calculated values.

- (1) $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Fe, Mn) Cl_2 - H_2O ;
- (2) $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Ca, Mn) Cl_2 - H_2O ;
- (3) $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Ca, Fe) Cl_2 - H_2O and
- (4) $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Ca, Fe, Mn) Cl_2 - H_2O .

II. Experimental method

A stoichiometric mixture of reagent-grade CaO , Al_2O_3 and SiO_2 was used as a starting material for a grossular component. We used stoichiometric mixtures of reagent-grade metallic iron or manganese powder, Al_2O_3 and SiO_2 as starting materials for almandine and spessartine components, respectively. We had some difficulties in the synthesis of grossular-almandine solid solution, especially in the almandine-rich side. Thus, synthetic almandine containing a small amount of a spessartine component was used as a crystal seed in the experiments. Ion exchange experiments were

conducted using various starting compositions. Anthracene($\text{C}_{14}\text{H}_{10}$) was used as a reducing agent in order to keep iron and manganese ions in a divalent state during the experiments.

The starting material (10–40 mg) and 2N CaCl_2 , FeCl_2 and/or MnCl_2 aqueous solution (15–50 μl) were enclosed into a gold capsule with a few milligrams of anthracene. The charged capsule was kept at 600°C and 1 kb in a standard cold-seal pressure vessel for 4 to 9 days. The temperature was monitored with a chromel-alumel thermocouple attached on the outer wall of the pressure vessel, and the pressure was measured by a Heise gauge. The temperature was controlled within $\pm 5^\circ\text{C}$ and the pressure within ± 10 bars.

After the termination of the run, the pressure vessel was quenched with cold water. Gold capsules were opened and the run products were washed away into a beaker with distilled water. Solid phases were separated from a liquid phase with a membrane filter and were identified by the polarizing microscope, the X-

Table 2. Experimental data for the ion exchange in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Ca, Mn) Cl_2 - H_2O at 600°C and 1 kb

Run No.	Duration days	Starting Materials				Run Products					
		Solid	mg	Solution	μl	Garnet		Solution			
						Gro	Spe	Σm_{Ca}	Σm_{Mn}	m_{CaCl_2}	m_{MnCl_2}
205	7	Spe	30.6	CaCl_2	20	0.088	0.912	0.323	0.677	0.153	0.508
206	7	Spe	20.8	CaCl_2	40	0.187	0.813	0.458	0.542	0.257	0.344
207	7	Gro	30.8	MnCl_2	30	0.824	0.176	0.864	0.136	0.773	0.054
208	7	Gro	20.3	MnCl_2	40	0.715	0.285	0.781	0.219	0.647	0.093
221	7	Gro	29.7	MnCl_2	20	0.886	0.114	0.906	0.094	0.839	0.036
222	7	Gro	24.0	MnCl_2	25	0.848	0.152	0.884	0.116	0.804	0.045
223	7	Gro	18.7	MnCl_2	30	0.757	0.243	0.823	0.177	0.710	0.072
224	7	Gro	15.0	MnCl_2	40	0.542	0.458	0.694	0.306	0.525	0.144
225	7	Spe	22.5	CaCl_2	20	0.132	0.868	0.381	0.619	0.193	0.434
226	7	Spe	17.5	CaCl_2	25	0.158	0.842	0.424	0.576	0.228	0.382
228	7	Spe	15.1	CaCl_2	30	0.204	0.776	0.474	0.526	0.272	0.327
247	7	Spe ₅₀ Gro ₅₀	25.1	CaCl_2	30	0.468	0.532	0.662	0.338	0.482	0.165
248	7	Spe ₅₀ Gro ₅₀	27.8	MnCl_2	20	0.361	0.639	0.607	0.393	0.414	0.205
249	7	Spe ₅₀ Gro ₅₀	15.9	MnCl_2	30	0.294	0.706	0.547	0.453	0.345	0.256
250	7	Spe ₅₀ Gro ₅₀	13.5	MnCl_2	40	0.267	0.733	0.518	0.482	0.315	0.283

* Calculated values.

Fig. 1. Ion exchange data in the system $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Fe, Mn) Cl_2 - H_2O at 600°C and 1 kb. The starting and final compositions are connected with dashed lines.

ray diffractometer (Rigaku RAD-IB) and the scanning electron microscope (JEOL JSM-5400). The chemical compositions of the solid phases were determined on the crystal surfaces by the energy dispersive-type microanalyzer

(Link QX-200JI). In some cases, cations in the solid products were analyzed by the atomic absorption spectrophotometer (Shimadzu AA-610S) after dissolution with HF and HCl. The molar ratio of the cations in the liquid phase was also determined by the atomic absorption spectrophotometer.

III. Results

1. Almandine-spessartine-(Fe^{2+} , Mn^{2+}) Cl_2 - H_2O system

The experimental results are summarized in Table 1, and the ion exchange isotherm is shown in Fig. 1. Almandine and spessartine form a complete solid solution with each other.

The ion exchange isotherm suggests that Fe/Mn ratio in the garnet solid solution is nearly equal to that in the coexisting aqueous chloride solution. The grain size of the synthesized garnets reached up to 100 μm . All synthesized garnets have a shape of dodecahedron (Fig. 2-A).

Fig. 2. Secondary electron images of synthesized garnets. A: Alm₇₆Spe₂₄ (run no. 215), B: Gro₉Spe₉₁ (run no. 205) and C: Gro₈₆Alm₁₄ (run no. 315).

2. Grossular-spessartine-(Ca²⁺, Mn²⁺)Cl₂-H₂O system

The experimental results are summarized in Table 2, and the ion exchange isotherm is shown in Fig. 3. Grossular and spessartine also form a continuous solid solution. Manganese ion is slightly preferentially partitioned into the garnet solid solution compared with calcium ion.

The synthesized garnet has a shape of dodecahedron (Fig. 2-B). The grain size decreases with an increase of grossular component from 50 μ m to 2 μ m.

3. Grossular-almandine-(Ca²⁺, Fe²⁺)Cl₂-H₂O system

The experimental results are compiled in Table 3. Grossular(Gro) and almandine(Alm) form solid solutions in the limited compositional ranges from Gro₀Alm₁₀₀ to Gro₈Alm₉₂ and from Gro₇₂Alm₂₈ to Gro₁₀₀Alm₀ under the experimental conditions (Fig. 4). The Ca/(Ca+Fe) molar ratio of the coexisting aqueous chloride solution is about 0.21 for the mineral assemblage of garnet(Gro₈Alm₉₂)+fayalite+anorthite, about 0.52 for that of fayalite+hedenbergite+anorthite+wustite, and about 0.80 for that of hedenbergite+anorthite+wustite+garnet(Gro₇₂Alm₂₈). The bulk chemical compositions of solid products containing the mineral assemblages of fayalite+anorthite and hedenbergite+anorthite+wustite were determined by the atomic

Fig. 3. Ion exchange data in the system Ca₃Al₂Si₃O₁₂-Mn₃Al₂Si₃O₁₂-(Ca, Mn)Cl₂-H₂O at 600°C and 1 kb. The starting and final compositions are connected with dashed lines.

absorption spectrophotometer after dissolution with HF and HCl. Their bulk compositions are plotted in Fig. 4. Mineral assemblages of fayalite+anorthite and hedenbergite+anorthite+wustite appeared in the intermediate compositions. The schematic phase relation in the system CaO-FeO-Al₂O₃-SiO₂ is shown in Fig. 5. This figure is a projection onto the CaO-FeO-SiO₂ plane from Al₂O₃. The anorthite-wustite-hedenbergite plane intersects the grossular-almandine line in the middle point (Gro₅₀Alm₅₀), and the anorthite-fayalite line intersects the grossular-almandine line in the composition of Gro₃₃Alm₆₇.

The synthesized garnet in this system has

Fig. 4. Ion exchange data in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Ca, Fe) Cl_2 - H_2O at 600°C and 1 kb. The starting and final compositions are connected with thin dashed lines. Bold dashed line is an estimated ion exchange isotherm between garnet solid solution and aqueous chloride solution in the unstable region of garnet solid solution. Symbols: solid circles, Ga; open squares, Ga+Hd+An+Wu; solid squares, Hd+An+Wu; open circle, An+Hd+Fa+Wu; solid triangles, Fa+An. Abbreviations: Ga, garnet; Hd, hedenbergite; An, anorthite; Fa, fayalite; Wu, wustite.

also a shape of dodecahedron (Fig. 2-C), and the grain size decreases with an increase of grossular component from 50 μm to 2 μm .

4. Grossular-almandine-spessartine-(Ca^{2+} , Fe^{2+} , Mn^{2+}) Cl_2 - H_2O system

The experimental results are summarized in Table 4. Compositions of garnets synthesized in this system are plotted in Fig. 6. Garnet solid solutions with the compositions corresponding to the semicircular area in Fig. 6 were not stable. The mineral assemblages fayalite+anorthite and hedenbergite+anorthite+wustite appeared in the semicircular area.

Fig. 7 shows concentrations of total Ca, Fe and Mn in the 2N aqueous chloride solution in equilibrium with garnet solid solution, calculated from the experimental results for binary

Fig. 5. The schematic phase relation in the CaO - FeO - Al_2O_3 - SiO_2 at 600°C and 1 kb, projected onto CaO - FeO - SiO_2 plane from Al_2O_3 . Abbreviations: Gro, grossular; Alm, almandine; Ga, garnet; Hd, hedenbergite; An, anorthite; Fa, fayalite; Wu, wustite.

and ternary systems by the least square method. In the calculation, the aqueous chloride solution was assumed to be an ideal solution (Kubo *et al.*, 1992).

IV. Thermodynamic considerations

Here we define unit formulae of garnet end members as follows:

grossular(Gro): $1/3(\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12})$

almandine(Alm): $1/3(\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12})$

and spessartine(Spe): $1/3(\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12})$.

The ion exchange reactions between garnet solid solution and aqueous chloride solution can be expressed using neutral aqueous species as follows:

Uchida *et al.* (1995) posed a question for the

Table 3. Experimental data for the ion exchange in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Ca, Fe) Cl_2 - H_2O at 600°C and 1 kb

Run Duration		Starting Materials				Run Products						
No.	days	Solid	mg	Solution	μl	Garnet		Solution				Phases
						Gro	Alm	ΣCa	ΣFe	$\text{CaCl}_2^{\#}$	$\text{FeCl}_2^{\#}$	
237	8	Gro	20.0	FeCl_2	30	0.784	0.216	0.878	0.122	0.822	0.075	Ga
315	8	Gro	24.7	FeCl_2	30	0.862	0.138	0.910	0.090	0.865	0.054	Ga
317	8	Gro	19.9	FeCl_2	40	0.771	0.229	0.765	0.235	0.676	0.154	Ga
350	4	Alm [*]	18.7	CaCl_2	30	0.063	0.937	0.199	0.801	0.127	0.730	Ga
353	4	Gro [*]	19.1	FeCl_2	30	0.849	0.151	0.803	0.197	0.724	0.126	Ga
356	4	Alm [*]	27.0	CaCl_2	20	0.055	0.945	0.189	0.811	0.120	0.743	Ga
357	4	Alm [*]	21.5	CaCl_2	30	0.071	0.929	0.182	0.818	0.115	0.752	Ga
358	4	Alm [*]	18.9	CaCl_2	40	0.081	0.919	0.196	0.804	0.124	0.734	Ga
366	4	Alm [*]	1.9	CaCl_2	40	0.693	0.307	0.787	0.213	0.704	0.138	Ga
399	7	Alm [*]	29.9	CaCl_2	20	0.039	0.961	0.128	0.872	0.078	0.823	Ga
403	7	Gro	30.3	FeCl_2	30	0.855	0.145	0.919	0.081	0.877	0.049	Ga
404	7	Gro	29.0	FeCl_2	40	0.862	0.138	0.884	0.116	0.830	0.071	Ga
406	7	Gro	19.5	FeCl_2	30	0.801	0.199	0.838	0.162	0.770	0.102	Ga
351	4	Alm ₅₀ Gro ₅₀ [*]	15.8	FeCl_2	30	0.262	0.738 ^{**}	0.486	0.514	0.384	0.397	An+Fa
360	4	Alm [*]	11.1	CaCl_2	40	0.274	0.726 ^{**}	0.419	0.581	0.302	0.467	An+Fa
361	4	Alm [*]	7.1	CaCl_2	30	0.275	0.725 ^{**}	0.471	0.529	0.350	0.412	An+Fa
395	4	No357	9.6	CaCl_2	20	0.413	0.587 ^{**}	0.526	0.474	0.404	0.357	An+Fa+Hd+Wu
A1	10	Gro	10.0	FeCl_2	40	0.522	0.478 ^{**}	0.799	0.201	0.719	0.129	An+Hd+Wu
A2	10	Gro	9.9	CaCl_2	10	0.577	0.423 ^{**}	0.744	0.256	0.650	0.170	Ga+An+Hd+Wu
				FeCl_2	30							
A3	10	Gro	9.8	CaCl_2	20	0.569	0.431 ^{**}	0.849	0.151	0.784	0.095	Ga+An+Hd+Wu
				FeCl_2	20							
A5	10	Alm ₅₀ Gro ₅₀	10.1	CaCl_2	20	0.476	0.524 ^{**}	0.596	0.404	0.478	0.292	An+Hd+Wu
				FeCl_2	20							

*, With crystal seed; **, Bulk composition; #, Calculated values.

Abbreviations: Ga, garnet; An, anorthite; Fa, fayalite; Hd, hedenbergite; Wu, wustite.

ideality of $2\text{N}(\text{Ca}, \text{Fe}, \text{Mn})\text{Cl}_2$ aqueous solution under supercritical conditions. The non-ideality is caused by the formation of FeCl_3^- and MnCl_3^- . Therefore, we calculated the molalities of the neutral aqueous species, $\text{CaCl}_{2\text{aq}}$, $\text{FeCl}_{2\text{aq}}$ and $\text{MnCl}_{2\text{aq}}$, solving the following four mass-balance and four mass-action equations iteratively:

$$\Sigma m_{\text{Ca}} = m(\text{Ca}^{2+}) + m(\text{CaCl}^+) + m(\text{CaCl}_2) \quad (4)$$

$$\Sigma m_{\text{Fe}} = m(\text{FeCl}_2) + m(\text{FeCl}_3^-) \quad (5)$$

$$\Sigma m_{\text{Mn}} = m(\text{MnCl}_2) + m(\text{MnCl}_3^-) \quad (6)$$

$$\Sigma m_{\text{Cl}} = m(\text{Cl}^-) + m(\text{CaCl}^+) + 2\{m(\text{CaCl}_2) + m(\text{FeCl}_2) + m(\text{MnCl}_2)\} + 3\{m(\text{FeCl}_3^-) + m(\text{MnCl}_3^-)\} = 2 \quad (7)$$

$$K(\text{CaCl}^+) = \gamma(\text{Ca}^{2+})m(\text{Ca}^{2+})\gamma(\text{Cl}^-)m(\text{Cl}^-) / \{\gamma(\text{CaCl}^+)m(\text{CaCl}^+)\} \quad (8)$$

Table 4. Experimental data for the ion exchange in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ -(Ca, Fe, Mn) Cl_2 - H_2O at 600°C and 1 kb

Run Duration			Starting Materials				Run Products									Phases
No.	days	Solid	mg	Solution	μl	Garnet			Solution							
						Gro	Alm	Spe	ΣCa	ΣFe	ΣMn	CaCl_2^*	FeCl_2^*	MnCl_2^*		
280	7	Gro ₉₅ Spe ₅	25.1	FeCl ₂	30	0.749	0.202	0.049	0.767	0.172	0.061	0.665	0.113	0.026	Ga	
281	7	Gro ₉₅ Spe ₅	19.7	FeCl ₂	40	0.700	0.250	0.050	0.715	0.224	0.061	0.601	0.151	0.027	Ga+An+Hd+Wu	
291	7	Alm ₇₅ Spe ₂₅	32.8	CaCl ₂	20	0.072	0.826	0.102	0.222	0.711	0.067	0.136	0.643	0.050	Ga	
293	7	Alm ₇₅ Spe ₂₅	20.6	CaCl ₂	30	0.084	0.718	0.198	0.237	0.625	0.138	0.142	0.562	0.108	Ga+An+Fa	
295	7	Alm ₅₀ Spe ₅₀	31.4	CaCl ₂	20	0.174	0.535	0.291	0.416	0.380	0.204	0.269	0.310	0.130	Ga+An+Fa	
296	7	Alm ₅₀ Spe ₅₀	25.4	CaCl ₂	25	0.195	0.465	0.340	0.403	0.358	0.239	0.254	0.295	0.156	Ga+An+Fa	
300	7	Alm ₂₅ Spe ₇₅	25.6	CaCl ₂	25	0.122	0.260	0.618	0.400	0.174	0.426	0.228	0.145	0.285	Ga	
311	8	Gro ₃₃ Alm ₃₃ Spe ₃₃	30.6	FeCl ₂	30	0.158	0.352	0.490	0.363	0.293	0.344	0.210	0.249	0.239	Ga	
313	8	Gro ₃₃ Alm ₃₃ Spe ₃₃	24.3	CaCl ₂	30	0.293	0.326	0.381	0.464	0.265	0.271	0.300	0.211	0.165	Ga	
314	8	Gro ₃₃ Alm ₃₃ Spe ₃₃	25.6	MnCl ₂	30	0.164	0.279	0.559	0.440	0.221	0.339	0.270	0.179	0.214	Ga	
319	8	Gro ₃₃ Alm ₃₃ Spe ₃₃	28.8	FeCl ₂	15	0.261	0.299	0.440	0.476	0.204	0.320	0.303	0.162	0.193	Ga	
				CaCl ₂	15											
320	8	Gro ₃₃ Alm ₃₃ Spe ₃₃	21.1	FeCl ₂	15	0.271	0.323	0.406	0.482	0.226	0.292	0.313	0.178	0.174	Ga	
				CaCl ₂	15											
322	8	Gro ₄₃ Alm ₄₃ Spe ₁₄	29.8	CaCl ₂	30	0.527	0.284	0.189	0.605	0.233	0.162	0.455	0.169	0.083	Ga+An+Fa	
323	8	Gro ₄₃ Alm ₄₃ Spe ₁₄	22.9	CaCl ₂	30	0.484	0.324	0.192	0.570	0.274	0.156	0.420	0.202	0.083	Ga+An+Fa	
324	8	Gro ₄₃ Alm ₄₃ Spe ₁₄	16.3	CaCl ₂	40	0.525	0.318	0.157	0.595	0.258	0.147	0.448	0.188	0.076	Ga+An+Fa	
325	8	Gro ₄₃ Alm ₄₃ Spe ₁₄	30.2	FeCl ₂	15	0.484	0.318	0.197	0.600	0.241	0.159	0.451	0.175	0.082	Ga	
				CaCl ₂	15											
331	9	Alm ₈₀ Spe ₂₀	35.3	FeCl ₂	10	0.027	0.607	0.366	0.154	0.520	0.326	0.080	0.490	0.282	Ga	
				CaCl ₂	10											
335	9	Gro ₃₃ Alm ₃₃ Spe ₃₃	19.0	CaCl ₂	30	0.306	0.318	0.376	0.487	0.249	0.264	0.321	0.195	0.156	Ga	
337	9	Gro ₅₀ Spe ₅₀	24.0	FeCl ₂	24	0.433	0.037	0.530	0.632	0.012	0.356	0.447	0.009	0.180	Ga	
				CaCl ₂	6											
338	9	Gro ₅₀ Spe ₅₀	16.5	FeCl ₂	24	0.488	0.058	0.454	0.628	0.026	0.346	0.444	0.019	0.176	Ga	
				CaCl ₂	6											

* Calculated values.

Abbreviations: Ga, garnet; An, anorthite; Fa, fayalite; Hd, hedenbergite; Wu, wustite.

$$K(\text{CaCl}_2) = \frac{\gamma(\text{CaCl}^+)m(\text{CaCl}^+)\gamma(\text{Cl}^-)m(\text{Cl}^-)}{\{\gamma(\text{CaCl}_2)m(\text{CaCl}_2)\}} \quad (9)$$

$$K(\text{FeCl}_3^-) = \frac{\gamma(\text{Cl}^-)m(\text{Cl}^-)\gamma(\text{FeCl}_2)m(\text{FeCl}_2)}{\{\gamma(\text{FeCl}_3^-)m(\text{FeCl}_3^-)\}} \quad (10)$$

and

$$K(\text{MnCl}_3^-) = \frac{\gamma(\text{Cl}^-)m(\text{Cl}^-)\gamma(\text{MnCl}_2)m(\text{MnCl}_2)}{\{\gamma(\text{MnCl}_3^-)m(\text{MnCl}_3^-)\}} \quad (11)$$

where Σm_i indicates the total molality of i-bearing aqueous species, $m(i)$ the molality of the aqueous species i , $\gamma(i)$ the activity coefficient of the aqueous species i , and $K(i)$ the

Fig. 6. Chemical compositions of garnets synthesized in the present experiments in the system $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $\text{Mn}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ - $(\text{Ca}, \text{Fe}, \text{Mn})\text{Cl}_2$ - H_2O at 600°C and 1 kb. Open circles show the chemical compositions of garnets in equilibrium with the mineral assemblages fayalite+anorthite and hedenbergite+anorthite+wustite, and solid circles show those in equilibrium with no other solid phases.

dissociation constant of the aqueous species i . The activity coefficients of the charged species were calculated using a Debye-Huckel equation:

$$\log \gamma(i) = -Z_i A I^{1/2} / (1 + a_i B I^{1/2}) \quad (12)$$

where Z_i is the ionic charge and I is the true ionic strength:

$$I = 1/2 \sum m(i) Z_i^2 \quad (13)$$

A and B are the Debye-Huckel coefficients and are taken from Helgeson and Kirkham (1974). a_i is the ion-size parameter and is taken from Kharaka and Barnes (1973). In the present study, the activity coefficients of the neutral species are assumed to be unity as done in most previous experimental studies (e.g., Frantz and Popp, 1979). Dissociation constants for $\text{CaCl}_{2\text{aq}}$ and $\text{CaCl}^+_{\text{aq}}$ are from Frantz and Marshall (1982) and dissociation constants for $\text{FeCl}_3^-_{\text{aq}}$ and $\text{MnCl}_3^-_{\text{aq}}$ from Uchida *et al.* (1995). In the

Fig. 7. Total molality of each cation in the aqueous chloride solution in equilibrium with garnet solid solution, calculated from the binary and ternary experimental data at 600°C and 1 kb by the least-square regression.

calculation, the presence of CO_2 derived from anthracene is neglected.

The calculated molalities of $\text{CaCl}_{2\text{aq}}$, $\text{FeCl}_{2\text{aq}}$ and $\text{MnCl}_{2\text{aq}}$ are included in Tables 1 to 4.

At equilibrium, we have the following relations corresponding to the reactions (1) to (3):

$$\Delta G_r(1) = \mu(\text{Alm}) + \mu(\text{CaCl}_{2\text{aq}}) - \mu(\text{Gro}) - \mu(\text{FeCl}_{2\text{aq}}) = 0 \quad (14)$$

$$\Delta G_r(2) = \mu(\text{Gro}) + \mu(\text{MnCl}_{2\text{aq}}) - \mu(\text{Spe}) - \mu(\text{CaCl}_{2\text{aq}}) = 0 \quad (15)$$

$$\text{and } \Delta G_r(3) = \mu(\text{Spe}) + \mu(\text{FeCl}_{2\text{aq}}) - \mu(\text{Alm}) - \mu(\text{MnCl}_{2\text{aq}}) = 0, \quad (16)$$

where ΔG_r is the Gibbs energy of reaction, and $\mu(i)$ the chemical potential of the component i . For the components constituting solid phases,

$$\mu(i) = \mu^\circ(i) + RT \ln X_i + \mu^{\text{ex}}(i) \quad (17)$$

and for aqueous species,

$$\mu(i) = \mu^\circ(i) + RT \ln(i) + RT \ln \gamma(i) \quad (18)$$

where $\mu^\circ(i)$ is the standard chemical potential of the component i , X_i the mole fraction of the component i in the solid solution, and $\mu^{\text{ex}}(i)$ the excess chemical potential of the component i .

Kakuda *et al.* (1991, 1994) derived a ternary regular solution model using a Bragg-Williams approximation. The excess Gibbs energy of mixing (G^{ex}) is written as

$$\begin{aligned} G^{\text{ex}} = & X_{\text{Fe}} X_{\text{Mn}} (X_{\text{Fe}} W_{\text{FeFeMn}} + X_{\text{Mn}} W_{\text{FeMnMn}}) \\ & + X_{\text{Mn}} X_{\text{Ca}} (X_{\text{Mn}} W_{\text{MnMnCa}} + X_{\text{Ca}} W_{\text{MnCaCa}}) \\ & + X_{\text{Ca}} X_{\text{Fe}} (X_{\text{Ca}} W_{\text{CaCaFe}} + X_{\text{Fe}} W_{\text{CaFeFe}}) \\ & + 2 X_{\text{Ca}} X_{\text{Fe}} X_{\text{Mn}} W_{\text{CaFeMn}}, \end{aligned} \quad (19)$$

where W_{ijk} represents the interaction parameter for solid solution.

If we adopt this mixing model for the ternary garnet solid solution, the excess chemical potential of each component can be expressed as follows (Kakuda *et al.*, 1991, 1994):

$$\begin{aligned} \mu^{\text{ex}}(\text{Gro}) = & -2 X_{\text{Fe}}^2 X_{\text{Mn}} W_{\text{FeFeMn}} \\ & -2 X_{\text{Fe}} X_{\text{Mn}}^2 W_{\text{FeMnMn}} \\ & + X_{\text{Mn}}^2 (X_{\text{Fe}} + X_{\text{Mn}} - X_{\text{Ca}}) W_{\text{MnMnCa}} \\ & + 2 X_{\text{Mn}} X_{\text{Ca}} (X_{\text{Fe}} + X_{\text{Mn}}) W_{\text{MnCaCa}} \\ & + 2 X_{\text{Ca}} X_{\text{Fe}} (X_{\text{Fe}} + X_{\text{Mn}}) W_{\text{CaCaFe}} \\ & + X_{\text{Fe}}^2 (X_{\text{Fe}} + X_{\text{Mn}} - X_{\text{Ca}}) W_{\text{CaFeFe}} \\ & + 2 X_{\text{Fe}} X_{\text{Mn}} (X_{\text{Fe}} + X_{\text{Mn}} - X_{\text{Ca}}) \\ & W_{\text{CaFeMn}} \end{aligned} \quad (20)$$

$$\begin{aligned} \mu^{\text{ex}}(\text{Spe}) = & X_{\text{Fe}}^2 (X_{\text{Ca}} + X_{\text{Fe}} - X_{\text{Mn}}) W_{\text{FeFeMn}} \\ & + 2 X_{\text{Fe}} X_{\text{Mn}} (X_{\text{Ca}} + X_{\text{Fe}}) W_{\text{FeMnMn}} \\ & + 2 X_{\text{Mn}} X_{\text{Ca}} (X_{\text{Ca}} + X_{\text{Fe}}) W_{\text{MnMnCa}} \\ & + X_{\text{Ca}}^2 (X_{\text{Ca}} + X_{\text{Fe}} - X_{\text{Mn}}) W_{\text{MnCaCa}} \\ & - 2 X_{\text{Ca}}^2 X_{\text{Fe}} W_{\text{CaCaFe}} \\ & - 2 X_{\text{Ca}} X_{\text{Fe}}^2 W_{\text{CaFeFe}} \\ & + 2 X_{\text{Ca}} X_{\text{Fe}} (X_{\text{Ca}} + X_{\text{Fe}} - X_{\text{Mn}}) \\ & W_{\text{CaFeMn}} \end{aligned} \quad (21)$$

and

$$\begin{aligned} \mu^{\text{ex}}(\text{Alm}) = & 2 X_{\text{Fe}} X_{\text{Mn}} (X_{\text{Mn}} + X_{\text{Ca}}) W_{\text{FeFeMn}} \\ & + X_{\text{Mn}}^2 (X_{\text{Mn}} + X_{\text{Ca}} - X_{\text{Fe}}) W_{\text{FeMnMn}} \\ & - 2 X_{\text{Mn}}^2 X_{\text{Ca}} W_{\text{MnMnCa}} - 2 X_{\text{Mn}} X_{\text{Ca}}^2 W_{\text{MnCaCa}} \\ & + X_{\text{Ca}}^2 (X_{\text{Mn}} + X_{\text{Ca}} - X_{\text{Fe}}) W_{\text{CaCaFe}} \\ & + 2 X_{\text{Ca}} X_{\text{Fe}} (X_{\text{Mn}} + X_{\text{Ca}}) W_{\text{CaFeFe}} \\ & + 2 X_{\text{Mn}} X_{\text{Ca}} (X_{\text{Mn}} + X_{\text{Ca}} - X_{\text{Fe}}) W_{\text{CaFeMn}}. \end{aligned} \quad (22)$$

Equations (14) to (16) are rewritten using equations (17) to (22) as follows:

$$\begin{aligned} \Delta \text{Gr}^\circ(1) + RT \ln(m(\text{CaCl}_2) X_{\text{Fe}} / m(\text{FeCl}_2) X_{\text{Ca}}) \\ = -2 X_{\text{Fe}} X_{\text{Mn}} W_{\text{FeFeMn}} - X_{\text{Mn}}^2 W_{\text{FeMnMn}} \\ + X_{\text{Mn}}^2 W_{\text{MnMnCa}} + 2 X_{\text{Mn}} X_{\text{Ca}} W_{\text{MnCaCa}} \\ + (2 X_{\text{Ca}} X_{\text{Fe}} - X_{\text{Ca}}^2) W_{\text{CaCaFe}} \\ + (-2 X_{\text{Ca}} X_{\text{Fe}} + X_{\text{Fe}}^2) W_{\text{CaFeFe}} \\ + (2 X_{\text{Fe}} X_{\text{Mn}} - 2 X_{\text{Mn}} X_{\text{Ca}}) W_{\text{CaFeMn}} \end{aligned} \quad (23)$$

$$\begin{aligned} \Delta \text{Gr}^\circ(2) + RT \ln(m(\text{MnCl}_2) X_{\text{Ca}} / m(\text{CaCl}_2) X_{\text{Mn}}) \\ = X_{\text{Fe}}^2 W_{\text{FeFeMn}} + 2 X_{\text{Fe}} X_{\text{Mn}} W_{\text{FeMnMn}} \\ + (2 X_{\text{Mn}} X_{\text{Ca}} - X_{\text{Mn}}^2) W_{\text{MnMnCa}} \\ + (-2 X_{\text{Mn}} X_{\text{Ca}} + X_{\text{Ca}}^2) W_{\text{MnCaCa}} \\ - 2 X_{\text{Ca}} X_{\text{Fe}} W_{\text{CaCaFe}} - X_{\text{Fe}}^2 W_{\text{CaFeFe}} \\ + (2 X_{\text{Ca}} X_{\text{Fe}} - 2 X_{\text{Fe}} X_{\text{Mn}}) W_{\text{CaFeMn}} \end{aligned} \quad (24)$$

$$\begin{aligned} \text{and } \Delta \text{Gr}^\circ(3) + RT \ln(m(\text{FeCl}_2) X_{\text{Mn}} / m(\text{MnCl}_2) X_{\text{Fe}}) \\ = (2 X_{\text{Fe}} X_{\text{Mn}} - X_{\text{Fe}}^2) W_{\text{FeFeMn}} + (-2 X_{\text{Fe}} X_{\text{Mn}} \\ + X_{\text{Mn}}^2) W_{\text{FeMnMn}} - 2 X_{\text{Mn}} X_{\text{Ca}} W_{\text{MnMnCa}} \\ - X_{\text{Ca}}^2 W_{\text{MnCaCa}} + X_{\text{Ca}}^2 W_{\text{CaCaFe}} \\ + 2 X_{\text{Ca}} X_{\text{Fe}} W_{\text{MnCaCa}} W_{\text{CaFeFe}} + (2 X_{\text{Mn}} X_{\text{Ca}} - 2 X_{\text{Ca}} \\ X_{\text{Fe}}) W_{\text{CaFeMn}}, \end{aligned} \quad (25)$$

where

$$\begin{aligned} \Delta \text{Gr}^\circ(1) \\ = \mu^\circ(\text{Alm}) + \mu^\circ(\text{CaCl}_{2\text{aq}}) - \mu^\circ(\text{Gro}) - \mu^\circ(\text{FeCl}_{2\text{aq}}) \end{aligned} \quad (26)$$

$$\begin{aligned} \Delta \text{Gr}^\circ(2) \\ = \mu^\circ(\text{Gro}) + \mu^\circ(\text{MnCl}_{2\text{aq}}) - \mu^\circ(\text{Spe}) - \mu^\circ(\text{CaCl}_{2\text{aq}}) \end{aligned} \quad (27)$$

$$\begin{aligned} \text{and } \Delta \text{Gr}^\circ(3) \\ = \mu^\circ(\text{Spe}) + \mu^\circ(\text{FeCl}_{2\text{aq}}) - \mu^\circ(\text{Alm}) - \mu^\circ(\text{MnCl}_{2\text{aq}}). \end{aligned} \quad (28)$$

Fig. 8. Excess Gibbs energies of mixing at 600°C and 1 kb, calculated using interaction parameters listed in Table 5-A. A: Almandine-spessartine solid solution, B: grossular-spessartine solid solution and C: grossular-almandine solid solution. Dashed lines show 1 σ deviation.

Interaction parameters W_{ijk} for the garnet solid solution and standard Gibbs energies of the reactions (1) to (3) can be obtained from the equations (23) to (25) by the least-square method using the binary and ternary ion exchange results. The results of the calculation are summarized in Table 5-A. For the comparison, interaction parameters obtained on the assumption that the molality of each neutral species is equal to the total molality of each cation are also listed in Table 5-B. The effect of the formation of $\text{FeCl}_3^-_{\text{aq}}$ and $\text{MnCl}_3^-_{\text{aq}}$ on the interaction parameters is considerable except for the almandine-spessartine system.

Fig. 8 shows excess Gibbs energies of mixing for the three binary garnet solid solutions calculated using interaction parameters in Table 5-A. The excess Gibbs energy of mixing for almandine-spessartine solid solution is slightly negative (Fig. 8-A), but grossular-spessartine solid solution shows positive deviation from ideality (Fig. 8-B). On the other hand, grossular-almandine solid solution shows positive deviation in the almandine side, but negative in the grossular side (Fig. 8-C).

Fig. 9 shows the excess Gibbs energy of mixing for the ternary almandine-spessartine-grossular solid solution calculated using the obtained interaction parameters (Table 5-A).

Table 5. Standard Gibbs energies of the ion exchange reactions and interaction parameters for garnet solutions at 600°C and 1 kb (kcal/mol of cation)

	(A)	(B)
W_{CaCaFe}	-1.091	-0.698
W_{CaFeFe}	1.140	1.852
W_{FeFeMn}	-0.238	-0.321
W_{FeMnMn}	-0.801	-0.841
W_{MnMnCa}	0.913	2.074
W_{MnCaCa}	0.454	1.336
W_{CaFeMn}	0.467	1.221
$\Delta G^\circ_r(\text{Gro-Alm})$	-0.993	-0.851
(s.d.)	(0.433)	(0.400)
$\Delta G^\circ_r(\text{Spe-Gro})$	1.610	1.209
(s.d.)	(0.262)	(0.213)
$\Delta G^\circ_r(\text{Alm-Spe})$	-0.375	-0.243
(s.d.)	(0.233)	(0.220)

(A) The molalities of the neutral aqueous species were calculated using the formation constants for $\text{FeCl}_3^-_{\text{aq}}$ and $\text{MnCl}_3^-_{\text{aq}}$ obtained by Uchida *et al.* (1995).

(B) Assumed that the total molality of each cation is equal to the molality of each neutral aqueous species.

*s.d.: standard deviation

It can be said that the garnet solid solution shows slight deviation from ideality.

V. Discussions

1. Unstable region of grossular-almandine-spessartine garnet solid solution

The equilibrium curve for the following reaction has been determined experimentally by Bohlen *et al.* (1983), Grafchikov and Fonarev

Fig. 9. Excess Gibbs energy of mixing (kcal/mol of cation) for grossular-almandine-spessartine solid solution at 600°C and 1 kb, calculated using interaction parameters in Table 5-A.

(1986), Anovitz and Essene (1987) and Berman (1990):

Extrapolation of their experimental results to lower pressures suggests that the equilibrium pressure for the reaction (29) is 2.5 to 3.7 kb at 600°C. The mineral assemblage fayalite + anorthite is stable at the lower pressures. The present experimental results at 1 kb are concordant with their experimental results.

No experiments have been carried out for the reaction anorthite + hedenbergite + wustite = garnet($\text{Gro}_{50}\text{Alm}_{50}$).

2. Mixing properties of garnet solid solutions

The excess Gibbs energy of mixing for almandine-spessartine solid solution was obtained by Ono (1980) and Pownceby *et al.* (1987, 1991) based on experimental studies of the partitioning of Fe and Mn between ilmenite and garnet. The exchange reaction can be expressed as

Fig. 10. Fe-Mn exchange isotherm between ilmenite and garnet solid solutions.

They gave -0.15 to 0.15 kcal/mol of cation as symmetric interaction parameter W_{FeMn} at 600 to 1,000°C and 2 to 10 kb, and concluded that almandine-spessartine solid solution behaves nearly ideally. From ionic size consideration, Ganguly and Kennedy (1974) also considered that spessartine mixes with almandine nearly ideally. The present experimental results show a small negative deviation ($W_{\text{FeFeMn}} = -0.24$ and $W_{\text{FeMnMn}} = -0.80$ kcal/mol) from ideality for almandine-spessartine solid solution.

Kubo *et al.* (1992) examined Fe-Mn exchange equilibrium between ilmenite and aqueous chloride solution at 600°C and 1 kb. Therefore, we can deduce the Fe-Mn exchange isotherm between ilmenite and garnet by combining their experimental data with the present results. The resultant isotherm is depicted in Fig. 10. The obtained isotherm is fairly concordant with that of Pownceby *et al.* (1987) at 600°C and 5 kb. As volume change for the reaction is very small (-0.0067 cm³/mol calculated from JCPDS card), the pressure effect can be neglected.

Fig. 11. Comparison of mixing property of grossular-almandine solid solution.

There are few studies on the mixing property of grossular-spessartine solid solution. Ganguly and Kennedy (1974) roughly estimated the mixing property of grossular-spessartine solid solution based on ionic radius, and concluded that grossular-spessartine solid solution has a small positive excess Gibbs energy of mixing ($0 < W_{\text{CaMn}} \ll 1.355$ kcal/mol). Based on displaced equilibrium experiments for the reaction $\text{anorthite} = \text{grossular} + 2\text{kyanite} + \text{quartz}$, Koziol (1990) concluded that grossular mixed with spessartine nearly ideally. The results presented here indicate a small positive deviation ($W_{\text{MnMnCa}} = 0.91$ and $W_{\text{MnCaCa}} = 0.45$ kcal/mol) from ideality.

There are several investigations on the mixing property of grossular-almandine solid solution (Fig. 11). Cressey *et al.* (1978) and Koziol (1990) obtained excess Gibbs energy of mixing for grossular-almandine solid solution by analyzing chemical compositions of garnet solid solution in equilibrium with anorthite, sillimanite/kyanite and quartz. Geiger *et al.* (1987) measured enthalpy of mixing for this series garnet using high-temperature solution calorimetry and calculated the excess Gibbs energy of mixing. Fig. 11 is obtained from

their experimental data on the assumption that interaction parameter for entropy is zero (Ganguly and Saxena, 1984). As a result, grossular-almandine solid solution shows positive deviation from ideality in the grossular side, but negative in the almandine side. This is obviously different from the present result which suggests that grossular-almandine solid solution shows positive deviation from ideality in the almandine side, but negative in the grossular side. Pownceby *et al.* (1991) gave positive deviation for grossular-almandine solid solution in the entire compositional range based on the experimental study of the Ca effect on Fe-Mn exchange equilibria between ilmenite and garnet. Thus, thermodynamic property for grossular-almandine solid solution obtained in the present study has large uncertainty due to a large unstable region of the garnet solid solution.

3. Summary and conclusions

- (1) Grossular and spessartine, and almandine and spessartine form continuous solid solutions at 600°C and 1 kb, respectively.
- (2) Mineral assemblages fayalite + anorthite and hedenbergite + anorthite + wustite are stable in the intermediate compositional range of the grossular-almandine join at 600°C and 1 kb.
- (3) Calcium ion is slightly preferentially partitioned into aqueous chloride solution against garnet solid solution compared with ferrous and manganese ions.
- (4) Almandine-spessartine solid solution shows slightly negative deviation from ideality, whereas grossular-spessartine solid solution shows slightly positive deviation.
- (5) Mixing property of grossular-almandine solid solution was not well determined due to the large unstable region.

Acknowledgements: We would like to express our sincere thanks to Emeritus Prof. R.

Otsuka and Prof. S. Tsutsumi of Waseda University for facilities of hydrothermal apparatus.

References

- Ackermann, D., Karl, F. and Raase, P. (1972), Granate mit Zusammensetzungen Zwischen Almandine und Grossular aus den westlichen Hohen Tauern, Österreich. *Contrib. Mineral. Petrol.*, **37**, 29-38.
- Anovitz, L.M. and Essene, E.J. (1987), Compatibility of geobarometers in the system CaO-FeO-Al₂O₃-SiO₂-TiO₂(CFAST). Implication for garnet mixing models. *J. Geol.*, **95**, 633-645.
- Berman, R.G. (1990), Mixing properties of Ca-Mg-Fe-Mn garnets. *Amer. Mineral.*, **75**, 328-344.
- Bohlen, S.R., Wall, V.J. and Boettcher, A.L. (1983), Experimental investigation and application of garnet granulite equilibria. *Contrib. Mineral. Petrol.*, **83**, 52-61.
- Brown, E.H. (1969), Some zoned garnets from the greenschist facies. *Amer. Mineral.*, **54**, 1662-1677.
- Cressey, G., Schmid, R. and Wood, B.J. (1978), Thermodynamic properties of almandine-grossular garnet solid solutions. *Contrib. Mineral. Petrol.*, **67**, 397-404.
- Frantz, J.D. and Marshall, W.L. (1982), Electrical conductances and ionization constants of calcium chloride and magnesium chloride in aqueous solutions at temperatures to 600°C and pressures to 4000 bars. *Amer. J. Sci.*, **282**, 1666-1693.
- Frantz, J.D. and Popp, R.K. (1979), Mineral-solution equilibria I. An experimental study of complexing and thermodynamic properties of aqueous MgCl₂ in the system MgO-SiO₂-H₂O-HCl. *Geochim. Cosmochim. Acta*, **43**, 1223-1239.
- Fron del, C. and Ito, J. (1965), Stilpnomelane and spessartine-grossularite from Franklin, New Jersey. *Amer. Mineral.*, **50**, 498-501.
- Ganguly, J. and Kennedy, G.C. (1974), The energetics of natural garnet solid solution: Mixing of aluminosilicate end-members. *Contrib. Mineral. Petrol.*, **48**, 137-148.
- Ganguly, J. and Saxena, S.K. (1984), Mixing properties of aluminosilicate garnets: constraints from natural and experimental data and application to geothermobarometry. *Amer. Mineral.*, **69**, 88-97.
- Geiger, C.A., Newton, R.C. and Kleppa, O.J. (1987), Enthalpy of mixing of synthetic almandine-grossular and almandine-pyropes from high-temperature solution calorimetry. *Geochim. Cosmochim. Acta.*, **51**, 1755-1763.
- Grafchikov, A.A. and Fonarev, V.I. (1986), Experimental evidence on coexisting garnet, clinopyroxene, and quartz in the FeO-CaO-Al₂O₃-SiO₂-H₂O system. *Geochem. Inter.*, **23**, 158-169.
- Hariya, Y. and Nakano, S. (1972), Experimental study of the solid solution between the grossular-almandine series. *J. Fac. Sci. Hokkaido Univ. Ser. IV*, **15**, 173-178.
- Helgeson, H.C. and Kirkham, D.H. (1974), Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. Debye-Huckel parameters for activity coefficients and relative partial molal properties. *Amer. J. Sci.*, **274**, 1199-1261.
- Hsu, L.C. (1980), Hydration and phase relations of grossular-spessartine garnets at P_{H₂O} = 2 Kb. *Contrib. Mineral. Petrol.*, **71**, 407-415.
- Ito, J. and Fron del, C. (1968), Synthesis of the grossular-spessartine series. *Amer. Mineral.*, **53**, 1036-1038.
- Kakuda, Y., Uchida, E. and Imai, N. (1991), A new thermodynamic model for ternary solid solutions. *J. Mineral. Soc. Japan*, **21**, 25-32 (in Japanese).
- Kakuda, Y., Uchida, E. and Imai, N. (1994), A new model of the excess Gibbs energy of mixing for a regular solution. *Proc. Japan Acad.*, **70**, Ser. B, 163-168.
- Kharaka, Y.K. and Barnes, I. (1973), SOLMNEQ; solution mineral equilibrium computations. *NTIS Technical Rep.*, **PB214-899**, 82 p.
- Koziol, A.M. (1990), Activity-composition relationships of binary Ca-Fe and Ca-Mn garnets determined by reversed, displaced equilibrium experiments. *Amer. Mineral.*, **75**, 319-327.
- Kubo, T., Uchida, E., Furukawa, Y. and Imai, N. (1992), Experimental study on ion exchange equilibria between ilmenite solid solution (Fe²⁺, Mn²⁺, Mg)/TiO₃ and aqueous (Fe²⁺, Mn²⁺, Mg)/Cl₂ solution. *J. Mineral. Soc. Japan*, **21**, 59-67 (in Japanese).
- Nemec, D. (1967), The miscibility of the pyrospite and grandite molecules in garnets. *Mineral. Mag.*, **36**, 389-402.
- Ono, A. (1980), Partitioning of Fe and Mn between garnet and ilmenite: an experimental study. *J. Japan. Assoc. Min. Petr. Econ. Geol.*, **75**, 160-160.
- Pownceby, M.I., Wall, V.J. and O'Neill, H.St.C. (1987), Fe-Mn partitioning between garnet and

- ilmenite: experimental calibration and applications. *Contrib. Mineral. Petrol.*, **97**, 116-126.
- Pownceby, M.I., Wall, V.J. and O'Neill, H.St.C. (1991), An experimental study of the effect of Ca upon garnet-ilmenite Fe-Mn exchange equilibria. *Amer. Mineral.*, **76**, 1580-1588.
- Shimazaki, H. (1977), Grossular-spessartine-almandine garnets from some Japanese scheelite skarns. *Can. Mineral.*, **15**, 74-80.
- Shoji, T., Tsukada, H. Mariko, T. and Kaneda, H. (1995), Immiscibility of the grossular-spessartine series under a water pressure of 100 MPa. *Mineral. J.*, **17**, 313-321.
- Uchida, E., Goryozono, Y., Naito, M. and Yamagami, M. (1995), Aqueous speciation of iron and manganese chlorides in supercritical hydrothermal solutions. *Geochem. J.*, **29**, 175-188.

600°C, 1 kb におけるザクロ石と 2N 塩化物水溶液間の Ca²⁺, Fe²⁺ および Mn²⁺ イオンの交換実験

内田 悦生・儀満 雅隆・今井 直哉

グロシュラー—アルマンディーン—スペサルティン系ザクロ石の安定関係と固溶に関する熱力学的性質を調べるために 600°C, 1 kb においてザクロ石と 2N 塩化物水溶液間における Ca²⁺, Fe²⁺ および Mn²⁺ イオンの交換実験を行った。実験結果は Ca²⁺ は Fe²⁺ および Mn²⁺ に比べて塩化物水溶液にやや濃集することを示した。また、グロシュラー—アルマンディーン—スペサルティン系ザクロ石ではグロシュラー—アルマンディーン系に沿った半円形の領域を除いて固溶体が生成された。この半円形の領域では、ザクロ石固溶体の代わりにファヤライト—灰長石およびヘデン輝石—灰長石—ウスタイトの鉱物組み合わせが出現した。塩化物水溶液中における FeCl₃^{-aq} と MnCl₃^{-aq} の存在を考慮に入れて実験結果からザクロ石固溶体の熱力学的性質を求めた結果、アルマンディーン—スペサルティン固溶体は理想固溶体から負のずれを示し、グロシュラー—スペサルティン固溶体は逆に正のずれを示した。グロシュラー—アルマンディーン固溶体の混合に関する熱力学的性質はこの系における広い不安定領域のため精度良く求めることができなかった。