

Synthesis of pyrope–grossular garnets: an experimental study at P = 2.5 GPa

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Received August 28, 2001; revised version accepted July 23, 2002

Published online February 24, 2003; © Springer-Verlag 2003

Editorial handling: B. de Vivo

Summary

In order to evaluate the stability of Mg–Ca garnets at P = 2.5 GPa/T = 800–1500 °C, some experiments were performed using both natural and synthetic starting materials. Particular attention was paid to the investigation of the Ca rich side of the pyrope–grossular join and the maximum pyrope content in grossular was found to be about 10 mol.%. The addition of Cr to the system only slightly increases the observed pyrope solubility in grossular whereas Na stabilises melilite and merwinite. Clinopyroxene with a composition lying on the diopside – Ca Tschermak join appears to be the only stable crystalline phase in the middle part of the pyrope–grossular join.

Introduction

The join pyrope ($\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$)–grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$) pertains to the CMAS system which is very important in modelling mantle petrology (e.g. *Yoder and Tilley, 1962; O'Hara, 1968; Sekine and Wyllie, 1983*). Furthermore, eclogitic garnets often consist of multicomponent solid solution (e.g. *Evans et al., 1979*). The miscibility between pyrope and grossular is therefore of some interest in high grade metamorphic petrology. In the past several experimental studies under crustal and upper mantle conditions were performed in order to determine phase relationships across the $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ – $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ join: they were performed at atmospheric pressure (*Chinner and Schairer, 1959*), at P = 1 GPa (*Yoder and Chinner, 1960*) and at P = 3 GPa (*Chinner et al., 1960; Boyd, 1970; Malinovskii et al., 1976; Maaløe and Wyllie, 1979; Sekine and Wyllie, 1983; Surkov and Gartvich, 1997*). Besides, *Ganguly et al. (1993)* and *Bosenick et al. (1995)* successfully synthesised

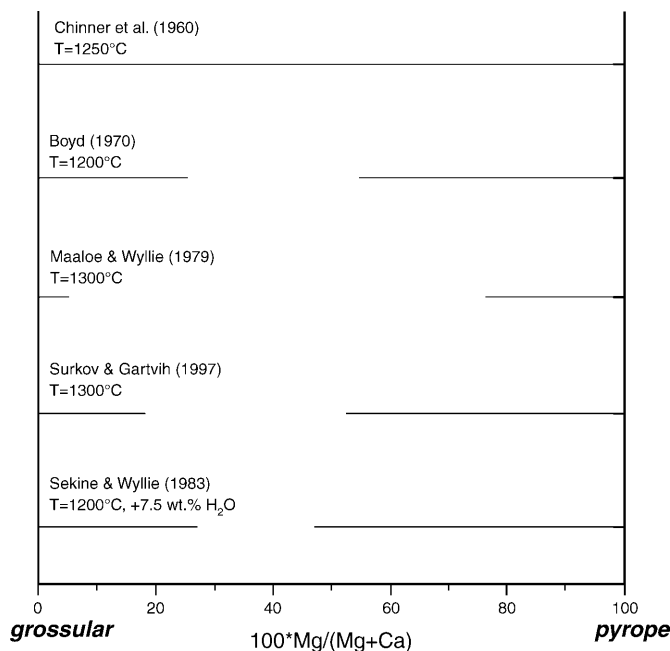


Fig. 1. Miscibility range (lines) between pyrope and grossular, as resulted from various experimental works at $P = 3$ GPa and $T = 1200$ – 1300 °C

homogeneous garnets of several intermediate compositions between pyrope and grossular at pressures up to 5 GPa, at $T = 1000$ – 1400 °C.

The results of the experimental studies performed at the highest pressure are not concordant (Fig. 1) probably because of the different starting materials used and the different amounts of water added to the runs. In fact, considering the anhydrous system at $P = 3$ GPa, *Chinner* et al. (1960) reported complete solid solution between pyrope and grossular at $T = 1250$ °C; *Boyd* (1970) at $T = 1200$ °C reported intermediate garnets (between 25 and 54 mol.% pyrope) to be unstable with respect to clinopyroxene whereas *Maaløe* and *Wyllie* (1979), using mixtures of synthetic pyrope and grossular as starting materials, reported the instability range to be between 5 to 76 mol.% pyrope at $T = 1300$ °C and 7 to 71 mol.% pyrope at $T = 1525$ °C. Considering the system pyrope–grossular – 7.5% H_2O , *Sekine* and *Wyllie* (1983) found a gap in the solid solution between 27 and 47 mol.% pyrope at $T = 1200$ °C while reporting complete solid solution for $T < 1100$ °C. *Surkov* and *Gartvich* (1997) reported complete solid solution below 1075 °C and a break at 1300 °C between 18 and 52 mol.% pyrope. In all these papers clinopyroxene is indicated as the main stable phase in the regions where no intermediate garnets are present.

Haselton and *Newton* (1980) studying the thermodynamics of pyrope–grossular solutions at $P = 3$ GPa evidenced that the solid solution region could be wider than that determined by *Boyd* (1970) and *Maaløe* and *Wyllie* (1979), even if uncertainties in the thermophysical properties values allow agreement with the experimental studies at $T > 1000$ °C. On the other hand, *Ganguly* et al. (1996), in their experimental work on the thermodynamics of aluminosilicate garnet solid solution, showed that the critical temperature (T_c) in pyrope–grossular system is about 625 °C at $P \leq 4$ GPa. *Wang* et al. (2000) report direct observation of immiscibility in Mg–Fe–Ca natural garnet formed at $P \sim 2.0$ GPa and T between 600 and 650 °C.

This observation is compatible with the thermodynamic solution properties deduced by *Ganguly et al. (1996)*.

At $P = 1$ GPa, *Yoder and Chinner (1960)* found the only stable garnet to be a grossular with a maximum pyrope content between 5 and 11 mol.% whereas *Chinner and Schairer (1959)* did not detect any stable garnet across the join at atmospheric pressure and $T > 1000$ °C.

The aim of the present study is to investigate the pyrope–grossular join at P intermediate between 1 and 3 GPa; 2.5 GPa was chosen also on the basis of the work of *Evans et al. (1979)* who reported the presence of garnets from 84 pyralspite – 16 ugrandite to 42 pyralspite–58 ugrandite in eclogites and metarodriguesites from Cima di Gagnone (Ticino, Switzerland), which were inferred to have equilibrated at $T = 800$ °C and $P \sim 2.5$ GPa. The experiments were performed mostly between 1100 and 1500 °C in order to enhance chemical reactivity. Both synthetic and natural starting materials were utilised, and in a few runs the system was made chemically complicated by adding the components Cr_2O_3 and Na_2O .

Experimental methods

The following chemical reagents (from Aldrich) were used to prepare synthetic starting materials: SiO_2 (>99.995%), Al_2O_3 (>99.99%), MgO (>99.99%), CaCO_3 (>99.95%). All reagents were dried at 110 °C prior to weighing. Mixtures with the following bulk compositions were prepared: $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (*py*), $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ (*gr*), $\text{Mg}_{0.75}\text{Ca}_{2.25}\text{Al}_2\text{Si}_3\text{O}_{12}$ (*py25gr75*), $\text{Mg}_{1.20}\text{Ca}_{1.80}\text{Al}_2\text{Si}_3\text{O}_{12}$ (*py40gr60*), $\text{Mg}_{2.25}\text{Ca}_{0.75}\text{Al}_2\text{Si}_3\text{O}_{12}$ (*py75gr25*). Using chemical reagents Cr_2O_3

Table 1. *Experimental conditions and results. All the runs were performed at $P = 2.5$ GPa*

N°	Starting material	T (°C)	Duration*	Phases detected
110	<i>py</i>	1400	1 ^h , 20 ^m , 4 ^h 40 ^m	Gr _t (100), glass
111	<i>gr</i>	1400	1 ^h , 20 ^m , 4 ^h 40 ^m	Gr _t (0), glass
125	<i>py25gr75</i>	1500	1 ^h	Gr _t (8), Cpx(33–37), glass
120		1400	1 ^h , 20 ^m , 4 ^h 40 ^m	Gr _t (8), Cpx(32–33), glass
126			1 ^h , 10 ^m , 28 ^h	Gr _t (7–8), Cpx(30–37), glass
123		1350	1 ^h , 30 ^m , 4 ^h 30 ^m	Gr _t (5–10), Cpx(28–43), glass
137		1100	1 ^h , 40 ^m , 28 ^h 20 ^m	Gr _t (6–8), Cpx(34–42), Crn, Qtz, glass
132	<i>Cr-py25gr75</i>	1400	1 ^h , 20 ^m , 27 ^h 40 ^m	Gr _t (12–14), Cpx(30–32), glass
136	<i>Na-py25gr75</i>	1400	1 ^h , 20 ^m , 28 ^h 40 ^m	Cpx(29–31), glass
138		1300	1 ^h , 40 ^m , 27 ^h 20 ^m	Mel(14–17), Cpx(31–38), Gr _t (7), Merw(23–24), glass
122	<i>py40gr60</i>	1400	1 ^h , 20 ^m , 4 ^h 40 ^m	Cpx(37–41), glass
127			1 ^h , 40 ^m , 28 ^h 20 ^m	Cpx(34–41), glass
134		1100	15 ^m , 40 ^m , 30 ^h 5 ^m	Cpx(38–42), glass
145		800	1 ^h , 2 ^h 20 ^m , 96 ^h 40 ^m	Cpx(36–41), Gr _t (1–5), (glass)
135	<i>py40grnat60</i>	1350	30 ^h (<i>no pre-heating</i>)	Cpx(36–40), Crn, glass
113	<i>py75gr25</i>	1400	1 ^h , 20 ^m , 4 ^h 40 ^m	Gr _t (82–87), Cpx(51–62)

Mineral symbols after *Kretz (1983)*; *Merw* merwinite. Numbers in parentheses refer to the 100* $\text{Mg}/(\text{Mg} + \text{Ca})$. * = duration at $T = 1500$ °C, during cooling to the stated value and at the stated value respectively

Table 2. Representative EPMA analyses of synthetic garnets. Py = pyrope, Uv = uvarovite

Run	111	125	120	126	123	123	137
Start. Mat.	<i>gr</i>	<i>py25gr75</i>	<i>py25gr75</i>	<i>py25gr75</i>	<i>py25gr75</i>	<i>py25gr75</i>	<i>py25gr75</i>
T(°C)	1400	1500	1400	1400	1350	1350	1100
SiO ₂	40.49	41.24	40.79	41.22	40.53	40.47	40.80
Al ₂ O ₃	22.74	22.56	22.32	22.93	22.99	22.73	22.67
MgO	–	2.21	2.19	2.25	2.77	1.81	2.20
CaO	37.57	34.99	35.09	34.41	33.92	35.50	34.35
Cr ₂ O ₃	–	–	–	–	–	–	–
Na ₂ O	–	–	–	–	–	–	–
Sum	100.80	101.00	100.39	100.81	100.21	100.51	100.02
<i>Cations on the basis of 12 oxygens</i>							
Si	3.008	3.031	3.022	3.030	2.998	2.999	3.025
Al	1.995	1.958	1.953	1.990	2.008	1.989	1.985
Mg	–	0.242	0.242	0.247	0.306	0.200	0.243
Ca	2.991	2.755	2.785	2.709	2.688	2.818	2.729
Cr	–	–	–	–	–	–	–
Na	–	–	–	–	–	–	–
Sum	7.994	7.990	8.002	7.975	7.999	8.006	7.982
<i>Mol. %</i>							
Py	0.00	8.08	7.99	8.34	10.21	6.63	8.19
Uv	–	–	–	–	–	–	–

(>98%) and Na₂CO₃ (>99.5% heated at 950 °C for 4 hours to convert Na₂CO₃ into Na₂O), the *py25gr75* composition was complicated adding 5 wt.% of either Cr₂O₃ (*Cr-py25gr75*) or Na₂O (*Na-py25gr75*). In order to increase the kinetic of the reactions, in the runs performed at 1100 °C about 25 wt.% H₂O was added to the experimental charges.

A run was also performed using natural grossular from Asbestos (Quebec, Canada) kindly provided by the Mineralogical Section of the Natural History Museum, Florence (the average and standard deviation of 4 electron microprobe analyses in wt.% is: SiO₂ = 39.17 ± 0.38, TiO₂ = 0.42 ± 0.03, Al₂O₃ = 21.96 ± 0.05, Cr₂O₃ = 0.03 ± 0.03, FeO = 1.55 ± 0.16, MnO = 0.59 ± 0.04, MgO = 0.03 ± 0.01, CaO = 35.89 ± 0.30). The experimental charge (*py40grnat60*) had a bulk composition corresponding to *py40gr60* and was prepared mixing natural grossular (*grnat*) to chemical reagents. In this experiment pre-heating at T = 1500 °C (see below) was not performed in order to preserve the garnet lattice.

All experiments were performed in a 0.5" piston-cylinder using 3.0 mm diameter Pt capsules and a salt-pyrex sleeve; a modified "hot piston out" procedure was followed. Temperature was measured by a Pt₁₀₀-Pt₉₀Rh₁₀ thermocouple; no correction for the effect of pressure was applied to the thermocouple emf, and on the basis of *Presnall et al. (1973)* no correction for drifting was deemed necessary. For most of the runs, the temperature was initially held at 1500 °C for 1 h in order to approach superliquidus conditions, decreased at a rate variable between 2.5 and 10 °C/min down to the desired value and maintained for durations ranging from

137 <i>py25gr75</i> 1100	145 <i>py40gr60</i> 800	145 <i>py40gr60</i> 800	132 <i>Cr-py25gr75</i> 1400	132 <i>Cr-py25gr75</i> 1400	113 <i>py75gr25</i> 1400	138 <i>Na-py25gr75</i> 1300	138 <i>Na-py25gr75</i> 1300
40.68	40.59	40.19	39.28	39.70	43.62	41.20	41.64
22.76	22.04	22.29	18.16	19.60	25.40	22.75	22.40
1.99	0.45	1.29	3.73	3.80	24.23	1.96	1.97
35.15	37.52	36.05	32.25	32.98	7.22	34.74	34.74
–	–	–	6.70	4.29	–	–	–
–	–	–	–	–	–	0.26	0.72
100.58	100.60	99.82	100.12	100.37	100.47	100.91	101.47
3.008	3.020	3.004	2.969	2.974	2.972	3.032	3.050
1.987	1.936	1.967	1.621	1.734	2.044	1.977	1.938
0.219	0.050	0.144	0.420	0.424	2.462	0.215	0.215
2.784	2.991	2.887	2.611	2.647	0.527	2.738	2.726
–	–	–	0.400	0.254	–	–	–
–	–	–	–	–	–	0.037	0.102
7.999	7.997	8.002	8.021	8.032	8.006	7.999	8.032
7.31	1.64	4.75	13.87	13.82	82.37	7.28	7.32
–	–	–	19.81	12.78	–	–	–

4.5 to 96 hours. Pressure was calibrated using the reaction ferrosilite = fayalite + quartz at $T = 1000\text{ }^{\circ}\text{C}$ (Bohlen et al., 1980). Further experimental details can be found in Orlando and Borrini (2001).

All the synthetic products were analysed with a JEOL JXA-8600 electron microprobe using an accelerating voltage of 15 kV, a beam current of 10 nA, and counting times ranging from 20 to 40 seconds. Data were corrected for the matrix effect using the Bence and Albee (1968) method and errors were estimated according to Vaggelli et al. (1999).

Experimental results

The experimental results obtained using the different starting materials are shown in Table 1 together with the ranges in $100^*\text{Mg}/(\text{Mg} + \text{Ca})$ values for the detected phases. Representative analyses for garnets, clinopyroxenes, melilites and merwinites, are reported in Tables 2, 3, and 4 respectively. Besides garnet, the main phase found in the products is clinopyroxene with a composition lying on the join diopside–Ca Tschermak; this is due to the intersection of pyrope–grossular join with the diopside–Ca Tschermak join, as shown in the enstatite–wollastonite– Al_2O_3 section of the CMAS system (Fig. 2).

Pure end-members (run 110 and 111, Table 1) are easily synthesised and they are the only mineral phases among the products. Difficulties arise when trying to

Table 3. Representative analyses of synthetic clinopyroxenes. Di = diopside, Ca-Ts = Ca Tschermak, Jd = Jadeite, bdl = below detection limit

Run	125	120	123	137	122	134	145	135	113	132	136	138
Start. Mat.	py25gr75	py25gr75	py25gr75	py25gr75	py40gr60	py40gr60	py40gr60	py40grmat60	py25gr75	Cr-py25gr75	Na-py25gr75	Na-py25gr75
T(°C)	1500	1400	1350	1100	1400	1100	800	1350	1400	1400	1400	1300
SiO ₂	44.08	41.91	40.25	45.82	41.47	46.70	43.36	43.43	50.35	39.82	38.77	45.22
TiO ₂	-	-	-	-	-	-	-	0.17	-	-	-	-
Al ₂ O ₃	19.65	23.67	26.20	16.90	23.89	14.57	21.48	21.47	13.08	24.08	23.19	19.88
Cr ₂ O ₃	-	-	-	-	-	-	-	bdl	-	2.51	5.43	-
FeO	-	-	-	-	-	-	-	0.33	-	-	-	-
MnO	-	-	-	-	-	-	-	0.16	-	-	-	-
MgO	10.13	9.23	7.53	11.52	10.67	13.25	10.88	11.11	15.59	8.56	7.64	10.07
CaO	26.25	25.52	25.99	26.09	24.21	25.22	24.88	23.48	20.79	25.26	24.67	24.02
Na ₂ O	-	-	-	-	-	-	-	0.21	-	-	0.73	1.14
Sum	100.11	100.33	99.97	100.33	100.24	99.74	100.60	100.36	99.81	100.23	99.70	100.33
<i>Cations for 6 oxygens</i>												
Si	1.596	1.512	1.461	1.653	1.488	1.688	1.552	1.559	1.810	1.448	1.433	1.621
Al ^{IV}	0.404	0.488	0.539	0.347	0.512	0.312	0.448	0.441	0.190	0.552	0.567	0.379
Sum T	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Al ^{VI}	0.435	0.518	0.582	0.372	0.498	0.309	0.457	0.468	0.364	0.480	0.443	0.460
Fe ³⁺	-	-	-	-	-	-	-	0.000	-	-	-	-
Ti	-	-	-	-	-	-	-	0.005	-	-	-	-
Mg	0.547	0.482	0.408	0.620	0.488	0.688	0.541	0.528	0.636	0.448	0.398	0.538
Cr	-	-	-	-	-	-	-	0.000	-	0.072	0.159	-
Fe ²⁺	-	-	-	-	-	-	-	0.000	-	-	-	-
Sum M1	0.982	1.000	0.989	0.992	0.986	0.997	0.998	1.000	1.000	1.000	1.000	0.999

(continued)

Table 3 (continued)

Run	125	120	123	137	122	134	145	135	113	132	132	136	138
Start. Mat.	py25gr75	py25gr75	py25gr75	py25gr75	py40gr60	py40gr60	py40gr60	py40gr60	py25gr75	Cr-py25gr75	Cr-py25gr75	Na-py25gr75	Na-py25gr75
T(°C)	1500	1400	1350	1100	1400	1100	800	1350	1400	1400	1400	1400	1300
Na	—	—	—	—	—	—	—	0.015	—	—	—	0.051	0.079
Mn	—	—	—	—	—	—	—	0.005	—	—	—	—	—
Ca	1.018	0.986	1.011	1.008	0.931	0.977	0.954	0.903	0.801	0.984	0.977	0.961	0.922
Fe ²⁺	—	—	—	—	—	—	—	0.010	—	—	—	—	—
Mg	0.000	0.014	0.000	0.000	0.083	0.026	0.040	0.067	0.199	0.016	0.023	0.054	0.000
Sum M2	1.018	1.000	1.011	1.008	1.014	1.003	0.993	1.000	1.000	1.000	1.000	1.066	1.001
M1 + M2	2.000	2.000	2.000	2.000	2.000	2.000	1.992	2.000	2.000	2.000	2.000	2.000	2.000
O	6.015	6.015	6.021	6.012	6.000	6.000	6.003	6.011	6.087	6.000	6.018	6.000	6.001
Di	0.56	0.48	0.41	0.63	0.49	0.69	0.54	0.53	0.64	0.48	0.47	0.34	0.49
Ca-Ts	0.44	0.52	0.59	0.37	0.51	0.31	0.46	0.47	0.36	0.52	0.53	0.60	0.42
Jd	—	—	—	—	—	—	—	—	—	—	—	0.05	0.09
Mg/(Mg+Ca)	0.35	0.33	0.29	0.38	0.38	0.42	0.38	0.40	0.51	0.32	0.30	0.29	0.37

Table 4. *Representative analyses of melilites and merwinites*

Run	138	138	138	138	138	
Phase	melilite	melilite	melilite	merwinite	merwinite	
Start. Mat.	<i>Na-py25gr75</i>	<i>Na-py25gr75</i>	<i>Na-py25gr75</i>	<i>Na-py25gr75</i>	<i>Na-py25gr75</i>	
T(°C)	1300	1300	1300	1300	1300	
SiO ₂	41.26	41.36	40.37	37.11	38.15	
Al ₂ O ₃	17.10	17.31	18.41	2.22	5.97	
MgO	4.50	3.82	4.22	10.61	9.43	
CaO	31.61	30.27	31.50	48.61	44.90	
Na ₂ O	5.98	6.67	5.60	1.09	2.54	
Sum	100.45	99.43	100.10	99.64	100.99	
<i>Cations per 7 oxygens</i>			<i>Cations per 8 oxygens</i>			
Si	1.814	1.832	1.779	Si	2.017	2.012
Al	0.888	0.905	0.958	Al	0.142	0.372
Mg	0.295	0.252	0.277	Mg	0.860	0.742
Sum	2.997	2.990	3.014	Ca	2.830	2.536
				Na	0.115	0.260
Ca	1.489	1.437	1.487	Sum M	5.965	5.922
Na	0.510	0.573	0.478			
Sum	1.999	2.010	1.965			
				Mg/(Mg + Ca)	0.23	0.23
Sum cations	4.997	5.002	4.979			
<i>End-members (mol.%):</i>						
Akermanite	29.69	25.45	28.22			
Gehlenite	19.02	16.77	23.10			
Soda melilite	51.29	57.78	48.68			
Mg/(Mg + Ca)	0.17	0.15	0.16			

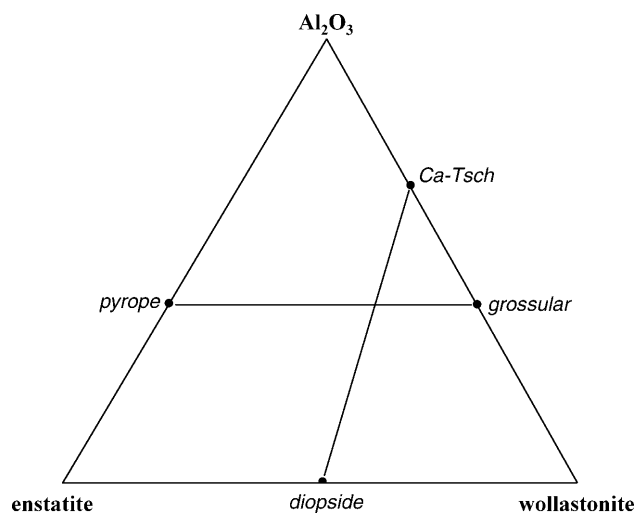


Fig. 2. The enstatite–wollastonite–Al₂O₃ section of the CMAS system. The intersection of pyrope–grossular join with the diopside–Ca Tschermak join (Ca-Tsch) is shown

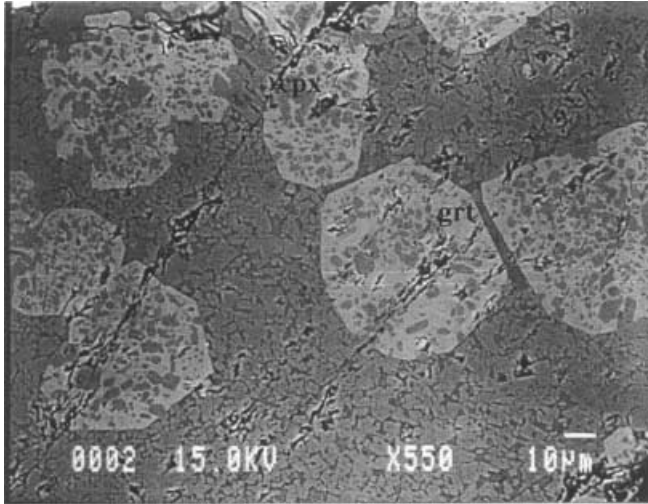


Fig. 3. Electron microprobe microphotography showing large garnet (grt) crystals including clinopyroxenes (cpx). Interstitial glass is also observable [Run 123, P = 2.5 GPa, T = 1350 °C, *py25gr75* starting material]

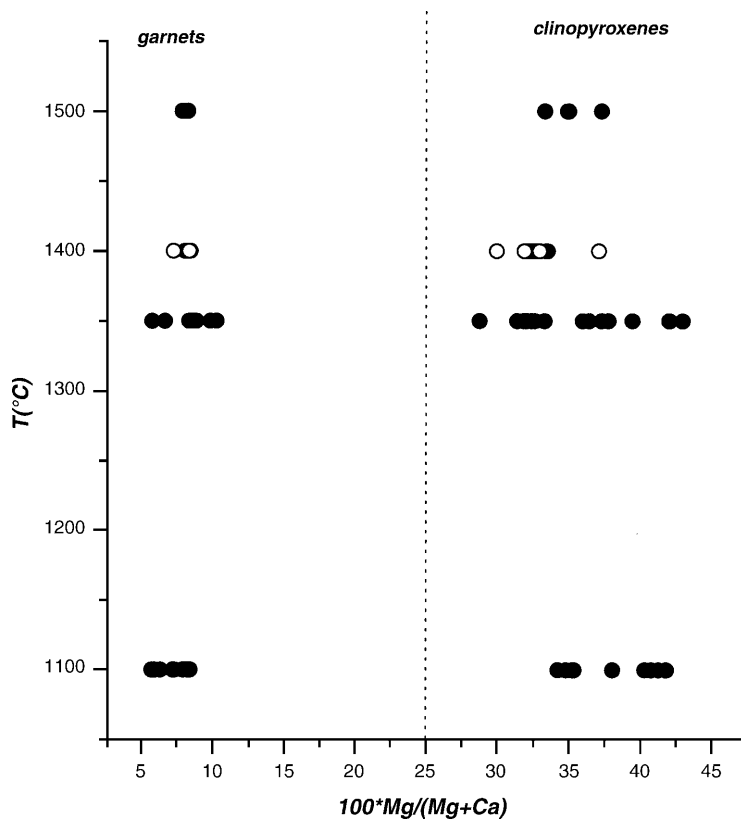


Fig. 4. 100 * Mg / (Mg + Ca) vs T plot for garnets and clinopyroxenes synthesised using *py25gr75* starting material (dotted line). Open and solid circles at 1400 °C represent analyses of runs 126 (long duration) and 120 (short duration) respectively

synthesise garnets with intermediate compositions. Using the *py25gr75* starting material, the synthesised euhedral garnets (up to 80 μm) with a pyrope contents in the 6–10 mol.% range coexist with subeuhedral clinopyroxene (generally less than 10 μm) often including them (Fig. 3). These results are in agreement with *Maaløe* and *Wyllie* (1979) who performed some reversal experiments to bracket the phase boundary and reported a maximum pyrope content in grossular of about 8 mol.% at $P = 3$ GPa. The results are summarised in Fig. 4 in which temperature is plotted against $100^* \text{Mg}/(\text{Mg} + \text{Ca})$ for both phases. The scatter of the data generally increases with decreasing T from 1500 to 1350 $^{\circ}\text{C}$ because of the sluggish kinetics at lower temperatures. At $T = 1100$ $^{\circ}\text{C}$ the water added to the charges increased reaction kinetics so that data are less scattered compared to the results obtained at $T = 1350$ $^{\circ}\text{C}$. Nevertheless, the presence among the run products of scarce unreacted starting materials (Table 1) points out that equilibrium was only approached but not fully achieved. These data clearly indicate that solid solution of pyrope in grossular is limited under the explored P-T conditions; in fact at $P = 2.5$ GPa and $T \geq 1100$ $^{\circ}\text{C}$, and starting from the grossular end, continuous solid solution of garnet extends to ~ 10 mol.% pyrope. Furthermore, the solubility between the two end-members appears to be rather constant in the range 1350–1500 $^{\circ}\text{C}$, the average values being about 8 pyrope mol.%, and slightly

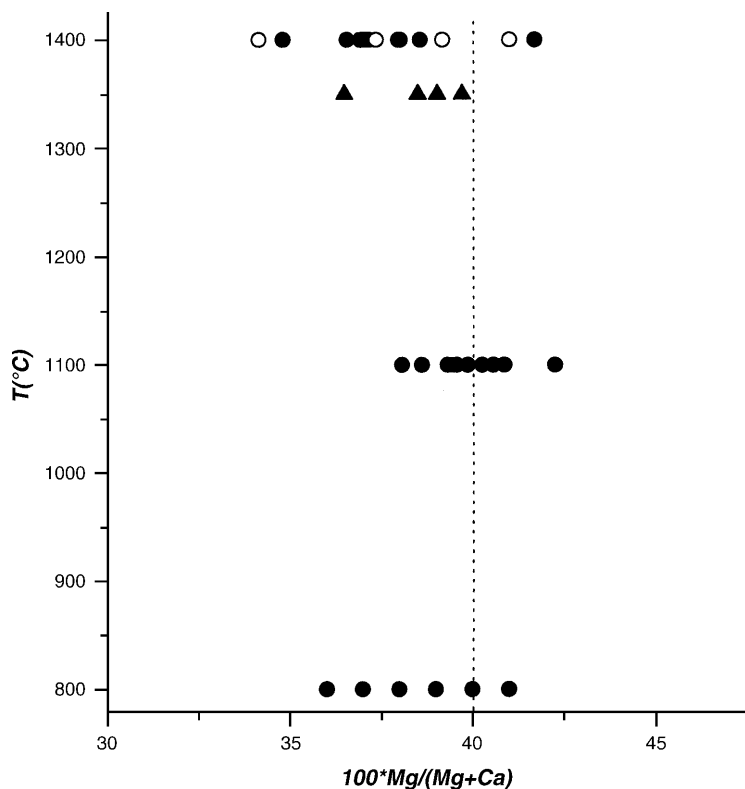


Fig. 5. $100^* \text{Mg}/(\text{Mg} + \text{Ca})$ vs T plot for clinopyroxenes synthesised using *py40gr60* (circles) and *py40grnat60* (triangles) starting materials (dotted line). Open and solid circles at 1400 $^{\circ}\text{C}$ represent analyses of runs 127 (long duration) and 122 (short duration) respectively

decreasing to 7 mol.% at 1100 °C. Correspondingly, $100^*Mg/(Mg + Ca)$ average values for clinopyroxenes are about 35 for $T \geq 1350$ °C and slightly increase to 37 at $T = 1100$ °C.

Using the *py40gr60* starting material, garnet was found only in the lowest temperature run (800 °C) as almost pure grossular ($100^*Mg/(Mg + Ca) = 1 - 5$, Table 1); in all the other runs clinopyroxene and glass were the only phases detected. The $100^*Mg/(Mg + Ca)$ values for clinopyroxenes are reported in Fig. 5, together with the values obtained at 1350 °C using the *py40grnat60* starting material. The average values range from 37–38 at 1350–1400 °C to 40 at 1100 °C; this is due to the presence of decreasing amounts of glass with decreasing T so that clinopyroxenes composition approaches ideality at the lowest T. The results for the synthetic + natural starting material fit well the trend depicted by the data collected using the synthetic starting material. In the run at 1350 °C, very rare crystals of corundum were found as remnants of unreacted starting material due to the fact that pre-heating to 1500 °C was not carried out in this experiment.

Finally, in the run performed using *py75gr25* starting material, pyrope rich garnets (82–87 mol.%, Tables 1–3) coexisting with clinopyroxenes ($100^*Mg/(Mg + Ca) = 51–62$) were found. No glass was detected because of the higher refractory nature of pyrope with respect to grossular.

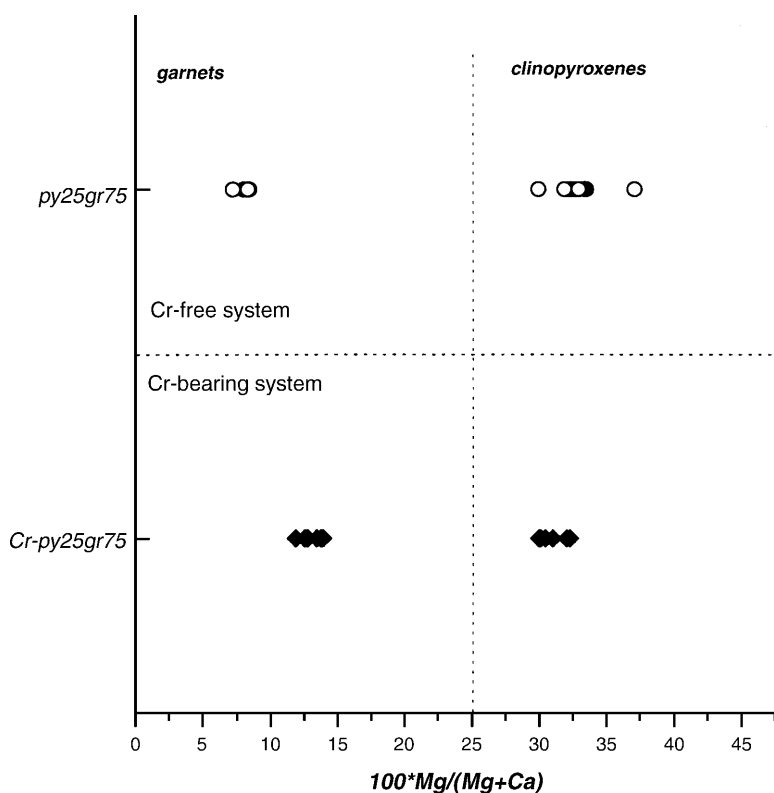


Fig. 6. $100^*Mg/(Mg + Ca)$ for garnets and clinopyroxenes using the *Cr-py25gr75* starting material at 1400 °C (diamonds). The results are compared with the same phases from Cr-free experiments at the same T

Attempts to increase the solubility between pyrope and grossular were made by adding additional components. Cr was chosen because its entry into the M1 site of clinopyroxene could vary its $Mg/(Mg + Ca)$ value; furthermore, its entry as uvarovite component in garnet could change its $Mg/(Mg + Ca)$ value, possibly extending the miscibility between pyrope and grossular end-members. The phases detected in the experimental products obtained from the Cr-doped starting material (*Cr-py25gr75*) at $T = 1400^\circ\text{C}$ are the same as in the experiment performed in the Cr-free system at the same temperature (Tables 2–3). These results are depicted in Fig. 6 where $100 * Mg/(Mg + Ca)$ values of garnets and clinopyroxenes are compared with the values of the same phases obtained at the same T in the Cr-free system. The pyrope contents for garnets in Cr-doped system are rather constant being in the range 12–14 mol.%; these values are a little bit higher than the values obtained using the Cr-free system while the $100 * Mg/(Mg + Ca)$ values for clinopyroxenes are similar for both systems.

Na component was chosen because its entry in the M2 site of clinopyroxene as jadeite component (Ca substitute) could again affect its $Mg/(Mg + Ca)$ ratio and possibly change the same ratio in garnet. In the experiment performed at 1400°C no garnet was formed (Fig. 7), whereas few crystals of clinopyroxenes (with the same $Mg/(Mg + Ca)$ ratio of the clinopyroxenes synthesised in Na-free

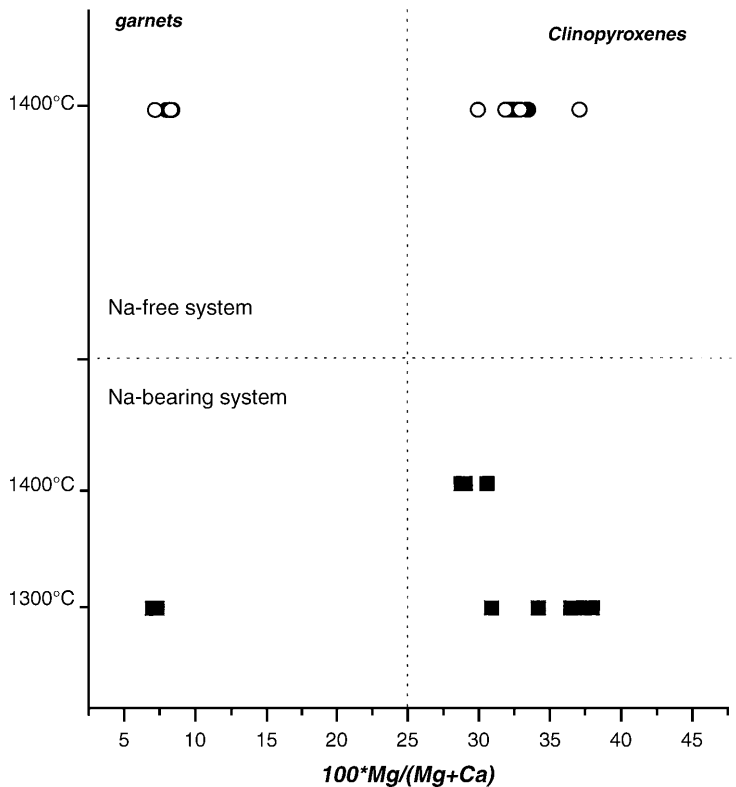


Fig. 7. $100 * Mg/(Mg + Ca)$ for garnets (left) and clinopyroxenes using the *Na-py25gr75* starting material at 1400 and 1300°C (squares). The results are compared with the same phases from Na-free experiments at 1400°C

system) coexist at the liquidus with a great amount of homogeneous glass. At lower T (1300 °C) this scenario changes completely: subeuhedral crystals of melilite (akermanite = 22–30 mol.%, gehlenite = 17–24 mol.%, soda melilite = 49–59 mol.%, Table 4) and clinopyroxene ($100^* \text{Mg}/(\text{Mg} + \text{Ca}) = 31\text{--}38$) coexist with minor garnet (7 mol.% pyrope) and merwinite crystals, beside very small amounts of glass. In clinopyroxenes of both experiments Na enters as jadeite component with values in the range 0.04–0.10 mol.% (Table 3).

Discussion and conclusions

Attainment of equilibrium

Even if reversal experiments were not performed, the following considerations suggest that, in general, run products may not be far from equilibrium conditions:

- a) experiments performed at the same temperature for different durations (run 120–run 126, run 122–run 127, Table 1) yielded the same phases with almost the same chemical compositions;
- b) experiments performed at similar P-T conditions using different starting materials (synthetic or synthetic + natural; runs 122, 127–run 135, Table 1) produced mainly the same phases with very similar chemical compositions.

Stability of pyrope–grossular garnets

The present study clearly reveals that at $P = 2.5$ GPa and $T \geq 1100$ °C, mixed pyrope–grossular garnets are stable only for end-member rich compositions, the extent of solid solution between grossular and pyrope appearing to be greater on the Mg-rich side in accordance with the experimental data for 3 GPa (Boyd, 1970; Maaløe and Wyllie, 1979; Sekine and Wyllie, 1983; Surkov and Gartvich, 1997).

Clinopyroxene with a composition lying on the diopside–Ca Tschermak join is a stable phase at all the intermediate compositions since the relatively high temperatures allow the entrance of tetrahedral Al needed to compensate the Si deficiency in the clinopyroxene lattice (e.g. White, 1964; Herzberg and Chapman, 1976). Moreover, for a relatively Mg-rich composition (*py40gr60* starting material) the only stable crystalline phase at $T \geq 1100$ °C is a clinopyroxene with a $100^* \text{Mg}/(\text{Mg} + \text{Ca})$ varying between 34 and 42. This suggests that the field in which clinopyroxene is the only stable phase is wider at $P = 2.5$ GPa than at 3.0 GPa. In fact, in the experiments performed at this latter pressure, Maaløe and Wyllie (1979) found clinopyroxene as the only stable phase in the range 33–37 mol.% pyrope.

The results of the Cr and Na doped experiments performed in the Ca-rich region with the aim to significantly increase the compositional range for pyrope–grossular garnets were not fully satisfactory. The addition of 5 wt.% Cr_2O_3 , in fact, only slightly increased the maximum pyrope content in grossular (from 7–8 to 12–14 mol.%, Table 2) whereas the addition of 5 wt.% Na_2O did not affect garnet composition but stabilised “exotic” phases such as melilite and merwinite (Table 1). The presence of melilite is in agreement with the study of Velde and Yoder (1976) on the chemical composition of melilite-bearing eruptive rocks. These authors

reported that the addition of alkalis to a nephelinite composition could produce a melilite-bearing lava; the *Na-py25gr75* starting material has in fact a composition of a nephelinite having 39.14 wt.% SiO₂, 4.76 wt.% Na₂O and a normative nepheline content equal to 21.81.

These findings are not in contrast with *Miyashiro's* (1994) results that Ca and Mg substitute almost completely in natural Ca–Mg–Fe–Mn garnets equilibrated at $P \geq 3$ GPa and $T > 1000$ °C. Moreover *Evans et al.* (1979) give equilibration temperature and pressure estimates of 800 °C and ~ 2.5 GPa for eclogites and garnet peridotites containing Ca–Mg–Fe–Mn garnets.

On the other hand, *Ganguly et al.* (1996) showed that the critical temperature (T_c) of the pyrope–grossular solvus lies at ~ 625 °C at $P \leq 4$ GPa. It is evident therefore that no miscibility gap exists in the P–T range investigated in the present work and the observed reduced stability of intermediate Ca–Mg garnets is to ascribe to extrinsic instability (e.g. *Ganguly and Saxena*, 1987). This holds at least down to 1100 °C since *Ganguly et al.* (1993) succeeded in synthesising Ca–Mg garnets in almost the entire compositional range from glasses under hydrous conditions at $P = 2.5$ GPa at $T = 1000$ °C. Nonetheless, a certain degree of clinopyroxene metastability cannot be excluded in our experiments because of the relatively high cooling rate below 1500 °C. The poor kinetic efficiency of solid state reactions in the run performed at 800 °C may have hindered an extended garnet crystallisation thus preserving metastable clinopyroxene crystals.

In conclusion, assuming that the run duration were adequate to closely approach equilibrium, the results of this work (combined with the results of the past experimental papers) suggest that is improbable that mixed garnets between *py10gr90* and *py85gr15* are stable in natural systems equilibrated at $P \leq 3$ GPa and $T \geq 1100$ °C.

Acknowledgements

The authors wish to thank *L. Ungaretti*, *S. Conticelli*, and *M. Boiocchi* for useful discussions and *F. Olmi* for electron microprobe analyses. A review by *J. Ganguly* has significantly improved the manuscript. The work is part of a research program supported by Italian MURST through “Cofin 1998” (national and local coordinators are *C. A. Ricci* and *S. Tommasini*, respectively) and by C.N.R. through grant #9800584CT11.

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