

Mn-Mg OLIVINES OF LÅNGBAN-TYPE AND THEIR SYNTHETIC EQUIVALENTS

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ABSTRACT: Tephroites and Mn-Mg olivines are the major olivines in the Långban ore region, while forsterite is rare. Forsterite solid solution in tephroite varies over a wide range, from $\text{Fo}_{60}\text{Te}_{40}$ to pure tephroite. Compositions in the range of $\text{Fo}_{90}\text{Te}_{10}$ to $\text{Fo}_{60}\text{Te}_{40}$ have not been encountered in the studied population of 30 samples. Most of the Mn-Mg olivines, especially those from the Långban mine, have a nearly ideal "picrotephroite" composition which is half-way between forsterite and tephroite. With occasional exceptions the olivines may be considered as binary systems with only subordinate amounts of other cations which makes it possible to determine cation ordering from plotting a- against b-axis and to estimate the crystallisation temperature. The Långban "picrotephroites" are approximately 62–94% ordered, with a mean ordering of 75%. Such extensive ordering implies that the crystallisation temperature of the olivines could not have been very high. Synthesis experiments have been performed in the forsterite-tephroite system at temperatures below 700° C and at a pressure of 1 kbar. The results are not very conclusive because of the sluggishness of the reactions but they may suggest a temperature range of 500–600° C and moderate to low pressures for the formation of the Långban "picrotephroites".

Key words/phrases: Binary system, cation-ordering, miscibility gap, solid solution, synthesis experiments

INTRODUCTION

The Långban district (Fig. 1), which includes the deposits of Långban, Pajsberg/Harstign and Jakobsberg, is presently a dump area and is located near the town of Filipstad in Värmland, south-central Sweden. The deposit is well known for its great diversity of mineral species, especially rare minerals, which probably resulted from the presence of certain cations usually not found together, such as Mn, As, Sb, Ba and Be (Moore, 1970).

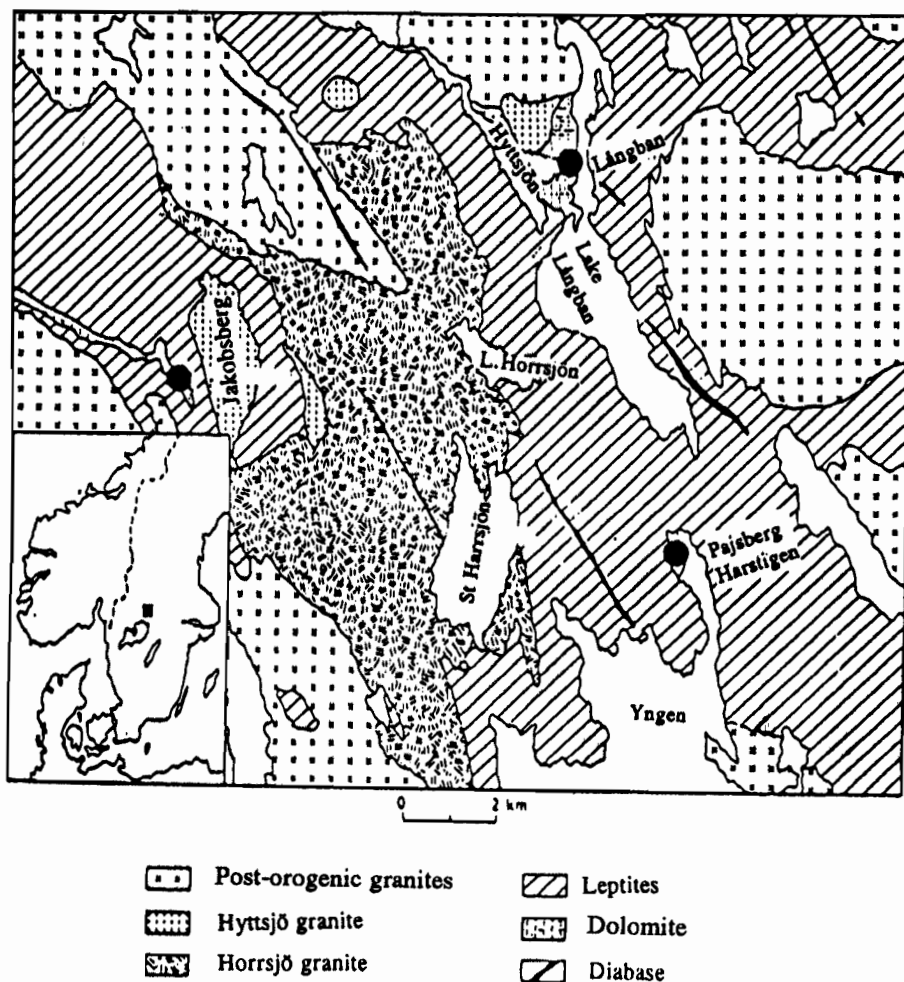


Fig. 1. Geological map of the Långban ore district [after Magnusson (1925), a simplified version].

Iron and manganese ores, which are the major ores of the Långban district, occur in the lower part of the Svecofennian supracrustal formation, which consists of a limestone- and dolomite-bearing leptite complex. To the supra-

crustal formation also belong slates, graywackes, hällflintas and spilitic greenstones.

The later rocks, granitic intrusions, and regional folding provided heat for metamorphic and metasomatic reactions which affected the whole of the Långban ore district. All rocks older than intrusives show extensive folding and fracturing. The rocks hosting the Fe and Mn ores are variously metamorphosed, ranging from the greenschist to the amphibolite facies and, at places, even to granulite facies.

The iron and manganese ores, which are in proximity with each other but well separated, are accompanied by characteristic reaction skarn silicates. Of the skarn silicates accompanying the iron ores, andradite, diopside and tremolite constitute the major ones. The manganese skarns consist primarily of Mn-bearing phases of andradite, diopside, aegirine-augite, richterite, mica, tephroitic olivines and of rhodonite.

Of the multitude of Mn-bearing rock-forming minerals of the Långban district, Mn-Mg olivines have been dealt with in this study. Other Mn-bearing skarn silicates, such as micas and glaucochroite from the same locality, have been dealt with elsewhere (Endale Ketefo, 1989; 1995).

Pure tephroites and solid solution phases intermediate between tephroite and forsterite, so-called "picrotephroites" (Pajkull, 1877), are among the more common skarn minerals accompanying the manganese ores of the Långban district, Filipstad. Picrotephroite is not an internationally valid mineral name but will be used throughout this paper as a convenient term for compositions close to $\text{Fo}_{50}\text{Te}_{50}$.

Pajkull's (1877) original analysis of what he labelled picrotephroite yielded 12.17 wt% MgO , corresponding to only 26 mol% of forsterite. In 1918, Magnusson published an analysis of picrotephroite containing 39 mol% forsterite. The most Mg-rich variety (66.6 mol% forsterite) published so far was analyzed by R. Blix, Stockholm, and referred to by Sundius (1963). All these picrotephroites are from the Långban district. In a recent paper, Francis (1985)

reported olivine compositions from Långban spanning over nearly the entire forsterite-tephroite series.

Mg-rich tephroites are also known from Franklin and Ogdensburg, New Jersey. These olivines are, however, not binary because they contain substantial amounts of Zn (Francis, 1985).

In the present investigation 31 samples of Mn-Mg olivines of various paragenetical types from Långban and its satellite localities were used to study the frequency of different solid solution compositions in an attempt to establish possible miscibility gaps in the binary tephroite-forsterite system.

The potential use of intracrystalline cationic distribution in olivine structures as geothermometers has recently attracted the attention of mineralogists and petrologists. The general criteria governing cation ordering in olivines are ionic size differences (Ghose, 1962), the degree of covalent bonding (Ghose *et al.*, 1975) and crystal field effects (Burns, 1970). In the case of Mn-Mg olivines only the first-mentioned criterion is important. The difference in size between the two octahedral cations involved (Mn, 0.83 Å; Mg, 0.72 Å) is much larger than that between Mg and Fe (0.78 Å). In the forsterite-fayalite series, the degree of cationic ordering is therefore much less pronounced.

Lumpkin and Ribbe (1983) constructed a diagram based upon the lengths of crystallographic a- and b-axes, from which the degree of cation ordering can be quantified. In a slightly modified version this diagram has been used in this paper to study the order-disorder relations of the same suite of Mn-Mg olivines as mentioned above. Hydrothermal synthesis experiments were also carried out in an attempt to relate the degree of cation ordering in Mn-Mg olivines to temperature of formation.

EXPERIMENTAL PROCEDURE

The chemical composition of the olivines was determined using a scanning electron microscope equipped with energy-dispersive spectrometer (EDS). Based

on four oxygens, the number of octahedral cations are shown in Table 1. For intermediate compositions, the standard deviation of the given values is $\pm 2\%$.

Table 1. Octahedral composition of Mg-Mn olivines from the Långban ore district.

Nop	Sample	Loc.	Octahedral cation proportions			Mg(Mg + Mn) ⁻¹ × 100
			Ca	Mn	Mg	
1	g15952a	J	-	0.08	1.92	96
2	140537	L	-	0.12	1.88	94
4	640974	L	-	0.82	1.18	59
3	170717	L	-	0.86	1.14	57
5	10100	L	-	0.86	1.14	57
6	g15935	L	-	0.88	1.12	56
7	g15952b	J	-	0.90	1.10	55
8	620758	L	-	0.90	1.10	55
9	g15934	L	-	0.94	1.06	53
10	140523	L	-	0.94	1.06	53
11	571021	L	-	0.96	1.04	52
12	251441	L	-	0.96	1.04	52
13	15879	L	-	0.98	1.02	51
14	170718	L	-	1.00	1.00	50
15	65:0083	P	0.02	1.02	0.96	48
16	090232	L	-	1.06	0.94	47
17	g15913	P	-	1.16	0.84	42
17a	255879	L	-	1.18	0.82	41
18	6778	P	0.09	1.11	0.80	40
19	670802	L	0.05	1.19	0.76	38
20	g15961	P	-	1.28	0.72	36
21	251242	L	-	1.36	0.64	32
22	74:0211	P	-	1.40	0.60	30
23	280344	L	-	1.42	0.58	29
24	332308	L	-	1.56	0.44	22

Table 1. (Contd).

Nop	Sample	Loc.	Octahedral cation proportions			Mg(Mg+Mn) ⁻¹ x100
			Ca	Mn	Mg	
25	g15976	P	-	1.70	0.30	15
26	670970	L	-	1.76	0.24	12
27	532657	P	-	1.80	0.20	10
28	331794	P	-	1.84	0.16	08
29	331825	P	-	1.86	0.14	07
30	532633	P	0.10	1.80	0.10	05

Abbreviations: Nop, Numbers of points on Fig. 2; L, Långban; J, Jakobsberg; P, Pajsberg.

Unit cell dimensions (Table 2) were calculated from X-ray powder diffraction data. The well-powdered specimen was mixed with a silicon internal standard ($\text{CuK}\alpha_1 = 1.5405 \text{ \AA}$) and run on a Philips X-ray diffractometer unit (PW 1730) equipped with a crystal monochromator. A Nova 4/X-type computer was employed to compute the cell parameters from the powder data using the CELREF programme (Nord and Forsberg, 1982). The estimated standard deviation is less than 0.005 Å.

Table 2. Observed cell parameters and estimated site occupancy of Långban and synthetic Mg-Mn olivines.

Nop	Sample	a(Å)	b(Å)	c(Å)	Mg(Mg+Mn) ⁻¹ (%)		Cation dist.		order (%)
					obs	from a-b	%Mg in M1	%Mn in M2	
3	170717	4.787	10.496	6.122	57	57.5	98	83	94
6	g15935	4.794	10.478	6.117	56	56.5	89	76	76
7	g15952b	4.800	10.499	6.124	55	51.5	85	82	70
8	620758	4.800	10.492	6.128	55	52.5	85	80	69
9	g15934	4.809	10.502	6.132	53	48.0	77	81	62
10	140523	4.795	10.498	6.129	53	54.0	90	82	78
11	571021	4.794	10.496	6.125	52	55.0	92	82	81

Table 2. (Contd).

Nop	Sample	a(Å)	b(Å)	c(Å)	Mg(Mg+Mn) ⁻¹ (%)		Cation dist.		order (%)
					obs	from a-b	%Mg in M1	%Mn in M2	
12	251441	4.798	10.502	6.132	52	52.0	87	83	72
13	15879	4.800	10.512	6.137	51	50.5	87	86	73
14	170718	4.802	10.513	6.138	50	49.5	85	86	71
16	090232	4.799	10.535	6.143	47	48.0	88	92	84
17	g15913	4.818	10.533	6.160	42	41.0	71	89	73
17a	255879	4.814	10.544	6.166	41	41.5	76	93	83
18	6778	4.814	10.537	6.158	40	42.5	76	91	78
20	g15961	4.835	10.540	6.180	36	34.5	58	89	66
24	332308	4.859	10.585	6.202	22	20.5	39	98	85
F1	F6	4.773	10.351	6.055	77	78.0	99	43	85
F2	F8	4.782	10.406	6.083	68	68.5	94	57	80
F3	F10	4.810	10.540	6.149	46	44.0	80	92	83
F4	F11	4.827	10.549	6.170	37	36.0	64	92	80
G1	G&W	4.811	10.421	6.116	53	55.0	67	57	24
N1	N&M	4.818	10.447	6.130	50	50.0	64	64	25
N2	N&M	4.855	10.536	6.204	25	27.0	38	84	40
N3	N&M	4.782	10.339	6.063	75	74.5	87	38	45
E1	409	4.814	10.485	6.148	47	47.5	71	76	48
E2	410	4.868	10.577	6.212	12	18.0	31	95	64
E3	001	4.879	10.602	6.243	6	10.5	20	98	85
E4	002	4.895	10.611	6.235	3	4.5	08	99	90

Abbreviation: Nop, numbers of points on Fig. 2; Obs, observed; a-b, determination from the a-b plot after Lumpkin *et al.* (1983); F1-F2, correspond to F6, F8, F10 and F11 in Lumpkin *et al.* (1983); G&W, synthetic Mg-Mn olivine heat treated at 1000° C (Ghose and Weidner, 1974); N&M, Mg-Mn olivine synthesized at 1300° C (Nishizawa and Matsui, 1972); E1-E4, synthetic Mg-Mn olivines (this study).

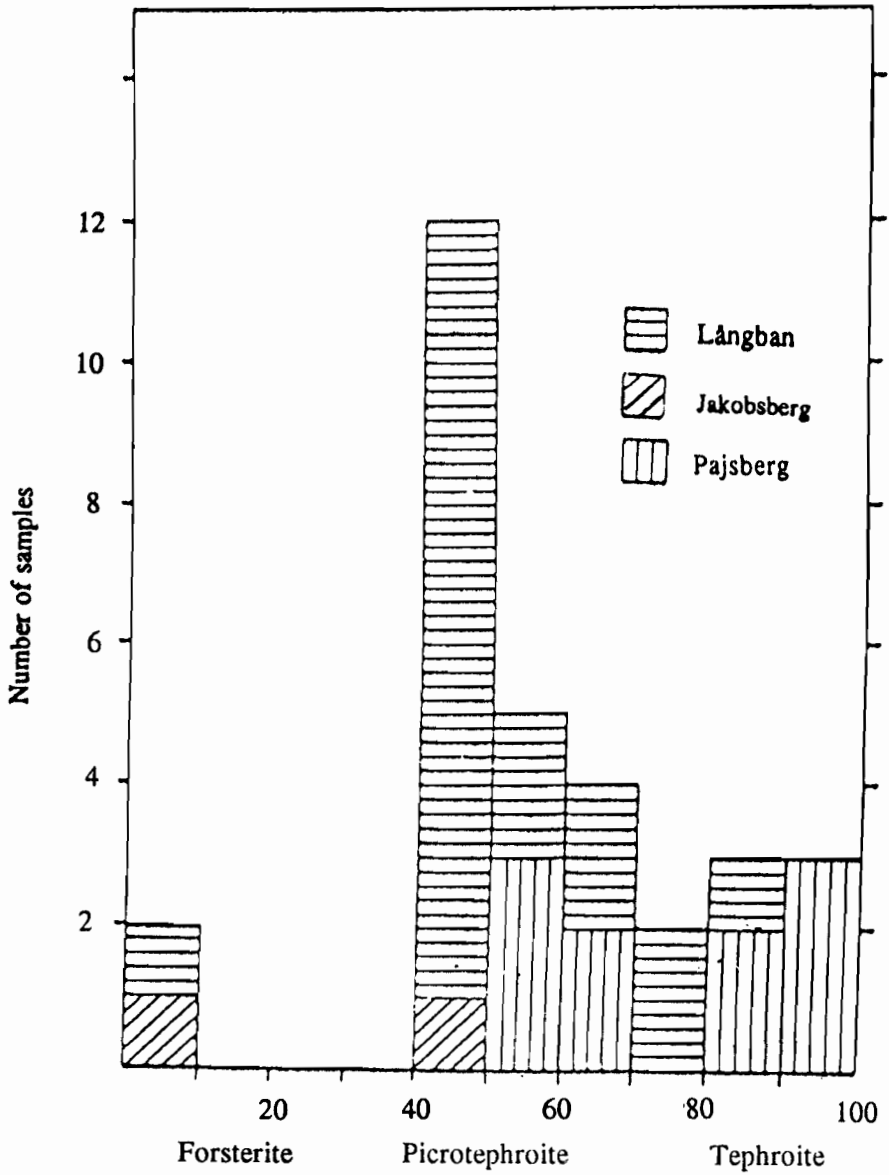


Fig. 2. Distribution of Mn-Mg olivines in the Långban ore region.

Synthetic olivines were obtained by heating fine-grained oxide mixtures (MnO, MgO, SiO₂) in autoclaves using water as pressure medium (T=500–700° C, P=1kb). The samples were kept in gold capsules to which trace amounts of water was added to promote crystallization. Run times varied from 1.5 hours to one week in most cases and 3 to 4 weeks in a few cases. A chromel-alumel thermocouple, believed to be accurate within $\pm 5^\circ$ C, was used to measure temperature of the samples. When the desired run time was attained, the oven was removed from the sample causing the temperature to drop and quenching the reaction.

Brief description of the Mn-Mg olivine samples

The investigated olivines were all selected from the collections of the Swedish Museum of Natural History. A brief description of these olivines is given in the Appendix. The sample labels refer to catalogue numbers.

Composition of the Mn-Mg olivines of the Långban region

From the chemical analysis of the studied Mn-Mg olivines, the numbers of octahedral cations were calculated on the basis of four oxygens as compiled in Table 1. The forsterite solid solution in tephroite seems to vary over a wide range, from picrottephroite of composition Fo₆₀Te₄₀ to pure tephroite (Fig. 2). With respect to composition and frequency the population may be split into four groups: 1) tephroites, 2) forsterites, 3) picrottephroites and 4) phases intermediate between tephroite and picrottephroite. The peak of frequency is clearly located at compositions of nearly ideal picrottephroite, especially for samples from the Långban mine. The Pajsberg samples, on the other hand, are more or less evenly distributed along the range from pure tephroite to picrottephroite. The forsterite group, finally, contains only two samples with a maximum tephroite content of 6%.

Figure 2 suggests the existence of a miscibility gap between forsterite Fo₉₀Te₁₀ and picrottephroite Fo₆₀Te₄₀ and an increased stability of the picrottephroite structure as compared to Mg-richer varieties. The gap could possibly be due to a compositional bias in the sampling. In analogy with an investigated population of manganoan phlogopites (Endale Ketefo, 1989) which show a rather continuous decrease in the Mn:Mg ratio, olivines intermediate between picrottephroite and forsterite should still be expected to be found, if stable. Francis (1985) who studied a smaller population of Långban olivines, reports

a composition of $\text{Fo}_{77}\text{Te}_{23}$, thus indicating a continuous solid solution series, possibly initiated by a local temperature increase.

The Mn-Mg olivines of the Långban region are nearly binary systems containing only subordinate amounts of Al and Fe (less than 4% and 1% of the octahedral sites, respectively). Leaving aside the Ca-rich tephroite observed at Långban and Jakobsberg (Endale Ketefo, 1995), an earlier unknown mineral, small amounts of Ca has also been noted in four of the Mn-Mg olivines (less than 5% of the octahedral sites). In forsterite-rich olivines, calcium is present in concentrations rarely exceeding one weight percent CaO (Simkin and Smith, 1970). The calcium content is usually higher in Mn-Fe olivines than in forsterites, and calcium concentrations up to 2.32 (Smith *et al.*, 1944) and 2.63 wt% CaO (Nambu *et al.*, 1966) in tephroite and knebelite ($\text{Fa}_{66}\text{Te}_{34}$) respectively have been reported. These values correspond to an occupancy of 4% and 4.6% of the octahedral sites respectively. Unlike the olivines at Franklin, New Jersey, which contain up to 13 wt. % ZnO (Francis, 1985), Långban Mg-Mn olivines are almost Zn-free.

Cation ordering in Långban Mn-Mg olivines

The olivine structure consists of a slightly distorted hexagonal close packed array of oxygen anions in which one-half of the available octahedral sites are filled with divalent cations and one-eighth of the tetrahedral sites are filled with silicon cations. The major structural feature is the zigzag chains of two occupied octahedra (M1 & M2) parallel to the c-axis, the M1 octahedron being located at centres of symmetry and the M2 octahedron forming mirror planes in the structure. The SiO_4 tetrahedron shares its basal edges with two M1 and one M2 octahedra (Fig. 3)

Brown *et al.* (1970) observed negative departure from linearity in a plot of the a-axis length against mean octahedral cation radius, and Ganguli (1977) recognized a positive deviation from linearity in a similar plot of the b-axis length. With the help of regression equations, $a = 0.932r(\text{M1}) + 0.236r(\text{M2}) + 3.918$ and $b = 0.505r(\text{M1}) + 3.211r(\text{M2}) + 7.535$, Lumpkin and Ribbe (1983) defined the effect of cation ordering on unit cell parameters. The regression equations show that the a-axis length is highly dependent on the size of the M1 cations, while the b-axis is mainly affected by the size of the M2

cations. On the basis of these variations in the a- and b-axes, Lumpkin and Ribbe (1983) constructed a plot to predict cation ordering in Mn-Mg olivines. When applying the regression equations to the binary Mn-Mg olivine system, the obtained values have to be corrected to fit the observed unit cell dimensions of the two end-members, as has also been done by Lumpkin and Ribbe (1983). Using the average of the end-member corrections, the dimensions of a fully ordered intermediate compound of picrotephroite composition, $MnMgSiO_4$, may be calculated.

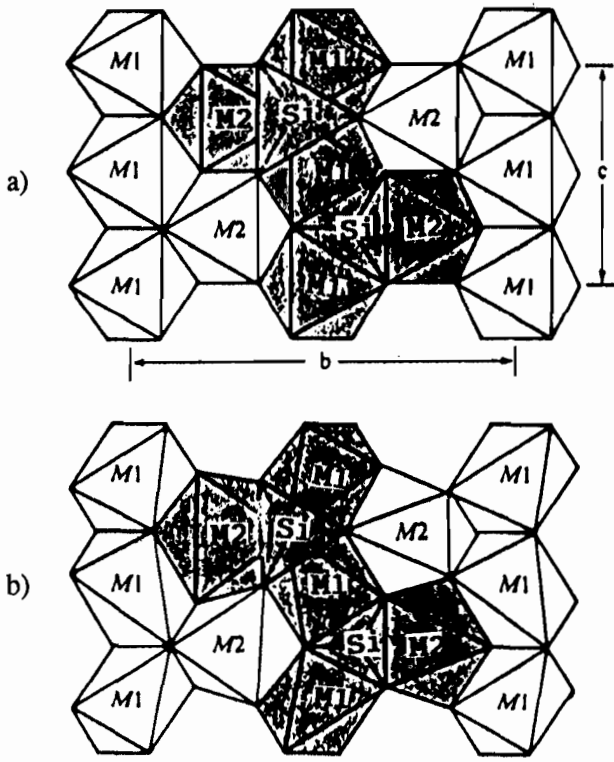


Fig. 3. Olivine structure parallel to (100) plane showing relationship of (a) ideal hexagonal close packing model, (b) actual structure (after Hazen, 1976).

For the present studies, calculated values of this intermediate phase have then been used to construct the diagram in Fig. 4. This diagram slightly differs from that given by Lumpkin and Ribbe (1983) in as much as the plotted tephroite data represent mean values of four tephroites ($a=4.904 \text{ \AA}$, $b=10.618 \text{ \AA}$, $c=6.259 \text{ \AA}$), synthesized at the present laboratory. The plotted b-axis of pure tephroite is thus 10.618 \AA as compared to the value 10.598 \AA used by Lumpkin and Ribbe (1983), whereas the a-axis is the same (4.904 \AA). For forsterite are chosen the same averaged values ($a=4.753 \text{ \AA}$, $b=10.193 \text{ \AA}$) as used by Lumpkin and Ribbe (1983).

In the a-b plot (Fig. 4), the points for cell parameters of the forsterite end-member, the tephroite end-member and the fully ordered MgMnSiO_4 phase ($a=4.791 \text{ \AA}$, $b=10.555 \text{ \AA}$, as calculated) are joined by broken lines, representing completely ordered phases, whereas the straight line between forsterite and tephroite represents completely disordered olivines. The NW-SE running lines represent each the locus of samples with constant total Mg content. From the position of a point on such a line, the degree of ordering can be read. The ordering, expressed as number of Mn ions per M2 site, may also be read for varying total compositions along lines drawn parallel to the join Mn_2SiO_4 -ordered MgMnSiO_4 . The usefulness of the diagram is at best for intermediate olivine compositions but is successively restricted when approaching the pure end-members.

The unit cell dimensions of 16 intermediate Mn-Mg olivines from the Långban region were refined with a standard deviation usually better than ± 0.003 and not exceeding ± 0.005 (Table 2).

When plotting the obtained values in the a-b diagram, the degree of cation ordering in these olivines may be predicted to vary between 62 and 94%. The mean value is 75%, pointing to such extensive ordering that it would be justified to regard intermediate olivine of picrotephroite type as a separate mineral according to accepted nomenclature rules.

Earlier similar determinations, performed on Långban olivines by Lumpkin *et al.* (1983), yielded still higher values of ordering centred around 90%. This deviation, however, is just an effect of the alternative choice of unit cell parameters for pure tephroite used in the construction of the diagram.

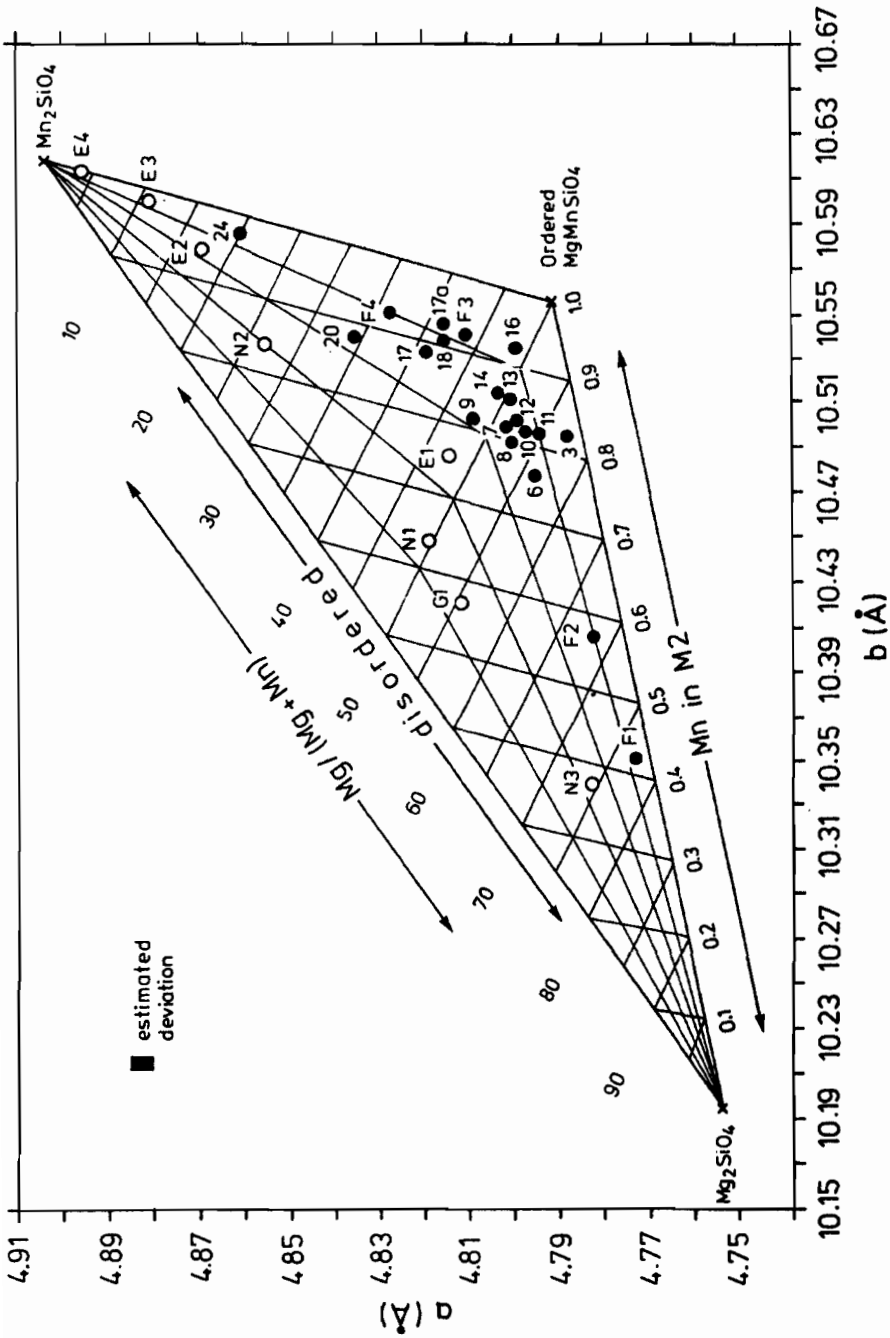


Fig. 4. An a-b plot constructed for natural (from Langban ore region) and synthetic Mn-Mg olivines (after Lumpkin *et al.*, 1983). Open and filled circles refer respectively to synthetic and natural olivines. Data for the plot is given in Table 2.

As the total octahedral composition also may be read from the a-b plot, the reliability of the diagram may be evaluated by comparison with the actually observed analytical figures (Tables 1 and 2). Taking into account the errors in unit cell parameters (generally less than ± 0.003 Å) and in the chemical measurements (less than ± 1 mole %), the agreement seems to be fairly good except for a couple of samples. Such an exception is sample g15934 for which the lowest degree of ordering has been recorded (62%).

Synthesis of solid solutions of tephroite and forsterite

On the basis of synthesis experiments along the join $\text{Mg}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4$, Glasser and Osborn (1960) concluded that the system was characterized by complete solid solution between the two olivine end members and that the liquidus and solidus temperatures rose regularly from the melting point of tephroite (1345° C) to that of forsterite (1890° C). Nishizawa and Matsui (1972) prepared intermediate solid solutions $(\text{Mg,Mn})_2\text{SiO}_4$ from mixtures of the end-members by heating them under controlled oxygen fugacity at 1300° C for half a day, with the aim of studying cation distribution over the non-equivalent octahedral sites.

All the synthetic studies hitherto done on the forsterite-tephroite join are related to high temperatures ($> 1000^\circ$ C). Here it is dealt with syntheses within the same system but at low temperatures (450–700° C) in order to examine the extent of solid solubility of Mg in tephroite and the impact of run time on olivine crystallization. An attempt to relate the degree of cation ordering in Mn-Mg olivines to temperature of formation has also been done.

The experimental conditions and results are compiled in Tables 3 and 4. The reactions involved in the formation of intermediate olivine from oxide mixtures are very sluggish in character. Short runs produce far from complete olivine yield which is witnessed by the presence of unreacted oxides. The chance of attaining equilibrium states is small even at prolonged duration of the experiments. Despite this and despite difficulties in analysing fine-grained synthetic products it is still possible to draw some limited and tentative conclusions from the experiments.

Table 3. Hydrothermal runs in the system Mn_2SiO_4 - Mg_2SiO_4 .

Run no.	Cationic prop.			Run time	Temp. ($^{\circ}$ C)	P bar	Crystalline products
	Mn:	Mg:	Si:				
517	1	1	1	33 days	450	1000	tep, (for), bru
516	1	1	1	10 days	500	1000	tep, for, pic, bru
001	1	1	1	4 days	520	1000	tep,(for)(pic) bru
002	1.5	0.5	1	4 days	520	1000	tep, (for)
003	0.5	1.5	1	4 days	520	1000	tep for bru pyr
407	1	1	1	2 days	580	1000	tep (for) bru
408	0.5	1.5	1	2 days	580	1000	(tep) (for) bru
409	0.8	1.2	1	2 days	580	1000	pic, (for) (tep)
505	1	1	1	42 hours	600	1000	tep for pic bru
508	0.5	1.5	1	2 hours	600	1000	tep (for)
506	0.5	1.5	1	42 hours	600	1000	for, tep, bru
509	1.5	0.5	1	2 hours	600	1000	tep for bru
507	1.5	0.5	1	42 hours	600	1000	tep, (for), bru
510	0.5	1.5	1	7 days	600	1000	for, (tep)
511	1.5	0.5	1	7 days	600	1000	tep,pic,for, (kan)
503	1	1	1	7 days	650	800	tep,for,pic
501	1	1	1	21 days	650	1500	tep,pic,kan,(for)
410	1	1	1	5 days	700	1300	tep,for,pic,(kan)

Abbreviations: tep, tephroite; for, forsterite; bru, brusite; pyr, pyroxene; kan, kanoite; pic, picrotephroite.

DISCUSSION AND CONCLUSION

In spite of low yield, X-ray powder diffraction patterns of the synthetic products repeatedly reveal the presence of at least two phases with a composition close to the two end-members (Fig. 5). With proceeding crystallization the formation of additional olivine with intermediate composition is usually observed, with the exception of the most Mn-poor bulks which seem to be least reactive. Even though the yield is generally limited, it is thus possible to trace the formation of a picrotephroite phase at such a low temperature as 500° C. The erratic

character of the results, compiled in Tables 3 and 4, is not only obvious from the unexplainable variation of the intermediate olivine composition (which could partially be due to analytical difficulties) but also from the fact that the only really good yield was obtained from the run 409 of rather short duration at the moderate temperature of 580° C. Anyway, the successful synthesis of this intermediate olivine indicates that its stability is higher than the end-member pair, at the expense of which it was formed. It also shows that extraordinarily high temperatures need not be involved in the picrotephroite formation.

Table 4. The Mn content of the synthetic olivine phases*.

Run no.	bulk Mn%	temp ° C	time hours	100Mn/(Mn+Mg)			100Mn/(Mn+Mg)		
				Te	Pic	Fo	Te	Pic	Fo
508	25	600	2	-	-	-	87	-	8
506	25	600	42	95	-	8	100	-	7
510	25	600	168	88	-	16	88	-	11
409	40	580	48	94	53	1	96	51	2
516	50	500	240	95	-	9	96	-	7
001	50	520	96	96	-	6	96	-	4
505	50	600	42	94	37	4	96	36	4
503	50	650	168	91	34	9	92	35	9
501	50	650	504	96	55	1	96	52	2
410	50	700	120	88	-	11	92	-	9
509	75	600	2	94	-	1	100	-	3
507	75	600	42	91	-	13	96	-	15
511	75	600	168	94	70	11	96	73	9

* as measured by electron microscope (left) and as calculated from X-ray diffraction peaks (Francis, 1985) (right).

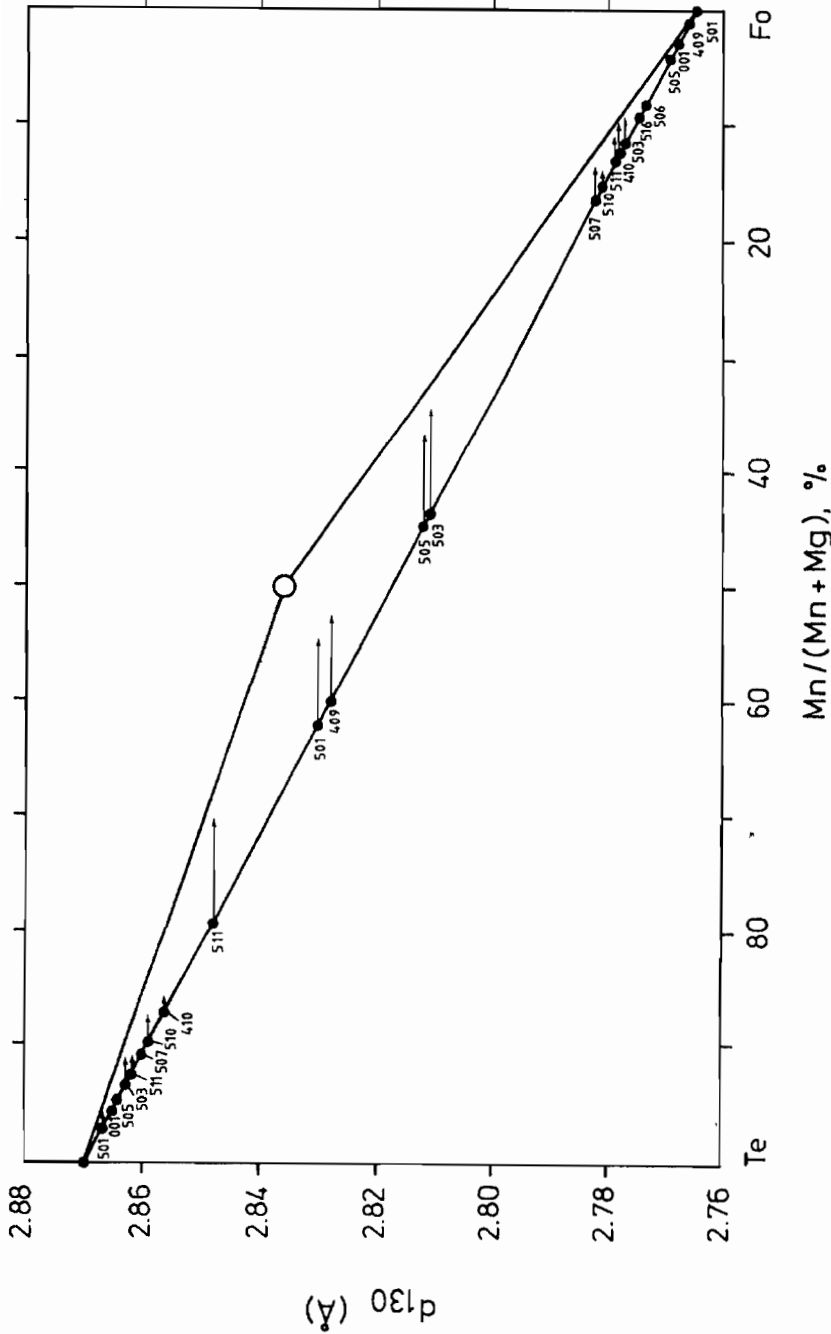


Fig. 5. A plot of d_{130} (Å) versus composition for synthetic (Mn, Mg) olivines. Arrows show the mean measured compositions, d_{130} for the end-member olivines are calculated from the cell dimensions of synthetic tephroite ($a=4.904$ Å, $b=10.618$ Å, $c=6.259$ Å, this study) and forsterite [$a=4.754$ Å, $b=10.197$ Å, $c=5.981$ Å, Schwab and Kustner (1977)]. Open circle refer to calculated d_{130} for ordered pictotephroite ($a=4.791$ Å, $b=10.555$ Å, $c=6.081$ Å).

At higher temperatures, some experiments of longer duration yielded a clinochroite phase of a composition close to $MnMgSi_2O_6$ (Tables 5 and 6). This phase which has earlier been synthesized by Lindqvist (1982) is stabilized by increasing pressure relative to picrotephroite as the dissociation of the latter into pyroxene and oxides is accompanied by a volume decrease of 3%. The product which is called kanoite is also known as a natural mineral, first reported by Kobayashi (1977) from metamorphic manganese rocks in Japan (Tables 5 and 6). Despite the occurrence of corresponding Mn-Mg olivines at Långban and its satellite deposits, kanoite has not been observed there so far. The exclusive occurrence of picrotephroite assemblages at Långban could possibly imply low-pressure environment and formation at relatively shallow levels.

Table 5. X-ray powder data for synthetic and natural kanoites.

Synthetic run no. d, (Å)	kanoite* 501				Natural kanoite (Kobayashi, 1977)**				
	h	k	l	I	d, (Å)	h	k	l	I
6.411	1	1	0	-	6.422	1	1	0	2
4.613	2	0	0	-	4.616	2	0	0	5
4.447	1	1	-1	-	4.446	1	1	-1	5
3.327	0	2	1	5	3.328	0	2	1	10
3.205	2	2	0	90	3.211	2	2	0	100
3.018	2	2	-1	80	3.022	2	2	-1	90
2.924	3	1	-1	40	2.926	3	1	-1	80
2.907	3	1	0	100	2.910	3	1	0	90
2.572	1	3	-1	20	2.576	1	3	-1	30
2.499	0	0	2	80	2.493	0	0	2	40
2.462	2	2	1	10	2.463	2	2	1	20
2.365	1	3	1	5	2.368	1	3	1	15
2.238	3	1	1	15	2.237	3	1	1	20
2.144	3	3	-1	20	2.147	3	3	-1	30
2.051	4	0	-2	10	2.050	4	0	-2	25
2.036	0	4	1	10	2.040	0	4	1	15
2.007	2	4	0	-	2.012	2	4	0	5
1.825	3	3	1	-	1.826	3	3	1	5
1.807	5	1	0	5	1.808	5	1	0	10

Table 5. (Contd).

Synthetic run no. d, (Å)	kanoite* 501				Natural kanoite (Kobayashi, 1977)**				
	h	k	l	I	d, (Å)	h	k	l	I
1.788	1	3	2	5	1.788	1	3	2	10
1.732	4	2	1	-	1.732	4	2	1	5
1.626	5	3	-1	40	1.629	5	3	-1	40
1.543	3	5	0	10	1.546	3	5	0	20

* a = 9.73(2) Å; b = 8.92(4) Å; c = 5.27(1) Å; β = 108.5(3)°; cell volume = 433.61(Å)³.

** a = 9.739 Å; b = 8.939 Å; c = 5.260 Å; β = 108.56°; cell volume = 434.1 (Å)³.

Table 6. Cationic proportions on the basis of 6 oxygens of synthetic and natural kanoites.

	Synthetic kanoite run no.		Natural kanoite (Kobayashi, 1977)
	501	511	
Si	2.04	2.01	1.973
Al	-	-	0.002
Fe ³⁺	-	-	0.012
Fe ²⁺	-	-	0.087
Mn	0.95	0.99	1.040
Mg	0.97	1.00	0.885
Ca	-	-	0.024
Na	-	-	0.002
K	-	-	0.002

The binary olivine phases (Table 2, nop. N1 and G1) that have been synthesised at high temperatures by Nishizawa and Matusi (1972) and Ghose and Weidner (1974) show a very low degree of ordering (25%) relative to the natural Mn-Mg olivines from the Långban region (62–94% ordered). For the low temperature synthetic Mn-Mg olivine (T=580° C, P=1kb, 2 days) with an observed

composition of $\text{Fo}_{47}\text{Te}_{53}$ (Table 2, Nop. E1) a 50% ordering is recorded, a value more or less intermediate between those for high-temperature synthesis phases and natural Långban olivines. Taking into consideration the slow rate generally characterising order-disorder reactions, it is safe to assume that the intra-crystalline cation distribution of the synthetic phase, showing 50% ordering at 580° C, has not reached equilibrium. Summing up all indications presented here it is concluded that the formation of intermediate Mn-Mg olivines of Långban-type is the result of reactions within the temperature range of 500 to 600° C.

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REFERENCES

1. Brown, G.E., Novak, G.A., Robinson, K.G., Gibbs, G.V. and Ribbe, P.H. (1970). Crystal Chemistry of the orthosilicates. *Geol. Soc. Am., Ann. Meet. Abstr.* 504-505.
2. Burns, R.G. (1970). Crystal field spectra and evidence of cation ordering in olivine minerals. *Amer. Mineral.* 55:1609-1632.
3. Endale Ketefo (1989). Trioctahedral micas of the Långban-type deposits in Värmland, Sweden. In: *Meddelanden från Stockholms Universitets Geologiska Institution*, N:r 276.
4. Endale Ketefo (1995). Glaucochroite from Jakobsberg, Filipstad, Sweden. *SINET: Ethiop. J. Sci.* 18(Suppl.):49-63.
5. Francis, C.A. (1985). New data on the forsterite-tephroite series. *Amer. Mineral.* 70:568-575.
6. Ganguli, D. (1977). Crystal chemical aspects of olivine structures. *Neues Jahrbuch für Mineralogie Abhandlungen* 130:303-318.

7. Ghose, S. (1962). The nature of Mg^{2+} - Fe^{2+} distribution in some ferro-magnesian silicate minerals. *Amer. Mineral.* **47**:338–394.
8. Ghose, S., Wan, C., Okamura, F.P., Ohashi, H. and Weidner, J.R. (1975). Site preference and crystal chemistry of transition metal ions in pyroxenes and olivines. *Acta Cryst.* **A31(Suppl.)**:S76.
9. Ghose, S. and Weidner, J.R. (1974). Site preference of transition metal ions in olivine (abstr). *Geol. Soc. Amer. Abstracts with Programs* **6**:751.
10. Glasser, F.P. and Osborn, E.F. (1960). The ternary system MgO - MnO - SiO_2 . *J. Amer. Cer. Soc.* **43**:132–140.
11. Hazen, R.M. (1976). Effects of temperature and pressure on the crystal structure of forsterite. *Amer. Mineral.* **61**:1280–1293.
12. Kobayashi, H. (1977). Kanoite (Mn^{2+} , Mg)₂(Si_2O_6), a new clinopyroxene in the metamorphic rock from Tatehira, Oshima Peninsula, Hokkaido, Japan. *J. Geol. Soc. Japan* **83**:537–542.
13. Lindqvist, B. (1982). Indirect mineral information from hydrothermal synthesis studies of some manganese compounds. In: *Proceedings of the First International Symposium on Hydrothermal Reactions 1982*, pp. 643–648. Japan.
14. Lumpkin, G.R. and Ribbe, P.H. (1983). Composition, order-disorder and lattice parameters of olivines. I. Relationships in silicate, germanate, beryllate, phosphate and borate olivines. *Amer. Mineral.* **68**:164–176.
15. Lumpkin, G.R. Ribbe, P.H. and Lumpkin N.E. (1983). Composition, order-disorder and lattice parameters of olivines: determinative methods for Mg-Mn and Mg-Ca silicate olivines. *Amer. Mineral.* **68**:1174–1182.
16. Magnusson, N.H. (1918). Beitrag zur Kenntnis der Optischen Eigenschaften der Olivinegruppe. *GFF*, Bd. 40.
17. Magnusson, N.H. (1925). Pesbergs malmtrakt Beskrivningarver mineralfyndigheter, Vol. 3: Kungl Kommerskollegium, Stockholm, 231 pp.
18. Moore, P.B. (1970). Mineralogy and chemistry of Långban-type deposits in Bergslagen, Sweden. *Mineralogical Record* **1**:154–172.
19. Nambu, M., Tanida, K. and Kitamura, T. (1966). Mineralogical study of the manganese silicate ores in northern Japan (1), Knebelite from Hakozaki mine, Iwate Prefecture. *Bull. Res. Inst. Min. Dress. and Metall. Tohoku Univ.* **22**:63–75.

20. Nishizawa, O. and Matusi, Y. (1972). An experimental study on partition of magnesium and manganese between olivine and orthopyroxene. *Physics of the Earth and Planetary Interiors* 6:377-384.
21. Nord, A.G. and Forsberg, L. (1982). A program system for mineral x-ray data including search-match routines. *Geol. Fören. Stock. Förhandl.* 103:343-348.
22. Pajkull, S.R. (1877). Mineralogiska notiser. Picrotephroite från Långban. *GFF* 3(40).
23. Schwab, R.B. and Kustner, D. (1977). Präzisionsgitterkonstantenbestimmung zur festlegung röntgenographischer Bestimmungskurven für synthetische Olivin der Mischkristallreihe Forsterit - Fayalit. *Neues Jahrbuch für Mineralogie, Monatshefte*, pp. 205-215.
24. Simkin, T. and Smith, J.V. (1970). Minor-element distribution in olivine. *J. Geol.*, 78:304-325.
25. Smith, W.C., Bannister, F.A. and Hey, M.N. (1944). Banalsite, a new barium felspar from Wales. *Min. Mag.* 27:33-46.
26. Sundius, N. (1963). Benstonite and tephroite from Långban. *Arkiv. Miner. Geol.*, 3(21):407-411.

Appendix Below is given a brief description of the Mn-Mg olivines from Långban and related localities.

Sample g15952a (Jakobsberg) — a light rose forsterite coexists with a dark rose picrotephroite variety (sample g15952b). The picrotephroite is intergrown with hausmannite and colourless calcite, whereas white dolomite was observed along the margins of the slightly serpentinized olivine.

Sample 670974 (Långban) — Light brownish pink olivine closely associated with tetraferriphlogopite and jacobsite in a calcite rock.

Sample 10100 (Långban) — Fine- to medium-grained, light brownish pink olivine in a jacobsite-mica layer of a banded skarn rock.

Sample 170717 (Långban) — Light to medium brownish pink, massive olivine enclosing scattered grains of calcite, thin mica flakes, rounded hausmannite and occasionally berzeliite. Calcite with inclusions of hausmannite also occurs as separate grains in contact with olivine.

Sample g15935 (Långban) — Slightly serpentinized fine to medium-grained, brownish pink to medium brown olivine located in a calcite - hausmannite rock.

Sample g15952b: see g15952a.

Sample 620758 (Långban) — Coarse- to medium-grained, brownish pink olivine in close association with calcite, nearly Mn-free phlogopite, hausmannite, berzeliite, hedyphane and norsethite. Berzeliite and hedyphane frequently occur as inclusions in the olivine.

Sample g15934 (Långban) — Partially serpentinized, massive, generally dark rose olivine associated with manganian diopside.

Sample 140523 (Långban) — Massive, light rose olivine intergrown with calcite. Traces of serpentine are present.

Sample 571021 (Långban) — Massive, dark rose olivine, containing inclusions of mica and calcite. Aegirine-augite and K-bearing manganian richterite are also associated with the olivine which is slightly serpentinized.

Sample 251441 (Långban) — Dark rose, massive olivine associated with brownish-red manganian phlogopite, manganian diopside, manganian richterite, hausmannite and calcite which also appears as inclusions in olivine.

Sample 15879 (Långban) — Coarse-grained, light rose olivine, accompanied by idiomorphic hausmannite crystals, orange berzeliite and yellow hedyphane in a calcite-rich skarn rock.

Sample 65:0083 (Pajsberg) — Fine- to medium-grained, brownish pink olivine scattered in massive hausmannite ore along with manganian diopside, manganian richterite and calcite.

Sample 170718 (Långban) — Coarse- to medium-grained, brownish pink olivine irregularly scattered in a hausmannite-bearing calcite rock. Inclusions of brown to orange berzeliite in olivine are occasionally observed.

Sample 090232 (Långban) — Coarse- to medium-grained, light brownish pink to medium brown olivine with inclusions of reddish-brown manganian phlogopite. Manganian richterite is closely associated with olivine. Native copper has also been observed on olivine grain boundaries.

Sample g15913 (Pajsberg) — Medium-grained, grey olivine (with pink shade) associated with jacobsonite, pyroxene and calcite.

Sample 255879 (Långban, "Ireland") — Medium- to coarse-grained, brownish pink olivine in a manganian phlogopite-calcite skarn.

Sample 6778 (Pajsberg) — Brownish pink olivine embedded in Mn-bearing calcite in a fine-grained amphibole-jacobsonite-carbonate skarn rock.

- Sample 670802 (Långban) — Massive, grey olivine (with violet shade) associated with reddish-brown Mn-bearing andradite, dark-green manganian amphibole, quartz and calcite.
- Sample g15961 (Pajsberg) — Medium- to coarse-grained, dark grey (pink shade) olivine associated with calcite and fine-grained hausmannite. Rhodonite occurs as inclusions in olivine.
- Sample 251242 (Långban, "Ireland") — Dark brown olivine is a major component of a coarse-grained skarn also consisting of jacobsite, and calcite and occasional berzeliite of light yellow colour.
- Sample 74:0211 (Pajsberg) — Brownish-red olivine closely associated with amphibole, jacobsite and calcite, forming a fine-grained skarn rock.
- Sample 280344 (Långban) — Fine-grained skarn consisting of dark rose to greyish olivine, jacobsite, rhodonite, manganian richterite, reddish-brown Mn-bearing andradite, barite and calcite. Olivine is often enclosed in jacobsite.
- Sample 332308 (Långban) — Medium- to coarse-grained, dark grey olivine associated with elongated, prismatic crystals of yellow manganian diopside, reddish pink rhodonite and calcite, in which brownish caryinite is observed.
- Sample g15976 (Långban) — Fine- to medium-grained, dark grey olivine irregularly interwoven with calcite and hausmannite.
- Sample 670970 (Långban) — Medium- to coarse-grained, dark grey olivine in skarn rock consisting mainly of manganian varieties of phlogopite, diopside, richterite and calcite.
- Sample 532657 (Pajsberg) — Medium-grained, dark grey olivine in jacobsite located in a micaceous rock.
- Sample 331794 (Pajsberg) — Dark rose, euhedral, prismatic olivine crystals, 2–4 mm in size, in fine-grained jacobsite. An intermediate member of the kentrolite-melanotekite series is occasionally observed in contact with olivine.
- Sample 331825 (Pajsberg) — Fine-grained crystals of grey olivine associated with jacobsite, yellowish-brown Mn-bearing andradite and calcite.
- Sample 532633 (Pajsberg) — Medium- to coarse-grained, dark grey olivine associated with yellowish-brown andradite and rhodonite.