GARNETS FROM THE ECLOGITES OF THE MUENCHBERGER GNEISS MASSIF (NE BAVARIA)

P. HAHN-WEINHEIMER and W. LUECKE

Mineralogical Institute, University of Frankfurt/Main (Germany)*

ABSTRACT

The mineralogical composition of eleven eclogitic rocks from the Muenchberger gneiss massif, together with three from other localities, has been investigated and the individual mineral phases separated. Major, minor and trace elements were determined in the separated garnets, together with their lattice constants and refractive indices. The results are presented diagrammatically.

The garnets from the lowermost parts of the Muenchberger gneiss massif are a little more basic in composition than those of the overlying rocks. The former contain noteworthy traces of Ni, Co, V and Sc, while Sr appears to be concentrated in the latter. The differences observed in the chemical compositions of the garnets are in agreement with those already observed in the corresponding eclogitic rocks themselves. In source material favourable to the formation of eclogitic rocks, it is demonstrated that the growth of garnet in a dry facies with increasing P/T conditions began with the appearance of the spessartine and almandine phases, in conditions corresponding to a "pre-eclogitic stage." Under higher P/T conditions, culminating in those of the so-called "Druck-sonderfazies" abundant pyrope makes its appearance. Appreciable concentrations of pyrope, few or no inclusions in the garnets, and the usual formation of omphacite are all characteristic features of the eclogites of the Muenchberger gneiss massif, as for the eclogites of other regions. The presence of elements characteristic of ultrabasic materials points to the influence of such materials in the genesis of these rocks.

INTRODUCTION

The genesis of the Muenchberger gneiss massif has occupied the attention of geologists for some decades. Up to the present, however, purely geological and petrographic methods have in the main been employed in attempts to solve the many outstanding problems posed by these rocks. For some years attempts have been made in this Institute to solve one of the problems of the Muenchberger gneiss massif, that of the genesis of the eclogitic rocks, with the help of geochemical methods. A broad investigation of the eclogitic rocks themselves along these lines was carried out by Hahn-Weinheimer (1959), but in order to carry the work a stage further it was considered necessary to separate and analyse the individual mineral phases. The garnets from eleven eclogitic rocks of the Muenchberger gneiss massif were selected, together with three from other localities for purpose of comparison. The minerals were analysed for major trace elements by physical and chemical methods.

*A further contribution towards the problem of the genesis of these rocks (II). The work on garnets is the subject of an unpublished Diploma thesis by W. Luecke, Frankfurt/Main 1962.

THE ECLOGITIC ROCKS IN THE GEOLOGICAL SETTING OF THE MEUNCHBERGER GNEISS MASSIF

The Muenchberger gneiss massif situated in NE Bavaria (Germany) consists of ancient basement rocks. It is bordered to the south by a marginal zone of amphibolites, to the south-east and east by a zone of prasinites* and phyllites, and to the north, north-west and west by a marginal schist series. The results of the more recent geological work are to be found in the publication of Wurm (1960).

The crystalline rocks of the central gneiss massif may conveniently be divided into a lower and an upper series (Fig. 1). The lower series is called the "Acid Gneiss Series," because of its main rock-types. These are paragneisses (muscovite-biotite-garnet-gneisses), metahornfels, graphite schists, and lime-silicates, all metamorphic rocks of pelitic and psammitic sediments. The upper series mainly consists of banded hornblende gneisses and amphibolites. These metamorphic rocks are partly of sedimentary origin; relicts of alternating greywacke and marly limestone. but also meta-igneous materials such as tuffs and diabase can be observed. Basic and acid magmas were intruded into both series at various times. Because of the intense metamorphic alternation of the rocks it has not yet proved possible to establish the time sequence of the individual tectonic events which have affected the area. Neither in the bordering Palaeozoic rocks, nor in the Muenchberger gneiss massif itself, can any indication of Caledonian folding be observed, but evidence of the Sudetic phase of the Variscan folding as well as possible Assyntian structures are to be seen; the former is especially important in connection with the deformation and metamorphism of the Muenchberger gneiss massif. For the genetic interpretation of the metamorphic rocks it is important to consider the mineralogical facies of the rocks before the Sudetic folding. Metamorphosed magmatic rocks of acid composition, representing the latest material to be added to the complex, are older than this folding, which has left its imprint upon them. Recent results suggest that the starting materials before their metamorphism must have been exceedingly variable. The various mineral facies produced may be taken as evidence of primary differences in source material; it must on the other hand be borne in mind that differing mineral facies may arise from the same starting material under different P/T conditions.

Basic complexes, lenses of gabbro, amphibolite and serpentinite are included within the gneiss massif. In addition, highly metamorphosed rocks of eclogitic composition occur in both the lower and upper series.

*Basic rocks with mainly amphiboles of the epidote-amphibolite-facies leading to the glaucophane-schist-facies.

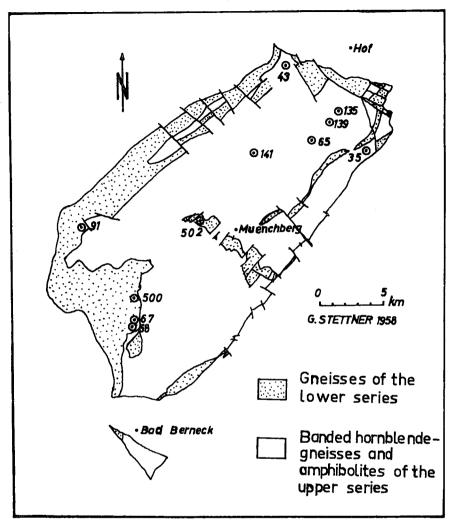


Fig. 1. Geological sketch-map of the Muenchberger gneiss massif and the surrounding formations.

These are to be classified, according to their metamorphic grade during their formation, as true eclogites (with pyrope and omphacite), eclogiteamphibolites, or garnet-amphibolites.

In order to study the garnet phases in the eclogitic rocks, five samples were taken from the lower series of the Muenchberger gneiss massif and five from the upper series. The garnet-amphibolite (141) from Ahornberg is somewhat exceptional both petrographically and chemically, and was

investigated because of its proximity to the single occurrence of marble in the Muenchberger gneiss massif. All these samples come from the Saxo-Thuringian zone (after P. Kossmat and F. E. Suess) within the region of the Variscan orogenetic belt which includes the Muenchberger gneiss massif. For purpose of comparison with these specimens two further samples were taken from the Moldanubian, another paleotectonic zone north of the Saxo-Thuringian. Specimen 201 was taken from the Dunkelsteiner granulite massif in the Mitterbachgraben near Aggsbach in Austria, and 86 from the Tannenbodenhalde, the only known occurrence of this type in the Black Forest.

The minerals of all these samples are believed to be of metamorphic origin, while the remaining sample studied (78) is a griquaite* from Robert's Victor mine in South Africa, thought to be of magmatic origin.

Geological horizon	No.	Sampl	e Rock type	Locality
Lower series	1	67	eclogite	Weissenstein
of the	$ar{f 2}$	68	eclogite	Weissenstein
Muenchberger	$rac{2}{3}$	500	eclogite	Stammbach
gneiss massif		91	eclogite-amphibolite	Gruenlas
B	$rac{4}{5}$	$5\overline{02}$	garnet-amphibolite	Muenchberger Querzone
Upper series	6	141	garnet-amphibolite	Ahornberg
of the	7	35	eclogite	Fattigau
Muenchberger	8	65	eclogite-amphibolite	Martinsreuth-South
gneiss massif	9	135	garnet-amphibolite	Schaumbergholz
6	10	139	eclogite-amphibolite	Wustuben
	11	43	eclogite-amphibolite	Woellbattendorf
Other localities	12	86	garnet-amphibolite	Tannenbodenhalde, Black Forest
	13	201	eclogite-amphibolite	Mitterbachgraben, Austria
	14	78	griquaite	Robert's Victor mine, South Africa

TABLE 1. PROVENANCE OF GARNET SAMPLES INVESTIGATED

As well as the characteristic minerals garnet and pyroxene (partly occurring as omphacite) the eclogitic rocks of the Muenchberger gneiss massif may contain hornblende, white mica and quartz. Whether this last represents a primary constituent typical of the eclogitic facies is still an open question (Eskola, 1921). In addition, kyanite, clinozoisite, rutile, plagioclase and iron-ore may be developed. Further descriptions of accessory minerals are given by Hahn-Weinheimer (1959).

The grain size of the garnets is variable, from medium grained (3.3 to 1.0 mm.) to fine grained (1.0 to 0.33 mm.), the crystals sometimes being

^{*}Eclogite-like inclusions of magmatic origin in Kimberlite (Troeger, 1935. Spezielle Petrographie der Eruptivgesteine, p. 289).

stretched out in one direction. The garnet normally forms idiomorphic crystals more or less free from inclusions. The number of inclusions in the garnets diminishes with progressive metamorphism, an observation already recorded by Backlund (1935, 1936). It is also observed how, because of its high power of crystallization, the garnet has pushed pre-existing minerals to one side or has enclosed them poikiloblastically. Kelyphitic rims are seldom observed in the rocks of the Muenchberger gneiss massif. These reaction rims, indicating retrograde metamorphism, are however seen in the Gilsberg eclogite (Hentschel, 1937) and also in thin sections of the griquaite from South Africa (sample 78).

Garnets of an eclogite in contact with ultrabasic rocks are known to be almost free from inclusions. This observation may be taken to indicate that the high temperatures obtained from contact rocks, together with high pressure, favour the assimilation of inclusions in garnet. In some of the eclogites of the Muenchberger gneiss massif, as well as in the griquaite (78), the garnets are almost completely free from inclusions. This purity provides a good criterion for true eclogites. The second critical mineral component is omphacite. This mineral was not present in all the thin sections investigated, confirming that the appropriate conditions for the formation of a true eclogite were not always attained. It occurs unfailingly, however, in all samples in which the garnets carry few or no inclusions. The samples studied by means of thin sections may thus be divided into three groups:

- (1) In the *true eclogites* (samples 67, 68, 500, 35 and 78) the garnet is generally idiomorphic in habit and inclusions are sparse or lacking. The principal constituent of the garnet is pyrope (Mg). The pyroxenes comprise omphacite, diopside and sometimes common augite. Hornblende (probably of secondary formation), rutile, quartz and opaque ores occur as minor constituents. White mica was only found in samples 67, 68 and 35. Kyanite was represented only in samples 67 and 68 of the Weissenstein complex. Some of the rock samples (68, 500 and 35) are fine grained, while others (67 and 78) are coarser.
- (2) Some eclogitic rocks carry practically no omphacite, and the garnets commonly carry numerous inclusions up to $1000\,\mu$ in size. Since it is scarcely conceivable that such larger inclusions continued to grow in the garnets during a retrograde metamorphism, after the rock had already passed through a true eclogitic stage, these rocks are supposed to belong to a pre-eclogitic stage and should thus be referred to as eclogite-amphibolites (samples 91, 65, 139, 43 and 201). The garnets are not so rich in pyrope as in the true eclogites. Some omphacite is present, and occasionally aegirine-augite, but the predominant pyroxenes are diopside and augite. Hornblende, quartz, rutile, some mica and iron-ore occur as accessory minerals. Sample 91 is noteworthy for its high content of iron-ore and gar-

net. Samples 65 and 139 contain some kyanite, 201 some plagioclase and no mica. The garnets of the eclogite-amphibolites are xenomorphic in habit and the rocks vary from fine grained (91 and 43) to coarse grained (65, 139 and 201).

(3) The third group comprises the garnet-amphibolites (502, 135 and 86), which contain no omphacite. The garnets generally carry numerous inclusions. Augite, hornblende, quartz, white mica, feldspar and iron-ore are seen in thin section. Sample 502 contains an unusually high proportion of quartz, while 135 contains some kyanite.

Sample 141 is exceptional. In terms of its chemical composition and modal analysis (Tables 2, 3, and 4) it cannot be grouped with the truly eclogitic rocks. Its garnet content, especially pyrope, is low, while its quartz content is quite considerable. The rock is dark and fine grained with a foliated groundmass in which occur isolated porphyroblasts of dark red garnet, full of inclusions and up to 3 mm. across. In the thin section, augite, pleochroic hornblende, abundant quartz, some mica and iron-ore are to be observed.

Mineral separations carried out on these eclogitic rocks yielded three principal concentrates. The garnet concentrate often contains small amounts of paramagnetic ore (pyrite, chalcopyrite); the concentrates of dark minerals consists mainly of pyroxene and subordinate hornblende together with rare accessories such as kyanite, rutile, apatite, some feldspar, etc. The third concentrate consisted of quartz and white mica (muscovite and sericite). The results of the mineral separations are given in Table 2.

		LABLE	Z. WIODAL AI	MALISIS OF EC	LOGITIC ROCKS	
			Garnet & para- magnetic ore	Ferro- magnetic ore	Pyroxene & subordinate hornblende	Light minerals (quartz & mica)
No.	Sample	Rock type	G >3.33 weight %	weight %	G <3.33 & >2.90 weight %	G < 2.90 weight %
1	67	е	30.9	<0.1	64.0	5.1
2	68	e	22.6	< 0.1	72.0	5.4
2 3	500	e	22.1	0.2	77.7	0
4	91	e-am	43.2	2.3	51.6	2.9
$egin{array}{c} 4 \\ 5 \\ 6 \\ 7 \end{array}$	502	g-am	17.4	0.7	67.5	14.4
6	141	g-am	9.0	< 0.1	64.7	26.3
7	35	ě	39.0	< 0.1	57.0	4.0
8	65	e-am	38.2	< 0.1	53.2	8.6
8 9	135	g-am	20.2	0.2	68.1	11.5
10	139	e-am	36.7	0.9	$\boldsymbol{45.5}$	16.9
11	43	e-am	21.8	0.1	69.2	8.9
12	86	g-am	16.7	0.9	37.1	45.3
13	201	e-am	46.2	0.1	52.0	1.7
14	78	griq	32.2	< 0.1	67.8	0

TABLE 2. MODAL ANALYSIS OF ECLOGITIC ROCKS

e: eclogite. e-am: eclogite-amphibolite. g-am: garnet-amphibolite. griq: griquaite.

Relation Between n_D , a_0 and Chemical Compositions of the Garnets

The results of measurements of lattice constants and refractive indices, together with the chemical analyses, are presented in Table 3. The values for a_0 vary between 11.531 Å and 11.612 Å, and those for n_D between 1.748 and 1.796.

Figure 2 shows diagrammatically the close relationship between a_0 and the contents of calcium, magnesium, aluminum, total iron and manganese determined by analysis. The cell edge increases with increasing contents of iron, titanium, manganese and calcium, aluminum and silicon remaining constant, as well as with decreasing content of magnesium. Iron, titanium and manganese increase the size of the garnet cell edge up to one tenth of an Ångstrom unit, while the incorporation of magnesium on the contrary causes diminution in the cell edge.

Since the total number of aluminum and silicon ions to be balanced remains more or less constant, while the calcium content also varies but little, it is the ratio of magnesium to iron which is of special importance. According to Fyfe, Turner & Verhoogen (1958) a high content of both these elements is especially characteristic of eclogitic garnets. The cation contents of the garnets of the Muenchberger gneiss massif fall within a very narrowly restricted field, whereas the cation contents of garnets from other localities (78, 86 and 201) lie outside this field. The Muenchberger gneiss sample 500 forms an exception. In this case, a low iron content is compensated by magnesium and titanium. The cation contents of sample 141 likewise fall outside the series here, and an unusually low magnesium content is compensated by calcium and manganese. The low calcium content in the griquaite (78) is compensated by iron and magnesium. In sample 86, the values for calcium and magnesium are low in comparison to those of the Muenchberger gneiss massif: these values are compensated by higher values for iron and manganese. The somewhat low values for iron and titanium in 201 are balanced by higher values for calcium and magnesium.

Figure 3 shows the relationship between refractive index and the total Fe + Ti + Mn and Mg + Ca respectively. With increasing contents of Fe + Ti + Mn, the refractive index likewise increases up to a certain limit, while the sum of Ca + Mg has the opposite effect. It is the varying iron content which chiefly determines the variation in refractive index. A lower iron content in garnets is made up by a higher content of Ca + Mg. The fields for Ca + Mg and Fe + Ti + Mn therefore run in opposite directions in Fig. 3. The exceptional case of sample 500 is also striking in this regard, especially when compared with sample 139. The

Table 3. Physical Constants and Chemical Composition of the Garnets

MnO	0.24	0.26	0.20	0.21	0.20	0.32	0.21	0.20	0.21	0.30	0.22	0.36	0.20	0.21
CaO	00.6	8.22	9.04	7.75	7.23	10.15	8.80	8.58	8.32	7.20	7.40	5.33	8.83	2.99
MgO	8.04	5.63	11.55	6.05	10.90	1.68	6.40	9.03	7.08	11.09	9.24	4.98	10.29	14.81
FeO	18.82	23.03	14.90	22.80	14.46	23.68	23.11	17.05	19.73	14.81	19.37	24.63	9.73	15.19
TiO_2	0.52	0.65	79.0	2.13	0.23	1.69	0.45	0.92	0.72	0.19	0.37	0.24	0.08	0.25
Cr2O ₃	0.03	0.01	0.05	0.00	0.01	0.00	0.02	0.01	0.01	0.05	0.00	0.00	0.15	0.12
Fe_2O_3	1.72	1.54	2.13	1.65	1.36	2.60	1.33	1.04	1.32	0.43	0.23	2.47	0.82	0.63
Al ₂ O ₃	21.13	19.47	21.43	19.10	21.78	20.96	19.57	19.94	20.26	21.27	21.19	23.40	26.78	24.20
SiO2	40.50	41.20	40.03	40.31	43.83	38.92	40.11	43.23	42.35	44.76	41.98	38.59	43.15	41.60
ПD	1.7771 ± 0.0008	1.7899 ± 0.0008	1.7600 ± 0.0010	1.7889 ± 0.0009	1.7490 ± 0.0010	1.7958 ± 0.0010	1.7855 ± 0.0005	1.7688 ± 0.0007	1.7725 ± 0.0005	1.7624 ± 0.0012	1.7671 ± 0.0020	1.7943 ± 0.0010	1.7484 ± 0.0005	1.7598 ± 0.0013
ao (Å)	11.580 ± 0.004	11.604 ± 0.004	11.585 \pm 0.004	11.608 ± 0.003	11.561 ± 0.003	11.612 ± 0.003	11.594 ± 0.006	11.571 ± 0.004	11.591 ± 0.003	11.557 ± 0.002	11.575 ± 0.004	11.577 ± 0.003	11.561 ± 0.004	11.531 ± 0.004
Sample	29	89	500	91	502	141	35	65	135	139	43	8 6	201	78
No.	H	87	က	4	īΟ	9	2	œ	6	10	11	12	13	14

0.00: Value below limit of detection.

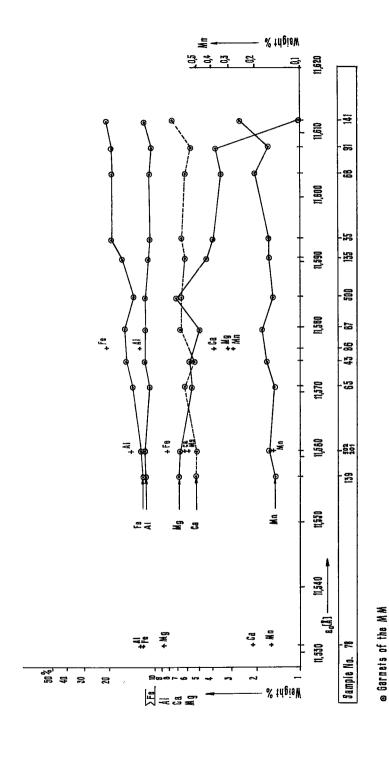


Fig. 2. Principal constituents and lattice parameters of the analysed garnets (MM = Muenchberger gneiss massif).

+ barnets from other localities

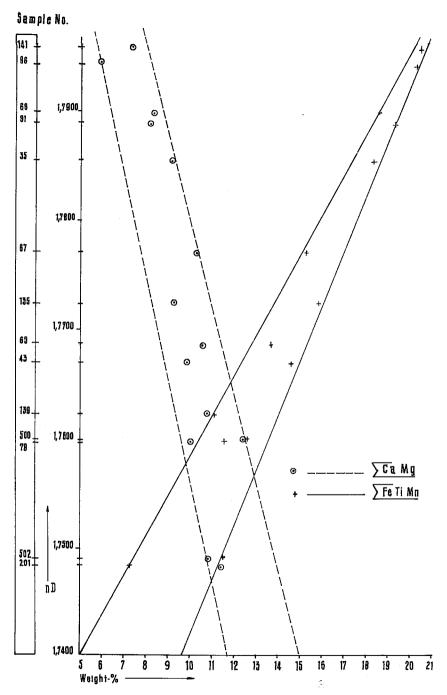


Fig. 3. Relation between refractive index and cation-composition of the garnets.

iron contents of both the samples differ but little from one another, as may be deduced from the similar refractive indices. In spite of this, however, sample 500 has a larger cell edge than 139, and this may well be due to differing contents of titanium.

Sample	n_D	$a_0(\text{Å})$	%Fe	%Ti
500	1.7600	11.585	13.08	0.40
139	1.7624	11.557	11.81	0.11

The relationship between a_0 and n_D is shown in Fig. 4. Here the determined points for the garnets from the Muenchberger gneiss massif also fall inside a relatively small field, while the garnets from eclogites from other localities (78 and 86) lie outside this field. Both these latter samples have high contents of iron and thus higher refractive indices. Their low titanium contents are doubtless responsible for the smaller values for a_0 .

In Fig. 5 the quotient (FeO + Fe₂O₃)/(FeO + Fe₂O₃ + MgO) = (Q), which involves both the typical cations in the garnets of eclogitic rocks, is plotted against the SiO₂ content of the garnets. As was shown earlier (Hahn-Weinheimer, 1959) the eclogitic rocks of the lower series in the western part of the Muenchberger gneiss massif are more basic than those of the upper series in the north-eastern part of the massif. This is now further reflected in the garnets separated from the corresponding eclogitic rocks. With one exception (sample 502) the SiO₂ contents of the garnets from the lower series, where the rocks are more basic in overall chemistry, vary between 39 and 42 per cent by weight. Again with a single exception (35) the garnets of the upper series, on the other hand, vary in silica content between 42 and 45 per cent by weight. The garnet amphibolite (141) is not comparable with the remaining eclogitic rocks of the Muenchberger gneiss massif. On the field evidence, it is not clear whether or not sample 35 really belongs to the upper series: its trace-level content of elements characteristic of ultrabasic rocks indicates affinity with the lower series. The garnets from other localities also do not fit into the scheme.

TRACE ELEMENTS

The content of trace elements in the eclogites and their garnets determined spectrochemically, are given in Table 4. First, the high chromium contents (100 to 300 p.p.m.) of some of the garnet samples from the Muenchberger gneiss massif are striking in comparison with the average value of 50 p.p.m.: samples 67, 500, 35 and 139, as well as 201 and 78 from other localities. Cobalt and nickel show the same behaviour, as does also scandium, though to a lesser extent. Titanium, on the other hand, behaves in the opposite fashion. Hahn-Weinheimer (1959) found that

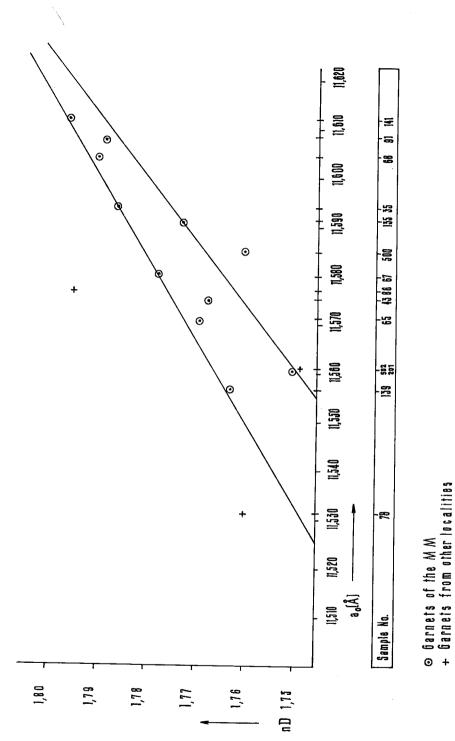
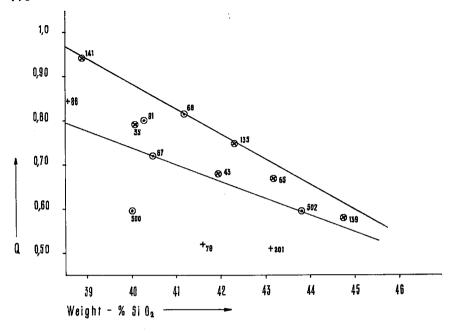


Fig. 4. Lattice parameters and refractive indices of the garnets (MM = Muenchberger gneiss massif).



- Garnets of the underlying series 0
- Garnets of the overlying series
- Garnets from other localities

Fig. 5. Plot of the ratio $\frac{\text{FeO} + \text{Fe}_2\text{O}_3}{\text{MgO} + \text{FeO} + \text{Fe}_2\text{O}_3} = (Q) \text{ against SiO}_2.$

eclogitic rocks which had possibly been in contact with ultrabasic material carried enhanced trace concentrations of nickel, cobalt and chromium, and this is found to extend to the garnet phase as well. Magnesium is relatively enriched in these eclogitic rocks as well as in their garnets, so that we might conclude that there has been an addition of those elements (Cr, Ni, Co and Mg) characteristic of ultrabasic environments. But on the other hand it is also possible that some isochemical process has taken place, magnesium and the three other trace elements having originated in the parent material from which they were mobilized and incorporated into the crystal lattices of the garnet phase. According to Backlund (1935 and 1936) high-grade metamorphism should strongly favour the assimilation of the inclusions in garnet. If the chemical and thermal influence of ultrabasic material is assumed to be significant in the samples under discussion, freedom from inclusions in the garnets and enhanced contents of ultrabasic trace elements should go together. This is in fact observed in the particularly chromium-rich samples 67, 500, 35, 139, 201 and 78.

The similarity of the griquaite (78) with the Austrian eclogite (201) is

of interest. Both contain particularly high concentrations of chromium, nickel, cobalt and magnesium, while the strontium contents are low. This is also true of samples 67, 68, and 500. With respect to its trace element content also, the garnet amphibolite (141) is an exception. Its content of chromium, nickel and copper is low, while it is enriched in strontium and calcium.

The garnet amphibolite (86) from the Black Forest is noteworthy for its content of boron, barium, scandium, strontium and zirconium, an enrichment in elements characteristic of a sedimentary environment. The small B⁸⁺ ion (radius 0.23 Å) appears to play its part in compensating valency charges in conjunction with the larger trace element ions, although this, of course, is no explanation for its presence. Rather, the trace element contents reflect the variable composition of the parent materials, and the relatively high boron content of the eclogite (86) is in accord with the boron contents of other basic to ultrabasic metamorphic rocks from the same district.* Since boron and carbon are elements which become strongly enriched in sediments, the relatively high content of these elements observed combined with the petrological and geological results, at any rate in the Black Forest rocks, lend weight to the opinion that the parent material of these rocks was probably sedimentary. This is in accordance with the field observations of Metz & Rein (1958).

The trace element content of the eclogitic rocks of the Muenchberger gneiss massif, as well as of its contained garnets, vary between wide limits. This supports the view that the parent material of these rocks was inhomogeneous; some rocks are perhaps of sedimentary origin. As well as purely local differences in trace element content, the difference in silica content between the upper and lower series is also confirmed by the trace elements. The eclogitic rocks of the lower series in the west of the Muenchberger gneiss massif, and their contained garnets, are more basic and richer in nickel, cobalt, vanadium and scandium than those of the upper series with a higher silica content and an enrichment in strontium and barium. Any discussion of the origin of the eclogites of the lower series in terms of the composition must take into account either the possible participation of basic rocks in the metamorphic processes, or the influence of neighbouring ultrabasic intrusions. These latter could be considered as a possible source of heat, and the true eclogites of the lower series may have originated in this way. The trace element levels determined seem to be too low, and the trace element contents too variable, to indicate the same magmatic origin for the whole parent material. The genetic conditions for the formation of eclogitic rocks seem to have been more favourable in the lower series than in the upper.

^{*}Unpublished results of the authors.

	B	E	Na %	a ppm	S dd	Sc ppm	V V	" "	Cr	.	<u> </u>	Co ppm
Sample	ecl.	gar.	ecl.	gar.	ecl.	gar.	ecl.	gar.	ecl.	gar.	ecl.	gar.
67	=	88	2.89	13.3	19	64	275	17	235	190	45	43
. œ	11	4	20.04	13.5	19	32	285	31	96	83	43	36
200	5.7	53	1.63	10.2		56	1	16	395	335	110	40
91	200	34	2.30	16.6	52	26	\sim 1000	36	150	33	22	53
502	13	21	1.63	25.2	l	37	1	36	119	56	62	16
141	9	28	1.80	12.6	9	42	105	35	40	18	36	23
35	17	34	1.93	10.9	30	69	350	34	102	143	16	20
50	∞	27	2.23	12.7	19	19	240	55	263	49	12	55
135	∞	32	1.98	16.4	24	56	135	11	155	75	86	16
139	9	28	1.62	10.8	16	13	200	24	54	325	64	16
43	11	29	2.03	14.9	33	22	130	9	273	83	53	83
86	~400	15	2.46	9.5		285	1	7		40	[35
3 03	}	, <u>rc</u>	1.12	11.3	1	54	[34	l	1030		32
282	7	22	1.71	8.1	0	83	~	18	870	810	 	47

Table 4 (cont'd)

	[d	Ni ppm	id	Cu ppm	ld ld	Ba ppm	3 Id	Sr ppm	Z _r ppm	. F
Sample	ecl.	gar.	ecl.	gar.	ecl.	gar.	ecl.	gar.	ecl.	gar.
29	61	ಣ	8.0	17	<100	155	250	2	105	62
89	57	ī	32	16	<100	163	81	٠	144	158
200	193	3.4	150	16	1140	150	194	2	22	25
91	143	2.4	7	18	ļ	163	130	20]) rc
205	0	2.4	8.4	20	180	155	270	14	18	4
141	0	1.5	4.6	රා	0	160	63	06	176	8
35	40	7	150	65	250	163	185	55	2	88
65	99	2.5	12	6	250	165	130	4	8	02
135	83	7	23	17	820	165	395	25	126	9
139	115	7	I	∞	0	163	270	9	22	84
43	82	τĊ	18	48	270	163	300	20	9	6 4
98	l	2		23		165		180		118
201]	18	[40	l	150		e c	1	41
78	730	27	\sim 1500	18	170	150	113	ı.	44	£
0 · Value below limit of detection	w limit of do	tootion								

0 : Value below limit of detection.- : Value not determined.

Certain regularities are to be observed in the trace element contents. As iron increases so does zirconium, and the same is true of the pairs of elements Mg and Cr, Mg and Ni, Ti and V, Ti and Zr, Co and Sc, and Zr and B. A typical example of replacement by ionic capture is provided by magnesium and scandium. With decreasing content of Mg^{2+} (r = 0.66 Å) the content of Sc^{3+} (r = 0.81 Å) increases. The charge balance is possibly compensated by trivalent aluminum or titanium. Replacement of Si^{4+} by the trivalent elements aluminum, iron and titanium may well be possible (Zemann, 1962).

The explanation of the sympathetic relationship between magnesium and nickel could lie in the markedly antipathetic relationship between iron and nickel, as discussed by Ringwood (1956) in the case of the olivine lattice. The difference in electronegativity between Mg and O is less than that between Fe or Ni and O, and hence the Mg-O link is the stronger. This strong bonding of magnesium appears to be the reason why, during progressive metamorphism, first Mn and then Fe in the parent material are mobilized, and Mg last, and only under conditions of high pressure and temperature. In this special case, the formation of pyrope from a relatively large amount of magnesium mobilized out of the source material during the metamorphic process, is a criterion of high P/T conditions favourable to the formation of eclogitic rocks. The replacement of some of the major elements in the garnets by certain parallel trace elements also affects the cell size and some extrapolations may be made. If the behaviour of the two elements concerned is concordant, they will occupy similar positions in the lattice. If their ionic radii are similar as well, mutual replacement in the lattice is probable. This is the case in particular with the ions V^{3+} (0.74 Å), Ti^{3+} (0.76 Å) and Zr^{4+} (0.79 Å), discussed earlier, which can replace Al3+ in the lattice.

In the light of the previous work carried out by Hahn-Weinheimer on the trace elements of the eclogitic rocks themselves, the partition of the trace elements between the garnet phase and the remaining phases may now be examined. Barium, copper and titanium are strongly enriched in the garnets, while boron, cobalt, chromium, manganese, scandium and zirconium are enriched to a lesser extent. Strontium and vanadium are about equally distributed between garnet and the whole eclogite. Sodium and nickel were strongly enriched in the more melanocratic constituents (Figs. 6, 7, and 8). A considerable amount of lead (30 p.p.m.) was found in the garnet phase of sample 500 while the pure pyroxene phase was free of this element.

The nickel content of the garnets is about ten times lower than the cobalt content. Nickel is constantly higher than cobalt in the eclogitic rocks, but this relationship is reversed in the garnet phase. Cobalt is

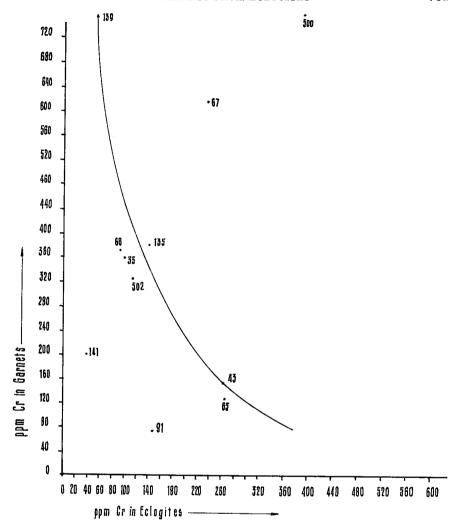


Fig. 6. Distribution of chromium between garnets and eclogites.

preferentially enriched in the garnet while nickel, on the contrary, is enriched in the pyroxene of the eclogitic rocks. Since pyroxene always predominates in the investigated eclogites, cobalt is lower than nickel in an analysis of the whole rock.

THE GARNET PHASE

The chemical analyses have been recalculated in terms of mineralogical molecules (Table 5). Some doubt remains as to whether part or all of the

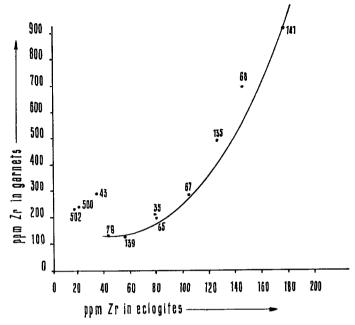


Fig. 7. Distribution of zirconium between garnets and eclogites.

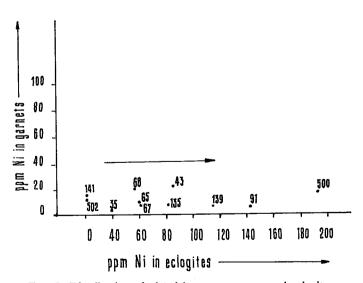


Fig. 8. Distribution of nickel between garnets and eclogites.

Fe³⁺ content was really present as such in the mineral from the beginning, or whether it arose from the oxidation of ferrous iron either during the grinding of samples or during the analysis for FeO. Philipsborn (1928) even considered it possible that some divalent iron might suffer later oxidation in the rock itself. One reason for believing in this possibility was that all analyses seemed to show an excess of Al₂O₈. An amount of trivalent iron corresponding to this excess was recalculated as FeO and allotted to the almandine phase. The allocation of titanium always poses particular difficulty. Since it is impossible in chemical analysis to distinguish between Ti3+ and Ti4+ in the presence of iron, and since investigation of the reflection spectrum can yield no definite information about the valency of titanium in the presence of Fe2+ and Fe3+, the deficit in aluminum found in the present work in samples 67, 68, 500, 91, 35, 65, 135 and 43 have been made up by allotting tetravalent titanium in its place. This gives rise to a titaniferous grossularite molecule 3CaO. TiO₂. 3SiO₂. The actual presence of trivalent titanium is improbable, however, as the presence of this ion can usually be recognized by the dark colour it confers upon the mineral, as in the melanites, but the garnets whose analyses indicate the presence of this titaniferous grossularite molecule are no darker in colour than the remainder. Because only small traces of sodium could be determined in these garnets, recalculation in terms of a titaniferous andradite, in which CaFe⁸⁺ is partly replaced by NaTi⁴⁺ (Strunz, 1957) is impossible. Even the melanite from Kaiserstuhl (Black Forest), which was examined in connection with this problem, was found to contain only 13 p.p.m. Na. From a consideration of the various oxidation potentials, the coexistence of Fe2+ and Ti4+ is more likely than coexisting Fe³⁺ and Ti³⁺ (Verhoogen, 1962). The Ti³⁺ ion will only be able to replace aluminum if all the iron was in the divalent state during the formation of the rock. According to Fyfe, Turner & Verhoogen (1958) quite low P/T conditions are necessary for the formation of andradite, while for the formation of grossularite pressures of about 10,000 bars and temperatures of 600-900° C. are required. The high proportions of the grossularite molecule in comparison with pyrope in the analysed garnets indicate that pressure and temperature during the metamorphism were very high. Because of the limited mobilization of titanium in the rocks, we may assume that it does not enter the andradite but becomes first incorporated in place of aluminum in the grossularite molecule.

Seven different end members of garnet molecules were recalculated. As in the case of earlier analyses (Fleischer, 1937; Wolff, 1942) a small excess of SiO_2 and a deficit of divalent cations with respect to R_2O_3 were found in contrast to the theoretical molecular ratios $RO:R_2O_3:SiO_2=3:1:3$. The average ratios yielded by the garnets of the Muenchberger gneiss massif

Table 5. Composition of the Garnet Phases

															1					ī
Mol-Relations RO:R ₂ O ₃ :SiO ₂	2.97:1:3.16	3,00:1:3,35	9 00:1:9 00	9.00:1:9.00	2.89:1:3.12	2.82:1:3.37	2.52:1:2.87	2 11.1.2 94	0.11.1.0	3.00:1:3.46	2.93:1:3.40	67 67 100	2.91:1:0.00	2.99:1:3.29		2.50:1:2.77	04 0 1 01 0	Z. 10:1:Z. (Z	2.65:1:2.87	
Σ mol%	100.00	100 00	200	100.00	100.00	100.00	100.00	100 00	100.00	100.00	100 00	000	100.00	100.00	20100	100.00		100.00 100.00	100.00	
Spessartine Uvarovite Almandine Andradite Grossularite Ti-grossularite	1.94	3 07	100	3.78	6.07	1	l	69 6	60.7	5.52	9, 10	i	1	- X	20.1	1			1	
Grossularite	23.26	17.90	07.11	T8.68	13.29	21 03	31 67	100	G/ · /T	18.96	99, 10	01.00	20.72	18 92	10.04	16.30	20.01	27.83	2 98	22
Andradite	!	9 65	2.6	1.61	i	1	j		5.91	ļ]	l	i]		[l	l	
Almandine	49. 79	100	07.70	32.42	52.86	34 21	80.08	00.70	26.UG	30 04	46.20	±0.0±	33.91	A9 GE	47.00	R1 44	H. 10	25.20	33 68	3
Uvarovite	20 0	200	0.0	0.14	ļ	0 07	5	1 3	0.0	U U	2.00	0.0	0.15		l]	0.50	0 27	5.5
Spessartine	0 53	3.5	60.0	0.42	0 49	0.10	100	0.0	0.48	0.45	1 5	0.4(0.46	9	0.49	00 0	00.0	0.50	78	OF. 70
Pyrope	91 41	91.41	77.74	42.95	06 76	74.92	11.65	67.7	24.84	25 06	20.00	68.87	44. 76	000	50.US	00	21.23	45.97	7	10.10
Sample	7.0	70	8	200	0.0	102	200	141	č.	, eq	3 6	135	130	9	43	8	200	201	101	e

are $RO:R_2O_3:SiO_2 = 2.96:1:3.26$. The principal molecules are pyrope, almandine and grossularite, so that the garnets of the Muenchberger gneiss massif may be represented on a ternary diagram (Fig. 9).

Sriramadas (1957) prepared a diagram, based on his own investigations, from which the principal mineral molecules of a garnet could be estimated from measurements of a_0 and n_D , so that chemical analysis should no longer be necessary. Since we have measured the values of a_0 and n_D in the garnets we have investigated, as well as having calculated the garnet composition from the analyses, we may use them to check Sriramadas' pyrope-almandine-grossularite diagram. The calculated compositions (b), and the compositions read off from Sriramadas' diagram (s) are compared in Table 6. The comparison shows that the values derived from Sriramadas' diagram are on the whole in good agreement with those calculated from the analyses and involve only relatively small errors. Sriramadas' diagram generally suggests too much almandine (+7.8%) and grossularite (+2.6%) and too little pyrope (-12.4%).

DISCUSSION OF RESULTS

Clearly, we must compare our results with the results and conclusions of other authors. Eskola (1921), in his work on the eclogite facies, dealt in some detail with the ternary diagram pyrope-almandine-grossularite and delimited a field characteristic of the chemical compositions of eclogitic garnets of varying provenance. Hentschel (1937) divided off a still smaller pyrope-rich field specific to the garnets of ultrabasic rocks. The recalculated garnet analyses in the present work are plotted on such a diagram in Fig. 9, in which the compositional fields defined by both the above authors are indicated. The grossularite component contains all calcium-rich garnet molecules, as well as titaniferous grossularite, uvarovite and andradite. The almandine component has been added to the subordinate spessartine phase.

The garnets of all the rocks investigated from the Muenchberger gneiss massif, with the exception of the garnet-amphibolite (141), fall within the field defined by Eskola. The griquaite (78) from South Africa falls at the edge of the field defined by Hentschel for the garnets of eclogites from ultrabasic rocks. Samples 201, 502, 139 and 500 with pyrope contents greater than 40 mol. per cent plot very closely together within the broad field and also quite close to the region appropriate to eclogites connected with ultrabasic rocks. Sample 86, from the Black Forest, plots close to the lower boundary of the main field, and belongs with the garnet-amphibolites. The garnet-amphibolite (141) plots outside the field. We may conclude that the P/T conditions were not favourable for the forma-

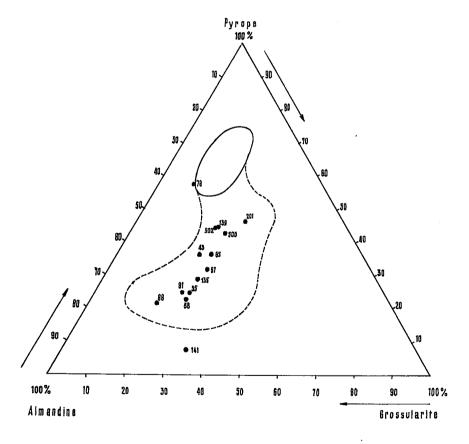
Table 6. Relation of Garnet Phases after Analysis and after a Diagram from Sriramadas (1957)

									Pyr.	Alm.	Gross.
						Pyr.	Alm.	Gross.		(b-s). 1000Z	
No.	Samples	άδ	Pyrope	Almandine	Grossularite	s-q	s—q	s-q		q q	
٦	29	þ	31.41	42.79	25.20						
		s	27.5	51.0	21.5	+3.9	-8.2	+3.7	+12.4%	-19.2%	+14.7%
67	89	p	22.74	52.78	21.17						į
		- vo	14.0	61.0	25.0	+8.7	-8.2	-3.8	+38.3%	-15.5%	-18.0%
က	200	p Q	42.95	32.42	22.46				1	,	:
		vo.	39.5	35.0	25.5	+3.5	-2.6	-3.0	+8.2%	-8.0%	-13.4%
4	91	q	24.29	52.86	22.36	7	1	-	6	74	700 01
)	S	os +	13.0	60.5 34.5	20.5 21.5 21.5	+11.3	9.7-	1.4.1	+40.9%	-14.4%	-18.9%
c	70c	Ω v.	52.0	26.0	22.09 22.09	-7.8	+8.2	-1.0	-17.6%	+24.0%	-4.8%
9	141	۰, ۵	7.29	60.26	31.67						
		w	7.0	0.99	27.0	+0.3	7.9	+4.7	+4.1%	-9.5%	+14.8%
2	35	٠,	24.84	50.32	20.38						:
		ß	18.0	58.5	23.5	+6.8	-8.2	-3.1	+27.4%	-16.3%	-15.5%
œ	65	q	35.96	39.04	24.48		,			,	0
(,	σ,	35.0	43.5	$\frac{21.5}{21.5}$	+4.5	-4.5	+3.0	+2.8%	~e'11'-	+12.3%
O	135	q	28.85	46.32	24.29		1	i	200	5	5
ç	061	w	27.0	48.0 33.0	25.0 20.73	+1.9	-1.7	7.0-	%9·9+	-3.7%	-2.9%
27	108	o s	42.5	38.5 38.5	19.0	+2.3	-4.6	+1.7	+5.1%	-13.6%	+8.2%
Ξ	43	. д	36.09	42.65	20.77		1	6	100 61	11 807	100 2
		S	36.0	42.0	22.0	+0.1	+0.7	-1.2	+2.8%	+1.0%	0%e.e_
12	98	.		61.44	16.39					;	,
	;	w.		67.0	18.0	+6.3	-5.6	-1.6	+29.6%	-9.1%	-9.8%
13	201			25.20 25.20	27.83	ì		1	1	1	200 00
7	1	or t		25.0 95.60	22.0	0.7	+0.2	8.c+	%z:c1-	%s:)+	+20.9%
T4	0	သော	50.0	37.0	13.0	+7.5	-3.3	-5.0	+13.0%	-9.8%	-62.7%

LEGEND: b: calculated garnet-phases from analysis. s: garnet-phases after Sriramadas.

tion of eclogite in the latter case: pressure and temperature was insufficient to mobilize sufficient magnesium from the pyroxenes to promote the growth of pyrope.

Miyashiro (1953), in his work on the garnets of metamorphic rocks, showed that the formation of individual members of the isomorphous solid solution series spessartine-almandine-pyrope was dependent upon temperature. With increasing temperature, the manganese content of the garnets decreases and hence, because of the large ionic radius of Mn (0.80 Å), so does a_0 ; while the iron contents and hence n_D increase. As



Eclogitic garnets from ultrabasic rocks (after HENTSCHEL)
---- Eclogitic garnets of all occurences (after ESKOLA)

Fig. 9. Distribution of the garnet phases from eclogites in the ternary system: almandine-pyrope-grossularite.

the temperature increases further, magnesium enters the garnet phase to an ever greater extent, and the iron content diminishes accordingly. Matthes (1961) came to similar conclusions; he found that with increasing pressure the iron content of cordierite decreases in favour of magnesium. It seems from the results of Matthes and Miyashiro that the P/T conditions attained affected the Mn-Fe-Mg ratios in garnet to a greater extent than in cordierite. The chief reason why first manganese, then iron and last magnesium under the highest P/T conditions, are mobilized in that order in the course of progressive metamorphism, seems to be the exceptional strength of the magnesium-oxygen bond. A liberal supply of magnesium, evidenced by the formation of pyrope, in this case indicates conditions of high pressure and temperature, conditions which are necessary for the formation of eclogites. A tendency towards inverse behaviour of the MgO and MnO contents with respect to P/T conditions is also to be noted in our garnets (Fig. 10). Decreasing MnO and FeO in the garnets naturally caused a parallel decrease in the values of a_0 , while the MgO content increases in the same order of the samples on the abscissa, reaching its highest value in the griquaite (78). This seems to reflect the high P/T conditions which were obtained during its genesis. Samples 86 and 141, with the smallest content of MgO and the highest of MnO, plot at the other end of the graph and are garnets which grew under relatively low P/T conditions, as is confirmed by other observations such as the analyses of the individual mineral phases and their microscopic characters.

These results allow some qualitative conclusions to be drawn as to the course of garnet formation during the genesis of eclogites. A suitable and dry source material was subjected to increasing pressure or stress and temperature, during which the crystallization of garnet began. Apart from the earliest formation of spessartine, which can probably occur at atmospheric pressure (Yoder & Keith, 1951) almandine was the first to form to any great extent, under P/T conditions appropriate to the amphibolite facies (Fyfe, Turner & Verhoogen, 1958). With further increase in temperature and pressure the formation of garnet continues, the Fe²⁺ component decreasing in favour of Mg2+ which is steadily becoming mobilized and increasingly available. At a temperature of about 700° C. and a pressure of about 13,000 bars the stability field of pyrope, and also the field of the eclogite facies is reached ("Drucksonderbedingungen" of Schueller, 1961). The core of a garnet porphyroblast formed in this way will be richer in the spessartine and almandine molecules, while the outer shells will in contrast be richer in pyrope. This is in accord with the investigations of Wolff (1942) who investigated the core and margin of the garnets from an eclogite of the Muenchberger gneiss massif chemically and optically. The core was richer in manganese and iron and had a higher refractive index than the margin, which in contrast contained more magnesium.

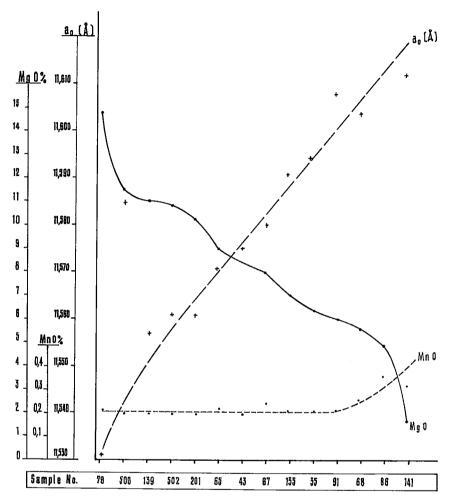


Fig. 10. Contents of MgO, MnO, and the lattice parameters of the garnets.

Composition of Garnet from the Eclogite of Silberbach (= Sample 65) (Wolff 1942)

	Spessartine	Almandine	Pyrope
Garnet core	1.26 mol.%	36.57 mol.%	39.66 mol.%
Garnet margin	0.76 mol.%	29.44 mol.%	48.71 mol.%

Moreover, Wolff found that the cores of the garnets contained abundant inclusions while the outer zones were almost free from inclusions. The same observation could, for example, be made about sample 35 in the present work, although on the other hand some of our garnets carry many

inclusions. This point should not be overlooked in any discussion about the formation of garnet in eclogitic rocks. We may assume that this took place under more or less continuously increasing conditions of pressure and temperature. The power of crystallization of the garnet caused the growing crystals to include fragments of foreign minerals such as quartz, mica, feldspar, etc. The earliest mobilized manganese and iron were incorporated into the spessartine and almandine phases and the stability field of almandine was reached under the conditions characteristic of the amphibolite facies. With further increase in pressure and temperature, magnesium also is more readily mobilized, under conditions corresponding to the stability field of pyrope and the field of the eclogite facies. Under these higher P/T conditions, inclusions of foreign minerals which remained resistant under the conditions of almandine formation and hence remained as inclusions, are no longer stable and are broken down and incorporated into the garnet lattice. In this way the freedom from inclusions of the pyrope-rich margins of the garnets may be interpreted. The almandinerich phase provides a kind of protection around its inclusions. In the case of garnets which contain no inclusions at all it may be envisaged that pressure and temperature rose so rapidly during their formation that the pyrope phase began to form very early and all the inclusions were assimilated. These garnets all carry a high proportion of the pyrope molecule. The remaining garnets, carrying numerous inclusions right up to the margins of the crystals, apparently never reached the optimal P/T conditions for eclogite formation, so that little of the pyrope molecule was formed and the inclusions were not assimilated. Such eclogitic rocks are referred to here as eclogite-amphibolites; they contain little pyrope, more almandine and grossularite, little omphacite and hence more diopside, augite and sometimes hornblende.

CHEMICAL COMPOSITION OF THE GARNET-FREE RESIDUAL PHASES OF THE ECLOGITIC ROCKS

Whole-rock analyses of samples 67, 68, 91, 141, 35, 65 and 78 had previously been made and it was thus possible to calculate the composition of the residual material after subtracting the contribution due to the (analysed) garnet. The result was recalculated into a hypothetical garnet molecule (Table 7, column A) representing the garnet which might have come into being at the expense of the modal eclogitic minerals plagioclase, omphacite, diopside, hornblende, etc. The result of the recalculation in the case of the griquaite (78) has been placed in brackets, since the recalculation yields an extremely problematical garnet with 13.02 mol. per cent pyrope, 12.6 mol. per cent andradite and 2.38 mol. per cent

grossularite. The recalculations show that the amounts of "virtual" garnet in the residual material are considerable, amounting to as much as 82.67 mol. per cent in one case. However, if the composition of the residual material is recalculated in terms of the proportions of pyrope, almandine and grossularite corresponding to the actual compositions of the garnets present in the rocks (Table 7, column B) then the virtual garnet in the residual material is always very much less. The figures in column B represent garnet which could have been formed under the conditions of pressure and temperature under which the actual individual garnets of the Muenchberger gneiss massif crystallized. The amounts of this additional virtual garnet vary from 6 to 29 mol. per cent for the eclogitic rocks of the Muenchberger gneiss massif. In the case of the griquaite (78) however, the additional formation of a garnet with 57.51 mol. per cent pyrope, 33.68 mol. per cent almandine and 7.98 mol. per cent grossularite would no longer have been possible. The conditions of the "Drucksonderfazies" were such that the equilibrium of the garnet-forming reaction was completely displaced in favour of garnet.

If the calculations of virtual garnet in column B of Table 7 are carried out, not on the residual materials, but on the whole rock analyses (column C of Table 7) the values shown are the amounts which would have been added to the amounts of garnet (Table 7, column D) actually occurring in the rocks, on the assumption that the equilibrium of the garnetforming reaction is completely displaced in favour of garnet. The figures in column C lead to the following conclusions. When the amounts of

TABLE 7. CALCULATED	GARNET	CONTENTS O	OF ECLOGITIC	Rocks
---------------------	--------	------------	--------------	-------

Sample	$_{ m mol.\%}^{ m A}$	$_{ m mol.\%}^{ m B}$	C mol.%	$_{ m mol.\%}^{ m D}$
67	69.00	14.99	10.46	30.23
68	82.67	17.04	13.23	22.38
91	76.50	28.69	16.23	43.44
141	61.81	60.10	54.61	9.14
35	57.84	5.78	3.60	37.81
65	58.29	23.98	15.24	36.42
43	62.51	28.63	22.66	20.84
78	(28.00)	0	0	31.40

A—Percentages of potential garnet, calculated without regard to mineralo-

A—Percentages of potential garnet, calculated without regard to mineralogical molecules actually present, corresponding to the residual phases of the rocks after subtraction of the actual garnet present. Residual phases recalculated to 100 mol.%.

B—Percentages of virtual garnet in the residual mineral phases of eclogitic rocks, assuming the virtual garnet to have the same composition as the modal garnet phase of the rocks. Residual material recalculated to 100

C—Percentages of virtual garnet calculated as in column B but referred to the whole rock analysis. Whole rock recalculated to 100 mol.%. D—Actual garnet in the whole rocks. Whole rock = 100 mol.%.

additional potential garnet in column C lie within the range 3 to 13 mol. per cent, the rock is a true eclogite, corresponding to the first group in the classification proposed earlier in this paper. Samples 67, 68 and 35 belong to this first group. The values in column C ranging between 15 and 23 mol. per cent comprise the pre-eclogitic stage, rocks which we call eclogite-amphibolites, and samples 91, 65 and 43 fall within the second group. Sample 141, with 54.61 mol. per cent virtual garnet in column C of Table 7, does not belong with the eclogitic rocks, the P/T conditions during its formation having been so low that only 9 mol. per cent of an almandine-grossularite-garnet rich in inclusions, could be formed. The results of these recalculations reinforce the conclusions set out in the previous section of this paper with regard to the genesis of the eclogitic garnets. They are also in accord with our earlier investigations of the eclogites of the Muenchberger gneiss massif and perhaps constitute a further contribution to the solution of the genetic problems posed by the eclogites.

EXPERIMENTAL METHODS

The rock samples were crushed to a grain size varying from 0.5 mm. to 10μ depending on the grain size of the rock, sieved, and its minerals separated with a magnetic separator (after Forrer) and heavy liquids.

The cell edge of the garnet sample was determined by measurement of x-ray powder photographs. Refractive indices were determined by the immersion method in mixtures of methylene-iodide and sulphur kept at constant temperature. To take account of variability from grain to grain in a single sample, the refractive indices of 70 separate garnet grains were measured for each sample and the average taken.

The chief chemical constituents of the garnets were determined in a solution of 1.2 g. of the microscopically checked garnet concentrate, decomposed with perchloric and hydrofluoric acids. Calcium and magnesium were determined by titration with versene using Calcon and Eriochrome black T as indicators. Total iron was determined volumetrically using ceric sulphate with ferroin as indicator, after reduction of the iron in a cadmium reductor.

Titanium was determined spectrophotometrically using Tiron, and masking the iron with sodium dithionite (Shapiro & Brannock, 1956). Sodium was determined by flame photometry. The determination of ferrous iron was carried out by the micro-method of Wilson (1960). Six separate portions of each garnet were dissolved by standing for 70 hours in hydrofluoric acid to which a known excess of a 0.139N solution of ammonium-metavanadate was added. After solution was complete, the excess pentavalent vanadium was back titrated with ferrous ammonium

sulphate solution using barium-diphenylamine sulphonate as indicator.

The trace elements As, B, Ba, Be, Co, Cu, Cr, Ni, Pb, Sc, Sr, V and Zr were determined by the D-C arc emission spectrograph, using a mixture of the powdered mineral and carbon in the ratio 1:2 and electrodes, shape C400 after Ultra Carbon Products Company. The intensities of the spectral lines for As, B, Ba, Ni and Zr were measured using a standard paper density scale (Addink, 1950), which is useful when the background on either side of the line is similar and the intensities relatively low. The method yields a precision of ± 10 per cent. Co, Cu, Cr, Pb, Sc, Sr and V were determined by micro-photometric measurement of the spectral lines on the photographic plates. This was essential to determine the correct background intensities for these elements; this was of importance also in avoiding interfering lines when determining Sr and Co.

The determination of manganese in the garnets, and of Co, Ni and Cu in eclogitic rocks was carried out spectrographically using hydrochloride acid solutions and the vacuum cup electrode technique (Zink, 1959). Ti, Cr, Mn, Fe, Sr and Zr in the eclogitic rocks were determined by x-ray fluorescence spectrography.

The standard deviations for duplicate analyses, after Youden (1959), in the garnet analyses are as follows:

```
Total Fe \pm 0.65\%

Fe<sup>2+</sup> \pm 0.24\% (6 determinations made on each sample)

Ca \pm 0.54\%

Mg \pm 5.24\%

Mn \pm 6.18\%

Ti \pm 0.52\%

Na \pm 8.27\%
```

(In all cases these are percentages of the amount of the constituent present).

ACKNOWLEDGMENTS

The authors are indebted to the Deutsche Forschungsgemeinschaft for financial help. They want to thank Professor E. A. Vincent, Manchester, who kindly read and corrected the English manuscript.

REFERENCES

ADDINK, N. W. H. (1950): A rapid and accurate method of measuring line intensities in spectrochemical analysis, *Spectrochim. Acta* 4, 36-42.

BEARTH, P. (1959): Ueber Eklogite, Glaukophanschiefer und metamorphe Pillowlaven, Schweiz. min. petroger. Mitt. 39, 267–286.

BECK-Mannagetta, P. (1961): Zur Deutung der Eklogite im Koralpenkristallin (Zentralalpen), Tschermaks min. petrogr. Mitt. 7, 437–450.

- Behr, H-J. (1961): Beitraege zur petrographischen und tektonischen Analyse des saechsischen Granulitgebirges, Freib. Forsch.-Hefte C 119, 1–118.
- DITTLER, E. (1929): Zur Frage der Oxydationsstufe des Ti in den Silikaten, Sitz. ber. Akad. Wiss. Wien 138, Abt. I 371-412.
- Duell, E. (1902): Ueber die Eklogite des Muenchberger Gneiss gebietes. Diss. University of Erlangen.
- ERDMANNSDOERFFER, O. H. (1938): Eklogit im Schwarzwald und seine retrograde Umwandlung, J. Geol. 46, 438-447.
- ESKOLA, P. (1921): The mineral facies of rocks, Norsk. Geol. Tids. 6, 143.
- EIGENFELD-MENDE, I. (1948): Metamorphe Umwandlungserscheinungen an Metabasiten des Suedschwarzwaldes, Mitt. bad. geol. L. NF.1, 1–112.
- FLEISCHER, M. (1937): The relation between chemical composition and physical properties in the garnet group, Am. Mineral. 22, 751-759.
- Ford, W. E. (1915): A study of the relations existing between chemical, optical, and other physical properties of the members of the garnet group, Am. J. Sci. 40, 33-49.
- Fyfe, W. S., Turner, F. J., & Verhoogen, J. (1958): Metamorphic reactions and metamorphic facies, Geol. Soc. Am. Mem., 73.
- Hahn-Weinheimer, P. (1959): Geochemische Untersuchungen an den ultrabasischen und basischen Gesteinen der Muenchberger Gneismasse (Fichtelgebirge), N. Jb. Mineral. Abh. 92, 203–278.
- ——— (1960 a): Alterseinstufung von eklogitischen Gesteinen mit Hilfe des C 12/C 13-Isotopenverhaeltnisses von Graphit- und Karbonat-Kohlenstoff, Geol. Rund. 49, 308-314.
- ——— (1960 b): Bor- und Kohlenstoffgehalte basischer bis intermediaerer Metamorphite der Muenschberger Gneismasse und Ihre C12/C13-Isotopenverhaeltnisse, Int. Geol. Congr. 21 Sess. Norden, Part 13, 431-442.
- HENTSCHEL, H. (1937): Der Eklogit von Gilsberg im saechsischen Granulitgebirge und seine metamorphen Umwandlungsstufen, Min. petr. Mitt. 49, 42–88.
- Kaiser, H., & Honerjaeger-Sohm, M. (1944): Beruecksichtigung des Untergrundes bei der Messung von Intensitaetsverhaeltnissen, Spectrochim. Acta 2, 396-416.
- Kretz, R. (1959): Chemical study of garnet, biotite, and hornblende from gneisses of Southwestern Quebec, with emphasis on distribution of elements in co-existing minerals, J. Geol., 67, 371–402.
- Kunitz, W. (1936): Die Rolle des Ti and des Zr in den gesteinsbildenden Silikaten, N. Jb. min. Abt. A. 70, 385-466.
- MACKOWSKY, M.-T (1938): Zusammenhaenge zwischen Optik und Chemismus der Granate, Diss. University of Bonn.
- MATTHES, S. (1961): Ergebnisse zur Granatsynthese und ihre Beziehungen zur natuerlichen Granatbildung innerhalb der Pyralspitgruppe, Geochim. Cosmochim. Acta 23, 233–294.
- (1961): Einige Betrachtungen zur Bildung von Pyralspitgranat und Cordierit aus dem derzeitig verfuegbaren experimentellen Befund, N. Jb. Mineral. Abh. 96, 180–183.
- METZ, R. & REIN, G. (1958): Erlaeuterungen zur geol. petrog. Uebersichtskarte des Suedschwarzwaldes, Moritz Schauenburg Verlag.
- MIYASHIRO, A. (1953): Calcium-poor garnets in relation to metamorphism, Geochim. Cosmochim. Acta 4, 179-208.
- MILTON, INGRAM, & BLADE (1961): Kimzeyite, a zirconium-garnet from Magnet Cove, Arkansas, Am. Mineral. 46, 533-548.
- Philipsborn, H. v. (1928): Beziehungen zwischen Lichtbrechung, Dichte und chemischer Zusammensetzung in der Granatgruppe, Abh. saechs. Acad. Wiss. 40, No. 3.1-43.
- RINGWOOD, A. E. (1956): Melting relationship of Ni-Mg-olivines and some geochemical implications, *Geochim. Cosmochim. Acta* 10, 297-303.
- Scheumann, K. H. (1961): Faziesprobleme der metamorphen Gesteine, N. Jb. Mineral. Abh. 96, 131–320.

Schueller, A. (1961): Die Druck-, Temperatur- und Energiefelder der Metamorphose, N. Jb. Mineral., Abh. 96, 250-290.

Shapiro & Brannock, (1956): Rapid analysis of silicate rocks, U.S. Geol. Survey Bull. 1036-C, 36.

Sriramadas, A. (1957): Diagrams for the correlation of unit cell edges and refractive indices with the chemical composition of garnets, Am. Mineral. 42, 294–298.

STETTNER, G. (1960): Ueber Bau und Entwicklung der Muenchberger Gneismasse, Geol. Rund. 49, 350-375.

STRUNZ, H. (1957): Mineralogische Tabellen.

Tertsch, H. (1921): Studien am Westrande des Dunkelsteiner Granulitmassives, Tschermaks min. petrogr. Mitt. 35, 177-214.

TROEGER, E. (1959): Die Granatgruppe: Beziehungen zwischen Mineralchemismus und Gesteinsart, N. Jb. Mineral. Abh. 93, 1-44.

TURNER & VERHOOGEN, (1960): Igneous and metamorphic petrology.

Verhoogen, J. (1962): Distribution of titanium between silicates and oxydes in igneous Rocks, Am. J. Sci., 260, 211-220.

WEINELT, W. (1958): Petrologische Untersuchungen der mineralfaziell Zustandsbedingungen im SW-Teil der Muenchberger Gneismasse, Tschermaks min. petrogr. Mitt. 6, 281–375.

WILSON, A. D. (1955): Chemical determination of FeO, Geol. Survey, Bull. Gt. Britain, 9, 56-58.

——— (1960): Microdetermination of FeO in silicate minerals, Analyst, 85, No. 1016, 823. Winchell, H. (1958): Composition and physical properties of garnet, Am. Mineral. 43, 595-600.

Wolff, T. v. (1942): Methodisches zur quantitativen Gesteins- und Mineraluntersuchung mit Hilfe der Phasenanalyse, *Min. petr. Mitt.* 54, 1–122.

WRIGHT, W. I. (1938): The composition and occurrence of garnets, Am. Mineral. 23, 436-445.

WURM, A. (1960): Ueber einige grundlegende Fragestellungen in der Muenchberger Gneismasse, Geol. Rund. 49, 343-350.

Yoder, H. S., & Keith, M. L. (1951): Complete substitution of Al for Si. *Am. Mineral.* **36**, 519-533.

Youden (1959): Statistical methods for chemists. N.Y.

ZEMANN, J. (1962): Zur Kristallchemie der Granate, Beitr. min. petr. 8, 180-188.

ZINK, TH. H. (1959): A vacuum cup electrode for the spectrochemical analysis of solutions, Appl. Spectroscopy, 13, 94-97.

Manuscript received March 27, 1963