Eclogites from the Minugrat, Siviez-Mischabel nappe (Valais, Switzerland)

by *Meinert Rahn*[1]

Abstract

In the southern part of the Turtmann valley, at Minugrat, eclogites are found in the polymetamorphic basement of the Siviez-Mischabel nappe. These eclogites occur as small lenses and layers in a boudinaged unit of mainly mafic and felsic rocks that form a mega-lens of varying thickness (15 to 90 m).

Thin section observations reveal a primary eclogitic paragenesis of garnet + omphacite + rutile ± quartz ± clinozoisite ± kyanite which was overprinted by three consecutive retrograde events: the first retrograde phase is characterized by phengite, barroisitic amphibole and "atoll" garnet, the second phase generates a fine-grained symplectite of plagioclase + bluegreen amphibole replacing the omphacite, and the third phase forms the transition to an epidote-amphibolite by recrystallization and associated coarsening of the symplectite.

Electron microprobe analyses show a pronounced zoning of the garnet with a core rich in grossularite and almandine, but poor in pyrope component. The omphacite is unzoned and exhibits a very constant jadeite content ($X_{jd} \approx 0.50$).

Application of three versions of the Fe–Mg exchange geothermometer between coexisting garnet and clinopyroxene produced significant differences in the resulting temperatures. While the data of ELLIS and GREEN (1979) seem to yield too high temperatures, the temperatures derived with the data sets of KROGH (1988) and PATTISON and NEWTON (1989) agree well, inferring equilibration temperatures of 550–600 °C at a minimum pressure of 12–13.5 kbar as determined by the jadeite content of the clinopyroxene. The replacement of kyanite by paragonite can be observed in thin section yielding another possibility of pressure determination based on the reaction jadeite$_{50}$ + kyanite + H_2O → paragonite. However, the P-T conditions for this reaction are very dependent on a_{H_2O} which has not been determined.

Possible pseudomorphs after lawsonite and small amounts of crossite can be observed in amphibolites. They might represent traces of a nearly extinct high P / low T event in the Siviez-Mischabel nappe after the eclogitization. Therefore an eo-Alpine age for the eclogites from Minugrat seems unlikely.

Keywords: Eclogite, geothermometer, polymetamorphism, Minugrat, Siviez-Mischabel nappe, Bernard nappe, Valais.

Introduction

The large middle-penninic Bernard nappe is located to the south of the Rhone valley (Valais, Switzerland), and was originally defined by LUGEON and ARGAND (1905). Recently it has been been divided into several sub-units (Fig. 1) with the Siviez-Mischabel nappe as main part (ESCHER, 1988). Its rocks form a large recumbent fold rising gently towards north. The Siviez-Mischabel nappe consists lithostratigraphically of a lower polymetamorphic and an upper monometamorphic part (Marthaler, 1984; SARTORI, 1988). The polymetamorphic part is divided into a lower "Ergischhorn" unit,

consisting mainly of micaschists and paragneisses with inlayered metabasites, and an upper "Barneuza" unit rich in metabasic rocks which occur especially at the bottom and at the top ("amphibolites rubanées" and "complexe rubané", SARTORI and THÉLIN, 1987). In the normal limb of the anticline four outcrops of eclogite and retroeclogitic metabasites are known (Fig. 1): BEARTH (1980) described an eclogitic amphibolite near the Augstbordhorn between Turtmann valley and Matter valley (locality 1 in Fig. 1), a second outcrop is located in the Val de Moiry further to the west (locality 2; HALM, 1945; LENGELER, 1988), and two occurrences are found in the southern part of the Turtmann valley,

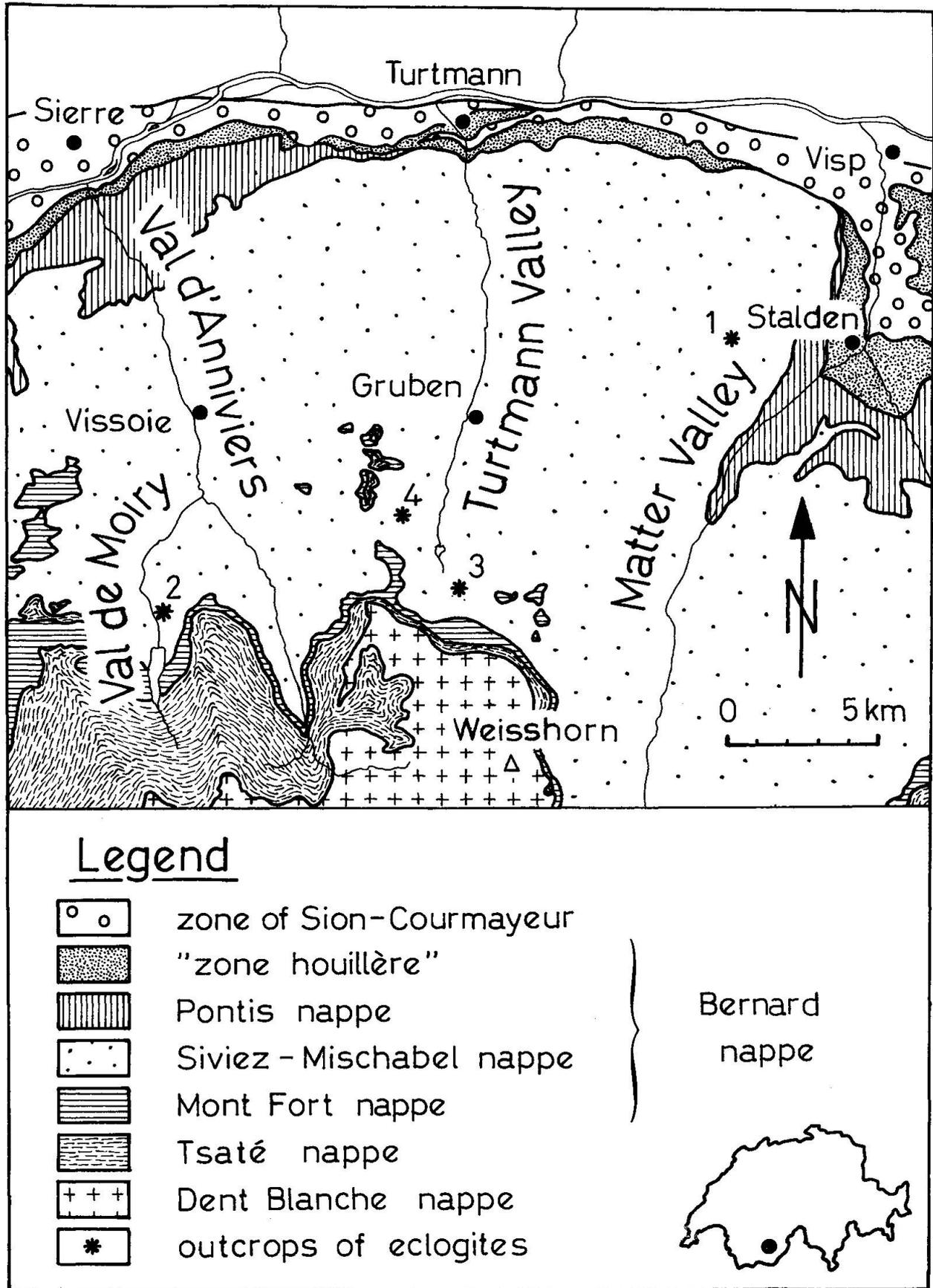[1] Mineralogisch-Petrographisches Institut, Bernoullistrasse 30, CH-4056 Basel, Switzerland.

Fig. 1 Tectonic map of the Bernard nappe between Matter Valley and Val d'Anniviers. The numbers indicate eclogitic outcrops: 1. Augstbordhorn, 2. Moiry valley, 3. Adlerflüe, 4. Minugrat. Modified after EscHER (1988), MARTHALER (1984) and SARTORI (1988).

at Adlerflüe (locality 3; SARTORI, 1988; THÉLIN et al., 1989 and 1990) and at Minugrat (locality 4; GILLIÉRON, 1946; RAHN, 1989; THÉLIN et al., 1990). The eclogites are restricted to the polymetamorphic lower part of the nappe and are mainly found near the contact between the Ergischhorn and the Barneuza units. The surrounding rocks are imprinted by the Alpine metamorphism, so the eclogites represent metamorphic islands in a sea of Alpine greenschist facies.

At Minugrat all eclogites occur with only one exception in the lowest part of the Barneuza unit ("banded amphibolites", THÉLIN et al., 1990), a layer of varying thickness forming a megaboudin structure (Fig. 2). It mainly consists of banded amphibolites and, subordinately, of micaschists and felsic rocks. Within these rocks the eclogites form ribbons and lenses of few metres of thickness. One outcrop of eclogite only was found in the uppermost part of the Barneuza unit ("banded complex", THÉLIN et al., 1990); this eclogite shows a pronounced retrograde overprinting.

Microscopic observations, electron microprobe data and thermodynamic calculations on the eclogites from the Minugrat will be presented in this paper.

Petrography

Most eclogites show a distinct retrograde overprint, and fresh omphacite is rarely preserved in these rocks. Nevertheless the eclogites can be well distin-

guished from the surrounding amphibolites which contain no garnet and are significantly darker. Fresh areas exhibit either a decussate texture or a good orientation of the omphacite. The size of the garnets varies from 0.5 to 3 mm. Other primary phases are rutile, clinozoisite, magnetite, kyanite and probably also some quartz. Grains of rutile and magnetite normally form small aggregates at the grain boundaries of garnet and omphacite; kyanite can be found within decussate omphacite textures.

Retrograde transformation begins along thin cracks or grain boundaries: a fine-grained symplectitic seam of bluegreen amphibole and plagioclase develops and replaces step by step the whole omphacite. Sometimes large amphiboles can be observed already in the hand specimen, and are appearing as colourless poikiloblasts in the microscope (Fig. 3c). The growth of these poikiloblasts must have taken place early after the eclogitic phase, because they often surround fresh grains of omphacite. Within these areas aggregates of phengite occur, and the kyanite is replaced by paragonite, later by margarite. Garnet and rutile seem to be the most stable primary eclogitic phases. Sometimes garnet is surrounded by a rim of bluegreen amphiboles and is replaced by chlorite, plagioclase, epidote and quartz in very retrograded eclogites. In the latter rutile is often rimmed by sphene.

The different types of amphiboles found in thin section and their chemical aspects are discussed below. With the disappearance of omphacite and

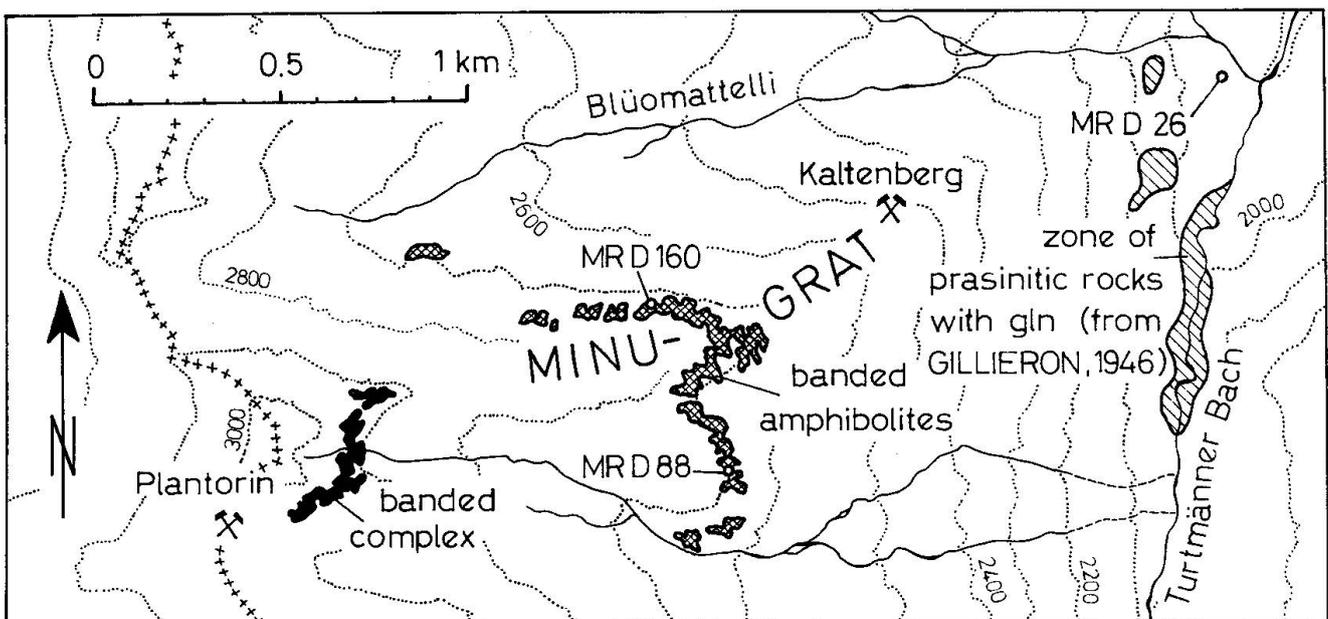Fig. 2   Map of the Minugrat showing the occurrence of the uppermost and the lowermost part of the Barneuza unit and the zone of prasinitic rock with glaucophane from GILLIÉRON (1946), all lying within the polymetamorphic basement of the Siviez-Mischabel nappe. In addition, the localities of the two analyzed eclogitic samples, MR D 88 and 160, as well as of the analyzed amphibolite with sodic amphiboles, MR D 26, are indicated.
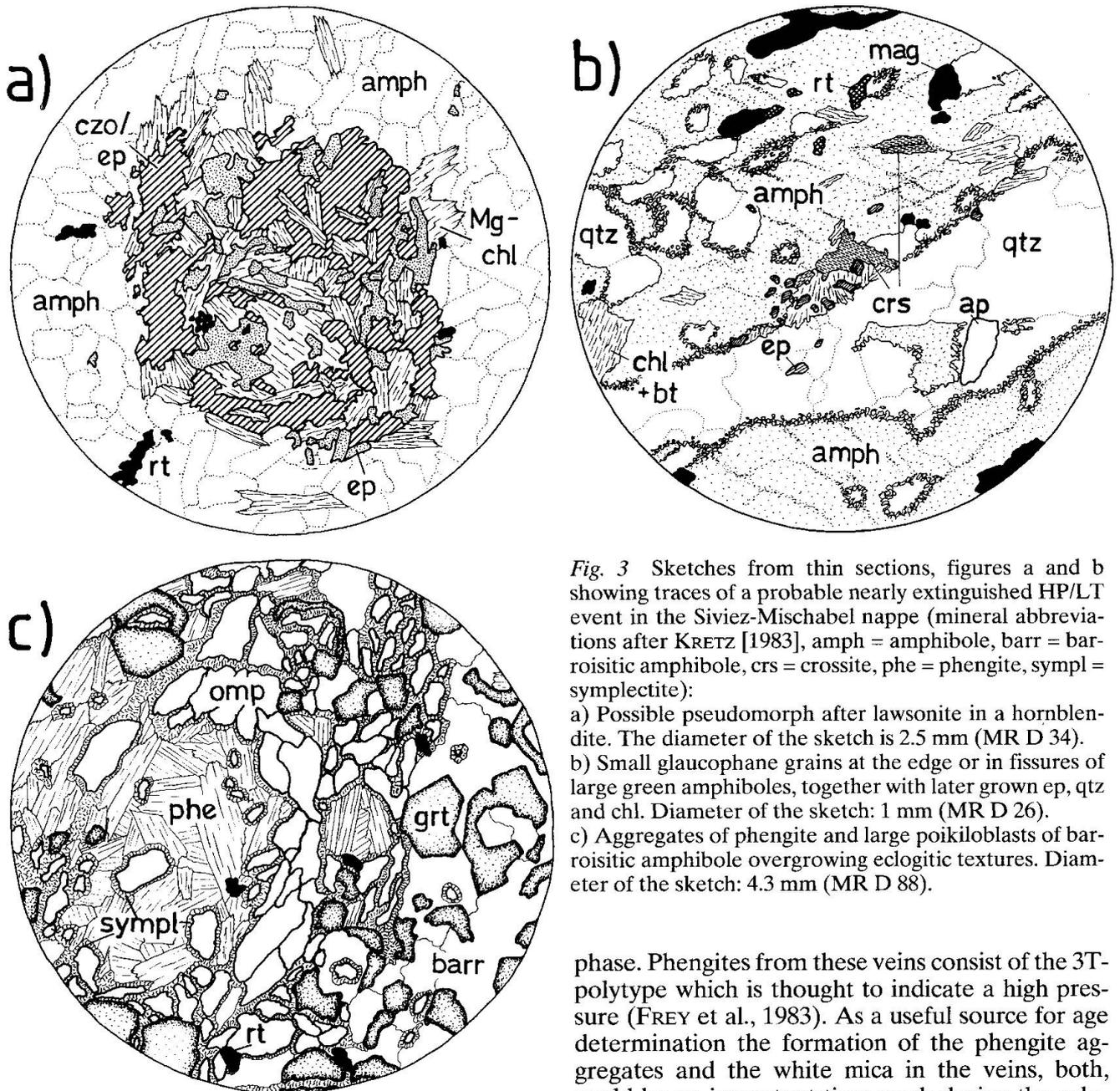
Fig. 3 Sketches from thin sections, figures a and b showing traces of a probable nearly extinguished HP/LT event in the Siviez-Mischabel nappe (mineral abbreviations after KRETZ [1983], amph = amphibole, barr = barroisitic amphibole, crs = crossite, phe = phengite, sympl = symplectite):

a) Possible pseudomorph after lawsonite in a hornblendite. The diameter of the sketch is 2.5 mm (MR D 34).

b) Small glaucophane grains at the edge or in fissures of large green amphiboles, together with later grown ep, qtz and chl. Diameter of the sketch: 1 mm (MR D 26).

c) Aggregates of phengite and large poikiloblasts of barroisitic amphibole overgrowing eclogitic textures. Diameter of the sketch: 4.3 mm (MR D 88).

coarsening of the amphibole-plagioclase symplectite a continuous transformation to a fine-grained garnet-bearing amphibolite is indicated. In the coarsening symplectite small needles of epidote often grow in rosettes.

No white mica seems to belong to the eclogitic paragenesis. Together with the growth of poikiloblastic barroisitic amphiboles, aggregates of phengite overgrow the eclogitic textures as a first retrograde paragenesis (Fig. 3c). However, at several places veins of quartz and/or phengite occur in the fresh eclogitic rocks, and sometimes these veins are kyanite-bearing. Their chronological relation to the eclogites is not yet clear; thus it is difficult to decide whether or not this phengite is a primary

phase. Phengites from these veins consist of the 3T-polytype which is thought to indicate a high pressure (FREY et al., 1983). As a useful source for age determination the formation of the phengite aggregates and the white mica in the veins, both, could be an important time mark during the eclogitic and/or retrograde evolution.

No traces of a preceeding blueschist facies (e.g. inclusions of glaucophane in garnet) as known from outcrops in the Matter valley (e.g. BEARTH, 1963; FRY, 1972; BARNICOAT and FRY, 1986; GANGUIN, 1988), could be found in the eclogites at Minugrat. But in the metabasites of the Ergischhorn unit, possible pseudomorphs after lawsonite (Fig. 3a) and small grains of a blue-violet amphibole (Fig. 3b) probably represent a nearly extinguished high pressure event, although no outcrop has been found, where both features can be observed within the same rock. On his map GILLIÉRON (1946) describes a zone of only optically determined "glaucophane"-bearing prasinitic rocks which can be found in the gorge of the "Turt-

männer Bach" and upwards towards "Blüomattel-li" (Fig. 2). This occurrence of sodic amphibole could be confirmed in one outcrop only, where within a large lense of amphibolitic rocks a very coarse-grained core with large dark green amphiboles has been found (Fig. 2). A detailed description of the outcrop is given in RAHN (1989). As already mentioned by GILLIÉRON (1946) grains of 20 to 150 μm in size occur as inclusions at grain boundaries and along fissures within the large green amphiboles showing a distinct blue-violet pleochroism. Textural evidences suggest the sodic amphiboles having newly formed within the large amphiboles; they do not seem to be relics of an earlier amphibole generation.

Mineral chemistry

Chemical analyses have been obtained using the JEOL JXA-8600 electron microprobe of the Geochemical Laboratory, Basel University (operated at 20 kV and a sample current of 20 nA; beam size = 5 μm). In order to analyze simultaneously for the elements listed in tables 1 and 2, a combined energy and wavelength dispersive system has been used. Special care was taken for the analysis of the garnet-omphacite pairs used for geothermobarometry; the distance between the two analyzed spots was always 20 μm or less.

Garnet: Most garnets show a good zoning with a core rich in almandine and grossularite and containing many inclusions (rutile, phengite and amphibole), and a rim rich in pyrope with only a few inclusions. Thus, the cores show compositions of typical B-eclogitic garnets, while the rims exhibit a chemistry characteristic for garnets in C-eclogites (COLEMAN et al., 1965). Typical compositions are (RAHN, 1989):

core:
$$X_{alm} = 0.58, X_{grs} = 0.30, X_{prp} = 0.08, X_{sps} = 0.04,$$

rim:
$$X_{alm} = 0.45, X_{grs} = 0.18, X_{prp} = 0.36, X_{sps} = 0.01.$$

A calculation of Fe^{3+} values after RYBURN et al. (1976) yields $X_{adr} \approx 0.02$ for the rim and negative values for the core. This zoning indicates a continuous growth of the garnets during changing P-T conditions, the rim probably being in equlibrium with the surrounding grains of omphacite.

No evidences for a continued growth of the garnets during retrograde conditions can be found. Especially in retrograde eclogites, garnets are crosscut by fissures. These fissures often are perpendicular to the orientation of omphacite grains and of late green amphibole blasts. The presence of the fissures is probably responsible for the lack of original inclusions belonging to the former history of the garnets preserved in the rims. However, all observed inclusions are either part of the eclogitic paragenesis or also found as retrograde phases in the matrix.

An interesting point is the formation of "atoll" garnets during growth of the colourless amphibole blasts. Analyses of the "atoll" garnets reveal the same composition as in the rims of the eclogitic garnets (see above). This is suggesting that the "atoll" shape was formed by replacement of the core during amphibole growth.

Omphacite: Only microprobe data of domains with a good orientation of the clinopyroxene were carried out. This microstructure yields important evidence for dynamic recrystallisation and therefore for attained equilibrium which meets the requirements for the use of the grt-cpx geothermometer (LARDEAUX et al., 1986). The analyzed pyroxenes show no zonation, and all of them lie in the omphacite field of MORIMOTO (1988). Omphacite shows only a small variation in its jadeite content: X_{jd} varies between 0.47 and 0.55. Several calculation models are available for estimation of the Fe^{3+} content (e.g. RYBURN et al., 1976; CARPENTER, 1979; LAIRD and ALBEE, 1981) but their application yields very small and often negative values. Therefore, it seems reasonable to neglect X_{acm} and to assume that $Fe_{tot} = Fe^{2+}$, although this assumption has an important influence on the temperature calculations. The content of Cr in clinopyroxene normally is very low, but the highest values reach up to 1.1 wt%; Mn, Ti and K are negligible (see Tab. 2).

Amphiboles: Analyses were carried out mainly in eclogitic and retroeclogitic rocks. One amphibolite with small sodic amphiboles has been analyzed by electron microprobe (see further below).

By optical observations in retrograde stages of former eclogites six different types of amphiboles can be distinguished, but not all of them show an individual chemical composition when analyzed by microprobe. All these amphibole data were calculated on the basis of 22 oxygens with the computer program of ROCK and LEAKE (1982).

– The first growing amphiboles are large colourless poikiloblasts with inclusions of nearly fresh clinopyroxenes and "atoll" garnets. The description fits well with that given by THÉLIN et al. (1989, 1990) for their pargasites in the eclogites of the "Adlerflüe", but microprobe analyses show barroisitic chemistry for these blasts: $(Na + K)_A << 0.5$; $Mg / (Mg + Fe^{2+}) > 0.95$.

– The bluegreen amphiboles in the very fine symplectite show varying composition. Especially the Ca content can range from 1.1 to 1.8 atoms per formula, while the content of Na is nearly constant

Tab. 1 Garnet analyses of the eclogites from the Minugrat and the calculated mineral formulas on the basis of 8 cations. Localities of the samples are shown in figure 2.

Sample Number	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88
Analysis	B1	B3	C1	C4	C5	C7	C9	C11	C14	C17	C19	C21	C22
SiO_2	39.50	39.66	39.37	39.21	39.31	39.38	38.71	38.98	39.09	39.37	39.63	39.03	39.29
Al_2O_3	22.67	22.63	22.64	22.45	22.75	22.62	22.47	22.59	22.71	22.85	22.82	22.41	22.60
TiO_2	0.00	0.00	0.10	0.00	0.00	0.00	0.09	0.06	0.00	0.00	0.00	0.05	0.00
Cr_2O_3	0.06	0.05	0.06	0.06	0.00	0.00	0.05	0.06	0.08	0.03	0.07	0.00	0.00
FeO	21.69	22.43	22.98	22.11	20.99	21.70	21.63	22.17	21.51	22.01	22.12	23.33	22.38
MnO	0.56	0.63	0.68	0.48	0.66	0.63	0.52	0.57	0.62	0.58	0.51	0.36	0.64
MgO	8.82	8.99	8.09	7.38	8.53	8.02	6.90	8.21	8.65	8.21	8.84	6.31	7.79
CaO	6.95	6.34	6.68	8.34	7.81	7.94	9.43	7.24	7.42	7.51	6.70	8.98	7.81
Na_2O	0.00	0.02	0.00	0.00	0.00	0.02	0.00	0.00	0.06	0.03	0.02	0.04	0.04
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.25	100.75	100.60	100.03	100.05	100.31	99.80	99.88	100.14	100.59	100.71	100.51	100.55

Mineral formulas: atoms per 8.00 cations

	B1	B3	C1	C4	C5	C7	C9	C11	C14	C17	C19	C21	C22
Si	2.996	2.996	2.994	3.000	2.986	2.994	2.971	2.978	2.967	2.984	2.994	2.991	2.987
Al	2.027	2.015	2.030	2.025	2.037	2.027	2.033	2.034	2.032	2.041	2.032	2.024	2.025
Ti	0.000	0.000	0.006	0.000	0.000	0.000	0.005	0.003	0.000	0.000	0.000	0.003	0.000
Cr	0.004	0.003	0.004	0.004	0.000	0.000	0.003	0.004	0.005	0.002	0.004	0.000	0.000
Fe^{2+}	1.376	1.417	1.461	1.415	1.333	1.380	1.388	1.416	1.365	1.395	1.397	1.495	1.423
Mn	0.036	0.040	0.044	0.031	0.042	0.041	0.034	0.037	0.040	0.037	0.033	0.023	0.041
Mg	0.997	1.012	0.917	0.842	0.966	0.909	0.789	0.935	0.979	0.927	0.995	0.721	0.883
Ca	0.565	0.513	0.544	0.684	0.636	0.647	0.776	0.593	0.603	0.610	0.542	0.737	0.636
Na	0.000	0.003	0.000	0.000	0.000	0.003	0.000	0.000	0.009	0.004	0.003	0.006	0.006
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Sample Number	MRD 160	MRD 160	MRD 160	MRD 160	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 88	MRD 160	MRD 160
Analysis	E2	E4	E6	E9	12.6	12.9	12.11	11.1	11.3	11.5	15.2	16.2
SiO_2	39.73	39.90	39.34	39.72	39.29	39.35	38.89	38.80	39.18	39.27	38.72	39.37
Al_2O_3	22.43	22.60	22.11	22.41	22.38	22.26	22.25	21.86	22.29	22.28	22.06	22.50
TiO_2	0.19	0.03	0.04	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.05	0.00
Cr_2O_3	0.05	0.05	0.03	0.07	0.07	0.05	0.00	0.00	0.00	0.00	0.05	0.12
FeO	22.62	22.59	23.41	21.80	20.64	20.99	21.58	21.23	22.56	21.91	23.53	22.05
MnO	0.52	0.54	0.28	0.58	0.63	0.61	0.64	0.93	0.63	0.71	0.87	0.53
MgO	8.66	9.43	6.74	7.95	8.24	8.53	8.27	4.16	9.17	8.67	6.80	9.24
CaO	6.64	5.56	8.41	8.11	8.44	8.20	8.01	13.09	6.41	6.97	7.80	6.64
Na_2O	0.00	0.00	0.02	0.06	0.05	0.00	0.03	0.03	0.00	0.00	0.05	0.00
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.84	100.70	100.38	100.70	99.74	99.99	99.67	100.30	100.24	99.81	99.93	100.45

Mineral formulas: atoms per 8.00 cations

	E2	E4	E6	E9	12.6	12.9	12.11	11.1	11.3	11.5	15.2	16.2
Si	3.006	3.012	3.016	3.010	2.995	2.993	2.972	2.998	2.974	2.996	2.984	2.978
Al	2.001	2.011	1.998	2.002	2.011	1.995	2.005	1.991	1.994	2.004	2.004	2.006
Ti	0.011	0.002	0.002	0.000	0.000	0.000	0.000	0.012	0.000	0.000	0.003	0.000
Cr	0.003	0.003	0.002	0.004	0.004	0.003	0.000	0.000	0.000	0.000	0.003	0.007
Fe^{2+}	1.431	1.426	1.501	1.381	1.316	1.335	1.379	1.372	1.432	1.398	1.516	1.395
Mn	0.033	0.035	0.018	0.037	0.041	0.039	0.041	0.061	0.041	0.046	0.057	0.034
Mg	0.977	1.061	0.770	0.898	0.936	0.967	0.942	0.479	1.038	0.986	0.781	1.042
Ca	0.538	0.450	0.691	0.658	0.689	0.668	0.656	1.084	0.521	0.570	0.644	0.538
Na	0.000	0.000	0.003	0.009	0.007	0.000	0.004	0.004	0.000	0.000	0.007	0.000
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

($Na_{tot} \approx 1.0$). Interesting details are a low Fe content and a Cr content similar to the replaced clinopyroxenes.

– Bluegreen amphiboles forming seams around garnet show a similar chemical composition: Na is more or less constant ($0.8 < Na_{tot} < 1.1$), Ca is somewhat higher compared to the symplectitic amphiboles. Thus, all of these amphiboles are Ca-amphiboles (LEAKE, 1978). The calculated Fe^{3+}/Fe^{2+} ratio is apparently low.

Tab. 2 Omphacite analyses of the eclogites from the Minugrat and the calculated mineral formulas on the basis of 6 oxygens. Localities of the samples are shown in figure 2.

Sample Number Analysis	MRD 88 B2	MRD 88 B4	MRD 88 C2	MRD 88 C3	MRD 88 C6	MRD 88 C8	MRD 88 C10	MRD 88 C12	MRD 88 C15	MRD 88 C16	MRD 88 C18	MRD 88 C20	MRD 88 C23
SiO_2	56.15	56.42	56.70	56.28	56.40	56.59	56.08	56.28	56.30	56.77	56.79	56.46	55.97
Al_2O_3	12.75	12.24	11.74	12.77	12.41	12.66	12.87	12.43	12.25	12.46	12.23	12.79	11.64
TiO_2	0.12	0.04	0.22	0.07	0.00	0.12	0.11	0.13	0.04	0.11	0.09	0.05	0.14
Cr_2O_3	0.14	0.08	0.17	0.07	0.09	0.08	0.11	0.10	0.08	0.06	0.05	0.08	0.10
FeO	2.47	2.42	2.04	2.49	2.38	2.43	2.52	2.40	2.15	2.42	2.11	2.42	3.03
MnO	0.00	0.03	0.03	0.03	0.00	0.04	0.00	0.06	0.00	0.03	0.00	0.00	0.00
MgO	7.94	8.36	8.71	8.01	8.19	8.04	7.90	8.16	8.57	8.35	8.46	7.97	8.38
CaO	12.75	13.21	13.74	12.75	13.13	12.84	12.77	12.93	13.29	13.13	13.14	12.89	13.55
Na_2O	7.04	7.13	6.85	7.26	7.23	7.39	7.33	7.20	7.15	7.20	7.13	7.35	7.11
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	99.36	99.93	100.20	99.73	99.83	100.19	99.69	99.69	99.83	100.53	100.00	100.01	99.92

Mineral formulas: atoms per 6.00 oxygens

Si	1.987	1.989	1.992	1.986	1.989	1.988	1.981	1.987	1.985	1.988	1.995	1.986	1.984
Al	0.532	0.509	0.486	0.531	0.516	0.524	0.536	0.517	0.509	0.514	0.507	0.530	0.486
Ti	0.003	0.001	0.006	0.002	0.000	0.003	0.003	0.003	0.001	0.003	0.002	0.001	0.004
Cr	0.004	0.002	0.005	0.002	0.003	0.002	0.003	0.003	0.002	0.002	0.001	0.002	0.003
Fe^{2+}	0.073	0.071	0.060	0.073	0.070	0.071	0.074	0.071	0.063	0.071	0.062	0.071	0.090
Mn	0.000	0.001	0.001	0.001	0.000	0.001	0.000	0.002	0.000	0.001	0.000	0.000	0.000
Mg	0.419	0.439	0.456	0.421	0.431	0.421	0.416	0.429	0.450	0.436	0.443	0.418	0.443
Ca	0.483	0.499	0.517	0.482	0.496	0.483	0.483	0.489	0.502	0.493	0.495	0.486	0.515
Na	0.483	0.487	0.467	0.497	0.494	0.503	0.502	0.493	0.489	0.489	0.486	0.501	0.489
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Sample Number Analysis	MRD 160 E1	MRD 160 E3	MRD 160 E5	MRD 160 E8	MRD 88 12.7	MRD 88 12.8	MRD 88 12.10	MRD 88 11.2	MRD 88 11.4	MRD 88 11.6	MRD 160 15.1	MRD 160 16.1
SiO_2	56.38	56.20	56.51	56.10	56.40	56.73	55.70	56.64	56.48	56.48	55.91	56.18
Al_2O_3	11.51	11.93	10.18	11.94	12.07	12.68	12.51	12.65	12.79	12.69	11.26	11.63
TiO_2	0.21	0.10	0.07	0.14	0.06	0.06	0.00	0.11	0.17	0.13	0.09	0.00
Cr_2O_3	0.12	0.09	0.13	0.07	0.17	0.05	0.11	0.16	0.08	0.16	0.00	0.07
FeO	3.52	3.63	3.36	3.52	2.40	2.47	2.33	2.58	2.57	2.39	2.95	3.94
MnO	0.00	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.06	0.00
MgO	8.03	7.97	9.01	7.77	8.53	8.40	8.05	8.09	8.09	8.18	8.77	7.93
CaO	13.10	12.67	14.56	12.82	13.33	12.94	12.96	12.94	12.90	13.00	13.61	12.60
Na_2O	7.15	7.22	6.27	7.30	7.43	7.77	7.53	7.57	7.69	7.66	7.03	7.93
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00
Total	100.02	99.86	100.09	99.66	100.39	101.10	99.22	100.74	100.85	100.69	99.68	100.28

Mineral formulas: atoms per 6.00 oxygens

Si	1.996	1.992	2.004	1.992	1.983	1.979	1.980	1.983	1.976	1.978	1.987	1.991
Al	0.480	0.498	0.426	0.500	0.500	0.521	0.524	0.522	0.528	0.524	0.472	0.486
Ti	0.006	0.003	0.002	0.004	0.002	0.002	0.000	0.003	0.004	0.003	0.002	0.000
Cr	0.003	0.003	0.004	0.002	0.005	0.001	0.003	0.004	0.002	0.004	0.000	0.002
Fe^{2+}	0.104	0.108	0.100	0.105	0.071	0.072	0.069	0.076	0.075	0.070	0.088	0.117
Mn	0.000	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.002	0.000
Mg	0.424	0.421	0.476	0.411	0.447	0.437	0.426	0.422	0.422	0.427	0.464	0.419
Ca	0.497	0.481	0.553	0.488	0.502	0.484	0.494	0.485	0.484	0.488	0.518	0.478
Na	0.491	0.496	0.431	0.503	0.506	0.525	0.519	0.514	0.522	0.520	0.484	0.545
K	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000

– At several places large bluegreen amphiboles with a visible zonation occur in the symplectite. They are NaCa-amphiboles (LEAKE, 1978) and typically show high Fe^{3+}/Fe^{2+} ratios (> 1.0).

– Bluegreen amphiboles as inclusions in garnets yield a chemical composition between the seam-forming amphiboles and the large amphiboles in the symplectite. These NaCa- and Ca-amphiboles show intermediate Fe^{3+}/Fe^{2+} ratios. Their chemistry

seems to be markedly influenced by the surrounding garnet.

– A last group, found mostly in late fissures or recrystallized symplectite and optically recognized by a yellowish green pleochroism, are Ca-amphiboles poor in Na, but rich in Fe and Ti.

From optical observations, the following growth sequence was established for these six amphibole groups: The earliest amphiboles are colourless barroisitic poikiloblasts followed by a second group comprising all bluegreen amphiboles. Green amphiboles probably belong to a last generation. This sequence shows two developments in chemical composition: Ca and Fe_{tot} increase during evolution. The first trend most likely is linked to a decrease in the anorthite content of the symplectitic plagioclase. The first retrograde plagioclase may have been andesine or oligoclase but most measurements show albitic composition ($X_{an} <$ 0.10).

The sodic amphiboles in one hand specimen have been a special focal point. Both, the large green amphiboles and the blue-violet grains within the former have been analyzed and calculated with the computer program EMP-AMPH of MOGESSIE et al. (1990). Six analyses of the large amphiboles show mainly tschermakitic hornblende with (Ca + Na)$_B$ = 2.00 and 6.18 < Si < 6.40. No zonation was observed. Eight analyses were made in blue-violet grains yielding crossite composition with Fe^{3+}/Fe^{3+} + Al^{VI} ranging from 0.40 to 0.62 and Mg/Mg + Fe^{2+} ≥ 0.6 (Fig. 4).

Phengite: Typical for the phengites growing together with the large barroisitic poikiloblasts (Fig. 3c) is a Si content between 3.36 and 3.45 (calculated on the basis of 11 oxygens) and up to 0.5 wt% of both Cr_2O_3 and BaO. The same chemical composition without Cr can be found for phengite
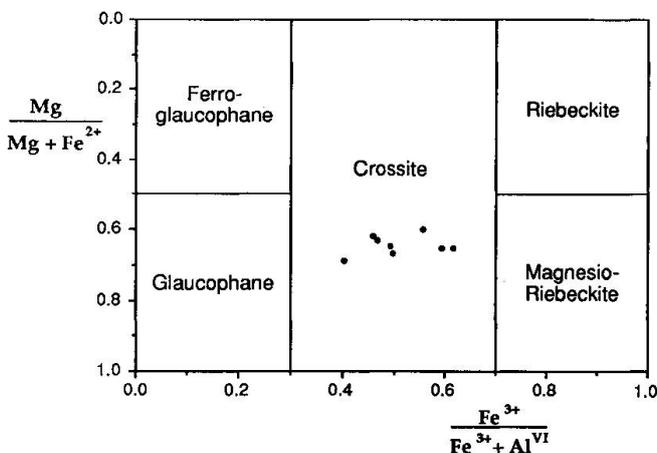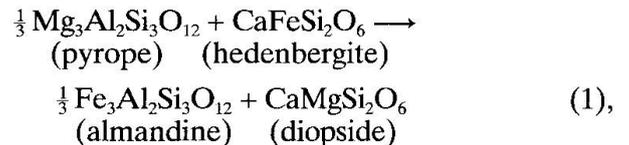

Fig. 4 Amphibole classification scheme of sodic amphiboles after LEAKE (1978) with the analyzed crossites from sample MR D 26.

inclusions in garnets and small phengite leaves in the symplectite.

Geothermobarometry

The use of the Mg–Fe exchange between coexisting clinopyroxene and garnet as indicator of temperature is very popular. The chemical reaction is:

$$\tfrac{1}{3} Mg_3Al_2Si_3O_{12} + CaFeSi_2O_6 \longrightarrow$$
(pyrope)   (hedenbergite)

$$\tfrac{1}{3} Fe_3Al_2Si_3O_{12} + CaMgSi_2O_6 \qquad (1),$$
(almandine)   (diopside)

with a distribution coefficient

$$K_D = \frac{X_{Fe}^{grt} \cdot X_{Mg}^{cpx}}{X_{Mg}^{grt} \cdot X_{Fe}^{cpx}} \qquad (2).$$

This equilibrium was first calibrated by RÅHEIM and GREEN (1974), and later by ELLIS and GREEN (1979) who proposed a correction for the Ca content of the garnet. For constant pressure and temperature they found a linear equation relating X_{Ca} in garnet to ln K_D using data from experiments at 24–30 kbar pressure and 750–1300 °C temperature. A reinterpretation of the data by KROGH (1988) is expressed by the equation

$$T\,(°C) =$$
$$\frac{-6173(X_{Ca}^{grt})^2 + 6731 X_{Ca}^{grt} + 1879 + 10P(kbar)}{\ln K_D + 1.393}$$
$$- 273 \qquad (3),$$

which shows a quadratic relationship between ln K_D and X_{Ca} at constant P and T. Another calibration with new experiments was developped by PATTISON and NEWTON (1989). They used reversal experiments at 15 and 29 kbar and 700–1200 °C. Their thermodynamic expression for the calibration is:

$$T\,(°K) = \frac{a'X^3 + b'X^2 + c'X + d'}{\ln K_D + a_oX^3 + b_oX^2 + c_oX + d_o} +$$
$$+ 5.5(P-15) \qquad (4),$$

where a'–d' and a_o–d_o are experimentally determined parameters for different X_{Ca} in garnet, X is the Mg number of the garnet (= Mg / (Mg + Fe)) and P is the pressure in kbar. All three equations were used here to obtain temperature conditions for the eclogitization.

For the pressure determination the following reaction was used:

$$jd_{50} + qtz \rightarrow ab \qquad (5),$$

where jd_{50} is the analyzed X_{jd} = 0.50 in the clinopyroxene. The reaction was calculated with the data
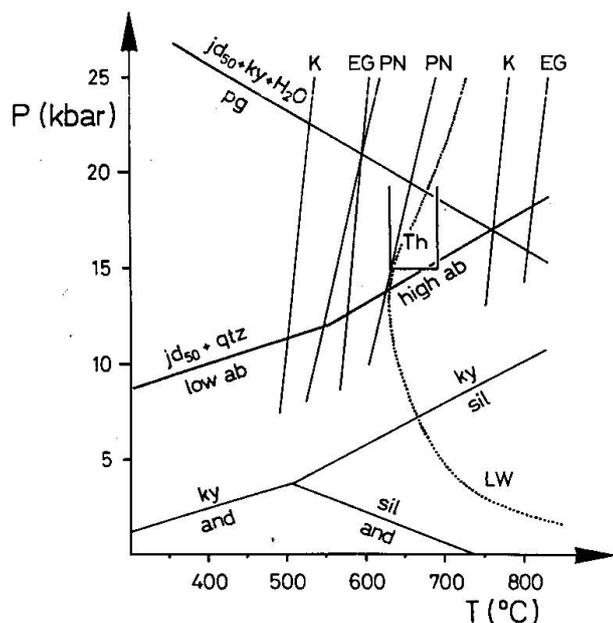
Fig. 5 P-T diagram showing the calculated conditions for the Minugrat eclogites: the subvertical lines show lower and upper limits of the following grt-cpx geothermometers: EG = Ellis and Green (1979), K = Krogh (1988), PN = Pattison and Newton (1989). Th = Conditions for the Adlerflüe eclogites from Thélin et al. (1990) calculated after Ellis and Green (1979). All inserted reaction curves have been calculated with the thermodynamic data base of Berman (1988) and the GE0-CALC computer program of Brown et al. (1988) in the system Na–Al–Si–O–H. (Dotted line: wet eclogite solidus curve of Lambert and Wyllie, 1972.)

base of Berman (1988) using the Ge0-Calc computer program of Brown et al. (1988). Both low and high albite were taken into account and it was assumed that $a_{jd} = X_{jd}$, which seems reasonable for omphacites close to the composition $jd_{50}di_{50}$ (Holland, 1983 and 1990). Furthermore it was assumed that the analyzed clinopyroxenes are structually ordered P2/n omphacites which is normally the case at temperatures below 850 °C (Carpenter, 1979 and 1981; Carswell and Harley, 1989). The intersection of reaction (5) with the calibrated curves for K_D between garnet and omphacite yields minimum pressure and temperature conditions for the eclogitization.

For the P-T estimations 25 clinopyroxene-garnet pairs were used. Because of very low calculated Fe^{3+} contents no correction for Fe^{3+} was applied to the data. The results are shown in figures 5 and 6. Two features are very obvious when comparing the results of the different calculations:

– The temperature values calculated after Ellis and Green (1979) and Krogh (1988) exhibit a considerable spread, ranging from 575 °C (12.5 kbar) to 810 °C (18 kbar) and 500 °C (11.5 kbar) to 760 °C (17.5 kbar), respectively (see Fig. 5). How-
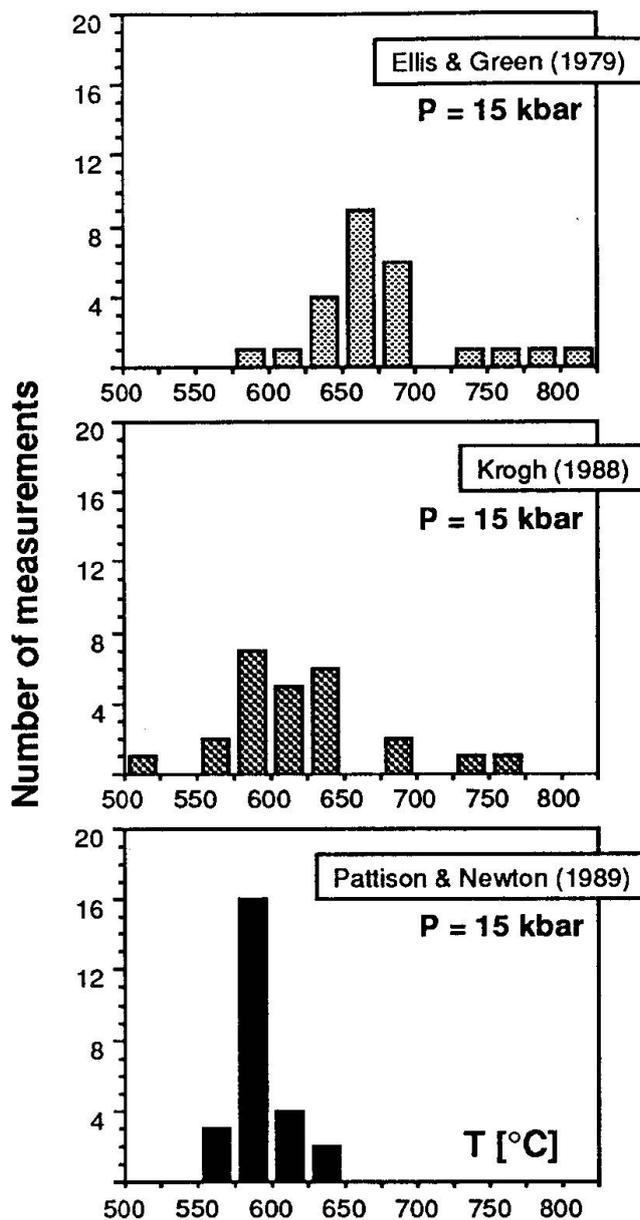

Fig. 6 Calculated temperatures at a pressure of 15 kbar for three different calculation methods of the Mg–Fe exchange between grt and cpx. The number of measurements always is 25.

ever, both data sets yield a distinct temperature maximum displayed in the histograms of figure 6, i.e. between 560 and 640 °C for the Krogh (1988) expression and between 620 and 690 °C for the Ellis and Green (1979) calibration, at corresponding minimum pressures defined by the stability of clinopyroxene with $X_{jd} = 0.50$ (Fig. 5). The values confirm the difference of about 50° between these two methods as already mentioned by Krogh (1988).

– The range of variation of the data calculated after Pattison and Newton (1989) is much smaller (from 545 to 625 °C at corresponding minimum pressures, see Fig. 5), with a sharp maximum at

560–580 °C (Fig. 6). These results agree well with those obtained of KROGH (1988), but the temperature maximum lies below the maximum obtained with the ELLIS and GREEN (1979) data.

A reasonable upper limit of pressure is not available. The replacement of kyanite by paragonite, observed in thin section, could be described by the following reaction:

$$jd_{50} + ky + H_2O \rightarrow pg \qquad (6).$$
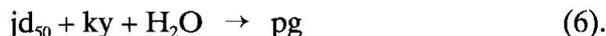
The P-T conditions of this reaction have been experimentally determined by HOLLAND (1979) and confirmed by BERMAN (1988). If the eclogites have equilibrated above this curve we must assume minimum pressures of 20–22 kbar at temperatures of 550 to 650 °C (Fig.5). However a great problem of the calculated reaction is the unknown water activity. With $a_{H_2O} = 0.6$ the reaction curve of (4) would yield minimum pressures of 14–15 kbar for 550–600 °C.

In the evaluation of minimum pressure conditions by reaction (5), high and low albite was used as end-member. Often the symplectite is too fine-grained to obtain reasonable plagioclase microprobe analyses. Even by reducing the beam diameter to 1 μm (normally 5 μm) nearly all data are mixed analyses of plagioclase and amphibole. Out of 17 useful analyses of symplectitic plagioclase 11 are albites, 4 are oligoclases and only 2 are andesines (RAHN, 1989). It is not clear whether the fine-grained symplectite continuously changed its composition during recrystallization or still retained its primary composition as replacement product of omphacite; the latter is more probable according to the textural observations. However, taking oligoclase as primary composition of the symplectitic plagioclase, reaction (5) would not be distinctly shifted to higher pressures: for $X_{ab} = 0.8$ the activity of albite (a_{ab}), estimated after PERKINS and NEWTON (1981), is approximately 1. Even for $X_{ab} = 0.5$, a_{ab} is still above 0.9. Thus, a small anorthite content has a negligible influence on the position of reaction (5).

Discussion

Comparison of the three versions of the clinopyroxene-garnet geothermometer, applied to the data of the eclogites from Minugrat, has shown significant differences in the resulting temperatures. The maximum of the calculations after ELLIS and GREEN (1979) coincides with the P-T conditions of THÉLIN et al. (1990) who estimated temperatures of 620–680 °C at a minimum pressure of 15 kbar (Fig. 5) by using the calibration of ELLIS and GREEN (1979). These temperatures partly lie above the solidus curve for wet eclogites determined experimentally

by LAMBERT and WYLLIE (1972) which shows a minimum temperature of 630 °C at 13–14 kbar. Moreover, ELPHICK et al. (1982) have pointed out that diffusion in garnets becomes an important process at temperatures above 600 °C and would produce a homogenization of the garnets. However, the analyzed garnets still show a distinct zoning (see above). Thus, the temperatures obtained with the expressions of KROGH (1988) and PATTISON and NEWTON (1989), i. e. temperatures of 550–600 °C at minimum pressures of 12–13.5 kbar, are thought to be the most probable conditions of formation for the eclogites from Minugrat. Therefore, the most likely evaluated P-T conditions are lower than the estimated conditions for the Adlerflüe eclogites (THÉLIN et al., 1990; calculated after ELLIS and GREEN, 1979). When ELLIS and GREEN developed their model, they used the results of experiments performed in a pressure range of 24–30 kbar and a temperature range of 700–1300 °C. This calibration, therefore, has to be extrapolated considerably, in particular with regard to pressure. PATTISON and NEWTON (1989) used experiments at 15 and 29 kbar at 700–1200 °C temperature. Their experimental conditions, thus, are much closer to the most likely conditions expected in the studied region (THÉLIN et al., 1989, 1990) and in the present study. The small range of K_D lines (Fig. 5) also is a good argument for the usefulness of this method for these eclogites.

The age of the eclogitization of the Siviez-Mischabel nappe is still an unsolved problem. THÉLIN et al. (1989, 1990) discuss arguments for a pre-or eo-Variscan versus an Alpine age. Their arguments for a pre-Alpine age are supported by age determinations of ZINGG (1989) who limits the age of eclogitization between two events, before and after a high pressure metamorphism at 546 ± 21 Ma and 490 ± 10 Ma, respectively. Nevertheless, no age determinations have been made on the actual eclogitic rocks. From field and optical observations one point shall be highlighted here: as mentioned above, possible pseudomorphs after lawsonite and small amounts of crossite are potential indicators of another nearly extinguished high P/low T event (e. g. BROWN, 1978; CHATTERJEE et al., 1984) in the Siviez-Mischabel nappe. Such a metamorphic phase is well known in the upper-lying Mont Fort nappe and supposed to be an eo-Alpine event (ESCHER, 1988), although the eo-Alpine evolution in the central and western Alps is still a matter of discussion (HUNZIKER et al., 1989).

Thin section observations suggest that the possible pseudomorphs after lawsonite and the small grains of crossite both have grown after a probably strong retrograde event during which the eclogitic paragenesis has disappeared in the main part of the

metabasic rocks and has been replaced partly by large green amphiboles (Fig. 3b). If we assume an eo-Alpine age for this second high P/low T event with estimated minimum P-T conditions of about 7–9 kbar and 350–400 °C (RAHN, 1989), the eclogitization must have been a pre-Alpine event.

A possible indication for the age of the eclogites is given by the penetrating veins of quartz and/or phengite. Their chronological relation with the eclogites has not been completely clarified, but the occurrence of kyanite and of 3T-phengites are good arguments for their formation under high pressure, probably still under eclogitic conditions.

Acknowledgements

References

BARNICOAT, A.C. and FRY, N. (1986): High pressure metamorphism of the Zermatt-Saas ophiolite zone, Switzerland. J. Geol. Soc. London 143, pp. 607–618.

BEARTH, P. (1963): Contribution à la subdivision tectonique et stratigraphique du cristallin de la nappe du Grand St-Bernard dans le Valais (Suisse). Livre mém. Paul Fallot 2, pp. 407–418, Soc. géol. France.

BEARTH, P. (1980): Erläuterungen zum Blatt St. Niklaus, Geologischer Atlas der Schweiz, Nr. 71, Schweiz. Geol. Komm., Basel.

BERMAN, R.G. (1988): Internally-Consistent Thermodynamic Data for Minerals in the System Na₂O–K₂O–CaO–MgO–FeO–Fe₂O₃–Al₂O₃–SiO₂–TiO₂–H₂O–CO₂. J. Petrol. 29/1, pp. 445–522.

BROWN, E.H. (1978): A P-T-grid for metamorphic index minerals in high pressure terranes. Geol. Soc. Amer. Abstracts with Programs 10/7, p. 373.

BROWN, T.H., BERMAN, R.G. and PERKINS, E.H. (1988): Ge0-Calc: Software package for calculation and display of pressure-temperature-composition phase diagrams using an IBM or compatible personal computer. Computers and Geosciences 14, pp. 279–290.

CARPENTER, M.A. (1979): Omphacites from Greece, Turkey and Guatemala: composition limits of cation ordering. Amer. Mineralogist 64, pp. 102–108.

CARPENTER, M.A. (1981): Time-temperature-transformation (TTT) analysis of cation disordering in omphacite. Contr. Mineral. Petrol. 78, pp. 433–440.

CARSWELL, D.A. and HARLEY, S.L. (1989): Mineral barometry and thermometry. In: CARSWELL, D.A. (ed.): Eclogite Facies Rocks. Blackie, Glasgow and London, 396 p.

CHATTERJEE, N.D., JOHANNES, W. and LEISTNER, H. (1984): The system CaO–Al₂O₃–SiO₂–H₂O: new phase equilibria data, some calculated phase relations, and their petrological applications. Contr. Mineral. Petrol. 88, pp. 1–13.

COLEMAN, R.G., LEE, D.E., BEATTY, L.B. and BRANNOCK, W.W. (1965): Eclogites and eclogites: Their differences and similarities. Geol. Soc. Amer. Bull. 76, pp. 483–508.

ELLIS, D.J. and GREEN, D.H. (1979): An experimental study of the effect of Ca upon garnet-clinopyroxene Fe–Mg exchange equilibria. Contr. Mineral. Petrol. 71, pp. 13–22.

ELPHICK, S.C., GANGULY, J. and LOOMIS, T.P. (1982): Experimental study of Fe–Mn interdiffusion in aluminumsilicate garnet. Geol. Soc. Amer., Abstr. with Progr. 14, p. 483, Nr. 05659.

ESCHER, A. (1988): Structure de la nappe du Grand St-Bernard entre le val de Bagnes et les Mischabel. Rapp. Serv. hydr. géol. Suisse, 7.

FREY, M., HUNZIKER, J.C., JAEGER, E. and STERN, W.B. (1983): Regional distribution of white K-mica polymorphs and their phengite content in the central Alps. Contr. Mineral. Petrol. 83, pp. 185–197.

FRY, N. (1972): A study of metamorphic eclogite, with particular reference to the rocks of the Täschtal, Switzerland. Ph.D. Thesis, University of Manchester.

GANGUIN, J. (1988): Contribution à la caractérisation du métamorphisme polyphasé de la Zone Zermatt-Saas Fee. Ph. D. Thesis, ETH Zürich Nr. 8731.

GILLIÉRON, F. (1946): Geologisch-petrographische Untersuchungen an der Ni-Co-Lagerstätte Kaltenberg (Turtmanntal, Wallis). Beitr. Geol. Schweiz, geotechn. Ser., 25.

HALM, E. (1945): Die Kupfer-Wismut-Lagerstätten im oberen Val d'Anniviers (Wallis). Beitr. Geol. Schweiz, geotechn. Ser., 22.

HOLLAND, T.J.B. (1979): Experimental determination of the reaction Paragonite ↔ Jadeite + Kyanite + H₂O, and internally consistent thermodynamic data for part of the system Na₂O–Al₂O₃–SiO₂–H₂O, with applications to eclogites and blueschists. Contr. Mineral. Petrol. 68, pp. 293–301.

HOLLAND, T.J.B. (1983): The experimental determination of activities in disordered and short-range ordered jadeitic pyroxenes. Contr. Mineral. Petrol. 82, pp. 214–220.

HOLLAND, T.J.B. (1990): Activities of components in omphacitic solid solution. An application of Landau theory to mixtures. Contr. Mineral. Petrol. 105, pp. 446–453.

HUNZIKER, J.C., DESMONS, J. and MARTINOTTI, G. (1989): Alpine thermal evolution in the central and western Alps. In: COWARD, M.P., DIETRICH, D. and PARK, R.G. (eds) (1989): Alpine tectonics. Geol. Soc. Spec. Publ. No. 45, pp. 353–367.

KRETZ, R. (1983): Symbols for rock-forming minerals. Amer. Mineralogist, 68, pp. 277–279.

KROGH, E.J. (1988): The garnet-clinopyroxene Fe–Mg geothermometer – a reinterpretation of existing experimental data. Contr. Mineral. Petrol. 99, pp. 44–48.

LAIRD, J. and ALBEE, A.L. (1981): High-pressure metamorphism in mafic schist from Northern Vermont. Amer. J. Sci. 281, pp. 97–126.

LAMBERT, I.B. and WYLLIE, P.J. (1972): Melting of gabbro (quartz eclogite) with excess water to 35 kilobars, with geological applications. J. Geol. 80, pp. 693–708.

LARDEAUX, J.-M., CARON, J.-M., NISIO, P., PÉQUIGNOT, G., BOUDEULLE, M. (1986): Microstructural criteria for

reliable thermometry in low-temperature eclogites. Lithos 19, pp. 187–203.

LEAKE, B.E. (1978): Nomenclature of amphiboles. Amer. Mineralogist 63, pp. 1023–1052.

LENGELER, R. (1988): Pétrographie et géologie de la région de Grimentz. Les éclogites du socle Siviez-Mischabel (Val de Moiry et Val de Tourtemagne, Valais). Unpubl. Diplomarbeit, Universität Lausanne.

LUGEON, M. and ARGAND, E. (1905): Sur les grandes nappes de recouvrement du Piémont. C. R. Acad. Sci. (Paris), 15. Mai.

MARTHALER, M. (1984): Géologie des unités Penniques entre le val d'Anniviers et le val de Tourtemagne (Valais, Suisse). Eclogae geol. Helv. 77, pp. 395–448.

MOGESSIE, A., TESSARDI, R. and VELTMAN, C.B. (1990): EMP-AMPH – A Hypercard program to determine the name of an amphibole from electron microprobe analysis according to the international mineralogical association scheme – Computers and Geosciences 16, pp. 309–330.

MORIMOTO, N. (1988): Nomenclature of pyroxenes. Schweiz. Mineral. Petrogr. Mitt. 68, pp. 95–111.

PATTISON, D.R.M. and NEWTON, R.C. (1989): Reversed experimental calibration of the garnet-clinopyroxene Fe–Mg exchange thermometer. Contrib. Mineral. Petrol. 101, pp. 87–103.

PERKINS, D. and NEWTON, R.C. (1981): Charnockite geobarometers based on coexisting garnet-pyroxene-plagioclase-quartz. Nature 292, pp. 144–146.

RÅHEIM, A. and GREEN D.H. (1974): Experimental determination of the temperature and pressure dependence of the Fe–Mg partition coefficient for coexisting clinopyroxene and garnet. Contrib. Mineral. Petrol. 48, pp. 179–203.

RAHN, M. (1989): Petrographie und Geologie des Minugrates im hinteren Turtmanntal (VS). Unpubl. Diplomarbeit, Basel, 193 p.

ROCK, N.M.S. and LEAKE, B.E. (1982): The international mineralogical association amphibole nomenclature scheme: computerization and its consequences. Mineral. Mag. 48, pp. 211–227.

RYBURN, R.J., RÅHEIM, A. and GREEN, D.H. (1976): Determination of the P,T paths of natural eclogites during metamorphism – record of subduction. A correction to a paper by RÅHEIM and GREEN (1975). Lithos 9, pp. 161–164.

SARTORI, M. (1988): L'unité de Barrhorn. Un lien entre les Préalpes médianes rigides et leur socle paléozoïque. Thesis, Universität Lausanne, 150 p.

SARTORI, M. and THÉLIN, PH. (1987): Les schistes œillés albitique de Barneuza (Nappe de Siviez-Mischabel, Valais, Suisse). Schweiz. Mineral. Petrogr. Mitt. 67, pp. 229–256.

THÉLIN, Ph., LENGELER, R. and SARTORI, M. (1989): Les éclogites du socle Siviez-Mischabel: occurrence, paragénese, âge présumé (Val Tourtemagne et Val Moiry, Valais). Abstr. in: Schweiz. Mineral. Petrogr. Mitt. 69, p. 130.

THÉLIN, Ph., SARTORI, M., LENGELER, R. and SCHAERER, J.-P. (1990): Eclogites of paleozoic or early alpine age in the basement of the pennine Siviez-Mischabel nappe (Wallis, Switzerland). Lithos 25, pp. 71–88.

ZINGG, M. (1989): Die Siviez-Mischabel-Decke: Entstehung und Entwicklung eines Altkristallins. Ph. D. Thesis, ETH Zürich Nr. 8997, 177 p.