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Autor(en): **Widmer, Timo / Ganguin, Jacques / Thompson, Alan Bruce**

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Ocean floor hydrothermal veins in eclogite facies rocks of the Zermatt-Saas Zone, Switzerland

by Timo Widmer¹, Jacques Ganguin² and Alan Bruce Thompson¹

Abstract

Mg-rich, irregular garnet-chloritoid-talc veins and schists occur in the eclogites of the ZS-Zone. This metamorphic assemblage formed during subduction at pressures of at least 20 kbar. They are interpreted as former oceanic hydrothermal veins and show similarities with smectite-chlorite veins of ocean drilling cores (e.g. ODP hole 504B) produced during metasomatic alteration of ocean floor basalt by seawater.

Keywords: high-pressure, hydrothermal veins, eclogite facies, ocean floor, metasomatism.

1. Introduction

Four different high-temperature low-pressure alteration trends can be distinguished in metabasaltic rocks, now high-pressure eclogites, of the Zermatt-Saas (ZS) Zone. These metasomatic trends have been observed in altered oceanic basalts and from fluid-rock interaction experiments between sea water and ocean floor volcanics. Four familiar trends of ocean floor fluid-rock interaction have been recognised:

(1) *spilitisation*: Na enrichment whereby magmatic plagioclase is altered to albite (BEARTH, 1959; BEARTH and STERN, 1971) by interaction with sea water having high Na/Ca ratios (CANN, 1969; SEYFRIED et al., 1978) and low Mg, high Si contents (ROSENBAUER et al., 1988).

(2) *rodingitisation*: Ca from pyroxene alteration in ocean-floor peridotite added to adjacent basalt; (COLEMAN, 1977; EVANS et al., 1981).

(3) *epidotisation*: Ca enriched sea water precipitates epidote at the expense of magmatic plagioclase; (HONNOREZ et al., 1983; ALT et al., 1986; ALT, 1995). However, this type of alteration appears to be more common in ophiolites than in sea-floor alteration (J. ALT, personal communication, November, 1999).

(4) *chloritisation*: enrichment in Mg and depletion in Ca, due to precipitation of chlorite and smectite at the expense of volcanic glass, magmat-

ic plagioclase, olivine and pyroxene (HUMPHRIS and THOMPSON, 1978; MOTTL, 1983).

An unusual metasomatic rock type in the eclogite facies ZS-Zone has been identified. The occurrence of chloritoid-garnet-talc (Ctd-Gr-Tc) schists enclosed by Ctd-Tc eclogites or glaucophanites (including glaucophane schists, marked as horizontal striped areas in Fig. 1) is presented here. These rocks bear chemical similarities to the *chloritisation* metasomatic type (4) listed above. In addition to Ctd-Gr-Tc these schists can contain small amounts of glaucophane, jadeite and rutile. Some garnets have Ca-rich cores with inclusions of ilmenite, titanite, quartz and ulvöspinel. Some Ctd-Gr-Tc schists are retrograded to chlorite-garnet schists (GANGUIN's 1988, "chloritoschiste").

The best outcrops of these unusual veins are found on a rocky promontory 300 metres north of the Pfulwepass. The Ctd-Gr-Tc rocks are found as veins (Fig. 2a) from several centimetres to several decimetres size, as well as forming irregular patches (Fig. 2b) of quite different volumes in glaucophanites and Ctd-Tc eclogites (Fig. 2).

2. Oceanic metasomatic trends in Zermatt eclogitic rocks

The chemical analyses of Ctd-Gr-Tc veins and their enclosing rocks have been portrayed using

¹ Institut für Mineralogie und Petrographie, Dept. Erdwissenschaften, ETH Zürich, CH-8092, Switzerland. <alan@erdw.ethz.ch>

² Amt für Gewässerschutz und Abfallwirtschaft des Kt. Bern, Reiterstr. 11, CH-3011 Bern, Switzerland.

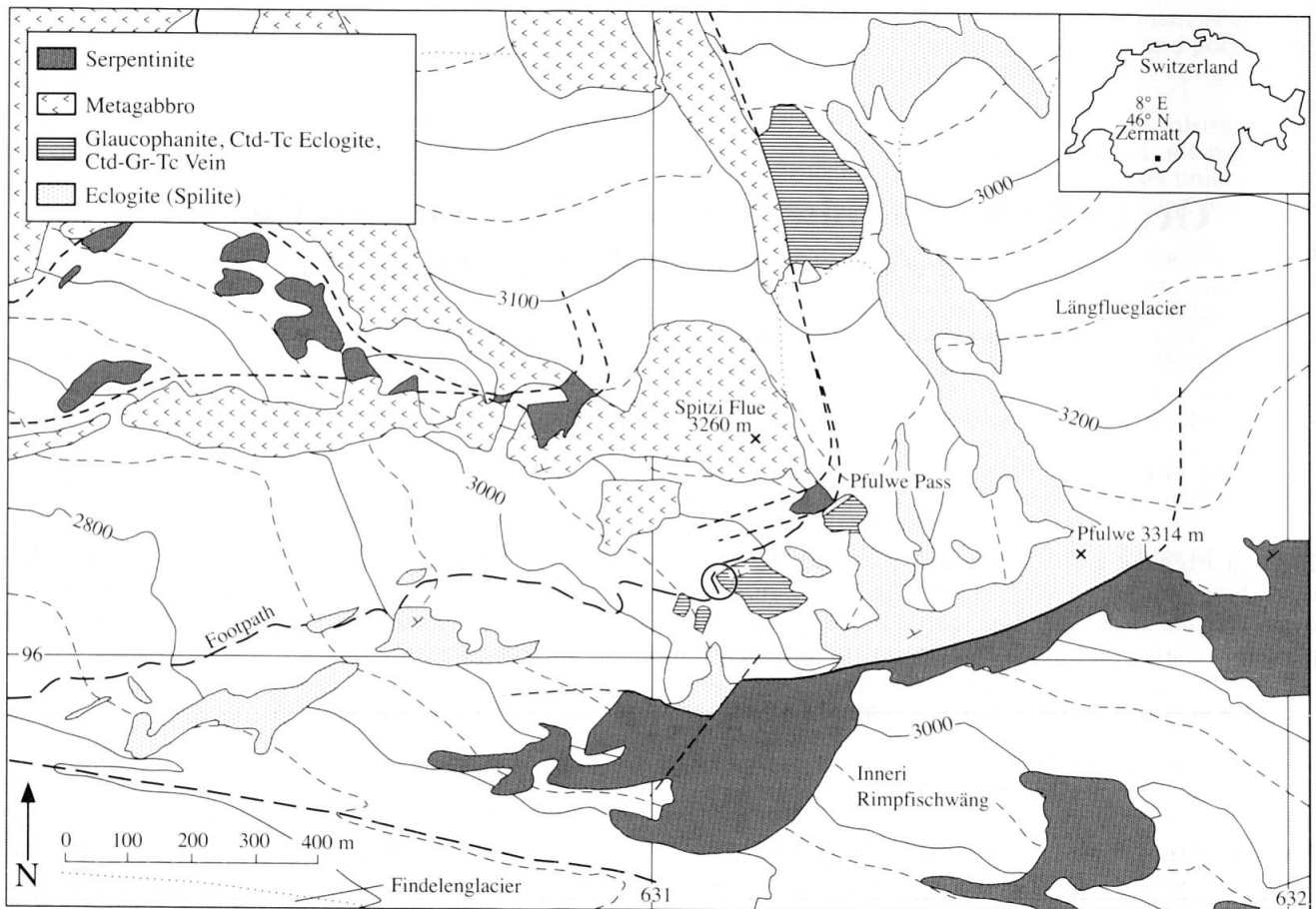


Fig. 1 Map of the Pfulwe region (WIDMER, 1996, p. 28) with various basalt lithologies and serpentinite. The location of the most important Ctd-Gr-Tc veins is shown by the open circle south of Spitzflue.

several projection schemes. To understand whether during hydrothermal alteration some elements remained unchanged, it was initially assumed that the ratio wt% Ti/wt% Zr remained constant.

Comparison of the chemical analysis of metabasalts from the ZS-Zone with analyses of mid-ocean ridge basalts (MORB, e.g. SCHILLING *et al.*, 1985) provides fundamental information on metasomatic events. PFEIFER *et al.* (1989) have shown using trace element analyses (REE, Zr-Y-Ti, Cr-Ni) that the eclogite facies mafic rocks of the ZS zone have a distinct MORB composition.

Of the ten oxide versus TiO_2 variation diagrams constructed by WIDMER (1996, p. 35–37) a plot of FeO^*/MgO vs TiO_2 (wt%) is shown here (Fig. 3). The differentiation trend of Fe- and Ti-enrichment can be seen for all metabasic rocks of the ZS-Zone. Sometimes Ctd-Gr-Tc schists and chlorite schists contain more than 2 wt% TiO_2 (Fig. 3). It is expected that vein fillings precipitated from ocean-floor hydrothermal solutions would be virtually devoid of Ti in view of its low solubility in natural waters (J. ALT, personal communication, November, 1999). However, as we were reminded

by A. BARNICOAT (personal communication, November, 1999), rutile crystals up to 5 cm are found in cross-cutting veins in the ZS-Zone, suggesting that some circumstances clearly favour Ti transport. Alternatively, the patchy occurrences of Ti minerals in the Ctd-Gr-Tc schists and chlorite schists suggest therefore partly a replacement origin involving metasomatic interaction of ocean-floor hydrothermal fluids in fractures with the wall-rocks, where the Ti in new minerals could be incorporated from the residue. The elements Ti, Zr, Cr, Ni, Fe and Al appear all to have behaved as immobile, whereas the elements K, Si, Mn, Ca, Mg and Na have different concentrations relative to MORB.

The differentiation trend of MORB (Fig. 4) is also represented by individual rock types among the eclogite facies metabasites at Zermatt. As shown by the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--}10\text{TiO}_2$ plot in figure 4a, most metabasalts of the ZS-Zone show little chemical differences from MORB. However, the Ctd-Gr-Tc veins (open square symbols in Fig. 4) show higher SiO_2 (Fig. 4a) and Na_2O (Fig. 4b) and CaO (Fig. 4d) with slightly lower MgO concentrations relative to MORB (Fig. 4c). In contrast many

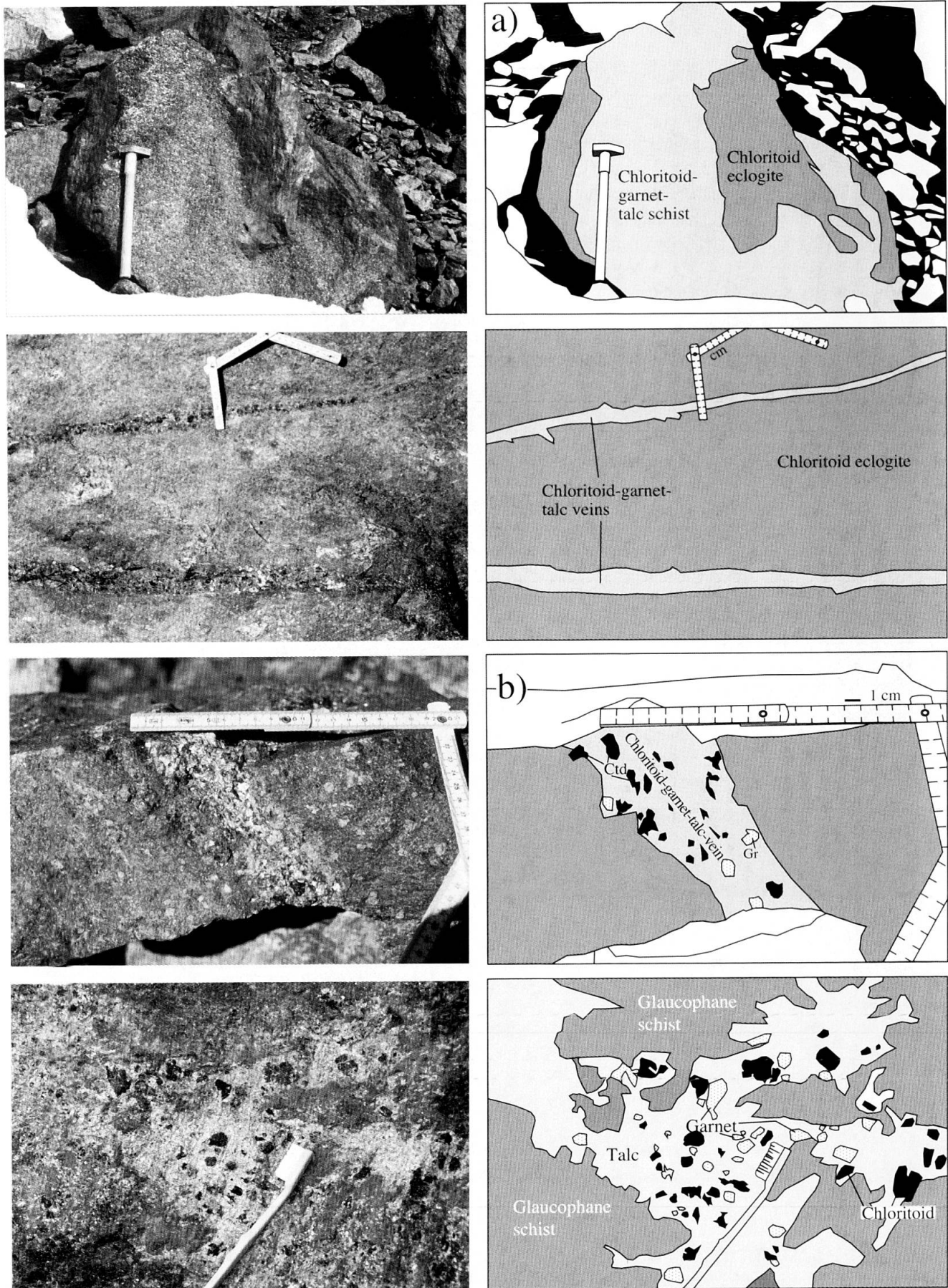


Fig. 2 Chloritoid-Garnet-Talc veins (CGT) in (a) chloritoid eclogite, (b) glaucophanite; from the rock promontory NW of the Pfulwepass (Map coordinates: 631.150/096.110; 3100 m).

eclogites and metabasalts of the ZS-Zone show noticeably higher Na compared to MORB (Fig. 4b).

Most of these differences have dramatic effect on the position of analyses relative to MORB in the AFM (alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$): $\text{FeO}_{\text{total}}$: MgO) diagram used to distinguish the major magmatic fractionation trends (Fig. 5). Here the Ctd-Gr-Tc veins appear to reflect primitive magmatic compositions compared to the enclosing glaucophanitic eclogites, and the Na-enriched eclogites, which appear to be more fractionated and/or metasomatically altered.

2.1. METASOMATIC TRENDS IN ZERMATT METABASITES

Each of the major metasomatic trends can be seen in the $\text{MgO}-\text{CaO}-\text{Na}_2\text{O}$ plot of bulk rock analyses through ZS Zone (Fig. 6). Evidence for spilitisation (Na-enrichment), chloritisation (Mg-increase, Ca-decrease, $\text{Mg}_{+1}\text{Ca}_{-1}$) and epidotisation

(Ca-enrichment) is clear. The mineralogy appropriate to basalt and their metamorphic equivalents in the zeolite and greenschist facies is shown. The composition of smectite is projected on the basis of analyses for "mixed-layer" clay minerals by ALT et al., (1985, 1986) from ODP borehole 504B.

2.2. $\text{Mg}_{+1}\text{Ca}_{-1}$ METASOMATISM ON THE OCEAN FLOOR

MOR basalts with high Mg and low Ca contents have been described by HUMPHRIS and THOMPSON (1978) and MOTTI (1983) among others. They are rich in the greenschist facies mineral chlorite which replaces magmatic olivine and glassy regions. These workers also described hydrothermal veins in MORB rich in chlorite with some quartz. Such rocks which have lost all Ca are either basalts strongly altered at high fluid-rock ratios, or direct precipitates from high temperature hydrothermal fluids (sea water partly exchanged

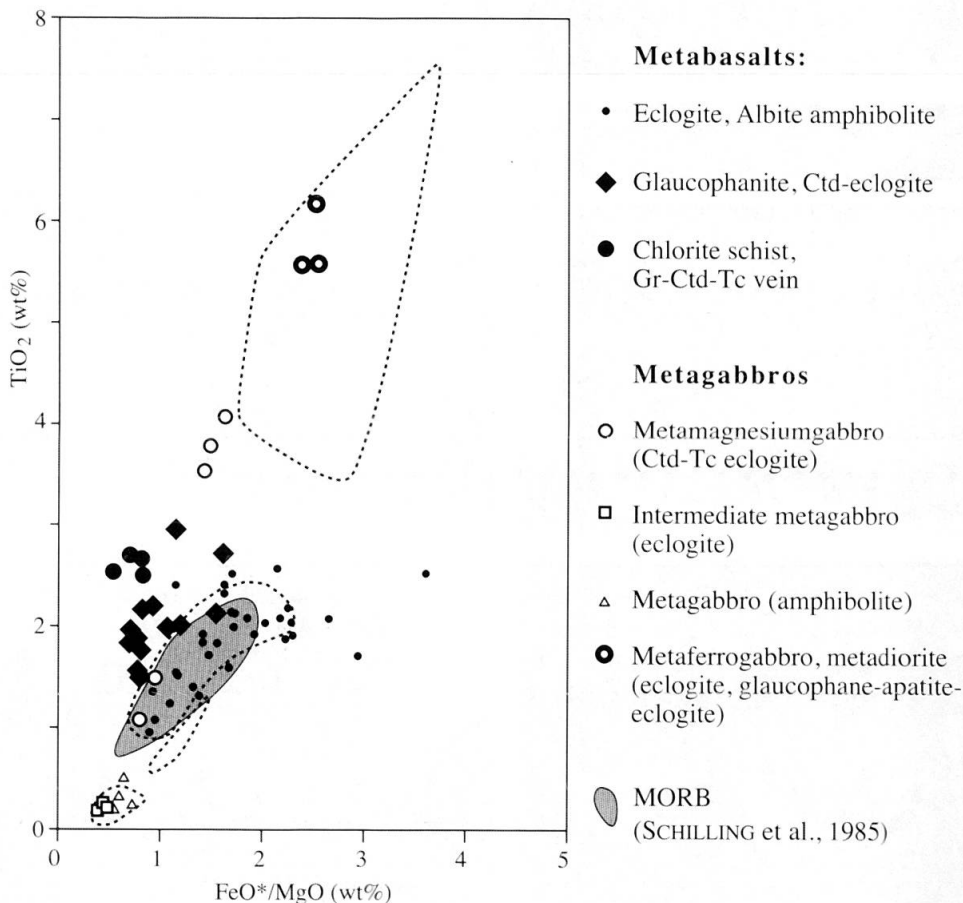


Fig. 3 FeO^*/MgO vs TiO_2 diagram (wt%) of metabasic rocks of the ZS-Zone (Ganguin, 1988) to illustrate magmatic differentiation ($\text{FeO}^* = \text{FeO} + 0.8998 \cdot \text{Fe}_2\text{O}_3$). Also shown are the compositional fields of metabasic rocks from the Apennines (dotted lines, MESSIGA et al., 1983; BECCALUVA et al., 1984; SERRI, 1980) and MORB (SCHILLING et al., 1985). Glaucophanites, Ctd-eclogites, Gr-Ctd-Tc-veins and chlorite schists lie outside the compositional field of MORB, in accordance with ocean-floor hydrothermal alteration trends.

with MORB). In the ODP drillhole 504B Mg-enriched and Ca-depleted veins contain chlorite with smectite-vermiculite clays and sometimes actinolite.

CANN, 1979; SEYFRIED et al., 1988). Metabasalts in the ZS-Zone with these chemical characteristics appear as glaucophanites and chloritoid-talc eclogites.

3. Hydrothermally altered Mg-rich basalts and hydrothermal veins

Sea water-basalt interaction on the ocean floor leads to Mg-enrichment and Ca-depletion (e.g.

3.1. GLAUCOPHANE SCHISTS AND CHLORITOID-TALC ECLOGITES

The *chloritoid-talc eclogites* often also contain epidote, rutile and pyrite in addition to omphacite and garnet. Three different parageneses have

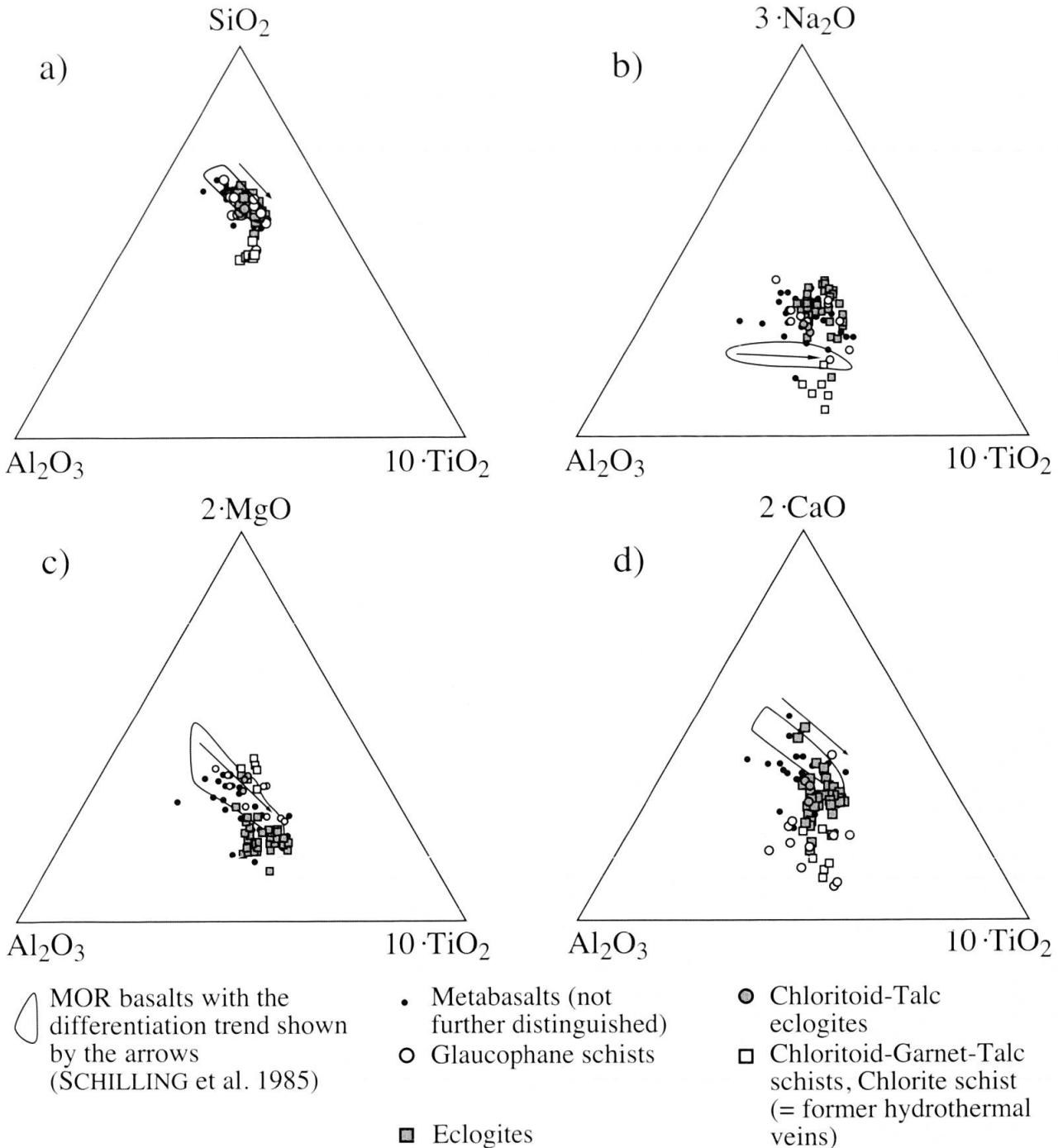


Fig. 4 Chemical analyses of the eclogite facies mafic rocks (WIDMER, 1996, p. 281–286) and MOR basalt with the differentiation trend shown by the arrows (SCHILLING et al., 1985), (a) $SiO_2-Al_2O_3-10 TiO_2$ (wt%); (b) $3 Na_2O-Al_2O_3-10 TiO_2$ (wt%); (c) $2 MgO-Al_2O_3-10 TiO_2$ (wt%); (d) $2 CaO-Al_2O_3-10 TiO_2$ (wt%).

been recognised in the *glaucophanites* – all containing glaucophane and garnet with small amounts of rutile and pyrite:

(i) paragonite, phengite, omphacite, epidote (sometimes with zoisite, dolomite, apatite),

(ii) chloritoid, paragonite, phengite, epidote (sometimes with omphacite, zoisite, dolomite, apatite),

(iii) talc, chloritoid (sometimes dolomite).

There appear to be gradual changes in chemistry from the three types of glaucophanite to-

wards the hydrothermal veins. Mg-rich minerals such as talc and Mg-rich chloritoid are only found in former hydrothermally altered MOR basalts.

The chemical composition of the Ctd-Tc eclogites and the glaucophanites of the ZS-Zone vary only slightly. Thus the slightly different parageneses could reflect small variation in chemical composition, or indicate progressive metamorphic pressure-temperature conditions.

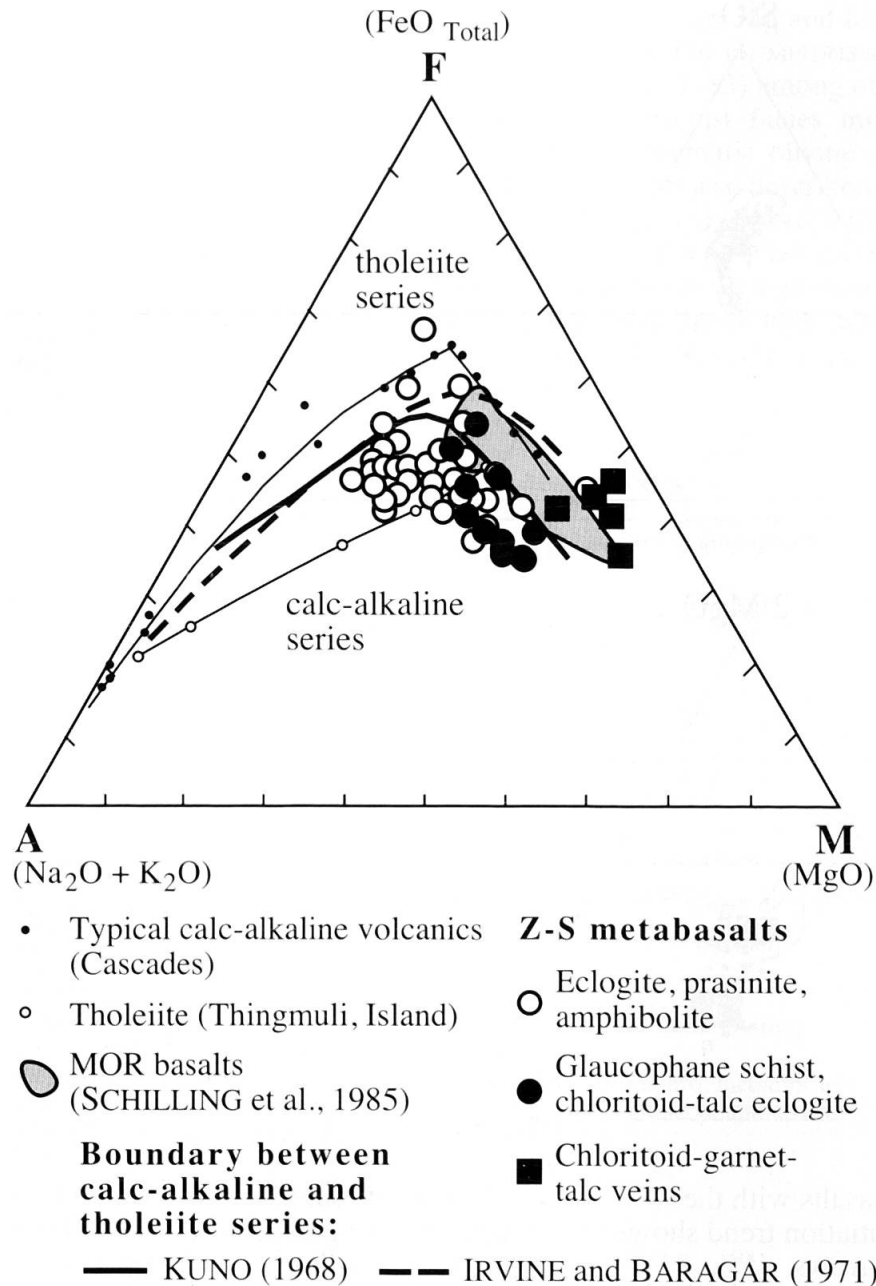


Fig. 5 Chemical analyses for ZS-Zone metabasalts (WIDMER, 1996, p. 281–286) plotted in a magmatic AFM diagram (wt%), which also shows the boundaries between calc-alkaline and tholeiite series (from KUNO, 1968; IRVINE and BARAGAR, 1971). The analyses of eclogites + prasinites + amphibolites, glaucophanites, Ctd-Tc-eclogites and the Ctd-Gr-Tc veins may be compared to typical calc-alkaline volcanics (Cascades), tholeiite (Thingmuli, CARMICHAEL, 1964) and MOR basalt (SCHILLING et al., 1985). The chloritisation trend appears here as the inverse of the magmatic fractionation trend.

3.2. CHLORITOID-GARNET TALC SCHISTS AS FORMER HYDROTHERMAL VEINS

These veins consisting of Ctd-Gr-Tc show great variation in the proportions of the three minerals

and their grain size. Because of these variations in the veins and the enclosing rocks, modal determinations needed to be made from image analysis (Adobe Photoshop) of scanned photographs. For the calculations of chemical analyses, measured

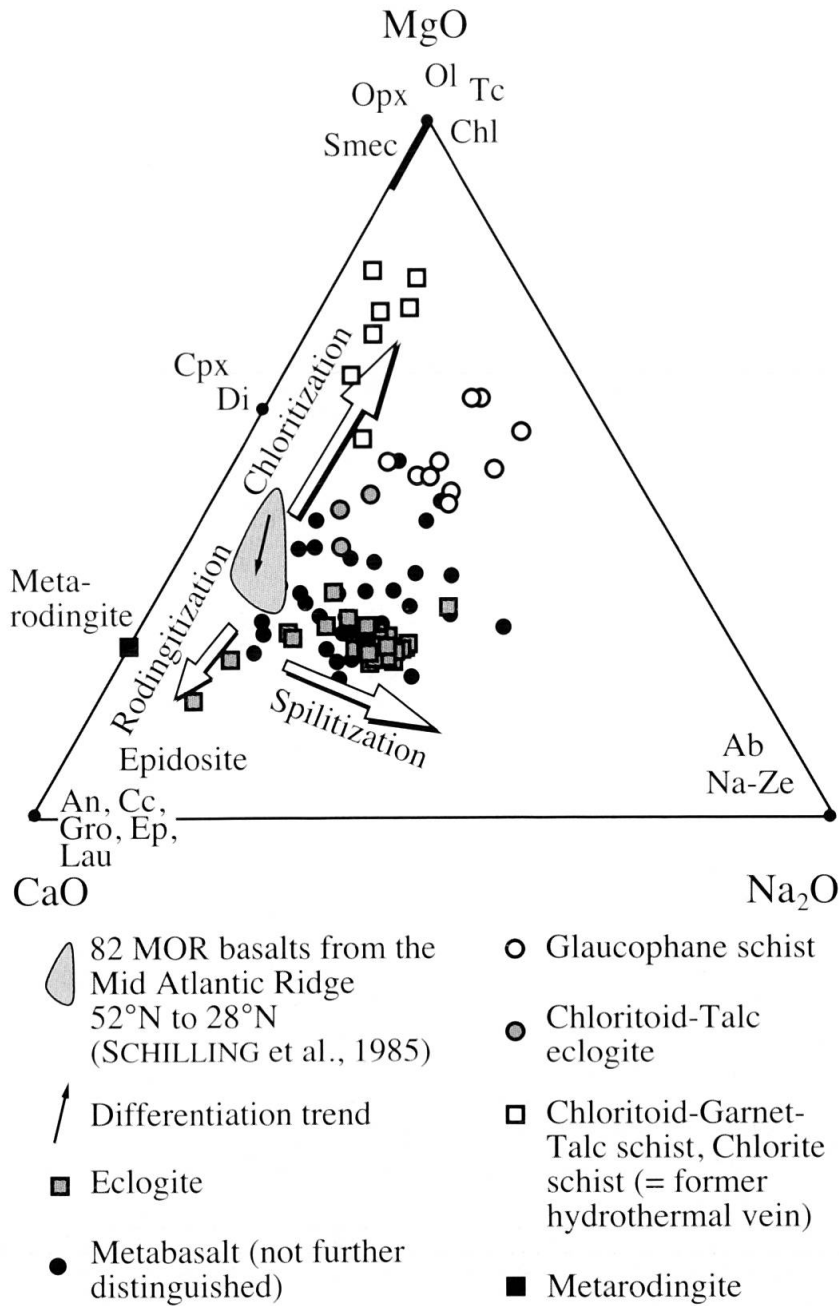


Fig. 6 Chemical analyses of ZS-Zone metabasalts (WIDMER, 1996, p. 281–286) shown on MgO–CaO–Na₂O (wt%). Four distinct ocean floor metasomatic alteration trends are preserved by the ZS metavolcanics: (i) spilitisation (Na-enrichment), (ii) chloritisation (Mg₊₁Ca₋₁), (iii) rodingitisation (Ca-enrichment, Mg and Na depletion) and (iv) epidotisation (Ca₊₁Mg₋₁).

The mineral compositions for magmatic basalt and for metabasalt in the zeolite/greenschist facies are indicated. The composition of smectite is plotted from an analysis from ALT et al. (1986) for a "mixed layer" clay mineral from ODP borehole 504B.

The metasomatic trends originate during precipitation of low-grade metamorphic assemblages replacing the magmatic mineralogy reacting with heated sea water. The Ctd-Gr-Tc-rocks most likely represent eclogite facies metamorphism of chloritised metasomatites (ii above), or similar veins.

Abbreviations: (Ol = olivine; Opx = orthopyroxene; Smec = smectite; Chl = chlorite; Tc = talc; An = anorthitic plagioclase; Cc = calcite; Gro = grossular; Ep = epidote; Lau = laumontite; Ab = albite; Na-Ze = sodic zeolites).

Tab. 1 Electron microprobe analyses of garnet-talc-chloritoid from Pfulwepass (sample ZS303B, GANGUIN, 1988), and the modal analyses of veins obtained from image analyses of photographs.

Weight %		Garnet 303 B01		Talc 303 B02		Chloritoid 303 B01	
SiO ₂	Si	39.43	2.9929	61.78	3.9917	25.86	1.0059
TiO ₂	Ti	0.02	0.0012	0.00	0.0017	0.00	0.0000
Al ₂ O ₃	Al	22.39	2.0029	0.00	0.0000	42.75	1.9595
Fe ₂ O ₃	Fe ³⁺	0.21	0.0118	0.00	0.0000	0.98	0.0287
FeO	Fe ²⁺	24.07	1.5273	3.21	0.1733	12.14	0.3949
MnO	Mn	0.51	0.0327	0.00	0.0003	0.06	0.0018
MgO	Mg	7.93	0.8969	29.43	2.8348	10.50	0.6087
CaO	Ca	6.53	0.5314	0.01	0.0007	0.01	0.0004
Na ₂ O	Na	0.02	0.0029	0.05	0.0065	0.00	0.0000
K ₂ O	K	0.00	0.0000	0.01	0.0005	0.00	0.0000
H ₂ O	OH	0.00	0.0000	4.64	2.0000	7.70	2.0000
Molecular weight		461.05 gr/Mol		384.90 gr/Mol		233.70 gr/Mol	
Oxygen atoms p.f.u.		12		7		12	

	Talc	Chloritoid	Garnet
vein 1:			
volume%	84.0%	9.0%	7.0%
mol%	78.9%	14.5%	6.6%
weight%	82.2%	9.5%	8.3%
vein 2:			
volume%	27.0%	66.0%	7.0%
mol%	18.4%	76.9%	4.8%
weight%	25.3%	66.7%	8.0%

mineral analyses and the modal data for two vein samples were used (Tab. 1).

4. Talc-chloritoid stability along the subduction PT path

The subduction path for the ZS Zone has been deduced from the successive mineralogies of metabasites (Fig. 7). A selection of experimentally investigated equilibria and thermodynamic calculations in NCMASH is shown in figure 7, together with previous estimates for the P-T of metamorphism for the ZS-Zone (BARNICOAT and FRY, 1986; GANGUIN, 1988). Changes in modal mineralogy along the subduction path have been calculated for specific bulk compositions in terms of their modal mineralogies compared to measured mineral compositions.

The finding of the veins containing Mg-rich chloritoid with talc and garnet requires that the PT subduction path be extended beyond the region enclosed by the solid box in figure 7. Indeed for reactions in MASH the stability of the vein assemblage Tc + Ctd is restricted to a small region near 30 kbar and 740 °C (between the numerals IV, V and VI along the subduction path illustrated in Fig. 7).

The subduction path for the ZS-Zone did not reach as far as crossing VIII in figure 7, because

talc is not replaced by enstatite + coesite there (A. BARNICOAT, personal communication, November, 1999).

Now because Fe²⁺ enters chloritoid (and garnet) more than chlorite (talc takes very little Fe²⁺) the natural stability field compared to MASH will be extended to lower pressures and temperatures, just about backwards along the indicated subduction path shown in figure 7 (see WIDMER, 1996, p. 110).

TARTAROTTI et al. (1986) have described "garnet-chloritoid (X_{Mg} = 0.33) bearing talc schists" from the St. Marcel Ophiolite in the Aosta valley. These rocks have undergone a similar history to those described here from the ZS-Zone (WIDMER, 1996, p. 29). Chemical profiles of zoned garnets, made as part of our study, show zoning Ca to Fe through the core and then Fe to Mg towards the rim. These profiles also support the notion of garnet growth via the continuous reactions illustrated in figure 7, in the P-T region denoted by the arrow numbered with Roman numerals up to VI.

5. Conclusions

The high-Mg lower-Ca rock compositions represented by the chloritoid-garnet-talc schists are considered to reflect eclogite facies metamor-

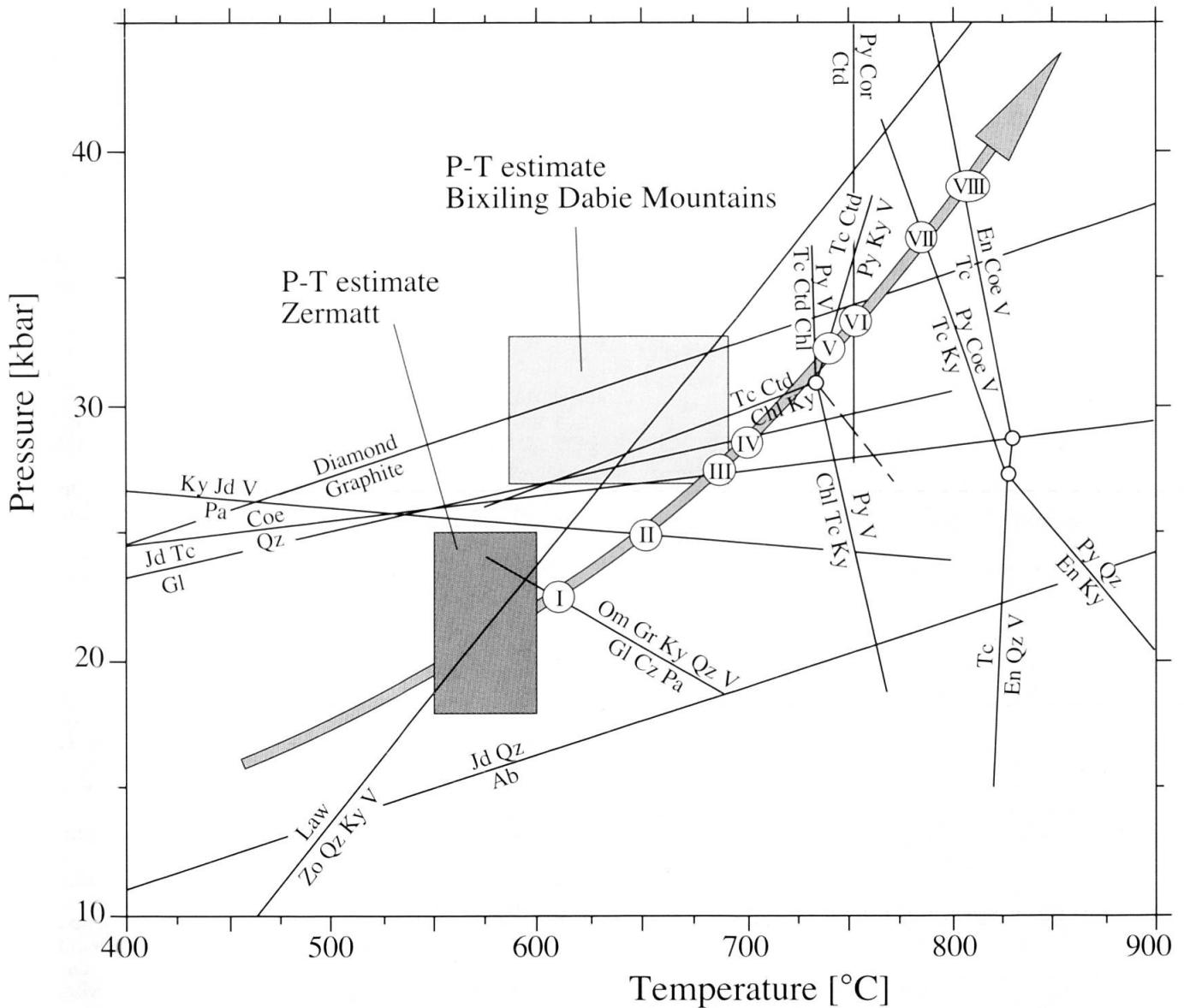


Fig. 7 Experimentally determined and calculated equilibria relevant to the high pressure metamorphism in the ZS-Zone and other subduction related high pressure zones.

- 1) albite = jadeite + quartz (HOLLAND, 1980)
- 2) graphite = diamond (BERMANN, 1979)
- 3) quartz = coesite (MIRWALD and MASSONNE, 1980)
- 4) talc + chloritoid = chlorite + kyanite (CHOPIN and SCHREYER, 1983)
- 5) chlorite + talc + kyanite = pyrope + H₂O (SCHREYER, 1968; SCHREYER, 1988)
- 6) talc + chloritoid + chlorite = pyroxene + H₂O and talc + chloritoid = pyrope + kyanite + H₂O (topography from CHOPIN, 1984)
- 7) glaucophane = jadeite + talc (KOONS, 1982)
- 8) paragonite = kyanite + jadeite + H₂O (HOLLAND, 1979)
- 9) enstatite + kyanite = pyrope + quartz (MASSONNE, 1983)
- 10) talc = enstatite + quartz + H₂O (KITAHARA et al., 1966)
- 11) talc + kyanite = pyrope + coesite + H₂O (CHOPIN, 1986)
- 12) talc = enstatite + coesite + H₂O (YAMAMOTO and AKIMOTO, 1977)

Metamorphic conditions for ZS-Zone estimated on the basis of several of the above geobarometers and oxygen isotope thermometry (GANGUIN, 1988); those for Dabie Shan and Bixiling, China from ZHANG et al. (1995). The crossings of the various reactions along the subduction path for the ZS-Zone is indicated by Roman numbering up to VI. Further abbreviations: Om = omphacite; Jd = jadeite; Ky = kyanite; Coe = coesite; Qz = quartz; Py = pyrope; En = enstatite; Cz = clinozoisite; Pa = paragonite; Law = lawsonite; Zo = zoisite; V = H₂O.

phism of hydrothermal veins formed in a previous metasomatic episode in an ocean floor hydrothermal system. The ocean floor metamorphism involved extensive chemical exchange with heated seawater producing smectite-chlorite (Mg-rich, Ca-poor minerals, probably with some quartz) veins in the greenschist facies. During subduction chlorite remains stable along the subduction PT-path but the reactions that converted mixed-layer clays to talc and Mg-chloritoid can only be inferred. While their MgO/FeO values overlap those of primitive mantle magmas on an AFM diagram (Fig. 5), these Ctd-Gr-Tc schists have lower CaO relative to such magmatic rock compositions (Fig. 6).

Despite the intense Alpine tectonic overprint that exhumed the metabasic and metaultramafic zones of the ZS-Zone (see also LEMOINE et al., 1987), signatures are to be found of the subduction path in the mineralogy of partly preserved eclogitic parageneses. In addition, part of the earlier ocean floor metamorphic episodes are preserved as veins or patchy domains (as also noted by BEARTH, 1959, 1973; OBERHÄNSLI, 1980; POGNANTE, 1989; BARNICOAT and FRY, 1986; BARNICOAT and BOWTELL, 1995; BARNICOAT and CARTWRIGHT, 1995). Thus these Ctd-Gr-Tc veins, among the other observed vein types, represent high-pressure subduction-zone metamorphism of rock compositions produced metasomatically on the ocean floor by interaction of heated seawater with MOR basalt. These observations are additional suggestions that the ZS-Zone has had quite different tectonometamorphic history than obducted ophiolites (eg. Semail in Oman; LIPPARD et al., 1986).

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