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Aspects of petrographical, structural and stable isotope geochemical evolution of ophicarbonate breccias from ocean floor to subduction and uplift: an example from Chatillon, Middle Aosta Valley, Italian Alps

by *Thomas Driesner*[1]

Abstract

A detailed study of an ophicarbonate breccia from the high-pressure metamorphic Zermatt-Saas ophiolites near Chatillon, Middle Aosta Valley, reveals various pre-Alpine and Alpine features that constrain the evolution of the rock from Jurassic extension and later brecciation in an ocean floor environment to Alpine subduction and uplift. Extension related features include a tectonitic fabric, several types of veins and retrograde growth of chlorite in the ultramafic protolith followed by ocean floor hydrothermal calcite veins and tectonosedimentary brecciation.

The predominant reaction observed in the rocks is diopside + dolomite + water = antigorite + calcite + CO_2 and probably took place under conditions of approximately 500 °C and 0.8 to 1.2 GPa. The reaction was driven by infiltration of an external fluid and was accompanied by extensive veining under moderate NW-directed shear stress. A younger steeply dipping NE–SW striking ductile deformation zone was probably formed at 480–490 °C and 0.35 to 0.4 GPa.

Several Alpine vein types indicate further deformation and various events of fluid-rock interaction. Oxygen isotopes show distinct values for different vein systems and the rock, indicating fluid-channeling and a lack of large scale isotopic equilibration. The carbon isotopic composition of all calcite samples lies in the marine range.

Keywords: Ophicarbonate, stable isotopes, serpentinization, veining, P-T conditions, Chatillon, Aosta Valley, Italian Alps.

1. Introduction

Ophicarbonate breccias occur as an abundant constituent of the Alpine and Apennine ophiolites. Usually the breccias are found on top of serpentinized ultramafics and are themselves overlain by pelagic sediments thus indicating an anomalous ocean-floor stratigraphy. Models proposed to explain these observations comprise various tectonosedimentary scenarios: deposition in or along active submarine fault systems (DECANDIA and ELTER, 1972; BONATTI et al., 1974; LEMOINE, 1980; WEISSERT and BERNOULLI, 1985), formation during the uncovering of mantle rocks in the initial extensional opening of the Tethys (LEMOINE et al., 1987) or deposition on an unusual ultramafic-gabbroic ocean floor resembling examples from the modern Mid-Atlantic Ridge (LAGABRIELLE and CANNAT, 1990). Obviously ophicarbonate breccias play a key role in evaluating the genesis of the Tethys ocean floor and can serve as an indicator for various paleotectonic and paleogeographic features.

Ophicarbonate rocks also have a great potential for the study of metamorphism. TROMMSDORFF and EVANS (1977 a, b) and TROMMSDORFF and CONNOLLY (1990) demonstrated this in the Bergell contact aureole and the recent presentation of P-T-X phase relations by CONNOLLY and TROMMSDORFF (1991) strongly suggests that ophicarbonates could be an interesting tool for studies of regional metamorphism, even such of high pressure type. In additon a stable isotope study on ophicarbonates from Eastern Switzerland (FRÜH-GREEN et al., 1991) showed that complex fluid evolutions can be detected in this type of rocks.

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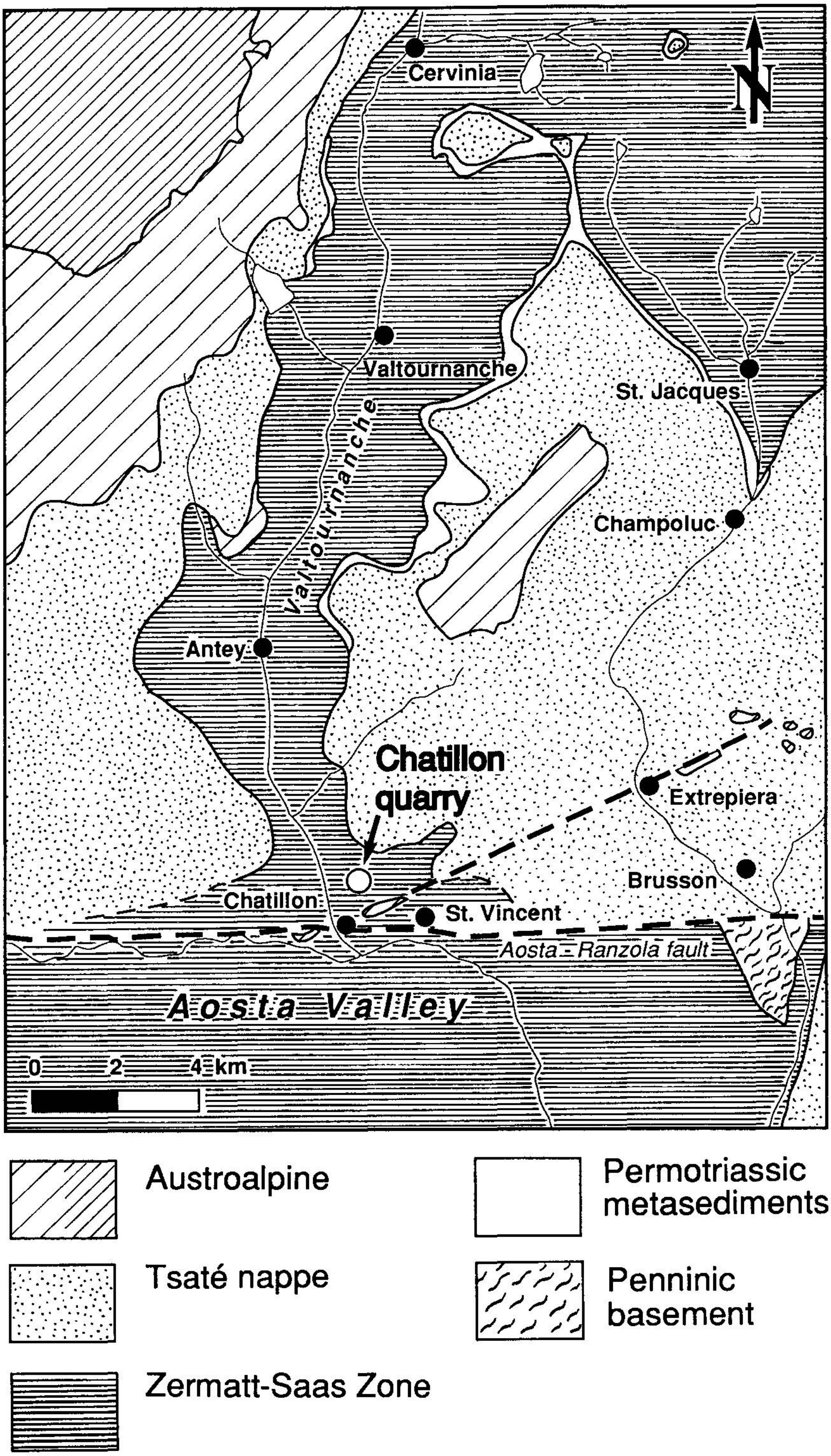

Fig. 1 Generalized tectonic map of the Middle Aosta Valley region (modified from DAL PIAZ, 1988).

In the present study an attempt is made to apply the concepts and experiences mentioned above to an ophicarbonate occurrence near Chatillon, Middle Aosta Valley (Fig. 1). It will be shown that although the rocks experienced high pressure metamorphism during Alpine subduction the preservation potential for pre-Alpine features was high. Also various stages of the Alpine petrographical, structural and stable isotope geochemical evolution can be traced in detail.

The breccia is part of the Zermatt-Saas ophiolites (Fig. 1) that for a long time have been recognized as remnants of the Tethys ocean floor separating the African/Apulian and European continents from Jurassic to Tertiary times. During Alpine subduction the rocks were affected by high to very high-pressure metamorphism and show partial to complete greenschist facies overprint probably related to the uplift path (e.g. BEARTH, 1967, 1973, 1974; ERNST and DAL PIAZ, 1978; MEYER, 1983; REINECKE, 1991). The Zermatt Saas Zone is tectonically underlain by Penninic basement and cover nappes representing the former European continental margin and is tectonically overlain by the Combin Zone and the Austroalpine nappes. The Combin Zone has recently been revised and divided into distinct nappes and units (SARTORI, 1987; ESCHER et al., 1987; DAL PIAZ, 1988), the most prominent of which is the Tsaté nappe comprising mainly calcschists and slices of ophiolitic material. An apparent lack of subduction-related high-pressure metamorphism and the structural style of the Tsaté nappe make an interpretation as a former accretionary prism plausible (MARTHALER and STAMPFLI, 1989). The uppermost tectonic element, the Austroalpine, is generally interpreted as part of the southern plate continental basement. Alpine high pressure metamorphism indicates that also these units were involved in the subduction process. The details of the regional tectonic evolution are still a matter of debate (see e.g. DAL PIAZ, 1988) and no coherent picture of the interference of deformation and metamorphism has been derived so far.

2. Macroscopic appearance

2.1. THE OPHICARBONATE BRECCIA

The rock of Chatillon quarry forms a matrix-supported breccia of mostly subrounded serpentinitic clasts in a macroscopically homogenous serpentinitic-carbonate matrix. Clast sizes range from millimeters to nearly one meter. Three main petrographic types of clasts can be distinguished:

– a *tectonite-type* (≥ 95%), i.e. serpentinites that exhibit a pre-brecciation tectonitic fabric (Fig. 2a) traced by millimeter-thick layers rich in diopside or pseudomorphs after diopside. Occasionally these clasts show old (pre-brecciation but post-tectonitic) calcite veins. Other veins of simi-

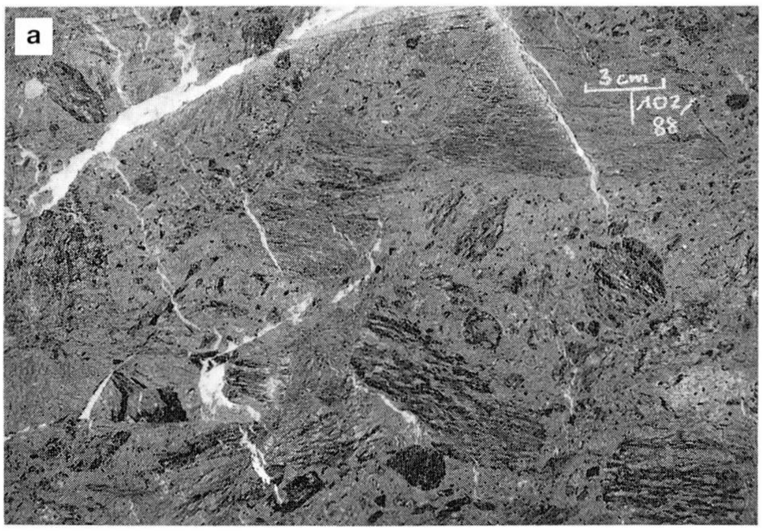

Fig. 2 a) Typical clasts with tectonitic fabric in breccia, scale bar 3 cm. b) Folded clast with complex relations between pre-brecciation veins, serpentinization (dark parts) and folding. White calcite veins along foliation are probably Alpine in age.

lar relative age have an antigorite, antigorite-diopside or diopside-calcite filling. All veins usually show either simple black-green or more complex reaction rims of mm to cm thickness.

– a *homogeneous* (i.e. without macroscopic internal structures) *black-green type* and

– *fragments of calcite* veins with or without serpentinitic wallrock.

Although rarely observed macroscopically, alteration phenomena like reaction rims around clast are rather abundant in thin sections. Therefore clast shapes and sometimes even internal structures should only with care be regarded as primary. This holds also true in the single case of a clast of apparently rebrecciated older ophicarbonate breccia whose structure might simply be the result of incomplete metasomatic alteration during metamorphism.

Only in one case a clast of folded serpentinitic rock with complex internal fabrics has been observed (Fig. 2b).

In the southeastern part of the quarry a zone of strong ductile deformation with a NE–SW striking and steeply dipping foliation could be observed up to June 1990 but has then been removed during quarry operations. Shear sense indicators like pressure shadows around clasts and some asymmetric folding of the foliation imply an upward movement of the southern part. Almost all types of veins are deformed in this zone, implying a relatively young age.

2.2. VEINS

Numerous types of veins can be distinguished according to macroscopic appearance, orientation and mineralogy. In most cases the relative ages could not be determined properly because of polyphase reactivations or lacking of cross-cutting relationships.

A classification into twelve groups seems to be adequate (Tab. 1), the four most prominent of which will be discussed in the following.

Large carbonate-filled fractures

These fractures range in thickness from a few decimeters to several meters and form a network with individual branches reaching up to 30 meters or more (Fig. 3a). There seems to be a preferred E–W trend in strike but this observation should not be generalized because of the small outcrop area.

The main component of the filling is a white to greenish grey calcite with grain sizes of usually 0.2 to 0.5 mm. Numerous fragments of the surrounding ophicarbonate breccia ranging from mm to some dm in size can make up more than 80% (average around 20–30%) of the fracture filling. A diffuse zoning of the vein filling can sometimes be observed perhaps indicating polyphase filling. Rather abundant are mm to cm sized fragments consisting of fine grained diopside or coarse yellowish dolomite. In thin sections the diopside shows alteration to tremolite whereas the dolomite is often partly altered to calcite.

On the wall-rock/vein interface up to three lineations (mainly antigorite-fibers) indicate polyphase tectonic reactivation (Tab. 1). Macroscopic "flow" textures of the calcite-filling and lineations on the surfaces on rock fragments in the vein filling strongly indicate temporary ductile deformation of the calcite.

The veins terminate either diffusely in fractured, calcite-cemented ophicarbonate-breccia or in smaller veins of type B described below.

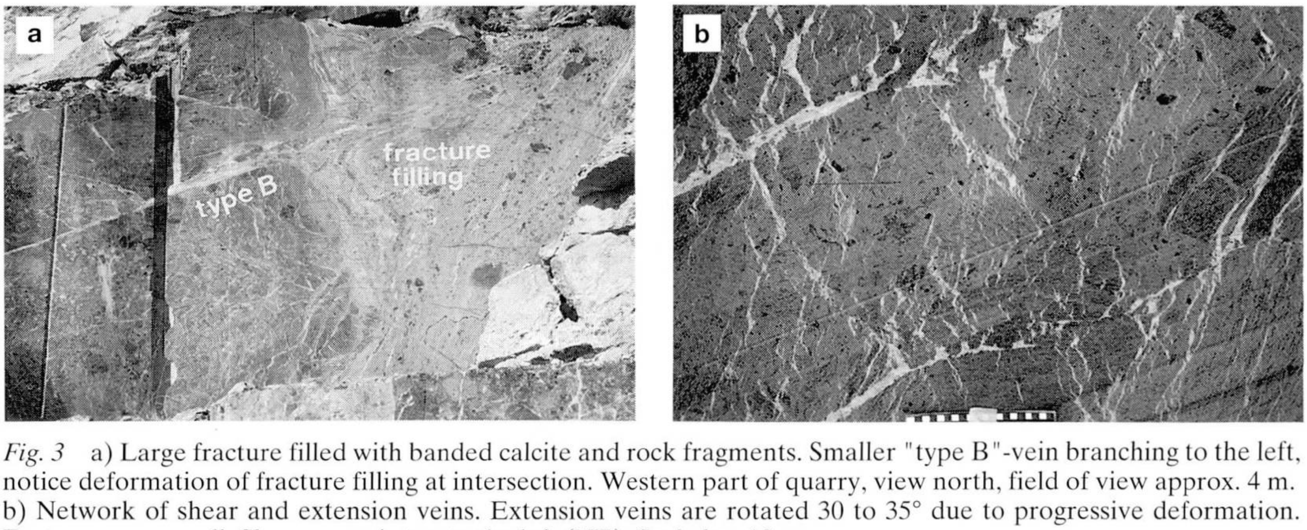

Fig. 3 a) Large fracture filled with banded calcite and rock fragments. Smaller "type B"-vein branching to the left, notice deformation of fracture filling at intersection. Western part of quarry, view north, field of view approx. 4 m. b) Network of shear and extension veins. Extension veins are rotated 30 to 35° due to progressive deformation. Eastern quarry wall. Shear sense is top to the left (NE). Scale bar 10 cm.

Tab. 1 Alpine vein types cross-cutting the ophicarbonate breccia of Chatillon quarry.

Vein type	Thickness	Length	Filling (remarks)	Abundance (No. of observed veins)	Typical structural data L: Lineations or fibres on interface to wallrock Atg: Antigorite
large fractures	0.2 –> 5 m	10–> 30 m	fine-grained white and grey calcite, fragments of ophi-carbonate breccia, fragments of fine-grained diopside; fragments of coarse dolomite	4	a) 210/75–200/85 L1 134/22–122/16 (Atg) L2 150/55–141/56 (Atg) L3 261/70 average thickness 0.4 m b) strike approx. 100–110 steep, thickness > 5 m c) strike approx. 120–130 0.2–0.5 m d) 326/35, 0.5 m thick
"type b"-veins	1–15 cm	several m	usually white calcite, some-times banded, banding can be internally folded; diopside and dolomite fragments like those above; often closely related to large fractures (example c is isotopically identical to shear and extension veins)	> 20	highly variable, e.g. a) 192/20 L 184/18 (Atg) b) 008/70 L 330/68 (Atg) c) 294/48 L1 240/40 L2 342/40 d) 220/30 L1 155/5 (Atg) L2 195/15 (Atg)
shear veins	0.2–2 cm	several m	white calcite, antigorite fibres	> 100	312/36 L1 325/35 (Atg) L2 016/25 (Atg) shear sense top NW (L1) shear sense top NNE (L2)
extension veins	0.1–1 cm	cm (-dm)	white calcite; very rarely Antigorite or tremolite fibres	10^3–10^4	a) 125–145/60–85 310–330/60–90 b) 200/70 (very rare)
calcite-antigorite veins (two sub-types)	1–3 cm	0.5–2 m	a: calcite and antigorite in palisade-like aggregates (cut by extension veins) b: fibrous antigorite in calcitic matrix, often higly deformed	~5 ~5	only in section 250/44–205/42 087/39 125/46
calcite-tremolite veins (four sub-types)	4 cm 1 cm 0.2 cm 4 cm	> 0.5 m > 0.2 m 3 cm 6–10 cm	a: deformed fibrous tremolite in fibrous calcite b: similar, but recrystallized calcite c: extension vein with fibrous tremolite d: system of transtensional openings with fibrous tremolite and calcite	1 1 1 1	292/78 strike approx. 300 strike approx. 320, steep strike approx. 220, steep
big, SW-dipping extensional veins	2–5 cm	3–5 m	calcite (removed during quarry operations, in SE part)	3	gently SW dipping
"back-shear" veins (two subtypes)	3–7 cm 0.5–1 cm	> 3 m 10–30 cm	calcite with rock fragments calcite	1 3	approx. 130/25, shear sense top to SE only section, shear sense top to SE (several more shearband-like structures can be observed on the same wall)
complex serpen-tinitic vein	8–10 cm	> 6 m	antigorite + calcite, complex filling texture; cut by "back shear" vein	1	only in section, apparent dip 20° S to SE
veins of pseudo-morphed clinopyroxene	several mm	dm to several m	antigorite (± calcite) pseudomorph after cpx; light green; cutting matrix and clasts; cut by ext. veins	> 5	only sections; mostly steep
green calcite vein	3 cm	> 40 cm	deformed green calcite	1	069/62
fissures with free-grown calcite xls.	0.5–1 cm	> 50 cm	free, milky calcite crystals on fibrous antigorite	1	found on a block
various examples of uncertain type and age			variable, mostly calcite and antigorite		

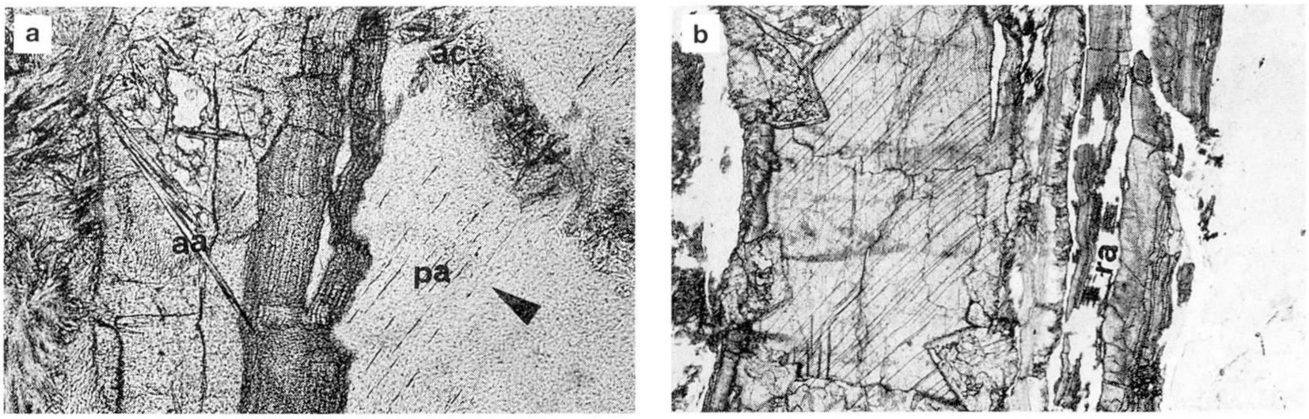

Fig. 4 a, b Photomicrographs of an old calcite vein in a serpentinitic clast. Outer, sinter-like parts resembling "modern" analogues (see text) may indicate original aragonite. The intermediate zone with idiomophic calcite crystals may possibly be taken as evidence for hydrothermal formation in an open fissure. The inner part is filled with coarse sparry calcite. ra: partial replacement by antigorite in outer zone, pa: antigorite pseudomorphs after pyroxene in the wall rock, aa: alpine antigorite, ac: small calcite filled alpine cracks. Field of view 3.5 mm in a, 5.5 mm in b.

Calcite veins "type B"

"Type B" calcite veins are often closely associated with the large fracture-fillings and form a part of that network (Fig. 3a). They are usually a few cm thick with an often polyphase calcite filling of grain size comparable to that in the large fractures. Rarely coarser (several mm) calcite grains make up a central part of the veins. Strong ductile shearing, folding of individual bands within the filling and up to three lineations on the interface to the wallrock are abundant reactivation phenomena. Diopside- and dolomite-fragments like those described above are not rare in these veins.

The orientations of "type B"-veins varies significantly although some trends seem to prevail (Tab. 1). Therefore it cannot be excluded that the "type B" as a field classification may represent more than one generation of veins.

Shear veins

A big number of calcite-filled shear veins dipping 25° to 36° NW is observed in the eastern part of Chatillon quarry (Fig. 3b) and a much smaller one in the western part. This uneval distribution might be due to the higher abundance of older faults/veins in the western part, the reactivation of which could have prevented the formation of new shear faults.

The thickness of the calcite filling ranges from less than 1 mm to 2 cm sometimes showing pinch and swell structures. At least two brittle or semi-brittle movements took place, the older one represented by slickenslides with azimuth between 320° and 335° and the younger one by slickenslides with azimuth 010° to 020°. Shear sense deduced from displaced markers and fiber-shadows is top to NW and top to NNE respectively. Displacement along the shear veins is between 3 and 15 cm where it could be measured from displaced markers. In the more homogenous rock in the easternmost part of the quarry a regular spacing of roughly 30 cm between individual shear veins can be observed. Neglecting ductile deformation of the rock this gives an overall shear strain γ (RAMSAY and HUBER, 1983) of 0.15 to 0.4.

Unambiguous cross-cutting relationships with the large fractures or type B veins have not been observed so far but indirect criteria from reactivation phenomena etc. indicate a younger age for the shear veins.

Calcite-filled extension veins accompanying shear veins

These form a dense (cm-scale), flame-like network (Fig. 3b) throughout the quarry that makes up 10 to 17% of the total rock volume. The filling consists of white fibrous calcite. Where measurable the individual branches show a 50° to 60° conjugation. Locally en-echelon arrays or single veins are found. Rock-inhomogeneities like the contact between matrix and clasts in the breccia or tectonitic fabric in clasts sometimes act as preferential sites of vein formation.

The extension veins are always striking NE–SW except a second, younger set that appears very rarely and shows a NNW–SSE strike. They are cut off by the shear veins indicating close genetic relationship between both types. This is supported by analysis of the geometric relationships between shear veins, extension veins, slickenslides and calcite fibres in the veins (DRIESNER, 1991).

Contemporaneous shear and extension failure requires $p_{fluid} \approx p_{lith}$ during vein formation and a weak to moderate shear stress not higher than a few tens of MPa (e.g. SIBSON, 1981).

3. Microscopic observations

Both matrix and clasts consist mainly of antigorite, calcite and diopside in varying amounts with minor chlorite and tremolite. Most of the fabrics can be interpreted in terms of the metamorphic equilibrium diopside + dolomite + H_2O = antigorite + calcite + CO_2 ("main reaction" in the following). Depending on the relative age four categories of fabrics are distinguished:

- older than brecciation
- younger than brecciation but older than the "main reaction"
- fabrics of the "main reaction" and
- fabrics of unknown age

Minerals + fabrics of the first two categories are often only preserved as pseudomorphs whereas those of the "main reaction" comprise both pseudomorphs (reactands) and unaltered minerals (products). As there is little doubt on the ocean floor age of the brecciation, fabrics older than the brecciation were formed during the ocean floor crustal or even the mantle evolution of the ultramafic protolith, whereas younger fabrics are of Alpine age.

3.1. FABRICS OLDER THAN BRECCIATION

Fabrics of this category are cut off at the contacts between clasts and matrix and mainly comprise the old *tectonitic fabric* of clasts and old veins (sometimes with reaction rims) in clasts. The old tectonitic fabric consists of alternating mm-thick serpentine- and diopside-layers. Serpentine-layers are formed by foliated antigorite, diopside-layers with their very often macroscopically granoblastic or spotted appearance by minor antigorite and either anhedral granular diopside or pseudomorphs of antigorite + calcite after diopside.

Additional pseudomorphic structures are *"mesh"-antigorite* (with high certainty after olivine) and some oriented intergrowth of antigorite and calcite that could be *pseudomorphs after orthopyroxene*. The overall appearance indicates a lherzolitic protolith.

The fabric of one old calcite vein (Fig. 4) resembles closely modern analogues from the atlantic ocean floor (BONATTI et al., 1974, 1980) or examples from Liguria or Eastern Switzerland (FRÜH-GREEN et al., 1991). In comparison to those examples aragonite might have been formed as the primary mineral in the outer sinter-like parts of the vein but is not preserved.

Old veins of bladed antigorite can sometimes be observed. Whether or not this antigorite is a primary mineral or replaces other minerals cannot be decided.

One of the rare macroscopically visible *reaction rims around old veins* has been studied in detail (DRIESNER, 1991). In this case the reaction rims are grouped around an old vein parallel to the tectonitic fabric that is cut off at the clast-matrix contact. The vein is now mainly filled with alpine calcite and only few diopside relics are observed. As there are no reaction rims developed around the normal Alpine calcite-filled extension-veins cutting the same clast it is concluded that the reaction rims are truly related to the diopside vein and not to its later replacement by calcite. The most interesting feature of the clast are aggregates of skeletal *chlorite-plates* of 0.5 to 2 mm size with a rim of *14 Å-antigorite* (GROBÉTY and DRIESNER, 1993) that are oriented in the tectonitic fabric. The same type of oriented aggregates is found in the innermost reaction rim (now consisting of antigorite matrix). This implies a relic character of the aggregates that therefore should be older than the reaction rims. Thus at least some of the ultramafic protolith was a chlorite peridotite. Whether or not antigorite is the primary mineral of the reaction rim is not yet clear.

3.2. FABRICS DEVELOPED AFTER BRECCIATION BUT PRIOR TO "MAIN REACTION"

General criteria of this relative age are the occurrence in both the matrix and clasts, especially when cutting or overgrowing matrix-clast contacts on the one hand and being overgrown by fabrics of the "main reaction" on the other. Probably more fabrics and minerals (antigorite in clasts) than those mentioned below belong to this group but cannot be classified due to lacking age criteria.

Former *(clino-)pyroxene veins* cross-cut both matrix and clasts, reach lengths up to several meters and thicknesses to 1 cm (compare Tab. 1). The pseudomorphs after pyroxene are formed by two almost perpendicular sets of antigorite crystals. Relictic diopside grains are rare.

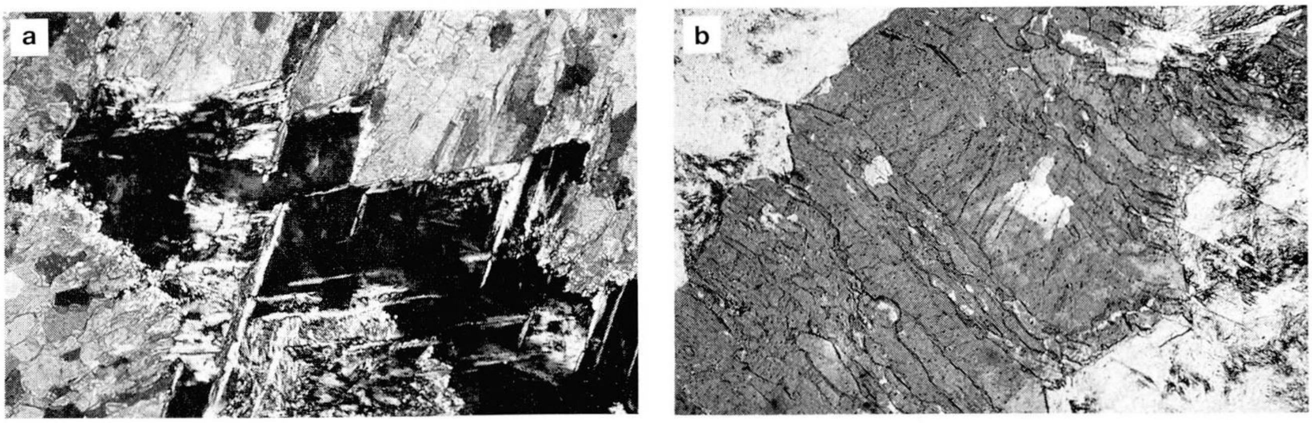

Fig. 5 a) Pseudomorphic replacement of dolomite by antigorite. Note how a calcite filled extension vein broke up along the former dolomite cleavage. Field of view 1.4 mm.
b) Extension vein cross-cutting pseudomorph analogous to a). Several fluid inclusion trails subparallel to the walls indicate crack-and-seal type filling mechanism. Field of view both 1.4 mm.

Pseudomorphs of *antigorite + calcite after dolomite or diopside* and relic diopside are abundant and will – as the pseudomorphic replacement is a feature of the "main reaction" – be discussed below.

3.3. FABRICS OF THE "MAIN REACTION"

Microscopically the matrix of the breccia shows a prevailing fabric of antigorite + calcite pseudomorphs after diopside + dolomite.

Diopside as in the veins mentioned above is usually replaced by two almost perpendicular sets of platy antigorite and minor fine-grained calcite. All stages from almost none to complete replacement can be observed. In rare cases rather coarse-grained (max. 1–2 mm) calcite forms the main mass of the pseudomorphs. The arrangement of pseudomorphs indicates cm-sized aggregates of anhedral diopside grains prior to replacement.

Pseudomorphs after dolomite reach sizes up to more than 1 cm and likewise consist mainly of antigorite, here in two forms: first as strictly oriented plates along the former dolomite-cleavage and second as dense flaky fillings between the oriented plates (Fig. 5a). Calcite usually is the minor component and forms fine-grained aggregates within the pseudomorphs. Arguments for dolomite being the replaced minerals are that calcite is one of the replacing minerals, further the dolomite fragments in the large fractures and "type B" veins and finally relic dolomite grains in material from Chatillon found by TROMMSDORFF (pers. comm. 1990).

In addition to unequivocal pseudomorphs after dolomite and diopside regular calcite-antigorite intergrowths indicate further pseudomorphic structures. These intergrowths consist of stacks of antigorite-plates with very fine grained calcite enriched along the cleavage planes and may either be interpreted as pseudomorphs after (ortho-) pyroxene or (less likely?) in comparison to material from St. Denis quarry (6 km to the west) represent a special type of pseudomorphs after dolomite. At the moment their true nature remains unclear.

Closely related to the reaction are the abundant calcite-filled extension veins described above. Their fibrous calcite-filling shows a median line of tiny wall-rock fragments and several trails of very small fluid inclusions (< 1 μm) parallel to the walls (Fig. 5b). This indicates antitaxial growth sense (innermost parts youngest, growth takes place at the vein-wall rock boundary) and a crack-and-seal type filling mechanism. The close age relationship to "main-reaction"-fabrics is especially shown by rather spectacular fabrics developed where the extension veins cross-cut former dolomite grains: here the veins are bound by the former dolomite cleavage (Fig. 5) indicating vein opening when dolomite was still present. Parts of the pseudomorphic fabrics are continous across the veins and others are not. Additionally platy antigorite fragments are found as trails reaching from an antigorite plate along the former dolomite cleavage on one side to its continuation on the other. The last two observations can be taken as indication for replacement of dolomite going on during opening of the vein. This would imply that the main reaction and formation of the extension veins took place *simultaneously.* As the extension veins formed simultaneously with the shear veins, $p_{fluid} \approx p_{lith}$ (s. above) can be assumed for the main reaction.

3.4. FABRICS AND MINERAL ASSEMBLAGES OF UNKNOWN RELATIVE AGE

No unequivocal age criteria could be established for some reaction rims in clasts, small veinlets and aggregates of chlorite + antigorite or chlorite in the matrix and in some clasts, some fabrics in clasts and a locally developed very weak cleavage. The latter has an orientation subparallel to the shear veins and could therefore be of the same age.

Almost all fabrics within the ductile deformation zone should be treated in this category. In thin sections of carbonate-rich parts (probably strongly deformed veined rock) two generations of dolomite appear, the older forming large grains up to several mm, the younger smaller grains recrystallizing from the older ones. Calcite forms either xenomorphic twinned grains or strongly stretched and sheared fibre-like fabrics. Tremolite is very abundant and forms fibrous, often sheared or folded, probably synkinematic aggregates that are often intergrown with antigorite or rare chlorite. Diopside seems to be restricted to rock fragments in that zone. From these observations it seems plausible that the assemblage in the deformation zone can be described in terms of the equilibrium antigorite + calcite + CO_2 = tremolite + dolomite + H_2O.

4. Mineral chemistry

Electron microprobe analysis were carried out on calcite, dolomite, chlorite and antigorite using a Cameca SX50 electron microprobe. Analytical conditions were 15 kV, 10 nA beam current, 5 or 10 μm probe diameter and 10 or 20 s counting time for carbonates and 15 kV, 20 nA, 5 μm, 20 s for chlorite and antigorite. The precision is assumed to be better than 1% relative for major elements (including Mg in calcite).

Calcite chemistry varies strongly with petrographical position. Vein calcites are usually very poor in Mg, Fe, Mn (Tab. 2) independent of vein type. In the rock itself coarse pseudomorphs after diopside show high (Mg,Fe,Mn)-contents in the core and somewhat lower ones in the rim. Due to its very fine-grained nature no matrix calcite could be analysed. The overall picture of the calcite chemistry implies that the cores with their higher (Mg,Fe,Mn)-contents are closest to equilibrium with former dolomite and can serve as minimum constraints for geothermometry (see next chapter). Those parts with low (Mg,Fe,Mn)-contents (rims, vein calcite) were probably affected by fluids during or after the "main reaction" that were no longer in equilibrium with dolomite. From this also the matrix calcite is expected to have only low trace element concentration.

The highest contents of Mg, Fe and Mn were found in samples from the ductile deformation zone where calcite grains occur together with preserved dolomite. These high contents are restricted to the core of larger calcite grains, whereas rims and smaller recrystallized grains vary strongly down to contents almost as low as in vein calcite. From these analyses it is clear that the chemical situation in ductile deformation zone calcites is highly complex and even for a single thin section only a very extensive microprobe survey could unravel the systematics. In addition no simple connection between cathode luminescence and chemistry could be established.

The antigorite in the old pre-brecciation reaction rims mentioned above has homogenously high iron contents of 7.9 wt% (Fe_{total} as FeO), even higher than the adjacent chlorite. The latter is an Mg-Al-chlorite with only 3.2 to 3.3% FeO. Its chemical composition is practically identical with that of chlorites from Alpe Arami peridotites as reported by ERNST (1978). In consistence with the petrographical constraints this may indicate that the chlorite preserved its original mantle or high-pressure metamorphic composition.

5. P-T-X-conditions of metamorphism

Satisfactory P-T-X-constraints could be derived for the "main reaction" (diopside + dolomite + H_2O = antigorite + calcite + CO_2). The *minimum temperature* for this event is deduced from the composition of the cores of coarser calcite pseudomorphs after diopside. With the calibration curve of ANOVITZ and ESSENE (1987) "temperatures" of 459 to 470 °C could be derived. The uncertainty arising from data scatter, analytical precision and an assumed maximal calibration error of 20 °C should be in the order of 30 °C.

In comparison calcites from the ductile deformation zone with the highest Mg, Fe and Mn contents observed yield "temperatures" of 485 °C and are within the analytical uncertainty in chemical equilibrium with adjacent dolomite grains. This higher temperature seems surprising as from the field relations the deformation should be younger (deformation of extension veins!) than the "main reaction". The most probable ex-

Tab. 2 Typical results of electron microprobe analyses of minerals from Chatillon quarry. All analyses were not normalized for this table.

	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	Fe as FeO	MnO	MgO	CaO	Na_2O	K_2O	NiO	total
chlorite	31.7	0.03	17.5	1.81	3.28	0.00	32.5	0.04	0.02	0.03	0.27	87.18
antigorite	43.5	0.00	1.22	0.26	7.93	0.08	35.8	0.03	0.00	0.00	0.32	89.14

	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$	total
calcite ps. after diopside: core	95.9 – 96.2	2.93 – 3.07	0.54 – 0.78	0.19 – 0.46	99.98 – 100.04
dito: rim	96.2 – 98.4	1.62 – 2.49	0.51 – 0.79	0.14 – 0.42	99.77 – 100.07
vein-calcites	98.9 – 99.6	0.27 – 0.75	0.01 – 0.15	0.03 – 0.20	99.98 – 100.55
calcites from					
ductile def. zone	95.6 – 99.34	0.39 – 3.32	0.02 – 0.81	0.01 – 0.33	99.81 – 100.09
dolomite, ductile def. zone	53.4 – 54.1	42.3 – 44.7	2.49 – 3.07	0.04 – 0.59	98.91 – 100.42

planation is that even the data from the cores of calcite pseudomorphs after diopside of the "main reaction" were not in equilibrium with dolomite thus giving to low temperatures. It might be concluded that the "main reaction" took place under temperatures higher than 485 °C, possibly around 500 °C.

Constraints on pressure and fluid composition can only be derived from a combination of petrographical observations and geothermometry with the calculated phase relations in the ophicarbonate system. CONNOLLY and TROMMSDORFF (1991) showed that the assemblage diopside + dolomite (+ antigorite) + fluid – predating the "main reaction" – is stable only at pressures higher than 0.5 GPa for fluid saturated conditions. The "main reaction" is restricted to the same field of the P-T-projection (Fig. 6) and bound by the curves of diopside + dolomite + fluid = antigorite + calcite + tremolite and the breakdown of antigorite + calcite. From this the *minimum pressure* is 0.5 GPa, the *maximum temperature* approximately 560 °C. $p_{fluid} = p_{lith}$ for this event is strongly implied from simultaneous formation of shear and extension veins as mentioned before. A *maximum pressure* of 1.2 GPa is given by the calcite-aragonite transition. From CONNOLLY and TROMMSDORFF (1991) the fluid needed for the reaction has to be extremely water rich if only C–O–H fluid compositions are considered.

Fluid inclusions suitable for microthemometry have only been found in dolomite grains in the ductile deformation zone. They form innumerable crystal negatives of maximal 10 μm (average 5 μm) size and appear to be primary. The two-phase filling consist of a liquid phase and a small gas bubble. Homogenization into the liquid phase occurs very consistently at 223 ± 0.5 °C. Freezing experiments indicate an aqueous liquid with less than 5 equiv. weight % NaCl. The isochores of these inclusions intersect with the 485 °C from calcite-dolomite thermometry at around 350 to 400 MPa (Fig. 6). This is consistent with the P-T position of the postulated reaction tremolite + dolomite + H_2O = antigorite + calcite + CO_2.

6. Calcite C and O stable isotope characteristics

C and O stable isotope compositions of 105 calcite samples have been measured with a VG 903 isotope ratio mass spectrometer using standard extraction techniques (McCREA, 1950). Reproducibility (1 σ) is assumed to be better than 0.1 for $\delta^{13}C$ and 0.2 for $\delta^{18}O$. All values given are relative to PDB standard for $\delta^{13}C$ and SMOW standard for $\delta^{18}O$ respectively.

$\delta^{13}C$ values scatter rather uniformly (± 0.4) around a mean of +0.4 whereas $\delta^{18}O$ shows significant variation from 13.3 to 16.7 (Fig. 7a). One sample from 2 mm size, free grown calcite crystals from a late fissure shows higher $\delta^{18}O$ (18.9) and lower $\delta^{13}C$ (–0.7).

Plotting $\delta^{18}O$ with respect to petrographic calcite types reveals distinct differences between these types (Fig. 7b). Values from large fracture

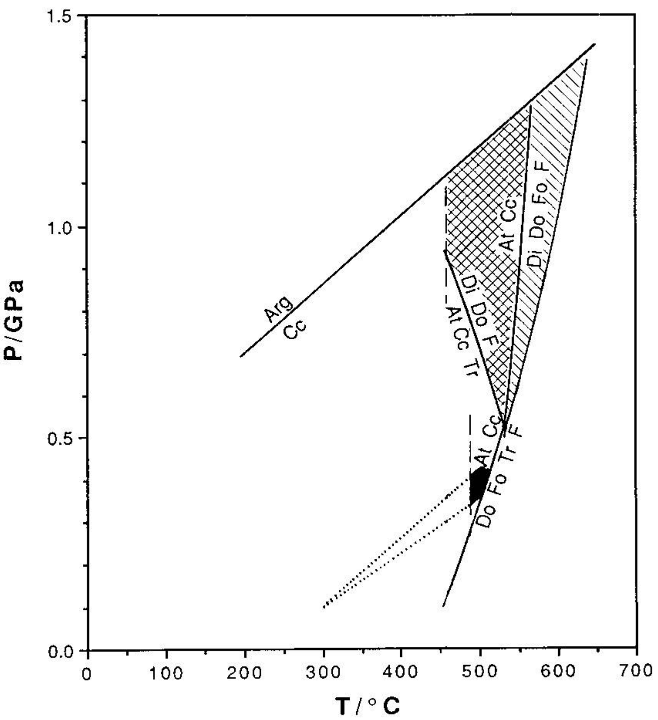

Fig. 6 P-T constraints for mineral assemblages in Chatillon ophicarbonate breccia. Hatched: stability field of diopside + dolomite + fluid overlapping with stability field of "main reaction" (cross-hatched). Black: P-T conditions for ductile deformation zone. Dotted lines: upper and lower limit for isochores of fluid inclusions in dolomite from ductile deformation zone. Dashed lines: calcite thermometry data. Arg = aragonite, At = antigorite, Cc = calcite, Di = diopside, Do = dolomite, F = fluid, Fo = forsterite, Tr = tremolite. Curves from CONNOLLY and TROMMSDORFF (1991).

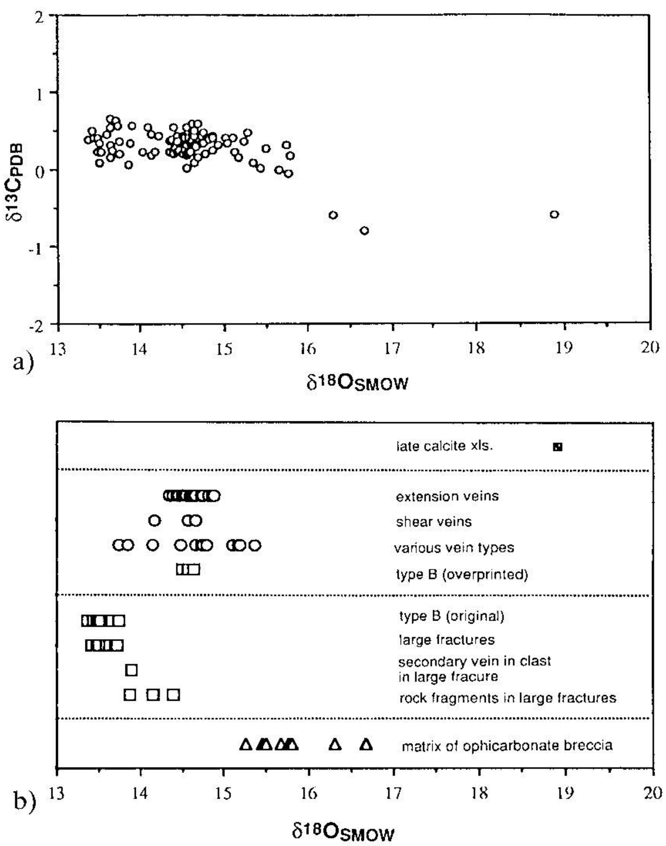

Fig. 7 a) $\delta^{13}C$ vs $\delta^{18}O$ for calcites from Chatillon. b) $\delta^{18}O$ plotted for various petrographic calcite types.

fillings and the structurally related type B veins are lowest (13.5 ± 0.3), the shear and extension veins show intermediate values with a mean of 14.7 (± 0.3 with three slightly higher values) and matrix calcite from the breccia is highest (15.6 ± 0.3 for matrix calcite; 16.3 to 16.7 for calcite from clasts rich in partly pseudomorphed diopside which show also a significantly lower $\delta^{13}C$ of –0.6 to –0.8).

Whether or not the scatters of ± 0.3 reflect real variations or are the result of accumulated errors during sampling, extraction and analysis cannot be evaluated with certainty. It seems plausible that there is a unique isotopic ratio at least in the extension vein subsystem indicating isotopic equilibrium on the outcrop scale.

Profiles across extension veins with spatial resolution down to 0.2 mm show no significant variation (maximum ± 0.1 for both $\delta^{18}O$ $\delta^{13}C$) indicating isotopic equilibrium at least in single veins.

At the rim of a large fracture filling, however, a diffusion profile with a length of 4 mm and $\delta^{18}O$ ranging from 13.4 in the filling to 14.7 at the contact to the ophicarbonate breccia can be observed. Calcite in ophicarbonate breccia fragments in the large fracture fillings is isotopically correlated to the filling although values are slightly higher.

The isotopic compositions of less abundant vein types show a scatter of values over almost the entire range mentioned above.

In general the $\delta^{13}C$ seems to reflect an only slightly modified originally marine signal, whereas the $\delta^{18}O$ values are clearly metamorphic. This interpretation is in good agreement with the observations on non to low-grade metamorphic ophicarbonates in Liguria and Eastern Switzerland (WEISSERT and BERNOULLI, 1984; GREEN, 1982; FRÜH-GREEN et al., 1991), where $\delta^{13}C$ shows typical marine values as well and $\delta^{18}O$ decreases with increasing metamorphic grade.

In detail the disequilibria in $\delta^{18}O$ between different petrographic calcite types are quite striking. Most likely they represent different events of fluid-rock interaction. The isotopic signals of these were preserved because limited exchange between the rock and a fluid channeled in the vein systems prevented larger scale equilibration. Such disequilibria between veins and country rock are not uncommon in metamorphic environments (e.g. KERRICH et al., 1978; TAYLOR and BUCHER-NURMINEN, 1986). They are usually interpreted as the result of incomplete equilibration due to small amounts of fluid, fluid channeling or slow exchange kinetics.

Fluid channeling is particularly suggested by the diffusion profile at the rim of a large fracture filling: an older signal was preserved in the interior while a later fluid (probably related to the "main reaction") was channeled along the tectonically reactivated filling-wall rock interface. This observation also implies a very low permeability for the fine grained calcite filling and/or a rather short duration of the infiltration event responsible for the formation of the shear and extension veins.

The disequilibrium between the extension veins and the matrix calcite on the one hand and between the matrix and clast calcite on the other are not easily interpreted as these calcites should petrographically result from the same event. It may be explained by a special "micro-hydrology" (dispersive/diffusive exchange between vein and rock) during the reaction(s) and/or kinetic isotope fractionation effects or simply by slow exchange kinetics. A detailed discussion of this problem will be given elsewhere.

7. Interpretation of data: tectonic and metamorphic evolution of the rocks

Crucial to any interpretation of ophicarbonate breccias are constraints on the time of brecciation. In this case the lower (older) time limit is given by the pre-brecciation calcite veins in the serpentinite clasts that with high certainty formed in ocean floor hydrothermal processes. The upper (younger) time limit is given by the "high" pressure-assemblage diopside + dolomite (± antigorite) that can be correlated with alpine subduction. Thus the brecciation took place either on the sea floor or during early subduction. The marine carbon isotope signal of the matrix carbonate is a strong indicator for pelagic sedimentation and therefore an ocean floor tectonosedimentary origin seems to be the most likely interpretation.

Accepting this interpretation the relative age relations of macroscopic and microscopic rock features allow the reconstruction of the rock's petrographical and structural history from mantle evolution of the ultramafic protolith through the ocean floor crustal stage to different stages of its Alpine tectonometamorphic evolution. A summary is given in table 3.

7.1. MANTLE AND CRUSTAL EVOLUTION OF PROTOLITH; BRECCIATION

The original petrographic and geochemical nature of the ultramafic protolith cannot be evaluated in detail. From pseudomorphic textures it is obvious that clinopyroxene and olivine were present. As already mentioned the former presence of orthopyroxene cannot be shown unambigously but seems almost certain. The relative age of oriented chlorite blasts in the tectonitic fabric and as relics in pre-brecciation reaction rims indicates a formation during retrogressive evolution (extension related uplift?) of the protolith.

The old concordant and discordant veins with diopside (and/or other not detected minerals?) and their reaction rims postdate the chlorite formation in the protolith and therefore can be attributed to the uplift path of the mantle material as well. Possibly the serpentine observed in the reaction rims is a relic of this stage and may therefore represent the oldest serpentine generation.

The next event that can be detected was hydrothermal activity in the ocean floor's crust resulting in the formation of calcite (and aragonite?) veins in the ultramafics. Serpentinization is indicated by the black serpentine rims around the calcite veins. Future investigations using hydrogen and oxygen stable isotope ratios of the silicates should allow a more detailed interpretation of the serpentine genesis.

For the formation of ophicarbonate breccias on the Tethys ocean floor at least the three different scenarios mentioned in the introduction are possible: a tectonosedimentary origin in fracture zones like in modern Atlantic examples (BONATTI et al., 1974), deposition in the proximitiy of ultramafics exposed along mid ocean ridges (known from the modern Mid Atlantic Ridge; LAGABRIELLE and CANNAT, 1990) or a formation during the denudation of mantle material during the initial opening of the Tethys (LEMOINE et al., 1987). There is no evidence to prefer one of these for the breccia of Chatillon but at least it can be stated that the pre-Alpine history of the rock is more complex than the evolutionary scheme of LEMOINE et al. (1987).

The lithification history cannot be constrained as there is no unequivocally resedimented breccia but it should be expected that lithification took place before the breccia was subducted.

Tab. 3 Overview of tectonic, petrographical, structural and stable isotope geochemical evolution of the rock.

Stage/tectonic environment	Process/mineral reactions	Veining/structural features	$\delta^{13}C_{PDB}/\delta^{18}O_{SMOW}$ in calcite	Remarks
jurassic extension a) mantle evolution of protolith	retrograde evolution of protolith: growth of chlorite in tectonitic fabric	tectonitic fabric in protolith		
	cpx- and other veins in protolith, formation of reaction rims (possibly serpentine I)	veins concordant and discordant to tectonitic fabric		
b) crustal evolution of protolith	veining with aragonite or calcite veins, serpentinization (II) along veins and in rock	carbonate veins discordant to tectonitic fabric	not preserved?	
	deformation (folding of some tectonites prior to breccia-tion)			
c) brecciation, sedimentary evolution	no mineral reactions, mechanical mixing with pelagic carbonate sediments lithification?		marine	$\delta^{13}C$ later homogenized but generally preserved $\delta^{18}O$ not preserved
subduction ("eo-Alpine")	further serpentinization (III) during early subduction?			
	high-pressure metamorphism with formation of diopside + dolomite temperature maximum higher than 485 °C	clinopyroxene veins large fractures	0.5/13.3–13.7	exact relative age of both vein types uncertain
early uplift path (late "eo-" to "meso-Alpine")		calcite-antigorite veins, subtype b	0.2/13.8–14.7	age relation uncertain
		calcite-trem. veins, subtype a+b?	0.2/15.2 (a)	
		calcite-antigorite veins, subtype a	0.2/15.3	single determination
	infiltration by aqueous fluid, T > 460 °C, P > 8 kbar (?); diopside + dolomite → antigorite + calcite; locally tremolite	dense network of shear- and extension-veins; top NW shearing (uncertain if thrust- or extension-related); change of shearing direction to NNE	0.2–0.4/14.3–14.8 0.2/15.5 (breccia matrix)	
		calcite-tremolite veins, subtype c+d	not determined	
		ductile deformation zone (?, probably active over longer periods, could have originated before infiltration event)		
progressive uplift (late "meso-" to "neo-Alpine")	no mineral reactions unam-bigeously of this age	backshearing veins green calcite vein some veins postdating ductile deformation zone fissures with free calcite xls.	not determined 0.4/15.1 e.g. 0.2/13.7 –0.6/18.9	relative age relations of these types uncertain

7.2. PROGRADE PATH OF ALPINE METAMORPHIC EVOLUTION (SUBDUCTION)

No information about the early stages of subduction could be obtained. The oldest unambiguous subduction-related feature of the rocks is the (now mainly pseudomorphed) mineral assemblage diopside + dolomite (+antigorite). This assemblage is stable at pressures higher than 5 kbar (CONNOLLY and TROMMSDORFF, 1991) but there are no field constraints on either P or T. Also the exact time of the formation of this assemblage cannot be deduced although an upper relative time limit is given by its decomposition to antigorite + calcite on the retrograde metamorphic path (see below). A prograde formation seems most plausible because the stability field of this assemblage was reached during subduction well below peak metamorphic conditions of the Zermatt-Saas zone.

A second probably subduction-related feature are the large calcite filled fractures and the probably contemporaneous "type B" calcite veins which both contain fragments of diopside and dolomite.

The "high-pressure" characteristics of these features imply an "eo-Alpine", i.e. Cretaceous age (e.g. HUNZIKER et al., 1989). This is possible but nevertheless a model subduction accompanied by continous offscraping and uplift of slices of oceanic crust (e.g. PLATT, 1986) also allows a tertiary age. As long as no detailed geochronology of the Zermatt-Saas zone is established the absolute age remains unclear.

Perhaps related to the dolomite-diopside assemblage are the now pseudomorphed clinopyroxene-veins which are offset by the extension veins related to the retrograde path (s. below).

7.3. RETROGRADE PATH OF ALPINE METAMORPHIC EVOLUTION (UPLIFT)

The question which features of the rock are related to the retrograde path of the Alpine metamorphic evolution can only be answered by comparing P-T-constraints with P-T-data determined for other rock types within the Zermatt-Saas zone (Fig. 8). This comparison strongly implies that at least the "main reaction" event (plus the contemporaneous formation of shear and extension veins) is located on the retrograde path although still under "high pressure" conditions. The most plausible conditions are approximately 500 °C and 0.7 to 1.2 GPa for the "main reaction". During that time the rock was affected by a small to moderate shear stress (probably a few tens of MPa) that resulted in an overall top to the NW shearing during the formation of the shear and extensional veins. The geometry could have been thrust like, i.e. todays low angle normal fault geometry is only the result of post-nappe folding (MILNES et al., 1981) although it would also fit in the PLATT-model (1986) with uplift of high pressure rocks by extensional movements in an "accretionary wedge". The direction of shearing is no time constraint at the moment, because several stages of regional deformation can show similar movement directions (see for example, STECK, 1989).

Of special interest for the evaluation of the uplift characteristics is the infiltration by externally derived aqueous fluids. Possible sources are for example dehydrating serpentinitic rocks below (e.g. antigorite + brucite = olivine + H_2O) or eclogite transition of mafic rocks. The P-T-estimates of BARNICOAT (1986) for albite-veining in eclogites from the Zermatt area are broadly consistent with those for the "main reaction", perhaps implying larger scale fluid infiltration. BARNICOAT (1986) considered the underlying Monte Rosa nappe as a possible source for the fluids. Further regional mapping and P-T-constraining of veining is needed.

Veins that predate the "main reaction/veining" event like the rare antigorite-calcite- and some of the tremolite-calcite-veins may also be part of the retrograde evolution. As there are no direct P-T-estimates available for this stage their exact location on the P-T path remains unclear.

The relative age of the ductile deformation zone is given by its position on the P-T path although its role in the tectonic evolution remains unclear. Interestingly its formation coincides with onset of a "normal" geothermal gradient in the rock. The isochores of the fluid inclusions in dolomite grains and their combination with calcite thermometry data imply a formation under greenschist facies conditions at approximately 485 °C and 0.35 to 0.4 GPa i.e. well after the "main reaction". This conclusion agrees with the observation of deformed "main reaction" related extension veins in the deformation zone. At the moment these data are probably the best constraints for the greenschist-facies part of the P-T path of the Zermatt-Saas zone.

Some of the "back shear-veins" (Tab. 1) may be related to the uplift path but due to their very local appearance no special importance can be attributed. This holds true also for some small calcite- and calcite-serpentine- or -tremolite-veins (not mentioned in Tab. 1) that crosscut the ductile deformation zone.

Probably the youngest mineralization are the idiomorphic calcite crystals in open fissures

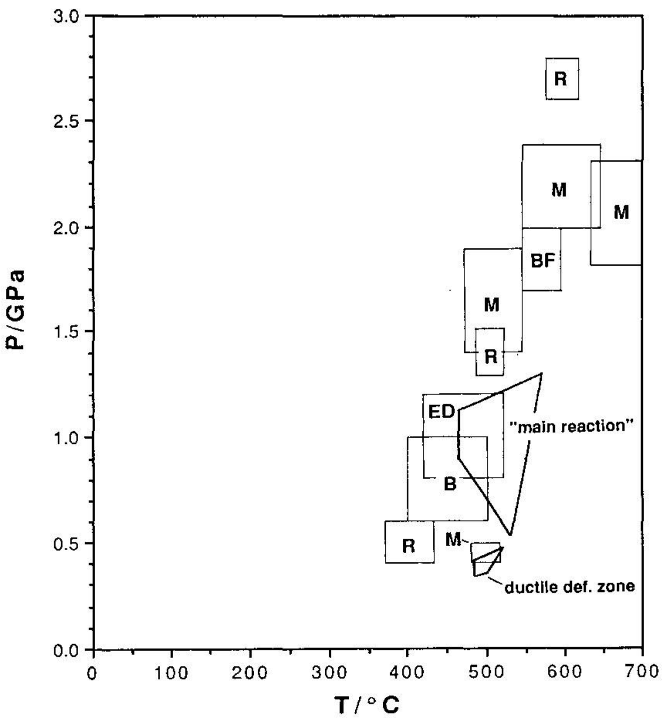

Fig. 8 P-T conditions from figure 6 in comparison to other estimates for the Zermatt-Saas zone. B: BARNICOAT (1986, albite veins in eclogite), BF: BARNICOAT and FRY (1986, eclogites, Zermatt), ED: ERNST and DAL PIAZ (1978, eclogites from Breuil – St. Jacques), M: MEYER (1983, Allalin-gabbro), R: REINECKE (1991, metasediments with coesite, Valtournanche).

that were rarely found in the middle part of the quarry.

7.4. CONCLUSIONS

The study of the ophicarbonate breccia of Chatillon clearly demonstrated that ophicarbonates are a valuable probe for evaluating and constraining both origin and metamorphic evolution in ophiolitic units.

For the first time it is demonstrated that the P-T-projections calculated by CONNOLLY and TROMMSDORFF (1991) can successfully be used to constrain P-T-X conditions of various parts of the Alpine subduction cycle. Especially for the ductile deformation zone the combination with calcite thermometry and fluid inclusion data yields an excitingly narrow defined "point" on the P-T path. The derived P-T estimates are in good aggreement with results from other rock types indicating consistency of the various petrogenetic grids.

On the other hand it was shown that in high pressure metamorphic ophicarbonate breccias the preservation potential for old, pre-Alpine features is very high. The inhomogeneous nature of the breccia seems to hinder mineralogical and structural as well as isotopical and chemical equilibration. Therefore even parts of the pre-brecciation history of the protolith can be traced.

Somewhat surprisingly no pervasive fluid flows seem to have occurred in the rocks. Fluid movement was mainly restricted to fractures and veins, at least during the retrograde evolution. Hydrogen and oxygen isotope studies of the silicates involved could clearly help to constrain this problem more accurately in the future.

Besides the major advantage of yielding much information the inhomogeneity of the rock has the disadvantage that it is not clear whether the details presented in this paper are really representative for the Chatillon ophicarbonate breccia or are only a restricted part of the information still obtainable. It seems to be almost certain that further detailed work on this and other ophicarbonate outcrops could contribute significantly to unravel the details of the evolution of the Zermatt-Saas zone.

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