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The reaction between olivine and plagioclase as a consequence of fluid-rock interactions during sub-seafloor metamorphism (Al-Mg-gabbros, Northern Apennine ophiolites, Italy)

by *Bruno Messiga¹* and *Riccardo Tribuzio¹*

Abstract

Corona textures between plagioclase and olivine characterize the hydrothermal alteration of olivine-bearing gabbros from the Northern Apennine ophiolites during the sub-seafloor metamorphism.

The following four different mineral layers can be found in the same rock type as well as in the same outcrop:

1) olivine + serpentine / chlorite / plagioclase (Na-rich) + prehnite; 2) serpentine / chlorite / plagioclase (Na-rich) + prehnite; 3) serpentine / tremolite / chlorite / plagioclase (Na-rich) + prehnite; 4) chlorite (2) / tremolite / chlorite / plagioclase (Na-rich) + prehnite.

Different steps of the reaction progress are recorded by the above steady layer sequences, indicating that local equilibrium was attained with different ratios of component diffusion.

The possible reaction mechanism for the attainment of the reaction at low P and T conditions involves a metamorphic fluid with low water activity, in an open fluid metamorphic environment. This is consistent with the infiltration of a hydrothermal fluid circulating in the rocks mainly derived from seawater. During the reaction progress the increase of volume produces both fluid confinement and overpressure in the reaction zone.

The reaction mechanism shifts from external versus local control of fluid composition, and requires a finite overstepping along the reaction boundary. The overstepping mechanism proceeds until the fluid pressure produces veining phenomena. The subsequent decrease of pressure stops the reaction progress.

The different coronitic features indicate that the sub-seafloor alteration metamorphism can be regarded as a patchy type process in which kinetic and/or fluid parameters can locally change. Consequently, the different sub-systems attained the partial metamorphic equilibrium following different pathways, each of them prevalently controlled by both fluid composition and reaction mechanism, rather than by intensive parameters such as temperature and pressure.

Keywords: Ophiolite, gabbro, Northern Apennines, seafloor metamorphism, fluid.

Introduction and geological setting

The Northern Apennines ophiolitic sequences consist of ultramafic, gabbroic and basaltic rocks (BECCALUVA et al., 1980; SERRI, 1980; HEBERT et al., 1989), which constitute the stratigraphic base of the allochthonous Jurassic-Paleocene Vara Super-group (ABBATE and SAGRI, 1970). Disregarding the sedimentary and volcanic sequences, the main lithotypes consist of mantle-derived ultramafites and gabbroic intrusives. The ultramafic rocks are tectonic lherzolites with plagioclase and/or spinel facies. The intrusive rocks are represented by: ul-

tramafic and mafic cumulates consisting of plagioclase dunites, wherlites, anorthosites, troctolites, olivine gabbros, gabbro norites and differentiated gabbros such as Fe-Ti-gabbros and Fe-diorites (SERRI, 1980). Detailed geochemical investigations of such rocks may be found in SERRI (1980) and HEBERT et al. (1989).

The intrusive rocks exhibit paragenetic signatures of an oceanic-type retrograde metamorphic evolution, characterized by low pressure conditions (CORTESOGNO et al., 1977; CORTESOGNO and LUCCHETTI, 1982, 1984). An early metamorphic event in the high grade amphibolite facies (often accompa-

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nied by ductile deformation) is overprinted by a polyphase event connected to hydrothermal circulation of seawater-derived fluids (sub-seafloor metamorphism). The metamorphic conditions of the sub-seafloor metamorphism range from the amphibolite to prehnite-chlorite-actinolite facies.

In such a metamorphic environment, the kinetic controls of the reaction progress are exerted by deformations and fluid-rocks interactions. The latter are controlled by grain boundaries and veins in rocks: mass transport in the intergranular region can occur, grain boundary fluid films are relatively thick and the fluid/rock ratios are high (SPOONER et al., 1977). Water consuming reactions, such as spilitization of basalts and serpentinization of ultramafics, are the best evidences of the involvement of water during the oceanic metamorphism. In particular, rocks interact with seawater derived fluids, the circulation of which is related to seafloor hydrothermal system (SPOONER and FYFE, 1973; SPOONER et al., 1977). The fluid movements are driven by thermal gradients (WALTHER and HELGESON, 1977). Owing to the low lithostatic pressure, the rocks are subjected to brittle deformations with consequent veining and increase of rock permeability. The ideal permeability is achieved when the fluids consumed by metamorphic reactions balance the fluids supplied by the hydrothermal reservoir (BRUTON and HELGESON, 1983). In such a hydrothermal system, hydrostatic pressure and lithostatic pressure may occur in veins and bulk rock, respectively, as demonstrated by BRUTON and HELGESON (1983) for geothermal systems.

In the Al-Mg-rich mafic rocks (troctolites and olivine gabbros) from Northern Apennine ophiolites, the main petrological evidence for the attainment of the low grade phase of the sub-seafloor metamorphism is given by the presence of the prehnite + chlorite + tremolite + albite assemblage. Oxygen isotopic compositions indicate exchange with a hydrous fluid enriched in ^{18}O with respect to normal seawater, for temperatures ranging between 200 and 300 °C (RÖSLI, 1987; BARRET and FRIEDERICHSEN, 1989). These temperature estimates agree with the $P_{\text{fluid}}-T$ paragenetic grid for basaltic rocks in the NCMASH system (LIU et al., 1985), which yield temperatures in the range 200–350 °C and P_{fluid} lower than 2.5 kb for the prehnite-chlorite-actinolite facies.

The aim of this work is to investigate the olivine-plagioclase reaction occurring in the Al-Mg-rich gabbros from Northern Apennine ophiolites during sub-seafloor alteration. The P-T equilibrium conditions together with the relationships between fluid composition and reaction progress are discussed. The paper proposes a simple reaction

model taking into account the actual microtextures in the investigated rocks.

Petrography and microtextures

The investigated rock-samples have been collected in a single outcrop from the Bracco ophiolite Unit (CORTESOGNO et al., 1987) in the Eastern Liguria. In this outcrop (along the Mezzema stream) troctolites and olivine gabbros are the most representative lithologies. The magmatic assemblage of the troctolites consists of euhedral chromite and plagioclase, subhedral olivine and anhedral clinopyroxene. The main microtextural features related to the sub-seafloor alteration are: i) pseudomorphic replacements of primary magmatic minerals; ii) coronitic rims between olivine and plagioclase; iii) presence of veins.

The petrographic statements presented derive from a careful comparative microtextural investigation between unaltered troctolites preserving their magmatic assemblage, and altered troctolites displaying different extents of low grade metamorphic overprint.

Relics of magmatic plagioclase are often preserved. The plagioclase exhibits small prehnite lamellae, either as irregular masses or veinlets. Moreover, semi-opaque aggregates consisting of fine intergrowths of phrenite and albite are scattered throughout the plagioclase grains; quartz has never been found. Chlorite veinlets radiating from the coronitic textures and spreading over the plagioclase occur frequently.

The olivine is replaced by either chlorite + tremolite aggregates, or by mesh textured serpentine. Olivine relics are occasionally preserved. Thin and discontinuous relics of magmatic clinopyroxene bounding the olivine grains allow to recognize the outermost boundary of the primary olivine.

Generally, the magmatic clinopyroxene is preserved. In some cases, it is partially replaced by granoblastic aggregates of brown hornblende and neoblastic clinopyroxene. However, this transformation is probably related to the early high grade event of the oceanic metamorphism (CORTESOGNO and LUCCHETTI, 1982, 1984).

The coronas occur between olivine and plagioclase with variable width, depending on the reaction progress. In the samples preserving the olivine relics, the corona is represented by a chlorite rim towards the plagioclase (Fig. 1a). If the olivine is completely replaced, a double tremolite-chlorite corona frequently bounds, the serpentine meshes (Fig. 1b). The most common coronitic texture consists of an external double tremolite-chlorite corona bounding mesh-textured chlorite aggregates on

the pristine olivine domain (Fig. 1c). Scattered grains of pyrite occur throughout the coronitic layer.

Sharp boundaries outline the contact between tremolite and chlorite aggregates. Owing to the

presence of thin magmatic clinopyroxene relics primarily bounding the olivine crystals, the tremolite-chlorite boundaries described above are inferred to occur exactly at the primary olivine-plagioclase grain boundary (Fig. 1a-c). No reaction rims are

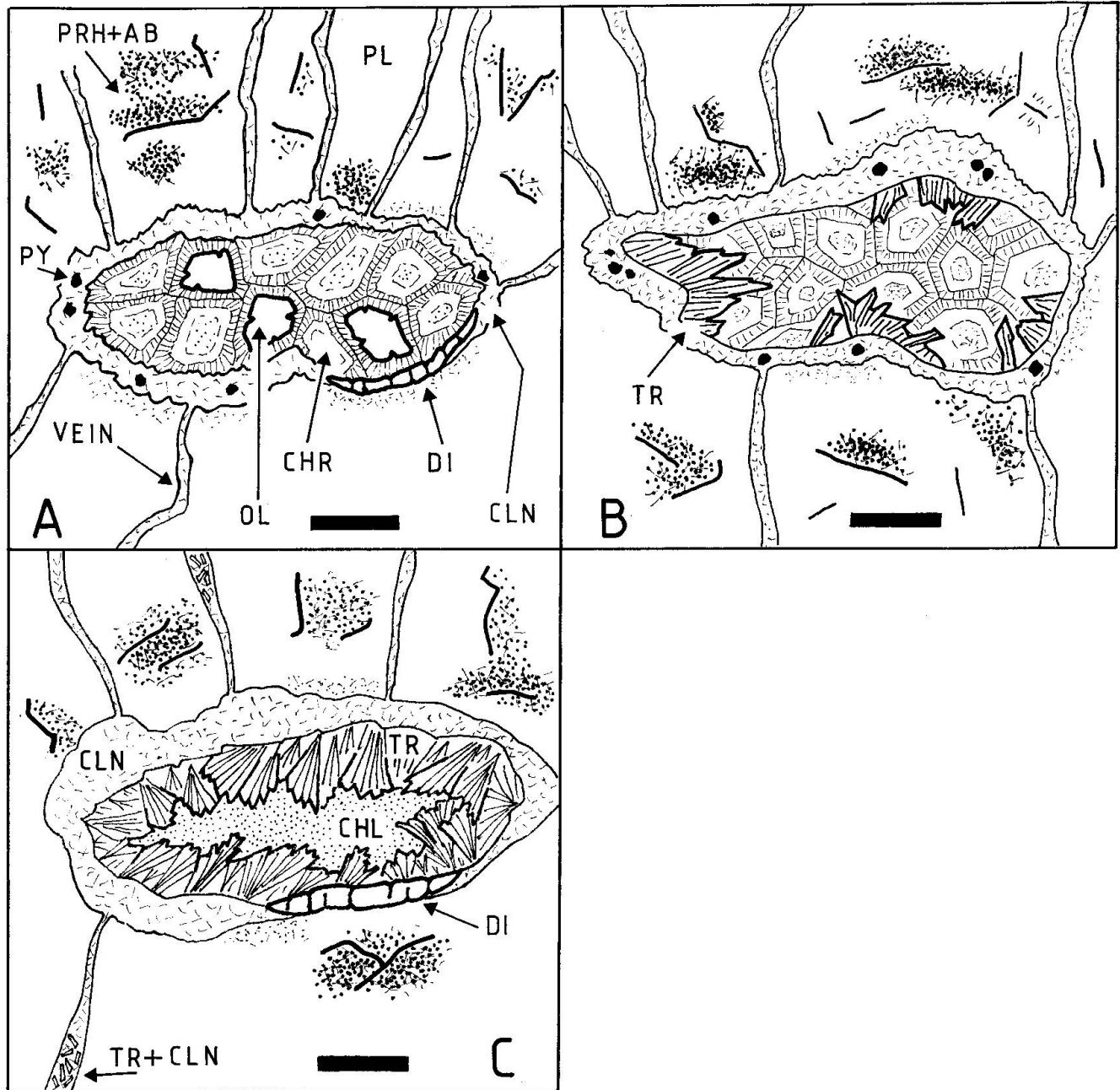


Fig. 1 Microtextural features of the reaction zone, marked by different steady layer sequences. Scale bar = 0.5 mm. a) Olivine relics (OL) are preserved in mesh-textured serpentine (CHR). A thin rim of primary clinopyroxene (DI) marks the primary boundary between olivine and plagioclase. The chlorite (CLN) bounds the pseudomorphs after olivine and contains scattered pyrite (PY) grain. The veins spread from the reaction zone over the plagioclase which in turn is partially transformed to prehnite + albite (PRH + AB). b) The olivine is completely replaced by serpentine and is bounded by a continuous rim of chlorite. At the boundary between chlorite and serpentine, radiating aggregates of tremolite (TR) may grow. c) Coronitic texture consisting of a double tremolite-chlorite corona bounding chlorite aggregates (CHL). When the olivine-plagioclase reaction is completely developed, the corona exhibits an external rim of needle-shaped tremolite crystals, which radiate towards the olivine pseudomorphs. In veins tremolite + chlorite aggregates (TR + CLN) are sometimes found. The presence of pyrite (PY) and primary clinopyroxene are not ubiquitous. The veins / plagioclase volumetric ratios are only indicatively drawn.

Tab 1 Representative microprobe analyses

	1	2	3*	4	5	6	7	8*	9
SiO ₂	38.52	49.80	51.93	45.59	54.23	56.79	31.24	34.16	28.79
TiO ₂	–	1.42	0.07	–	–	0.10	–	0.07	–
Al ₂ O ₃	–	3.98	29.73	–	2.52	0.60	18.19	16.60	21.59
FeO	18.11	3.56	–	4.79	4.24	3.11	9.17	7.34	11.13
MnO	0.35	0.23	–	–	0.08	0.15	–	0.05	0.26
MgO	43.02	16.73	–	41.54	23.73	24.51	32.59	31.59	27.80
CaO	–	22.96	13.74	–	12.65	13.32	0.06	0.28	0.13
Na ₂ O	–	0.66	4.00	–	0.77	0.25	0.08	0.05	0.03
K ₂ O	–	–	0.02	–	–	–	–	0.01	–
Cr ₂ O ₃	–	0.91	–	–	–	–	–	–	–
TOT	100.00	100.25	99.78	92.02	98.22	98.83	91.33	90.16	89.73
MgO/FeO	2.38	4.70	–	8.67	5.57	7.88	3.55	4.30	2.50

1) olivine; 2) clinopyroxene; 3) plagioclase; 4) serpentine in pseudomorphs after olivine; 5) tremolite from corona, rim towards plagioclase; 6) tremolite from corona, rim towards olivine; 7) chlorite from corona, rim towards plagioclase; 8) chlorite from corona, rim towards olivine; 9) chlorite, veins on plagioclase.

* Data from MESSIGA (1984). Hyphens represent values lower than the microprobe detection limit (< 0.01 wt%).

detected between clinopyroxenes and plagioclases, whereas a tremolite rim characterizes the olivine-clinopyroxene boundary.

Moreover, the investigated rocks are marked by the occurrence of veins. Two types of veins, radiating from the reaction zone, can be distinguished: (1) veins spreading through the plagioclase; (2) veins crosscutting the olivine pseudomorphs. Type (1) veins are usually filled with the corona-forming minerals, dominantly chlorite, while type (2) veins always consist of tremolite. Type (1) veins are volumetrically more abundant than type (2). The veins (1) cut the plagioclase laths but also occur along sub-grain boundaries; their width increases from the reaction zone towards the plagioclase (Fig. 1). In the presence of the tremolite-chlorite corona, type (1) veins may exhibit a peculiar change in mineral composition: at the contact with the corona, these veins are always filled with chlorite which in turn is progressively replaced by tremolite moving towards the plagioclase.

Mineral chemistry

Mineral compositions have been determined by electron microprobe using minerals as standards. Microprobe analyses have been performed using a JEOL 840 Microanalyzer equipped with three WDS and one EDS spectrometers installed at "Centro Grandi Strumenti, Università di Pavia".

All the FM phases exhibit high MgO/FeO ratios (always higher than 2.3; Tab. 1). This allows to approximate the calculation of mineral reactions using pure Mg-end members. The analytical survey

on minerals also indicates that anions other than OH⁻ are minor of the detection limit of the microprobe (< 0.01 wt%).

Reactions

The phase relationships have been investigated in the system CaO–MgO–Al₂O₃–SiO₂–H₂O–CO₂ with the following phases: anorthite (AN), calcite (CC), carbon dioxide (CO₂), chlinoclore (CLN), diopside (DI), forsterite (FO), prehnite (PRH), α-quartz (aQZ), tremolite (TR), chrysotile (CHR) and water (H₂O). These phases were selected as representative of minerals characterizing both the magmatic and the sub-seafloor assemblages for Al-Mg-rich rock compositions (CORTESOGNO *et al.*, 1977; CORTESOGNO and LUCCHETTI, 1982; RÖSLI, 1988).

Sub-systems have been selected for the different aspects to be discussed. They have been analyzed using the GEO-CALC computer program written by BROWN *et al.* (1988), based on the internally consistent data base of BERMAN (1988).

Table 2 lists stable and metastable equilibrium reactions which may have occurred in the investigated rocks.

MICROTEXTURAL CONSTRAINTS

The microtextures of the investigated rocks reduce the number of possible reactions if the following constraints are taken into account:

a) the absence of PRH in the reaction rim between olivine and plagioclase;

Tab. 2 Equilibrium reactions

- 1) $aQZ + 2 PRH + 2 CLN = 4 AN + 5 FO + 10 H_2O$
- 2) $CLN + 6 PRH + 3 aQZ = 5 DI + 7 AN + 10 H_2O$
- 3) $7 CLN + 5 PRH + TR = 20 FO + 12 AN + 34 H_2O$
- 4) $3 TR + 15 PRH + CLN = 16 AN + 20 DI + 22 H_2O$
- 5) $2 TR = 4 DI + 3 FO + 5 aQZ + 2 H_2O$
- 6) $TR + 3 PRH = 3 AN + 5 DI + aQZ + 4 H_2O$
- 7) $2 TR + 4 CLN = 4 AN + 15 FO + 5 aQZ + 18 H_2O$
- 8) $2 CC + 2 CLN + 3 aQZ = 5 FO + 2 AN + 8 H_2O + 2 CO_2$
- 9) $6 CC + CLN + 9 aQZ = 5 DI + AN + 4 H_2O + 6 CO_2$
- 10) $5 CC + 3 TR = 2 FO + 11 DI + 3 H_2O + 5 CO_2$
- 11) $CC + 3 PRH + TR = 5 DI + 2 AN + 3 H_2O + CO_2$
- 12) $5 CC + 11 CLN + 3 TR = 35 FO + 11 AN + 47 H_2O + 5 CO_2$
- 13) $TR + 2 aQZ + 3 CC = 5 DI + 3 CO_2 + 2 H_2O$
- 14) $aQZ + 3 FO + 4 H_2O = 2 CHR$
- 15) $2 AN + H_2O = PRH + SiO_2 + Al_2O_3$

- b) the absence of CO_2 -bearing phases;
- c) the absence of reaction between plagioclase and clinopyroxene;
- d) the presence of serpentine as breakdown product of FO;
- e) the occurrence of AB and PRH after the plagioclase breakdown.

THERMODYNAMIC CONSTRAINTS

The equilibria listed in table 2 represent all the possible reactions which occurred in the investigated rocks. The investigation of the phase relationships in the studied rocks indicates that:

a) both primary mineral pairs FO + AN and DI + AN may be in equilibrium with TR + PRH + CLN, along a univariant curve, for water present and quartz absent compositions (reactions 3 and 4). Moreover, both pairs can also be stable with CLN + PRH + aQZ (reactions 1 and 2);

b) the presence of CO_2 in the fluid phase produces the crystallization of CC (reactions 8, 9, 10, 11, 12 and 13).

Therefore, only three forsterite-anorthite reactions are consistent with CO_2 absent compositions: (1) SiO_2 producing reaction, together with PRH

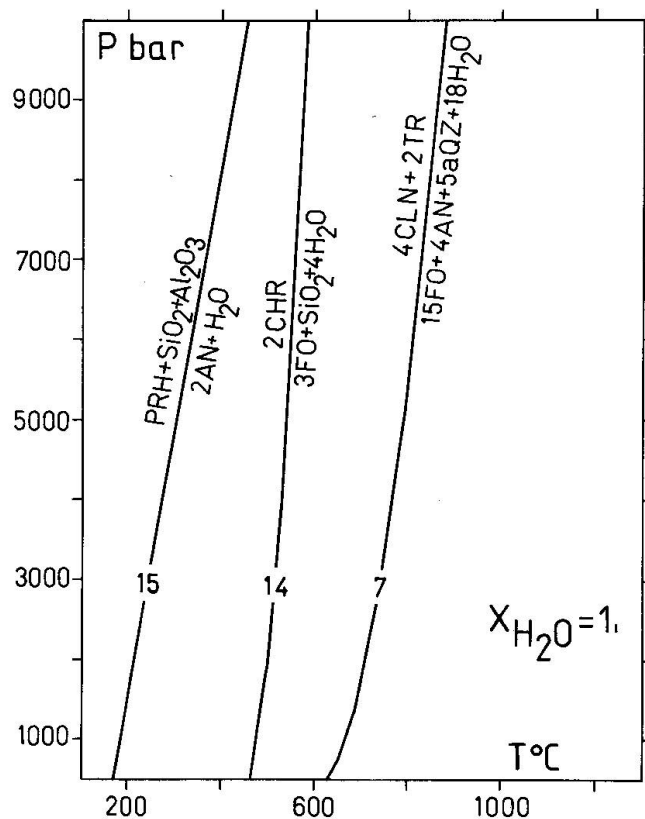


Fig. 2 P-T diagram showing the sequence of retrograde reactions pertaining the investigated rocks.

and CLN; (3) SiO_2 preserving reaction evolving a CLN + TR + PRH assemblage; (7) SiO_2 consuming reaction, producing TR + CLN.

Taking into account the microtextural constraints, the forsterite breakdown (reaction 14) and reaction (7) are the SiO_2 consuming reactions inferred to have occurred in the investigated rocks. On the contrary, the anorthite breakdown (reaction 15) is the only reaction producing SiO_2 .

In figure 2, positions and slopes of reactions 7, 14 and 15 indicate the possible reaction sequence that the investigated rocks may have experienced along a retrograde P-T path. These equilibria on the P-T diagram show a positive slope and are much more dependent on temperature rather than pressure.

Fluid-rock interactions

The reaction behaviour can now be discussed considering either a reaction model in which SiO_2 and H_2O are externally controlled components (K-component, according to THOMPSON, 1970) dissolved in the fluid phase or a reaction model in which only H_2O is a K-component.

SiO_2 AND H_2O EXTERNALLY CONTROLLED

In this case, water and SiO_2 are supplied by a fluid phase circulating in the reaction system.

The isothermal P- $a_{\text{H}_2\text{O}}$ diagram evidences that the equilibrium (7) is almost insensitive to pressure (Fig. 3a). In contrast, the isobaric diagram T- $a_{\text{H}_2\text{O}}$ (Fig. 3b) clearly shows that the equilibrium temperature is strictly controlled by water activity. In the reacting behaviour, the dropping of water activity allows the attainment of the equilibrium conditions at low temperature. The low water activity in the metamorphic fluid would be due to the dilution of H_2O by other components, even if the presence of CO_2 in the fluid phase can be excluded since rocks display a CC absent paragenesis. SPOONER and FYFE (1973) evidenced seawater-rock interactions during sub-seafloor metamorphism, considering the seawater as a fluid in which water could be diluted by other ion and/or molecular species.

H_2O EXTERNALLY CONTROLLED

In this model the SiO_2 is considered as a system component (THOMPSON, 1970), supplied by the anorthite breakdown (reaction 15). This reaction must be attained earlier along the retrograde P-T path experienced by the investigated rocks, in or-

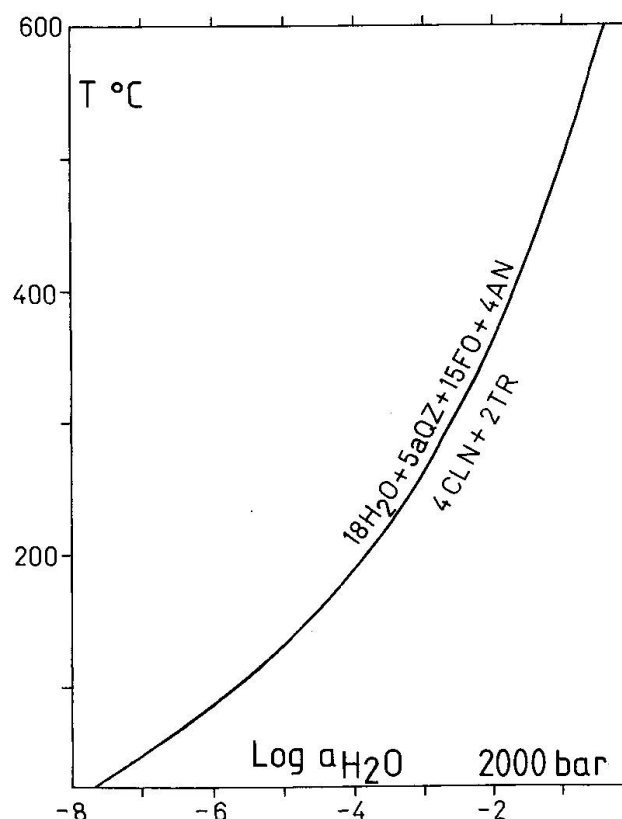
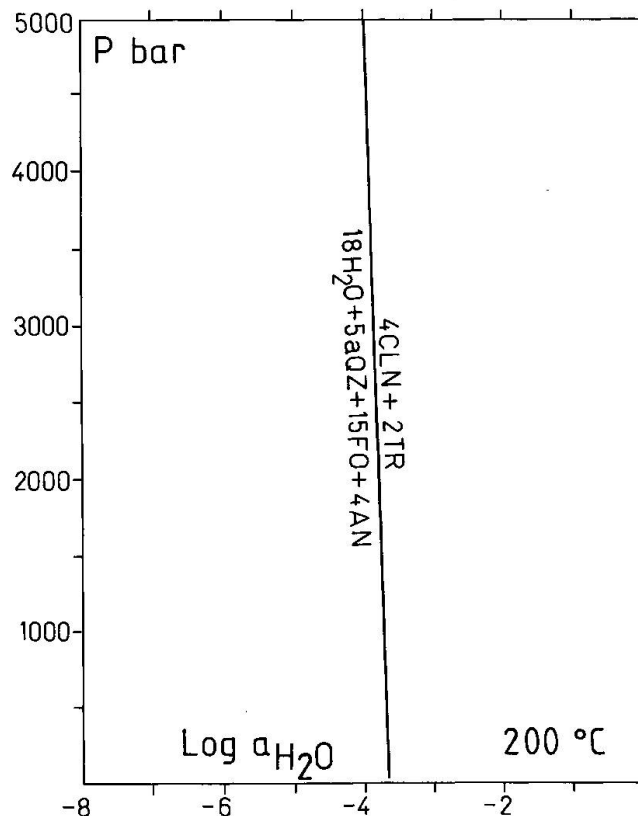


Fig. 3 a) Isothermal $\text{Log } a_{\text{H}_2\text{O}}$ -pressure and b) isobaric $\text{Log } a_{\text{H}_2\text{O}}$ -temperature diagrams for equilibrium (7).

der to evolve the SiO_2 consumed by reactions (14) and (7). However, the P-T grid (Fig. 2) clearly demonstrates that the breakdown reaction of AN is the last reaction that rocks may have suffered along a retrograde P-T path. Therefore, rocks could have escaped the earlier attainment of the equilibrium conditions for reactions (7) and (14), as a result of the absence of SiO_2 .

FLUID PRESSURE

The irreversible reaction (7) occurs with a negative ΔV value and the volume increase is linearly correlated to the number of moles of water involved. This suggests that the reaction progress produces:

- 1) a decrease of $a_{\text{H}_2\text{O}}$ in the fluid, since only pure water is allocated in the produced hydrous phases;
- 2) a volume increase and, consequently, closure of the pores in which fluid circulated.

As a consequence, the reaction behaviour changes from open to closed fluid reacting system, causing a pressure increase in the reaction zone. As the $a_{\text{H}_2\text{O}}$ -pressure diagram shows (Fig. 3a), this pressure increase results in a displacement of the equilibrium (7) towards the products. The reacting system moves along the equilibrium curve, and the reaction progress, enhanced by increasing pressure, is reduced by decreasing water activity.

THE VEINING MECHANISM

When the pressure in the reaction zone overcomes the strength of the plagioclase crystals, veining mechanism takes place thus producing both spreading of fluids and decrease in pressure in the reaction environment. Such a pressure decrease results in the displacement of equilibrium (7) towards reactants and, consequently, the reaction ends.

The composition of the metamorphic fluid present in the reaction zone is presumably controlled by the interactions with the reacting minerals (see GREENWOOD, 1975). The composition of the fluid can be qualitatively estimated to be richer in components involved in metamorphic reactions, such as SiO_2 , H_2O , MgO , CaO , and Al_2O_3 .

As a matter of fact, the presence of tremolite or chlorite in the veins is related to the thermodynamic concentration of the components in the fluid, i.e. different Al_2O_3 and MgO activities. Moreover, the replacement of chlorite by tremolite, occurring in some veins moving outwards from the reaction zone, is probably related to lowering of the MgO activity in the fluid phase.

Discussion

The microtextures of the different investigated rocks display different steady-layer arrangements characterized by different mineral assemblages, each related to the olivine-plagioclase reaction. Four different steady layers have been observed:

- 1) olivine + serpentine / chlorite / plagioclase + prehnite;
- 2) serpentine / chlorite / plagioclase + prehnite;
- 3) serpentine / tremolite / chlorite / plagioclase + prehnite;
- 4) chlorite (2) / tremolite / chlorite / plagioclase + prehnite.

The different steady layer sequences are probably generated by diffusion controlled reactions under chemical potential gradients and reflect different ratios of component diffusion (MESSIGA and TRIBUZIO, 1991). The mineral sequences in the corona reflect different ratios for fluxes of Al_2O_3 , CaO , MgO . In particular, the steady layers (1) and (2) can be ascribed to a very short range diffusion for Al_2O_3 and MgO across the reaction boundary. The steady layer (3) reflects an increase in the $\text{Al}_2\text{O}_3/\text{MgO}$ and CaO/MgO ratios diffusion in the reaction zone. The steady layer (4) could represent a further increasing of Al_2O_3 flux beyond the plagioclase boundary towards the olivine.

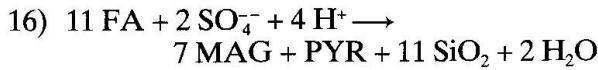
The different steady layer sequences can be governed either by different moments in which the metamorphic reactions started, or by the fluid composition controlling the reaction rate and progress. A whole spectrum of reaction rates is possible during a metamorphic event characterized by fluid-rock interactions, depending on:

- water saturation or undersaturation of the intergranular region (RUBIE, 1986);
- buffering operated by mineral reactions on the fluid phase composition (TROMMSDORFF, 1972; GREENWOOD, 1975; TROMMSDORFF and SKIPPEN, 1986);
- different fluid compositions that change the reaction mechanism and, consequently, the steady layer sequence (KRIDELBAUGH, 1973; TANNER et al., 1985);
- changes of reaction mechanism from diffusion through an aqueous fluid phase to a grain boundary diffusion (RUBIE, 1986).

The investigated reaction can be considered as representative of hydrothermal processes acting during the sub-seafloor metamorphism. The fluid circulated in the rocks along pores and grain boundaries, as well as veins (according to the model proposed by ETHERIDGE et al., 1983).

The presence of CO_2 in the fluid phase is not evident, standing the absence of carbonates among the reaction products. This could be consistent with

a sea-floor environment in which the hydrothermal fluid is mainly composed of seawater. According to SPOONER and FYFE (1973) the fluid can be considered an oxygenated aqueous electrolyte whose anion content is dominated by Cl^- , Br^- , HCO_3^- , CO_3^- and SO_4^- . The occurrence of the disseminated presence of sulfur – bearing phases in the reaction zone can be due to redox reaction such as:



which can cause massive oxidations (SPOONER and FYFE, 1973). Moreover, the fluid interacts with mafic and ultramafic rocks: consequently, a low silica activity is inferred.

The presence of a reacting system either open or closed to the SiO_2 component leads to different conclusions about the water activity in the metamorphic fluid:

- a) SiO_2 and H_2O open reaction system: the water activity in the fluid was low, in order to allow the attainment of the reaction at low temperature;
- b) SiO_2 closed and H_2O open system reaction behaviour: the silica is produced at low temperature by the breakdown of anorthite.

Consequently, the silica availability allows the attainment of reaction (14) and (15) at lower temperatures, even for high values of water activity in the fluid phase. In this aspect, the magmatic assemblage of the rock may be metastably preserved until the occurrence of reaction (15).

Indeed, either externally supplied or internally produced, the silica component is driven to the reaction zone as dissolved species in the fluid phase. It is worth noting that a low SiO_2 activity in the reaction behaviour produces a decrease in the equilibrium temperatures (Fig. 4a). Moreover, an increase in pressure results in the displacement of the equilibrium towards the $\text{CLN} + \text{TR}$ stability (Fig. 4b).

The reaction starts at low temperature and runs at first with a mechanism in which the diffusion of elements is driven by an aqueous fluid phase. Subsequently, the increase of reactants volume probably leads to the closure of grain boundaries channels, trapping water inside the reaction zone. At this point the reaction mechanism could be controlled by grain boundary diffusion and by steady mineral layers growth. The increase of product volume shifts the equilibrium towards products consequently enhancing the decrease of water activity in the trapped fluids. This resulted in increasing of fluid pressure and then veining. Veins are formed when the effective pressure ($P_e = P_{\text{lito}} - P_{\text{fluid}}$) overcomes the strength of plagioclase. The opening of veins produces de-

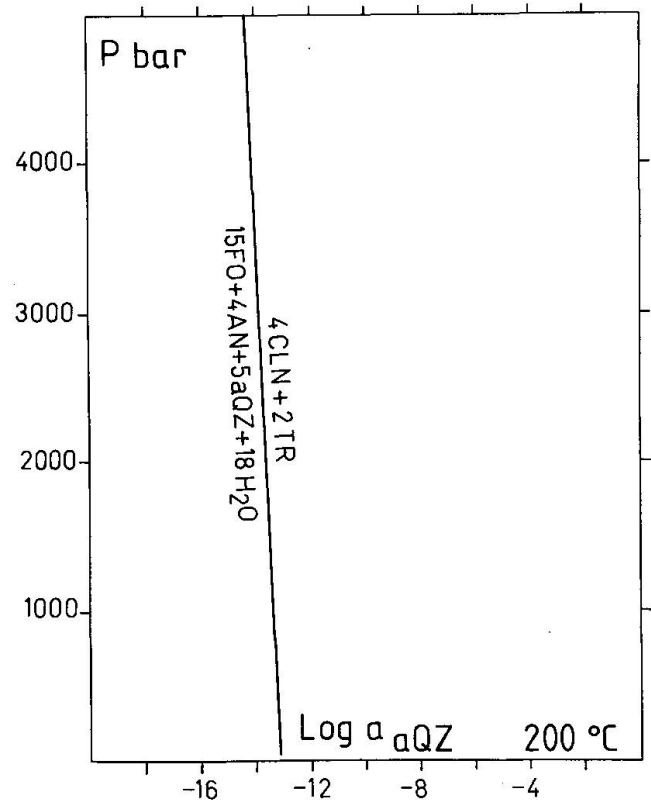
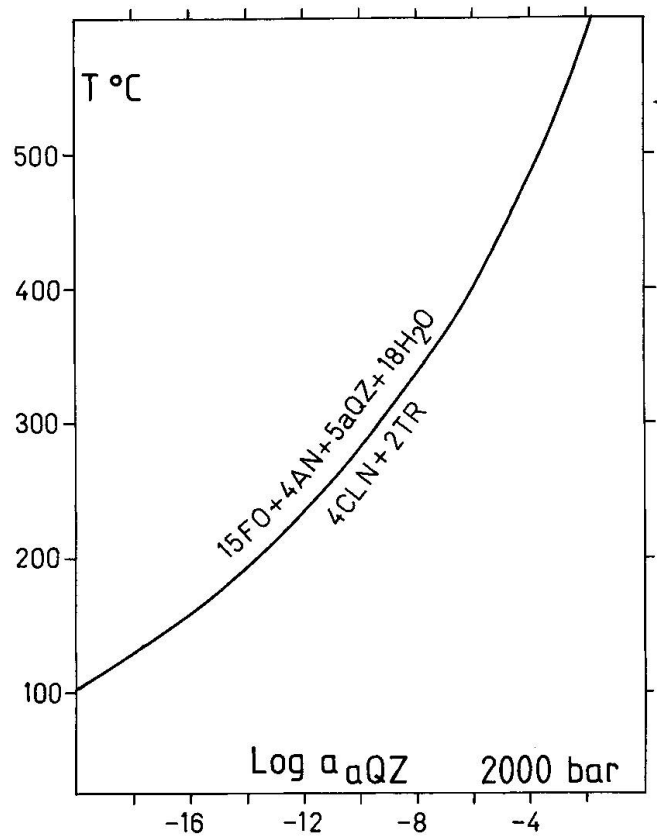


Fig. 4 a) Isothermal $\text{Log } a_{\text{SiO}_2}$ -pressure and b) isobaric $\text{Log } a_{\text{H}_2\text{O}}$ -temperature diagrams for equilibrium (7).

creasing of pressure and shifting of equilibrium towards reactants.

The presence of veins filled with the same mineral phases present in the different steady layer sequences stresses out that the fluid was confined in the reaction zones and played a catalytic effect on the reaction kinetic, enhancing the diffusion of the elements involved in the metamorphic reactions.

The reaction mechanism controlling the reaction progress in the investigated rocks is constrained by an external versus local control of fluid compositions. This mechanism requires a finite overstepping (KERRICK, 1974) along the equilibrium boundary, each step marked by increasing of pressure followed by an isobaric change in the fluid composition to the equilibrium curve. The overstepping mechanism proceeds until the fluid pressure produces veining phenomena. The subsequent decrease in pressure stops the reaction progress.

Conclusions

Since the investigated rocks belong to a single outcrop, they experienced the same P-T history. Therefore, the different steady layer mineral associations represent different steps in the reaction progress, generated by local changes of kinetic factors. In the P-T-t space, the metamorphic evolution can be regarded as a continuous mechanism in which each rock portion recorded, at different times, different segments of the whole metamorphic history. The earlier steps are evidenced by the development of the steady layer (1) and (2), whereas steady layers (3) and (4) represent the later ones. The rocks displaying the steady layer (4) could have been subjected to all the former steps.

The metamorphic behaviour is governed by kinetic factors such as: – fluid availability; – presence of pores and/or intergranular channels; – changing of the reaction mechanism from open-fluid to closed-fluid controlled; – fluid composition buffered by the reaction. All of them may control the different steps of reaction development in the Mg-Al-gabbros.

A single rock outcrop may be regarded as constituted of different sub-systems which attained the metamorphic equilibration following different pathways, each of them more controlled by both fluid composition and reaction mechanism than intensive parameters, such as temperature and pressure. Consequently, the sub-seafloor metamorphism represent a process in which the reaction controlling parameters can locally change, resulting in patchy distribution of the modal amount of the metamorphic reaction products.

Owing to the low metamorphic grade, the reaction kinetic should be very low. However, the conditions for the metamorphic equilibration are attained by the presence of fluids and by their catalytic effect enhancing reaction kinetics.

In absence of interactions with fluid, the rocks metastably preserved the magmatic assemblages and did not record any evidence of the sub-seafloor metamorphism.

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References

- ABBATE, E. and SAGRI, M. (1970): The eugeosynclinal sequences. In: G. SESTINI ed., *Development of the Northern Apennines Geosyncline*. *Sediment. Geol.*, 4, 251–340.
- BARRET, T.J. and FRIEDRICHSEN, H. (1989): Stable isotopic composition of atypical ophiolitic rocks from East Liguria, Italy. *Chem. Geol.*, 80, 71–84.
- BECCALUVA, L., PICCARDO, G.B. and SERRI, G. (1980): Petrology of Northern Apennine Ophiolites and comparison with other Tethyan ophiolites. In: A. PANAJOTOU ed. *Proceedings International Ophiolite Symposium, Cyprus*. *Geol. Surv. Dept., Nicosia*, pp. 413–331.
- BERMAN, R.G. (1988): Internally-consistent thermodynamic data for minerals in the system $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{CaO}-\text{MgO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{H}_2\text{O}-\text{CO}_2$. *J. Petrol.*, 29, 445–522.
- BROWN, T.H., BERMAN, R.G. and PERKINS, E.H. (1988): GE0-CALC: II. PTA-SYSTEM. Software for calculation and display of pressure-temperature-activity phase diagrams. University of British Columbia, Vancouver.
- BRUTON, C.J. and HELGESON, H.C. (1983): Calculation of the chemical and thermodynamic consequences of differences between fluid and geostatic pressure in hydrothermal systems. *Am. J. Sci.*, 283-A, 540–588.
- CORTESOGNO, L., GIANELLI, G. and MESSIGA, B. (1977): Le rocce gabbriche dell'Appennino settentrionale: III. Caratteristiche petrografiche: evoluzione metamorfica in ambiente oceanico ed orogenico, confronti con metagabbri a metamorfismo alpino-tipo. *Ofioliti*, 2, 75–113.
- CORTESOGNO, L. and LUCCHETTI, G. (1982): Il metamorfismo oceanico nei gabbri ofiolitici dell'Appennino Ligure: aspetti mineralogici e paragenetici. *Rend. Soc. It. Min. Petr.*, 38, 561–579.
- CORTESOGNO, L. and LUCCHETTI, G. (1984): Ocean-floor metamorphism of metagabbros and stripped amphibolites (T. Murlo, Southern Tuscany – Italy). *Neues Jh. Min. Abh.*, 148, 276–300.

- CORTESOGNO, L., GALBIATI, B. and PRINCIPI, G. (1987): Note alla "Carta geologica delle ofioliti del Bracco" e ricostruzione della paleogeografia Giurassico-Cretacea. *Ofioliti*, 12, 261–342.
- ETHERIDGE, M.A., WALL, V.J. and VERNON, R.H. (1983): The role of the fluid phase during regional deformation and metamorphism. *J. Metam. Geol.*, 1, 205–226.
- GREENWOOD, H.J. (1975): Buffering of pore fluids by metamorphic reactions. *Am. J. Sci.*, 275, 573–593.
- HEBERT, R., SERRI, G. and HEKINIAN, R. (1989): Mineral chemistry of ultramafic tectonites and ultramafic to gabbroic cumulates from the major oceanic basins and Northern Apennines ophiolites (Italy): A comparison. *Chem. Geol.*, 77, 183–207.
- KERRICK, D.M. (1974): Review of metamorphic mixed-volatile (H_2O-CO_2) equilibria. *Am. Min.*, 59, 729–762.
- KRIDELBAUGH, S.J. (1973): The kinetics of the reaction: Calcite + Quartz = Wollastonite + Carbon dioxide at elevated temperatures and pressures. *Am. J. Sci.*, 273, 757–777.
- LIU, J.G., MARUYAMA, S. and CHO, M. (1985): Phase equilibria and mineral parageneses of metabasites in low-grade metamorphism. *Min. Mag.*, 49, 321–333.
- MESSIGA, B. (1984): Relationships between the chemical domains inherited from the ocean-floor metamorphism and the eclogitic domains equilibration in Ligurian Ophiolitic metagabbros. *Ofioliti*, 9, 499–526.
- MESSIGA, B. and TRIBUZIO, R. (1991): Steady mineral sequence generated by reaction between olivine and plagioclase during sub-seafloor metamorphism in Al-Mg-gabbros, Northern Apennine Ophiolites, Italy. *Ofioliti*, in press.
- RÖSLI, U.E. (1988): Geochemische und mineralogische Untersuchungen an Metarodingiten. Ph. D. Thesis E.T.H. Nr. 8589. 170 pp.
- RUBIE, D.C. (1986): The catalysis of mineral reactions by water and restrictions on the presence of aqueous fluid during metamorphism. *Min. Mag.*, 50, 399–415.
- SERRI, G. (1980): Chemistry and petrology of gabbroic complexes from Northern Apennines ophiolites. In: PANAJOTOU, A. ed. *Proceedings International Ophiolite Symposium*, Cyprus. Geol. Surv. Dept., Nicosia, pp. 296–311.
- SPOONER, E.T.C. and FYFE, W.S. (1973): Sub-sea-floor metamorphism, heat and mass transfer. *Contrib. Mineral. Petrol.*, 42, 287–304.
- SPOONER, E.T.C., BECKINSALE, R.D., ENGLAND, P.C. and SENIOR, A. (1977): Hydration, ^{18}O enrichment and oxidation during ocean floor hydrothermal metamorphism of ophiolitic metabasic rocks from E. Liguria, Italy. *Geochim. and Cosmochim. Acta*, 41, 857–871.
- TANNER, S.B., KERRICK, D.M. and LASAGA, A.C. (1985): Experimental kinetic study of the reaction: Calcite + Quartz = Wollastonite + Carbon dioxide, from 1 to 3 kilobars and 500 to 850 °C. *Am. J. Sci.*, 285, 577–620.
- THOMPSON, J.B. (1970): Geochemical reaction and open systems. *Geochim. and Cosmochim. Acta*, 34, 529–551.
- TROMMSDORFF, V. (1972): Change in T-X during metamorphism of siliceous dolomitic rocks of Central Alps. *Schweiz. Mineral. Petrogr. Mitt.*, 52, 567–571.
- TROMMSDORFF, V. and SKIPPEN, G. (1986): Vapour loss ("Boiling") as a mechanism for fluid evolution in metamorphic rocks. *Contrib. Mineral. Petrol.*, 94, 317–322.
- WALTHER, J.W. and HELGESON, H.C. (1977): Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures. *Am. J. Sci.*, 277, 1315–1351.

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