Periodico di Mineralogia (2015), 84, 3B (Special Issue), 751-777 DOI: 10.2451/2015PM0453

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on Environment, Archaeometry and Cultural Heritage

Fluid rock interactions as recorded by Cl-rich amphiboles from continental and oceanic crust of italian orogenic belts.

Gisella Rebay[1,*], Maria Pia Riccardi[1] and Maria Iole Spalla[2]

[1] Università degli Studi di Pavia, Dipartimento di Scienze della Terra e dell'Ambiente, Via Ferrata, 1, 27100 Pavia, Italy
[2] Università degli Studi di Milano, Dipartimento di Scienze della Terra "A. Desio", Via Mangiagalli, 34, 20133 Milano, Italy
[*] Corresponding Author: *gisella.rebay@unipv.it*

Abstract

Several samples of Cl-rich amphiboles coming from oceanic and sub-continental gabbro bodies has been studied in order to compare their microstructural and compositional peculiarities and to investigate the fluid-rock interactions in different geodynamic contexts. The development of a first group of amphiboles outcropping in the Northern Apennines was the result of a hydration event that has been ascribed to oceanic metamorphism. The second group was collected from a slice of continental crust subducted during Alpine collision, in a subcontinental metagabbro from the Sesia-Lanzo Zone of Italian Western Alps. Their development has been ascribed to a hydrothermal event that took place after the exhumation of the metagabbro during pre-Alpine lithospheric extension. The Cl-amphiboles are found in veins, as granoblastic aggregates in different microstructures, or as rims of zoned amphiboles, where brown-amphibole cores (sometimes Ti-rich), and successive green amphibole, are rimmed by the Cl-rich amphibole. All amphiboles show edembergite to pargasite compositions up to glaucophane and crossites when reequilibrated under HP conditions, with a direct correlation between Fe and $Na_{(A)}$ vs. Cl content, and inverse correlation of Mg and $Na_{(M4)}$ vs. Cl. A comparison with other Cl-amphiboles that have been observed both in oceanic and continental settings, allow discussing the role played by Cl-rich fluids infiltration both in oceanic and continental crust, during lithospheric extension. The large variations in Si, Al^{IV}, Al^{VI}, Fe, Mg, K and Cl may be related to the combination of different factors, such as Cl-content and related cristal-chemical constraints, whole rock composition, PT conditions of reequilibration, the microdomains where the amphibole grows and the variable $a_{HCl/fluid}/a_{H_2O/fluid}$ ratio of the fluid in equilibrium with the amphiboles at various stages of the metamorphic evolution. Amphiboles that locally contain extremely high Cl contents (up to 4% wt) could have been in equilibrium with a locally enriched Cl-fluid. As suggested by the fact that the Cl content of amphibole into the veins is generally lower than in amphibole rims far from the veins, these equilibrium conditions probably were reached at places where the system was locally closed. In addition, hydration reactions consumed the H_2O component of the fluid, leading to a re-equilibration of the crystallising amphibole with the remaining Cl-enriched fluid. Equilibration temperatures up to 350 °C can be attributed to the Northern Apennines amphiboles, and up to 550 °C to the ones from the Sesia-Lanzo Zone.

Key words: Cl-amphibole; Northern Apennine; Sesia-Lanzo Zone; Cl-rich fluids.

Introduction

The study of fluids circulating in the Earth's crust and contributing to its transformations is extremely important as it can give insights on the mechanisms governing fluid rock interactions in different geodynamic environments and at different structural levels. These fluids can be investigated with various methods, but special attention needs to be given to the vein filling minerals and "hydrous" assemblages.

Amphiboles are amongst the most common hydrous minerals present in mafic rocks and in addition, thanks to the large number of independent crystallographic sites with varying coordination numbers (Ungaretti, 1981; Hawthorne, 1983; Rossi and Ungaretti, 1989), various isomorphic substitutions, either iso- or etero-valent are possible. The resulting wide range of possible compositions allows their crystallization in a broad interval of P-T conditions making them a sensitive indicator of PT variations. Investigating into their crystallographic, chemical and geochemical characters provides a key to understanding the metamorphic evolution of their host rocks and the mechanisms of mineral reactions.

Cl-bearing minerals are evidence of the Cl content of the fluids circulating during metamorphic processes. In particular, Cl-rich amphiboles have been recognized in various geological contexts and rocks types around the world (see Kullerud, 1999).

In the present article we will focus on the comparison between the microstructural and compositional character of two groups of Cl-rich amphiboles included in gabbro bodies coming from different paleotectonic scenarios.

The first group of amphiboles is found in gabbros from the Northern Apennines (from different localities, i.e. Bonassola, Monte Capra), and is related to the ophiolitic units. These amphiboles developed in mafic rocks subsequently to a hydration event ascribed to oceanic metamorphism (Riccardi, 1994). The second group of amphiboles is found in subcontinental Corio and Monastero gabbros from the Sesia-Lanzo unit of the Western Alps, the widest tectonic slice of continental crust subduced during Alpine collision. The development of the above amphiboles has been ascribed to a hydrothermal event that took place after the exhumation of the metagabbros in pre-Alpine times and before their subduction (Rebay and Spalla, 2001).

Geologic setting and field relations

Ophiolitic rocks surfacing in the outer units of the Apennine orogeny (Figure 1) represent the remnants of the ancient Jurassic lithosphere of the Ligure-Piemontese oceanic basin, originally interposed between Europe and Adria plates (Decandia and Elter, 1972; Dal Piaz, 1974; Beccaluva et al., 1980; Pognante and Piccardo, 1984; Lemoine et al., 1987; Piccardo et al., 1990).

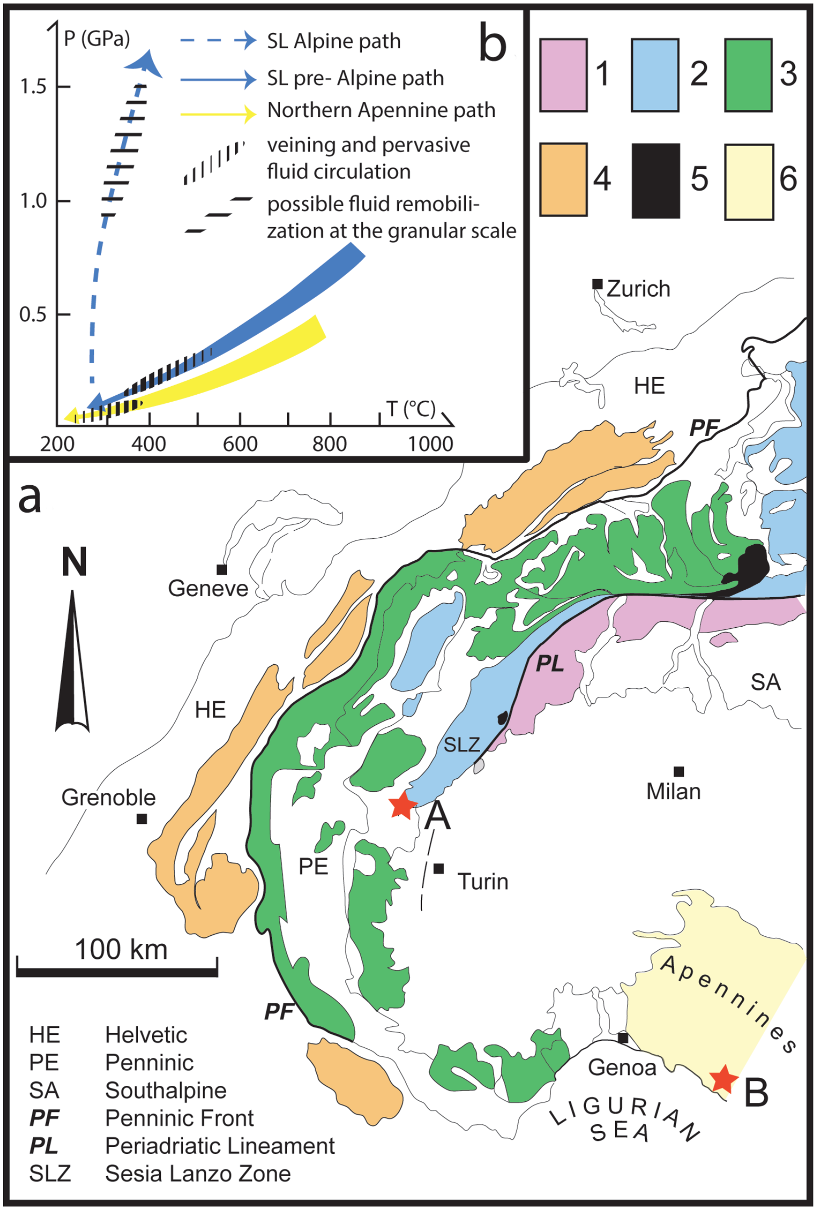


Figure 1. a) Location of the sampling areas: A = Sesia Lanzo zone, Corio and Monastero metagabbro; B = Liguria, Northern Apennine, Bonassola and Monte Capra gabbros. 1 = Helvetic basement; 2 = Penninic basement; 3 = Austroalpine basement; 4 = Southalpine basement; 5 = Tertiary intrusive stocks; 6 = Apennines. b) PT evolution for the Northern Apennines gabbros (Riccardi, 1997; Molli,1996) in yellow, and for the Sesia Lanzo metagabbro (Rebay and Spalla, 2001) in blue. Ornamentation evidences PT conditions at which fluid infiltration occurred.

The ophiolitic rocks outcropping in the Northern Apennine sequence comprise gabbros, intruding variably serpentinized peridotites. These gabbros derive from the fractional crystallization of MORB fluids within shallow magmatic chambers (Serri, 1980; Piccardo, 1984; Hebert et al., 1989; Rampone, 1998; Renna and Tribuzio, 2011). They are covered by mono- and polygenic brecciae (Gianelli and Principi, 1974), that are often intercalated with basaltic lavas (Abbate et al., 1980; Serri, 1980) locally forming thick, doleritic bodies, or displaying pillow structures, often associated with ialoclastites and pillow brecciae. Single basaltic dykes or dyke swarms are also found within the serpentinites, the gabbros and the brecciae. These rocks are covered by a sedimentary sequence made of clastic rocks, with clasts deriving from the ophiolites (Cortesogno et al., 1987), followed by jaspers, limestones ("*Calcari a Calpionelle*") and pelites ("*Argille a Palombini*"), (Abbate and Sagri, 1970; Decandia and Elter, 1972; Principi et al., 2004).

The ophiolitic rocks of Northern Apennine, preserve evidences of a poliphase retrograde evolution followed by re-equilibration under amphibolite and then greenschist facies conditions associated with pervasive hydration, during oceanic metamorphism. The hydrothermal alteration of the oceanic lithosphere took place from amphibolite- to greenschist-facies conditions, when fluids pervasively affected all lithologies. All the phases of this hydration are accompanied by growth of amphiboles, collected from reconstruction of the metamorphic evolution. The inferred evolution implies gabbro intrusion at moderate depths followed by their exhumation, accompanied by intense deformation along shear zones under amphibolite facies conditions. The last stages imply fluid circulation and exhumation up to greenschist-facies conditions associated with ductile-brittle deformation (Cortesogno and Lucchetti, 1982; 1984a; 1984b; Messiga and Tribuzio, 1991; Molli, 1992; Molli, 1996; Tribuzio, 1992; Riccardi et al., 1993; Riccardi, 1994; Tribuzio et al., 2004; Sanfilippo and Tribuzio, 2011; Tribuzio et al., 2014). It is likely that hydrothermal fluids were ocean derived, but a complex interaction with late magmatic fluids has also been postulated (Tribuzio et al., 2014) for part of the evolution. This retrograde metamorphic evolution is associated with high T/P ratios, in an extensional regime consistent with an ocean ridge environment (Figure 1). Absolute ages of ophiolite formation and of the hydrothermally assisted metamorphism range between 180 Ma and 150 Ma (Beccaluva et al. 1980; Bortolotti et al., 1990).

Amphiboles are present in deformed rocks (tectonitic flaser gabbros and mylonites), and in coronitic, unfoliated rocks. Pseudomorphs of green to blue-green amphiboles after mafic primary minerals (pyroxene and olivine) are widespread. Continuous or discontinuous coronitic textures, green or colorless aggregates after brown-red amphiboles, and compositional zonations of tardo-magmatic amphiboles are all the result of the interaction of igneous rocks with hydrothermal fluids. Moreover widespread fractures (from one mm to several dm wide) filled by amphibole crosscut foliated and massive gabbros. The different magmatic and hydrothermal events are marked by different parageneses, all involving amphiboles of different compositions, replacing the original igneous mineral assemblages. Hydrothermal fluids permeated the gabbros not only through fractures, but also along grain boundaries or along foliations (Riccardi, 1994; Tribuzio et al, 2014).

At Bonassola, successive fractures associated with different hydration episodes are pervasively developed and overprinting relationships are evident: i) a system of parallel, millimetric veins filled by green amphibole is associated to shear zones. These veins crosscut at a high angle the metamorphic foliation. ii) A later system of conjugate fractures, from few mm to some cm wide, filled by green amphiboles, crosscut the previous veins and the metamorphic foliation.

They generally occur as larger, centimetric veins surrounded by smaller micro-veins, few millimetres wide. The walls of the veins are sharp and open, with no displacements. Some of these veins may be up to 10 cm wide (Riccardi, 1994; Tribuzio et al., 2014).

The Sesia-Lanzo Zone (Figure 1) is a polymetamorphic basement mainly consisting of continental crust with intruded subcontinental gabbros pervasively eclogitised during Alpine times. This basement comprises metapelites, metagranitoids, scattered mafic and ultramafic bodies and marbles (Compagnoni et al., 1977). The main Alpine eclogitic imprint is dated at 75-65 Ma (Duchene et al., 1997; Rubatto et al., 1999; Meda et al., 2010; Roda et al., 2012) with portions that preserve older HP imprints at 85-75 Ma (Regis et al., 2014 and references therein), up to 130 Ma (Hunziker et al., 1992). Little is known about the pre-Alpine configuration and evolution because of the widespread Alpine high pressure re-equilibration. Some relics of pre-Alpine granulites and amphibolites have been described in the metapelites, both in the northern and southern parts of the Sesia-Lanzo Zone (Compagnoni et al., 1977; Lardeaux et al., 1982; Spalla et al., 1983; Pognante et al., 1987; Lardeaux and Spalla, 1991; Rebay and Spalla, 2001; Rebay, 2003). Lardeaux and Spalla (1991) describe the P–T evolution of basic and acid "granulitic" relics. A granulite facies imprint at T = 700-800 °C, P = 0.7-0.9 GPa, is followed by an amphibolite (T = 600 °C, P = 0.4-0.5 GPa) to greenschist facies re-equilibration (T about 500 °C).

Consistently, Rebay and Spalla (2001), describe the structural and metamorphic pre-Alpine evolution of the Corio and Monastero metagabbros as recording a re-equilibration following the emplacement in the deep crust (P = 0.6-0.9 GPa and T = 850° ± 70 °C), exhumation through amphibolite facies conditions (P = 0.5-0.35 GPa and T = 570-670 °C), with a successive greenschist facies imprint (0.25 ≤ P < 0.35 GPa and T-550 °C). This exhumation was associated with different episodes of fluid infiltration in the gabbro, testified by different generations of veins. Acid granulite relics are present in the surroundings of the Corio and Monastero metagabbros, where the Sesia-Lanzo Zone (Figure 1) has experienced - at least since the early Alpine stages - a common deformation history together with the ophiolitic units of the Piedmont ocean and the ultramafics of the Lanzo Massif (see also Gosso et al., this volume). The retrograde pre-Alpine P–T evolution, which is reconstructed thanks to its preservation in less deformed domains within mostly eclogitised rocks (see Gosso et al., this volume), suggests that the exhumation occurred under a high thermal regime, such as that resulting from lithospheric thinning announcing continental rifting, as proposed for the Southalpine and Austroalpine domains during Permian times (Diella et al., 1992; Schuster et al., 2001; Marotta et al., 2009).

Rock description and microstructures

Common elements in both Apennines and Alps are the type of rocks where the Cl-amphiboles are found, i.e. intrusives of mafic composition, and the microstructural position of the Cl-amphiboles. The latters are either found in veins or as rims of complexly zoned grains or as aggregates in different microdomains. Zoning usually involves brown-amphibole cores (Ti-rich high temperature hornblendes), and green amphibole rims (intermediate temperature green hornblende), with the Cl-rich amphibole rimming the latter. Finally in both cases no other Cl-bearing minerals have been detected in the studied samples.

Cl-amphiboles are found in a series of different microstructures. In the Northern Apennine, the study of 15 samples allowed to recognise that inFe^- and Mg-gabbros (Figure 2 a,b) three different microstructures may be distinguished

(Figure 3):

a) rims of brown or green hornblende;

b) veins in plagioclase microdomain;

c) acicular aggregates (coronae between mafic minerals and plagioclase, or aggregates within the plagioclase microdomain);

in the Sesia Lanzo Zone metagabbros (Figure 4), the analysis of 20 samples allowed to recognise that Cl-amphiboles are found:

a) as rims of brown or green hornblende;

b) in veins through plagioclase, pyroxene or brown amphibole;

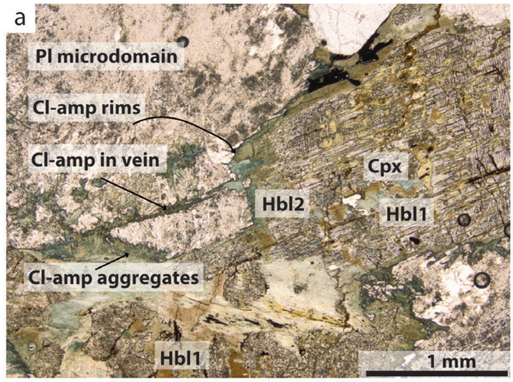
d) as granoblastic zoned aggregates in a carbonate bearing microdomain;

e) as acicular aggregates in the plagioclase microdomain.

In the Northern Apennines, in Fe-gabbros the presence of a green amphibole rim pseudomorphing the magmatic brown-amphibole, and the acicular aggregates usually formed at the original grain boundaries on the plagioclase microdomain, is strictly associated with the presence of veins (Figure 2a).

In addition, a more Cl-rich amphibole rim developed around zoned amphiboles (brown hornblende core and green hornblende mantle) (Figure 3a). Green and colorless acicular Cl-amphiboles are found as coronae or as rounded fibrous aggregates around primary minerals (Figures 2 a,b), in microfractures (Figure 3b) and along the twinning planes of igneous plagioclase (Figure 3c).

In veins the most common paragenesis is green Cl-amphibole, chlorite and interstitial colorless amphibole; amphiboles rim the veins towards the plagioclase microdomain (Figure 3b). When veins crosscut primary mafic minerals, there is a partial to total replacement by green amphibole (Figure 3c). Plagioclase is mostly pseudomorphosed by albite and crosscut by veins (Figures 2 a,b and 3 b,c), with the following mineral sequence: large idioblastic green amphiboles (Hbl_2 in Figure 3d), Cl- and Fe-rich amphibole (Figure 3d) and late colorless amphiboles.



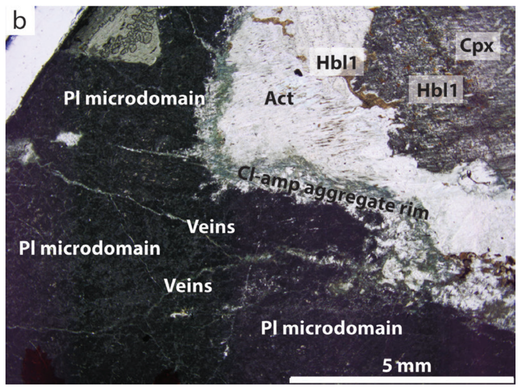
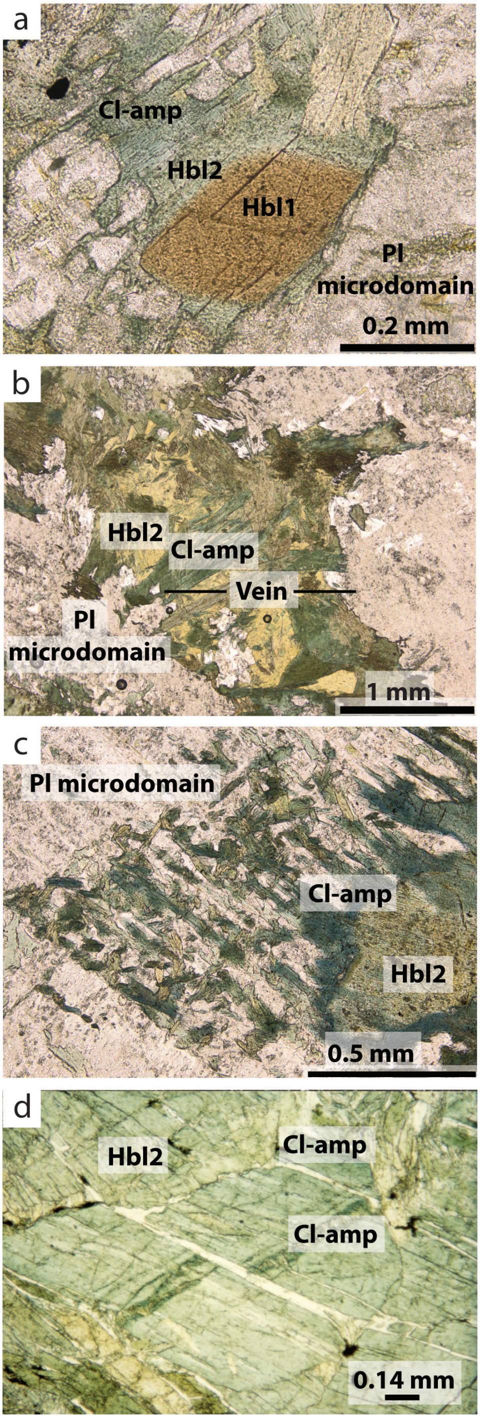


Figure 2. Microphotographs, in plane polarized light, of a) Fe-gabbros and b) Mg-gabbros from the Northern Apennines (Monte Capra and Bonassola). Plagioclase is in both examples not preserved and substituted by an intergrowth of albite + epidote + chlorite (plagioclase microdomain). Dark green-bluish Cl-amphiboles are found as rims around brown to green amphibole, in veins crosscutting the plagioclase microdomain and in acicular aggregates along the primary minerals.

In Sesia Lanzo metagabbros the Cl-amphiboles microstructures partially coincide with those from the Northern Apennines. Successive different generations of veins recognizable in the field contain distinctive minerals such as Cl-amphiboles or chlorite. Carbonates (calcite and



ankerite) with lozenge-shaped opaque inclusions, and Fe–Ti-oxides are sometimes overgrown, and often completely replaced, by Cl-rich green-blue amphibole. These amphiboles are also found in millimeter to centimeter veinlets that crosscut all microdomains (epidote, albitic plagioclase, pseudomorphs after plagioclase, talc after orthopyroxene), and they rim brown and green amphiboles. Locally, they are rimmed by a yellowish edenitic hornblende. All these observations point to fluid circulation related to these fluids to be pre-Alpine.

A second set of veins is chlorite bearing. Its relationship with the Cl-amphibole-bearing veins has not been observed so far in the field, but in coronitic rocks chlorite growth is successive to Cl-amphibole. An-rich plagioclase is not transformed when crosscut by wide (up to 1 cm) chlorite veins. In contrast, mafic minerals such as orthopyroxene, clinopyroxene and brown amphibole are replaced, respectively, by talc, green amphibole and chlorite + talc + opaque minerals. Where chlorite veins are thin, widespread and closely spaced, a pervasive mineral replacement, giving rise to a homogenisation of the different microdomains, occurs. Plagioclase is replaced by an aggregate of albite$_2$, epidote$_2$, amphibole$_2$, and chlorite. Retrogressive transformations are more effective in shear zones where fine-grained epidote, plagioclase, amphibole, chlorite and opaques developed.

Figure 3. Microphotographs of details of Cl-amphibole textures in Fe-gabbros from Northern Apennines. a) zoned amphibole has red-brown hornblende core and green hornblende mantle. The green-blue rim is Cl-amphibole; b) in veins through plagioclase microdomain, green amphibole and Cl-amphibole are present; c) Cl-amphibole rims around green amphibole and pyroxene, as well as along cleavage of substituted plagioclase; d) in veins, green idioblastic hornblends (Hbl$_2$) are crosscut by Cl-amphiboles.

In undeformed rocks retaining "magmatic" or granoblastic textures, Cl-amphibole rims zoned, brown to green hornblende (Figure 4a), fills veins crosscutting the plagioclase and mafic mineral domains (Figure 4b) and develops in aggregates replacing the plagioclase microdomain (Figures 4 a,c). In rare coronitic samples a microdomain characterized by a carbonate (calcite, ankerite), with Fe-oxides aligned at 120°, testifies the circulation of CO_2-rich fluids. Dark-green extremely Cl-rich zoned amphiboles grow in this microdomain, and are rimmed by actinolites and a garnet corona. In more deformed rocks this microdomain is characterized by an aggregate of granoblastic Cl-amphiboles, with a calcic amphibole core, a sodic-calcic mantle and a sodic blue amphibole rim, all Cl-bearing. In completely eclogitised samples, this site is replaced by a single crystal of blue amphibole, with small Cl-amphibole inclusions in the core (Figure 4d). Glaucophane may replace brown amphibole, actinolitic amphibole and Cl-rich amphiboles, completely or partially, starting from the rims. In these cases it is possible to locally find Cl-amphibole that are calcosodic-or sodic (see also Table 2) pointing to a recrystallization at high-P conditions of amphiboles locally in equilibrium with Cl-enriched fluids. These observations

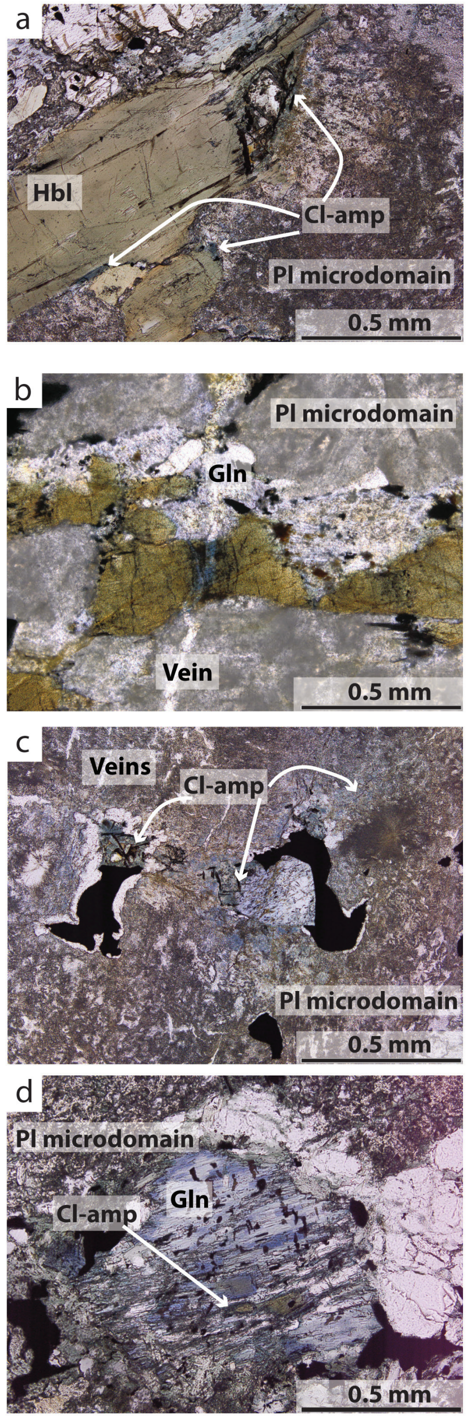


Figure 4. Microphotographs of details of Cl-amphibole textures in Fe-metagabbronorite from Sesia Lanzo zone. a) Cl-amphibole (deep blue-green) rimming brown-green hornblende (lower left side of image) and in the carbonate microdomain. Note the small vein across plagioclase microdomain in the upper right corner; b) a vein crosscutting all microdomains. Cl-amphibole (dark blue) grows only when the veins crosses the brown hornblende. Glaucophane (Gln) partially substitutes mafic minerals; c) Cl-amphibole aggregate in the carbonate microdomain and overgrowing the plagioclase microdomain; d) Cl-amphibole thin rim around brown hornblende core in a glaucophane crystal.

indicate that Cl-amphibole developed before HP metamorphism, and that only in limited cases these amphiboles have recrystallized locally (as rims) during the prograde alpine path.

Cl-amphiboles are also found in other microdomains:

- in veins, in the plagioclase microdomain crosscutting the aggregate of epidote, albite + chlorite and amphibole after plagioclase, and in mafic mineral microdomains along pyroxene cleavage planes;
- as rims of brown hornblende;
- in granoblastic aggregates in plagioclase microdomain toghether with chloritoid (in this case the Cl-amphibole is sodic or calco-sodic);
- in up to 50 cm wide bands made of green amphibole (as a mantle rim between a brown amphibole core and an actinolitic rim or in veins cutting larger actinolitic amphiboles), probably representing amphibole rich veins similar to those observed in ophiolites.

Mineral Chemistry

Minerals were analysed with a JEOL JXA-840A microprobe of Centro Grandi Stumenti, Università di Pavia. Natural silicates and oxides were used as standards, and 11 elements were measured, using the program TASK and the PRZ correlation matrix, with an estimated precision of 3% on major elements and 10% on minor elements. The accelerating voltage was 20 kV with a 20 nA current, on a 5 µm area in order to reduce matrix effects. The structural formulae were calculated using the program AMPH ETH, Zurich; amphibole formulae were recalculated on the basis of 23 oxygens, according to the method described by Laird e Albee (1981) and the IMA classification of Leake et al. (2004), and using a diagram comparing $(Na+K)_A$ and Al^{IV}, thus visualising the edenitic and tschermakitic substitutions which are very important in Cl-bearing amphiboles (Figure 5). Representative mineral compositions of Cl-amphiboles with indications of the microstructural domains where amphibole are found and the type of rocks hosting them are listed in Table 1 for the Northern Apennine and in table 2 for Sesia Lanzo.

The crystallization of Cl-amphiboles depends from several factors: a) the amphibole structure (Vollfinger et al., 1985; Makino et al., 1993; Oberti et al., 1993 and references therein); b) the PT conditions of crystallization; c) whole rock composition; d) the composition of the fluids (Kullerud, 1996; Kullerud & Erambert, 1999; Kullerud et al., 2001).

According to some authors the Cl content of amphibole is principally controlled by the Fe/Mg ratio (Volfinger et. al., 1985), whereas others (Oberti et al., 1983) have pointed out that there are several consequences on amphibole structure when Cl is incorporated (more K in the A site and substitution of Al for Si in the tetrahedral site). However, the implications of the two models of incorporation of Cl in amphibole are substantially different: the first one is based on the assumption of a constant composition of the fluid, whereas the second implies that variations in amphibole Cl content are controlled by the a_{Cl-}/a_{OH-}.

Cl incorporation in the amphibole structures is in the O3 site, more exactly in the satellite site O3’ (Oberti et al., 1993). Cl has a large ionic radius and substitutes the OH^- group. This substitution is favoured by an enlargement of the tetrahedric chain and of the octahedral ribbon. The enlargement of these two structural units can be achieved by Al-Si substitution in the tetrahedric chain and with the contemporaneous entrance of Fe in the octahedral sites (Ito and Anderson, 1983; Oberti et al., 1993 and references therein). Therefore the chemical composition of Cl-amphiboles in terms of Na, K, Fe, Al and Si is dependent on Cl content for the same whole rock composition and (P) T conditions (Morison, 1991; Oberti et al., 1993; Kullerud 1996; Sato et al., 1997; Markl and

Table 1. Representative analyses of Cl-amphiboles from the Northern Apennine.

	Mg-gabbro						
	rims of AMP			veins in PL - 1			
	Parg-Hb	Parg-Hb	parg-Hb	Ed	Mg-Hb	Ed-Hb	Ed
SiO_2	44.21	45.97	47.31	48.40	48.98	46.45	48.41
TiO_2	2.26	1.21	1.44	0.38	0.14	0.43	0.33
Al_2O_3	13.51	9.03	8.18	8.88	5.70	9.24	8.89
Cr_2O_3	0.01	0.00	0.00	0.00	0.00	0.00	0.00
FeO	10.81	12.18	11.57	10.64	18.42	12.17	11.59
MnO	0.14	0.22	0.20	0.13	0.20	0.18	0.14
MgO	14.02	14.55	15.01	16.15	12.27	15.88	16.09
CaO	11.15	11.66	11.87	11.96	11.57	12.03	12.16
Na_2O	2.33	2.15	1.84	1.87	1.26	2.04	1.92
K_2O	0.24	0.28	0.21	0.12	0.11	0.13	0.10
Cl	0.18	0.22	0.20	0.20	0.18	0.20	0.16
Tot	99.22	97.42	97.78	98.68	98.79	98.70	99.75
Si	6.32	6.75	6.88	6.91	7.20	6.66	6.85
Ti	0.29	0.13	0.16	0.04	0.01	0.05	0.03
Al	2.28	1.57	1.40	1.49	0.98	1.57	1.49
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.02	0.03	0.03	0.02	0.02	0.02	0.02
Mg	2.99	3.19	3.25	3.44	2.69	3.40	3.40
Ca	1.71	1.83	1.85	1.83	1.82	1.85	1.84
Na	0.65	0.61	0.52	0.52	0.36	0.57	0.53
K	0.04	0.05	0.04	0.02	0.02	0.02	0.02
Cl	0.04	0.06	0.05	0.05	0.04	0.05	0.04
Fe^{3+}	0.00	0.00	0.00	0.06	0.21	0.43	0.20
Fe^{2+}	1.10	1.33	1.26	1.04	1.94	1.31	1.02
Al^{IV}	1.68	1.25	1.12	1.09	0.80	1.34	1.15
Al^{VI}	0.60	0.32	0.28	0.40	0.18	0.23	0.34
Na_{M4}	0.10	0.00	0.02	0.00	0.00	0.00	0.00
Na_A	0.55	0.61	0.50	0.52	0.36	0.57	0.53

Table 1. Continued…

	Mg-gabbro			Fe-gabbro				
	veins in PL - 2			aggregates				
	Mg-Hb	Mg-Hb	Mg-Hb	FeHb-parg	FeHb-parg	FeHb-parg	FeHb-parg	FeHb-parg
SiO_2	49.07	47.73	48.51	40.79	40.98	40.46	39.48	40.86
TiO_2	0.09	0.10	0.10	0.12	0.24	0.13	0.00	0.00
Al_2O_3	6.88	7.59	7.30	15.34	11.46	12.65	12.01	11.78
Cr_2O_3	0.00	0.00	0.00	0.05	0.07	0.09	0.08	0.08
FeO	16.04	16.37	13.63	19.97	25.36	27.15	27.11	27.44
MnO	0.21	0.19	0.22	0.27	0.32	0.26	0.13	0.27
MgO	13.13	13.06	13.63	7.74	5.34	4.26	4.09	4.32
CaO	11.75	11.29	11.72	11.51	11.38	11.64	11.47	11.43
Na_2O	1.54	1.74	1.74	2.72	2.41	2.49	2.36	2.33
K_2O	0.13	0.12	0.13	0.07	0.22	0.16	0.12	0.16
Cl	0.33	0.12	0.41	0.33	0.39	0.44	0.52	0.57
Tot	99.10	98.48	99.53	98.84	98.08	99.63	97.25	99.11
Si	7.14	7.01	7.03	6.13	6.38	6.24	6.24	6.34
Ti	0.01	0.01	0.01	0.01	0.03	0.02	0.00	0.00
Al	0.67	1.31	1.25	2.72	2.10	2.30	2.24	2.15
Cr	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01
Mn	0.03	0.02	0.03	0.03	0.04	0.03	0.02	0.04
Mg	2.85	2.86	2.94	1.73	1.24	0.98	0.96	1.00
Ca	1.83	1.78	1.82	1.85	1.90	1.92	1.94	1.90
Na	0.43	0.49	0.49	0.79	0.73	0.74	0.72	0.70
K	0.02	0.02	0.02	0.01	0.04	0.03	0.02	0.03
Cl	0.08	0.09	0.10	0.08	0.10	0.12	0.14	0.15
Fe^{3+}	0.05	0.13	0.16	0.18	0.30	0.41	0.52	0.42
Fe^{2+}	1.73	1.60	1.48	2.18	2.90	3.01	3.01	3.04
Al^{IV}	0.34	0.99	0.97	1.87	1.62	1.76	1.76	1.66
Al^{VI}	0.33	0.32	0.28	0.85	0.48	0.54	0.48	0.49
Na_{M4}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_A	0.43	0.49	0.49	0.79	0.73	0.74	0.72	0.70

Table 2. Representative analyses of Cl-amphiboles from the Sesia-Lanzo zone (Corio and Monastero).

	meta-Fe-gabbro norite											
	granoblastic aggregates						veins in PL		veins in PX			
	Al-rich	Al-rich	Al-rich	Al-rich	Al-rich	Al-rich	Al-rich	Al-rich	Fe-Barr	Al-rich	Barr	Al-rich
SiO_2	36.75	38.88	38.43	37.68	37.68	36.09	37.76	37.86	37.68	38.88	38.20	52.65
TiO_2	0.40	0.58	0.29	0.28	0.18	0.52	0.37	0.39	0.30	0.12	0.12	0.29
Al_2O_3	14.45	12.15	12.44	10.26	14.19	12.49	16.35	14.23	11.72	15.39	15.04	1.66
Cr_2O_3	0.07	0.09	0.00	0.06	0.00	0.11	0.08	0.08	0.08	0.02	0.02	0.07
FeO	28.02	28.68	26.16	27.24	25.98	30.86	26.79	26.95	27.59	26.93	26.03	17.72
MnO	0.19	0.19	0.11	0.15	0.09	0.23	0.18	0.19	0.13	0.15	0.12	0.04
MgO	2.92	2.65	3.82	3.82	3.32	1.51	2.64	3.25	3.45	2.13	2.42	12.77
CaO	10.43	9.98	10.52	10.73	10.03	10.42	9.92	10.04	10.86	9.47	9.19	11.77
Na_2O	3.56	3.75	3.31	3.96	3.39	3.38	3.72	3.77	3.38	3.83	3.24	1.25
K_2O	1.22	0.91	0.83	0.95	0.87	1.14	1.00	1.00	1.00	0.92	0.91	0.14
Cl	3.22	2.71	2.83	4.20	2.82	3.09	2.82	3.04	3.76	2.90	2.67	0.13
Tot	101.23	100.57	98.74	99.33	98.55	99.84	101.63	100.80	99.95	100.74	97.96	98.49
Si	5.82	6.18	6.17	6.23	6.03	5.90	5.85	5.96	6.72	6.09	6.09	6.11
Ti	0.05	0.07	0.04	0.04	0.02	0.06	0.04	0.05	0.05	0.01	0.01	0.04
Al	2.70	2.28	2.35	2.00	2.68	2.41	2.99	2.64	1.67	2.84	2.83	2.24
Cr	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.01
Mn	0.03	0.03	0.02	0.02	0.01	0.03	0.02	0.03	0.02	0.02	0.02	0.02
Mg	0.69	0.63	0.91	0.94	0.79	0.37	0.61	0.76	1.17	0.50	0.58	0.84
Ca	1.77	1.70	1.81	1.90	1.72	1.82	1.65	1.69	1.62	1.59	1.57	1.89
Na	1.09	1.16	1.03	1.27	1.05	1.07	1.12	1.15	1.01	1.16	1.00	1.06
K	0.25	0.18	0.17	0.00	0.18	0.24	0.20	0.20	0.17	0.18	0.19	0.21
Cl	0.86	0.73	0.77	1.18	0.76	0.86	0.74	0.81	0.73	0.77	0.72	1.03
Fe^{3+}	0.68	0.48	0.42	0.20	0.57	0.70	0.60	0.59	0.35	0.41	0.63	0.40
Fe^{2+}	3.03	3.33	3.09	3.57	2.91	3.52	2.87	2.96	3.01	3.12	2.84	3.35
Al^{IV}	2.18	1.82	1.83	1.77	1.98	2.10	2.15	2.04	1.28	1.91	1.91	1.89
Al^{VI}	0.52	0.45	0.52	0.23	0.70	0.30	0.84	0.61	0.39	0.94	0.92	0.36
Na_{M4}	0.23	0.30	0.19	0.10	0.28	0.18	0.35	0.31	0.38	0.41	0.43	0.11
Na_A	0.86	0.86	0.84	1.17	0.77	0.90	0.77	0.85	0.64	0.75	0.57	0.95

Table 2. Continued…

meta-Fe-gabbro norite

	veins in AMP			rims of AMP					aggregates	
	Fe-Barr	Fe-Barr	Cross	Al-rich	Fe-Barr	Al-rich	sl46i	sl623	Act	Act
SiO_2	40.44	41.59	38.78	36.87	40.36	38.50	36.87	36.45	46.52	49.48
TiO_2	0.06	0.09	0.42	0.32	0.09	0.00	0.32	0.24	0.30	0.16
Al_2O_3	8.45	9.15	12.24	11.83	7.02	15.89	11.83	13.51	5.80	5.77
Cr_2O_3	0.19	0.24	0.13	0.18	0.27	0.05	0.18	0.03	0.09	0.04
FeO	25.00	25.42	27.33	26.00	24.83	24.69	26.00	23.93	23.09	15.94
MnO	0.14	0.15	0.20	0.14	0.17	0.15	0.14	0.06	0.18	0.25
MgO	5.05	4.81	3.30	2.64	4.62	3.57	2.64	4.26	8.18	13.77
CaO	10.22	10.28	10.62	8.94	9.92	8.97	8.94	10.23	9.17	8.13
Na_2O	2.43	2.59	3.22	4.43	2.38	2.98	4.43	1.62	2.88	2.53
K_2O	0.56	0.54	1.05	1.17	0.45	0.51	1.17	3.25	0.41	0.18
Cl	2.20	2.24	3.70	3.84	2.34	2.07	3.84	4.69	1.22	0.19
Tot	94.74	97.10	100.99	96.36	92.45	97.38	96.36	98.27	97.84	96.44
Si	6.64	6.66	6.18	6.22	6.84	6.00	6.22	6.00	7.73	7.58
Ti	0.01	0.01	0.05	0.04	0.01	0.00	0.04	0.03	0.03	0.02
Al	1.64	1.73	2.30	2.36	1.40	2.92	2.36	2.62	0.29	0.51
Cr	0.03	0.03	0.02	0.02	0.04	0.01	0.02	0.00	0.01	0.01
Mn	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.01	0.01	0.02
Mg	1.24	1.15	0.78	0.66	1.17	0.83	0.66	1.05	2.80	2.72
Ca	1.80	1.76	1.81	1.62	1.80	1.50	1.62	1.80	1.85	1.71
Na	0.77	0.80	1.00	1.45	0.78	0.90	1.45	0.52	0.36	0.46
K	0.12	0.11	0.21	0.25	0.10	0.10	0.25	0.68	0.03	0.04
Cl	0.61	0.61	1.00	1.10	0.67	0.55	1.10	1.31	0.03	0.06
Fe^{3+}	0.55	0.46	0.39	0.16	0.38	1.07	0.16	0.51	0.00	0.00
Fe^{2+}	2.88	2.94	3.25	3.52	3.14	2.15	3.52	2.78	2.18	2.33
Al^{IV}	1.36	1.34	1.82	1.78	1.16	2.00	1.78	2.00	0.27	0.42
Al^{VI}	0.28	0.39	0.48	0.58	0.24	0.92	0.58	0.62	0.02	0.09
Na_{M4}	0.20	0.24	0.19	0.38	0.20	0.50	0.38	0.20	0.11	0.11
Na_A	0.57	0.57	0.81	1.07	0.58	0.40	1.07	0.32	0.25	0.35

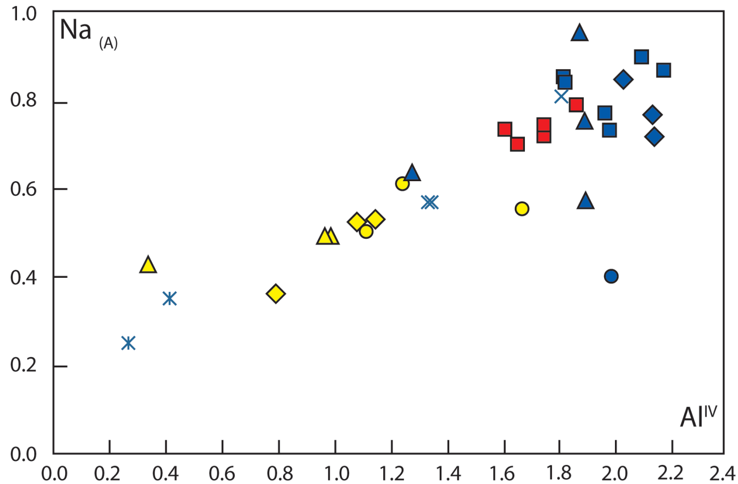


Figure 5. $Na_{(A)}$ vs Al^{IV} in amphiboles from the Northern Apennines (red and yellow symbols, indicating Fe-gabbro and Mg-gabbro respectively) and Sesia Lanzo (blue symbols). Different symbols represent microdomains where Cl-amphiboles are observed. Yellow circle = rims of brown or green amphibole; yellow lozenge = veins in plagioclase (1); yellow triangles = veins in plagioclase (2); red squares = acicular and granoblastic aggregates. Blue star = granoblastic aggregates; blue lozenge = veins in plagioclase; blue triangles = veins in pyroxene; blue crosses = veins in amphibole; blue circles = brown or green amphibole rims; blue square = aggregates on plagioclase. See text for a detailed explanation of textures.

Bucher et al., 1998; Kullerud & Erambert, 1999; Liu et al., 2009): there is a positive correlation between Cl and Fe, Al, K and $Na_{(A)}$ (or A site occupancy) and a negative correlation between Cl and Mg, Si and $Na_{(M4)}$ (or Mg/(Mg+Fe) ratio). These trends are observed in both the Northern Apennine and Sesia Lanzo amphiboles, but are very evident in the Sesia Lanzo amphiboles, whose Cl contents span over a wide range as they can have up to 4 wt% Cl (Figures 5, 6 and 7). Cl-amphiboles are more common in Fe-Ti rich rocks than in Mg rich ones, as evidenced by their abundance in Fe-gabbros and rarity in Mg-gabbros. In the latter they have the highest Cl contents. In the Northern Apennines Mg-gabbros, Cl-amphiboles with Cl contents of 0.05 - 0.18 wt% are found in veins and as rims of mafic minerals. They vary from Edenites, to Edenitic hornblendes, to Pargasites.

As a consequence of the influence of Cl content on other cations, Cl-amphiboles have a wide range of compositions and are classified in many different types (following Leake et al., 2004). In the Northern Apennines all the Cl-amphiboles are calcic and range in composition from Edenites to Hornblendes. In Sesia Lanzo, where the Cl contents are more extreme, and Cl-amphiboles recrystallize at different times and PT conditions, they can be either calcic (from Edenites, Pargasites to Hornblendes to Actinolites in rims, veins or acicular aggregates on plagioclase), calco-sodic (Fe-Barroisites and Barroisites in rims or overgrowing veins), sodic (Crossites and Glaucophanes, overgrowing veins or in the plagioclase domain aggregates toghether with epidote and chloritoid) or Al-rich amphiboles (Pargasites to Sadanagaites, according to Thompson, 1982). The presence of Na- and Ca-Na- amphiboles in Sesia Lanzo metagabbro is not only an effect of Cl content on

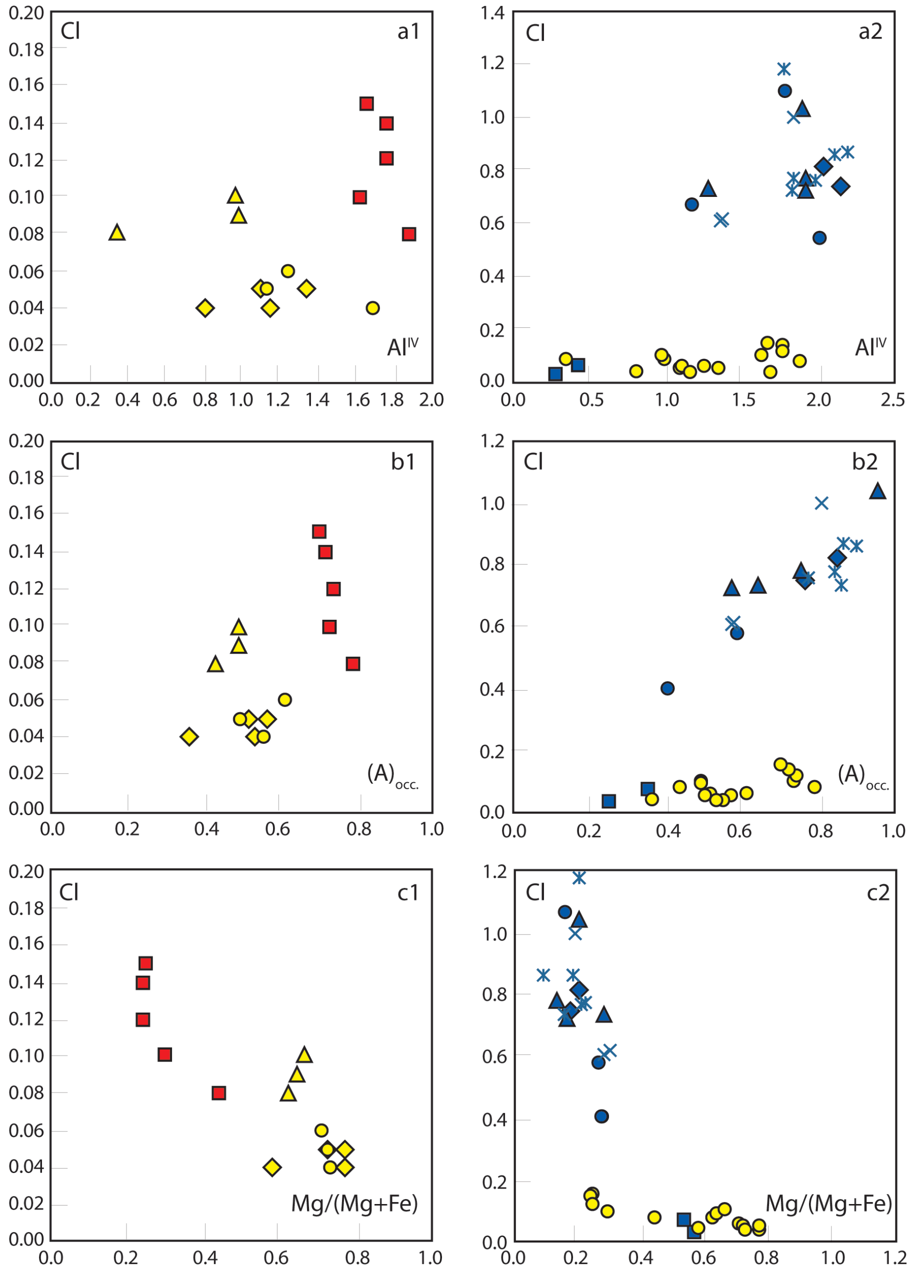


Figure 6. Cl vs Al^{IV} (a), Cl vs A site occupancy (b) and Cl vs Mg/(Mg+Fe) in amphiboles from the Apennines (column 1) and from Sesia Lanzo and Apennine for comparison (column 2). Note the different scales, and the clear compositional trends associated to Cl content in amphibole. In column 2 yellow symbols represent amphiboles from the Northern Apennines to facilitate comparisons. See Figure 5 caption for explanation of symbols.

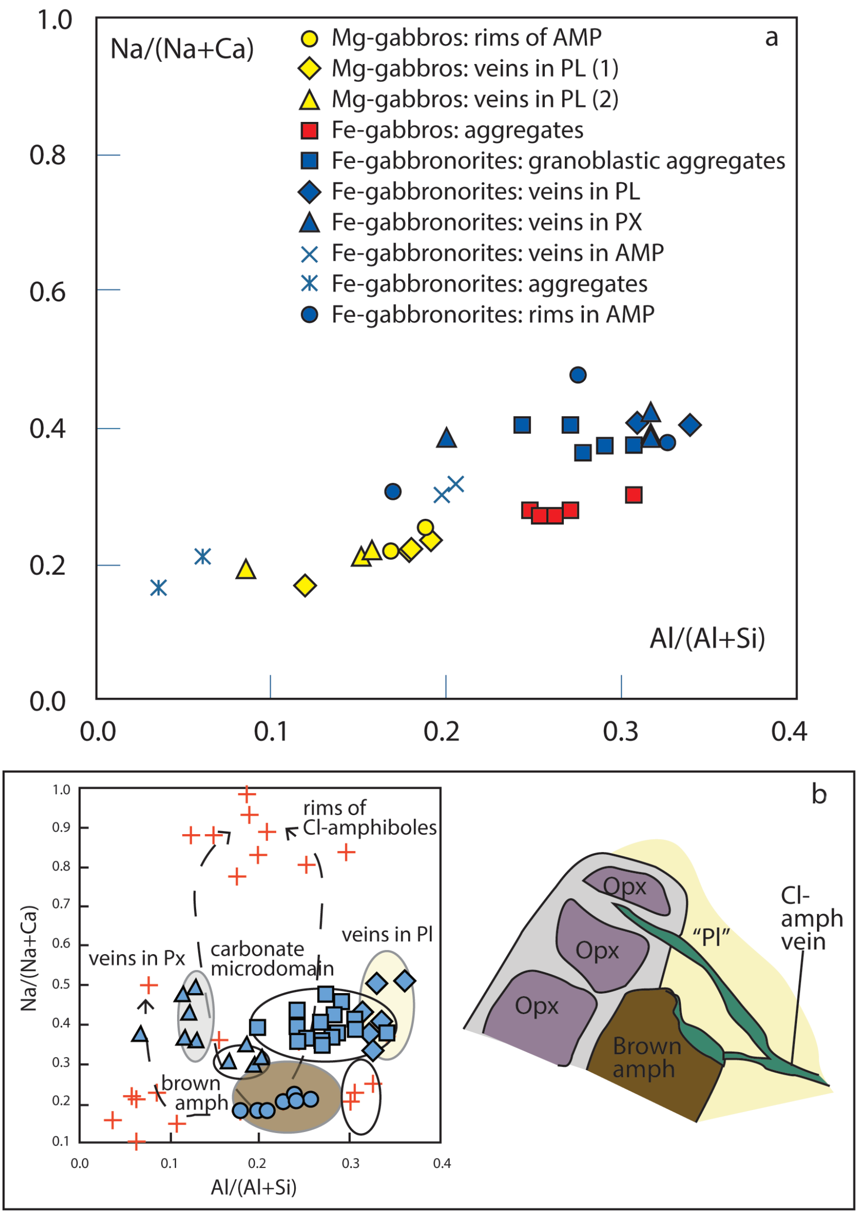


Figure 7. Na/(Na+Ca) vs Al/(Al+Si) in Cl amphiboles from the Northern Apennines and Sesia Lanzo zone (a), and within a single sample of meta Fe-gabbronorite from SL zone, according to microdomain in (b). Symbols as in legend and Figures 5 and 6. The red crosses identify amphibole with intermediate textural positions and/or very low Cl-contents.

amphibole composition, but also a consequence of successive amphibole recrystallization at different PT conditions (namely, growth at low P, medium to low T conditions during exhumation and then recrystallization at HP conditions, see Rebay and Spalla, 2001; Rebay, 2003; Rebay and Messiga, 2007 and Gosso et al., this volume), as testified by the relationships between composition and microstructures, and composition and growth stage (Figures 6 and 7).

In Mg-gabbros Cl-amphiboles pseudomorphing brown Hornblendes have Cl contents between 0.20 and 0.25 wt%, being Pargasitic Hornblendes with Al^{IV} and $Na_{(A)}$ contents between 1.1 and 1.7 apfu and 0.5-0.6 apfu respectivey, with Ti between 0.1 and 0.3 apfu. Green amphiboles in veins are Edenites, Edenitic Hornblendes, Mg-Hornblendes up to Actinolites (see Figure 3d and Table 1). The first three types of amphibole have Cl of 0.1-0.2 wt% and are cut by fractures where hydrothermal fluids circulated causing the crystallization of Cl-rich Mg-Hornblendes (Cl up to 0.4 wt%). In later fractures colorless actinolitic Hornblendes and Actinolites have less edenitic substitution and Al^{IV} between 0.05 and 0.34 apfu.

The maximum Cl content is found in the acicular aggregates present in Fe-gabbros: they are Fe Pargasitic Hornblendes in which Cl reaches 0.6 wt%, and with Al^{IV} between 1.7 and 1.9 apfu, $Na_{(A)}$ between 0.7 and 0.8 and the lowest X_{Mg} of 0.2-0.5.

Within the major trends, in the different analysed samples, Cl contents of amphibole are not only dependent on the available quantity of Cl in the system and on (P) T conditions of formation: they also change according to the microstructure in which they develop or to the whole rock composition (Figures 6 and 7).

In the Northern Apennines, Cl-amphiboles always have Cl < 1wt%, and Cl content are usually positively correlated to Al^{IV} and $(Na + K)_A$, that is to say, from Edenitic to Pargasitic substitution (Figure 6) and to Fe content of amphibole.

In Fe-gabbros they are found in late aggregates and in veins. In the aggregates constituting coronae between amphibole and plagioclase microdomain, Cl content is higher in rims than in cores of each crystal of the aggregate. The Cl content increases also towards the mafic minerals (Figures 5 and 6).

Amphiboles in veins have a wide compositional range. Within a single vein, multiple generations of often zoned amphibole are recognised thanks to their superposition relationships. The earliest amphiboles are Edenitic Hornblendes with high edenitic substitutions ($Na_{(A)}$ = 0.7 apfu) and Ti around 0.1 apfu, suggesting that the first fractures were formed under high T hydrothermal conditions. Later amphiboles are characterized by a decrease in Ti and $Na_{(A)}$, suggesting a progressive lowering of temperatures. X_{Mg} in veins is similar to that of the green metamorphic amphiboles in the host rock. It is higher in Mg-Al gabbros than in Fe-Ti gabbros, suggesting a strict control of the bulk rock composition on amphiboles in veins. Within this general behaviour, in less deformed samples amphiboles in smaller veins have different composition according to the microdomain crosscut by the vein: the ones on plagioclase have higher Al and Na contents, those on pyroxene have higher Fe and Mg. These same variations and Cl contents have been already observed in present day ocean in the MARK area gabbros (Mével and Cannat, 1991; Gillis et al., 1993; Coogan et al., 2001; Cortesogno et al., 2004) and described by Tribuzio et al. (2014), in the Northern Apennines.

In the Corio (Sesia Lanzo) metamorphosed Fe-gabbronorite (see Table 2 and Figure 7), the Cl amphiboles growing in veins crossing the plagioclase microdomain always have Al/(Al+Si) > 0.3, whereas those in the same veins have Al/(Al+Si) = 0.1 when crossing the pyroxene microdomain, even if they have comparable Cl contents. This is in good agreement with the different compositions of the microdomains, as plagioclase is more Al-rich than the mafic minerals. Cl-amphiboles rims around hornblendes have the highest K contents at comparable Cl contents, as hornblendes have the highest K content of all amphibole. This points to the influence of amphibole composition when reactions depend on diffusion at the intergranular scale along short distances. Cl-amphiboles from carbonate-bearing microdomain and rimming Hornblendes have the highest Cl contents, Al/(Al+Si) between 0.16 and 0.3 and V_2O_5 up to 2.5 wt% (EDS, semiquantitative analyses).

Na amphiboles after Cl-amphiboles in veins are Fe-Glaucophanes in the plagioclase microdomain, with a lower Na/(Na+Ca) than the Crossites in the carbonate-bearing microdomain, which have, on the other hand, higher Si contents. A similar evolution is observed in the rims around pyroxene, where Na-Ca amphibole develops, during the prograde evolution, following an Actinolite rim, with higher Si and lower Al contents than those that develop after the carbonate growth.

A comparison with other Cl-amphiboles observed both in oceanic and continental settings and ascribed to the infiltration of Cl-rich fluids is presented in Figure 8. The analysed amphiboles show large variations in Si, Al^{IV}, Al^{VI}, Fe, Mg, K and Cl, and this may be related to the ratio $a_{HCl/fluid}/a_{H2O/fluid}$ of the fluid in equilibrium with the amphiboles at various stages of the metamorphic evolution of the gabbroic rocks. Amphiboles that locally are characterized by extremely high Cl contents could thus suggest equilibration with a locally enriched Cl-fluid, probably formed in places where the system resulted locally closed, and are more common in continental settings than in oceanic ones, as evident also in the examples discussed here. In such a case hydration reaction consumed the H_2O component of the fluid, leaving a Cl-enriched fluid re-equilibrated with the crystallising amphibole. This also suggests that the volumes of fluids interacting with the continental crust could be lower than those interacting with the oceanic crust. As a matter of fact, the Cl content of amphibole in veins is generally lower, whereas the highly variable Cl-contents of rims may be extremely high.

Calculations based on amphibole thermometry suggest temperatures of equilibration of the Cl-amphiboles up to 350 °C for the amphiboles from the Apennines, and up to 550 °C for those from the Sesia-Lanzo Zone (Rebay and Spalla, 2000; Riccardi, 1994).

Discussion

Cl-rich fluids in different geological contexts

Cl-amphiboles (Ito and Anderson, 1983; Mével, 1984; Vanko, 1986) found in present day oceanic rocks (Fe-Ti gabbros, diorites, foliated amphibolites) have positive Cl-Fe and Cl-K and Cl-Al^{IV} correlations (Dick and Robinson, 1979; Kaminemi et al., 1982; Mével, 1984). These correlations are more evident in rocks with Cl contents > 1-2 wt%. Amphiboles that are poor in Si and Mg and rich in Al and Fe are therefore those that can accommodate the maximum Cl (Mével, 1984).

As already pointed out, Cl-amphibole crystallization is dependent upon various factors: 1) chemical composition of the whole-rock system; 2) chemical composition and evolution of the circulating fluids; 3) structure of the amphibole; 4) P-T conditions of crystallization. The most favourable "chemical" conditions for the growth of Cl-amphibole are those offered by the most differentiated rocks (Fe-Ti gabbros and diorites), and by the presence of evolved, Cl-rich hydrothermal fluids.

The content of Cl in Fe-Ti gabbro from Northern Apennines amphiboles is less than 1%. Usually it is well correlated with Al^{IV}, Fe_{tot} and $(Na+K)_A$, i.e. consistent with the Edenitic substitution (see Figure 6). Relating the chemical composition of amphiboles

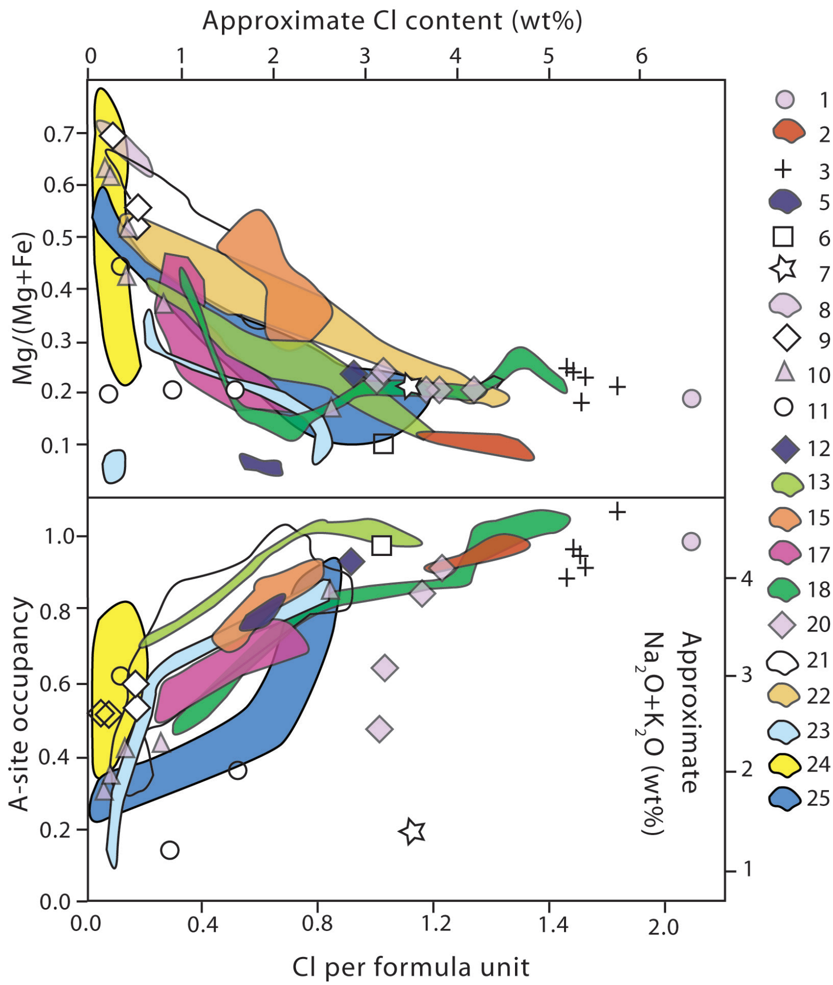


Figure 8. Cl vs X_{Mg} and A site occupancy in different Cl-amphiboles from the world (redrawn after Kullerud, 1999) with present wok data added for comparison. 1 = Krutov, (1936); 2, 3, 4 = Data from Kullerud (1999 and references therein); 5 = Dick and Robinson (1979); 6 = Sharma (1981); 7 = Kamineni et al. (1982); 8 = Vielzeuf (1982); 9 = Ito and Anderson (1983); 10 = Vanko (1986); 11 = Rao and Rao (1987); 12 = Suwa et al. (1987); 13 = Castelli (1988); 14 = Mora and Velly (1989); 15 = Morrison (1991); 16 = Tracy (1991); 17 = Enami et al. (1992); 18 = Oen and Lustenhouwer (1992); 19 = Sonnenthal (1992); 20 = Jiang et al. (1994); 21 = Kullerud (1995, 1996); 22 = Léger et al. (1996); 23 = Sato et al. (1997); 24 = Northern Apennine, Bonassola and Monte Capra, this work; 25 = Sesia Lanzo Zone, Corio and Monastero, this work.

with their growth history during the complex metamorphic evolution, it is clear that amphibole composition depends upon T of crystallization, fluid phase composition (Tribuzio et al., 2014) and microstructural domain in which they crystallize. Microprobe and single crystal X-ray diffraction data (Riccardi, 1994) on these amphiboles show evidence of the fact that all have: 1) low $Na_{(M4)}$, indicating low P conditions of formation; 2) low Ti contents and edenitic substitution in Cl absent amphiboles due to a progressive T decrease; 3) a higher cummingtonitic substitution ($Ca_{(M4)}$<1.34 apfu) in Fe-Ti gabbros than in Mg- Al gabbros; 4) an increase in Fe_{tot}, Al^{IV} and A site occupancy at the increase of Cl.

In the Northern Apennines gabbros, metamorphic reactions following the ductile deformation event (Molli, 1996) are all related to hydrothermal fluid infiltration. LREE and trace element composition of amphiboles suggest that the fluids derived from marine waters (Riccardi, 1994; Tribuzio et al., 1995; Tribuzio et al., 1997; Tribuzio et al., 2014).

The chemical evolution of amphiboles developed after the ductile deformation event in oceanic gabbros is clearly indicative of a temperature decrease, from amphibolite- to greenschist-facies to very low-grade conditions. This is suggested also by the decrease in edenitic substitution and Ti contents.

The low $Na_{(M4)}$ content suggests an evolution at low P conditions. It is convenient to point out that the late amphiboles are sometimes characterized by an increase in tschermackitic and/or edenitic substitution. However such increases are strictly associated with higher Cl or Fe^{3+} contents. In all the lithologies, the chemical changes of amphiboles with time are the same as in veins and in the country rock, suggesting that the same fluid phase permeated the rock through the veins and the crystal boundaries.

Coronitic and pseudomorphic amphiboles postdating magmatic and HT minerals allow the recognition of the influence exerted by the microdomain in which they grow on their composition. In this case, not only the intergranular fluids, but also the domain in which nucleation takes place, play an important role. For instance, coronitic amphiboles around Ti-Pargasites, are more Al-rich towards plagioclase than towards pyroxene, indicating diffusion-assisted growth at high temperatures. In coronitic amphiboles, Edenitic substitution decreases towards the rim, where Edenitic Hornblendes and then Actinolites/Tremolites indicate a decrease in T to greenschist-facies conditions. The increase in Fe^{3+} content can be related to fluid circulation.

In the Sesia Lanzo Zone metagabbros, the chemical evolution of amphiboles indicates a decrease in temperature from granulite- to amphibolite- to greenschist-facies (see Rebay and Spalla, 2001 for a detailed description of PT conditions of these rocks). In this case hydrothermal fluid circulation is confined to the late pre-Alpine evolution, during final stages of exhumation. Peculiar of this situation is the presence of Cl-bearing sodic amphiboles that are present only as pseudomorph after pre-Alpine Cl-amphiboles and grow during the prograde Alpine evolution, pointing to remobilization of Cl at granular scale. In this case Cl is found only in rims of pre-existing Cl-bearing amphiboles. Differently from the Apennines, in Sesia Lanzo Zone gabbros the carbonate microdomain hosts the amphiboles with the highest Cl contents (up to 4 wt%).

Formation of saline fluids during fluid-rock interaction - a summary

As pointed out above it is likely that the systematic compositional variations observed in Cl-amphiboles are in part related to gradual variations in the composition of the equilibrium fluid during growth. As pointed out by Kullerud (1999), potential mechanisms of enrichment in Cl in a fluid are:

1. fluid immiscibility, where the Cl-bearing fluid separates in two phases, one Cl-rich and the other Cl-poor;
2. fluid filtration;
3. preferential extraction of H_2O;
4. dissolution of Cl-rich minerals.

The most likely mechanism prevailing in the studied rocks was the preferential extraction of H_2O from a Cl-bearing fluid in both cases.

H_2O was consumed during crystallisation of OH bearing minerals (among which amphiboles, as testified by the observed zonations). Several fluid influxes allowed the formation of complex zonations, as the originally open system became closed after different fluid influx episodes. For the subcontinental gabbro of the Sesia Lanzo Zone, the observed growth of Cl-amphibole, not only in veins but also in carbonate-bearing microaggregate, could suggest a further acting mechanism: that is, a Cl-bearing fluid could have split into two immiscible fluids due to CO_2 addition.

In the Northern Apennines, veins within the gabbro were associated with migration of seawater-derived H_2O-rich fluids along micro-fractures and grain boundaries. Cl-amphibole forming reactions were triggered by fluids, but in most cases they were active locally, as suggested by the amphibole compositions varying in different microdomains or along a single vein crosscutting different microdomains.

In Sesia Lanzo, Cl-amphibole bearing veins are common in widely re-equilibrated Fe-Ti gabbros. All the veins are pre-eclogitic, as testified by the growth of HP minerals (garnet, glaucophane, chloritoid) at the vein boundaries and crosscutting microdomains.

The definition of the postgranulitic – pre-eclogitic fluid phases is important as it can offer a hint on the setting in which the gabbro was exhumed. Metamorphic assemblages indicate that the gabbro intruded in the mid crust, recrystallized at granulite facies PT conditions and was exhumed, through amphibolite- and greenschist-facies conditions to low depths, under a very high TP ratio, typical of divergent margins (Rebay and Spalla, 2001). Even though isotopic or fluid inclusion analyses are lacking for the Sesia Lanzo rocks, it is nonetheless possible to make some considerations about fluids on the basis of parageneses, their superpositions and the textural evolution of rocks, from low strain to high strain domains.

Most of the minerals found in veins are hydrous silicates, implying that water was an important component of the hydrothermal fluid phase. The occasional presence of carbonates is evidence of occurrence of a CO_2 fraction in the fluid. Carbonates predate Cl-amphiboles, therefore it is possible that there were different timing of fluid circulation carachterized by different composition. Indeed Cl-rich fluid did permeate the gabbro partially.

Ideally the Cl concentration in the fluid could be deduced from the Cl content of minerals, once the pH and the partition coefficient between fluid and mineral is known (Kullerud, 1996 and references therein). Unfortunately, in the absence of fluid inclusions analyses, inferences on the composition of fluids cannot reasonably be made, because amphibole is the only Cl-bearing present phase, with a composition also influenced by crystal-chemical factors, as explained above (with strong correlations Fe-Cl, K-Cl ed Al^{IV}-Cl).

The zoning of Cl-amphiboles, with rims richer in Cl than cores, could be, alternatively, due to two different mechanisms. Assuming a closed system, the Cl-bearing fluid would progressively be enriched in Cl while the less Cl rich amphiboles crystallize. With the crystallization of the first amphiboles, the fluid would have higher a_{Cl} /a_{H2O} in equilibrium with the amphiboles. This could explain also the fact that the Cl richer amphiboles often form thin discontinuos rims between green Hornblende and Actinolite.This texture indicates that fluid circulation occurred not only through veins, but also along grain boundaries at the low pressure amphibolite facies conditions. However the occurrence of an open system, in which the Cl content of the fluid increases with time due to an external source that gets richer in Cl content (brines?), cannot be excluded.

The lack of quantitative isotopic data on the fluid allows to make only conjectures on the possible origin of such Cl enriched fluids in a thinned continental crust. Two principal reservoirs are envisageable:

- fluids coming from nearby units that are being metamorphosed and are dehydrating (Heinrich, 1982)
- hydrothermal fluids coming from an external source, such as, for example, brines in an extensional setting.

Indeed, whereas CO_2 rich and aqueous fluids are very common in every metamorphic environment, the presence of extremely Cl rich brines is not so common, unless in granulite facies environment and when magmatic fluids are involved. Even if reference to a nearby large acid intrusions postdating the gabbro emplacement are lacking, it is interesting to note that acid prealpine dykes are present within the metagabbros crosscutting the granulitic fabric and developing chilled margins (Rebay and Spalla, 2001).

Conclusions

Two kinds of conclusions can be drawn integrating of petrological and structural analyses on rocks containing Cl-rich amphiboles from the ophiolitic rocks of the Apennines and the continental rocks of the Alps: i) crystallochemical considerations on Cl-incorporation in amphiboles and the role of Cl-bearing fluids and ii) insights on the tectonometamorphic evolution traced by these amphiboles. Cl-amphibole composition is simultaneously controlled by several interplaying factors, whose predominance may vary in different portions of the same gabbroic body:

1) crystal-chemical factors pose constraints on amphibole structure that directly influence their composition as the Cl content is positively correlated to the edenitic substitution in amphibole;

2) in coronitic rocks, where reactions take place at the submillimetric or millimetric scale, amphibole composition is dependent also on the composition of the microdomains where they develop, and not only on the bulk composition of the host rock.

3) the Cl-amphibole composition is dependent on the fluid composition evolution. The assumed transition from open to closed system may give rise to different Cl concentrations in the fluid, and therefore to different Cl contents in the amphibole, as probably indicated by Cl zoning in late, granoblastic amphibole and rims.

4) Finally Cl-amphibole composition is dependent also on the PT conditions at which amphibole crystallize.

The interactions between the above factors are difficult to assess quantitatively, even though it is possible in single cases to evaluate which is the predominant one. For example, taking into account that in the Northern Apennines Cl contents of amphiboles are always higher in Fe-gabbros than in Mg-gabbros, and that Fe is positively correlated to Cl, it is likely that the factors 1) and 2) predominate there within each step of re-equilibration during exhumation.

Our results demonstrate that multiscale structural analisys, separating deformation gradients, once the relative chronology of superposed fabrics has been established, allows the individuation of significant samples allowing the deciphering of the tectonometamorphic evolution in both orogenic belts (Alps and Apennines). In the Northern Apennines case such an approach allows to discriminate the specific stage in which Cl-rich fluids interacted with rocks, during the oceanic metamorphic evolution. In the Sesia Lanzo Zone it allows to distinguish Cl-rich amphiboles grown during the pre-Alpine evolution in the context of a Permian lithospheric thinning from those growing during burial in the subduction system. In both the considered examples, the Cl enriched fluids permeate the gabbroic rocks once they were exhumed at the upper crust structural levels in a divergent geodynamic setting with an anomalously high-T gradient. In the Northern Apennine case such high T gradient implies the thermal influence of the ridge zone, whereas the case of the Sesia

Lanzo Zone is consistent with a thinned crust during the initial phases of a continental rift. The hydration is achieved by fluid circulation through main conduits (represented by decimetre up to metric amphibole-rich veins and bands where deformation is concentrated), and also, on a smaller scale, through a network of millimetric to submillimetric veins pervading undeformed domains of the intrusive bodies. This shows that hydrothermal circulation takes place at shallow crustal level in contrast with the localization of Cl-bearing phases in shear zones occurring in deep crustal granulites. In veins permeated volumes the chemistry of the system is not homogenized at the microdomain scale, and therefore within a single hand-specimen equilibrium is attained at the microdomain scale, even though the fluid circulation may be widespread. Finally, in less deformed domains, fluids also circulated along grain boundaries. All these considerations point to the fact that in collisional orogenic belts remnants of hydration of the oceanic and continental crust in divergent geodynamic settings can be found. Evolution in Sesia Lanzo Zone shows that Cl stored in amphibole in divergent environment remains available during the prograde path in the subduction zone, demonstrating that the hydration of originally anhydrous rocks is one of the most powerful mechanisms to recycle "surface" fluids in the deep crust and mantle once PT conditions for dehydration are reached.

Acknowledgements

Silvana Martin and an anonymous reviewer helped us substantially improve the first draft of the manuscript. Also the suggestions from Gaetano Ortolano and Michele Lustrino improved the paper. Funding from PRIN 2011 "Birth and death of oceanic basins: geodynamic processes from rifting to continental collision in Mediterranean and Circum-Mediterranean orogens" is gratefully acknowledged. Bruno Messiga helped with thorough discussion and suggestions to clarify many points of Apennine and Austroalpine petrology. Pino Guzzetta for critical reading and appreciated suggestions.

References

Abbate E. and Sagri M. (1970) - The eugeosynclinal sequences. In: G. Sestini ed. Development of the Northern Apennines Geosyncline. *Sedimentary Geology*, 4, 251340.

Abbate E., Bortolotti V. and Principi G. (1980) - Apennine ophiolites: a peculiar oceanic crust. In: Tethyan ophiolites, *Ofioliti*, 1, 59-96.

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 Geological Survey Department, Nicosia, 413331.

Bortolotti V., Cellai D., Vagelli G. and Villa I.M. (1990) - $^{49}Ar/^{39}Ar$ of apenninic ophiolites: I. Ferrodiorites from La Bartolina quarry, southern Tuscany, Italy. *Ofioliti*, 15, 1-15.

Castelli D. (1988) - Chloropotassium ferro-pargasite from Sesia-Lanzo marbles (Western Alps): a record of highly saline fluids. *Rendiconti della Sociatà Geologica Italiana di Mineralogia e Petrologia*, 43, 129-138.

Compagnoni R., Dal Piaz G.V., Hunziker J.C., Gosso G., Lombardo B. and Williams P.F. (1977) - The Sesia–Lanzo zone, a slice of continental crust with alpine high pressure–low temperature assemblages in the western italian Alps. *Rendiconti della Sociatà Geologica Italiana di Mineralogia e Petrologia,* 33, 281-334.

Coogan L.A., Wilson R.N., Gillis K.M. and MacLeod C.J. (2001) - Near-solidus evolution of oceanic gabbros: insights from amphibole geochemistry. *Geochimica and Cosmochimica Acta*, 65, 4339-4357.

Cortesogno L. and Lucchetti G. (1982) - Il metamorfismo oceanico nei gabbri ofiolitici dell'Appennino Ligure: aspetti mineralogici e paragenetici. *Rendiconti della Sociatà Geologica Italiana di Mineralogia e Petrologia*, 38, 561579.

Cortesogno L. and Lucchetti G. (1984a) - Ocean floor metamorphism of metagabbros and stripped amphibolites (T. Murlo, Southern Tuscany Italy).

Neues Jahrbuch für Mineralogie Abhandlungen, 148, 276300.

Cortesogno L. and Lucchetti G. (1984b) - Ocean - floor metamorphism of the volcanic and sedimentary sequences in the northern Apennine ophiolites: mineralogical and paragenetic features. *Ofioliti*, 9, 363-400.

Cortesogno L., Galbiati B. and Principi G. (1987) - Note alla "Carta geologica delle ofioliti del Bracco" e ricostruzione della paleogegrafia Giurassico-Cretacica. *Ofioliti*, 12, 261-342.

Cortesogno L., Gaggero L. and Zanetti A. (2004) - Rare earth and trace elements in amphiboles of oceanic gabbros (MARK area, Mid-Atlantic Ridge) at medium- to low-temperature seafloor alteration. *Ofioliti* 29, 107-123.

Dal Piaz G.V. (1974) - Le metamorphisme de haute pression et basse temperature dans l'evolution structurale du bassin ophiolitique alpino appeninique II. *Schweizerische Mineralogische und Petrographische Mitteilungen*, 54, 399424.

Decandia F.A. and Elter P. (1972) - La "zona" ofiolitifera del Bracco nel settore compreso fra Levanto e la Val Graveglia (Appennino Ligure). *Memorie della Società Geologica Italiana*, 11, 503-530.

Dick L.A. and Robinson G. W. (1979) - Chlorine-bearing potassian hastingsite from a sphalerite skarn in southern Yukon. Canadian Mineralogist, 17, 25-26.

Diella V., Spalla M.I. and Tunesi A. (1992) - Contrasted thermo-mechanical evolutions in the Southalpine metamorphic basement of the Orobic Alps (Central Alps, Italy). *Journal of Metamorphic Geology*, 10, 203-219.

Duchene S., Blichert-Toft J., Luais B., Télouc P., Lardeaux J. M. and Albaréde F. (1997) - The Lu–Hf dating of the Alpine high pressure metamorphism. *Nature*, 387, 586-589.

Enami M., Liou J.G. and Bird D.K. (1992) - Cl-bearing amphibole in the Salton Sea geothermal system, California. *Canadian Mineralogist*, 30, 1077-1092.

Gianelli G. and Principi G. (1974) - Studies on mafic and ultramafic rocks 4 - Breccias of the ophiolitic suite in the Monte Bocco area (Ligurian Apennine). *Bollettino della Società Geologica Italiana*, 93, 277-308.

Gillis K.M., Thompson G. and Kelley D.S. (1993) - A view of the lower crustal component of hydrothermal systems at the Mid-Atlantic Ridge. Journal of Geophysical Research, 98, 19597-19619.

Gosso G., Rebay G., Roda M., Spalla M.I., Tarallo M., Zanoni D. and Zucali M. - Taking advantage of petrostructural heterogeneities in subduction-collisional orogens, and effect on the scale of analysis. This volume.

Hawthorne F.C. (1983) - The crystal chemistry of the amphiboles. *Canadian Mineralogist*, 21, 173-480.

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. *Chemical Geology*, 77, 183-207.

Hunziker J.C., Desmons J. and Hurford A.J. (1992) - Thirty-two years of geochronological work in Central and Western Alps. *Memoires Geologiques Lausanne*, 13, 59.

Ito E. and Anderson A.T. (1983) - Submarine metamorphism of gabbros from the mid-Cayman rise: petrographic and mineralogic constraints on hydrothermal processes at low-spreading ridges. *Contributions to Mineralogy and Petrology*, 82, 371-388.

Jiang S.-Y., Palmer M.R., Xue C.-J. and Li Y.-H. (1994) - Halogen rich scapolite-biotite rocks from the Tongmugou Pb-Zn deposit, Quinling, north-western China: implications for ore forming processes. *Mineralogical Magazine*, 58, 543-552.

Kamineni D.C., Bonardi M. and Rao, A.T. (1982) - Halogen-bearing minerals from Airport Hill, Visakpatnam, India. *American Mineralogist*, 67, 1001-1004.

Krutov G.A. (1936) - Dashkesanite: a new chlorine amphibole of the hastingsite group. *Mineralogical Abstracts*, 6, 438.

Kullerud K. (1995) - Chlorine, titanium and barium-rich biotites: factors controlling biotite composition and implications for garnet-biotite geothermometry. *Contributions to Mineralogy and Petrology*, 120, 42-59.

Kullerud K. (1996) - Chlorine-rich amphiboles: interplay between amphibole composition and an evolving fluid. *European Journal of Mineralogy*, 8, 355-370.

Kullerud K. (1999) - Occurrence and origin of Cl-rich amphibole and biotite in the Earth's crust-implications for fluid composition and evolution. In: Hydrogeology of Crystalline Rocks (eds. I. Stober and K. Bucher), 205-225.

Kullerud K. and Erambert M. (1999) - Cl-scapolite, Cl-amphibole, and plagioclase equilibria in ductile shear zones at Nusfjord, Lofoten, Norway: Implications for fluid compositional evolution during fluid-mineral interaction in the deep crust. *Geochimica et Cosmochimica Acta*, 63, 3829-3844.

Kullerud K., Flaat K. and Davidsen B. (2001) - High pressure fluid-rock reactions involving Cl-bearing fluids in lower crustal ductile shear zones of the Flakstadøy Basic Complex, Lofoten, Norway. *Journal of Petrology*, 42**,** 1349-1372.

Lardeaux J.M., Gosso G., Kienast J.R. and Lombardo B. (1982) - Relations entre le métamorphisme et la déformation dans la zone Sésia-Lanzo (Alpes Occidentales) et le problème de l'éclogitisation de la croûte continentale. *Bulletin de la societé géologique de France*, 24, 793-800.

Lardeaux J.M. and Spalla M.I. (1991) - From granulites to eclogites in the Sesia zone Italian Western Alps: a record of the opening and closure of the Piedmont ocean. *Journal of Metamorphic Geology*, 9, 35-59.

Leake B.E., Woolley A.R., Birch W.D., Burke E.A.J., Ferraris G., Grice J.D., Hawthorne F.C., Kisch H.J., Krivovichev V.G., Schumacher J.C., Stephenson N.C.N. and Whittaker E.J.W. (2004) - Nomenclature of amphiboles: additions and revisions to the International Mineralogical Association's amphibole nomenclature. *Mineralogical Magazine*, 68, 209-215.

Léger A., Rebbert C. and Webster J. (1996) - Cl-rich biotite and amphibole from Black Rock Forest, Cornwall, New York. *American Mineralogist*, 81, 495-504.

Lemoine M., Tricart P. and Boillot G. (1987) - Ultramafic and gabbroic ocean floor of the Ligurian Tethys (Alps, Corsica, Apennines): In search of a genetic model. *Geology*, 15, 622-625.

Liu J., Liu W., Ye K. and Mao, Q. (2009) - Chlorine-rich amphibole in Yangkou eclogite, Sulu ultrahigh-pressure metamorphic terrane, China. *European Journal of Mineralogy*, 21, 1265-1285

Makino K., Tomita K. and Suwa K. (1993) - Effect of chlorine on the crystal structure of a chlorine-rich hastingsite. *Mineralogical Magazine*, 57, 677-685.

Markl G., Ferry J. and Bucher K. (1998) - Formation of saline brines and salt in the lower crust by hydration reactions and partially retrogressed granulites from the Lofoten Islands, Norway. *American Journal of Sciences*, 298**,** 705-757.

Marotta A.M., Spalla M.I. and Gosso G. (2009) - Upper and lower crustal evolution during lithospheric extension: numerical modelling and natural footprints from the European Alps. *Geological Society of London Special Publications*, 321, 33-72.

Meda M., Marotta A.M. and Spalla M.I. (2010) - The role of mantle hydration into the continental crust recycling in the wedge region. *Geological Society of London Special Publications*, 332, 149-172.

Messiga B. and Tribuzio R. (1991) - The reaction between olivine and plagioclase as a consequence of fluid-rock interactions during sub-seafloor metamorphism (Al-Mg-gabbros, Northern Apennine ophiolites, Italy). *Schweizerische Mineralogische und Petrographische Mitteilungen*, 71, 405-414.

Mével C. and Cannat M. (1991) - Lithospheric stretching and hydrothermal processes in oceanic gabbros from slow-spreading ridges. In Ophiolite Genesis and Evolution of the Oceanic Listhosphere (eds. T.J. Peters, A. Nicolas and R.G. Coleman). Kluwer Academic Hingham, pp. 293-312.

Mével C. (1984) - Le métamorphisme dans la croute océanique: apport de la pétrologie à la comprehension des phénomènes de circulation hydrothermale et de déformation (exemples dans l'Atlantique). Thèse Doct. Univ. Paris VI, 434 p.

Molli G. (1992) - Evoluzione strutturale di shear zones nel complesso gabbrico del Bracco (Appennino Settentrionale). *Atti Ticinensi di Scienze della Terra*, 35, 19-23.

Molli G. (1996) - Pre-orogenic tectonic framework of the northern Apennine ophiolites. *Eclogae Geolocicae Helveticae*, 89, 163-180.

Mora C.I. and Valley J.W. (1989) - Halogen-rich scapolite and biotite: implications for metamorphic-fluid interactions. *American Mineralogist*, 74, 721-737.

Morison J. (1991) - Compositional constraints on the incorporation of Cl into amphiboles. *American Mineralogist*, 16, 1920-1930.

Oberti R., Ungaretti L., Cannillo E. and Hawthorne F. C. (1993) - The mechanism of Cl incorporation in amphibole. *American Mineralogist*, 78, 746–752.

Oen I.S. and Lustenhouwer W.J. (1992) - Cl-rich biotite, Cl-rich hornblende and Cl-rich scapolite in meta-exhalites: Nora Bergslagen, Sweden. *Economic Geology*, 87, 1638-1648.

Piccardo G.B. (1984) - Le ofioliti metamorfiche del Gruppo di Voltri, Alpi Liguri: caratteri primari ed interpretazione geodinamica. *Memorie della Società Geologica Italiana*, 28, 95-114.

Piccardo G.B., Rampone E. and Vannucci R. (1990) - Upper mantle evolution during continental rifting and ocean formation: evidences from peridotite bodies of the western Alpine-northern Apennine system. *Mémoires de la Société Géologique de France*, 156, 323-333.

Pognante U. and Piccardo G.B. (1984) - Petrogenesi delle Alpi Occidentali. *Memorie della Società Geologica Italiana*, 29, 79-92.

Pognante U., Talarico F., Rastelli N. and Ferrati N. (1987) - High pressure metamorphism in the nappes of the Valle dell'Orco traverse (western Alps). *Journal of Metamorphic Geology*, 5, 397-414.

Principi G., Bortolotti V., Chiari M., Cortesogno L., Gaggero L., Marcucci M., Saccani E. and Treves B. (2004) - The pre-orogenic volcano-sedimentary covers of the Western Tethys oceanic basin: a review. *Ofioliti*, 29, 177-212.

Rampone E., Hofmann A.W. and Raczek I. (1998) - Isotopic contrasts within the Internal Liguride ophiolite (N. Italy): the lack of a genetic mantle-crust link. *Earth and Planetary Sciences Letters*, 163,175-189.

Rao A.T. and Rao P.C.S. (1987) - Halogen bearing potassium hastingsite from the charnokites of Eastern Ghats. *Indian Mineralogist*, 28, 1-5.

Rebay G. and Spalla M.I. (2001) - Emplacement at granulite facies conditions of the Sesia-Lanzo metagabbros: early record of Permian rifting? *Lithos*, 58, 85-104.

Rebay G. (2003) - A metamorphic map of the Corio and Monastero gabbro (Southern Sesia-Lanzo zone, NW Italy). *Memorie di Scienze Geologiche di Padova*, 55, 21-30.

Rebay G. and Messiga B. (2007) - Prograde metamorphic evolution and development of chloritoid bearing eclogitic assemblages in subcontinental metagabbro (Sesia-Lanzo zone, Italy). *Lithos*, 98, 275-291.

Regis D., Rubatto, D., Darling J., Cenki-Tok B., Zucali M. and Engi M. (2014) - Multiple Metamorphic Stages within an Eclogite-faciesTerrane (Sesia Zone,Western Alps) Revealed byTh U-Pb Petrochronology. *Journal of Petrology*, 55, 1429-1456.

Renna M.R. and Tribuzio R. (2011) - Olivine-rich troctolites from Ligurian ophiolites (Italy): evidence for impregnation of replacive mantle conduits by MORB-type melts. *Journal of Petrology*, 52, 1763-1790.

Riccardi M.P., Tribuzion R. and Caucia F. (1994) - Amphibole evolution in the metagabbros from East Ligurian ophiolites (Northern Apennines, Italy): constraints on the ocean-floor methamorphism. *Memorie della Società Geologica Italiana*, 48, 203-208.

Riccardi M.P. (1994) - Gli anfiboli legati al metamorfismo oceanico dei metagabbri ofiolitici dell'Appennino settentrionale: aspetti composizionali e cristallochimici. PhD thesis, Pavia, 1994.

Roda M., Spalla M.I. & Marotta A.M. (2012) - Integration of natural data within a numerical model of ablative subduction: a possible interpretation for the Alpine dynamics of the Austroalpine crust. *Journal of Metamorphic Geology*, 30, 973-996.

Rossi G. and Ungaretti L. (1989) - The crystal chemistry of clinopyroxenes and amphiboles in high pressure metamorphism. *Proedimenti. Atti dei convegni Lincei*, 80, 297-323.

Rubatto D., Gebauer D., Compagnoni R. (1999) - Dating of eclogite-facies zircons: the age of Alpine metamorphism in the Sesia–Lanzo Zone Western Alps. *Earth and Planetary Sciences Letters*, 167, 141-158.

Sanfilippo A. and Tribuzio R. (2011) - Melt transport and deformation history in a non volcanic ophiolitic section, northern Apennines, Italy: implications for crustal accretion at slow spreading settings. *Geochemistry, Geophysics, Geosystems*, 12, 7.

Sato H., Yamaguchi Y. and Makino K. (1997) - Cl incorporation into successively zoned amphiboles from the Ramnes cauldron, Norway. *American Mineralogist*, 82, 316-324.

Schuster R., Scharbert S., Abart R. and Frank W. (2001) - Permo-Triassic extension and related HT/LP metamorphism in the Austroalpine-Southalpine realm. *Mitteilungen der Gesellschaft der Geologie und Bergbaustudenten in Oesterreich*, 45, 111-141.

Serri G. (1980) - Chemistry and petrology of gabbroic complexes from Northern Apennines ophiolites. Proceedings International Ophiolite Symposium, Cyprus 1979, 296311.

Sharma R.S. (1981) - Mineralogy of a scapolite-bearing rock from Rajastan, northwest peninsular India. *Lithos*, 14, 165-172.

Sonnenthal E.L. (1992) - Geochemistry of dendrite anorthosites and associated pegmatites in Skaergard intrusion, East Greenland: evidence for metasomatism by a chlorine-rich fluid. *Journal of Volcanoligical and Geothermal Research*, 52, 209-230.

Spalla M.I., De Maria L., Gosso G., Miletto M., Pognante U. (1983) - Deformazione e metamorfismo della zona Sesia–Lanzomeridionale al contatto con la Falda Piemontese e con il Massiccio di Lanzo, Alpi occidentali. *Memorie della Società Geologica Italiana*, 26, 499-514.

Suwa K., Enami M. and Horiuchi T. (1987) - Chlorine-rich potassium hastingsite from West Ongul Island, Lutzow-Holm Bay, East Antarctica. *Mineralogical Magazine*, 51, 709-714.

Thompson J. B. Jr. (1982) - Composition space: an algebraic and geometric approach, in Reviews in Mineralogy, v. 10 (ed. J.M. Ferry) 33-51, Mineralogical Society of America.

Tracy R.J. (1991) - Ba-rich micas from the franklin marble, Lime crest and Sterlin Hill, New Jersey. *American Mineralogist*, 76, 1683-1693.

Tribuzio R. (1992) - Distribuzione delle terre rare e di alcuni elementi in tracce nei principali minerali dei meta-Fe-gabbri delle ofioliti liguri: aspetti cristallochimici ed implicazioni petrogenetiche. Tesi di Dottorato, Università di Pavia, 148 p.

Tribuzio R., Riccardi M. P. and Messiga B. (1997) - Amphibolitization of Mg- and Fe-rich gabbroic dykes within mantle derived serpentinites from northern Apennine ophiolites evidence for high-temperature hydration of the oceanic lithosphere. *Ofioliti*, 22, 71-79.

Tribuzio R., Riccardi M.P. and Ottolini L. (1995) Trace element redistribution in high temperature deformed gabbros from East Ligurian ophiolites (northern Apennines, Italy): constraints onthe origin of syndeformation fluids. *Journal of Metamorphic Geology*, 13, 367-377.

Tribuzio R., Thirwall M.F. and Vannucci R. (2004) - Origin of the gabbro–peridotite association from the Northern Apennine ophiolites (Italy). *Journal of Petrology*, 45, 1109-2277.

Tribuzio R., Renna M.R., Dallai L. and Zanetti A. (2014) - The magmatic–hydrothermal transition in the lower oceanic crust: Clues from the Ligurian ophiolites, Italy. *Geochimica et Cosmochimica Acta*, 130, 188-211

Ungaretti L. (1981) - I contributi della cristallografia strutturale alle Scienze della Terra. *Rendiconti della Sociatà Geologica Italiana di Mineralogia e Petrologia*, 37, 575-596.

Vanko D.A. (1986) - High-chlorine amphiboles from oceanic rocks: Product of highly saline hydrothermal fluids. *American Mineralogist*, 71, 51-59

Vielzeuf D. (1982) - The retrogressive breakdown of orthopyroxene in an intermediate charnockite from Saleix (French Pyrénées). *Bullettin de Mineralogie*, 105, 681-690.

Volfinger M., Robert J.L., Vielzeuf D., and Neiva A.M.R. (1985) - Structural control of the chlorine content of OH-bearing silicates (micas and amphiboles). *Geochimica et Cosmochimica Acta*, 49, 37-48.

Submitted, March 2015 - Accepted, November 2015