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High pressure coronites in the western Alps: a record of reaction pathways

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ABSTRACT. — This paper, after a short review on the historical development of the use of the term «corona texture» to indicate a layered mineral structure developed at the contact between two reacting minerals, describes methods and problems encountered in the study of coronitic rocks. Four well-known examples of high- and ultrahigh-pressure coronitic rocks from the western Alps (Monviso and Zermatt-Saas concerning eclogitized ophiolites and Monte Mucrone and Dora Maira concerning eclogitized continental crust) are presented and discussed as case studies.

It is stressed out that the study of coronitic rocks by means of classic microstructural and determination of chemical composition of reactants and products coupled with more recent thermodynamic modelling and mass-balance calculation enhance our understanding of reaction mechanisms, our knowledge of the role played by fluids and our ability to determine accurate P-T paths followed by rocks, involved in major tectonic processes.

RIASSUNTO. — Dopo una breve introduzione sullo sviluppo storico dell'uso del termine «tessitura coronitica» per descrivere una struttura a livelli concentrici che si sviluppano al contatto tra due minerali che reagiscono allo stato solido, vengono

discussi i metodi ed i problemi che si riscontrano nello studio di rocce coronitiche. Quattro esempi molto noti di rocce coronitiche di alta e ultra-alta pressione delle Alpi occidentali (Monviso e Zermatt-Saas per le rocce ofiolitiche eclogitiche e Monte Mucrone e Dora Maira per le rocce di crosta continentale eclogitizzata) sono presentati e discussi come casi studio.

Viene sottolineato come lo studio delle rocce coronitiche fatto attraverso i classici approcci microstrutturale e di determinazione della composizione chimica dei reagenti e prodotti insieme alla modellizzazione termodinamica ed ai calcoli di bilanci di massa migliori la nostra comprensione dei meccanismi di reazione, del ruolo della fase fluida e della nostra capacità di determinare in modo accurato i percorsi P-T seguiti dalle rocce coinvolte nei processi tettonici a grande scala.

KEY WORDS: *Coronite, eclogie-facies, western Alps*

INTRODUCTION

Corona textures indicated as «roughly concentric structures» were firstly proposed by Rosenbusch, and since the end of the 19th century the word corona has been commonly

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used to indicate reaction textures between minerals.

According to Sederholm (1916), the first time that a corona was mentioned would be in Muller (1846). He described a corona as shells of a green mineral around garnet in «serpentinite» (*i.e.* garnet peridotite) from Greifendorf in Saxony. In mafic rocks the first description of a corona texture was given by Törnebohm (1877) who described amphibole-bearing parageneses developing in troctolitic and gabbroic rocks along the contact between olivine and plagioclase; this rim was absent at pyroxene plagioclase boundaries. The author says, with reference to olivine: «at the metamorphism of the mineral (olivine) new crystals originate almost exclusively at the borders of the mineral grains [...]. These zones of newly formed mineral have obviously origin through the reaction between plagioclase and olivine, the outer green zone having formed at the expense of the plagioclase, the inner, light one, having replaced the olivine...» (Translation by Sederholm, 1916).

Sederholm, in his comprehensive work of 1916, compiled all previous studies and his own observations on different rocks from Finland, and gives an exhaustive picture of the ideas about sinanthetic structures at that time. Since then the term corona is used to indicate a layered, roughly concentric structure, formed at the contact between two reacting mineral grains under metamorphic conditions (secondary). Sederholm made a distinction between a «coating» of magmatic (primary) augite («very irregular in breadth») and the radially disposed fibres of hornblende developing at the contact of olivine with plagioclase, that he refers to a secondary process (*i.e.* metamorphic).

Important considerations, on coronitic troctolitic and gabbroic rocks, were made in the Alps by Bearth (1959, 1967) (following the observations of Bonney (1892) and Schäfer (1895) on the Allalin metagabbro) and in Norway, among others, by Griffin (1971) and Griffin and Heier (1973).

Of this period are also the first papers that try

to approach modelling of corona texture (see below). Rubie (1984, 1990) suggests that corona are incomplete reactions and he shows the importance of putting together the data collected at different observational scales, from optical microscope, to SEM and TEM in investigating disequilibrium microtextures. He shows that in unreacted domains relics are preserved, and these domains thus preserve the evidence of the onset of transformation reactions.

In Norway Mørk (1985) and in the Alps Pognante (1985 and 1989, Pognante and Kienast, 1987) have shown how it is possible to separate, at the mesoscale, volumes of coronitic rocks that preserve old parts of the metamorphic evolution and volumes of tectonic rocks that are homogeneously re-equilibrated and contain mineralogical associations with a lesser number of phases (Lardeaux and Spalla, 1991). These two end-members of the structural metamorphic evolution allow to reconstruct the reaction history and to investigate equilibrium vs. disequilibrium conditions.

Pognante (1985) describes in Rocciavre coronitic reactions in Mg-metagabbro showing: - corona microstructures; - pseudomorphic replacements of igneous microdomains; - compositional variations of phases (especially clinopyroxenes) in the different microdomains. In his work of 1989, where he compares metagabbro and trondhjemite, he summarizes the possible corona growth reactions for each microdomain. In such complex evolutions coronitic rocks may remain coronites or completely loose their character during successive deformation and vice-versa (Messiga and Scambelluri, 1988) as shown by Rebay *et al.*, (in press).

Minerals of the coronitic layers are compositionally zoned and give thus information about the diffusivity of components. The chemical potential gradient is the driving force which promotes the diffusion of chemical species during coronitic reactions. Microtextures allow to reconstruct the disposition of the mineral layers in the corona,

and when coupled with careful chemical analyses allow to calculate the mass balance of diffusing components (Gresens, 1966). Methods proposed by Joesten (1977) and Nishiyama (1983) allow the prediction of the disposition of layers in a corona texture and the modelling of metasomatic processes, a technique that dates back to the papers by Korzhinskii (1959) and Thompson (1959), and to the more specific works by Fisher (1973, 1977) and Johnson and Carlson (1990). A review on these topics was made in 1990 by Rubie.

Coronas form as a consequence of a reaction-diffusion process. At the prevailing P/T conditions, adjacent minerals become unstable, they dissolve and their components diffuse through the grain boundary network, causing the nucleation and growth of new stable phases making the corona.

It is because of the sluggishness of inter-crystalline diffusion that the phases are spatially ordered. Although these models allow to understand the spatial organisation of reagents and products minerals, difficulties are encountered when temperature and pressure are not constant or when chemically zoned minerals develop. In such situations it is necessary to set a system of reaction-diffusion equations, in order to describe the reaction kinetics and the coupling between inter- and intra-crystalline diffusion. To this end experimental studies are essential in order to assess the values of inter- and intra-crystalline diffusion coefficients (Chakraborty and Ganguly, 1991, 1992, Morioka and Nagasawa, 1991; Ganguly *et al.*, 1998), as well as the experimental modelling of corona textures as in Larikova and Zaráisky (2002) and in the works therein quoted.

CASE STUDIES AND EXAMPLES FROM THE WESTERN ALPS

In Italy coronitic rocks deriving from protoliths with different bulk chemistries and produced under high- to ultrahigh-pressure conditions are common in the Alps. We will

restrict our review to examples found in the Italian Western Alps, focussing on well known examples to describe coronitic reaction environments and their evolution.

OPHIOLITES

The detailed study of the northern Apennine ophiolites, which are devoid of eclogitic imprint, gave the opportunity to gather strong evidence of the large extent of oceanic transformations in these rocks and of its impact on the development of eclogitic assemblages in the Alpine rocks (Messiga and Scambelluri, 1988). Moreover the fluid-bearing environment in which oceanic metamorphism takes place represents, in undeformed rocks, the driving force that constrains the kinetics of eclogitic transformation.

Troctolites, that are SiO₂-undersaturated rocks, have a relatively simple mineralogy (they are almost biminerale) and a strong compositional contrast of the igneous minerals (olivine and plagioclase). So troctolites look, at a first sight, a simple petrologic system that has a high «reactivity» at different P-T conditions, giving rise to a high number of rocks with different textures and equilibrium assemblages. This accounts for the fact that olivine-plagioclase corona were among the first corona described and one of the most common.

Examples of polyphasic metamorphism are found in many troctolitic rocks of the Alps. Here an oceanic metamorphism episode predated the widespread eclogitic reequilibration, as proved by relics of low-grade hydrated minerals predating the eclogitic assemblages. In the Voltri Group, formation of serpentine pseudomorphs on primary olivine is followed by the growth of orthopyroxene during prograde metamorphic stages (Messiga *et al.*, 1995) (similar occurrences were observed by Mørk (1985) in the Flemsøy gabbro). A peculiar effect of this metamorphic imprint on metatroctolite is the fact that rocks originally undersaturated in SiO₂, as for instance troctolite, become quartz-bearing

because of the plagioclase transformation reactions: $Ab = Jd + Qtz$, $An = Gro + Ky + Qtz$ and $An = Ep + Ky + Qtz$. Minerals abbreviations follow Kretz (1983).

Monviso metatroctolite

The gabbroic sequence of the Monviso ophiolite complex (Lombardo *et al.*, 1978; Lardeaux *et al.*, 1987; Philippot and Kienast, 1989) shows an excellent example of eclogitisation of troctolites that had previously undergone oceanic transformations (Messiga *et al.*, 1999). In particular, Mg-troctolites have peculiar corona textures at the olivine-plagioclase and olivine-pyroxene boundaries (see also Kienast and Messiga, 1987). The presence of abundant H_2O-CO_2 bearing eclogitic phases (talc, amphibole, chloritoid, magnesite) supports the presence of a syn-eclogitic fluid phase, linked to pre-eclogitic hydration of these rocks. This pre-eclogitic stage also caused widespread chemical re-homogenisation of the different microdomains, allowing the development of peculiar chloritoid-talc bearing eclogitic assemblages.

In the Monviso metatroctolites, the igneous clinopyroxene relics are preserved, and have coronas showing asymmetric compositional zoning, thus indicating reactions developed between microdomains with strongly contrasting chemical compositions. In contrast, coronas developed at the olivine-plagioclase interfaces commonly display symmetric chemical zoning (Fig. 1). Consequently chemical potential gradients between plagioclase and olivine microdomains should have been smoothed before the eclogitic recrystallization. These features indicate that element diffusion was different in each microdomain. The components overcame the boundaries of the igneous mineral with different rates and/or at different times during the metamorphic recrystallization, even if all samples followed a common P-T path (peak conditions estimated as $P=2.4$ Gpa and $T = 620 \pm 50^\circ C$, supported by the presence of magnesiochloritoid, magnesite and garnet with

Py content up to 58 mol%). Monviso metatroctolites are thus an example of rocks that underwent a pre-eclogitic metamorphism possibly under high fluid activity conditions. Consequently the investigated metatroctolites most likely experienced different reaction kinetics as a consequence of the different amounts of hydration during ocean-floor metamorphism, in each microdomain.

Zermatt-Saas metatroctolite

The analytical/microstructural approach allows the reconstruction of the superposition of different static metamorphic episodes even when no relics are preserved, but the use of thermodynamic modelling allows to approach under a new perspective the problems connected to the mechanisms of reactions and their progression. Corona structures, being typical disequilibrium textures, are normally studied using mass balances and non-equilibrium thermodynamics. Recently Rebay and Powell (2002) applied, using the concept of equilibrium volume, an equilibrium thermodynamic approach to coronitic troctolites from the Western Alps. In completely eclogitized troctolites from the Zermatt-Saas unit it has been possible in this way, to understand the role played by fluids in preserving different equilibrium assemblages in the olivine and plagioclase microdomains, considered as equilibrium microdomains. Calculating pseudosections for each microdomain it is possible to unravel a complex metamorphic evolution in which fluid played a major role: while olivine microdomains react and dehydrate during prograde metamorphism and then preserve metastable assemblages developed during peak conditions, plagioclase domains, being fluid-undersaturated for most of the metamorphic evolution, react mainly during lawsonite breakdown, except if fluid coming from dehydration of adjacent olivine microdomains, enhances garnet formation at peak conditions. This hydration episodes are testified by cracks filled by garnet in plagioclase domains of some samples (Fig.

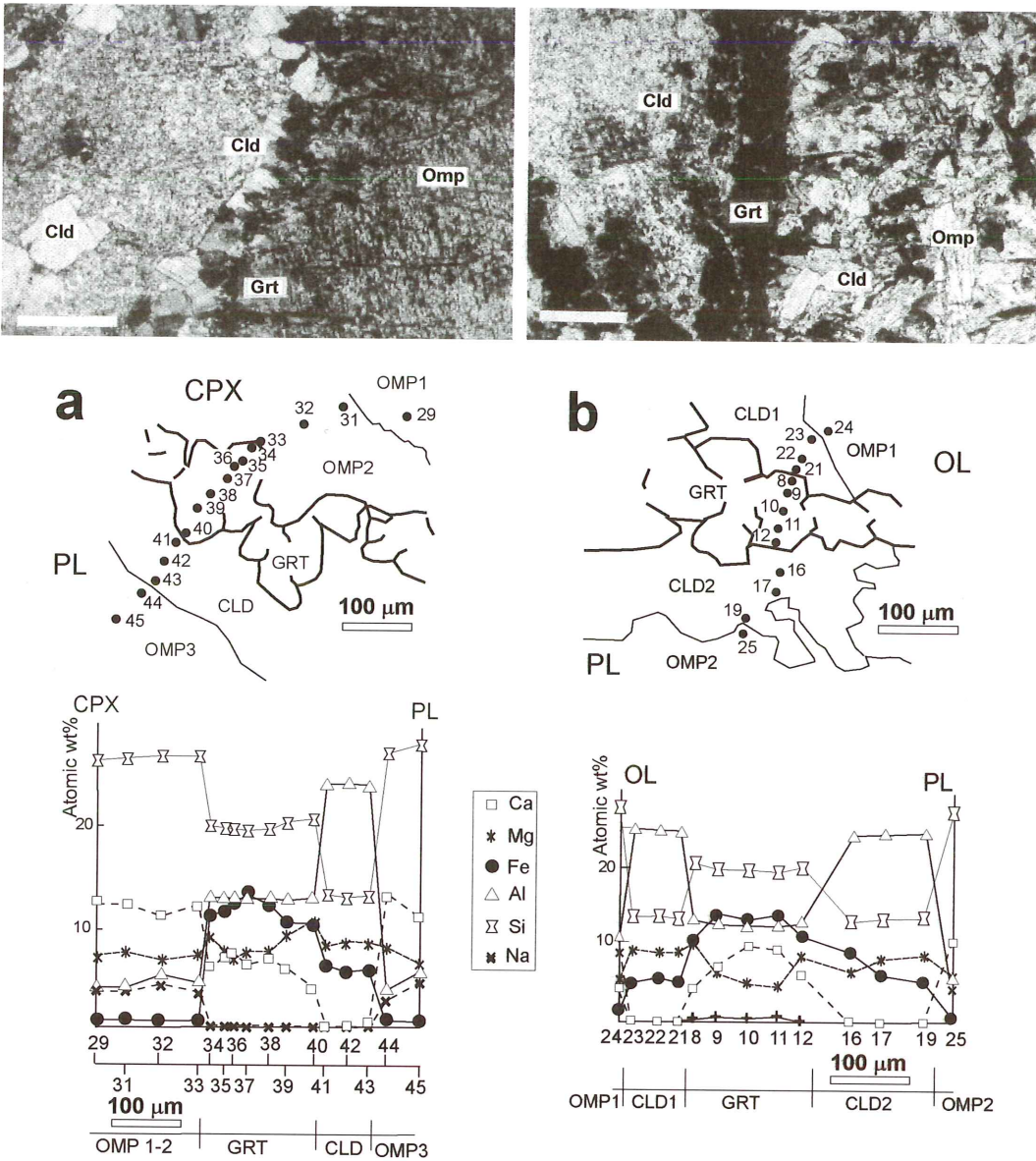


Fig. 1 – Compositional variation of major elements across corona from the Monviso metatroctolite (after Messiga *et al.*, 1999)

2a). Peak pressures are testified by the assemblage chloritoid + talc + garnet + omphacite preserved in olivine microdomains (indicating pressures higher than 2.0 GPa),

whereas the diagnostic plagioclase microdomain mineral assemblage clinzoisite + kyanite + quartz testifies somehow lower pressures (Fig. 2b).

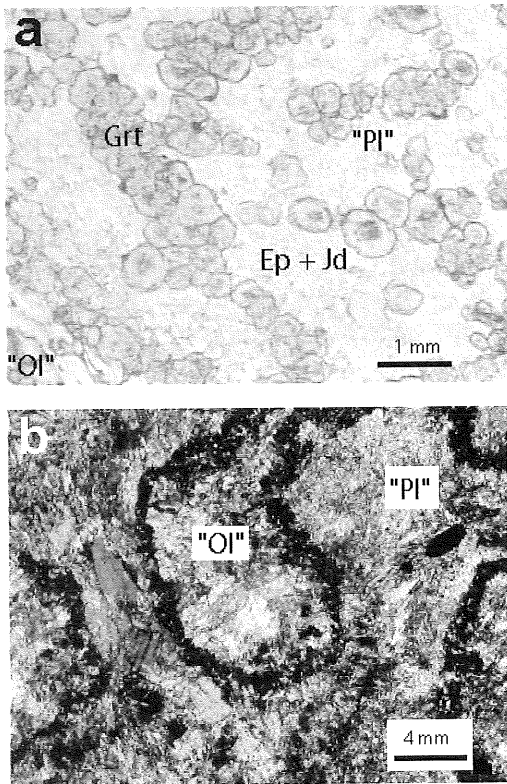


Fig. 2 – Microstructures observed in Zermatt-Saas troctolites: a) garnet veins in plagioclase microdomain (transformed to omphacite (jadeite), clinozoisite \pm kyanite \pm phengite \pm paragonite \pm chloritoid) and b) troctolite preserving igneous texture («Pl» and «Ol» indicate plagioclase and olivine microdomain respectively) but with eclogite-facies assemblages (see text for details).

CONTINENTAL CRUST

Two famous and well-known case studies are represented in the western Alps by the Mucrone metagranodiorite, the first studied example of eclogitized continental crust, and by the Dora Maira Unit, the first example of ultrahigh pressure metamorphism.

Monte Mucrone metagranodiorite

Coronitic textures developed at the original igneous biotite/plagioclase and biotite/K-feldspar contacts in the Monte Mucrone

metagranodiorite (MMM) from the Sesia-Lanzo Zone, Western Alps. The MMM crops out in the «Eclogitic Micaschist Complex» (EMC), which is one of the main subunits making up the Sesia-Lanzo Zone (Dal Piaz *et al.*, 1972; Compagnoni and Maffeo, 1973; Compagnoni, 1977; Compagnoni *et al.*, 1977; Koons *et al.*, 1982; Zucali *et al.*, 2002). The Sesia-Lanzo Zone is characterised by the widespread occurrence of eclogite facies assemblages in a wide spectrum of continental crustal lithologies. The EMC of the Sesia-Lanzo Zone is a fragment of Variscan continental crust, which was metamorphosed during the early Alpine HP subduction event (Oberhänsli *et al.*, 1985; Rubatto *et al.*, 1999).

The early Alpine HP stage is constrained at $T = 500\text{--}600^\circ\text{C}$ and $P = 1.6\text{--}2.0$ GPa (Compagnoni, 1977; Lardeaux *et al.*, 1982; Droop *et al.*, 1990; Tropper and Essene, 2002).

Composite corona developed at the contacts biotite/plagioclase (Fig. 3) and biotite/K-feldspar. The corona consists of an inner moat of phengite I surrounded by a moat of garnet and by an outer moat composed of quartz + phengite (Ph II) intergrowth (Rubbo *et al.*, 1999). The garnets are mainly almandine-pyrope-grossular solid solutions, with almandine concentration higher than 45% and spessartine concentration lower than 2.5%. The garnets show a marked asymmetric chemical zoning of iron and calcium: iron decreases while calcium increases towards feldspar.

These coronitic structures have been studied by Rubbo *et al.* (1999), who developed a modified model of segregation for garnet. In this model it is supposed that the amount of the grossular in garnet is controlled by the dissolution of feldspar, which is slow (Loomis, 1981). The zonings calculated with this model and those measured are in good agreement.

Dora-Maira metagranodiorite

Metagranodiorite samples from the Brossasco-Isasca Unit (Biino and Compagnoni, 1992; Bruno *et al.*, 2001), Dora-Maira Massif, western Alps, show coronitic textures where igneous minerals were partially replaced by

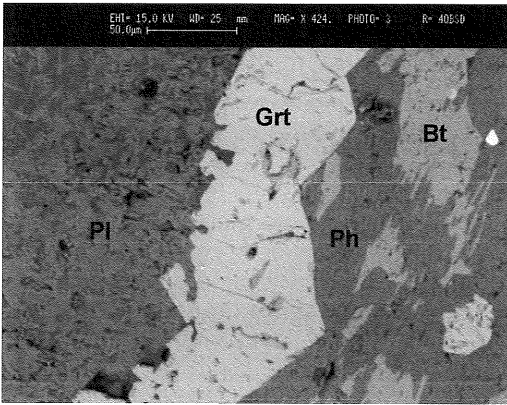


Fig. 3 – SEM backscattered image of the Monte Mucrone metagranodiorite. The igneous biotite is partially replaced by phengite, and a garnet corona developed between biotite and the igneous plagioclase, now replaced by a polycrystalline aggregate of Zo + Jd (partially replaced by Ab) + Qtz.

ultrahigh pressure (UHP) metamorphic assemblages. The Brossasco-Isasca Unit (BIU) is a slice of Variscan continental crust recrystallised under UHP metamorphic conditions during the Alpine orogeny (Chopin *et al.*, 1991; Compagnoni *et al.*, 1994, 1995). The metamorphic peak is estimated by many workers at $P = 3.3 \pm 0.3$ GPa and $T = 750 \pm 30^\circ\text{C}$ (Chopin, 1984, 1987; Chopin *et al.*, 1991; Kienast *et al.*, 1991; Schertl *et al.*, 1991; Sharp *et al.*, 1993; Compagnoni *et al.*, 1994), and, recently, by Hermann (2003) at about 4.3 GPa and 750°C . The metagranodiorite originally consisted of quartz, plagioclase, K-feldspar, biotite and accessory apatite, zircon and a Ti-rich phase, most likely ilmenite. During the Alpine metamorphism, the igneous minerals reacted and developed coronitic structures between biotite and quartz, biotite and K-feldspar (Fig. 4), and biotite and plagioclase. Specifically:

- At the original igneous biotite/quartz contact, a single continuous corona of weakly zoned garnet, with composition $\text{Alm}_{76-78}\text{Prp}_{21-23}\text{Grs}_{1-2}\text{Sps}_{1-2}$.

- Between biotite (partially replaced by phengite I) and K-feldspar, the composite

corona is made by (Fig. 4): i) a continuous corona of weakly zoned garnet ($\text{Alm}_{78-80}\text{Prp}_{15-17}\text{Grs}_3\text{Sps}_2$); ii) a continuous corona of garnet ($\text{Alm}_{78-80}\text{Prp}_{17-19}\text{Grs}_{2-3}\text{Sps}_{0-1}$) with vermicular quartz inclusions, elongated perpendicular to the corona; iii) a continuous corona of a quartz-phengite (PhII) symplectite in continuity with the garnet-quartz symplectite.

Between biotite and plagioclase, the composite corona is made by:

- i) a corona of garnet ($\text{Grs}_{49-50}\text{Alm}_{42}\text{Prp}_{7-8}\text{Sps}_{0-1}$) plus quartz; ii) a composite corona of idioblastic garnet ($\text{Grs}_{62-84}\text{Alm}_{16-32}\text{Prp}_{0-6}$) and jadeite. Garnet becomes richer in grossular and pyroxene richer in jadeite. Coronitic garnet is always asymmetrically zoned with Ca increasing and (Fe + Mg) decreasing, from biotite towards plagioclase. A retrograde phengite II developed outside the garnet corona.

Information on the metamorphic history of the metagranodiorite has been obtained by integrating petrographic observations of multivariant mineral associations with calculations of relative stability and composition of phases (Bruno *et al.*, 2001). The rock retains evidence of recrystallisation at a minimum pressure of 2.4 GPa at 650°C .

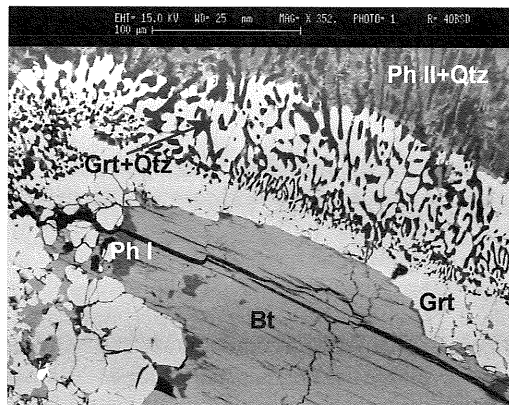


Fig. 4 – SEM backscattered image of the Dora-Maira metagranodiorite. Relic igneous biotite included in K-feldspar, and partly replaced by phengite (PhI). Note the development of a composite corona of garnet, garnet+quartz and quartz+phengite (PhII).

DISCUSSION AND CONCLUSIONS

In the above examples it is clear that a tectonite and a coronite having similar bulk compositions may have not only different textures, but also different minerals assemblages. This applies also to smaller volumes within these rocks. For instance in coronitic troctolite (Rebay and Powell, 2002) plagioclase and olivine microdomains display minerals assemblages that preserve information of the metamorphic evolution acquired in different moments along the P-T-t path. In particular olivine microdomains preserve assemblages equilibrated at peak pressure conditions, while plagioclase microdomains equilibrate during retrograde path when lawsonite reacts out. In Monviso, a similar troctolite displays a more complex mineralogical and textural evolution.

Besides the above example, where it was shown that in a coronite different microdomains may preserve different parts of the common evolution, it must also be stressed out that deformation gradients also play an important role: a coronite may develop from a tectonite and, in turn, may be transformed to a tectonite. Deformation has the role of enhancing, in this latter case, a sort of chemical mixing of the small equilibrium volumes that are formed during the coronitic stage, making them homogenous.

Another important feature is the compositional zonation of minerals defining the corona. These zonations testify the chemical gradients linked to the migration of components during corona-forming reactions. In the examples here shown, two different types of chemical zonation are observed: in Mucrone asymmetric zonation is the evidence that the reacting microdomains had contrasting chemical compositions at reaction onset; on the contrary in Monviso, the bell shaped zoning through the corona, indicates smoothing of the chemical compositional gradients due to pre-eclogitic reactions (oceanic metamorphism).

Coronitic rocks can be studied through equilibrium thermodynamics by defining small

equilibrium volumes: this approach is essential in the definition of the P-T conditions of re-equilibration. This must not prevent us from the pleasure of investigating also the disequilibrium features of these rocks, that can give essential hints on the mechanisms of reactions.

It is an exciting but quite difficult task to unravel the information encrypted in the path-dependent non-equilibrium features the coronas bearing rocks exhibit. Indeed it requires knowing the mechanisms of the transformations as a function of pressure, temperature and chemistry. The mechanism is a sequence of processes by which elements are released by the dissolving phases, migrate and are integrated in the growing minerals. Nowadays the kinetic models allow rationalizing the formation of these textures but we hardly can make quantitative calculations, lacking of kinetic databases. The situation is similar to the one prior the building of internally consistent thermodynamic properties of minerals and of solid solutions. A great deal of field and laboratory work has been necessary before being able to calculate petrogenetic grids and a similar effort should be produced to improve our capability to explain coronas formation.

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