Acta Mineralogica-Petrographica, Szeged, XXXVIII, Supplementum, 135–144, 1997

DIFFUSION CONTROLLED DOUBLE CORONA REACTION RIM AROUND KYANITE IN RETROGRADED ECLOGITE FROM THE SWISS CENTRAL ALPS

T. M. TÓTH[1]

Institut of Mineralogy, Geochemistry and Petrology
Attila József University, Szeged, Hungary

ABSTRACT

Retrograded eclogite samples at the village Gorduno in the Swiss Central Alps contain relics of ellipsoidal shape with double corona rim. The internal core consists of radial intergrowth of spinel and at places corundum. The fine-grained core is rimmed by plagioclase of composition An_{95} which is followed by an outer plagioclase rim. This second plagioclase is of An_{45-50}.

This mineralogy has formed due to a series of reactions between kyanite and other high pressure phases; pyroxene, garnet, zoisite. All these reactions separated the Al-, and Si-rich phases from each other. Because of the restricted mobility of Al the newly formed minerals created the double corona structure around kyanite.

Key words: eclogite, corona structure, mobility

INTRODUCTION

Amphibolite samples found in the Swiss Central Alps north of the village Gorduno contain mineral and textural relics of an earlier eclogite facies event. In addition to amphibole and plagioclase these samples also contain garnet, clinopyroxene, rutile and zoisite as HP phases. Pyroxene grains have been almost totally replaced by amphibole-plagioclase symplectitic intergrowth, garnet is surrounded by an amphibole-plagioclase corona, while rutile is rimmed by sphene. Zoisite has been replaced by a cluster of submicroscopic grains of undefined minerals. All these changes are typical of a breakdown of eclogite when decreasing pressure, and have been frequently observed in the Central Alps. In addition to the breakdown paragenesis common in retrograded eclogites, egg-shaped relics with double corona reaction texture also occur (PLATE I/1.). Their appearance in many localities as well as their mineralogy and textural characteristics were first described by FORSTER (1948).

This paper focuses on the possible development of the disequilibrium textural relics.

[1] ✉ H-6701 Szeged, P.O. Box 651, Hungary.
e-mail: mtoth@geo.u-szeged.hu

ANALYTICAL METHODS

In addition to optical microscopy quantitative chemical analysis as well as X-Ray mapping for selected elements were performed on a CAMECA SX-50 electron microprobe. Instrumental conditions for single crystal analysis were an accelerating voltage of 15 kV and a beam current of 20 nA. In the spectrometers LiF, PET and TAP crystals were used. Natural minerals (DIAMOND et al., 1994) were used as standards. On X-ray mapping acquisition time varied from 10 to 20 minutes depending on the concentration of the selected element.

PETROGRAPHY

Major part of the samples studied consists of amphibole and garnet. At places amphibole is intergrown with clinopyroxene; garnet usually has a radial rim of plagioclase and amphibole. Chemical composition of the relict garnet grains is consistent with an earlier HP metamorphic event, pyroxene, however, is low in jadeite component. Garnet is of composition $Alm_{45}Pyr_{26}Grs_{27}Sps_{2}$, pyroxene is diopside and hedenbergite (about 1:2 in proportion), with a very low amount of Al and Na.

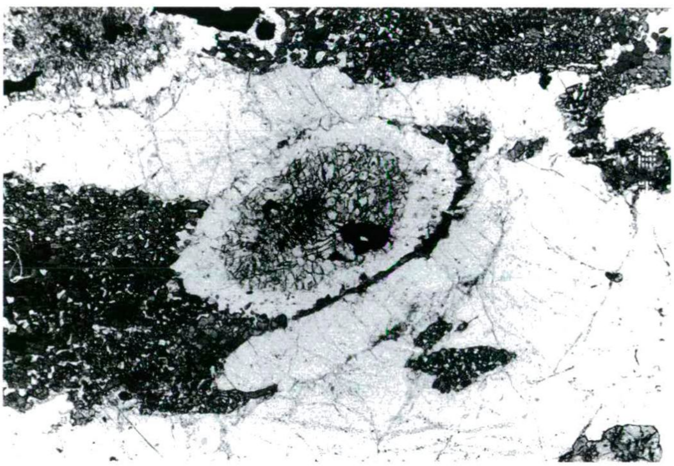

Plate I/1. Double corona microtexture with a dark grey internal and a white external rim. The textural relic is inbedded in a rock composed by amphibole and quartz. N1, 100x. 1-internal rim; 2-external rim; 3-amphibole; 4-quartz

The microfabric studied has ellipsoidal shape and a well-defined border towards the other phases around, usually quartz, amphibole and garnet (PLATE I/1., I/2.). The outer shell of the compouned corona structure consists of plagioclase with granoblastic texture, followed by an inner feldspar zone. The boundary is evident in a plain light owing to a sharp increase in relief (refractive index) and by a textural change as well (PLATE I/3.). Plagioclase grains of the inner shell are smaller in size and form radial overgrowth around the core without a well-developed granoblastic texture. The inner core consists of tiny mineral grains, usually submicroscopic in size, with brush-shaped aggregates of a conspicuous radial appearance (PLATE I/4.). Among the core-forming phases in some samples spinel may be recognized under the microscope. Other breakdown minerals cannot be identified in the core, however, one of the microtextures studied also contains a kyanite grain in the centre. The textural relations are consistent with the interpretation that kyanite represents the original high pressure phase which became unstable during exhumation of the eclogite. The subsequent mineral zones formed due to a reaction between kyanite and other high pressure phases like pyroxene, garnet or zoisite.

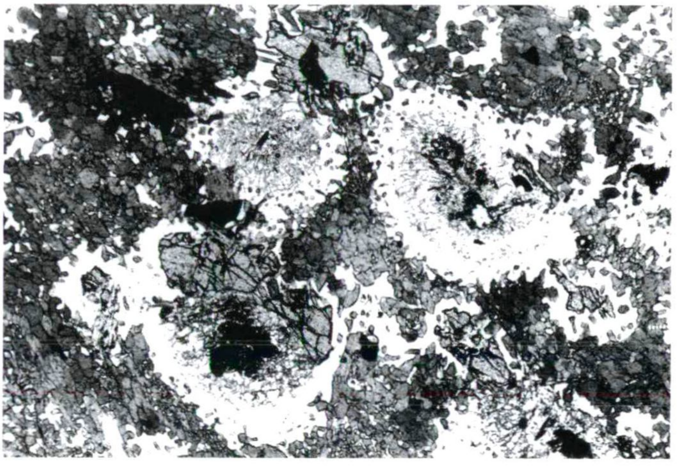

Plate I/2. Cluster of microtextures studied in a matrix composed mainly by amphibole (after pyroxene), plagioclase and garnet. N1, 50x. 1-amphibole; 2-plagioclase; 3-garnet

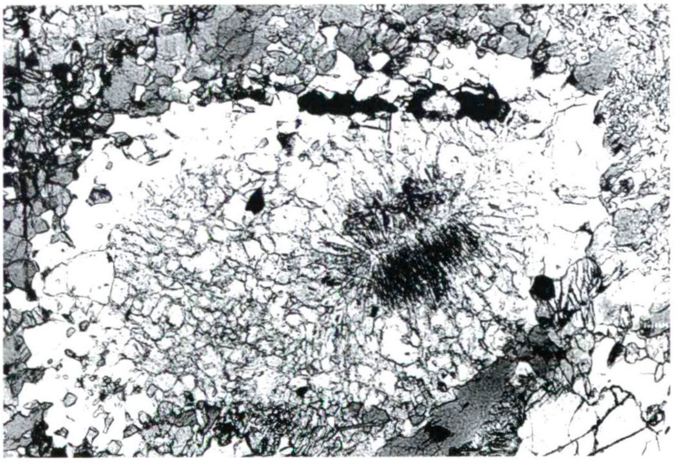

Plate I/3. The symplectitic internal core is rimmed by anorthite-rich plagioclase. The external rim is plagioclase of composition An_{45-50}. Note the significant difference in relief of the two feldspar phases. N1, 200x. 1-anorthite; 2-plagioclase

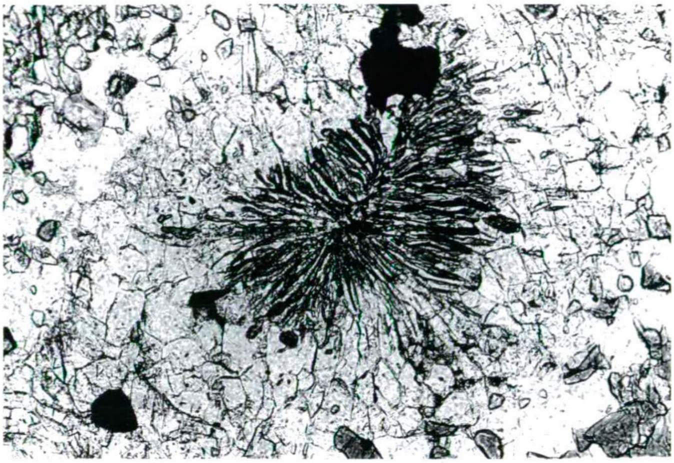

Plate I/4. Fine-grained symplectitic intergrowth of spinel and corundum forms radiating growth N1, 200x.
1-spinel (and corundum); 2-anorthite

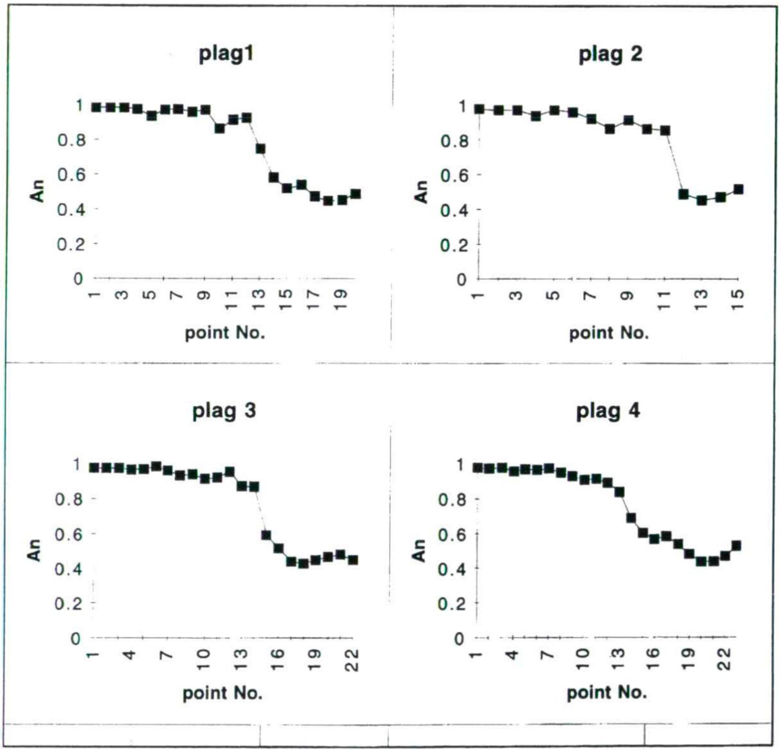

Fig. 1. Compositional change of plagioclase from core to rim in four different cases. Each step means 2 microns.

MINERAL CHEMISTRY

In order to be able to explain the formation of the microtexture, the exact composition of the subsequent minerals was measured by electron microprobe, and the submicroscopic mineral phases have been identified as well. For this purpose, element distribution (X-ray) maps were made by electron microprobe. The differences between the two outer plagioclase zones observed microscopically, may be explained by their chemical composition. The external shell consists of a feldspar of An_{50}, while the internal one of An_{95} plagioclase. The boundary is sharp, no continuous change was measured (fig. 1.). Based on the X-ray maps the spinel is principally hercynite, with significant amounts of Mg and Zn; other metals (Cr, Mn) were not detected (fig. 2/a-b.). However, the maps suggest a heterogenous composition of the spinel, the core being Mg-rich, while the rim contains more Fe. The qualitative results could be confirmed by quantitative point analyses on some relatively big spinel grains as well. In the average of four large grains, the spinel composition is the following: Hc: 79%, Sp: 13.5%, Gn: 7.5 %. The X-ray maps could supply also the last phase in the core: the exclusively Al-bearing mineral is corundum (fig. 3/a-b.).

In addition to the minerals mentioned the coronas also contain rutile inclusions, as well as late white mica flakes which appear sporadically without any relationship with the concentric breakdown structure. They are interpreted to be secondary to the corona formation.

DISCUSSION

Possible breakdown reactions

The textural relationships detailed above suggest that the corona-forming mineral intergrowth formed due to reactions between kyanite and other HP-phases, principally pyroxene. In retrograded eclogite kyanite is usually replaced by mica; margarite has been observed also in the Alps by many authors (e.g. BORGHII, 1991; BIINO, 1995). Appearance of the corona structure around kyanite described above suggests uncommon circumstances during the retrograde development. Possible plagioclase, spinel and corundum-forming reactions between different end-members of pyroxene and kyanite are the following:

kyanite + jadeite = albite + corundum	(1)
2 kyanite + hedenbergite = hercynite + anorthite + 2 quartz	(2)
2 kyanite + diopside = spinel + anorthite + 2 quartz	(3)
kyanite + Ca-Al-pyroxene = anorthite + corundum	(4)

Although the original composition of the clinopyroxene was not preserved, HP-pyroxene is generally low in Ca. Further reactions likely to have taken place when producing the anorthite are therefore:

3 kyanite + grossular = 3 anorthite + corundum	(5)
2 kyanite + almandine = 3 hercynite + 5 quartz	(6)
2 kyanite + pyrop = 3 spinel + 5 quartz	(7)
2 kyanite + 2 zoisite = 4 anorthite + corundum + H2O	(8)

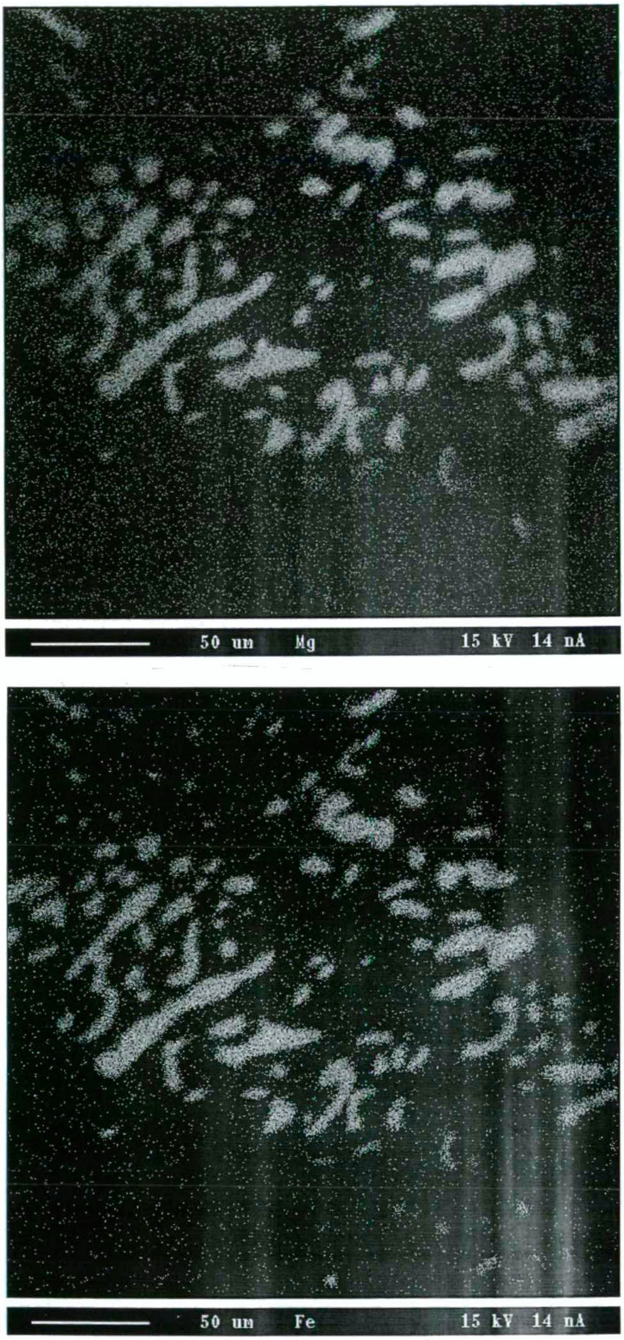

Fig. 2. X-ray maps of the spinel-bearing internal core. a) Mg; b) Fe

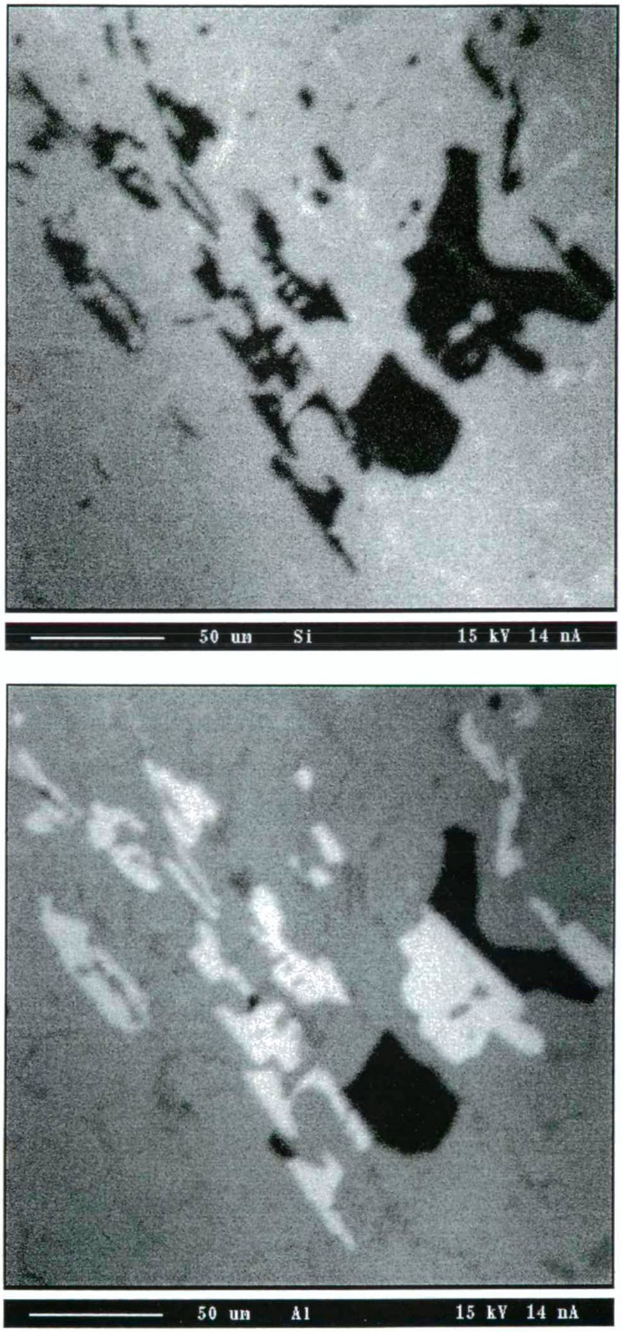

Fig. 3. X-ray maps of the corundum-bearing internal core a) Si; b) Al

Compound corona reaction rims may develop due either to sequential or simultaneous growth (GRANT, 1988). Subsequent reactions take place, for example, in forming garnet-bearing corona around olivin in metagabbros, where the primary spinel-clinopyroxene symplectite may be replaced by garnet later. In the given case there is no textural evidence of the replacement of earlier phases; all corona-forming minerals formed during the kyanite-pyroxene (garnet) reactions.

A complex corona structure may also form during the simultaneous reactions when the diffusion of certain elements is restricted. Resulting from the significant mobility differences, mineral zones with distinct composition may develop. In our case, kyanite serves Si and Al, while pyroxene and garnet Na, Ca, Fe and Mg to form the paragenesis stable under the new P, T conditions. Iron and magnesium appear in two phases. The starting pyroxene (garnet) and the core-forming spinel contain both elements, in about the same proportion. Similarly to calcium, they occur in the internal core suggesting free mobility. The behaviour of sodium, however, differs significantly from the first three cations. The only Na-bearing phase, the Ab-rich plagioclase, forms the external shell; the Ab-content of the internal feldspar zone is extremely low, less than 2 wt%. So, one clue to the development of the given corona structure should be the restricted mobility of Na.

In order to analyze the mobility of the kyanite-forming cations Si and Al, reactions (1)–(8) are instructive: on the right hand side the product minerals are those observed in the core (corundum, spinel) and in the rim (quartz, albite, anorthite) respectively. There is a conspicuous difference in the Si/Al ratio of these coupled mineral pairs. While the core contains no silicate phases (for both ideal spinel and corundum Si/Al=0) the outer shells are more and more rich in silica. Finally, the external zone is pure quartz. The increase of the Si/Al ratio towards the rim is presented along a hypothetic section of the microtexture (fig. 4.).

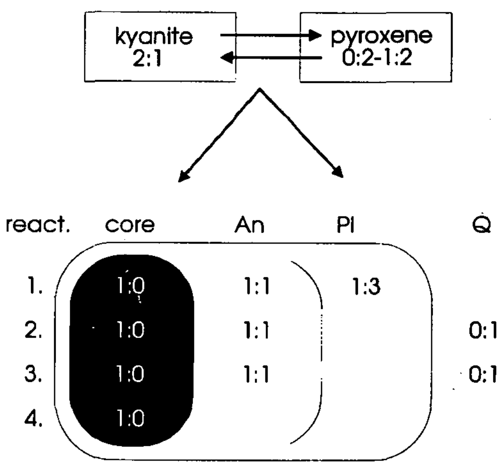

Fig. 4. Variation of the Al/Si ratio during the breakdown of the HP phases in the case of the reactions (1)–(4). Al-rich minerals are separated in the internal core.

The most significant difference among the subsequent zones of the microtexture studied appears in their Si/Al proportion. The main reason for the corona growth must have been the lower mobility of Al compared to Si during the breakdown of the high-P paragenesis. This process could result in a diffusive gain of Al relative to Si in the core, and finally lead to the disequilibrium coexistence of quartz and corundum in the same system. Between these two phases the outer plagioclase rim formed an effective barrier controlling the diffusion of Al and Si.

When plotting the stability fields of the reactions listed above on a P-T map, decreasing pressure, but slightly increasing temperature during the breakdown may be seen (fig. 5.). The reactions define a wide pressure range, and reaction (4) gives significantly higher pressure than the others. This shows that anorthite (and corundum) must have developed prior to the other phases. This evidence is in good agreement with the different textural and geochemical features of the two plagioclase shells, suggesting that anorthite grew earlier and formed a radial corona overgrowth around the kyanite. The more sodic outer plagioclase rim, which presents a mutual granoblastic texture, likely grew under higher temperature conditions. So, not only the sodic-intermediate plagioclase shell played a role as an the effective barrier, but also the primary anorthite zone could separate Al-rich and Al-poor phases (corundum in the core).

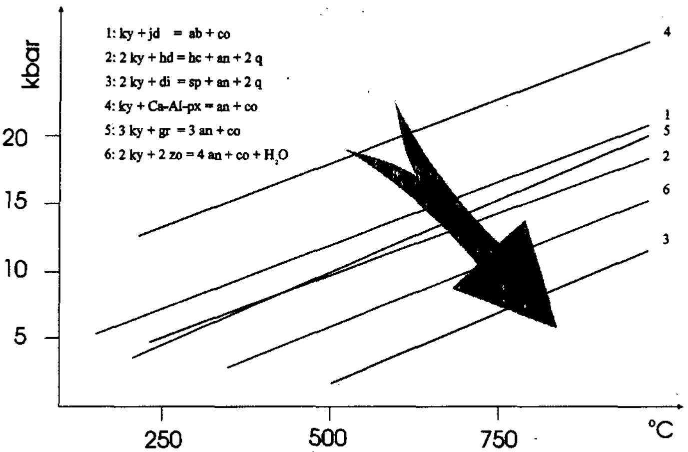

Fig. 5. Each reaction suggests increasing temperature during uplift. Thermodynamic calculations were performed with a TWQ software using the database of Berman (1988).

During a usual uplift both P and T decrease, the reheating refers to extreme geological conditions. Based on the current tectonic models for the Swiss Central Alps two solutions seem possible. Either the big granodiorite bodies found south-east of the eclogite locality intruded simultaneously with the uplift causing an extra heat-source, or the Adula nappe carried the heat when covering the underlying tectonic units (melon pit model, ENGI et al., 1995). When studying a breakdown microtexture of kyanite similar to the one described, HILL AND BALDWIN (1993) found a relationship with granodiorite bodies, which intruded due to the uplift of a metamorphic core complex in Papua New Guinea. To answer this question, however, we need more study.

Increasing temperature, of course, induced a more intensive sub-solidus diffusion, what lead to the corona growth around kyanite. At a certain value, however, also temperature had to drop and start decreasing. Because diffusion rate is an exponential function of temperature (PUTNIS, 1992), the diffusion and also the growth of the corona eventually stopped allowing the metastable microtexture to persist. During cooling, probably due to the following reactions all Al-rich phases were replaced by mica:

$$\text{corundum} + K^+ + H_2O = \text{muscovite} \quad (9)$$
$$\text{kyanite} + K^+ + H_2O = \text{muscovite} \quad (10)$$
$$\text{hercynite} + K^+ + H_2O = \text{annite (in a biotite)} \quad (11)$$
$$\text{spinel} + K^+ + H_2O = \text{phlogopite (in a biotite)} \quad (12)$$

In several samples studied also isometric sets of plagioclase and mica, or plagioclase and corundum remind the previous existence of kyanite.

CONCLUSIONS

Compiled corona forming processes in the eclogite samples at Gorduno in the Swiss Central Alps represent a series of diffusion-controlled reactions. The corona structure is a result of reactions between kyanite and other HP phases; pyroxene, garnet and zoisite. In the internal core Al-rich minerals (corundum, spinel) are separated, and the Al/Si ratio decreases towards the rim (anorthite, plagioclase, quartz). The observed mineralogy formed due to the restricted mobility of Al relative to Si in high temperature conditions.

Due to cooling diffusion rate had to decrease making the persistence of the double corona structure possible.

ACKNOWLEDGEMENT

Microprobe measurements were performed at the University of Bern, Switzerland. The microprobe laboratory was financially supported by the Swiss National Foundation (Grant No. 21-26579.89). Special thanks to M. ENGI and J. MEYER for their helpful comments.

REFERENCES

BERMAN, R. G. (1988): Internally-consistent thermodynamic data for stoichiometric minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2. J. Petrol. 29: 445–522

BIINO, G. (1995): Pre-Variscan evolution of the eclogitised mafic rocks from the Helvetic basement of the Central Alps. Eur. J. Mineral. 7: 57–70

BOCCHIO, R. (1975): Le eclogiti retrommetamorfiche di Gorduno. Periodico di Mineralogia – Roma. 44: 245–256

BORGHI, A. (1991): Margarite coronas after kyanite in the Seria dei Laghi (Southern Alps – northern Italy and Canton Ticino). Per. Mineral. 60: 45–54

ENGI, M.; TODD, C. S.; SCHMATZ, D. R. (1995): Tertiary metamorphic conditions in the eastern Lepontine Alps. Schweiz. Mineral. Petrol. Mitt. 75: 347–369

FORSTER, R. (1948): Geologisch-petrographische Untersuchungen im Gebiete noerdlich Locarno. Schweiz. Mineral. Petrol. Mitt. 13/2: 249–470

GRANT, S. M. (1988): Diffusion models for corona formation in metagabbros from the Western Grenville Province, Canada. Contrib. Mineral. Petrol. 98: 49–63

HILL, E. J.; BALDWIN, S. L. (1993): Exhumation of high-pressure metamorphic rocks during crustal extension in the D'Entrecasteaux region, Papua New Guinea. J. metamorphic Geol. 11: 261–277

PUTNIS, A. (1992): Introduction to mineral sciences. Cambridge University Press.