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EVOLUTION OF CARBONATE ROCKS DURING THE REGIONAL METAMORPHISM IN SOUTH CARPATHIANS AND GENESIS OF ASSOCIATED "REACTION SKARNS"*

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Affected by the regional metamorphism, the carbonate rocks are crystallizing like any other rock. During the greenschist facies metamorphism, below 500°C, the carbonate rocks crystallized into rocks showing a fine granoblastic texture without any reaction phenomenon at the contact with the host silico-alumonous crystalline schists. During the amphibolite facies metamorphism, above 500°C, the carbonate rocks crystallized into rocks showing a larger granoblastic texture. Because the carbonate rocks and the host silico-aluminous crystalline schists are chemically incompatible rocks, during the high-grade metamorphism between these rocks a bilateral diffusion of chemical elements manifested itself from a rock to another, there resulting the so-called "reaction skarns". The mineralogical composition of the "reaction skarns" depended on the composition of the carbonate rock, which reacted with the crystalline schists.

Key words: carbonate rocks; crystalline schists; incompatible rocks; "reaction skarns"; limestones; dolomites; iron carbonates.

INTRODUCTION

The carbonate rocks from the crystalline schists of South Carpathians being rocks of sedimentary origin, during the regional metamorphism underwent changes in their composition and structure. As the carbonate rocks and the host crystalline schists are chemically incompatible rocks, during the regional metamorphism interesting changes occurred at the contact of the two rock-types, there resulting the "reaction skarns". These changes depended on the intensity of the metamorphism. As this problem rouses a special interest, I decided to present in this paper the succession of the transformations of the carbonate rocks in different crystalline schist series from South Carpathians, the metamorphism intensity of which was different.

ORIGIN OF CARBONATE ROCKS FROM THE CRYSTALLINE SCHISTS

The carbonate rocks from the South Carpathian crystalline schists have been formed under aqueous, marine conditions either during the oceanic or the island arc stages from the evolution of the Pre-Variscan and the Variscan oceans.

During the oceanic stage carbonate rocks may occur as layers of chemically precipitations deposits, intercalated between the flows of ocean floor basalts like those from the Mures ophiolitic suture[1], which is not the case in the present study. On the ocean floor the carbonate rocks may undergo both the ocean floor metamorphism and the regional metamorphism. Such carbonate rocks (limestones, dolomites, ankerites and rhodochrosites) occur as layers in the basaltic flows, the thickness of which rarely surpassing 50 meters. In the Pre-Variscan crystalline schists the carbonate rocks occur as reduced occurrences.

The most important masses of carbonate rocks occur in the oceanic areas during the island arc stage. But such large masses of carbonate rocks are rarely found in the crystalline schist areas. An example of such large masses of carbonate rocks occurs in the crystalline schists of the Poiana Ruscă Mountains, metamorphosed under the greenschist facies conditions[2], which seems to be formed in the Variscan Ocean by the end of the island arc stage, during the transition toward an epicontinental sea, both as precipitation and reef carbonate rocks. When the convergent tectonic plates started moving, due to the subduction processes, the sedimentary deposits, including the carbonate rocks, underwent the regional metamorphism.

After the collision of the convergent tectonic plates and the closing of the Alpine ocean trench, for instance, epicontinental seas have been installed, in which important masses of carbonate rocks were formed, like those from North Dobrogea[3], which occurred under intra-plate tectonic conditions. But such carbonate rocks cannot be affected by the regional metamorphism processes of the respective tectono-magmatic cycle.

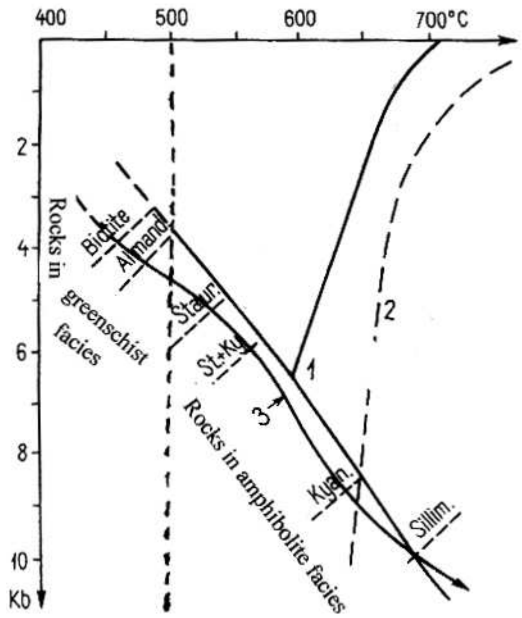

Fig. 1. PT diagram showing the curve of the regional metamorphism of Barrovian-type of the Sebes-Lotru series (Semenic Mountains) and the position of the low-grade and high-grade metamorphosed carbonate rocks. 1, triple point[4]; 2, melting curve of granite[5]; 3, curve of the Barrovian-type metamorphism of the Sebeş-Lotru series[6].

In the South Carpathians carbonate rocks affected by the regional metamorphuism are to be found in the crystalline schists of the Pre-Variscan Sebeş-Lotru series and other crystalline schist series, like the Variscan Poiana Ruscă series, in which the metamorphism manifested itself from the chlorite up to the sillimanite isogrades (Fig. 1). Within the South Carpathian metamorphic series carbonate rocks occur from the Semenic Mountains in the west, up to the Făgăraş Mountains in the east. The succession of the changes intervened in the structure and composition of the carbonate rocks during the Pre-Variscan and the Variscan metamorphism, under the conditions of the greenschist facies and the amphibolite facies are presented further down.

CARBONATE ROCKS FROM THE CRYSTALLINE SCHISTS OF THE GREENSCHIST FACIES

Within the South Carpathian crystalline schists metamorphosed in the greenschist (greenstone) facies occur in the Poiana Ruscă Mountains and in the south of the Semenic Mountains. These formations have been metamorphosed during the Pre-Variscan and the Variscan movements. In the Poiana Ruscă Mountains important masses of limestones and dolomites occur, sometimes iron carbonate rocks being associated with. All the carbonate rocks show a fine granoblastic texture (Table 1).

Table 1

Evolution of the carbonate rocks during the regional metamorphis

Metamorphism facies	**Limestones and dolomites**	**Ankerites and rhodochrosites**	**“Reaction skarns”**
Greenschist facies	Marble with fine granoblastic texture	-	-
Amphibolite facies	Marble with granulated texture	Rocks with fine granoblastic texture	“Reaction skarns” formed on limestones,dolomites and ankeritic rocks

Depending on the initial composition of the sedimentary deposits, represented mostly by calcareous rocks and dolomites, in Poiana Ruscă resulted, by the low metamorphism, sericite chlorite limestones, sericite dolomites, quartz limestones, quartz dolomites, and iron carbonates as well. In these rocks adequate mineral assemblages were formed[7–10, 2]), as follows:

1. Dolomite-calcite-quartz (-graphite-turmaline).
2. Dolomite-quartz-sericite (-epidote-rutile).
3. Dolomite –quartz

In the limestone *sensu stricto* the following mineral assemblages were formed under the conditions of the metamorphism manifested itself at temperatures lower than 500°C.

4. Calcite-quartz-graphite (-albite-sericite-magnetite).

5. Calcite- quartz-sericite-magnetite (-albite-epidote).

6. Calcite-sericite-albite-quartz-magnetite.

7. Calcite-quartz-chlorite-graphite (-sericite).

Besides these mineral assemblages there are other assemblages combined of the minerals presented in these mineral assemblages, which resulted from the transitional rocks between dolomites and limestones.

In the Semenic Mountains carbonate rocks occur in the crystalline schists metamorphosed under the greenschist facies conditions of the Miniş series[11,12]. In this series carbonate rocks occur as thin layer of limestone intercalated between biotite quartzites and amphibolites, a rock association characteristic for this series. In the crystalline limestones the following mineral assemblage was determined:

8. Calcite-muscovite (-magnetite-pyrite).

All these mineral assemblages occurred under the conditions of the regional metamorphism of Barrovian-type in the greenschist facies, which, according to Turner and Verhooge[13], manifested itself at temperatures of 300^o to 470^{o}C (see also Fig. 1). However, Winkler[14] supposed that in some cases the high temperature may increases up to 560^{o}C. Under these metamorphism conditions realized below 500^{o}C temperature, no metasomatic reaction between the carbonate rocks and the silico-aluminous host crystalline schists was reported.

CARBONATE ROCKS IN THE HIGH-GRADE METAMORPHOSED CRYSTALLINE SCHISTS

In the high-grade metamorphosed crystalline schists carbonate rocks occur within the eastern part of the Semenic Mountains and the Cimpa Mountains in the central area of the Sebeş-Lotru series, as well as in the Făgăraş Mountains. In these crystalline schists the carbonate rocks form either small lenticular bodies or layers of important length. In the last case sometimes there occur terminal interlayerings of carbonate rocks and silico-aluminous crystalline schists. The carbonate rocks from the amphibolite facies of the regional metamorphism are represented by crystalline dolomites and limestones, to which ‘reaction skarns’, ankeritic and rhodochrositic rocks are associated (Table 2).

The composition of the characteristic mineral assemblages from these carbonate rocks depended on the metamorphic zone in which they have been situated during the metamorphism. Thus in the staurolite-kyanite zone the following mineral assemblages occurred[11]:

9. Dolomite-phlogopite-quartz.

10. Calcite-diopside-tremolite (-phlogopite-opaque minerals).

In the manganese rocks from this metamorphic zone the following mineral assemblages have been detemined:

11. Rhodochrosite-spessartine-dannemorite

Table 2

Chemical composition of some carbonate rocks, iron rocks and “reaction skarns” affected by the high-grade regional metamorphism from the Semenic Mountains (data from Savu[11])*

Number	1	2	3	4	5	6	7	8	9	10	11
SiO_2	0.70	0.10	0.22	2.42	0.61	0.35	14.40	50.98	0.80	1.34	1.12
Al_2O_3	-	-	-	-	-	-	3.97	14.0	-	-	-
Fe_2O_3	-	0.50	0.44	1.18	1.21	1.19	-	4.4	4.78	19.93	76.62
FeO	0.65	0.73	1.52	1.50	2.30	4.20	4.31	0.72	11.2	11.25	20.98
MgO	0.40	20.47	20.52	19.32	20.05	20.0	14.7	5.0	12.8	1.8	0.16
CaO	55.8	31.72	31.2	31.02	30.09	30.16	27.58	19.88	30.8	25.0	-
Na_2O	-	-	-	-	-	-	3.92	2.51	-	-	-
K_2O	-	-	-	-	-	-	0.56	0.64	-	-	-
TiO_2	-	-	-	-	-	-	0.26	0.44	-	-	0.51
MnO	-	-	-	-	-	-	0.28	0.21	-	-	-
P_2O_5	-	-	-	-	-	-	0.10	0.08			
CO_2	40.21	45.48	44.43	42.67	44.6	43.84	29.0	0.18	-	-	-
S	0.06	0.1	0.12	0.12	0.29	0.02	0.30	-	0.17	0.04	-
H_2O^-	-	1.32	2.25	1.54	1.18	-	0.02	0.13	-	-	-
H^2O^+	-	-	-	-	-	-	-	0.70	-	-	-
Total	98.6	100.42	100.7	99.77	100.33	99.78	100.2	99.87	99.84	98.68	99.49

*The analyses in this table represent: 1, limestone; 2 – 6, dolomites; 7 – 9, “reaction skarns”; 10, alkerite; 11, magnetite.

12. Rhodochrosite-spessartine-rhodonite

13. Rhodochrosite-quartz-rhodonite

In the sillimanite metamorphic zone the following mineral assemblages have been reported, which represent both the recrystallized carbonate rocks and the "reaction skarns" in which the silicate minerals show that they have been formed at temperatures of 700^{o} to 800^{o}C (Fig.1). It is of note that the term of "reaction skarn" was introced in geology by Magnuson[15] since 1930[16].

14. Calcite-phlogopite.

15. Dolomite-magnetite (-pyrite).

16. Dolomite-tremolite-magnetite (-pyrrhotite).

17. Calcite-forsterite-tremolite-humite-magnetite-pyrite.

18. Garnet-diopside-hornblende-zoizite-epidote-lagioclase-calcite (-apatite-magnetite-pyrite).

19. Tremolite-calcite-quartz.

20. Diopside-calcite-quartz.

21. Diopside-forsterite-tremolite-calcite

22. Diopside-tremolite-plagioclase (-quartz-titanite-patite).

At Răscoala, in the Cimpa Mountains, thin magnetite and iron carbonate layers are intercalated in the biotite quartzo-feldspatic gneisses, metamorphosed under the kyanite isograde conditions (Fig. 2), which contain "eaction skarns" In such a 'reaction skarn' the following mineral assemblage was formed:

23. Fe-olivine-green clinopyroxene-redish garnet-mphibole-magnetite-calcite

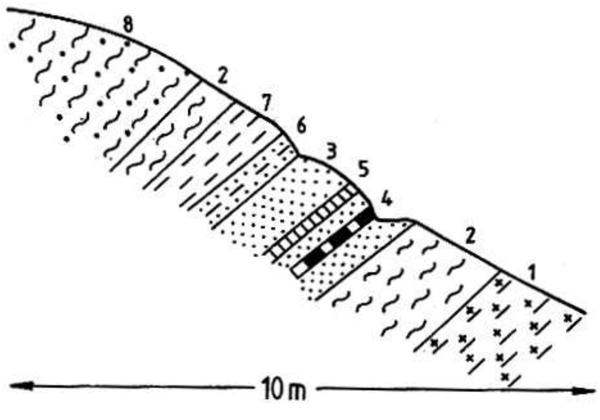

Fig. 2. Succession of crystalline schist layers outcropping in the Răscoala Valley (Cimpa Mountains). 1, quartzo-feldspatic gneiss; 2, biotite quartzitic schist; 3, magnetite and ankeritic layer; 4, pyroxene amphibolite; 5, iron carbonate rocks with "reaction skarn"; 6, pyroxene gneiss with magnetite bands; 7, pyroxene gneiss; 8, feldspatic quartzites.

The quartzo-feldspatic gneiss in contact with the iron "reaction skarn" changed into a clinopyroxene gneiss, the pyroxene of which is a light green variety (salite). Both the iron 'reaction skarn' and the pyroxene gneiss resulted from the reaction between the quartzo-feldspatic gneiss and the iron carbonate layer during the high-grade metamorphism.

According to their composition, all the mineral assemblages above presented show that, they have been formed under high temperature and moderate pressure conditions (see Fig. 1).

METAMORPHISM OF CARBONATE ROCKS AND GENESIS OF THE "REACTION SKARNS"

As shown above, the carbonate rocks from the South Carpathian crystalline schists have been metamorphosed under the conditions of the chlorite up to the sillimanite isogrades of the Barrovian-type regional metamorphism. The pressure varied from about 5 kb up to 10 kb and the temperature changed from about 200^{o} up to 800^{o}C (see Fig.1).

The metamorphosed carbonate rocks, represented by limesones, dolomites, magnetite dolomites and ankerites rarely by rhodochrosites and Mn-magnetites, resulted from sedimentary rocks with a close chemical composition (Table 1).

Inside the carbonate rock bodies the rocks recrystallized into rocks with a fine granoblastic texture, below 500^{o}C, and with a granulated texture above 500^{o}C. On the marginal zones of the bodies the carbonate rocks, metamorphosed at high temperatures, reacted with the silico-aluminous crystalline schists in course of metamorphism. Thus, there took place a bimetasomatic process manifested itself by diffusion of the chemical elements from a rock to another. Such a phenomenon is represented in the following set up, based on a contact between a dolomite layer and silico-aluminous crystalline schists occurring in a quarry northeast of Armeniş Village from the Semenic Mountains (Fig. 3).

Incompatible rocks in contact	Rocks resulted from the bimetasomatic process
Biotite gneiss	Biotite gneiss ± biotite bands Pyroxene gneiss ± pyroxene bands
Contact (bilateral metasomatism)	
Dolomite	Pyroxene-calcite-phlogopite 'reaction skarn' ± pyroxene bands Tremolite-calcite-'reaction skarn' ± tremolite bands Dolomite-tremolite-phlogopite-'reaction skarn' ± phlogopite bands

Fig. 3. Set up showing the manifestation of the bimetasomatic process between incompatible rocks during the metamorphism.

This set up shows that, in the presented structural circumstances and under the conditions of the high-grade metamorphism, from the initial sedimentary rocks H_2O, CO_2 and other gas components have been partially removed like hot metamorphic solutions. These solutions transported at the same time other elements, which were in excess during the recrystallization of the sedimentary rocks under high PT conditions[11], Fig. 11). The metamorphic solutions acted over the carbonate rock bodies, there resulting the “reaction skarns”, usually on the margin of the carbonate rock bodies.

Comparing the standard cell of a dolomite with that of the associated “reaction skarn” the above quoted author showed that, for the formation of the “reaction skarn” there have been introduced from the host biotite gneiss into the dolomite body the following cations in percentages: 0,8 K, 4.6 Na, 2.9 Fe, 15.8 Al, 48.6 Si, 0.2 S, 0.1 Mn and 0.2 Ti. From the dolomite have been removed 7.6 Ca and 18.0 Mg cations and 51.5 C like CO_2. The removed cations of Mg and Ca penetrated the host silico-aluminous rock, so that a zone of clinopyroxene (salite) gneiss resulted at the contact with the carbonate rock body. Sometimes, the excess of Mg cations determined the occurrence of some phlogopite aureola around the dolomite bodies.

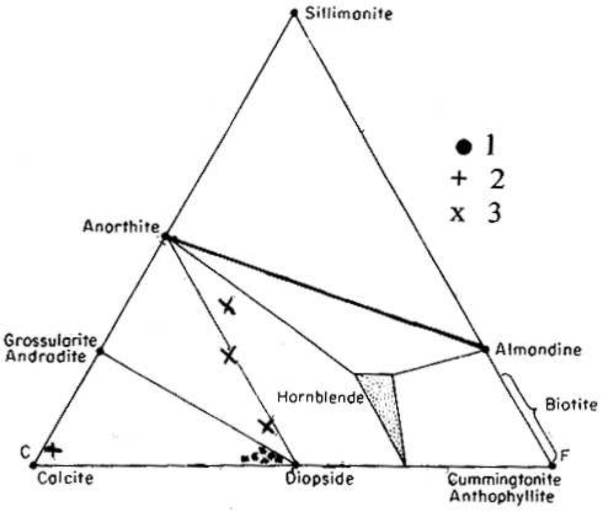

Fig. 4. ACF diagram for the characteristic mineral assemblages from the carbonate rocks and the related “eaction skarns” 1, limestone; 2, dolomites; 3, “eaction skarns”

The ACF diagram (Fig. 4) shows the characteristic assemblages of the recrystallized carbonate rocks and of the respective “reaction skarns”. Within this diagram the analyzed rocks are distributed as follows: the limestone is situated near the C angle and the dolomite rocks plot in the grossular-diopside-calcite mineral assemblage, near the diopside place. The “reaction skarns” are close to the anortite-diopside-hornblende mineral assemblage. These mineral assemblages correlate with those determined under microscope, as shown above.

CONCLUSIONS

Like any other sedimentary rocks the carbonate rocks are metamorphosed, the effects of metamorphism depending on the intensity of the PT conditions. Thus, during the regional metamorphism in the greenschist facies conditions, below 5OO°C, the carbonate rocks are crystallizing like rocks with a fine granoblastic texture without any evident reaction with the host silico-aluminous crystalline schists.

During the regional metamorphism under the amphibolite facies conditions the carbonate rocks are crystallizing as rocks with a granulated texture.

Because the carbonate rocks and the host silico-aluminous crystalline schists are chemically incompatible rocks, if they are in contact during the high-grade metamorphism, reacted to one another, there resulting the so-called “reaction skarns” in the carbonate rock bodies and of pyroxene gneisses in the crystalline schists.

The composition of the “reaction skarns” epended on the composition of the carbonate rock, which reacted with the silico-aluminous crystalline schist. If the reacting carbonate rock was represented by limestone, there occurred “reaction skarns” ontaining mostly tremolite and clinopyroxene as silicate minerals. In case of dolomites as reacting rocks the “reaction skarns” contained a forsteritic olivine, and if the reacting carbonate rock was an ankerite, the “reaction skarns” contained melanocratic minerals rich in iron.

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