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Occurrence of chloritoid and pyrophyllite in metaclastic rocks of Morava Zone

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Д. Милованович, М. Милосавлиевич, М. Каленич, В. Марчиг — Присутствие хлоритоида и пирофиллита в метакластических породах Моравской зоны. Метакластиты Моравской зоны (восточной части Сербо-Македонского массива) присутствуют в одном, двух и более последовательно расположенных изолированных горизонтах мощностью до нескольких десятков метров. Исследуемые метакластиты определены как первичные конгломераты и песчаники, отложившиеся в мелководной обстановке континентальной окраины. Хлоритоид, пирофиллит и биотит, образовавшиеся во время последнего метаморфического события, показывают, что температура метаморфизма достигала 350°C ±50°C. Давления определены менее точно и приняты 2—3 Kb. Упомянутые оценки указывают на условия более низкой ступени метаморфизма, чем в других исследованных районах. Хлоритоид и пирофиллит фактически присутствуют во всех породах Моравской зоны. Наличие этих минералов объясняется повсеместными гидротермальными изменениями в бассейне, вызванными инфильтрационными флюидами во время метаморфизма. Их образование не требует необыкновенных условий для седиментации выветрелых продуктов, диагенезиса или эпитермальной активности, чтобы образовались богатые алюминием составы, и временые границы выглядят несопоставимыми с таким объяснением.

Abstract. Metaclastics of the Morava Zone (eastern part of the Serbo-Macedonian Massif) occur in one, two or more successive discontinuos levels, up to several tens of meters in thickness. The investigated metaclastites were determined as primary conglomerates and sandstones deposited in shallow water environments at a continental margin. Chloritoid, pyrophyllite and biotite formed during the last metamorphic event indicate that metamorphic temperature reached 350°C, ±50°C. Pressure conditions are less well constrained, 2-3 Kb being inferred. The mentioned estimates indicate that metamorphic conditions were of lower grade than in other investigated areas. Chloritoid and pyrophyllite are present also in virtually all rocks in the Morava Zone. The occurrence of these minerals is attributed to basin-wide alteration by infiltrating hydrothermal fluid during metamorphism. Their formation do not require unusual condition for the sedimentation of weathering products, diagenesis or epithermal activity to produce the alumina rich assemblage, and timing constraints appear incompatible with such explanations.

Introduction

Metaclastic rocks of the Morava Zone are located in eastern part of the crystalline schists of the Serbo-Macedonian Massif, in a narrow belt over a length of 250 km, from Danube to Vlasina Lake. Metaclastites of the Morava Zone which contain chloritoid, pyrophillite and paragonite belong to the metamorphic rocks of the Serbo-Macedonian massif. These rocks follow the front of the Morava nappe (Fig. 1).

Metaconglomerates and metasandstones are dominant rocks of the Morava zone. They were first mentioned by Aleksić (1965); first detailed geological description was provided recently by Milosavljević (1992), who studied their sedimentological features. Previous studies have stressed on the opinion that metaclastites represent a hydrothermally altered pile of Paleozoic age (Jancović, 1990), or have acknowledged minor metamorphism without determining its grade, extent and the influence.

This paper aims to show that metamorphism has played an important part in the generation of the present metamorphic mineral assemblages in metaclastics rocks. Metamorphic studies could eventually be used to construct a tectonic model for the inves tigated area.

Petrography

The dominant rocks of the Morava Zone are highly siliceous metasediments with commonly absent diagnostic metamorphic assemblages.

Metaclastics occur in the Morava Zone in one, two or more successive discontinuous levels, up to several tens of meters in thickness. Metamorphic assemblage, chlo-

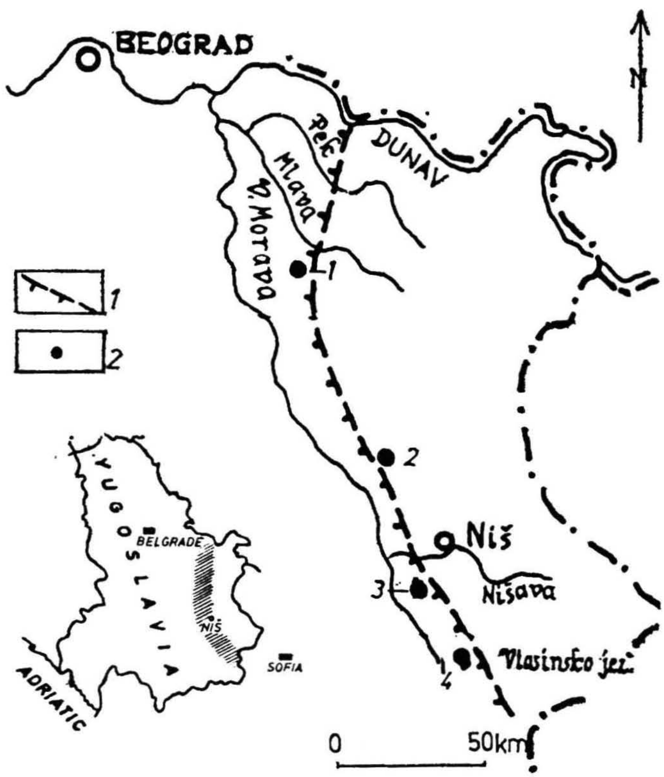

Fig. 1. Geographic position of Morava zone with occurrence of chloritoid and pyrophyllite *1* — Morava zone; *2* — Occurrence of chloritoid and pyrophyllite. 1. Čelava Glava, 2. Mratinja, 3. Gradiste, 4. Donji Dejan.

ritoid, pyrophyllite and biotite are abundant locally, in Ćelava Glava, Mratinja and Donji Dejan (Fig. 1). Paleopalynological analyses in several places were used in determining their lower Devonian age.

Based on preserved relict structures and textures, the metaclastites studied were determined as primary conglomerates and sandstones, deposited in shallow water conditions in continental-marginal enviroments.

Metamorphic features are apparent specially in the metaconglomerates. They mainly involve induration, dissolving and polygonization of quartz pebbles, and veins formed by pressure solutions.

The spatial control of the primary lithological types was not noted in broad frame. The more shaly units among metaconglomerates tend to be the areas of major deformation and thus represent zones of intense and heterogenous strain, representing local movement over long time periods, rather than discrete kinematic events.

Diagnostic metamorphic assemblages are sporadic in the metaclastics rocks, being absent in pebbles and grains but common in the matrix. They include chloritoid, pyrophyllite and muscovite with less common metamorphic biotite. Although chloritoid and pyrophyllite bearing rocks are relatively uncommon in nature and restricted to specific bulk rock compositions (H o s h e k, 1969) both minerals are present throughout the investigated metaclastites. Their distribution and geological setting have not been previously used to constrain the regional metamorphic conditions.

Mafic metaextrusives usually overlay the metaclastics rocks. These rocks are dark-green to green, foliated, composed of albite, chlorite, epidote, zoisite, leucoxene, quartz, sometimes with muscovite, chloritoide and calcite. The metabasic rocks are generally altered and useless as regional indicators of the metamorphic grade. The presence of chloritoid in metabasites and Morava metaclastites proves that metamorphism has affected both of these rocks types and it appears reasonable that the metamorphism was the same, or very similar in the metaclastites.

Mineral chemistry

Chloritoid

The chloritoid mainly forms poorly oriented blades up to 1 mm in length that usually overgrow the mica, pyrophyllite and / or chlorite fabric. This mineral is abundant locally: in metaclastites of Ćelava Glava, Mratinja and Donji Dejan (Fig. 1). Chloritoid is not always related to highly deformed zones probably in part because of its

Table 1

Chemical compositions of the chloritoid

	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	23,67	23,96	23,77	24,08	23,69	25,34	23,37	24,85	23,15	23,32	24,31	24,29
Al_2O_3	40,03	39,99	40,35	40,60	40,36	39,78	41,35	40,40	40,51	40,84	41,58	40,85
FeO	27,25	27,33	25,56	26,47	26,70	25,13	25,24	24,98	26,53	26,03	22,34	24,47
MnO	0,14	0,14	0,23	0,09	0,13	0,32	0,41	0,55	0,51	0,70	0,75	0,96
MgO	1,34	1,17	2,22	1,13	1,32	1,47	2,08	2,86	1,75	1,20	1,89	1,32
	92,43	92,59	92,13	92,37	92,20	92,04	92,45	92,64	92,45	92,09	90,87	91,89
					Number of cations per 12 oxigens							
Si	1,986	2,005	1,984	2,008	1,985	2,104	1,941	2.053	1.940	1.956	2.202	2.023
Al	3,958	3,944	3,970	3,991	3,986	3,892	4,047	3.934	4.001	4.038	4.076	4.011
Fe	1,912	1,912	1,784	1,846	1,871	1,745	1,753	1.726	1.859	1.826	1.554	1.705
Mn	0,010	0,010	0,016	0,016	0,009	0,022	0,029	0.038	0.036	0.050	0.053	0.068
Mg	0,168	0,146	0,276	0,276	0,165	0,182	0,257	0.229	0.219	0.150	0.234	0.164

tabular crystal habit. This type of occurrence suggests pre-date S_1-development. Chloritoid occurs in a number of different settings. It occurs with chlorite and pyrophyllite in the matrix of metaclastites and also in altered metabasites, as well as in shear zones (within metaclastites).

The tabulated data (Table 1, analyses 1-3 are from Ćelava Glava; 4-6 from Mratinja; 7-9 from Gradište and 10-12 from Donji Dejan) are nearly identical providing that the analytical precision is good and indicating that chemical variability from locality to locality is insignificant. Oxide totals range from 90.87 to 92.59, ignition loss is about 9%. Structurally on 12 oxigens, the cation proportions are in good agreement with the stoichiometric values 8. The presence of more than 3.9 Al atoms per formula unit strongly suggest that there is little ferric iron in sixfold coordination. Ashworth & Evirgen (1984) reached a similar conclusion for a number of chloritoid analyses from different localities.

It is necessary to mention that the studied chloritoid compositionally has a very high Fe / (Fe+Mg) ratio like other low grade chloritoid.

Table 2

Chemical composition of the chlorite

	1	2	3	4
SiO_2	23.95	23.18	23.88	22.43
Al_2O_3	21.84	22.69	21.00	23.25
FeO	33.20	34.15	34.39	36.53
MnO	0.21	0.15	0.20	0.17
MgO	9.24	8.16	8.33	7.66
	88.44	88.33	87.80	90.04
	Number of cations per 28 oxigens			
Si	5.226	5.094	5.289	4.898
Al	5.617	5.877	5.481	5.983
Fe	6.059	6.276	6.369	5.671
Mn	0.039	0.028	0.037	0.031
Mg	3.005	2.673	2.750	2.493

Table 3

Chemical composition of muscovite and paragonite

	1	2	3	4	5	6
SiO_2	47.90	47.34	47.58	48.08	48.22	47.25
TiO_2	0.12	0.08	0.06	0.00	0.00	0.00
Al_2O_3	36.16	36.06	36.12	40.19	40.12	40.14
FeO	1.81	1.39	2.11	0.00	0.00	0.00
MgO	0.41	0.45	0.53	0.00	0.00	0.00
Na_2O	1.17	0.77	1.03	6.50	6.81	6.94
K_2O	8.64	9.10	7.95	0.46	0.44	0.56
	96.21	95.19	95.38	95.23	95.59	94.89
	Number of cations per 22 oxigens					
Si	6.247	6.219	6.222	6.086	6.088	6.024
Ti	0.012	0.080	0.060	0.000	0.000	0.000
Al	5.558	5.583	5.567	5.996	5.970	6.032
Fe^{2+}	0.197	0.153	0.231	0.000	0.000	0.000
Mg	0.080	0.088	0.103	0.000	0.000	0.000
Na	0.296	0.196	0.261	1.595	1.667	1.716
K	1.436	1.525	1.326	0.074	0.071	0.091

Chlorite

Chlorite usually occurs as minor phase in the studied rocks. According to the classification of H e y (1954) the chlorites are mainly ripidolite with quite homogenous Si and Al content (Table 2; analyses 1 and 2 are from Ćelava Glava; 3 from Mratinja and 4 from Donji Dejan).

Muscovite and biotite

Muscovite and less abundant biotite occur in fine grains, up to 0.1 mm in size.

Muscovite is slightly enriched in FeO (up to 2.11 %) and MgO (up to 0.53%), (Table 3; analyse 1 is from Ćelava Glava, analyse 2 is from Mratinja and analyse 3 from Donji Dejan). The seladonite content of muscovite, being measured in terms of X_{si} (wehere X_{si}=(Si/2-3) for 22 O, varies from 0.11 to 0.12.

Biotite has been indentified optically in some thin sections. This mineral occurs as discrete light brown flakes making up to 2% modally. Many grains are retrogressed to chlorite.

Paragonite and pyrophyllite

Pyrophyllite and paragonite are abundant only locally, usually associated with chloritoid and / or muscovite and chlorite. These minerals appear as small flakes or build folded spurts or bands up to 0.5 mm in size. Pyrophyllite and paragonite usually show preffered orientation parallel to the schistosity. Paragonite (Table 3; analyse 4 is from Ćelava Glava, analyse 5 Mratinja, and 6 from Donji Dejan) and pyrophyllite are of homogenous compositions.

Metamorphism

The key metamorphic assemblage in the metaclastites includes chloritoid, pyrophyllite, chlorite and muscovite, with less common biotite. All the metamorphic minerals are sin- or post-tectonic with respect to the S_1 schistosity.

The origin of chloritoid and pyrophyllite has been explained in two different ways. First, both minerals could originate by isochemical metamorphism of different Fe- and Al-rich clay assemblages (H o s c h e k, 1969). Alternatively a post-sedimentary origin is suggested when the necessary bulk composition was produced during an introduction of the components needed by fluids after burial. In the first model, the metaclastics would provide vital environment informations for any sedimentary environment reconstruction. In the second, data constraining the provenance and depositional environments would be minimal, but critical information could be gained about post-burial fluids.

The genesis of chloritoid and pyrophyllite can be modelled by two simplified equations using Fe end-member composition, first to chloritoid (1) and then to pyrophyllite (2) taking into account the mobility of Fe, immobility of Al and representative chlorite composition:

chlorite=chloritoid+quartz (1)

chloritoid+quartz=pyrophyllite+Fe-oxides+H_2O (2)

The additional equations (3, 4 and 5) involving pyrophyllite, albite and muscovite provide the link between all main aluminous phases and expressed in terms of variable Na, K and H^+.

pyrophyllite+2K=muscovite+quartz (3)

pyrophyllite+2Na=paragonite+quartz (4)

and albite+muscovite=paragonite+pyrophyllite+K (5)

The major component not considered in the above systems that might influence the equations is Mg. Increased Mg / Fe ratio will destabilize the chloritoid formation relative to other phases. The Mg-rich nature of chlorite and Fe-rich nature of chloritoid would mean major Mg (but not Fe) loss by transition from chlorite to chloritoid.

Different experimental values for the lower limit of the pyrophyllite stability field have been obtained by Althaus (1966), Kerric (1968), Thomson (1970) and Hemley, Montoya, Marinenko & Luce (1980) among others. A recent discussion on the pyrophyllite stability field can be found in Hewitt & Wones (1984).

Compositionally, pyrophyllite is equivalent to low grade kaolinite plus quartz assemblages and to high-grade andalusite / kyanite plus quartz assemblage. For condition of water saturation at 1 Kb, kaolinite plus quartz is stable to 325°C and pyrophylite breaks down above 400°C (Thomson, 1970; Helgeson et al., 1978; Holland & Powell, 1985).

Since chloritoid sometimes coexists with pyrophyllite and magnetite (or hematite) the following chloritoid-producing reaction could be considered:

pyrophyllite (or kaolinite)+Fe-oxides=chloritoid+quartz+water (6)

In the absence of a specific reaction, experimental control on the temperature of biotite formation is unavailable. Ferry (1984) has demonstrated that initial biotite formation occurs by a number of different reactions in different rocks at approximate the same temperatures (just below 400°C). The presence of biotite in the investigated metaclastites probably indicates temperatures of 350-400°C.

Chloritoid, pyrophyllite and biotite indicate that temperatures reached about 400°C. Pressures are less well determined, 2-3 Kb (?) being inferred.

Water activity is not constrained independently of temperature, namely the main metamorphic reactions involve dehydration.

Conclusion

Dominant rocks of the Morava zone are highly siliceous metasediments. Rapid variations in the imposed assemblages might be attributed to silty, sandy and gravel horizons are easily distinguished, however diagnostic metamorphic assemblages are commonly absent.

Chloritoid, pyrophyllite and biotite indicate that metamorphic temperature reached 400°C. Pressures are less well determinable, 2-3 Kb being inferred (Fig. 2). The mentioned estimates indicate that metamorphic conditions were no lower than in other surroundings investigated area.

The inferred metamorphic conditions are those in which Mn-garnet and stilpnomelane may occur in rocks of suitable Fe-rich composition (Milovanović et al., 1994, in print).

The agreement between three independent determinations (pyrophyllite, chloritoid and biotite stability) in samples from all parts of the Morava Zone gives confidence that metaclastic rocks generally record peak metamorphism of a regional nature.

Chloritoid and pyrophyllite are present in virtually all rocks in the Morava Zone. The occurrence of these minerals is attributed to basin-wide alteration by infiltrating hydrothermal fluid during metamorphism. The origin of the mentioned minerals does not require unusual sedimentary conditions or precursors, weathering products, epithermal activity or diagenesis to produce the alumina-rich assemblage.

The alteration event is inferred to have been within the chloritoid and pyrophyllite stability field (and thus syn-metamorphic) as bulk chemical changes in metaclastites are from chlorite directly towards chloritoid and then pyrophyllite, rather to lower grade minerals such as kaolinite.

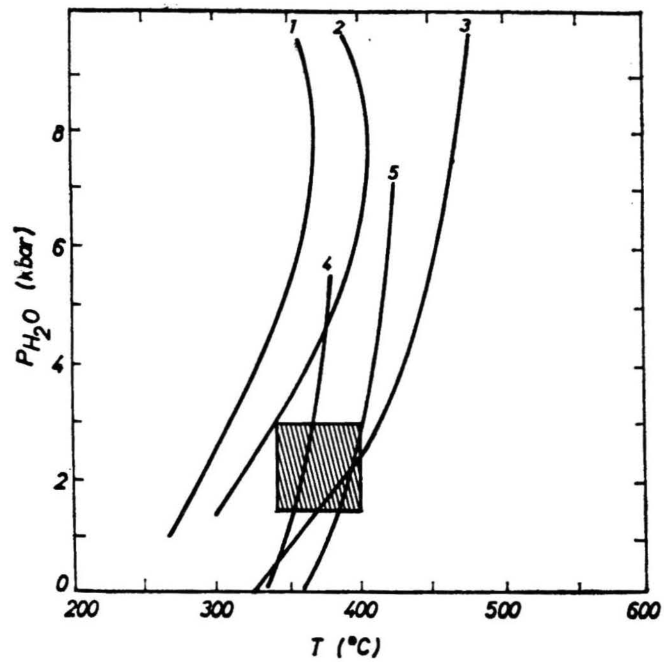

Fig. 2. P-T diagram showing the considered mineral reactions in investigated rocks (see text)
Reactions 1 (*kaolinite +quartz= pyrophillite+H_2O*), 2 (*kaolinite=pyrophyllite +diaspore +Quartz*) and 3 (*pyrophyllite=Al_2SiO_5+quartz+H_2O*) are from Chatterjee et al. (1984), reaction 4 is proposed themperature and pressure stability for chloritoide and reaction 5 is biotite stabillity after Ferry (1974)

Dating of metamorphism of rocks from the Morava Zone relative to deposition of these rocks is not established. The protolites of these metaclastics are of Devonian age. Post-Devonian metamorphic events in Serbo-Macedonian Massif, according to isotopic data took place during Carboniferous-Permian to Upper Jurassic-Lower Cretaceous, are reflected in Morava Zone metaclastites by low grade effects (350-400°C only) but it is not possible to specify which one controlled the formation of the characteristic metamorphic minerals (chloritoid and pyrophyllite).

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