Slovak Geol. Mag., 6, 4(2000),367–376

# Petrogenesis of Metamorphosed Ironstones Near Kokava nad Rimavicou (Veporicum, Western Carpathians)

MARTIN KOVÁČIK

Geological Survey of Slovak Republic, Mlynská dolina 1, 817 04 Bratislava, Slovakia
E-mail: kovacik@gssr.sk

*Abstract*: Primary ferruginous sediments shared together with their host metapsammites a basic regional tectono-metamorphic event in the condition of the amphibolite facies. This was followed by multistage Hercynian granitization with some periplutonic effects. An Alpine overprint caused only localised cataclasis and/or recrystallisation. At least six basic petrographical types are assigned to these ferruginous rocks. Magnetite is a frequent constituent in a characteristic metamorphic mineral assemblages built with garnet (almandine) - amphibole (grunerite) - apatite ± biotite (annite), quartz, chlorite (brunsvigite), graphite and allanite. Grunerite appears in many petrostructural positions (porphyroblasts, fine-grained aggregates, needles, swarms), which reflect polygenetic metamorphic reactions. Generally, deposition of sandstones, chamosite bearing ferrolites, black quartzites and the occurence of apatite-bearing laminae support an idea about a shallow-level sea sedimentary facies. The uniquity of (meta)ferrolites, among the more common rock association indicate a more specific environment (a bay or a deltaic system) of deposition. The occurrence of magnetite resulted from a complex combination of many factors. A case study of metamorphosed ironstones show an affinity of magnetite to a more pronounced pelitic character, corresponding also to a greater extent of $Fe^{3+}$. The original Eh of certain beds determine the nature of Fe-phases crystallisation (e.g. ilmenite vs. magnetite or grunerite vs. magnetite) in the process of regional metamorphism.

*Key words*: regional metamorphism, ironstone, ferrolite, grunerite, magnetite, annite, Hercynian basement, Western Carpathians

## Introduction

By the road in the valley 3 km from the Kokava nad Rimavicou site towards to Hriňová (the Hrabina area) there are occurrences of magnetite iron ore (Fig. 1). The site represents an unique accumulation of magnetite mineralization in the rock of the Western Carpathians crystalline complexes. This study includes a brief structural-geological descriptions, a division into lithotypes, petrology of the selected ferruginous schists, and assessing metamorphic development, magnetite generation and genetic aspects of the pre-metamorphic source. The basis for this article stems from research that was focused mainly on problems of graphite in the adjacent metaquartzites (Petro et al., 1998, Kováčik 1998).

## Overview of the Geological - Depositional Knowledge

The pilot mining - geological study of the magnetite mineralization was published by Šuf (1938). With respect to the irregularity of the deposit occurrences and of the great hardness of the ore-bearing rocks he considers the ore deposit as non-prospective. Migmatite was recognized as the basic host-rock and the studied area was integrated into the northern migmatite zone (Šuf 1937, 1938). The outlined area was later considered as part of the zone composed mainly of the so-called late-orogenic migmatites and granitoides (Hovorka in Kuthan et al., 1963). This zone is also designated as the hybrid zone, since its magmatic-metamorphic heterogeneousness (Bezák 1988).

During the 50-ies an intensive mining prospecting took place in the wider area of the prior-known occurrences. Zoubek and Nemčok (1951) localized the ore deposit into strongly granitized zone where migmatites and katazoned gneisses evolve from paragneisses. In the ore bearing rocks they distinguished the type composed of magnetite and garnet; garnetstones (without much magnetite) and biotitstones. The authors observed abundant occurrences of apatite and flaky biotite and emphasized a notable lack of hedenbergite. Although the deposit is conventionally classified as the „Kokava scarn“, in question of the genesis the preferred idea is that it is a regionally metamorphosed sedimentary ironstone deposit (Zoubek and Nemčok, 1951).

Based on the study of mineral paragenesis, Gubač (1957) proposed a contact-metasomatic origin of the deposit. He understood the original source material as regionally wide-spreaded gneisses of a claystone protolith that were changed by pneumatolitic - metasomatic effect of the pegmatites after the regional and subsequent contact metamorphism. He attributed the development of the

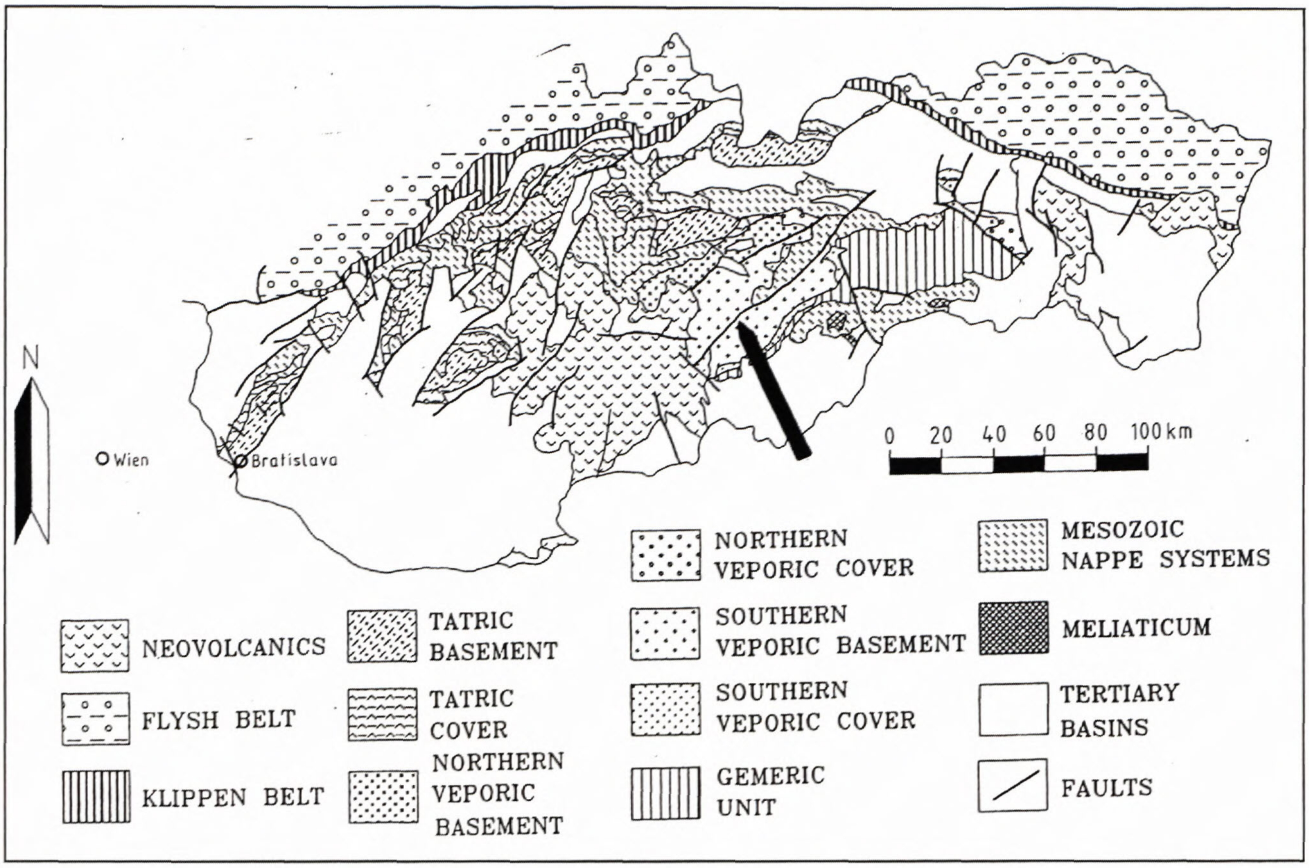


*Fig. 1A The geological scheme of the Slovak part of the Western Carpathians; the arrow points out the studied area.*

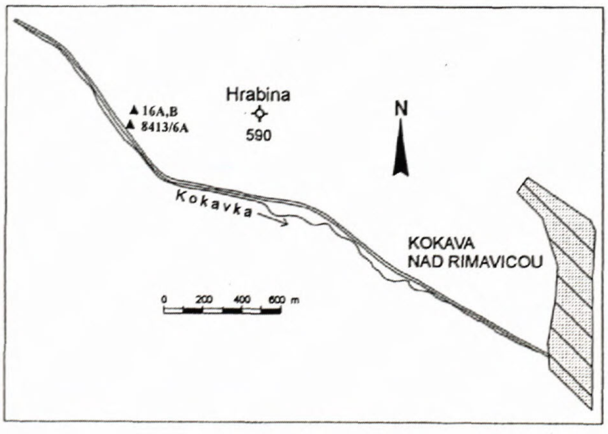


*Fig. 1B Site localization of the samples studied on electron microprobe*

magnetite ore and accumulation of biotite and garnet to the mineralization process of the pegmatite stage (so-called III. stage). Korikovskij et al., (1989) attributed a sedimentary origin to rock with a mineral assemblage of magnetite-garnet-grunerite. Phanerozoic chamosite ironstones are considered as the most probable source material and the metamorphic temperature is inferred to be about 550°C (Korikovskij et al., 1989). Radvanec (2000) viewed special petrologic questions about the ferruginous assemblages.

**Structural - Geological Observations**

The construction of a gneiss-migmatite substrate with lenses of graphite quartzites and gneisses, pure quartzites and magnetite-garnet gneisses show a conformable position. Alternations of various types of gneisses (basic gray fine-grained siliceous types, miscellaneous banded types, migmatitized varieties, coarse-grained garnet orthogneisses etc.) can be observed on a mezo- (x-dm) and macroscale. Lenses of greenish-gray amphibolite rocks occur rarely. The general dip of the rock complex is northward. Folds (many with cylindrical shape) are locally present as well, their shallow to sub-horizontally dipping b-axes are parallel to the strike. The question of the presence of the granitoids seems to be more complicated. Part of the granitoides, including also the dark-gray biotite-plagioclase granitoid rocks of the so called hybrid type, share a mutual deformation history with the gneissic substrate. This is also shown by the rare granite boudins in the gneiss-migmatite base rocks. The migmatitization is probably related to this oldest episode of granitoid formation. In places it can be observed that the biotite gneisses are injected by a light material ("neosome") which created quartz-feldspar eyes or also banded structure. Abundant enclaves of gneisses and oriented relics of graphitic substances enclosed in the later and predominant type of granitoids indicate magmatic assimilation of the metamorphic substrate.

These structures pierce several-decimeters-thick veins of light pegmatitic granite that also indicates formation in a synkinematic regime. In the rigid metaquartzites and in the magnetite-garnet gneisses, there are some nests of light granitic material and feldspathisation connected with silicification. The intrusions of this relatively younger leucocratic melt also indicate a assimilation or partial-anatectic effects on the basic biotite gneisses. In the light pegmatite granite, there are characteristic inclusions of gneiss relics containing as much as 1-2 cm large garnet porphyroblasts, which apparently originated as a result of periplutonic effects of this granite. However, the garnet phenocrysts are in places also present in these granites (residuum from incompletly assimilated gneisses?). Because of the variegated shape and composition each of the granitization-stage, the time and source relation between the predominant Veporic intrusion and the other plutonic events cannot be always expressed explicitly.

The sub-vertical east-west shear-deformation including gneisses and granitoides can be locally observed. Relatively weak sub-horizontal lineation with a similar orientation may indicate a younger Alpine phenomenon. Generally, it seems that the Alpine deformation-recrystallisation processes are not as intensive in the studied area as in the other areas of the southern Veporicum. This is probably caused by more resistant rheology of the rocks in investigated area. The Alpine deformation mostly uses inhomogenities of the pre-Alpine fabrics and it manifests mainly on the lithological boundaries, or follows directions of the Hercynian deformation. For example, the development of the omnidirectional biotitization on the contact with the granite vein penetrating into a fine-grained gneiss is most likely a Hercynian phenomenon. Afterwards, the biotite rims used to be deformed locally, and fine-grained micaceous mixture of presumably Alpine age were generated.

## Petrography and Geochemistry of the Rock-forming Minerals

Within the ferruginous rock ensemble there are a number of lithological variations that are often reflected in the banded mesostructure. Generally, the dark to black lithotypes with conspicuous red garnet and shiny faint-green amphibole clusters are dominant. Considerable sedimentary and polymetamorphic variability led to different petrographic division of these rocks (Zoubek and Nemčok 1951, Gubač 1957, Korikovskij 1989). (The rock divisions listed bellow are also only an incomplete overview of the ferruginous lithotypes). The rock composition also shows, that feldspars and white mica are not present here. The rock texture is usually homogeneous, sometime it has a massive, cherty character (for example, straight boundaries of polygonal quartz-grain texture in the fine-grained mineral assemblage in the rock type 2). According to the presence and quantitative abundance of the rock-forming minerals the following petrographic types of ferruginous metamorphic rocks are recognized:

*1) garnet > biotite > quartz > magnetite > amphibole;*
*2) garnet > quartz > magnetite;*
*3) garnet >> amphibole ≥ magnetite >> biotite;*
*4) garnet > amphibole ≥ quartz*
*5) garnet >> quartz > amphibole > magnetite > biotite*
*6) garnet >> magnetite > amphibole >> biotite*

***Garnet*** is the basic component of the rocks; rocks composed up to 90 by vol. % of garnet are assigned to (amphibole)-garnetstones. Garnet is here almost in a "cast" form, individual crystals reach 2 - 3 mm (for example, types 3, 5, 6). As it grows, the garnet encloses about 0.05 - 0.1 mm grains of magnetite, sometimes also tiny biotite, apatite, or grunerite, which probably represent relicts from pre-metamorphic or early-metamorphic stages of the rock development. According to the chemical analyses (Tab. 1, Fig. 2) the garnet is the *almandine type*. In mineral assemblages without magnetite (sample 16A, rock type 4) garnet contains up to 17% of the spessartite components. Garnet associated with magnetite (sample 16B, rock type 3) has up to 82 % of the almandine component and a little bit greater portion of Ca-, but it contains small amount of the Mn-component. A potential chemical zonality is not clear, the garnet can be considered more or less homogeneous.

*Tab. 1 Microprobe analyses of garnet in sample without - (16A) and with (16B) magnetite. The chemical composition is recalculated to 12 oxygens; ratio M/MF = $Mg/(Mg + Fe_{tot})$. (Mineral composition in Tabs. 1 - 3 was made on the device Jeol Superprobe 733 by RNDr. M. Köhlerová a ing. A. Sonáková.)*

| sample | 16A | | | 16 B | |
|---|---|---|---|---|---|
| | margin | between | centre | margin | centre |
| **$SiO_2$** | 36,73 | 36,681 | 36,556 | 36,651 | 36,913 |
| **$Al_2O_3$** | 21,443 | 21,411 | 21,4 | 21,253 | 21,627 |
| **MgO** | 1,084 | 1,371 | 1,158 | 0,99 | 1,075 |
| **FeO** | 31,488 | 31,256 | 31,101 | 36,058 | 35,708 |
| **MnO** | 7,382 | 7,026 | 7,398 | 2,056 | 1,975 |
| **CaO** | 2,146 | 1,997 | 2,175 | 2,982 | 2,958 |
| **total** | 100,273 | 99,742 | 99,788 | 99,99 | 100,256 |
| | | | | | |
| **Si** | 2,981 | 2,984 | 2,978 | 2,983 | 2,985 |
| **Al IV.** | 0,019 | 0,016 | 0,022 | 0,017 | 0,015 |
| | | | | | |
| **Al VI.** | 2,032 | 2,037 | 2,033 | 2,021 | 2,046 |
| **Mg** | 0,131 | 0,166 | 0,141 | 0,12 | 0,13 |
| **Fe2+** | 2,137 | 2,127 | 2,119 | 2,454 | 2,415 |
| **Mn** | 0,507 | 0,484 | 0,511 | 0,142 | 0,135 |
| **Ca** | 0,187 | 0,174 | 0,19 | 0,26 | 0,256 |
| **sum** | 4,994 | 4,988 | 4,994 | 4,997 | 4,982 |
| | | | | | |
| **Alm** | 72,147 | 72,077 | 71,564 | 82,46 | 82,255 |
| **Spes** | 17,117 | 16,401 | 17,258 | 4,77 | 4,598 |
| **Pyr** | 4,422 | 5,625 | 4,762 | 4,032 | 4,428 |
| **Gros** | 6,313 | 5,896 | 6,417 | 8,737 | 8,719 |
| | | | | | |
| **M/MF** | 0,058 | 0,072 | 0,062 | 0,047 | 0,051 |

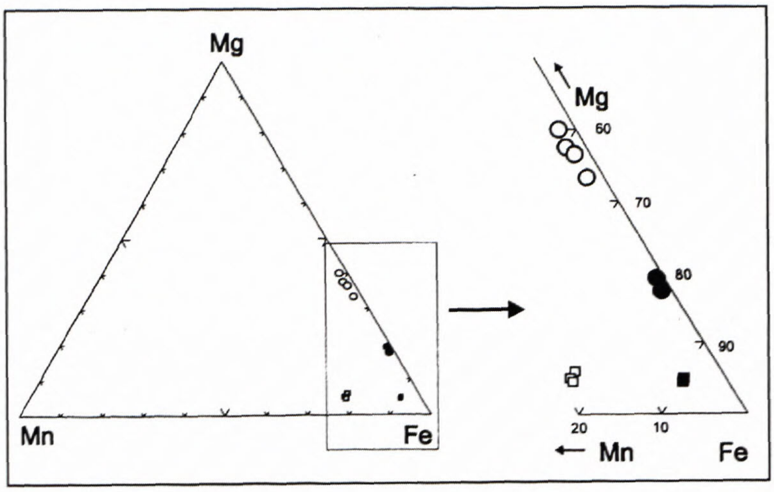


*Fig. 2 The projection of the garnet (rectangular) and grunerite (circle) composition in the sample without - (empty symbols) and with magnetite (full symbols). (For more information see the text and Tabs. 1 and 2). The basic mineral assemblage is garnet - grunerite - biotite.*

*Tab. 2 Microprobe analyses of grunerite recalculated on 23 oxygens. Ratio M/MF expresses also the percentage of cummingtonite component in the amphibole.*

| sample | 16A | | | | 16B | |
|---|---|---|---|---|---|---|
| | basic type | light phase | needle-type | needle-type | basic type | tiny type |
| **$SiO_2$** | 52,525 | 52,605 | 52,688 | 53,251 | 49,287 | 49,631 |
| **$Al_2O_3$** | 0,23 | 0,373 | 0,142 | 0,189 | 0,221 | 0,283 |
| **MgO** | 11,186 | 9,775 | 11,864 | 10,988 | 5,417 | 5,001 |
| **FeO** | 31,84 | 33,81 | 30,578 | 34,161 | 40,129 | 41,213 |
| **MnO** | 1,28 | 1,086 | 1,071 | 1,04 | 0,406 | 0,675 |
| **$TiO_2$** | 0 | 0,003 | 0 | 0 | 0 | 0 |
| **CaO** | 0,13 | 0,127 | 0,122 | 0,026 | 0,12 | 0,099 |
| **$K_2O$** | 0 | 0,127 | 0 | 0 | 0,035 | 0,003 |
| **$Na_2O$** | 0,077 | 0,105 | 0 | 0 | 0,035 | 0,002 |
| **total** | 97,268 | 97,906 | 96,464 | 98,453 | 95,624 | 96,908 |
| **Si** | 8,05 | 8,071 | 8,083 | 8,072 | 8,033 | 8,018 |
| **Al IV.** | | | | | | |
| **Al VI.** | 0,042 | 0,067 | 0,026 | 0,034 | 0,042 | 0,054 |
| **Mg** | 2,555 | 2,236 | 2,713 | 2,483 | 1,316 | 1,204 |
| **Fe** | 4,081 | 4,339 | 3,923 | 4,161 | 5,47 | 5,568 |
| **Mn** | 0,166 | 0,141 | 0,139 | 0,133 | 0,056 | 0,092 |
| **Ti** | 0 | 0 | 0 | 0 | 0 | 0 |
| **Ca** | 0,021 | 0,021 | 0,02 | 0,026 | 0,021 | 0,017 |
| **K** | 0 | 0,004 | 0 | 0 | 0,002 | 0,001 |
| **Na** | 0,023 | 0,031 | 0 | 0 | 0,011 | 0,001 |
| **sum** | 14,939 | 14,911 | 14,903 | 14,91 | 14,951 | 14,955 |
| **M/MF** | 0,385 | 0,34 | 0,41 | 0,374 | 0,194 | 0,178 |

The ***amphibole*** belongs to the group of the monoclinic Fe-Mg-Mn amphiboles and its composition (Tab. 2) fits the field of *grunerite* (Leake, 1997). The grunerite is non-pleochroic, it has mostly variegated interference colors. It commonly forms fine-grained aggregates, found in interstitial spaces among garnets. In a thin section, the grunerite aggregates are intergrown with magnetite (Fig. 3) or do not contain it. This fact may indicate a dependence upon the chemical composition of the primary crystallization domain. An interesting phenomena represents scarce diablastic intergrowths of magnetite and grunerite (Fig. 4), which also can be attributed to a high iron content in a local aluminiumpoor crystallization system. These structural forms, together with the 2-3 mm porphyroblasts, represent relatively the older grunerite generations. Locally also, a skeletal crystals developed - thin long needles or swarms of grunerite grow into quartz or biotite. Figures 5a and 5b illustrate the basic mineral assemblage (rock type 1) garnet - biotite - magnetite and grunerite, which occurs in two morphological forms. Incomplete crystallization of the "skeleton" grunerite in biotite probably indicates an excess of $Fe^{2+}$ in the system, along with a concurrent lack of aluminum and eventually also potassium. Because the metamorphic conditions in these metamorphic minerals are indicated also by the mutual distribution of Fe and Mg (or also Mn), neither the garnet nor the biotite were able to bind greater amount of FeO at the given metamorphic grade. A similar situation is found in the case of grunerite needles grown into quartz, which indicate the predominance of the two-valent iron, otherwise magnetite would be generated (rock type 5).

Within a studied sample, all forms of grunerite (i.e. porphyroblasts, fine-grained aggregates and needles) have practically identical chemical composition (see Tab. 2). This can indicate either equal conditions of metamorphic crystallization, or rather the fact that the metamorphic reactions are to a great extent controlled by the chemical composition of the protolith. The grunerite in the samples without magnetite contains an increased amount of Mg and Mn, analogously as in garnet. Microprobe analysis of the grunerite crystals also did not show a relevant metamorphic zoning.

***Biotite*** - the crystal size considerable depends upon its quantity. If insignificant, then it can be observed as a tiny (about 0.1 mm) inclusion in the garnet, if abundant, then it occurs in 1-3 mm large blasts, similar to garnet or grunerite (Fig. 5). Some of the non-directional biotite flakes were probably generated due to thermal and metasomatic (input of $K_2O$ and $H_2O$) effects of the surrounding granitoides. On the contrary to the garnet, the fine-grained inclusions of magnetite are not

*Tab. 3 Microprobe analysis of biotite and secondary chlorite that documents the ferruginous protolith (decreased $K_2O$ content in the biotite 16B indicates a dealkalization during the initial chloritization stages). Biotite is recalculated to 22 and chlorite to 28 oxygens.*

| sample | 16 B | | | | 8413/6A | |
|---|---|---|---|---|---|---|
| | Chl | Chl | Bt (dark ph.) | Bt | Bt | Bt |
| **SiO2** | 24,213 | 23,872 | 34,11 | 33,936 | 33,9239 | 34,132 |
| **Al2O3** | 17,716 | 17,676 | 16,004 | 16,191 | 14,6753 | 15,245 |
| **MgO** | 4,367 | 3,969 | 3,243 | 3,735 | 4,8022 | 5,258 |
| **FeO** | 39,879 | 40,257 | 33,051 | 32,46 | 31,259 | 31,189 |
| **MnO** | 0,18 | 0,215 | 0,041 | 0,035 | 0,1298 | 0,147 |
| **TiO2** | 0 | 0 | 1,506 | 1,504 | 1,882 | 1,774 |
| **CaO** | 0,04 | 0,021 | 0 | 0,033 | 0,064 | 0,275 |
| **K2O** | 0 | 0 | 5,662 | 5,73 | 8,32 | 7,893 |
| **Na2O** | 0 | 0 | 0,153 | 0,162 | 0,189 | 0,145 |
| **total** | 86,395 | 86,011 | 93,769 | 93,788 | 95,345 | 96,309 |
| **Si** | 5,659 | 5,627 | 5,556 | 5,516 | 5,5008 | 5,453 |
| **Al IV.** | 2,341 | 2,373 | 2,444 | 2,484 | 2,5008 | 2,547 |
| **Al VI.** | 3,318 | 2,538 | 0,629 | 0,618 | 0,304 | 0,324 |
| **Mg** | 1,521 | 1,395 | 0,787 | 0,905 | 1,161 | 1,252 |
| **Fe** | 7,794 | 7,936 | 4,503 | 4,412 | 4,238 | 4,167 |
| **Mn** | 0,036 | 0,043 | 0,006 | 0,005 | 0,018 | 0,02 |
| **Ti** | 0 | 0 | 0,184 | 0,184 | 0,229 | 0,213 |
| **Ca** | 0,01 | 0,005 | 0 | 0,006 | 0,011 | 0,047 |
| **K** | 0 | 0 | 1,177 | 1,188 | 1,721 | 1,609 |
| **Na** | 0 | 0 | 0,048 | 0,051 | 0,059 | 0,045 |
| **M/MF** | 0,163 | 0,15 | 0,149 | 0,17 | 0,215 | 0,231 |

characteristic for the biotite accumulations, whereas grunerite is there present more frecquently. For this reason it can be assumed that the biotite binds a certain amount of $Fe^{3+}$. The chemical composition of the biotite (Tab. 3) documents the genesis in the ferruginous - and aluminapoor environment. Considering the classification, the composition of the biotite is close to the end member - *annite* (Guidotti 1984). Comparison of the biotite from two samples (Tab. 3) indicates that a decrease of $Al_2O_3$ is accompanied by an increase of MgO (and MnO), which represents a certain shift from the siderophyllite to phlogopite component in the classification diagrams.

***Quartz*** occurs in variable abundance, some lithotypes of the ferruginous metamorphic schists do not contain it at all. The synsedimentary origin is indicated by lamina enriched with quartz (mostly to the detriment of garnet) and by quartz lenses with apatite or with the rosette-like grunerite inclusions. Quartz with a genetic relationship to the protolith is usually of finer-grained texture. The younger quartz depends upon the mass influx, connected either with granitization or later hydrothermal processes.

***Magnetite*** is scattered throughout the rock with a frequent grain size of 0.2-0.3 mm. In richer ore accumulation 1 mm or greater crystals are not rare. The coarse-grained magnetite occurs mostly at the contacts with garnet. The samples, in which the garnet encloses a quantum of tiny magnetites, these grains are not observed in grunerite or biotite blasts (Fig. 5a). This points to the development during early stages of metamorphism (or resistance or/and recrystallization in the diagenetic stage?), similarly as do the intergrowths of grunerite and magnetite (Figs. 3 and 4). The grunerite porphyroblasts in places enclose larger magnetite crystals, which can indicate a general increase of grain-size during the progressive metamorphic growths.

The magnetite presence depends to a great extent upon the composition of the primary lithologic domain and probably also upon the redox-potential form of the iron inside a sedimentary bed. The appearence of magnetite is the result of a combination of several factors, from which one example can be mentioned: on the contrary to the rock type 3 (sample 16B), in the rock type 4 (sample 16A) there is no magnetite, but it contains more quartz and grunerite. The absence of magnetite is caused mainly by a lower content of iron in the rock, which also has an effect on the composition of grunerite and garnet (Fig. 2). Except the high iron content in the sample with magnetite, from the mineral composition results, that the rock contains also increased amount of $Al_2O_3$ (90 vol. % of garnet, presence of biotite and chlorite). A similar situation also occurs in the 1. rock type.

The mineral assemblages are accompanied by ***apatite*** that frequently reach 1 - 3 vol.%, and in some cases even more. Apatite crystallized from the early metamorphic stages (e.g. inclusion in garnet) to the peak metamorphic stage (coarse crystals in textural relations with the basic metamorphic assemblage). It commonly reaches a size of about 0.15 mm, locally it creates up to 1 mm crystals. Apatite frequently forms fine-grained aggregates in lenses (width about 1-2 mm, length 5-10 mm) where it dominates over quartz. The metamorphic assemblages include also ***allanite*** with crystals up to 0.5 mm. ***Ilmenite*** occurs in these ferruginous schists where magnetite is not present (for example sample 16A). Similarly as in the surrounding gneisses and black metaquartzites, the ***graphite*** (this polymorph of carbon was proved by RTG diffract. analysis by Pulec 1989 and Očenáš in Petro 1998) is a not infrequent admixture of ferruginous schists. The petrographic textures show that it is a metamorphic product of synsedimentary organic substances.

From the ***secondary minerals***, rich-green ***chlorite*** is the typical one. It most frequently fills joints in the garnet; however, it also originates at the expence of biotite. Grunerite use to be replaced mainly near contacts with garnet, from which the chlorite probably gains $Al_2O_3$. The

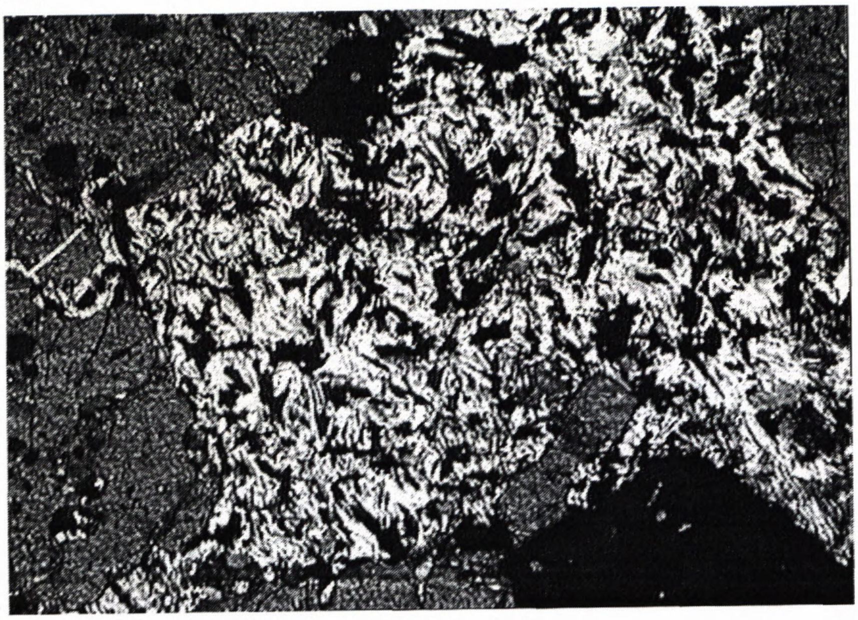

*Fig. 3 Fine-grained aggregate of grunerite (bright phases) and magnetite (black) enclosed in dark garnet matter (//N, 34x magnification)*

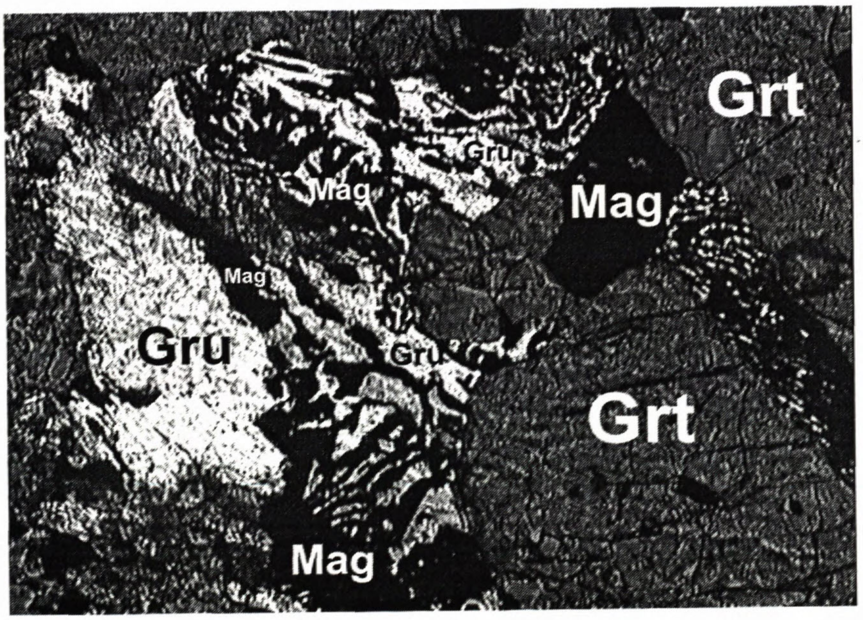


*Fig. 4 Diablastic intergrowth of grunerite with magnetite; the surrounding mass forms mainly garnet (//N, 185x magnification).*

chloritization, probably of the Alpine age, is locally very intensive and, on the contrary, in some domains it totally absents. The assemblage chlorite - magnetite - apatite indicates that along with magnetite apatite also underwent Alpine remobilization. Locally, the pre-Alpine origin of chlorite cannot be absolutely excluded, mainly if it occurs in the form of inclusions in the garnet. (Under middle pressure conditions Fe-chlorite can resists up to a temperature of about 600 °C, as experimentally proven by James et al., 1976). Also, it is not always clear whether part of the post-kinematic chlorite does not originate in periphery zones of the periplutonic effects of the granites. The chlorite can be classified as *brunsvigite* (Tab. 3), which projective point falls near the border with ferruginous ripidolite (sensu Hey 1954). The geochemical criteria for distinguishing of the potential chlorite generations were not recognized. From other secondary minerals we can mention rare *sulfide dissemination*, *carbonates* and clusters of dark *clay minerals*.

## Results and Discussion

### *A) Pre-metamorphic Genesis*

A specialty of the studied locality is, in the first order, the ferruginous protolith. In this relatively small area other unusual elements were also discovered; however, their areal exclusion cannot be confirmed so far. The increased content of apatite, not only in the Fe-rich rocks, is also characteristic. For example, in the fine-grained garnet-muscovite gneiss 1-2 mm thick intercalations containing 30 - 50 % apatite are present, and it is the same in some graphite metaquartzites. The spatial association of graphite metaquartzite and ferruginous gneisses is also noteworthy.

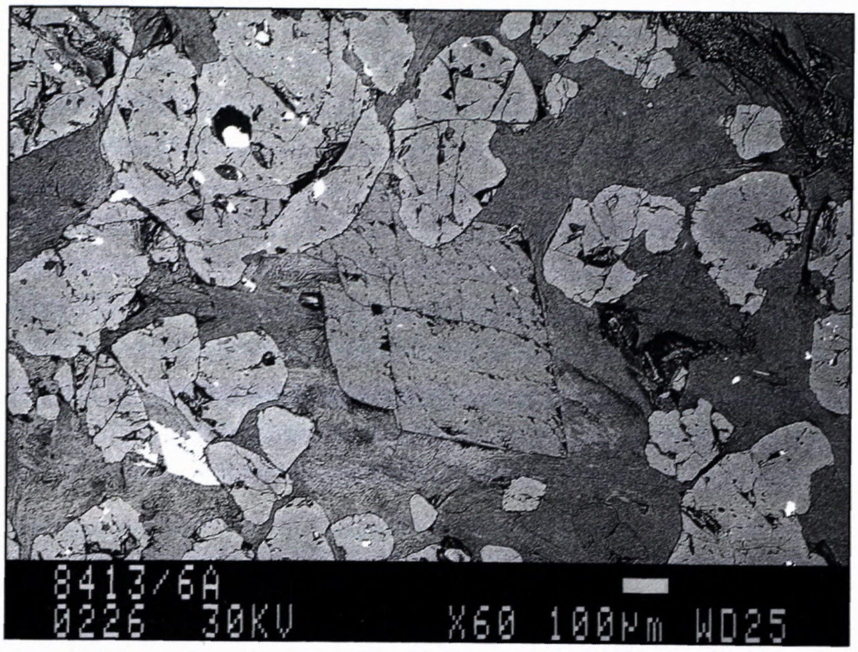


*Fig. 5a Two forms of the grunerite on the BSE image: in the middle part there are euhedral grunerite and fibrous clusters in the biotite (bright phase under grunerite crystal and also more to the left). Bright gray porphyroblasts represent garnet, the shining grains are magnetite.*

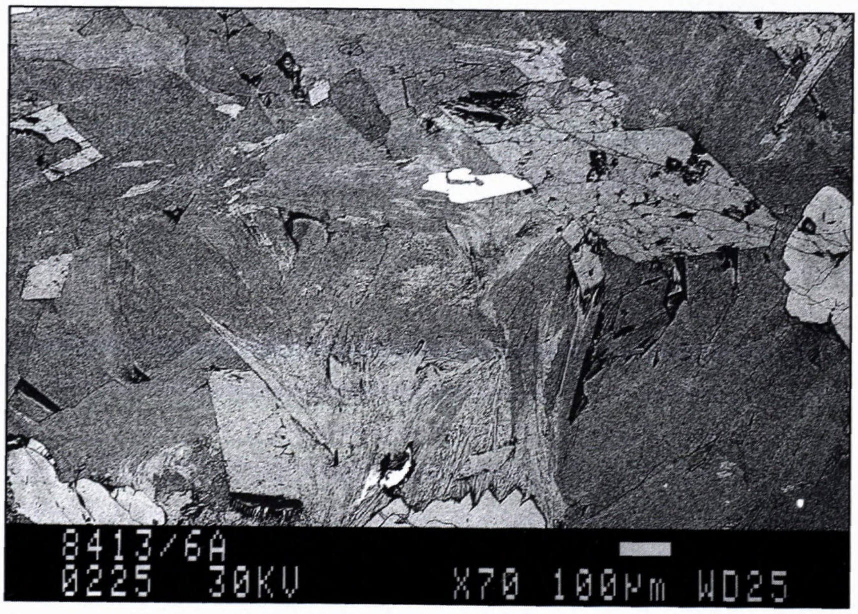


*Fig. 5b Detail of the incomplete grunerite development (brighter phases in the middle over the bottom margin) in a dark gray mass of the biotite (biotite composition in Tab. 3). (BSE images made RNDr. F. Caño on device JSM-840.)*

In the question of genesis of iron formation four basic facies are distinguished - oxide, carbonate, sulfide, and silicate - which can mutually overlap to a certain extent (James, 1954). Discussion regarding the origin of the investigate locality is naturally focused on the carbonate and silicate types. In the carbonate Fe-formations the content of the quartz is relatively constant (about 30-35%), whereas the composition of the Fe-silicate rocks vary significantly (James, 1954), which remains the Kokava deposit. The significant aluminum content resulting from the dominat abundance of the garnet designates the chamosite as the main mineral precursor of the studied rocks. The higher aluminum content is understood as a result of a more mature Phanerozoic crust, contrary to the low content of aluminum in Fe-silicate formation of the Precambrian (James, 1954, Bailey and James, 1973). These facts were also pointed out by Korikovskij et al. (1989); thus, we can join the conclusions of their and Zoubek and Nemčok (1951) work to characterize the Fe-protolith as the Phanerozoic chamosite ironstones. Phanerozoic ooidal ironstones were common in Ordovician and Devonian time (e.g. Petránek, Van Houten 1997), which is characterized by a high relative rate of marine sedimentation on the continents (Ronov at al. 1980).

The potential carbonate precursor of the main ferruginous rocks can also be excluded for other reasons: relicts of the synsedimentary layers of carbonates were not found; the increased content of Ca or Mg that are the usual components of Fe-carbonates (Haase, 1982, Tucker 1985), does not manifest itself in the rock composition; it is hard to explain the mechanism of material input (mainly aluminum) into the potential Fe-carbonate layers, as the metamorphics were formed in the pre-granitization stage. The composition and structures of the rocks reflect fairly well the original lithology; infiltration metamorphism of the carbonates (scarnization) generally results in garnet enriched in the andradite-grossularite composition, pyroxene of diopside-hedenbergite type, Ca-amphibole, epidote etc. (e.g. Němec 1991), thus minerals that are not known from the studied site. However, we can assume some siderite admixture in the Fe-protolith, because the carbonates (mostly of diagenetic origin) are common components of chloritic beds in the iron formation (James 1954, French 1973, Korikovskij et al., 1989).

We can assume that the ferruginous metamorphites originally represented fine-grained beds of pelitic to chemogenic character that were deposited in the environment of the sediments with prevailing psammite lithology (i.e. surrounding gneisses). The higher content of $Al_2O_3$ and eventually $K_2O$ suggests a more significant involvement with the clayey components into the development of ferruginous beds. The chamosite ores are generally considered as near-shore sediments with a diagenetic origin (Tucker 1985); however, there is a lack of the data about a more detailed elaboration about concrete paleoenvironment or sedimentary source. Considering the unique occurrence of the metaferrolites in a broad regional scale, it is probable that a certain specialty of the shallow-water depositional environment played its role, too. It can be attributed, for example, to a bay or a deltaic system prograding to the shelf zone. The accumulation of $P_2O_5$ reminds, in certain features, of accumulation of shallow-marine phosphorite that commonly is associated with limestones, sandstones, ferruginous sediments and black shales (Kukal 1991). The source of phosphor probably originates from calcareous shells of microorganisms. The minor phases as organic matter (changed to graphite), apatite, ilmenite and part of the magnetite can be considered for relicts from deposition, diagenetic and/or early metamorphic phase of ferruginous rocks development.

Within the rock-complex surrounding the ore deposit there are rarely found amphibole-clinozoisite schists. They are made of as much as 2/3 of clinozoisite, further contain amphibole of actinolite type, quartz, biotite, as well as ubiquitous tiny titanite grains. The clinozoisite belongs to the basic metamorphic assemblage, but it also partly takes place in corrosive reactions. The rock represents an unusual petrographic type that probably belongs to the group of hedenbergite - clinozoisite - quartzite schists described by Korikovskij et al. (1989). The authors recognized the source material as psammite enriched with Ca and eventually with Fe. From our standpoint it seems that the protolith was represented more probably by clayey - calciferous material, which is indicated by the low content of alkalies - $K_2O$ occurs only in biotite and a $Na_2O$-bearing mineral is not present at all (for example plagioclase). It can be suggested that these rocks are of similar origin to the calc-silicate hornfels with metamorphic assemblage amphibole - clinopyroxene (diopside-hedenbergite type) ± clinozoisite, which are occasionally found in the Kohút massif (Vrána 1964). The rocks with clinopyroxene signalize sporadic pre-metamorphic carbonate admixture in the highly metamorphosed "hybrid" rock-complex of the Kohút zone. The fact that these rocks also contain magnetite, and that the clinopyroxene represents hedenbergite is in accordance with the overall ferruginous character of the Kokava site.

### *B) Metamorphic Processes and the Questions of the Magnetite Mineralization*

The studied area belongs to a polymetamorphosed crystalline complex, where three metamorphic events took place. Regional metamorphism, most probably of Hercynian age, represents the basic metamorphic event (M1). This was followed by several, often unclear, mutually overprinting periplutonic phases of the Carboniferous granitoids, from which the effects of the acid pegmatite granites (M2) are the best distinguishable. The partial reworking of the regionally-metamorphic mineral parageneses caused by younger granitoid phases is a characteristic phenomena of the given area. Although such an importance cannot be attribute to this stage as Gubač (1957) does. In the ferruginous schists the periplutonic stage is manifested by the local development of the biotite, quartz and probably a certain portion of the skeletal grunerite is also developed there.

The Alpine metamorphic processes (M3) are shown in the ferruginous mineral assemblages mainly by chloritization, silicification, partly by sulfide mineralization, and carbonization etc. An intensive garnet cataclasis takes place locally in rheologically weaker domains, mostly in positions where quartz is abundant. In comparison with other areas of the southern Veporicum realm the Alpine thermal reworking in this area of the hybrid zone is not too significant. This is also indicated by the late Hercynian K/Ar and Rb/Sr ages of micas from the migmatized gneisses near the Chorepa saddle (Cambel et al., 1986).

The study of the ferruginous rocks indicate that the metamorphic reactions of the M1 stage strongly depended on the original geochemical microdomains (there is no pronounced metamorphic segregation as in the common metapelites). Similarly, it can be inferred that the original redox-potential of the individual positions was not considerably changed, and it greatly determines the character of later recrystallization (for example the relationship of the ilmenite and magnetite or grunerite and magnetite). The chamosite is considered to be the most likely primary precursor of the garnet, as assumed by Korikovskij et al. (1989).

The grunerite precursor is less apparent, but it was probably generated in several ways. In the cases where grunerite (mostly the needle-like swarms) intergrow with quartz, in part of the porphyroblasts, eventually in overgrowths with magnetite (Figs. 3 and 4), the generation of grunerite through the reaction of siderite with quartz can be expected. (If this case happened, then the content of the quartz probably significantly exceeded the Fe-carbonate content, which is absent in the primary mineral assemblages). The grunerite, frequently in the skeletal crystals (Fig. 5) grown within the biotite mass, could also represent the minnesotaite-phases in a stilpnomelane matrix. Stilpnomelane is the most probable biotite precursor and since it has a lower content of $Al_2O_3$, than the biotite, the grunerite could be generated, along with a high content of $Fe^{2+}$ in the system, as a byproduct of this transformation (Miyano and Klein, 1989). A similar situation can also take place in the case where there is a lack of aluminum and an abundance of iron (in the simplified reaction "chlorite + quartz = garnet"), compensated by the production of grunerite. However, in many cases and in accordance with actual observations (Beukes 1973, Klein 1982, Bayley and James 1973) also others, more complex reactions of several ferruginous reactants can be inferred.

The study case of the grunerite - garnet schists with - and without magnetite differs from the example of grunerite - garnet schists given by Korikovskij et al. (1989). Fig. 2 illustrates how the iron content of garnet and grunerite increase at the expense of the Mn and Mg contents in the sample with magnetite, whereas in the work of Korikovskij et al. (1989, see the sample HD-32 and HD-23 in Tabs. 1 and 2) it is to the contrary. The controversy of the both studies suggests that the presence/quantity of the magnetite is not generally related to the indicated geochemical parameters. However, we propone the idea that the presence of the magnetite is stimulated by the higher aluminum character of the protolith, where also the $Fe^{3+}$ form is probably more abundant. In the case of the Kokava locality, the relationship between magnetite content and degree of metamorphosis has not been proven.

Generally, it seems that the main mass of the magnetite was created during the progressive period of M1, less during its peak stage (some of the marginal garnet zones do not contain magnetite) or in the process M2. It can be inferred that under those conditions the crystallization system was already freed of the "surplus" 3-valent iron. An influence of the potential reducing effects of the organic substance was not observed. The presence of magnetite in the rocks with graphite can be explained by the fact that a part of the magnetite content was already created in the diagenetic/early metamorphic stage and the gradual oxidation of the organic substance does not proceed from degradation of the magnetite. (James 1954, published several cases of diagenetic magnetite generation in the presence of decaying organic substance.) In the case of the ilmenite inclusions in garnet (our sample 16A or sample HD-23 taken from Korikovskij et al., 1989) we similarly infer its pre- to early-metamorphic origin, which indirectly points out the primary absence of the magnetite.

Because of the uncertain $E_h$, dependence upon the $p_{H2O}$, rock composition, type of geological buffer etc., the more exact *determination of p-T conditions* of the metamorphism in the ferrous formations remains only very informative (for example Fonarev, 1985). The stability field of the Fe-cummingtonite - grunerite has a wide temperature range, from 350 °C to about 760 °C; it is similar also with the determination of the pressure (Lattard and Evans 1992, Fonarev 1981, Miyano and Klein 1986). The bimineral exchange geothermometry cannot be used (Ferry and Spear 1978, Perčuk and Lavrenteva 1983) because these systems are not calibrated for the ferruginous protolith (mainly Fe-biotite causes too high temperature evaluations). There have not been identified ferrohyperstene or olivine in the studied rocks, and the preliminary outlining of the metamorphic conditions can be made only with use of the petrogenetic grid or by looking for an analog rocks of other regions. The reaction "grunerite = fayalite + quartz + $H_2O$" runs out at middle pressure conditions (about 4 - 8 kb) at 650 °C - 700 °C (Miyano and Klein 1986), or at about 570 °C - 600 °C (Fonarev 1985). The maximum thermal stability of the pure grunerite in the invariant point of the reaction "ferrosilite = fayalite + quartz" is set at 650 °C at the pressure of 9.7 kb (Lattard and Evans, 1992). At a pressure of 2 kb the grunerite is stable up to 550 °C and the temperature, along with the pressure, continuously increases to the mentioned invariant point (Lattard and Evans, 1992). However, from real and experimental systems it results that the grunerite stability increases with an increasing content of MgO. On the basis of several data (Fonarev 1985, Miyano and Klein 1986, Haase 1982, etc.) we assume that the investigated ferruginous rocks were metamorphosed under the conditions of the middle (up to higher) part of the amphibolite facies (i.e. about 600 ± 50 °C).

Similarly, as indicated by Korikovskij et al. (1989), the petrological reconnaissance of the surrounding rocks revealed a higher iron content in the rock forming minerals than is common on a regional scale. The preliminary data obtained from the almost unzoned garnets (the homogenization is probably caused by diffusion processes at temperature over 550 °C, Spear 1991) from the garnet - biotite gneisses showed that the conditions of the basic regional metamorphism (M1), according to the method of Perčuk and Lavrentevova (1983) and Ghent and Stout (1981), were about 675 - 715 °C and a pressure of about 5kb (Kováčik, 1998). This data falls into span of the metamorphic conditions in the southern Veporicum migmatites (Siman et al., 1996). However, the systematic abundance of muscovite and absence of K-feldspar and Al-silicates may indicate that metamorphic temperatures in these gneisses did generaly not exceed 650 °C (Chatterje, Johannes, 1974). Frequent discontinuous incremental zones in the garnet margin of the metapelites are considered the result of the thermal - mass effects of the acid granites (terminal part of M2), which, according to preliminary geothermometric calculations, show similar or a little bit lower thermal condition than the M1 stage.

*Acknowledgement:* I am thankful to Prof. RNDr. A. Vozárová, DrSc. for her careful review. The impulse for the writing of this work comes from RNDr. M. Petro and ing. M. Radvanec, CSc.

## References

Bailey, R.W. a. James, H.L. 1973: Precambrian iron-formation of the United States. Econ. Geol., 68, 934-959

Beukes, N.J. 1973: Precambrian Iron-Formation of Southern Africa. Econ. Geol., 68, 960-1004

Bezák,V.1988: Tectonic development of the south-western part of Veporicum, West Carpathians. (In Slovak, Engl. summary.) Min. slovaca, 20, 131-142

Cambel, B., Korikovskij, S.P., Krasivskaja, I.S. &. Arakeljanc, M.M. 1986: Opredelenie vozrasta retrogradnovo metamorphizma v Zapadnych Karpatach K-Ar metodom po muskovitam. Geol. Zb. Geol. carpath., 36, 683-701

Chatterje, N. D. & Johannes, W., 1974: Thermal stability and standard thermodyname properties of syntetic $2M_1$-muscovite. Contr. Miner. Petr., 48, 89-114

Ferry, J.M. &. Spear, F.S.1978: Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. Contrib. Miner. Petrol., 66, 113-117

Fonarev, V.I. 1981: Thermodynamic functions of cummingtonite solid solutions: Geochem. Internat., 18, 1-11

Fonarev, V.I. 1985: Experimental study of equilibria involving Fe-Mg solid solutions, geological thermo-baro-oxometry. Geol. zb. Geol. Carpath., 36, 597-617

French, B.M. 1973: Mineral Assemblages in Diagenetic and Low-Grade Metamorphic Iron-Formation. Econ. Geol., 68, 1063-1074

Gubač, J. 1957: Paragenesis of the skarn bed near Kokava nad Rimavicou. (In Slovak, Engl. summary.) Geol. práce, Zprávy, Bratislava, 11, 89-99

Ghent, E.D. &. Stout, M.Z. 1981: Geobarometry and geobarometry of Plagioclase-Biotite-Garnet-Muscovite assemblages. Contrib. Miner. Petrol., 76, 92-97

Guidotti, Ch.V. 1984: Micas in metamorphic rocks. In Bailey, S.W. (ed.): Micas. Reviews in Mineralogy, 13, 357-468

Haase, C.S. 1982: Metamorphic petrology of the Negaunee Iron formation, Marquette District, Northern Michigan: Mineralogy, Metamorphic reaction, and phase equilibria. Econ. Geol., 77, 60-81

Hey, M.H. 1954: A new review of chlorites. Mineral. Mag.,30, 277-292

James, H.L. 1954: Sedimentary facies of iron-formation. Econ. Geol., 49, 235-293

James, R.S., Turnock, A.C. & Fawcett, J.J. 1976: The stability and phase relations of iron chlorite bellow 8,5kb $pH_2O$. Contrib. Min. Petr., 56, 1-25

Korikovskij, S.P., Dupej, J. &. Boronichin,V.A. 1989: High Fe metasediments from Kokava nad Rimavicou (Veporicum, Central Slovakia). (In Slovak, Engl. summary.) Min. slovaca, 21, 251-258

Kováčik, K. 1998: Contribution to petrogenesis of the area. In: Petro, M. (ed.): Kokava nad Rimavicou - graphite. (In Slovak). Open-file report, Geofond Bratislava, 1-25

Klein, C. 1982: Amphiboles in iron-formations. In Veblen, D. R. a. Ribbe, P.H.: Amphiboles, Review in Min.,9B, 88-97

Kukal, Z. 1991: Fe-, Mn-, and P-rich marginal facies of black shale formation. Proc. Internat. Conference IGCP 254, Rabat

Kuthan, M., Biely, A., Boehm, V., Čechovič, V., Fusán, O., Hovorka, D., Mazúr, E. &. Regásek, F. 1963: Explanations to geological map of ČSSR 1 : 200 000, M-34-XXXII Zvolen. (In Slovak.) Geofond-Bratislava, 131 s.

Lattard, D. &. Evans, B.W. 1992: New experiments on the stability of grunerite. Eur. J. Miner.,4, 219-238

Leake, B.E., Woolley, A.R., Arps, Ch.E., Birch,W.D., Gilbert, M.Ch., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev,V.G., Linthout, K., Laird, J., Mandarino, J.A., Maresch, W.V., Nickel, E.H., Rock, N.M., Schumacher, J.C., Smith, D.C., Stephenson, N.C., Ungaretti, L., Whittaker, E.J. &. Youzhi, G. 1997: Nomenclature of amphiboles: Report of Subcommitee on Amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. Am. Miner., 82, 1019-1037

Miyano,T. & Klein, C.1986: Fluid behavior and phase relations in the system Fe-Mg-Si-C-O-H: application to high grade metamorphism of iron-formations. Am. J. Sci., 286, 540-575

Miyano, T. &. Klein, C.1989: Phase equilibria in the system $K_2O$-FeO-MgO-$Al_2O_3$-$SiO_2$-$H_2O$- $CO_2$ and the stability limit of stilpnomelane in metamorphosed Precambrian iron-formations. Contrib. Min. Petrol., 102, 478-491

Němec, D. 1991: Regional typization of the iron skarns of the Bohemian-Moravian Heights (Českomoravská vrchovina). Acta Mus. Moraviae, Sci. nat., 76, 51-82

Perčuk, L.L. &. Lavrentjeva, I.V. 1983: Experimental investigation of exchange equilibria in the system cordierite-garnet-biotite. In: Saxena, S.K. (ed.): Kinetics and Equilibrium in mineral reactions. Adv. phys. geochem., 3, Springer Verlag, New York.., 199-239

Petránek, J. & Van Houten, F.B. 1997: Phanerozoic ooidal ironstones. Czech Geological Survey Special Papers, 7, Praha, 71pp.

Petro, M. 1998: Kokava nad Rimavicou - graphite. (In Slovak). Open-file report, Geofond Bratislava

Pulec, M. et al., 1989: Occurrence of crystalline graphite in paragneisses, granitoides, pegmatites and aplites of the crystalline complex of the West Carpathians. (In Slovak, Engl. summary.) Min. slovaca, 21, 53-57

Radvanec, M., 2000: Metapelite, amphibole schist, and origin of magnetite-graphite mineralization in Veporicum near Kokava nad Rimavicou. (In Slovak, Engl. summary.) Miner. slovaca, 32, 1-16

Ronov, A.B, Khain, V.E., Balukhovsky, A.N. & Seslavinsky, K.B. 1980: Quantitative analysis of Phanerozoic sedimentation. Sedim. Geol., 25, 311-325

Siman, P., Johan, V., Ledru, P., Bezák, V. & Madarás, J. 1996: Deformation and p-T conditions estimated in "layered migmatites" from southern part of Veporicum basement. Slovak Geol. Mag., 3-4/96, 209-213

Spear, F.S. 1991: On the interpretation of peak metamorphic temperatures in light of garnet diffusion during cooling. J. met. Geol., 9, 379-388

Šuf, J. 1937: Survey of economic mineral repositories with respect to geological setting in the surroundings of Hnúšťa in Slovakia. (In Czech.) Bánský svět, 2-4, Praha

Šuf, J. 1938: Report on geological setting and mineral deposits in the surroundings of Kokava in Slovakia. (In Czech.) Věstník SGÚ, Praha, 91-103

Tucker, M.E. 1985: Einführung in die Sedimentpetrologie. Ferd. Enke Verlag, Stuttgart, 265

Vrána, S. 1964: Petrogenese des Veporiden Kristallin in der Umgebung von Slavošovce. (In Czech, German summary.) Geol.práce, Zprávy 33, 5-30

Zoubek, V. &. Nemčok, A. 1951: Report on magnetite deposit near Kokava n./Rim. (In Slovak.) Open-file report, record office GÚDŠ, 13 pp.