

# Petrogenesis of the calc-silicate skarns from Garby Izerskie, Karkonosze-Izera block

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## ABSTRACT:

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The exocontact skarns of the Garby Izerskie mountain group in Izera Mts (Sudetes, Southern Poland), which occur as intercalations in hornfelsed schists, were characterized by means of the paragenetic analysis. A number of parageneses were found, consisting of hedenbergite, grossular, wollastonite, vesuvianite, albite, actinolite, calcite, epidote, quartz and fluorite. The skarn minerals formed in four stages of different physico-chemical conditions. Stage I, which took place during the prograde metamorphism in a quasi-isochemical system, resulted in crystallization of hedenbergite (ca. 500°C), wollastonite and grossular (ca. 600-650°C) at  $p_{\text{static}} = p_{\text{total}} = p_{\text{fluid}} = 2$  kbar. The latter two minerals formed at peak metamorphic temperatures, when at ca. 650°C the fluids had a CO<sub>2</sub> concentration of 30 molar percent. Stage II began the retrograde metamorphism, also in a quasi-isochemical system, and resulted in the origin of vesuvianite, actinolite, prehnite, epidote and calcite pseudomorphs after wollastonite. Vesuvianite was the earliest retrograde mineral, which had probably started growing when the temperature decreased below 600-580°C. Water activity increased during retrograde metamorphism at the expense of the CO<sub>2</sub> activity, whose concentration was lower than 2 molar percent during the prehnite formation. Stage III comprised mainly silicification which began at least at 410°C in an allochemical system; it could have partly overlapped stages I and II in time. Stage IV, which was mainly the fluorine metasomatism at 360 to 110°C developed also as an allochemical process. Thus, the skarns from Garby Izerskie are high-temperature calc-silicate varieties of the pyroxene-garnet-wollastonite type with the subsequent alteration of the calcic plagioclase to the sodic one, and the silica and fluorine metasomatism.

**Key words:** Contact metamorphism, Skarns, Silica metasomatism, Fluorine metasomatism

## INTRODUCTION

The skarns from Garby Izerskie have been characterized till present only in a preliminary mode from a petrographic point of view (SZALAMACHA & SZALAMACHA 1966), and afterwards brief petrogenetic suggestions have been given by KOZŁOWSKI (1978). This paper is intended to introduce the results of a study focused on the optical petrography and mineral chemistry of these skarns. From the data obtained from microscope observations of the relationships between

the skarn minerals the course of geochemical processes was reconstructed and the physico-chemical conditions during the contact metamorphism at Garby Izerskie were deduced.

## ANALYTICAL PROCEDURE

The rocks were examined in thin sections by optical microscopy. Selected samples were analysed in the WDS system by means of an ARL electron microprobe

at the University of Tübingen. The data from the electron microprobe have been corrected by use of the Magic IV and ZAF systems.

In this study the following abbreviations are routinely used:

p – static pressure = fluid pressure (kbar);  
 T – temperature (°C);  
 X<sub>CO<sub>2</sub></sub> – molar fraction of carbon dioxide;  
 Act – actinolite;  
 Ab – albite;  
 An – anorthite molecule in plagioclase;  
 And – andradite;  
 Cc – calcite;  
 Czo – clinozoisite;  
 Di – diopside;  
 Ep – epidote;  
 Fe-Act – ferroactinolite;  
 Hd – hedenbergite;  
 F – fluorite;  
 Gr – grossular;  
 Qtz – quartz;

Pl – plagioclase;  
 Prh – prehnite;  
 Tr – tremolite;  
 Wo – wollastonite;  
 Ves – vesuvianite;  
 Zo – zoisite.

#### THE GEOLOGY OF THE KARKONOSZE-IZERA BLOCK

The Karkonosze massif, which outcrops in the Sudetes Mts having a surface extent about 70 km long (E – W) and are 8 – 20 km wide, is a Variscan granitoid intrusion with a composite metamorphic cover. The age of this intrusion is 300-320 Ma (BORKOWSKA & *al.* 1980). The northern metamorphic cover in the Izer area consists of Izer gneisses and Rumburk granites having ages of 460 and 500 Ma, respectively. The gneissic and granitic complex of the Izer area is divided by four parallel mica-chlorite schist zones, formerly having been clayey sediment of possibly Algonkian age (SMULIKOWSKI 1958). At the southern bor-

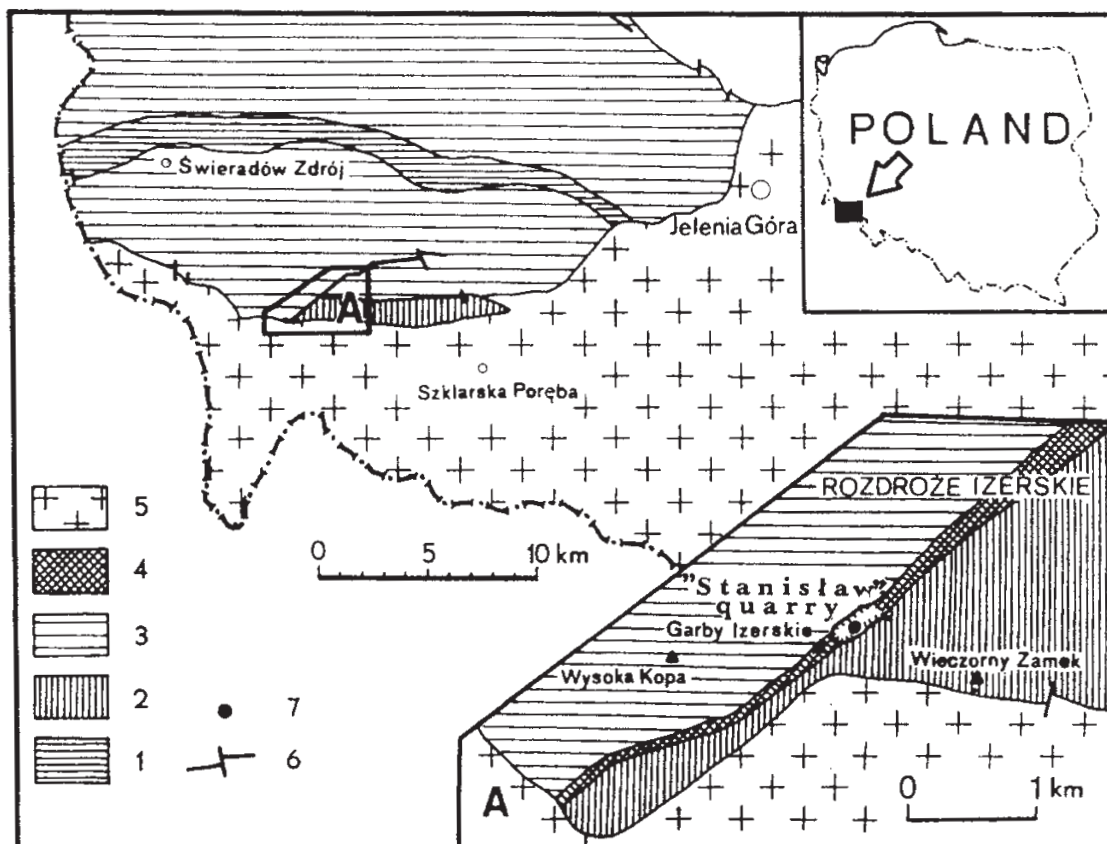


Fig. 1. Sketch geological map of part of the Karkonosze-Izera block, after A. KOZŁOWSKI (1978); 1 – mica schists, 2 – hornfelses, 3 – Izer gneiss and Rumburk granite, 4 – quartz vein, 5 – Karkonosze granite, 6 – faults, 7 – skarn location; A – Rozdroże Izerskie fault zone

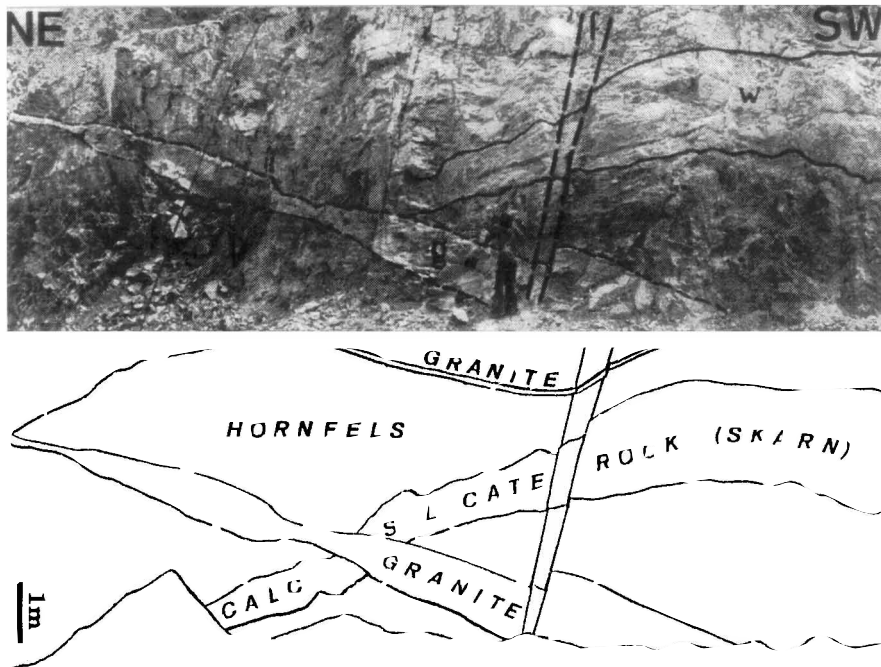


Fig. 2. The South-eastern wall of the "Stanisław" quarry at Garby Izerskie, the photo is after A. KOZŁOWSKI (1978)

der of the Izera area (Text-fig. 1), the schist zone of Szklarska Poręba, which contacts with the Karkonosze intrusion, was altered by thermal metamorphism in hornfelses. Northwards, the Czerniawa – Stara Kamienica, Mirsk and Złotniki Lubańskie zones, consist of schists regionally metamorphosed under greenschist facies conditions, in the quartz – albite – almandine subfacies (KOZŁOWSKI 1974).

The contact of the Karkonosze massif with the gneisses and hornfelses of the Izera area near Jakuszyce to the west of Szklarska Poręba is in part intrusive, and in part tectonic along the dislocation zone of Garby Izerskie – Rozdroże Izerskie (Text-fig. 1). This dislocation is several km long with SW – NE strike. The mineralised zone connected with this dislocation is 100-400 m wide and dips steeply to SE. The SW end of the zone contacts with the Karkonosze granite and its NE end may be observed as a diffused silicification at Mt. Jastrzębia. The zone was divided by a number of transversal dislocations into blocks, then shifted. The wall rocks on the SE side of the zone (Text-fig. 2) consist of hornfelsed schists bearing andalusite and pinite, with intercalations of skarns (SZAŁAMACHA & SZAŁAMACHA 1966, KOZŁOWSKI 1978). The intercalations of these skarns have a variable thickness from ca. 20 cm up to 1 m and can be seen at the open "Stanisław" mine at Garby Izerskie, which is about 5 km north of the contact. These skarns were formed in the

exocontact zone of the Karkonosze intrusion, and therefore are exoskarns (FILA 1994). The NW side is built up of blastomylonitic and fine-grained gneisses with biotite blasts; the eastern part of the dislocation zone cuts several varieties of gneisses. The dislocation zone is mineralised with quartz and a continuous increase in quartz content can be observed both in gneiss and hornfels toward the center of the zone, to form a monomineral quartz rock (LEWOWICKI 1965, SZAŁAMACHA 1965, KOZŁOWSKI 1978).

## PETROGRAPHY

The blastic and blastomylonitic structures, observable in microscope, are characteristic for these skarns. Their texture is directional and laminated, with microfolds of various size. The laminae consist either predominantly of quartz, or of calc-silicates. The quartz layers are built of interlocking quartz blasts. Large- and medium-sized blastic quartz (maximum dimension of approximately 3 mm) replaced other minerals as evidenced by a number of inclusions of different minerals in quartz. These quartz blasts have commonly undulose light extinction resulting from stress. The silicate layers have variable mineral composition. The mineral assemblages in the calc-silicate layers appear to be controlled by the

initial bulk compositions of the individual layers. Sometimes two mineral assemblages were observed in one thin section. This situation may reflect local variations in the initial bulk composition with domains smaller than a thin section. Generally, the following types of silicate layers were distinguished:

1) **Pyroxene – plagioclase layers** (Pl. 1, Fig. 1), which consist of pyroxene (max. 2 mm) and plagioclase (andesine) xenoblasts (max. 30  $\mu\text{m}$ ).

2) **Wollastonite – pyroxene – plagioclase layers** which are partly built of wollastonite fibroblasts (maximum width of 2  $\mu\text{m}$  and length sometimes exceeding 10  $\mu\text{m}$ ), pyroxene xenoblasts (variable dimensions up to 10  $\mu\text{m}$ ), irregular poorly translucent plagioclase (albite), and quartz (Pl. 1, Fig. 2-3). Locally, pyroxene, wollastonite, albite and quartz were replaced by fluorite (Pl. 1, Figs 3-4a). In general, the latter corroded in places all the skarn minerals and filled fissures developed between blasts. The above-mentioned silicate minerals were strongly fractured and cut by quartz veinlets of different orientation. In some parts of the investigated layers pyroxene and wollastonite were replaced by irregular calcite aggregates associated with anhedral fluorite and rounded quartz (Pl. 1, Fig. 4).

3) **Wollastonite – pyroxene layers with nest-like garnet swellings.** These layers are built of wollastonite fibroblasts, pyroxene xenoblasts and quartz xenoblasts of dimensions similar to those given above. At the contacts between the wollastonite-pyroxene layers and nest-like garnet swellings, the presence of the pseudomorphs of calcite after wollastonite was noted (Pl. 1, Fig. 5). Such calcite is associated with rounded quartz grains of the diameter of ca. 3  $\mu\text{m}$ . Nest-like swellings of the diameters up to several centimetres are mainly built of the garnet granoblasts. Pyroxene, quartz and irregular calcite blasts were observed in lesser quantities. In several areas the alteration of wollastonite, pyroxene and garnet into vesuvianite was observed (Pl. 1, Figs 6-7). The associated fine-grained masses contain relics of pyroxene and garnet, and automorphic sphene. Sphene was also identified in association with unaltered garnet and pyroxene. Sometimes, at the contact zones between the wollastonite-pyroxene layers and the garnet swellings, signs of fluorine metasomatism can be identified. Wollastonite, pyroxene and garnet were replaced there by anhedral fluorite and calcite. The grains building the layers with swellings are commonly strongly fissured and some of these fissures were filled by either quartz or calcite. Locally, in the strongly silicified parts of the rock, prehnite blasts can

be found. This mineral replaced garnet and filled fractures in the layers.

4) **Garnet – pyroxene layers**, which are built of garnet, pyroxene and quartz blasts of dimensions similar to those described above. Local alterations of the garnet and pyroxene grains were observed. Sometimes, aggregates of amphibole associated with amoeboid calcite were found in fine-grained masses as the alteration products of pyroxene (Pl. 1, Fig. 8). Some parts of the skarns built of garnet – pyroxene layers were extensively silicified, with the garnet and pyroxene blasts having been strongly fissured with the fissures filled with calcite and quartz.

5) **Garnet – epidote – calcite layers**, which are thin (max. 70  $\mu\text{m}$ ), probably of reduced thickness due to strong silicification. Epidote and irregular calcite were found as products of garnet alteration (Pl. 1, Fig. 9). Epidote occurred as fine globular grains, and only occasionally as prismatic crystals of up to 8  $\mu\text{m}$  in length.

In the skarns from Garby Izerskie the following parageneses were found, as resulted from the detailed analysis of the relations between the skarn minerals:

1. **Pyroxene – plagioclase (andesine)**
2. **Pyroxene – wollastonite – garnet – plagioclase (albite)**
3. **Pyroxene – wollastonite – garnet – vesuvianite**
4. **Amphibole – calcite**
5. **Epidote – calcite – quartz**
6. **Calcite (pseudomorphs after wollastonite) – quartz**
7. **Calcite – fluorite – quartz.**

## COMPOSITION OF THE SKARN MINERALS

### Pyroxene

The clinopyroxene from the skarns has a relatively wide variation of the element composition, as evidenced by 17 representative analyses from among 30 analyses made (Table 1). Nevertheless, the analyses in the pyroxene classification plot located in the **hedenbergite** area and showed certain differences in the content of  $\text{Fe}^{2+}$  and Mg (Text-fig. 3).

### Wollastonite

Wollastonite is a very characteristic mineral for the thermally altered limestones which originally contained

	Hd 4	Hd 9	Wo 1	Gr 4	Gr 9	Prh 1	Act 1
SiO <sub>2</sub>	48.41	52.51	51.20	39.44	37.12	42.89	50.96
TiO <sub>2</sub>	0.00	0.01	0.00	0.07	0.18	0.00	0.31
Al <sub>2</sub> O <sub>3</sub>	0.00	1.95	0.08	22.83	13.04	23.52	2.13
FeO	28.39	10.76	0.39	0.46	13.66	0.47*	17.99
MnO	0.54	0.60	0.09	0.00	0.57	0.15	0.42
MgO	0.01	9.72	-	-	0.12	0.00	12.65
CaO	22.49	23.66	48.17	36.29	34.34	27.27	11.93
Na <sub>2</sub> O	0.00	0.72	0.02	0.15	0.00	0.08	0.89
K <sub>2</sub> O	0.02	0.00	0.03	0.00	0.00	0.00	0.57
"H <sub>2</sub> O"	-	-	-	-	-	4.29	1.64
F	-	-	-	-	-	-	0.88
Si	2.00	1.99	5.96	5.96	6.08	3.00	7.58
Ti	0.00	0.00	0.00	0.01	0.02	0.00	0.04
Al	0.00	0.08	0.01	4.07	2.52	1.94	0.37
Fe <sup>+2</sup>	0.98	0.34	0.04	0.06	1.87	0.03#	2.24
Mn	0.02	0.02	0.01	0.00	0.08	0.01	0.05
Mg	0.00	0.55	-	-	0.03	0.00	2.81
Ca	1.00	0.96	6.01	5.88	6.03	2.04	1.90
Na	0.00	0.05	0.00	0.04	0.00	0.01	0.26
K	0.00	0.00	0.00	0.00	0.00	0.00	0.11
OH	-	-	-	-	-	2.00	1.63
F	-	-	-	-	-	-	0.05

Table 1. Chemical composition of hedenbergite, wollastonite, grossular, prehnite and actinolite from Garby Izerskie (analyses in weight percent, crystallochemical formulae in atoms p.f.u.); \* - Fe<sub>2</sub>O<sub>3</sub>, # - Fe<sup>3+</sup>

an admixture of quartz or were metasomatically enriched in silica. On the basis of 20 analyses it was shown that the chemical composition of the wollastonite from Garby Izerskie was very similar to its theoretical composition (Table 1).

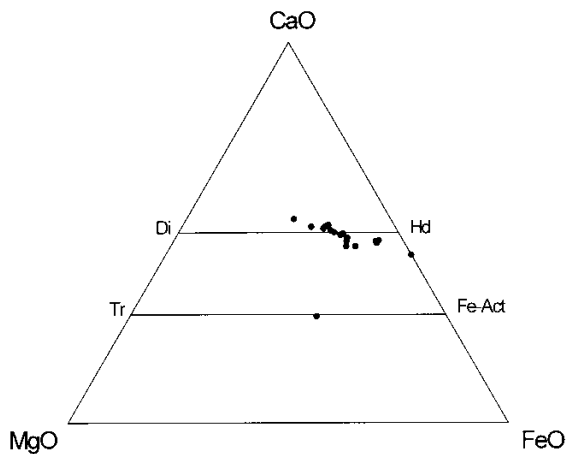


Fig. 3. Molar percent CaO – MgO – FeO plot for clinopyroxene and amphibole; abbreviations: Di – diopside, Hd – hedenbergite, Tr – tremolite, Fe-Act – ferroactinolite

**Garnet**

Considering 8 representative analyses from among 30 analyses made, it is obvious that the garnets from Garby Izerskie are of the **grossular** composition (Table 1 and Text-fig. 4).

Chemical analyses showed a low titanium content, despite the fact that the environment of the grossular was sufficiently rich in titanium for rutile crystallization. This may be evidence of titanium being reluctantly taken into the garnet structure due to unfavourable conditions, though titanium was present in the skarn formation medium.

**Plagioclase**

Two different compositions of plagioclase were identified, the first one, in pyroxene – plagioclase layers was, **andesine** (An<sub>32</sub> – An<sub>49</sub>), and the second one, in wollastonite – pyroxene – plagioclase layers, was **albite** (An<sub>10</sub> – An<sub>1</sub>).

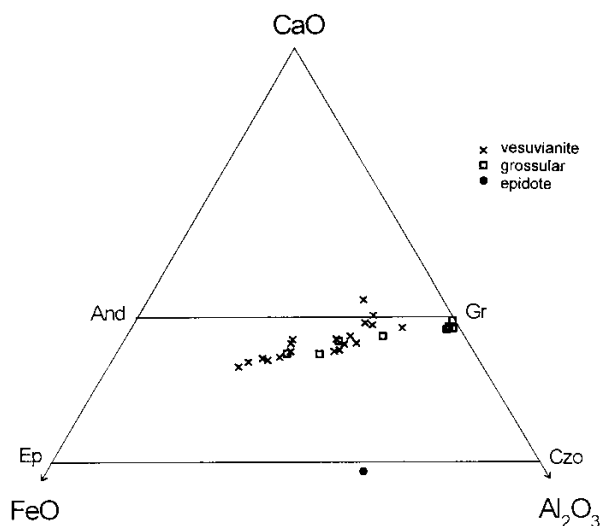


Fig. 4. Molar percent CaO – Al<sub>2</sub>O<sub>3</sub> – FeO plot for vesuvianite, grossular and epidote; abbreviations: And – andradite, Gr – grossular, Ep – epidote, Czo – clinozoisite, Ves – vesuvianite

### Vesuvianite

Based on 20 analyses it was shown that the vesuvianite from Garby Izerskie has a strongly variable content of certain oxides (Table 2 and Text-fig. 4). The “H<sub>2</sub>O” content was calculated only theoretically from the totals of the analyses, and the results obtained may be less precise than results gained directly by the analytical determination of water.

### Amphibole

It was only possible to perform one analysis (Table 1 and Text-fig. 3), because there were no other blasts of an appropriate size in the investigated preparations. The Mg/(Mg + Fe<sup>2+</sup>) ratio amounted 0.41 and indicated the composition of **actinolite**. The low total of H<sub>2</sub>O and F could result from the sum of analytical errors.

	Ep 1	Ves 1	Ves 2	Ves 5	Ves 6	Ves 14	Ves 18	Ves 23
SiO <sub>2</sub>	38.55	35.20	35.43	35.73	35.11	35.81	35.36	36.05
TiO <sub>2</sub>	0.00	0.46	0.48	0.21	0.54	0.48	0.03	0.61
Al <sub>2</sub> O <sub>3</sub>	21.46	11.21	9.46	12.50	16.76	15.66	19.28	15.44
FeO	13.81*	15.45	18.04	13.39	8.12	10.20	4.12	5.77
MnO	0.17	0.52	0.42	0.50	0.10	0.31	0.08	0.13
MgO	0.00	0.00	0.00	0.00	1.00	0.00	0.38	0.90
CaO	23.38	34.60	34.34	35.27	35.59	35.27	36.62	39.24
Na <sub>2</sub> O	0.05	0.00	0.04	0.00	0.03	0.00	0.08	0.06
K <sub>2</sub> O	0.00	0.00	0.02	0.00	0.03	0.00	0.02	0.02
"H <sub>2</sub> O"	1.87	1.77	1.45	2.16	1.47	1.95	2.87	0.52
F	-	1.36	0.64	0.41	1.99	0.55	2.01	2.17
BaO	-	0.00	0.00	0.00	0.10	0.00	0.00	0.00
Si	3.09	18.77	18.88	18.44	17.63	18.14	17.13	18.27
Ti	0.00	0.18	0.17	0.08	0.20	0.18	0.01	0.23
Al	2.03	6.90	5.94	7.60	9.92	9.35	11.02	9.23
Fe <sup>+2</sup>	0.83#	6.75	8.04	5.78	3.41	4.32	1.67	2.45
Mn	0.01	0.23	0.19	0.22	0.04	0.13	0.03	0.06
Mg	0.00	0.00	0.00	0.00	0.75	0.00	0.27	0.68
Ca	2.01	19.36	19.61	19.50	19.15	19.14	19.01	21.31
Na	0.01	0.00	0.04	0.00	0.03	0.00	0.08	0.06
K	0.00	0.00	0.01	0.00	0.02	0.00	0.01	0.01
OH	1.00	6.16	5.15	7.44	4.92	6.59	9.27	1.76
F	-	2.25	1.08	0.67	3.16	0.88	3.08	3.48
Ba	-	0.00	0.00	0.00	0.02	0.00	0.00	0.00

Table 2. Chemical composition of epidote and vesuvianite from Garby Izerskie (analyses in weight percent, crystallochemical formulae in atoms p.f.u.); \* – Fe<sub>2</sub>O<sub>3</sub>, # – Fe<sup>3+</sup>

**Epidote**

This mineral was observed sporadically and thus only one grain was found to be appropriate for the microprobe analysis (Table 2 and Text-fig. 4). The "H<sub>2</sub>O" content was calculated only theoretically. The total iron from the analysis was calculated as Fe<sub>2</sub>O<sub>3</sub>.

**Prehnite**

The representative analysis is shown in Table 1. The "H<sub>2</sub>O" content was calculated only theoretically. The total iron from the analysis was calculated as Fe<sub>2</sub>O<sub>3</sub>.

**SEQUENCE OF MINERALS AND SKARN PARAGENESIS FORMATION**

On the basis of the microscope investigations it was concluded that the skarns from Garby Izerskie were formed in four stages, characterised by different physico-chemical conditions.

The reactions which occurred during the rock metamorphism were determined under favourable conditions by careful microscope studies. Then, with the help of the isobaric T - X<sub>CO<sub>2</sub></sub> diagrams, and taking into account the chemical compositions of the minerals, the equilibrium data (conditions) of certain reactions were determined. The applied grids might have been used for the specific pressure condition: p<sub>static</sub> = p<sub>total</sub> = p<sub>fluid</sub> = 2 kbar (see HOVER-GRANATH & al. 1983, GOTTSCHALK 1997). HOVER-GRANATH & al. (1983) presented geological arguments which indicated that the lithostatic pressure during the contact event studied by her was ~2 kbar, based on an estimated overburden thickness of 6.2-6.5 km. In the case of the skarns from Garby Izerskie this method of estimating the pressure was not applicable. For the purposes of the study of the skarns from Garby Izerskie, a total pressure of 2 kbar was assumed. This pressure is compatible with the pressure determined by the method of the crossed H<sub>2</sub>O and CO<sub>2</sub> isochores from the investigations of fluid inclusions in garnets and pyroxenes. During the current discussion of the applied petrogenetic diagrams, the iron presence in the mineral structures was not taken into account.

**Stage I**

At the stage I, which was the stage of the prograde metamorphism, the crystallisation of **hedenbergite**, **wollastonite**, **albite** and **grossular** occurred.

The earliest mineral-forming reaction which could be deduced on the basis of the microscope observations of the investigated skarns, is the following one (see Text-fig. 5):

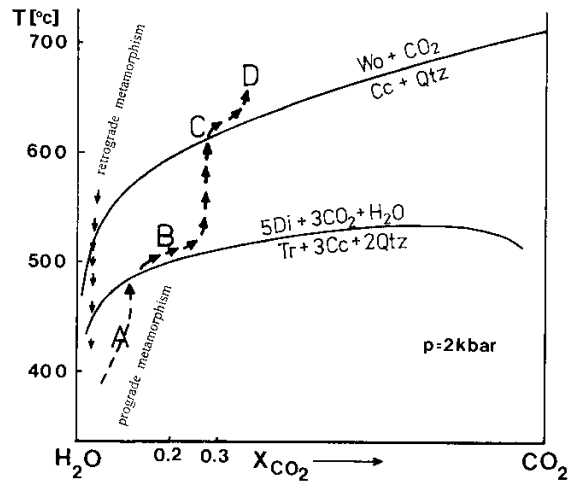
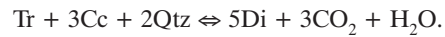
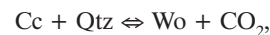


Fig. 5. Plots of 2 kbar - T - X<sub>CO<sub>2</sub></sub> equilibrium data of mineral reactions in the system CaO - MgO - SiO<sub>2</sub> - CO<sub>2</sub> - H<sub>2</sub>O, calculated from thermodynamic data set which was extracted from the experimental equilibrium data of mineral reactions by M. GOTTSCHALK (1997). Arrows represent the possible T - X<sub>CO<sub>2</sub></sub> paths during the metamorphism of the skarns from Garby Izerskie. Prograde metamorphism: A - tremolite formation, B - diopside formation, C - wollastonite formation, D - grossular formation

This reaction was extensively investigated by METZ (1964,1970), EGGERT & KERRICK (1981), DACHS & METZ (1988) and GOTTSCHALK (1997), however, these studies considered pure diopside as the reaction product. The clinopyroxenes from the studied skarns have a hedenbergite composition. Such a reaction could have occurred at temperatures between ca. 430 and ca. 535°C, when the mole fraction of CO<sub>2</sub> was from 0.02 to 0.75. The reaction resulting in the formation of hedenbergite was a reaction of calcite dissociation and tremolite dehydration. It resulted in the release of certain quantities of CO<sub>2</sub> and H<sub>2</sub>O, which are highly active at higher temperatures. It should be said that there were no relics of such primary minerals as tremolite and calcite in this mineral assemblage, which was stable after the formation of hedenbergite. On this basis one may conclude that they reacted completely.

Wollastonite is the product of the reaction (see Text-fig. 6):



the mechanism of which was investigated by GREENWOOD (1967), KERRICK & *al.* (1973) and HEINRICH & GOTTSCHALK (1994). Wollastonite is a common mineral of the contact-metamorphosed limestones, and found in regional metamorphic rocks (GREENWOOD 1967). According to the diagrams in Text-figs. 5 and 6, wollastonite may exist within a wide temperature range, but in the investigated case it probably occurred at ca. 600°C and  $X_{CO_2}$  of the approximate value of 0.3. The absence of any associated minerals indicates, that wollastonite could have crystallised under conditions of  $CO_2$  content lower than 0.3 molar fraction and at temperature below 600°C, suggests the given values as the lower limits of the considered parameters. The fact that a temperature distinctly higher than 600°C can only rarely be achieved in the contact metamorphic aureoles of granitic rocks is additional evidence that the estimated value is reasonable. The above-mentioned reaction resulted in the release of significant amounts of  $CO_2$ . The released  $CO_2$  probably migrated away from the skarns, otherwise a permanent increase of the partial pressure of  $CO_2$  would have occurred, which would have inhibited the formation of wollastonite. When  $X_{CO_2}$  increased, the temperature required for the crystallization of wollastonite had to increase as well. The primary calcite was not found in this association, which could be explained by

the complete dissociation of the calcite of the skarn protolith. In addition to calcite, silica was necessary for wollastonite formation. It may have come either from the protolith quartz or from inflowing silica-bearing solutions.

The process of grossular formation is more difficult to explain. Relics of wollastonite fibroblasts identified in grossular suggest that the following reaction occurred (KERRICK & *al.* 1973, MILKE 1998):



This reaction could have occurred at above 600°C (*see* Text-fig. 6). The absence of the primary calcite in association with garnet was most probably caused by a total dissociation of the protolith carbonate, as a result of the formation of hedenbergite, wollastonite and grossular. In the case of calcic plagioclase, it is possible that its relicts are not present in the assemblages in which we have garnet because of the total use of the anorthite molecules in the above-mentioned reaction. Calcic plagioclase grains were only observed in the hedenbergite – plagioclase layers. Albite that could have formed as a secondary mineral, replacing the plagioclase rich in the anorthite molecule, occurs in the assemblage wollastonite – albite – hedenbergite. For this reason it was probably present in the above reaction.

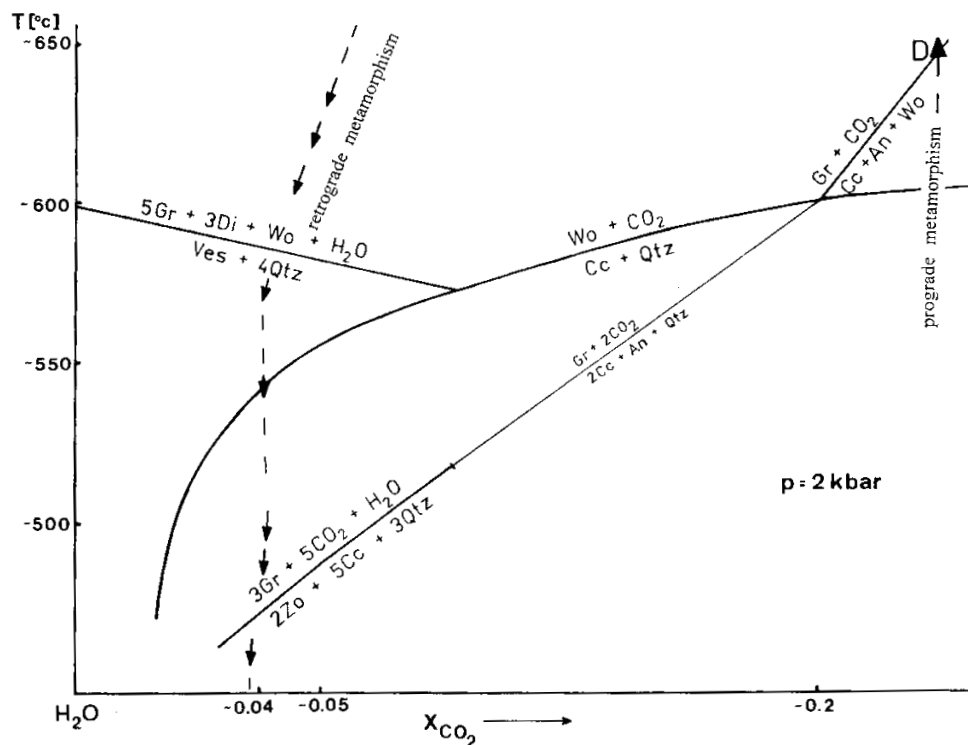


Fig. 6. Schematic and semiquantitative  $T - X_{CO_2}$  diagram at 2 kbar for di-bearing calc-aluminous rocks, after D. M. KERRICK & *al.* (1973) from V. C. HOVER-GRANATH & *al.* (1983); arrows represent the possible  $T - X_{CO_2}$  paths during the metamorphism of the skarns from Garby Izerskie



The direction of the metamorphic process at the stage I was progressive and the probable paths of metamorphism are shown in the respective diagrams (Text-figs 5 and 6).

On the basis of the evaluation of the element balance the reactions of the stage can be considered as developed under almost isochemical conditions. It is therefore likely that the bulk chemical composition characteristic for the skarn protolith did not differ distinctly from the present-day bulk composition of these skarns. That indicates that all changes took place in a quasi-closed system. However, during contact metamorphism water and carbon dioxide could have migrated outside the system (*see* RYKA & MALISZEWSKA 1982).

## Stage II

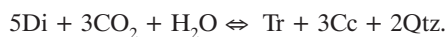
Stage II developed already during the retrograde metamorphism and it was marked by local replacements of hedenbergite, wollastonite and grossular by **vesuvianite, actinolite, prehnite, epidote and calcite**.

Taking into account the presence of the hedenbergite and grossular relics in vesuvianite and the relationship of vesuvianite to the other skarn minerals, the following hydration reaction can be suggested (KERRICK & *al.* 1973):



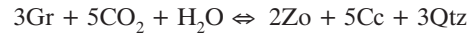
which probably started below, but closely to ca. 600–580°C. Vesuvianite had to begin its crystallization once conditions are below the equilibrium curve of this reaction (see the marked curve in Text-fig. 6). Calcite formation could have resulted directly after passing below the wollastonite equilibrium curve. Vesuvianite formation at the expense of hedenbergite, grossular and indirectly wollastonite started at the moment that the system reached the stage of chemical equilibrium involving vesuvianite. It was found that hedenbergite, grossular and wollastonite completely either partly transformed into vesuvianite, or they did not change at all. Since the temperature at a certain moment was uniform in the whole rock, the different progress in the alteration process reflected a different inflow of CO<sub>2</sub> and H<sub>2</sub>O into the rock.

It was also possible to find actinolite – calcite paragenesis in the investigated rock, formed at the expense of hedenbergite according to the following reaction (EGGERT & KERRICK 1981, PUHAN & METZ 1987, DACHS & METZ 1988, GOTTSCHALK 1997):



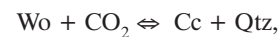
At an X<sub>CO<sub>2</sub></sub> lower than ca. 0.2 and at a temperature lower than ca. 500°C this reaction occurred (*see* Text-fig. 5).

The grossular relics existing together with epidote and calcite confirm the reaction (KERRICK & *al.* 1973)



which occurred below the equilibrium curve of this reaction, when the temperature decreased below 520°C (*see* Text-fig. 6).

The microscope investigations also revealed calcite – quartz paragenesis in some parts of the skarns. This is the effect of the reaction (GREENWOD 1967, KERRICK & *al.* 1973, HEINRICH & GOTTSCHALK 1994):



which is suggested by the pseudomorphs of calcite after wollastonite which were identified. The replacement process of wollastonite by calcite plus quartz had to initiate as soon as the T – X<sub>CO<sub>2</sub></sub> values decreased below the wollastonite equilibrium curve (*see* Text-fig. 6).

The relics of garnet occurring in prehnite suggest the following reaction:



which takes place below 400°C (*see* LIOU 1971). Prehnite is only stable in H<sub>2</sub>O-rich fluids with the compositions of X<sub>CO<sub>2</sub></sub> less than ≈ 0.02, and at temperatures less than ca. 380°C, as resulted from the isobaric (2 kbar) T – X<sub>CO<sub>2</sub></sub> diagram compiled by WINKLER (1979). This suggests that an influx of H<sub>2</sub>O-rich fluids, which should occur after the peak metamorphism episode.

The formation of vesuvianite, actinolite, prehnite, epidote and pseudomorphs of calcite after wollastonite probably took place in a quasi-isochemical system during a decrease of temperature and CO<sub>2</sub> partial pressure. A local migration of H<sub>2</sub>O took place in this skarn. The identified stage II minerals suggest that the liquid phase contained very low CO<sub>2</sub> concentrations during mineral formation, which meant high water activity.

## Stage III

The process of recrystallization of the mylonitised minerals of the wall rocks in the “Stanisław” quarry (SZALAMACHA 1965, SZALAMACHA & SZALAMACHA 1966) was accompanied by an intensive **silicification** in the dislocation zone. Metasomatic activity of the silica-bearing solutions seems certain (SMULIKOWSKI 1961, SZALAMACHA 1965, SZALAMACHA & SZALAMACHA

1966, KOZŁOWSKI 1978). Silicification took place after the process of cataclasis and mylonitisation (SZAŁAMACHA 1965, SZAŁAMACHA & SZAŁAMACHA 1966). The beginning of stage III could not be precisely determined because in the Garby Izerskie zone, the starting time for quartz metasomatite formation is difficult to ascertain (KOZŁOWSKI 1978). The possibility that stage III could have occurred during the same period as the earlier described stages should also be taken into consideration. KOZŁOWSKI (1978) states that although the schists were silicified, it is not clear whether they were already altered by contact metamorphism, or whether silicification developed before, or during and after the formation of the massif. In his opinion, the granitoid apophyses cutting the silicified hornfels (and skarns) formed their development before the final consolidation of the Karkonosze massif, and the thermal influence of these relatively thin apophyses on the cover rocks was very scarce.

The process of silicification that began at least at 410°C (KOZŁOWSKI 1978) changed the conditions of crystallization from quasi-isochemical to allochemical.

#### Stage IV

This is the stage of the predominant **fluorine metasomatism** which occurred at 360 to 110°C (KOZŁOWSKI 1978). Fluorite replaced the earlier minerals and filled voids. Fluorite, as one of the last components, appeared in the both quartz and calc-silicate laminae in the skarns. The paragenesis of fluorine minerals: **fluorite** and **apophyllite** with porous **white quartz** and **late calcite**, **stilbite** and **chlorite**, is the final mineral association in the skarns and fractured hornfels (KOZŁOWSKI 1978).

The crystallization of **sphene** can probably also be included in this stage. The titanium necessary for this mineral might have migrated into the system in the form of fluoride complex ions.

#### DISCUSSION

In this paper the possible prograde and retrograde paths of metamorphism were proposed. The prograde paths, illustrated in Text-figs 5 and 6 can be used to constrain the peak metamorphic temperature and fluid compositions during the high-grade metamorphism. The progressive metamorphism of these rocks has resulted in a sequence of prograde minerals that indicate fluid buffering in metamorphic reactions. The following assemblage was identified: hedenbergite, wol-

lastonite and grossular, which belong to the stage I of the skarn formation. These minerals constrain the peak metamorphic temperatures between ca. 500°C (the formation of hedenbergite) and ca. 600-650°C (the formation of wollastonite and grossular) at  $p_{\text{static}} = p_{\text{total}} = p_{\text{fluid}} = 2$  kbar. At ca. 650°C fluids had a CO<sub>2</sub>-concentration in the range of 30 molar percent. Stage I is characterized by a quasi-isochemical system.

After the peak metamorphism conditions were reached a change took place in the fluids to more H<sub>2</sub>O-rich compositions. Stage II was the first one during which this process was observed. This retrograde stage resulted in the origin of vesuvianite, actinolite, prehnite, epidote and calcite pseudomorphs after wollastonite also in a quasi-isochemical system as well. During the retrograde metamorphism the vesuvianite formation started probably below 600-580°C.

Stage III, which was essentially a period of silicification that began at least at 410°C in an allochemical system, could have partly overlapped in time with stages I and II.

Stage IV, which was fluorine metasomatism at 360 to 110°C was also an allochemical process.

Thus, the skarns from Garby Izerskie are the high-temperature calc-silicate varieties, with late silica and fluorine metasomatism. The high-grade metamorphism are characterized by the appearance of wollastonite, grossular and a change in plagioclase to more albitic compositions.

The progressive metamorphism of the protolith of these skarns has resulted in a variety of stage I miner-

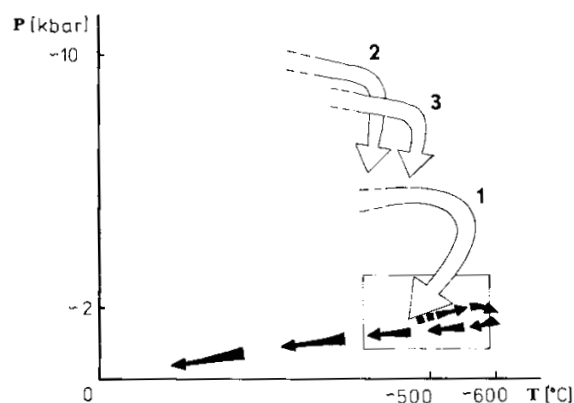


Fig. 7. Tentative p - T paths for particular tectono-litostratigraphic units of the southern part of the eastern metamorphic cover of the Karkonosze pluton, after R. KRYZA & S. MAZUR (1995); 1 - Kowary and Czarnów units, 2 - Niedamirów unit, 3 - Leszczyniec unit. The shaded box represents the approximate pT field of Lp - HT metamorphism related to the granite intrusion; black arrows represent the possible p - T paths during the metamorphism at Garby Izerskie

al assemblages which occur within small domains probably defined by the initial bulk composition of individual sedimentary layers.

The formation of vesuvianite, actinolite, epidote, pseudomorphs of calcite after wollastonite and prehnite probably took place in a quasi-isochemical system accompanied by a decrease in temperatures and CO<sub>2</sub> partial pressure. A local migration of H<sub>2</sub>O occurred. The identified skarn minerals of stage II suggest that the liquid phase contained very low CO<sub>2</sub> concentrations during mineral formation, which meant high water activity. The presence of prehnite replacing grossular particularly suggests that a possible influx of H<sub>2</sub>O-rich fluids occurred after peak metamorphism.

On the basis of 20 analyses it was shown that the vesuvianite from Garby Izerskie has a strongly variable content of certain oxides (Table 2 and Text-fig. 4). The vesuvianite analysis published in KARWOWSKI & *al.* (1996) was probably a chance composition of vesuvianite from this locality, one of many possible.

In KRYZA & MAZUR (1995) the tentative p – T paths for particular tectono-lithostratigraphic units of the southern part of the eastern metamorphic cover of the Karkonosze pluton were presented (Text-fig. 7). To their diagram the present author would like to introduce the path of the contact metamorphic conditions of the studied rocks, which belong to the northern metamorphic cover of the Karkonosze pluton. The black arrows in Text-fig. 7 represent the changes of temperature and presumable changes of pressure during the contact metamorphism at Garby Izerskie.

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## PLATE 1

## Skarns from Garby Izerskie, "Stanisław" quarry

- 1 – Pyroxene (*Px*) – plagioclase (*Pl*) layers, quartz (*Qtz*); nicols oblique
- 2 – Hedenbergite (*Hd*) – wollastonite (*Wo*) paragenesis; nicols oblique
- 3 – Crystallization of albite (*Ab*) after Ca-rich plagioclase, hedenbergite (*Hd*); wollastonite (*Wo*), fluorite (*F*); nicols parallel
- 4 – Fluorite metasomatism – formation of fluorite (*F*), calcite (*Cc*) and late quartz (*Qtz 2*); wollastonite (*Wo*), hedenbergite (*Hd*); nicols oblique
- 4a – Fluorite metasomatism – fluorite (*F*) as the product of early quartz (*Qtz 1*) alteration; nicols oblique
- 5 – Pseudomorphs of calcite (*Cc*) after wollastonite (*Wo*); grossular (*Gr*) quartz (*Qtz*); nicols oblique
- 6 – Formation of vesuvianite (*Ves*) after hedenbergite (*Hd*) and grossular (*Gr*); nicols parallel
- 7 – Crystallization of vesuvianite (*Ves*) after hedenbergite (*Hd*), wollastonite (*Wo*) and grossular (*Gr*), calcite (*Cc*) after wollastonite; nicols oblique
- 8 – Formation of actinolite (*Act*) after hedenbergite (*Hd*); nicols oblique
- 9 – Epidote (*Ep*) and calcite (*Cc*) as the product of grossular (*Gr*) alteration; quartz (*Qtz*); nicols oblique

