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# Pneumatolytic and hydrothermal activity in the Karkonosze-Izera block

ABSTRACT: The Karkonosze-Izera block in the Sudetes Mts (Southern Poland), consisting of the Karkonosze granite massif and its gneiss-schist cover, named the Izera area, bears numerous pegmatites and pneumatolytic-hydrothermal bodies: veins, silicified cataclastic zones, and metasomatites (leucogranites, greisens and tourmaline nests). A scheme of the formation of early zones of pegmatites by metasomatic recrystallization of aplite under pneumatolytic conditions is presented, being established on textural features. The mode of crystallization of the individual types of veins depended on the type of fracture and the changes of temperature during the fracture filling with minerals. Both pegmatites and veins from Karkonosze formed originally under action of pneumatolytic, and subsequently of hydrothermal fluids, contrary to veins and metasomatites in the Izera area, formed by an activity of essentially hydrothermal fluids. Measurements of temperatures of the homogenization of fluid inclusions and evaluation of the pressure permitted a discussion of real temperatures of the crystallization of hydrothermal mineral assemblages. Geochemistry of major elements in the inclusion fillings *i.e.* sodium, potassium, calcium, magnesium, aluminum, iron and chlorine, was characterized. High fluorine content in inclusions, expressed as atomic ratio 1000F/Cl, is typical of metasomatites and ore-bearing rocks in the Izera area, being a possible prospecting tool. Minor and trace elements in inclusion fluids, especially Li, Be and B, have characteristic regional distribution. Bromine content in inclusions gives some genetic suggestions on the origin of mineral-forming solutions. Discussed are also possible relations between diverse hydrothermal deposits in the metamorphic Izera cover and the Karkonosze granite massif.

# INTRODUCTION

In the present paper, hydrothermal process will be defined as activity of liquid solutions, usually, but not necessarily, with water as prevailing solvent, at temperature higher than temperature at the boundary of influence of annual atmospheric thermal changes in the Earth's crust in

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the area under study. Endogene processes are the source of heat. Activity of thermal gaseous solutions is named a pneumatolytic process, and both hydrothermal and pneumatolytic processes are called the activity of thermal fluids, including also strongly saline brines, *i.e.* hydrated saline melts. Other mineral-forming media will not be mentioned as thermal fluids in the present paper.

The writer investigated deposits formed by activity of thermal fluids under conditions of free growth (in cavities, opened fractures) as well as by metasomatosis.

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# GEOLOGY OF THE KARKONOSZE-IZERA BLOCK

The Karkonosze massif, cropping out on the surface about 70 km long (W - E) and 8 - 20 km wide, is a Variscan granitoid intrusion. In the massif some types of biotite granite sometimes bearing hornblende were distinguished. Berg (1920) on his maps gives three types as the main ones: i) porphyry granite (with porphyric feldspars), occurring throughout almost the whole area of the massif and occupying the greatest area; ii) even-grained granite, forming main chain of the Karkonosze Mts, and part of the Rudawy Janowickie Mts; iii) aplite-like granite, known from the eastern part of the massif and from vicinity of Szklarska Poreba. Borkowska (1966) distinguished other three types, only in part coinciding with Berg's division: i) central (porphyric) granites; ii) crest granite, without hornblende, poor in enclaves; iii) granophyric granite; she suggests two-stage scheme of intrusion: crest granite would be intruded earlier, and two other types — later. This assumption was however disavowed by Oberc (1972, p. 107) who regards the granite as a one-phased intrusion.

The Karkonosze granite bears numerous enclaves, presumably xenoliths of wall rocks, and schlieres mainly rich in biotite, and delineating internal structure of the massif (Cloos 1925), and aplite veins. Vein rocks often filled vertical fractures Q (NNE-SSW); vertical fractures S(NW-SE) and horizontal fractures L (cf. Cloos 1925) are weakly mineralized. Contacts of the intrusion with its cover are concordant, and only from Jeżów Sudecki to Piechowice (part of NNW boundary of the massif) they become discordant (Cloos 1922, 1923). The intrusion is about 4 km thick (Schwinner 1928) and it seemingly underlies its northern crystalline cover called the Izera area (Oberc 1972).



Fig. 1. Sketch geological map of the Karkonosze-Izera block 1 hornfelses and schists, 2 Izera gneiss and Rumburk granite, 3 leucogranite, 4 greisen, 5 Karkonosze granite, 6 faults, 7 locations of samples (LK location of samples cited after Karwowski 1977); detailed maps: A - Fig. 6, B - Fig. 7, C - Fig. 8, D - Fig. 9

The Izera area (Fig. 1) consists of polygenic Izera gneisses and Rumburk granites (Kozłowska-Koch 1965, W. Smulikowski 1972) of undefined age, divided into four parallel mica-chlorite schist zones, formerly being the clayey sediment of maybe Algonkian age (K. Smulikowski 1958). The southern range of the area is the zone of Szklarska Poręba, altered by thermal activity of the Karkonosze intrusion into hornfelses bearing andalusite and cordierite (SE part of Garby Izerskie fault zone is included here). Northwards, the zones of Stara Kamienica, Mirsk and Złotniki Lubańskie, consist of schists regionally metamorphosed under conditions of greenschist facies, quartz-albite-almandine subfacies (K. Kozłowski 1974). Metasomatic rocks, formed by alteration of gneisses: leucogranites and several varieties of greisens (Budkiewicz 1949; Kozłowska 1956, Wieser 1956; Heflik 1964; Pawłowska 1966, 1968; Karwowski 1977), associate spatially with the three northern zones. One may observe continuous transitions from microcline-oligoclase biotite gneiss through microclinized and albitized gneiss with decreasing amount of biotite and increasing amount of muscovite, through albite or microcline leucogranites, greisenized leucogranites with decreasing amount of feldspars and increasing quartz and light micas, to quartz-mica, quartz-topaz, quartz-tourmaline *etc.* greisens.

Numerous veins of quartz and silicified rocks are known from the Izera area (W. Smulikowski 1966, 1969). A part of them is believed to be developed in Assyntian tectonic zones (Kotowski 1969) and some veins connect with the formation of leucogranites and greisens, especially with the final stage of the process. Main directions of quartz veins are NW—SE, SW—NE and W—E.

# SELECTION OF SAMPLES

Over 500 samples were collected during field works 1969—1976 and after initial studies over 250 of them were accepted for further investigations. The writer also included 20 specimens from scientific collection of the Institute of Geochemistry, Mineralogy and Petrography, Warsaw University, and used a number of determinations of F and Cl in inclusions from papers of Kopaczewska (1976) and Karwowski (1977). Samples were arranged in five groups: series K — samples from the Karkonosze massif, series Gi — from the Garby Izerskie mineralized fault zone, series CK — from the Czerniawa — Stara Kamienica schist zone, series S — from the southern part of the Izera area, and series N — from northern part of Izera area (cf. Figs 1, 6—9).

Ten samples of quartz from the Karkonosze granite, both even-grained and porphyric types, and, on the other hand, both from fresh and altered (silicified, chloritized, hematitized) rock were studied because of numerous secondary inclusions of thermal fluids present in this quartz. Granite samples were taken from outcrops and from various depths of the borehole Jakuszyce. Four samples of quartz from aplite were coming from Michałowice and Szklarska Poreba quarries. Quartz from pegmatites (including granophyric intergrowths) and various veins was collected from the area of all Polish parts of the Karkonosze massif (Fig. 1).

Samples from the Izera area were chosen intending as uniform distribution as the outcrops permitted. Concentration of samples in the Izera Mts between Swieradów and Zakret Smierci, to the south of the road (Fig. 7) is caused by the occurrence of numerous tourmaline nests distant from other metasomatites.

All known types of quartz bearing inclusions of thermal fluids were collected from the Izera area. The collection consists of bluish blastic quartz from gneiss, rock-forming quartz from skarn, hornfels and greisens, quartz intercalations and veins in schists and quartz from veins in gneiss, leucogranite and greisen. All samples were taken from the Polish part of the Izera area.

### METHODS

Thin and polished sections were studied by routine microscopic methods of transmitted and reflected light. Fluid inclusions were investigated in double polished plates 0.3 - 2 mm thick. Homogenization temperatures (T<sub>H</sub>) of inclusions were measured in heating stage made by the writer, with accuracy  $\pm 2^{\circ}$ C. Methods of work and interpretation are described elsewhere (Kalyuzhnyi 1960, Roedder 1970a). Pressure was evaluated by the method presented by Naumov & Malinin (1968).

Handpicked quartz in grain class 1-2 mm weighing about 100 g was divided into two parts, about 50 g each. First part for water leachate for F and Cl determinations was washed for a week with water changed two times per day, until Na concentration in water after washing was equal that in pure water. Then, a sample was dried, ground in agate ball mill, weighed and leached with water at 60-70°C. The second part of quartz, for determination of cations and B in inclusions, was washed with HCl and aqua regia solutions 1:10 at 50°C till spectrographically found absence of Fe in washing solution, and then with water at 50-60°C till negative reaction for Cl with AgNO<sub>3</sub> solution. Dried, ground and weighed sample was leached with HCl water solution (pH = 2-2.5) at 50°C. The leachate was filtrated and precipitated by evaporation on spectral pure carbon (200-300 mg).

Fluorine, after distillation as HF from concentrated  $H_2SO_4$ , was determined colorimetrically with cerium and alizarine complexone; chlorine distilled as HCl was determined potentiometrically by titration with AgNO<sub>3</sub> solution (accuracy  $\pm 1$  to  $\pm 5^{\circ}/_{\circ}$ , depending on the amount of F or Cl). Control determinations of Cl by colorimetric method with methyl red, after distillation from  $H_2SO_4$  and  $KJO_4$  solution, gave a very good coincidence of results (in ppm of quartz mass):

Sample	Potentiometric determinations of Z. Jonca	Colorimetric determinations of A. Kozlowski
Gi034b	160	130
Gi035	36	40
N21	<b>51</b>	51
NSS	' <b>/280</b>	200

Fluorine determinations were controlled by three or five repetitions of leachates of each tenth sample.

Spectral emission determinations of cations and B were performed with use of ISP 28, ISP 51 and DFS 13 spectrographs and suitable methods (Kalinin & Fain 1969). Synthetic standards were applied; accuracy was evaluated as equal  $\pm 7$  to  $\pm 15^{\circ}/_{\circ}$  of the value found. In comparison with performed standard determinations of B by curcumin method, the spectrographical determinations of B had accuracy  $\pm 20^{\circ}/_{\circ}$ .

Leachates for determinations of cations and B were made with use only of laboratory vessels with hard polyethylene; nylon sieves were used. Applied water was triple distilled.

The amount of inclusions was determined by calcination method with accuracy  $\pm 10\%$  (Karwowski & Kozłowski 1971).

# STRUCTURAL, TEXTURAL AND MINERALOGICAL CHARACTERISTICS

# KARKONOSZE MASSIF

# PEGMATITES

In the Karkonosze massif numerous pegmatitic bodies occur but they are poorly investigated either during geological mapping (e.g. Berg 1926) or as a marginal problem of petrographical studies (Borkowska 1966). Geochemical studies were carried out on pegmatitic micas (Gadomski 1958), feldspars (Kowalski & Walenczak 1957, Kowalski 1967) and quartz (Walenczak 1969, Kozłowski 1973). First mineratogical studies were connected with exploitation of ceramic raw materials in the 19th century (Traube 1888). Further mineralogical notes were on feldspars (Krzywobłocka 1957), rare minerals (Gajda 1960a, b) and beryl (Sachanbiński 1970). The mentioned authors either accepted Fersman's hypothesis (1940) on the origin of pegmatites, or reported several different hypotheses without evaluation of a meaning of the features of the Karkonosze pegmatites for elucidation of their origin.

The writer would like to propose a scheme of origin of the Karkonosze pegmatites on the basis of the found structural and textural peculiarities and conditions of crystallization of quartz. This scheme connects with certain general hypotheses of pegmatite origin but it is not a tentation of proving of the reasonableness of any hypothese for all pegmatites.

Karkonosze pegmatites are nest- and vein-like, and they usually occur in aplites. In thick aplite veins or zones they often formed near the boundary with granite, sometimes touching it. Dimensions of pegmatites vary from some centimeters to several meters; the largest were found in the eastern part of the massif (Czarne, Karpniki, Trzcińsko).

Typical pegmatite (Fig. 2) is zonal: on aplite, a zone of granophyric intergrowths occurs, further — a zone consisting of albite and microcline with biotite and quartz. Towards the centre, the amount of quartz increases and it heals the cavity and forms the quartz core. If the central part of the cavity is empty, quartz and feldspars form druses and the last zone appears with cleavelandite, muscovite, zeolites, epidote and chlorites.

Component	Even-grained granite, Samotnia, sample K39	Aplite, Szklarská Poręba Hutá, sample K40a	Granophyric intergrowths, Szklarska Poręba Huta, sample K40b
8102	71.61	78.37	76,99
T102	0.29	0.07	0.04
A1203	14.17	12.73	12.20
Fe <sub>2</sub> 0 <sub>3</sub>	0.20	0.20	0.10
FeÖ	1.55	0.54	0.25
MnQ	0.05	0.05	y <b>0₊03</b>
Ng0	0.76	0.37	0.27
CaO	2.04	0.94	0.65
Na <sub>2</sub> 0	3.57	4.23	2.60
ĸ₂ō	4.65	3,90	6.08
H <sub>2</sub> 0+	0.77	.0.33	0.46
H20-	0.20	0.14	0.13
Total	99-88	99.87	99,80
Ignition	0.60	0,44	<b>0.61</b>

Table 1

Chemical compositions of granite, aplite and granophyric intergrowths from the Karkonosze massif; wt % Moreover, there occur extensively developed zones of granophyric intergrowths bearing small pegmatitic nests (Fig. 3A). The zones are arranged along planes being probably fractures or tensions in aplite (Fig. 3B). Some fragments of aplite are isolated relics in granophyres (Pl. 1, Fig. 1; cf. Fig. 7A). Granophyres healed even thin cracks of aplite fragments (Pl. 1, Fig. 2). Both aplite and granophyre have similar chemical composition, on the other hand differring from composition of granite (Table 1). Granophyric intergrowths are poorer in sodium and richer in potassium than aplite due to development mainly of microcline perthite. Such zones may be interpreted as formed by: a) injection of the melt in the net of fractures, b) recrystallization of possibly crushed aplite in zones of tension. The writer rather accepts the second interpretation because of the similarity of composition, absence of visible translation or rotation of aplite fragments in granophyric intergrowths and found aplite fragments floating in the intergrowths.

The boundary of pegmatite may be either sharp, or the pegmatite gradually passes into aplite. In the latter case, the transitional zone up to 20-30 cm thick, bears microcline and quartz grains of dimensions increasing little by little from aplite toward pegmatite (Fig. 4; PL 2, Fig. 1). These grains overgrew small fragments of aplite so that the transitional zone became rock with clear signs of metasomatosis. Also granophyric intergrowths, firstly fine (Pl. 3, Fig. 1), became much larger in pegmatitic zone (Pl. 3, Fig. 2). The mentioned process may be observed



Fig. 2. Scheme of typical pegmatite nest from the Karkonosze massif, quarry at Szklarska Poręba Huta

Gr granite, Ap aplite, Gi granophyric intergrowths, Bi biotite, Mi microcline, Ab albite, Qz quartz, Al allanite, Mu muscovite, Ep epidote, Cl cleavelandite, St strigovite (chlorite); Cc central cavity in the immediate neighbourhood of fractures and cracks where tensions and easier migration of the thermal fluids occurred.

Closely to the pegmatite/aplite boundary, euhedral quartz crystals up to 10 cm long, were found, sticking partly or almost completely in aplite (Pl. 2, Fig. 2; Pl. 4, Figs 1—2). Euhedral or subhedral microcline associates with this quartz. The described quartz formed from pneumatolytic and hydrothermal fluids, since it bears gaseous and gas-liquid inclusions. Such crystals contain, arranged along the growth zones, small fragments of aplite, isolated during the growth of a crystal from the aplite filling of the vein. Aplite sometimes penetrates under individual zones of the growth ("hoods") of quartz crystals. These features prove that quartz and feldspar crystals occupy the place of aplite dissolved by a metasomatic growth (Fig. 5).

Examples of similar occurrences and habits are known from pegmatites of the granitoid massifs at Strzegom (Pl. 5) and Strzelin (Pl. 6). Supposition that such structures were formed by an injection of aplite melt into fractures with crystals of quartz and feldspars rather cannot be accepted since this process had to destruct fine crystals in a fracture and mark itself as rapid increase of temperature (e.g. by decrepitation of fluid inclusions, cf. Voznyak & Kalyuzhnyi 1974), not observed here.

The above scheme of the formation of granophyre zones and metacrysts of quartz and microcline seems to be true for early stage of the origin of pegmatite. If recrystallization is associated with removal of a part of dissolved mineral sub-



Fig. 3. Blockdiagram of the system of granophyric intergrowth zones in aplite (A) and presumed orientation of the surfaces of mechanical stress, causing formation of these zones (B); quarry at Szklarska Poreba Huta

Gr granite, Ap aplite, Gi granophyric intergrowths, Pg pegmatite, F fracture in aplite healed with granophyric intergrowths; place where sample K40a, b, was taken (cf. Pl. 1 Fig. 1) is rectangled



stance, e.g. for reason of presence of net of fractures in the rock (cf. Fig. 1 in Dmitriev 1972), a cavity forms in the central part of pegmatite; it may be also an increase of thickness of a fracture or a crack. The formed cavity is filled by mineral-forming solution, where minerals can crystallize under conditions of free



Fig. 5. Scheme of formation of euhedral quartz crystals in aplite matrix, quarry at Szklarska Poręba Huta 1 quartz, 2 other minerals A-D — reconstruction, E — sample K75 growth. This cavity may be completely healed (quartz or quartz-feldspar core) or covered with druses.

During formation of cavity and growth of druses, intensive sodium metasomatosis appeared. Increasing sodium activity in solution causes strong albitization or microcline till prevailing of Ab over Or, and removal of Ca-ions from structure of pegmatite plagioclase with contemporaneous introduction of Na--ions into this structure, so that plagioclase alters in almost pure albite (Table 2), preserving morphology and twinnings of richer in Ca former plagioclases. This phenomenon was ascertained in pegmatites by A. Nowakowski by the use of his method (Nowakowski 1976). Albites with chemically found composition Ab<sub>95</sub>An<sub>2.5</sub>Or<sub>2.5</sub> (Pl. 14, Figs 1-3) have relic pericline composition plane (PCP) with angle  $\sigma = 7-3^{\circ}$ , the same as in very rarely preserved relics of oligoclase An<sub>20</sub>. Thus, recent secondary albite formerly were oligoclase An20, and the only primary albite in Karkonosze pegmatites seemingly forms thin transparent rims on post--oligoclase secondary albite and epitaxial cleavelandite on microcline. Pericline twins at the boundary primary albite/secondary albite immediately change direction of PCP and in the rim  $\sigma$ -value is typical for abite: 30-37° (oral communication, Nowakowski 1978).

#### Table 2

Chemical composition of pegmatitic feldspars from Marczyce and Trzcińsko, Karkonosze massif; wt %

	Micro	cline	Alt	ite
Component	Trzcińsko, sample K41	Marczyce, sample K72	Trzcińsko, sample K41	Marczyce, eample K72
Si02	65.97	64.96	66,85	67.42
T102	0.01	0.01	0.01	0.01
A1203	19.04	18.69	19.76	19,74
Total Fe <sub>2</sub> 03	0.43		0,25	
Fe <sub>2</sub> 0 <sub>3</sub>		0.04	• .	0.11
FeO	i	0.09		0.04
MnO	0.00	0.01	0.03	0.01
MgO	0.06	0.04	0.21	0.05
CaO	0.43	0.39	0.81	0.51
NegO	6.44	3,80	10.80	11.12
ĸ₂õ	7.09	10.93	0,50	0.40
H <sub>2</sub> 0+	0.24	0.25	0.60	0.31
· H_0-	0.31	0.73	0.10	. 0.10
Total	100.02	99,94	99.91	99,82
Ab	54,45	32.11	91.33	94.12
An	2.11	1.92	4.01	2.50
Or	41.98	64.60	2.95	2.31
Silice	+0.46	+0.23	+0.43	+0.13
Alumina	-	-0,09	-0.02	+0.09

Intensity of albitization is difficult for evaluation on the basis of studies of plagioclase, which probably was very susceptible for this process and albitized in pegmatites almost completely. Microcline associated with plagioclase is albitized in various degree, proving a different intensity of albitization in diverse pegmatites and even in particular parts of the same pegmatite: together with microcline without traces of albitization (Pl. 12B), crystals with weak (Pl. 12A) and strong signs of albitization (Pl 13, Figs 1-2) were ascertained.

High activity of sodium was followed by a moderate increase of potassium activity (sometimes together with lithium) causing formation of fine muscovite on albite rims (Pl. 14, Fig. 2), lithium muscovite and zinnwaldite.



- Relic of aplite in granophyric intergrowths (cf. Text-fig. 3; Sample K40, Szklarska Poreba
- Same, section perpendicular to the above; granophyric intergrowths (Gi) healing also a fracture in aplite (Ap)



- Aplite (Ap) being replaced towards the fracture by a coarse-crystalline ag-gregate of microcline (Mi), abite (Ab) and quartz (cf. Text-fig. 4); Sample K2, Snieżne Kotły
   Euhedral morion and feldspars (F), mainly microcline, replacing aplite (Ap); K74, Szklarska Poręba; nat. size



- Fine granophyric intergrowths, making up an initial stage of replacement of aplite (cf. Pl. 2, Fig. 1); Sample K2/132, nicols crossed
   Coarse-grained quartz-microcline aggregate bearing albite (Ab), adjacent to the fracture; K2/133, nicols crossed



- Euhedral gray quartz replacing aplite; relics of aplite are visible inside quartz in the growth zone (cf. Text-fig. 5); Sample K75, Szklarska Poręba
   Euhedral smoky quartz in aplite; relic of aplite between white feldspar zones is also visible; K76, Szklarska Poręba



Aplite vein in granite  $(G\tau)$ ; aplite partly replaced by large euhedral feldspars (F) and morions (Qz); Strzegom



 Aplite cutting granite (Gr); aplite contains large eubedral and subhedral feldspars
 (F), morions (Qz) and late, fine-crystalline iron sulfides (Is); specimen supplied by M. Stępisiewicz, M. Sc.; Gębczyce, Strzelin massif



Parallel growth of two zonal quartz crystals from a cavity of pegmatite at Czarne, Karkonosze massif



Quartz druse chipped naturally from cavity of pegmatite: A - upper view, B - side view, C - view of cleavage surface; Karpniki, Karkonosze massif



Piece of strongly cracked quartz (A-A), covered with a regeneration rim of parallel euhedral quartz crystals; Karpniki, Karkonosze massif



Japanese twin of A and B quartzes, both A and B quartzes consist of numerous parallel crystals; orientation of Z-axes of Japanese twin is given; Karpniki, Karko nosze massif



- Detail of zonal quartz (showed in PI. 7), rhombohedrons (r and z), and prism (m) of the crystals are visible, as well as heads of crystal on the edge of the outer zone of big quartzes
- 2 Regeneration of cleavage surface of quartz (showed in PI. 8C); numerous small rhombohedrons are visible



Microclines: A — with tiny epitaxial cleavelandites (Cl) as traces of albitization; B — without traces of albitization; both specimens from Trzcińsko pegmatite, Karkonosze massif



- 1 and 2 Micrcclines strongly albitized, corroded and with epitaxial cleavelandites; Sample K41, Trzcińsko
- 3 Reticulate post-inversion fractures (i) in pegmatitic quartz; orientation of fractures is concordant with rhombohedral cleavage (c) of quartz; Karpacz, Wilcza Poręba, Karkonosze massif
- 4 Three-phase inclusion of solution healing post-inversion fractures; sample same as above



- Secondary albite, albitized microcline (Mi) and guartz (Qz); Sample K41, Trzcińsko
- $2\, \,$  Tiny flakes of muscovite at the edges of albite crystals; same sample
- 3 Secondary albite and albitized microcline (Mi); K72, Marczyce



- Contact of quartz veinlet with granite (Gr); fq fine-grained quartz; small quartz veinlet in microcline is arrowed; Sample K15, Biała Dolina
- 2 Filling of a vein developed in cataclastic zone; granite, mainly feldspar fragments (F), cemented with milky vein-quartz, afterwards cracked again and cemented once more by fine-grained quartz with hematite; K77, Biała Dolina
- 3 -- Vein quartz with a fragment of strongly altered granite (Gr); K30, Szklarska Poręba, Wiciarka quarry



- Fractured amethyst vein, healed with jasperoid (j); Sample K24, Hala Szrenicka
   Filling of quartz vein: amethyst (A), fine-grained quartz (jq) and a fragment of altered
- granite (Gr); K16, Szrenica
- 3 Zoned vein amethyst; Kamieńczyk Falls, Karkonosze massif
- 4 Vein amethyst and milky quartz; Szrenica, Karkonosze massif

Changes of chemical composition of mineral-forming solution were probably caused by a fact that during a cooling of the massif both chemical activity of ions and stability of the minerals in solution have varied strongly. A mineral, when adapting its composition to changing conditions, influences mineral-forming solution. The process of albitization released significant amounts of Ca, partly immobilized next in Ca-zeolites, apophyllite, fluorite and calcite.

Changes of volume of a mineral-forming system may be another reason of chemical evolution. Such changes cause variations of temperature, pressure, boiling of solution and mixing of portions of solution from various parts of the system. This assumption needs formation of cracks and fractures during the development of pegmatite: it is proved by studies on morphology of pegmatitic minerals. Big quartz crystals are always twinned (Dauphiné, Brasil and rarer Japanese twins; Pl. 10), and they formed parallel growths (Pl. 7); quartz commonly grew in many points of a crystal simultaneously (Pl. 10), but zonally, forming hoods (Pl. 7; Pl. 11, Fig. 1) resulted from periodical break of growth. All these features prove unstable chemical composition and temperature of the mineral-forming fluid, resulting in interruptions in the crystallization process. Microscopically, inclusions of mineral crumbs were found, and these were changing the scheme of the crystal growth. Sometimes, cataclased quartz fragments occur, afterwards being cemented and overgrown by quartz of regeneration with euhedral habit (Pl. 9). Also quartz druses were chipped out from the walls of a cavity (Pl. 8A, B, C) and the former crack surface was covered with quartz of regeneration (Pl. 11, Fig. 2). This is the clear evidence of crushing stages during formation of pegmatite.

### VEINS

Veins may be divided into forms origined by filling of opened fractures and those formed by metasomatic replacement of cataclased wall rock. Taking into account the known fillings of veins in the Polish part of the massif, one may distinguish following types:

- a) feldspar-quartz veins, with muscovite, in opened fractures,
- b) metasomatic quartz veins with relic feldspars and with clay minerals,
- c) quartz ore-bearing veins,
- d) quartz (and amethyst) veins,
- e) quartz with hematite (jasperoid) veins.

Thickness of the veins ranges from one to several tens of centimeters, and their outcrops are from several to almost 2,000 m long.

Feldspar-quartz veins, with vein paragenesis; quartz + feldspar, consist of 80-90 vol. 9/6 of gray, milky or semitransparent quartz, sometimes with small miaroles in the center. Parallel growth of crystals occurs near the miaroles. Feldspar, almost exclusively subhedral microcline, sometimes slightly albitized, occurpies iess than 20 vol. 9/6, occurring mainly near the walls. Single flakes of muscovite are either associated with feldspar or dispersed in quartz mass; they occupy less than 1 vol. 9/6. Such a filling is presumably similar to microcline-quartz and quartz zones of pegmatites. Occassionally hematite appears as thin covers on quartz, or as several cm long subhedral crystals. Such veins that fill usually opened fractures, were found by the writer at Szklarska Poreba and Mysłakowice vicinities.

Metasomatic feldspar-quartz veins bear quartz, microcline, oligoclase and albite in very variable proportions with trace hematite. The veins developed in zones of cataclastic, often very compact breccia of granite. Microcline and oligoclase are granitic relics replaced by quartz with varying grain size (PL 17, Figs 1-2). Sometimes granitic quartz, slightly etched, is discernible in vein quartz. In different parts of the same vein the replacement was less or more intensive: e.g. in samples from the vein at Mysłakowice the content of granite relics ranged from 40-30 to less than 2 vol. 0/0.

Ore-bearing quartz veins, recognized by the writer and his collaborators (Karwowski, Olszyński & Kozłowski 1973; Kozłowski, Karwowski & Olszyński 1975), crop out at the quarry at Szklarska Poręba Huta. Ore minerals, mainly wolframite, partly altered into scheelite (Pl. 21, Figs 2—3), molybdenite, cassiterite, sulfides of copper, sulfides and oxides of iron, occupy from several to more than 80 vol. % of vein. Bismuth minerals: bismuthinite, emplectite, nuffieldite and native bismuth are associated with the latter minerals (Olszyński, Kozłowski & Karwowski 1976). These veins fill opened fractures, with small development of quartz metasomatosis.

Quartz veins, most common in Karkonosze massif, are almost monomineral (quartz content 95-99 vol. %). Autigenic or relic feldspars, hematite, sericite, clay minerals and iron hydroxides are the balance. Quartz is either massive, milky, gray, sometimes translucent, or it forms druses of euhedral or subhedral crystals. Massive quartz has coarse- and even-grained structure and random texture; only near the walls, a part of grains has Z-axis roughly perpendicular to the wall. Crystallization under continuous but not rapid decrease of temperature, or recrystallization of the former fine-grained quartz may result in such structure and texture (see Fig. 13).

Quartz druses, partly or completely healing fractures, usually grew on aggregate of fine-grained quartz, precipitated on the wall of the fracture (Pl. 15, Fig. 1). Such sequence is caused by rapid temperature drop at the beginning of the healing of the fracture and further isothermal conditions or weak temperature decrease (Fig. 13A, E, G, H, and J). Sometimes additional lamina of coarse-grained quartz (C in Pl. 17, Fig. 3) appeared between granite and fine-grained quartz A under quartz druse B. Fine-grained quartz A cannot heal fracture in coarse quartz B+C, since is gives preorientation for drusy quartz B, and geometrical selection (Lemmlein 1973) is apparent here. Coarse quartz C may origin under quiet conditions either before the temperature drop causing precipitation of fine quartz A, or in fractures between fine quartz and granite, approximately when drusy quartz B formed. Then, both vein and wall granite were cracked (Pl. 15, Fig. 1; place marked by arrow). Thus, even thin veins were several times fractured during and after healing.

In cataclastic zones, quartz druses overgrew granite chips (Pl. 15, Fig. 3) with simultaneous silicification of granite till its complete replacement by quartz. Such veins have nebulous boundaries in a silicified wall zone. Together with quartz, sericite and hematite crystallized; this is proved by changes of orientation of hematite crystals on the boundary of two quartz crystals according to quartz structure (Pl. 17, Fig. 4).

Formation of veins was renewed several times at the same place: crushed granite was silicified with good preservation of microcline. Then new, probably opened fractures formed, healed by milky quartz. This filling of vein was subsequently cataclased and cemented with fine quartz with hematite (Pl. 15, Fig. 2). In sample K77 from Biała Dolina, rotation of chips followed the crushing, *i.e.* the fracture was not tightened.

Amethyst veins, most common at Szklarska Poreba, Szrenica Mt. and Łabski Szczyt Mt, have formed by similar way. They are compact zoned druses of amethyst, milky and translucent quartz (Pl. 16, Figs 3-4). Silicification, crushing, and formation of jasperoids (Pl. 16, Figs 1-2) are also apparent here.

Quartz veins with hematite belong to the latest group of vein-like bodies. These veins consist of: 1) jasperoids; 2) fine-grained quartz aggregate (grain size <0.1 mm) with dispersed hematite. Some quartz aggregates filled thin opened fractures, but simultaneously with formation of jasperoid in wall rock. Moreover, completely altered wall rock, i.e. "perfect jasperoid", presumably is not discernible from that aggregate. Thus, the writer will not distinguish them, assuming that for both these varieties of simultaneous and closely connected origin, the name "jasperoid" may be applied, in agreement with Spurr's definition (Lovering 1972); jasperoid is the rock consisting essentially of silica, usually quartz, formed by epigenetic (hydrothermal) alteration of wall rocks. The Karkonosze jasperoids are essentially silica; intensive hematite colour needs as low amount as 0.4-2.2 wt % of Fe<sub>2</sub>O<sub>3</sub>, has not to be enriched in Fe<sub>2</sub>O<sub>3</sub> during silicification. The content of other components (Table 3) depends on the amount of granite relics.

Table	3
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Chemical composition of hydrothermal fine-grained quartz rocks from the Karkonosze-Izera block; wt %

Component	Jesperoid, Hala Szrenicka, semple K24	Jasperoid, Jakuszyce IG2, sample K36	Jaspercid, Szklarska Poręba, sample K42j	Fine-grained quartz aggre- gate, Izera Mountains, sampla S17
<b>Si0</b>	95,11	84.48	95.74	95.46
T10-	0.05	0.25	0.18	0,02
A1_0_	2.01	. 6,70	1.61	2.10
23 Fe-0-	0.75	2.25	0.63	0.40
-2-3 Fe0	trace	0.15	trace	0.34
MriO	0.03	0.05	0.03	0.01
MaO	0.29	0.71	0.32	0.54
CaO	0.41	0.70	0.25	. 0.40
No.O	0.02	1.37	0.01	0.16
K-0	0.70	2.12	0.50	0,30
12- H.04	0.48	1.11	0.47	0.22
H.0-	0.13	0.19	0.12	0.10
Total	99,98	100.08	99.86	100.05
Ignition loss	0.52	1.20	0.61	

Some jasperoids (e.g. K42j from Szklarska Poręba) are completely relicsfree (Pl. 18, Figs 1-2), and a supposition that they have formed by precipitation of gel-like silica, then having been crystallized, was discussed (Kozłowski 1977). However, further analysis of the network of fractures, earlier assumed as possibly being of syneretic origin (Pl. 18, Fig. 3) and the presence of intermediate stages between that jasperoid and slightly altered granite (Pl. 19) proved the metasomatic origin. Solubility of SiO<sub>2</sub> in water and salt solutions is low, even under elevated temperature and pressure, thus during rapid temperature decrease (cf. Fig. 13, B-C) only thin layer of fine-grained quartz may precipitate (Pl. 15, Fig. 1), at the initial stage of the opening fracture (cf. Golubev & Sharapov 1974, p. 187). Presumably, the formation of jasperoids is connected with: *i*) release of silica from silicates of granite and its precipitation almost in situ; *ii*) supplying and accumulation of a part of SiO<sub>2</sub>.

Quartz veinlets cutting jasperoid have normal sequence of crystals (Pl. 20, Fig. 1), testifying slow crystallization (cf. Fig. 13 D, J). Quartz grains from jasperoid walls were the nuclei of crystallization of quartz filling the veinlets.

Small muscovite flakes often occur between quartz grains in jasperoid, resulted from the increase of K and Al activity in the final stage of hydrothermal process (Pl. 20, Fig. 2). Jasperoids commonly bear cataclastic grains of quartz (Pl. 20, Fig. 3), especially when formed together with the crushing of veins. Then, typical of mechanically destroyed quartz grains, triangular ("dagger-shape") chips are apparent (Pl. 20, Fig. 4).

It is noteworthy that sometimes, *e.g.* at the initial stage of the jasperoid origin, granite quartz is dissolved earlier than feldspars, which are slowly replaced by new quartz. Presumably pH of early solutions was high.



Fig. 6. Geological map of the Czerniawa — Pobledna region (after Berg 1922; modified)

1 schist, 2 Izera gneiss, 3 granite-gneiss, 4 fine-grained gneiss, 5 leucogranite, 6 greisen, 7 tourmaline quartzite, 8 vein rocks, 9 quartz veins; CK1, N1, etc. — sample locations

# IZERA AREA

VEINS

Quartz veins at the Izera area (Figs 1, 6-8) are up to several meters thick and their outcrops range to some km. Three types of veins may be distinguished:

i) veins occurring in gneisses and not connected with metasomatites but probably with gneisses;

ii) veins occurring in metasomatites, but being earlier than metasomatosis, presumably connected with gneisses;

iii) veins occurring in metasomatites, formed during metasomatosis or somewhat later.



Fig. 7. Geological map of the Gierczyn — Świeradów — Wysoki Grzbiet Mts region; after Berg (1920) and Berg & Ahrens (1923)

1 schist, 2 Izera gneiss, 3 granite-gneiss, 4 porphyric granite-gneiss, 5 fine-grained gneiss, 6 Leucogranite, 7 vein rocks, 8 larger quariz veins, 9 sample locations A part of veins and similar bodies of the two first types may be the product of metamorphosis of primarily sandy intercalations in sediment then altered into paragneiss

"Vein" from Mt. Blizbor (S49) consisting of quartzite laminated with muscovite (Pl. 27, Fig. 4) is such an example, but a general identification is difficult and ambiguous.

Veins of type ii, passing sometimes both through gneiss and leucogranite (e.g. veins at Kotlina leucogranites) are rebuilt by metasomatosis in various degrees.

Veins of types *i* and *ii* fill opened fractures and they consist either of massive (Pl. 22, Fig. 3) and drusy quartz (Pl. 22, Fig. 2) or of products of silicification of tectonic breccia zones (Pl. 23, Figs 1—3). Massive quartz, contrary to that from Karkonosze, bears various stress translations of crystal lattice (Pl. 26, Figs 1—4). Single microclines (Pl. 22, Fig. 4) which grew in equilibrium with quartz, were afterwards weakly replaced by quartz (Pl. 27, Fig. 3). Quartz druses growing from both sides of a fracture are often asymmetric (Pl. 22, Fig. 2) with growth deformations of quartz habit, proving temperature gradients or influence of gravitation on the movement of solution. Fine-grained hematite-quartz aggregates with composition similar to jasperoids (Table 3, S17) were found rarely and only between crystals of druses (Pl. 22, Fig. 2 and Pl. 25, Fig. 3), being clearly of a primary, not metasomatic origin. This aggregate formed due to decrease of temperature at the end of the vein origin. Zoned quartz crystals often bear amethyst zones (Pl. 25, Fig. 1) resulting from pH change of solution (Walenczak 1969).

Cataclastic breccias were silicified beginning from the filling of spaces between fragments with druses and veinlets (Pl. 23, Figs 1—3) and afterwards an intensive silicification of gneiss fragments (Pl. 25, Fig. 2). Strong recrystallization sometimes effaced the texture of breccia, forming mimetic "vein of opened fracture".

Some metasomatic veins, e.g. S23, is filled by fine quartz (<0.1 mm dia.) with sericite (PI. 23, Fig. 4); they are similar to muscovite-quartz zones in greisens. Subsequent quartz veinlets cutting sericite-quartz filling are coarse-grained due to crystallization under almost isothermic conditions (Pl. 25, Fig. 4).

Veins and veinlets of gray-bluish quartz in gneiss have zonal distribution of rutile(?) inclusions, similarly as gneiss quartz (Pl. 28, Fig. 13) being presumably the oldest veins.

Veins in metasomatites (type *iii*), usually fill opened fractures. Vein quartz from leucogranites is commonly grained, milky or gray, and from greisens transparent or translucent. Fluorite and muscovite is common, although subordinated.

#### **METASOMATITES**

Quartz from metasomatites (cf. Figs 1, 6—7): leucogranites, greisens and tourmaline nests, differs from blastic gray-bluish quartz of parent gneisses. Zonal distribution of bluish color disappears and quartz becomes uniformly blue. This quartz is replaced by gray grained variety in tourmaline greisens and nests or light-gray one in leucogranites. These latter alter into translucent or transparent quartz in greisens.

Tourmaline nests in gneisses and leucogranites consist of typical tourmaline--quartz association with muscovite (Pl. 24, Figs 1—5 and Pl. 27, Figs 1—2). Nests in gneisses are always surrounded with a leucocratic rim, several mm to several cm thick (Pl. 24, Figs 4—5), consisting of quartz, albite and some microcline, *i.e.* being very similar to leucogranites. Likewise, greisens and leucogranites in large scale bodies, associate ones with the others in the Izera Upland (cf. Fig. 1).





1 Izera gneiss and Rumburk granite, 2 vein rocks, 3 quartz veins, 4 Quaternary sediments; N26 etc. — sample locations

# MICA-CHLORITE SCHISTS

2

Quartz in schists of the Czerniawa-Stara Kamienica zone (cf. Figs 1, 6-7) forms intercalations and various veinlets and veins. It is associated with all minerals of schists (muscovite, biotite, chlorites, garnet and feldspars). Extensive range of quartz varieties was found, from gray, milky and rock crystal to smoky quartz and true morion. Usually quartz is anhedral. Gray, grained quartz associates almost always with ore parageneses (cassiterite and sulfides); only ocassionally semitransparent or translucent massive quartz was found in ore associations.

Schists, very similar to those from the Czerniawa-Stara Kamienica zone, taking into account both chemical (Table 4) and mineral composition, were found as small intercalations in gneiss from Izera Mfs (e.g. sample *S18*; Pl. 22, Fig. 1). Quartz in these intercalations forms lenses of subhedral crystals.

# Table 4

Component	Muscovite-chlo- rite-quartz schist, Izera Mountsine, sample S18	Muscovite-bio- tite schist, Czerniewo- Zdrój, sample CK3	Biotite-Rusco- vite-chlorite schist, Krobice, sample OK11
S10,	76.91	45.89	44,63
T10	0.07	0.60	0.22
A1,0,	12.66	27.65	30,33
FegOg	0,25	2.28	2.11
FeO	0.75	5,12	4.76
MnO	0.01	0.08	0.08
MgO	0,65	3,39	2.29
CaO	0,76	0.73	0.94
NagO	0.20	0.67	0.86
ĸ	5.04	8.05	6.45
H_0+	2,14	4.42	5,84
H20-	0.55	0.84	0.75
Totel	99.98	99.82	99.46
Ignition loss		5.16	6.19

Chemical composition of mica-chlorite schists from the Czerniawa — Stara Kamienica zone and Izera Mts; wt %

#### MINERALIZED FAULT ZONE OF GARBY IZERSKIE

Dislocation zone of Garby Izerskie is several km long, in direction SW-NE (Fig. 9). Mineralized zone, connected with the dislocation, is 100-400 m wide and it dips abruptly to SE. The SW end of the zone contacts with the Karkonosze granite and its NE end may be observed as nebulous silicification at Mt Jastrzębia. The zone is divided with a number of transversal dislocations (Fig. 10) into blocks then shifted. Wall rocks on the SE side of the zone consist of hornfelsed schists bearing andalusite and pinite, with intercalations of the following kinds of skarn: diopside-quartz-wollastonite, garnet-vesuvianite-quartz-wollastonite, wollastonite with vesuviante plus fluorite, silicate-fluorite-calcite, etc. (Fig. 10; Pl. 29, Figs 1-3). The NW side is built up of blastomylonitic and fine-grained gneisses with biotite blasts: the NE part of the zone cuts some different varieties of gneisses. The dislocation zone is mineralized with quartz; one may observe continuous increase of quartz content both in gneiss and in hornfels toward the center of the zone, till monomineral quartz rocks (cf. cross-section in Fig. 21). Both wall rocks and quartz are cut with horizontal and slightly inclined veins (Fig. 10; Pl. 29, Fig. 1 and Pl. 30. Fig. 4) of granitoid composition (Table 5), and presumably connected with the Karkonosze granite. The above rocks, excluding skarns, were previously characterized from petrographic and tectonic points of view (Lewowicki 1965, Szałamacha 1965, Szałamacha & Szałamacha 1966), and the writer would like to add some new observations made mainly in "Stanisław" quarry (Fig. 9).

Durable process of recrystallization of minerals of wall rocks (Szałamacha & Szałamacha 1966) was accompanied by intensive silicification in the dislocation zone. A metasomatic origin seems to be undoubted. Quartz grains in quartz metasomatites are apparently larger (0.3—3 mm) than in parent hornfels (0.1—0.5 mm) and the most of other wall rocks. Similar increase of quartz grain size is obvious at the contacts of wall rocks with granitoid veins (Pl. 30, Fig. 4).

Hornfelses, probably after silicification, underwent to the activity of fluorinebearing solutions, and fluorite developed intensively (Pl. 30, Fig. 3), associating with pyrite and chalcopiryte (Pl. 31, Figs 1—2). Fluorite, as one of the last components, appears also in skarns, both in quartz and calcium silicate laminae.

# PNEUMATOLYTIC AND HYDROTHERMAL ACTIVITY



Fig. 9. Plan of the working pit of "Stanisław" quarry at Garby Izerskie (a); state in 1971; based on materials of JKSM and writer's observations; and geological map of Garby Izerskie zone (b); after Berg (1920)

OI GATDY IZCISE ZONG (D), GIOT ZONG (DOL) 1 Izera gneiss, 2 granite-gneiss, 3 porphyric granite-gneiss, 4 blastomylonitic gneiss, 5 cordieritebearing hornfels, 6 hornfels, 7 Karkonosze granite, 8 quartz vein, 9 vein rocks, 10 outcrops of granite apophyses, 11 sample locations

cs outcrop of calc-silicate intercalations (skarn; cf. Fig. 10), p cross-section line (cf. Fig. 21); 1012-1031 — height of exploitation levels (m a. s. l.)

Silicified hornfelses and quartz rocks, constisting of grains overlapping one another and with wavy light extinction (Pl. 30, Fig. 1), are cut with numerous fractures, partly or completely healed with subhedral quartz druses and aggregates. The filling of the fractures, being coarse-crystalline, precipitated without any initial layer of fine-grained quartz (Pl. 30, Fig. 2). Druses in cavities in metasomatic massive quartz are common (Pl. 35 D) as well as druses formed on the whole surface of massive quartz chips, found separately in tectonic cavities (Pl. 36 D). In the latter, the greater quartz crystals grew only on quartz grains of massive quartz, having favourable orientation; on other grains only thin covers formed (Fig. 11). The above assemblage of peculiarities testifies to slow crystallization of the healing quartz, under subisothermic conditions (cf. Fig. 13 D, J) and from solution with moderate concentration of SiO<sub>2</sub>.

Euhedral fluorite (Pl. 33, Fig. 3) and single scales of hematite associate with the latest healing quartz.

Besides of small quartz druses and veinlets, tectonic cavities (50-80 by 30-50 cm) were found occassionally, with walls covered by zoned, milky and transparent quartz crystals (Pl. 34 A-C), bearing inclusions of clay minerals, and arranged in the growth zones of the crystals. Some fractures in hornfels were healed with partial replacement of hornfels, by gray quartz and very late amethyst plus late calcite (Pl. 33, Fig. 2).

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Fig. 11. Orientation and intensity of growth of crystals in quartz druse (B) crystallized on the whole surface of a chip of massive quartz (A, dotted), both depending on orientation of Z-axis (C) of grains being the nuclei of crystallization; Garby Izerskie, "Stanisław" quarry

Paragenesis of fluorine minerals: fluorite (blue, green, pink and violet) and apophyllite (Pl. 32 C) with porous white quartz and late calcite (Pl. 33, Fig. 1) or stilbite and chlorite, are the final mineral association in skarns and fractured hornfelses.

Granitoids often form pegmatoid bodies consisting of quartz, microcline, albite and muscovite with rare euhedral hornblende (Pl. 32 A) and relatively common tourmaline (Pl. 32 B) and fluorite. Sometimes granitoids are cataclased and strongly chloritized along the cracks; pyrite follows chlorite (Pl. 31, Fig. 3).

Component	Aplite, sample G172	Altered aplite, sample Gi73
\$10 <sub>2</sub>	75.52	70,45
T102	0.06	0.04
A1203	12.90	16.80
Total Fe203	0.18	0,43
Mn0	0.04	0.04
Mg0	0.26	0,74
CaO	<b>0.9</b> 6	0.87
Na <sub>2</sub> 0	6.10	0.30
ĸ₂Ō	3.35	7.00
H20+	0.48	2.63
H20-	0.15	0.87
Total	100.00	99.97

 Table 5

 Chemical composition of aplites from Garby Izerskie; wt %

A part of granitoid vein rocks is disintegrated during alteration connected with the removal of SiO<sub>2</sub> from silicates and total alkalies; simultaneously these rocks become enriched in Al<sub>2</sub>O<sub>3</sub> and H<sub>2</sub>O (Table 5). Changes of amounts of MgO, total Fe and partly  $K_2O$  are controlled by variable content of muscovite. From these rocks, the clayey substance was extracted, being the product of feldspar alteration; this mineral was identified by X-ray powder pattern as halloysite. Electron microscope images show typical tubular crystals of halloysite (Pl. 38, Figs 11-12). This alteration process is one of the final phenomena in the studied rocks. Undoubted silicification of the vein rocks was not observed.
A. KOZŁOWSKI, FIG. 10

South-eastern wall of the "Stanisław" quarry at Garby Izerskie (cf. Text fig. 9a),



h hornfels, cs calc-silicate rocks (skarn), g granite apophysis, f transversal fault

In massive quartz, pockets and nests were found, filled essentially with halloysite, and bearing euhedral quartz crystals (Pl. 35 A; Pl. 36 A-C), colorless, milky, with smooth or frosty faces, as well as parallel (Pl. 35 BC) or oblique (Pl. 37 A-C) intergrowths of quartz. Variable morphology of crystals in the same nest and inclusions of clayey substance in quartz prove that crystals grew, in part at least, in halloysite mass.

# PHYSICO-CHEMICAL CONDITIONS OF PNEUMATOLYTIC AND HYDROTHERMAL ACTIVITY

# FLUID INCLUSIONS

### PEGMATITES

Special attention was paid to fluid inclusions in minerals, essentially in quartz, representing the microsamples of the mineral-forming fluid. Doubtless inclusions of the silicate melt, partly or completely crystallized, were ascertained in aplites surrounding pegmatites in the Karkonosze massif. Although homogenization temperatures  $(T_H)$  of these inclusions were not measured, due to their minute size, their presence testifies the melt origin of aplites. Searches of melt inclusions in granophyric intergrowths were not successful; only gas and liquid-gas, i.e. pneumatolytic inclusions were found. The ascertained pneumatolytic inclusions could not be accepted as surely primary ones for reason of an obscure relation to the growth zones of quartz, and hence the high-temperature granophyric intergrowths may be called the pneumatolytic assemblage only on condition of primary origin of inclusions found. Further searching either for the melt inclusions or for the doubtless primary pneumatolytic inclusions is, however, very desirable. Density of pneumatolytic solution inclusions, both in the intergrowths and in the block zone, was low, roughly 0.1 - 0.2 g/cm<sup>3</sup>.

Pneumatolytic solutions condensed, forming hydrothermal conditions of an one-phase fluid, although in fluid inclusions liquid CO<sub>2</sub> at room temperature is found, which homogenizes in water solution. Liquid CO2 is more common in pegmatites from the Eastern part of the Karkonosze massif, but it is assumed to be absent in larger amounts in pegmatites in the NW part of the massif; although liquid  $CO_2$  is a common component of secondary inclusions in magmatic quartz grains from fresh granite probably of the whole massif.

With condensation of pneumatolytic solutions, the existence of critical phenomena associated, and it resulted in fluid inclusions homogenizing in critical fluid. After general condensation, short events of pneumatolysis appeared due to the boiling of the hydrothermal solution. Condensation is also followed by two processes: (1) healing of reticulate postinversion cracks in former pegmatitic high quartz (Pl. 13, Fig. 3) with fluid that yielded inclusions bearing several percent of liquid CO<sub>2</sub> (PL 13, Fig. 4), as it was ascertained in pegmatite at Wilcza Poreba, and (2) crystallization of wolframite Fb77 (Pl. 21, Fig. 1), and presumably somewhat eanlier metamict allanite (Pl. 21, Fig. 4) in pegmatites at Szklarska Poreba.

Very numerous gas-liquid (hydrothermal) inclusions occur is massive and euhedral quartz of pegmatites, as well as relatively rare one-phase liquid low--temperature inclusions (cf. Plate 2 in: Kozłowski, Karwowski & Olszyński 1975). Moreover, albitization was also caused by hydrothermal fluids, since the gas-

-liquid inclusions were found in fractures of quantz, partly filled by albite.

#### VEINS

Fluid inclusions in vein quartz from Karkonosze massif are small (< 0.1 mm) and usually two-phase. Mineral-prisoners, such as hematite (specularite), muscovite, clay minerals, calcite (?) and opaque phases, are rare; none daughter minerals were found. Purely gas inclusions are extremely rare, liquid-gas ones, although more frequent, are less numerous than in pegmatites, so that the pneumatolytic stage is poorely developed, and veins are mainly of hydrothermal origin (cf. Plate 3 in: Kozłowski, Karwowski & Olszyński 1975). The latest inclusions bear one--phase filling of water solution.

Vein quartz from Izera area contains somewhat more variable inclusions. About 70% of all the investigated samples bear inclusions of water solutions (Pl. 28, Fig. 2 and 4), but almost 30% of the samples yield inclusions of water solutions with noticeable content of CO<sub>2</sub>, and forming own liquid phase at room temperature, that occupies 5—30 vol. % (Pl. 28, Figs 1 and 9). The CO<sub>2</sub>-bearing inclusions were found both in vein quartz from gneiss and from metasomatites. Several very minute, nonphotogenic inclusions with a cubic, isotropic daughter mineral (halite ?) were also ascertained. Pneumatolytic conditions were obviously absent, excluding two cases of heterogenic state of fluid, and necked down inclusions, with irrational phase content. Secondary hydrothermal inclusions, similar to those from the vein quartz, are common in blastic bluish quartz in gneiss (Pl. 28, Fig. 14).

### METASOMATITES

Metasomatites (leucogranites and tourmaline nests) bear inclusions similar to those described ealier for greisens (Karwowski 1977): mainly hydrothermal, two-phase aqueous (Pl. 28, Fig. 10) and three-phase aqueous with liquid CO<sub>2</sub> (Pl. 28, Fig. 8), occassionally with small ( $\leq 5$  vol.  $^{0}/_{0}$ ) halite crystals. Common in inclusions euhedral muscovite occupies a variable part of the vacuole volume and it occurs as solid inclusions in the same growth zone, being then obviously the entrapped mineral-prisoner (Pl. 28, Figs 5 - 7).

# MICA-CHLORITE SCHISTS

Quartz from mica-chlorite schists bears very small inclusions ( $\sim 1 - 5 \mu m$ ; Pl. 28, Fig. 3). Three types of the filling were here distinguished: aqueous solution + + gas bubble; liquid CO<sub>2</sub> + gas bubble; and aqueous solution + liquid CO<sub>2</sub> + gas bubble. Over 50 % of the studied inclusions bear a filling, the nature of which cannot be unambiguously determined; nevertheless, the great role of CO<sub>2</sub> in the mineral-forming solutions in schists is apparent.

#### ROCKS FROM MINERALIZED FAULT ZONE OF GARBY IZERSKIE

Inclusions are gas-liquid (hydrothermal); only occasionally in quartz from silicified hornfels and quartz-wollastonite skarns, pneumatolytic inclusions appeared. However, pneumatolytic inclusions are ubiquitous in the contact rocks at Szklarska Poręba Dolna, Zbójeckie Skały location (Pl. 28, Figs 11-12). Neither at Zbójeckie Skały nor at Garby Izerskie liquid  $CO_2$  was hitherto found.

Inclusions in late quartz from halloysite pockets at Garby Izerskie often bear the third phase except of water solution and gas. This phase is a mineral-prisoner, presumably halloysite, forming radial, loose or compact, not disordered aggregates, and being found only in primary inclusions (Pl. 38, Figs 2-4, and 8-9) in various parts of the crystal (Pl. 38, Fig. 1) together with two-phase hydrothermal inclusions (Pl. 39, Fig. 5). The mineral-prisoner is sometimes present at the "bottom" (taking into account the direction of crystal growth) of the inclusion, being the cause of the origin of primary inclusion (Pl. 38, Fig. 10); secondary inclusions are either two-phase gas-liquid or three-phase (Pl. 38, Figs 6-7) with a flake of muscovite (sericite ?). The above facts permit to assume that halloysite crystallized together with quartz and temperatures of the origin of quartz ought to be pertinent also to halloysite being trapped into primary inclusions, the situation being similar to that of the earlier studied quartz and kaolinite-smectite paragenesis at Jeglowa (Kozłowski & Karwowski 1972a, Karwowski & Kozłowski 1975).

#### TEMPERATURES

#### THEORETICAL CHANGES OF TEMPERATURE IN FRACTURE

Crystallization of minerals in veins, even monomineral, or almost monomineral ones like those being under study, is a complicated, rarely one-stage process. However, analysis of certain simple, essential events, would clarify the mode of the formation of often very composed vein fillings.

The opening fracture is filled with solution, the temperature of which in a given point of the system, that will be called the *initial point* of the solution migration (independently, whether it is another fracture-resorvoir able, with its solution, to fill the actually formed fracture or the pore, integranular solution of the wall rock), may change during the time t as follws (Fig. 12): A — no changes (Ts = const); B — increase ( $Ts_o < Ts_t$ ); C — decrease ( $Ts_o > Ts_t$ ); D reaching maximum after  $t_1 < t$ ; B — reaching minimum after  $t_1 < t$ . Such changes of the solution temperature just flowing into the discussed zone of the fracture, strongly influence, in addition to chemical composition of the solution, the course of precipitation and temperature regime in the fracture, being favorable, respectively, to: A — slow crystallization of big crystals, B — recrystallization and partial dissolution of the already crystallized minerals, C — crystallization of aggregates of fine crystals with defects, D — complicated phenomena like B at the initial stage, and healing of the etchings in the final stage, E — crystallization like C and further corrosion with possible overlapping of the initial parageneses.

These general models are modified by a change of temperature of the wall rock in the discussed zone of fracture, change of thickness of the fracture, and the kind of the movement of solution in the fracture (laminar or turbulent).

One may suppose that the temperature of formation of the successive zones of a single crystal is analysed. The crystal grows perpendicularly from the wall of the fracture to its center, so that after the time t (different from the previous t value) the crystal reaches the center of the fracture. For elimination of heat influence of the approaching walls of the healing fracture, we may consider only one crystal. The heat conductivity of the crystal, heat effects of crystallization, disturbances of solution flow around the orystal, and possible dissolution of the crystal during the temperature increase, are ignored.

#### PLATE 28

Fluid inclusions in quartz, Izera area: 1 — three-phase; vein in gneiss, sample N9, Mirsk; 2 — two-phase, vein in leucogranite, S56, Sosnka; 3 — two-phase, quartz layer in schist, CK14, Krobica; 4 — two-phase, vein in gneiss, S5; 5 — gaseousliquid with two muscovite crystals (mu); 6 — gaseous-liquid; 7 — muscovite crystal (mu) and unidentified mineral (x), all three inclusions in the same growth zone of quartz crystal, tourmaline nest, S14; 8 — three-phase with L CO<sub>2</sub>; tourmaline nest S14; 9 — three-phase with L CO<sub>2</sub>; vein in gneiss, S16; 10 — two-phase, tourmaline nest, S31, Górzyniec; 11—12 — pneumatolytic, two-phase, silicified hornfels, S43, Zbójeckie Skały. Scale bar for all inclusions.

13 — Blast of blue quartz from the Izera gnelss with zones of rutile (?) inclusions; C — cracks, sample S72; 14 — typical secondary inclusion in this blast.



Fig. 12. Possible cases of temperature changes of solution in the initial point of migration of the solution (reservoir) during time interval from 0 to t  $Ts_0$  — temperature of solution in time 0;  $Ts_t$  — temperature of solution in time t; other explanations in the text

The specific events, a part of which is to be discussed here (Fig. 13), may be divided into two essential groups:

I - connected with filling of the forming fracture with pore solution from the rock, then pressure of the solution in pores and small cracks is higher than in fracture (Pr > Pv)and possible metasomatic alterations in the wall rock connect with a removal of a part of the substance dissolved in pore solution, hitherto being in equilibrium with minerals, and possibility of influx of solution with different composition;

II – due to the filling of the fracture with solution from a "reservoir", then  $Pr \leq Pv$ and possible metasomatosis of the wall rock connects with penetration of the substance from the fracture to the rock (the walls of the fracture may be sometimes dissolved by the solution).

The above partition is theoretical. In general, one of the named processes may distinctly prevail. Presumably, the process II ought to be accompanied by the process I in the forehead of the opening fracture. Such influx of the pore solution, called the adiabatic mobilisation (Dolgov 1965), connects with strong temperature drop at the beginning and its following increase till almost the previous value (whereas Tr = const.). The initial temperature and pressure drop cause rapid crystallization of the dissolved substance (Fig. 19 A) and the fracture may be early healed (Fig. 13B-C). Any substance then precipitating, is fine-grained. A slow opening of the fracture may result in the growth of well developed big crystals (Fig. 19D). Such course of the temperature changes may be modified by variations of temperature of the whole system (Fig. 13E-F).

Fig. 13. Certain cases of temperature changes during the filling of a fracture, having been opened or existing in porcus material (rock); distance from wall to the middle of vein, from left to right side of each graph, respectively

Essential cases: I — influx of solution from pores to fracture, II — flow of solution along fracture

Pr pressure in pores of rock, Pv pressure in fracture

Temperatures: Ts — of solution, Tr — of rock,  $Tr_0$  — of rock in the initial moment of process,  $Tr_t$  — of rock in the final moment of process,  $Ts_0$  — of solution in the initial moment of process,  $Ts_t$  — of solution in the final moment of process Thick lines — temperature of solution; thin lines — temperature of rock or

temperature in reservoir; other explanations in the text



In group II, for Ts = const, if Ts > Tr, initial crystallization is rapid, forming fine-grained aggregates, and afterwards slowly growing larger crystals, with assumed recrystallization of the early fine-grained zone of the vein filling into coarser crystalline aggregate. When the flow was laminar, the change of the grain size ought to be more gradual, and when  $Ts \ge Tr$ , a vein may be filled by coarse-crystalline druses or aggregates (Fig. 13G—J). Changes of Ts ( $Ts_o > Ts_i$  or  $Ts_o < Ts_i$ ) modify temperature in the studied zone and temperature maximum may appear (Fig. 13K—L).

When Ts < Tr (Fig. 13 *M*—*R*), crystallization is rather impossible on the walls of the fracture, whereas the solution with increasing temperature may dissolve the walls of the fracture till achieving saturation. Crystallization is possible only in some cases (illustrated in Fig. 13*P*), if  $Tr_{t} = Ts_{t}$ .

When minerals crystallize in fracture filled with an immobile solution, generally the temperature consequently decreases.

### HOMOGENIZATION TEMPERATURES OF FLUID INCLUSIONS

Homogenization temperatures  $(T_H)$  of fluid inclusions (Table 6) may be accepted as minimum crystallization temperatures of the minerals. For evaluation of the real crystallization temperatures, the pressure correction value  $\Delta T$  should be added to  $T_H$  value (Roedder & Kopp 1975). Evaluation of the pressure of mineral-forming solution is difficult. Suggestions, based on the inclusion studies are rather only approximations, but if they represent the range close to true values of pressure, in the studied area the pressures ought decrease from about 1 kbar at elevated temperatures (600-400°C) to 0.4-0.3 kbar at low temperatures (200-150°C). Hence, the  $\Delta T$  values were calculated for 1, 0.5 and 0.25 kbar at elevated, moderate and low temperatures, respectively. Diagrams PTF and  $T_{y}/\Delta T$  for 10% and 5% NaCl solutions (cf. Lemmlein & Klevtsov 1973) were applied. Presumably, the values  $T_{\rm H} + \Delta T$  (Table 6) are the maximum crystallization temperatures, but they are assumed as being rather close to the true values. Pneumatolytic inclusions, due to their unknown composition, were omitted in calculations of the  $\Delta T$  values. Most of the inclusions ( $T_H$  given in Table 6) are primary or seemingly primary ones, except of those indicated.

The highest  $T_H$  (580°C) were found in pegmatitic quartz from paragenesis with former oligoclase (albitized) and microcline (sample K72, from Marczyce). So high temperatures, plus unknown  $\Delta T$  value, are confirmed by the occurrence of quartz with typical reticulate cracks in pegmatite at Karpacz; such cracks are formed during rapid high  $\rightarrow$  low quartz inversion at temperature ~600°C under pressure ~1 kbar (Pl. 13, Fig. 3).

These reticulate cracks were healed only after condensation of a pneumatolytic solution, with fluids bearing CO<sub>2</sub> and forming in inclusions under room conditions phase of liquid CO<sub>2</sub> (Pl. 13, Fig. 4). Rather rare CO<sub>2</sub>-bearing inclusions have  $T_H = 380 - 210^{\circ}$ C. Thus, the true temperatures  $(T_H + \Delta T)$  for later events in pegmatites can be evaluated (Table 6), but not, at least now, for the early stage: the only information is that pegmatites began formed at temperatures higher than  $800^{\circ}$ C.

Veins from the Karkonosze massif crystallized over a wide range of temperatures (Table 6); their crystallization probably began at temperature higher than 500°C, but difficulties named above, preclude the evaluation of the  $\Delta T$  value for gaseous inclusions. Active high-temperature pneumatolytic conditions appeared very distinctly in the Karkonosze massif. Condensation at 470–460°C ( $T_H = 380$ –  $370^{\circ}$ C) caused in ore-bearing veins an abundant precipitation of the ore minerals. Occasional pneumatolytic events at lower temperatures are connected with rapid pressure decreases and they are local. High-temperature silicification ( $T_H + \Delta T =$ 

### Table 6

Homogenization temperatures of fluid inclusions and calculated formation temperatures of associations crystallized under activity of thermal fluids, Karkonosze-Izera block

	- 0-		4	5	
Description	1 <sup>7</sup> H, <sup>-</sup> C	ι <sub>ή</sub> +ΔΤ),"C	data explained Selow		Remarks")
Karkonosza massif				<b>—</b>	
	680-380				E part of the second
regueraton	480-360		G	l č	W part of the meesif
	405-398		C	Ā	
	380-300	470-390	<u>L</u>	<u>c</u> .	persgenesis: allenite, wolfrésite
	366-330	440-490			elhitization
	290-270	380-360	1 T	B	P inclusions in cleavelandite
	320-200	410-250	L .	B	scheelitization of wolframite
	360-290	460-389	1 5	l c	snoky quartz
	250-160	340-210	1 1	Ιč	Another
	160-90	210-110	ĩ	č	paragenesis: hematite
	100-80		L	•	8 inclusions in cleavelandite
Feldsper-quertx veine	420-390		8	8	of. description in the text
	400-90	600-110		1 10	•
	380-330				a designed and the share of
Veins with quertz replacing feldepers	370-270	460-360	L	C	of, description in the text
Ore-bearing quartz veins	405-376	460-390	G L	ĉ	personesis: cossiterite personesis: cossiterite, molfra-
	340-150	440~200	L	Ð	paragenesis: scheelite, sulfides of Ho, Fe, Cu and Bi, sulfosalts of Cu, Pb and Bi
	170-100 (€40)	210-110	Ł	8	pangue quartz ons-phase inclusions
Quartz and meethyst voins	340-90	440-110	L	0	
Quartz veins with hemetite (issperoids)	280-100	340-110	L		
	140-80	180-100	L	•	quertz veinlets in jasperoid
izera area					
Quartz veine	340-300	440-390	(G), L	8	
-	280-170	370-210	Ľ.	0	
	190-100	230-120	L		
Metaeomatitee: greisens	450-300	550-390	(G), L		"), inclusione in topaz, quartz
	<b>330-90</b>	430-110	L		A tourmaine , inclusions in fluorite and late quartz
leucogranites	405-290	490-380	Ĺ	- c	inclusions in quartz
	250-90	340-110	L		"), inclusions in fluorite
TOURNELING NEELS	410-270	800-360			
Quertz from schlote	400-150	490-200	L	•	$T_{\rm D}$ of ceselterize = 390 - 380°C')
Zone of Garby Izerskie	]				
Hornfalses and skarna	430-310	7 -410	6.L	A	inclusions in quartz
Messive quartz	280-130	370-170	L	c	P and 8 inclusions not discornible
	280-140	370-180	-	c	his and anall druges
alogy durity	220-125	300-160	ĩ	č	quertz from helloyeite meste
Apophyllits-fluorits-quartz-calcite association	265-95	360-110	L	в	inclusions in fluorite

<sup>(9)</sup>Type of homogenization: G = in get phase, L = in liquid phase, C = dritical phenomena <sup>(9)</sup>Number of determinatione: A = <10; B = 10-80; C = 50-100; D = 100-800 <sup>(1)</sup> P = primery inclusions, S = secondary inclusions, T<sub>D</sub> = temperature of decrepitation

// - primery inclusions, 5 - sedanosry inclusions, 10 - temperature of decreg d)T<sub>H</sub> after Kerwowski (1977)

After Karwowski & Kozłowski (1974)

= 460--360°C) gave products different from the jasperoid low-temperature one  $(T_{\rm H} + \Delta T = 340 - \text{about 110°C})$ . The first type of silicification results in quartz almost nondiscernible from massive quartz, the second type does in fine-grained jasperoids with typical fracture.

Measurements of  $T_H$  for veins from the Izera area were seriously impeded by very small dimensions of the studied inclusions. Number of measurements in relation to the number of studied veins is too small for clear distinguishing of temperature-genetic types of the veins. Probably, three temperature stages of the vein formation occurred (Table 6): 440--390°C, 370-210°C and 230-120°C, either characteristic of individual vein, or overlapping one another in the same vein. In general, temperatures of the formation of veins in the Izera area are lower than in the Karkonosze massif.

Temperatures of the origin of leucogranites and tourmaline nests are very similar to the temperatures of the formation of greisens (Karwowski 1977). This is also the argument supporting the connection of the origin of these three kinds of metasomatites that formed at temperatures higher than quartz veins in the Izera area

The  $T_H$  measurements in quartz from schists, due to the finding of extremely small number of inclusions with dimensions sufficient for homogenization (6 inclusions), may be only the approximate values; however, upper range of  $T_H + \Delta T$  (490°C) is close to the temperature suggested for metamorphism of the schist zone (500-550°C; cf. K. Kozłowski 1974).

For the same reason, the  $T_H$  values for skarns and hornfelses determine only the range of temperatures; moreover, hitherto the advance of formation of the rocks which may be connected with the obtained temperatures, is nebulous. Better defined temperatures of the origin of quartz rocks and druses, vary weakly. Also fluorite crystallized at the similar temperature interval. Distinct decrease of the temperature occurred at the final stage of crystallization of drusy quartz and fluorite (cf. Pl. 36, Figs 1--6); earlier stages are almost isothermic, and changes of temperature did not exceed 20°C. The assumed crystallization of halloysite from  $\sim 300^{\circ}$ C to  $\sim 160^{\circ}$ C may be accepted, since its occurrences formed by the activity of hydrothermal solutions are known (cf. Gennaro, Franco & Stanzione 1973).

Data on temperature changes in the transversal section of the vein are scarce and incomplete, mainly due to small number of the larger inclusions. Of the sufficiently documented cases, two are the most common and doubtless:

i) lower temperature near the wall of the vein, and following increase to a higher level;

ii) almost constant temperature along the whole section, sometimes with weak decrease in a small, central part, connected with interruptions of crystallization.

The above cases agree with the schemes presented earlier (Fig. 13A, G, H, and Fig. 13D, J, P, respectively). The case (i) was ascertained as very common also in other areas (cf. Pavlov & Sharapov 1972, p. 94).

### DISCUSSION ON THE FORMATION OF PEGMATITES

The scheme of formation of the Karkonosze pegmatites, presented in the recent paper, refers to the Zavaritski's hypothesis (1939, 1947), elucidating the origin of pegmatites by an accumulative recrystallization of fine-grained rocks. That author disavowes in general the existence of pegmatitic melts sensu Fersman (1940). Such an idea appeared even earlier, expressed e.g. by Hess (1933, p. 462): "Pegmatite... rock... formed from the aqueous solutions of a freezing magma or from the combination of the solutions with previously existing minerals". Extensive discussion of opinions on metasomatic hypothesis of the pegmatite origin and critical evaluation of the presumptions and arguments proving the hypothesis on crystallization of the pegmatites from the silicate melt, is given elsewhere (Rudenko 1972).

An experienced investigator of fluid inclusions and pegmatites of the Ukrainian shield, Kalyuzhnyi, has hitherto never reported the presence of inclusions of the silicate melt in pegmatitic minerals, formally accepting the ready hypothesis of the origin of pegmatites from



Skarns from Garby Izerskie, "Stanisław" quarry; nat. size 1 -Contact of granite (Gr) vein with skarn composed of diopside (D), quartz (Qz) and wollastonite (W) 2 — Garnet (G)-vesuvianite (V)-quartz (Qz)-wollastonite (W) skarn 3 — Coarse-crystalline wollastonite with vesuvianite (V)



- Orientation of quartz crystals in druse (upper part), and defined by the orientation of respective grains of massive quartz (lower part); contact marked with triangles; Sample 81
  Anhedral massive quartz cut by a vein of subhedral quartz; Sample 82

- 3 Sulfide-bearing hornfels with fluorite (Fl); Sample 84
  4 Contact of granite vein with hornfels (right side); Sample 94
  Garby Izerskie, "Stanisław" quarry; nicols crossed



1 — Pyrite in hornfels; reflected light, one nicol

2 — Relics of chalcopyrite in limonite; reflected light, one nicol 3 — Chlorite (Ch) and pyrite (Py) in pegmatoid vein; Qz — quartz

Garby Izerskie, "Stanisław" quarry



Fluorine-bearing minerals from Garby Izerskie, "Stanisław" quarry: A — hornblende, B — tourmaline, C — apophyllite; the first two minerals are associated with microcline (*Mi*) and quartz (*Qz*)



- 1 Late calcite; association with apophyllite and fluorite 2 Hornfels (h) replaced by gray quartz (gq) and amethyst (A) with calcite; nat. size

3 — Fluorite (f) in quartz druse Garby Izerskie, "Stanisław" quarry



Two specimens of quartz (A and B), from large druses in massive quartz, and crosssection along the rhombohedron plane (C) to show their zonal structure Garby Izerskie, "Stanisław" quarry; nat. size



Euhedral quartz (A), parallel-grown quartz (B and C) from halloysite nests; and quartz druse (D) in massive quartz (qm) Garby Izerskie, "Stanisław" quarry



Euhedral quartz (A, B and C) from halloysite nests and quartz druse grown on a chip of massive quartz (D) Garby Izerskie, "Stanisław" quarry



Oblique intergrowth of quartz from halloysite nests: A — transparent crystals, B — crystals with frosted faces, C — milky and transparent crystal Garby Izerskie, "Stanisław" quarry



1 — Polished plate of quartz from halloysite nest; indicated are places of inclusions presented in micrographs 2—8 ( $T_H$  — homogenization temperature; mp — mineral-prisoner, probably halloysite; mu — muscovite); 9–10 — inclusions in another quartz crystal, and bearing various amount of mineral-prisoner; same scale bar for micrographs 2—10; 11—12 — halloysite crystals separated from altered aplite Gi73; electron image; Garby Izerskie, "Stanisław" quarry the remnant melts, and he clearly distinguishes the development of pegmatites into two stages: pre- and post-inversional (related to inversion temperature of high to low quartz). In his papers, the results of studies on the inclusions of post-inversional stage are reported, *i.e.* from temperatures  $< 600^{\circ}$ C (Kalyuzhnyi 1971, Kalyuzhnyi & Voznyak 1967, Kalyuzhnyi & Gigashvili 1972). Moreover, Gigashvili (1969) proved that gas-crystalline inclusions in quartz from the Ukrainian (Volhynian) pegmatites are not the relics of melts but the heterogeneous inclusions of pneumatolytic solutions with xenogene crystal phases (*i.e.* minerals-prisoners). The  $T_{iH}$  of those inclusions as high as 950°C does not indicate the temperature of the quartz origin, but it is only  $T_{iH}$  of heterogeneous systems.

However, reports on findings of melt inclusions in the external zones of pegmatites (Bakumenko 1966; Bazarov 1973; Bakumenko & Kosukhin 1975, 1976; Dolgov & al. 1976; Kosukhin 1976; Litovchenko 1976; Zakharchenko 1976), with  $T_H$  540—840°C, cannot be ignored, especially if the reports bear the detailed discussion on the possible heterogeneity of the recognized gas-crystalline (assuming formerly melt) inclusions. Some of the presumably melt inclusions, especially in minerals of the metamorphic pegmatites, related to migmatitization or anatexis (e.g. Chlebus 1977) need further studies. As low  $T_H$  as 540°C for melt inclusions are explained by a supposed presence of fluorine (Bakumenko & Kosukhin 1976), thus the inclusion melt evolutes to the ongonite composition (Kovalenko & al. 1976). Reports on parent melts of silexite veins (Ermakov 1976) submit data difficult now for verification.

Assumption, that inclusions consisting of gas, water solution, easily soluble salts plus rock-forming minerals (quartz, feldspar) prove the existence of strongly hydrated silicate melts, seems to be doubtful, if only the first three components homogenized at 400-600°C, but silicates after 4-6 hours run at temperature > 1000°C dissolved less than by half (Bazarov & al. 1975). The writer reckons that until homogenization, those inclusions cannot be called "inclusions of solution-melt".

The writer's studies (Kozłowski & Karwowski 1972b, 1974b; Karwowski & Kozłowski 1973) on high-temperature inclusions of hydrated salt melts in micropegmatitic granitoid rocks from Alam Kuh (Iran) prove that pegmatite-type aggregates may also form at elevated temperatures about 800-900 °C. Although in quartz from those micropegmatites only inclusions of hydrated salt melts were found (total of salts up to 84 wt %, the balance — water), undoubtedly this melt contained also minor silicate component. Such salt melt is immiscible with silicate melt, forming two co-existing phases (Roedder & Coombs 1967; Roedder 1970b, 1972a), thus in the case studied by the writer, the common activity of the silicate and salt melts in the formation of micropegmatites is very probable.



Fig. 14. Evolution of diluted (Karkonosze) and strongly saline (Alam Kuh) post--magmatic pegmatite-forming fluids Solidus line of granite saturated with water and isolines of saturation of the granite melt with water compiled from various reference data

The  $T_H$  of salt-melt inclusions from Alam Kuh, needing small  $\Delta T$ corrections, appears above the solidus of the system granite - H<sub>2</sub>O, saturated with water (Fig. 14), thus the micropegmatite formed originally from a silicate melt. Evaluation of position of the highest known temperatures compared with solidus is difficult for the Karkonosze pegmatites, due to unknown  $\Delta T$  correction for pneumatolytic inclusions. Theoretically, it is possible that magmatically grown crystals may bear inclusions of heterogeneous gaseous solution separated by the retrograde boiling or during crystallization of the silicate melt. However, the above described textures in early zones of pegmatites preclude an immediate growth from the melt in the Karkonosze pegmatites. Moreover, the saturation of magma with water in the Karkonosze massif is not proved, then crystallization temperatures of the pegmatite parts characterized by  $T_{\rm H} = 580^{\circ}$ C may be lower than solidus of this very granite. Recently, the proposed scheme of formation of the Karkonosze pegmatites is substantiated, excluding certain specific bodies in the Karkonosze massif, viz. the so-called "ball pegmatites" (Karwowski & Kozłowski 1972), the earliest parts of which are probably of melt origin.

The process of the "normal" pegmatite formation probably began closely after consolidation of the massif, by recrystallization of the newly intruded aplites at temperatures somewhat lower than the solidus temperature.

Probably, the application of the term "pegmatitic facies" (Vlasov 1965), including many agents like tectonics, dimensions of the intrusion and its composition, position of the pegmatites in the intrusion, physical and chemical composition of the mobile phase, temperature, pressure, etc., would cause the studying of pegmatite origin *a priori* more impartially and individually in various massifs.

The evaluation of the depth of the pegmatite formation is another difficult problem. Taking into account such criteria as temperature, pressure, mineral composition of pegmatites, etc. (cf. Lukashev 1976), Karkonosze pegmatites may be assumed as belonging to the group of shallow pegmatites and the depth may be very roughly evaluated for 3-5 km

# GEOCHEMISTRY OF ELEMENTS IN INCLUSION FILLINGS

Results of the composition of inclusion fillings obtained by leachate method, give a certain mean value of all generations of the inclusions leached. Thus, various concentrations, e.g.  $Ca^{2+}$  and  $F^-$ , cannot be interpreted as occurring in the same inclusion, since this should lead to precipitation  $CaF_2$  in the inclusion vacuole. Large excess of the leaching water permits the keeping of all those ions in solution. The Si-bearing ions were not determined due to obvious contamination with ground quartz.

# LITHIUM, SODIUM AND POTASSIUM

Alkalies are main cations in inclusions (Fig. 16), occupying 40 to 90 at. % of total cations. Total alkalies do not differ in samples from the Karkonosze massif and the Izera area. The Li concentrations, both related to host quartz (Table 7) and inclusion solution (Table 8) vary strongly. Lithium takes up to 31 at. % of total alkalies and up to 0.28 wt % in inclusion fluid; it is common even in Li-poor (in crystal lattice) quartz from the Izera area. Parent solutions of metasomatites bear rather low concentrations of Li (1-d1/2) of total alkalies); however, quartz from the Karkonosze massif, as well as in the studied samples from Garby Izerskie, crystallized from solutions enriched in Li (15-31)/0 of total alkali atoms; cf. Fig. 15).

Sodium is the main cation in inclusions; only rarely weight concentrations of Na and K are almost similar, essentially in samples from schists. These almost equal concentrations of Na and K are connected presumably with Na-poor conditions in schists (cf. Table 4). Low Na/K ratio, <50 by weight, typical of the studied inclusions, is caused by their hypogene origin or an action in hypogene processes. Sodium occupies 45-95 at. % and K 1-45 at. % of total alkalies (Fig. 15) with variations smaller in the Karkonosze massif and schist zones than in the Izera area, because the first two complexes are less polygenic than gneiss-metasomatic zones.

#### Table 7

No.of sample	Description	u	Na	ĸ	Be	Mg	Ca	Sr	Ba	Al	Min	Fe	8
izera area													
N2 N7 N9 N37 N39 N45 N49b		2.3 0.44 0.14 2.3 2.7 0.30	9.0 48 15 14 34 49 27	2.0 25 4.3 5.8 14 24 12	-	2.2 0.26 0.23 1.2 1.3	1.4 32 2 4.0 5.0 23 51 15	0.2 0.9 0.5 1.2 1.7	0.3	0.45 34 3.1 3.6 11 12	4.6	20	0.02 0.28 0.03 0.20 0.02
N51 81 834 841 850 854 859	-Vein quertz from gneies	0.10 0.34 2.0 0.14 0.30 0.63 2.0 1.7	11 8.1 38 5.6 14 5.0 26 14	9.2 1.3 1.0 3.6 0.3 4.3 18 5.6		0.32 0.15 1.6 0.12 0.31 0.33 0.48 0.19	2.5 2.3 27 1.9 10 5.8 8.6 8.4	0.1	0.2	10 4.6 17 2.5 6.0 3.3 7.3 6.0	2.5 1.5 1.6	33375	0.01
864 N3 N10 S14	y Vein quartz from greisen Quartz from tourmaline nest Blastic quartz from	0.74 0.09 0.22 1.0 0.93	27 5.6 21 20 18	23 6.4 25 6.0 3.7	-	1.2 0.47 1.1 3.3 1.7	15 3.6 12 9.7	0.2		2.4 1.0 3.6 5.8	1.6	12 6 23	0.02 0.09 0.09
S26 G1017 G1034a	gneiss White massive quartz Druse in massive quartz	1.2	12 42	19 21	0.02	1.7	5.4 29	0.1 1.1	~0.5	3.3 4.4	0.8	65	0.04
CK1 CK3 CK4 CK5 CK11 CK18 CK17 CK18 CK22 CK23	Intercalitions and veins in mica-chlorite schiete	0.09 0.17 0.28 0.12 0.21 2.8 0.38 0.75 0.08	.5.4 3.3 3.8 3.5 2.8 22 9.0 18 18 4.1	3.0 3.3 3.9 3.0 2.2 8.6 3.8 8.6 18 1.4		0.11 0.25 0.42 0.30 0.75 0.32 1.5	1.8 2.9 1.5 3.1 2.4 8.0 6.8 5.0 16 0.8	0.5	1,2	2.2 2.7 2.5 2.3 1.5 4.5 0.8 4.0 2.1	2.1	17	0.02
			Karl	kond	DSZE	e ma	Issit						ŀ
K12 K18 K20 K21 K29 K38	Pegmetitic quartz	2.3 1.2 0.92 1.8 1.8 3.1	14 17 13 12 15 18	5.5 9.6 4.2 2.0 10 11	0.1 0.05 0.1	0.65 0.81 0.22 0.17 0.38 1.8	8.8 9.6 2.6 5.9 6.8 13	0.4 0.2 0.2 0.3 0.5	1.2 0.8	16 17 6.9 5.4 15 23	0.3	4 11 3 6	0.04 0.06 0.02 0.02 0.02 0.02
K1 K19 K22 K24	Vein quartz	2.4 1.1 4.1 0.40	15 11 34 30	5.8 8.3 46 10	0.03 0.03 0.1 0.1	0.11 0.83 4.7 3.2	4.6 4.0 14 14	0.2 0.4 1.0	0.4	16 16 10 16	1.0 2.5	5 3 15 8	0.01 0.02 0.03
Detecti	on limit, ppm	0.03	0.1	0,1	0.01	0.03	0.1	0.1	0.1	<0.1	0.3	1 ·	0.01

Concentrations of cations and boron in leachates from quartz samples from the Karkonosze-Izera block; ppm of quartz weight

#0.7 ppm Ti was detected in inclusion filling

# MAGNESIUM, CALCIUM, STRONTIUM AND BARIUM

Total Mg + Ca is clearly lower than total alkalies and ranges from 5 to 40 at. % of total cations (Fig. 16). Magnesium is subordinate (Table 7) in relation to Ca; only the latter occurs in concentrations comparable with alkalies, being the third major cation in inclusions, together with Na and K.

Strontium and barium are trace elements in inclusions; their concetrations do not exceed 0.1 wt. 0/0 (Table 8) in solution. Neither Sr nor Ba are concentrated in any process over the Karkonosze-Izera area, but the distinct positive correlation Sr with Ca is apparent. Barium behaves differently than other alkaline earths and potassium (Table 7).

## ALUMINUM, IRON AND MANGANESE

Three named elements are rarely reported from inclusion fillings, since leachates are made usually with pure water (pH  $\approx$  7). Then respective salts hydrolize and their hydrolizates are sorbed by finely ground mineral. Acid



Fig. 15. Plots of composition of alkalies in fluid inclusions in quartz from the Karkonosze-Izera block; atomic percents of total alkalies

leachates proved, that Al, Fe and Mn occupy 2 to 40 at. % of total cations. Presumably Al, Mn and Fe display a greater role in hydrothermal solutions of the Karkonosze massif than in the Izera area (Fig. 16). Aluminum was found in all samples, but Fe and Mn in many samples occurred in concentrations lower than the detection limit (Table 7). Aluminum concentrations ranges from tenths to  $\sim 3$  wt. % Fe to  $\sim 4$  wt. % and Mn to  $\sim 0.4$  wt. % (Table 8).

Tabl	e 8
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Ranges of mean concentrations of elements in inclusion fluids in quartz from the Karkonosze-Izera block; wt %/

Description	LI	Na	ĸ	Ba	Ma	6	e.,				Τ	T _	1	1	
			ļ	1	1003		- 31		A	Min	Fe	F	CI	8	n*
izera area															
Vein quartz from gneise	0.00-	1-8.5	0.02-	.**	0.02-	0.3-	0.00-	0.00-	0.1-	0.00-	0.0-3	0.000-	1-19	0.000-	15
Vein quartz from greisen	0.02	1.5	1.7	-	0.13	1.0	0.06	_	0.3			1.1		0.02	
Quertz from tourmeline neet	0.17	3.4	1.0	_	0.56	1.6			1.0					0.02	1
Blastic quartz from gneiss	0.24	4.7	1.0	_	0.44	3.1			0.9		4	3.2	11	0.02	1
Quertz from mica-chlori- te schist	0.00- -0.28	0.7-4	0.3- -3.9	-	0.00- -0.13	0.02 -3.3	0.00- -0.02		0.1-	-	-	0.01- -1.4	a.8 1-15	- 0.000- -0.02	1 6
Karkonosze massif															
quertz	0.12	0.8	0.1	-	0.01	0.4	0.01	-	0.4	-	0.2	0.008	4.2	0.001	1
Vein quartz	0.04	2.8	0.9	0.01	0.30	1.3	0.09	0.04	1.5	0.23	0.7	0.06	15	-	11

\*number of determinations

\*\*no dete



Fig. 16. Plots of atomic percent participations of main groups of cations in fluid inclusions in quartz from the Karkonosze-Izera block

### BERYLLIUM AND OTHER METALS

Beryllium is a trace element in inclusions, and its differentiation has clearly regional pattern. Samples from the Karkonosze massif usually bear higher amounts of Be in inclusions, whereas the Izera area is poorer in this element (Table 7). Massive and drusy quartz from Garby Izerskie however displays remarkable concentrations of Be in inclusions, supporting the connection of its parent solutions with the Karkonosze massif. It is noteworthy, that some samples of quartz from schists, mainly ore-bearing ones (CK3, CK4, CK11, CK17, CK23), contained in inclusions traces of Be, quantitatively nondeterminable by the used method.

The enrichment of the Karkonosze massif in Be is expressed also by high Be concentrations in quartz lattice (Walenczak 1969, Kozłowski 1973) and beryl mineralizations (Sachanbiński 1970).

In leachates, trace amounts of copper usually were found, but only the further studies may elucidate whether copper ions occurred in inclusions.

In leachate from a sample of blue vein quartz (N7) titanium was determined (Table 7), but since this sample bears the micrometer-size rutile inclusions, one may not exclude the contamination.

#### CHLORINE AND FLUORINE

Chloride ion is one of the main anions in inclusions in the studied samples, and, on the other hand, its content varies strongly, from 4 to almost  $100 \ 0/0$  of total chemical equivalents (ch.e.) of anions (Fig. 117). Fluoride ion, however, occurs in smaller amounts, from extremely low to  $30 \ 0/0$  of total ch. e. of anions.

A cryptonym "other anions" means this amount of ch. e. of anions, which is necessary for equilibrating of the total ch. e. of cations in addition to chloride and fluoride ions. "Other anions", not determined immediately, are essentially carbonate and bicarbonate ions, as it is proved by the presence of Equid  $CO_2$  in inclusions. Sulfate, as well as HS-and S<sup>2</sup>- ions may also appear, but probably their concentrations are at best comparable with fluoride content. "Other anions" occupy from almost nil to 96% of total ch. e.



Fig. 17. Plots of composition of main anions in fluid inclusions in quartz from the Karkonosze-Izera block; in percents of chemical equivalents

Samples from the Izera gneiss and metasomatites (series N and S, Fig. 17) arrange along the side  $Cl^-$  — other anions with significant deviations toward the F<sup>-</sup> angle for samples connected with metasomatites (N3, N10, S14). Those samples have also significant (S14) or prevailing (N3, N10) amounts of the "other anions", i.e. here the carbonate ions.

Samples from schists place mainly in the field: 35 to  $52^{\circ}/_{0}$  of Cl- ch.e. and 0 to  $10^{\circ}/_{0}$  of F- ch.e. This field groups the samples of ore-bearing 'quartz and a part of gangue quartz; samples bearing almost purely chloride (CK5) or carbonate (CK16, CK18) solutions consists of gangue quartz.

Solutions from the Karkonosze massif group along the side: Cl - - other anions, and the content of F- does not exceed 3% of total ch.e. Concentrations of the "other" (i.e. presumably carbonate) anions also are lower than in samples from the Izera area.

Performed studies of fluoride and chloride ions in fluid inclusions in quartz revealed the futher peculiarities of the geochemical differentiation of those ions at the area under study. Atomic ratio 1000F/Cl was used as the index, *i.e.* number of fluorine atoms per one thousand of chlorine atoms. The studied population of samples may be divided into genetic groups differing in 4000F/Cl values (Table 9). Vein quartz from gneisses is characterized by low values of 1000 F/Cl (x = 10); its significant standard deviation (s = 16.5) and changeability index (v = 1.65) may testify to polygenic nature of the veins. High positive value of the obliqueness index ( $\gamma_4 = 2.94$ ) means that 1000F/Cl values groups closely to the lower limit

Table (	9
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Quartz	n	Range	$\overline{X}$	S	v	T <sub>1</sub>					
IZERA BLOCK											
vein from gneiss	93	0-62	10	16.5	1.65	2.94					
vein from leucogramites	8	140-1200	440								
vein from graisens, quartz- sericite veins and mins- rels from greisene and tourmaline mests")	13	420-2200	1100								
blastic from gneiss	9.	72-370	220			1					
gangue from schists	23	0-85	31	24	0.77	0.90					
ore-bearing from schiets	10	58-180	120	· (							
CONTACT	ZONE	AT G	ARBY	IZERSI	CIE						
from ore-bearing hornfels	3	770-1600				1					
from skarn	1	1000									
massive and from druses	8	12-58	40			1					
from pagentites and splites	3	37-390		1	l	ł					
к	ARKON	OSZE	MASSI	F							
vein and pegmatitic	57	0-44	9.1	9.7	1.1	2.1					
vein pegmatitic	27 30	0-44 1-37	9.1 9,0	11.1 8.2	1.2	2.2 1.5					
from splites and granite	14	12-210	100								

Statistical characteristics of atomic 1000F/Cl ratio for various genetic groups of minerals from the Karkonosze-Izera area

\*)includes eight samples of greisens with 1000F/Cl ratios calculated on the basis of Karwowski's data (1977).

of the range of changeability. Vein quartz from metasomatites achieves high values of 1000F/Cl (up to 2200, including  $\bar{x} = 440$  for veins from leucogranites, and  $\bar{x} = 1100$ for veins from greisens and greisen minerals). Other statistical characteristics were not calculated here and some further cases due to small number of determinations.

Blastic quartz from gneiss has  $(\bar{x} \text{ high (220)})$ , but clearly lower than from metasomatites, although certain portions of metasomatizing solutions used to be entrapped in secondary inclusions in blasts.

Gangue quartz from schists is characterized by 1000F/Cl values range similar to that from veins in gneisses, but it differs in the higher mean value ( $\bar{x} = 31$ ) and lower dispersion (s = 24, v = 0.77), and distinctly lower obliqueness index ( $\gamma_1 = 0.90$ ). This proves the less polygenic origin of quartz from schists, or the better homogenization of parent solutions. Ore-bearing quartz has higher values of 1000F/Cl  $\bar{x} = 120$ ).

Quartz from Karkonosze massif was divided into two groups: quartz from granite and aplites with higher 1000F/Cl values ( $\bar{x} = 100$ ) and quartz from veins and pegmatites with lower 1000F/Cl index ( $\bar{x} = 9.1$ ). Standard deviation (s = 9.7) and changeability index (v = 1.1) testify to smaller dispersion of 1000F/Cl values for post-magmatic quartz from the Karkonosze massif than for vein quartz from the Izera gneiss. Also obliqueness index ( $\gamma_1 = 2.1$ ) characterizes the tendency for grouping of the results near the lower limit of the range, the tendency itself being weaker, *i.e.* the statistical distribution less asymmetric.

Changes of 1000F/Cl ratio at individual areas are round (Figs 18-20). This testifies to the gradual changes of the process, causing the differentiation of F and Cl; by geological data it was rather increase than decrease of activity of the fluorine-rich solutions. Less or more abrupt steps about values 100 (Fig. 18) or "0"-10 ("0" means F content below the detection limit) presumably are connected with too small number of samples.



Fig. 18. Atomic 1000F/Cl ratios in fluid inclusions in quartz from gneiss (a) and from metasomatites (b), arranged increasingly, N part of the Izera area



Fig. 19. Atomic 1000F/Cl ratios in fluid inclusions in vein quartz from gneiss (a), and in quartz from blasts in gneiss and from metasomatites (b), arranged increasingly; S part of the Izera area

Consequent variations of 1000F/Cl ratio were found also in the Garby Izerskie mineralized zone (Fig. 21 and Table 9): from low values typical of massive quartz and druses occurring inside it (12-58) to high values ascertained in orebearing hornfelses, skarn and late amethyst (750-1600). Quartz from pegmatites and aplites at Garby Izerskie have 1000F/Cl ratio from 37 to 390.

The above characteristics of geochemistry of fluorine and chlorine proves that in the Izera area the post-gneiss metasomatic rocks formed under action of solutions enriched in F. Since with the metasomatites such ore minerals as ferberite, scheelite, chalcopyrite, native bismuth and Nb-bearing rutile associate (Karwowski 1977; Karwowski & Kozłowski 1974, 1977, Kozłowski & Karwowski 1975), thus high values of 1000F/Cl ratio may be assumed as a geochemical indi-





cator of the occurrence of metasomatites, being potentially ore-bearing ones. Also quartz, associated in schists with cassiterite and sulfides (Jaskólski & Mochnacka 1959, Sałaciński 1965, Do Van Phi 1974, Kowalski & al. 1978) has higher 1000F/Cl ratio than gangue quartz from schists (Fig. 22). One may assume that positive fluorine anomalies are the prospecting indicator, facilitating in the Izera area the localization of zones mineralized with ores. However, this indicator cannot be applied mechanically, without investigations of the geological structure and geochemical regularities of the region.







It is noteworthy that analysis of the anion composition of the studied inclusions (Fig. 17) permits the supposition on significant role of carbonates in metasomatosis. Then, metasomatites not connected with the positive F anomalies, but with increased  $CO_2$  ( $CO_3^{2-}$ ,  $HCO_3^{-}$ ) content, may be also expected.



Fig. 22. Plots of fluorine versus chlorine contents in fluid inclusions in quartz from the Karkonosze-Izera block. Izera area: S — southern part, N — nothern part, CK — Czemiawa — Stara

Izera area: S — southern part, N — nothern part, CK — Czenniawa — Stara Kamienica schist zone; K — Karkonosze massif Plot S: 1 vein quartz from gneiss, 2 quartz from metasomatites, 3 blastic quartz from gneiss

Plot N: 1 vein quartz from gneiss, 2 quartz from metasomatites Plot CK: 1 gangue quartz, 2 ore-bearing quartz

Plot K: i vein and pegmátithe quartz, 2 quartz from granite, 3 quartz from aplite Scale of 1000F/Ct values is drawn with dashed lines

More detailed distinguishing of genetic groups of hydrothermal bodies, based on the narrower ranges of 1000F/Cl ratio, has been presented previously (Kozłowski 1976, Kozłowski & Jońca 1977).

Variations of 1000F/Cl ratio, ascertained in the Polish part of the Karkonosze massif, have different pattern than in the Izera area. Ore-bearing zones in granite are less distinctly or not connected with high values of 1000F/Cl ratio. Secondary fluid inclusions in quartz from magmatic rocks (granite and aplites) bear high concentrations of F, if the rocks were not submitted to further metasomatic action of post-magmatic solutions (Fig. 22). On the other hand, quartz from altered granite has lower 1000F/Cl ratio, ranging from 10 to 50. Similar is the behaviour of  $CO_2$ , enough common in fresh-granite quartz, but rarer in postmagmatic bodies. Presumably, fluorine (and  $CO_2$ ) was removed during the subsequent hydrothermal alterations and carried away.

### BROMINE

Data concerning Br in inclusions are very scarce (cf. Osipov 1968, Etimova & al. 1972, Sabouraud & al. 1972, Wickman & Khattab 1972) due to methodic difficulty, although the necessity of such studies was emphasized (Roedder 1972b).

The writer determined Br concentrations in fluid inclusions in various minerals (Kozłowski & Karwowski 1969). Moreover, the determinations were performed in inclusions in hydrothermal quartz from the Strzegom and Karkonosze massif, and from the Izera area; methods and detailed tables of results were published earlier (Kozłowski & Karwowski 1973, 1974a). Content of bromine in inclusions ranges from 0.1 to 2.9 ppm of host mineral weight, whereas concentrations in inclusions from 0.003 to 0.2 wt  $\sqrt[9]{a}$ . Atomic Cl/Br ratio varies from 1200 to 39 and in individual parageneses the tendency of increase of Br concentration with the temperature decrease is apparent.

Comparison of 1000Br/Cl ratio of the studied relics of thermal fluids and sea water, including products of its concentration, is noteworthy. Mean 1000Br/Cl ratio for sea water equals 3.3, and for its concentrates values up to 22 were noted (Valyashko 1956). In brines from sedimentary rocks of marine origin the ratio is as high as 31 (Valyashko 1963). Also found 1000Br/Cl ratio for fluid inclusions ranges in the limits typical of sea water and products of its condensation (Kozłowski & Karwowski 1976). This testifies to a possible genetic connection between thermal fluids and solutions derived from the strata of marine origin. Sedimentary rocks are mainly of marine origin and they contain pore and adsorbed sea water (the so-called connate water), becoming hydrotherms during metamorphism.

Metamorphism, connected with origin of OH-bearing minerals takes a part of water from solutions; deep metamorphism submits additional water released from hydrated minerals ( $\sim 100$  mln t of water from 1 cubic km of metamorphosed rocks; cf. Belevisev 1970). These processes influence essentially the evolution of natural solutions. Origin of palingenic magmas also takes place in the presence of remnant, formerly marine solutions. Of course, part of water from magma melt is linked in OH groups in minerals and excluded from then originating thermal fluids.

The obtained results were placed in the 1000Br/Cl versus concentration of Cl plot (Fig. 23). Part of samples occur closely to the curve for sea water and products of its concentration, and the balance is replaced toward the lower Cl concentrations, especially low-temperature samples. The following cases are therefore assumed:

i). Concentrated solutions of formerly marine origin were diluted by weakly mineralized waters (meteoric, "distilled" from hydrothermal solution, etc.).

ii). Some inclusions bear more concentrated solution, and the others diluted. During leaching the both solutions mixed and hence the effect of dilution is apparent.

### BÒRON

Boron, occurring in thermal fluids presumably as  $BO_3^{s-}$ , although other borate ions are assumed, used to be determined in inclusions occassionally and rarely reported; systematic studies were not performed.

Boron (Tables 7—6) is common, although subordinate component of inclusion fillings from quartz in the northern part of the Izera area, as well as from quartz from tourmaline metasomatites. Fluids from the southern part of the Izera area are poorer in boron. Its content in inclusions in quartz from schists below the detection limit connects with the low number of extremely small inclusions in this quartz. In the zone of Garby Izerskie, where tourmaline is relatively com-





Plot for sea water: 1000Br/Cl versus chlorine concentration with points representing inclusion fluids from quartz from the Karkonosze-Izera block and Strzegom massif; for number data see Kozłowski & Karwowski (1973, 1976)

mon, B was found in inclusions. It is noteworthy, that in inclusions in quartz from the Karkonosze massif, the occurrence of B is ordinary, although boron minerals (tourmalines) in the massif are scarce (Traube 1888; and writer's observations).

# RELATIONS BETWEEN THE KARKONOSZE INTRUSION AND ACTIVITY OF THERMAL FLUIDS IN THE IZERA AREA

The recognition of physico-chemical and geological conditions of the formation of pneumo-hydrothermal rocks in the Karkonosze massif and its metamorphic cover arises the problem of a possibility of the reciprocal connections, mainly the influence of magmatic intrusion on hydrothermal mineralization in the cover. Distinguishing hydrothermal mineralization of different ages, especially pre-, syn- and post-intrusive (related to Karkonosze intrusion) in the cover, is very difficult, if possible at all. Age parallels of vein drawn e.g. by Oberc (1972), maybe are acceptable for tectonic deformations, but not for the mineral filling of veins, since the filling process used to be younger than deformation (fracture) over an unknown time; moreover, the process usually lasts long, and it is divided into some stages and renewed several times. On the other hand, the influence of the intruding magma has appeared in the studied area considerably earlier than the intrusion achieved the recent position inside the cover rocks; time interval of these processes is however also unknown. Intrusion was gotten ahead probably by front of mechanic stresses, as well as by thermal and chemical fronts. Mobilisation of elements and water should appear in the cover rocks. The direction

of migration may be not only from the ir trusion toward the cover rock, but also elements may move in the ranges of the cover, and the cover ought to influence the chemical composition of the intrusion, since enclaves (xenoliths of cover rocks) in granite are very common.

In the zone of Garby Izerskie, the lower time boundary of the formation of quartz metasomatite is difficult for ascertaining. Although schists were silicified, it is not clear whether they were already altered by contact metamorphism, or root yet, *i.e.* whether silicification developed before, or during plus after formation of the massif. Granitoid apophyses cutting silicified bounfels were not silicified themselves, then silicification finished before final consolidation of the massif. Thermal influence of relatively thin apophyses on the cover rocks was very scarce.

Crystallization of the late fluorite (plus late quartz) overlapped both silicified hornf els and granite apophyses. Increased content of Be in inclusions and L i in late quartz, testifies a connection with the Karkonosze massif. T.hus, presumably mineralization resulted from the activity of early solutions mobilised by intrusion plus certain influx of thermal fluids from the intrusion. Solutions were of the chloridecarbonate type. Subsequently, probably after consolidation of the intrusion, F-ricch solutions appeared and fluorine was carried from the intrusion (cc), difference in F content between fresh and hydrothermally altered g;ranites).

Source of solutions which caused metasomatosis of gneisses and formation of leucogranites and greisens is another problem. Similar tungsten-tin mineralization both in granite and in greisens, and postulated migration of fluorine and presumably CO2 from the massif to the cover may support an idea on the Karkonosze massif as the source of metasomatizing solutions. However, another way of fluorine accumulation is possible, mentioned also from the other areas (cf. Sotnikov & al. 1976), viz. decomposition of fluorine-bearing minerals (biotite) during metasomatosis of gneiss. Then, leucogranites almost free of fluorine minerals ought to form initially, and subsequently fluorite would crystallize or leucogranites would alter into greisens, i.e. fluorine-bearing minerals such as topaz, tourmaline, apatite and fluorite would appeer. Biotite from the Izera gneiss (preliminary determinations) bears 0.2-0.4 wt % of fluorine and up to 0.1 wt % of chlorine, thus its decomposition and including of F and Cl into mineral-forming solutions should increase the F content. The above scheme does not exclude the role of the Karkonosze intrusion as the factor initiating metasomatic processes, but it also does not submit new premises.

Age of leucogranites was not determined hitherto by geological methods. Chaloupsky's (1963, 1965) supposition on identity of the Izera leucogranites with pebbles of light granites found in the Upper Ordovician conglomerate south from Karkonosze, was refuted by K. Kozłowski (1974, pp. 84-85). Recently, facts excluding the connection of leucogranites with the Karkonosze intrusion are not known, however, the data used for supporting this idea, including a probable occurrence of the Karkonosze-type granite under the Izera area, are rather less or more significant premises, but not the evidences. Taking into account the general geological plane and mineral parageneses in the studied area, the writer assumes that this connection may be accepted as well-founded hypothesis being the base for further studies.

The origin of cassiterite mineralization in schists of the Czerniawa — Stara Kamienica zone is an open question. This mineralization, initially considered to be pneumo-hydrothermal (cf. Jaskólski & Mochnacka 1959; and references cited there), was also reconsidered as metamorphosed placer (sedimentary) deposit (Jaskólski 1963, Szałamacha 1967, Szałamacha & Szałamacha 1974). A proposed metasedimentary origin of cassiterite mineralization needs contemporaneously the explanation of the questions connected with the occurrence of very similar cassiterite in greisens of the Izera Upland (Karwowski 1975, 1977) and the hypothetical alimentation area and sedimentary basin. Greisen cassiterite cannot be the relic mineral from sedimentary strata, since parent solutions of greisen minerals, rich in F and Cl, ought to mobilize Sn.

The writer assumes that cassiterite association with chlorites may be explained as follows. Solutions found in fluid inclusions in quartz from the schist zone, have significant concentrations of halogens. Such solutions at elevated temperatures hydrolize with acid reaction (Kalinin 1973, Ganeev 1976). Presence of CO2 also results in acid reaction of solutions, and liquid CO2 was ascertained in inclusions in quartz from schists. Migration of tin in acid solutions appeared, presumably as complex compounds like  $H_2[SnCl_6]$ ,  $Sn(OH)_nCl_m$ ,  $SnF_4$ ,  $Sn(OH)_nF_m$ , Sn(OH)4, and, maybe Hs[Si(SnO2)6]. All these complex compounds at temperature 500-300°C decompose at pH  $\approx 5$  (Nekrasov 1976). Zones of rocks rich in Mg, Ca and Al were especially able to increase pH value of solution, resulting in precipitation of cassiterite after decomposition of complexes stable under acid conditions. Grainy quartz, co-existing with chlorites and together with sulfides being the association of cassiterite, was more permeable to penetration of solutions than massive quartz. For this reason rather this grainy quartz bears the oresi Positive fluorine anomalies, often treated as prospecting tool for post--magmatic tin mineralization (Isbihara & Terashima 1977) are the additional premise. Taking into account the above data, the writer assumes that ore mineralization (cassiterite plus sulfides) formed under action of hydrothermal solutions and the connection of the ore genesis with activity of the Karkonosze massif is substantiated, with limitations given in the discussion on metasomatite origin.

### ANDRZEJ KOZŁOWSKI

### CONCLUSIONS

Activity of thermal fluids in the Karkonosze-Izera area was essen tially hydrothermal; only at temperature >500 °C and occasionally be low 500 °C it was pneumatolytic.

Fluids at the Karkonosze massif were diluted water solutions (total of salts from  $\infty 5$  to  $\infty 15$  wt  $^{0}/_{0}$ ); only at marginal parts of the massif CO<sub>2</sub> appears in postmagmatic bodies. Contrary, CO<sub>2</sub> is the important component of thermal fluids in the Izera area, including the schist zone of Czerniawa — Stara Kamienica.

Alkalies are main cations of thermal fluids; fluids from the Karkonosze massif bear increased concentrations of Li, compared with the Izera area. Ca and Al are important cations by their concentrations, and Mg, Sr, Ba, Fe and Mn are subordinate or were found ocassionally. Higher concentrations of Al+Fe+Mn in total cations are typical of the Karkonosze massif. Beryllium is connected with thermal fluids of the Karkonosze massif, and in the Izera area it occurs in lower concentrations.

Chloride and carbonate anions are prevailing; in thermal fluids in the Karkonosze massif they occupy over  $95^{\circ}/_{\circ}$  of chemical equivalents (ch.e.) of total anions, whereas fluoride is subordinate. In ore-bearing quartz from schists the fluoride content increases to  $10^{\circ}/_{\circ}$  of total ch.e. of anions. Mineral-forming solutions from veins in gneiss are also chloride-carbonate; however, metasomatites (leucogranites and greisens) and veins connected with them formed from solutions rich in fluorides.

Atomic ratio 1000F/Cl, determined for fluid inclusions, and proposed for distinguishing certain genetic groups of hydrothermal deposits in the Izera area, presents as follows (arithmetic mean  $\bar{x}$ ): vein quartz from gneiss — 10, vein quartz from leucogranites — 440, vein quartz and rock-forming minerals from greisens — 1100, gangue quartz from schists — 31, ore-bearing quartz from schists — 120. Thus the ratio is a possible prospecting tool for the ore-bearing zones.

Results of studies on geochemistry of bromine are applicable for elucidation of the genesis of thermal fluids, especially their possible connection with former marine waters.

Boron concentrations in fluid inclusions from the Karkonosze massif are stable and their occurrence is common. In the Izera area, however, a significant differentiation appears and highest values are typical of tourmaline metasomatites.

Geochemical pattern of the Karkonosze massif and its cover (Izera area) includes the formation of aureole of mobile components ( $CO_2$ , F, B, Li, Na, Be) around the massif in cover rocks, in diverse distances for individual components.

Hydrothermal mineralization of the Garby Izerskie zone, formed at 370—110°C, should be connected with the Karkonosze massif. Unequivocal distinguishing of pre-, syn- and post-intrusive veins in the Izera area, in relation to the Karkonosze intrusion, is impossible by the methods used. The veins formed at temperature ranges: 440-390, 370-210, 230-120 °C.

Cassiterite mineralization in schists is assumed to be hydrothermal, formed at  $\sim 400^{\circ}$ C; quartz from schists orystallized presumably at 490—200°C. The ore mineralization might be caused by the Karkonosze intrusion.

Metasomatites: greisens, leucogranites and tourmaline nests, formed from hydrothermal solutions at 550—360°C; metasomatizing solutions probably were mobilized by the Karkonosze intrusion, with partial influx of solutions from the intrusion.

Pegmatites of the Karkonosze massif formed by accumulative recrystallization of aplites in zones of stress, under action of high-temperature pneumatolytic solutions, presumably beginning from 700-650°C; central cavity and free-growth minerals formed during the subsequent stage, essentially from hydrothermal solutions.

Main types of the veins in the Karkonosze massif, taking into account the kind of the vein filling, are as follows: feldspathic-quartz, high-temperature metasomatic, ore-quartz, quartz, and low-temperature metasomatic. High- and low-temperature quartz metasomatites (460—360 and 340—110°C, respectively) differ clearly: the first are coarse-grained and similar to filling of an opened vein, the second are typical finegrained jasperoids. Formation of veins lasted usually a long time and it was interrupted by cataclastic events.

Quartz veins in the Karkonosze massif crystallized in the temperature interval  $\sim 500 - \sim 40^{\circ}$ C. Transversal temperature distribution in veins formed without cataclasis events gives commonly either lower temperature near the wall and an increase toward the vein centre, or almost constant value for the whole section.

The performed studies proved the essential role of mobile (fluid) phase for the formation of all studied rocks and parageneses, and the final product of numerous geological processes depended upon the type of the fluid phase, its temperature, as well as upon the mode and direction of movement through the parent rocks or fractures.

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## A. KOZŁOWSKI

## UTWORY PNEUMATOLITYCZNO-HYDROTERMALNE BLOKU KARKONOSKO-IZERSKIEGO

## (Streszczenie)

Przedmiotem pracy jest odtworzenie warunków powstania utworów pneumatolityczno-hydrotermalnych występujących na obszarze bloku karkonosko-izerskiego (fig. 1 oraz 6—9). Cechy strukturalne i teksturalne pegmatytów masywu karkonoskiego (fig. 2—5 oraz pl. 1—14) oraz skład chemiczny ich minerałów (tab. 1—2), pozwalają stwierdzić, że we wczesnym etapie rozwoju badane pegmatyty tworzyły się drogą rekrystalizacji aplitów w warunkach pneumatolitycznych; roztwory hydrotermalne oddziaływały na ten zespół mineralny powodując silną albityzację skaleni oraz krystalizację m.in. kwarcu, albitu i zeolitów. W masywie karkonoskím wyróżniono wśród żył kwarconośnych: żyły skaleniowo-kwarcowe, wysokotemperaturowe metasomatyczne żyły kwarcowe, żyły kruszcowo-kwarcowe, żyły czysto kwarcowe oraz żyły jasperoidowe (niskotemperaturowe metasomatyczne); dokonano analizy sposobu ich powstania, składu mineralnego i chemicznego (tab. 3, fig. 12—13 oraz pl. 15—21). Zbadane podobnymi metodami utwory obszaru izerskiego: wkładki i żyły w łupkach łyszczykowo-chlorytowych z towarzyszącym im okruszcowaniem kasyterytowo-siarczkowym, metasomatyczne leukogranity, grejzeny i gniazda turmalinowe, oraz żyły kwarcowe w gnejsach i metasomatytach (tab. 4 oraz pl. 22—28) są pochodzenia zasadniczo hydrotermalnego, zaś warunki pneumatolityczne pojawiały się tylko sporadycznie. Asocjacje minerałów, utworzone w strefie tektonicznej Garbów Izerskich (tab. 5, fig. 10—11 oraz pi. 29—38), określono jako hydrotermalne.

Na podstawie badań inkluzji fluidalnych w poszczególnych minerałach przedstawiono ewolucję temperatur powstawania wymienionych utworów bloku karkonosko-izerskiego (tab. 6 oraz fig. 14), a także skład chemiczny i koncentracje roztworów macierzystych minerałów (tab. 7–8 oraz fig. 15–17). Zwrócono uwagę na regionalne różnicowanie się koncentracji Li, Be, B, CO<sub>2</sub> i F zawartych w badanych inkluzjach. Cechy geochemiczne Br w inkluzjach sugerują związek hydroterm z roztworami powstającymi podczas metamorfizmu formacji osadowych morskiego pochodzenia (fig. 23). Analiza koncentracji fluoru w inkluzjach i stosunku 1000F/Cl (tabl. 9 oraz fig. 18–22) pozwala wnioskować, iż dodatnie anomalie fluoru wiążą się ze strefami metasomatytów i innych utworów hydrotermalnych, które mogą być kruszconośne; spostrzeżenie to może mieć istotne znaczenie dla poszukiwań złóż kruszcowych.