Hydrothermal activity in the Karkonosze, Strzegom and Strzelin massifs – a fluid inclusion study

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Abstract: Fluid inclusions in post-magmatic minerals from the three Variscan granitoid intrusions: Karkonosze, Strzegom-Sobótka and Strzelin massifs, yielded temperatures and pressures of formation of the minerals, moreover compositions and concentrations of the parent solutions. The temperatures ranged from *ca*. 600 to less than 100ºC, pressures from *ca*.1.5 to 0.5 kbar and the solution concentrations from almost 20 to *ca*. 1 wt.%. Chlorides of sodium, potassium and calcium were the main dissolved salts in the parent solutions; their concentrations varied, however, according to a general pattern similar in all the three massifs. Continuous though not high presence of carbon dioxide was noted. The crushing events in the pegmatitic mineral assemblages were linked to the temperatures of the post-magmatic evolution of the massifs. A general scheme of the physico-chemical conditions of formation of the mostly hydrothermal mineral parageneses in the studied massifs was proposed.

Key words: fluid inclusion, post-magmatic, hydrothermal, temperature, pressure, solution composition, carbon dioxide, Karkonosze, Strzegom, Strzelin, Sudetes

INTRODUCTION

The three granitoid Variscan intrusions in the NE part of the Bohemian massif (Mazur *et al*. 2007) are important magmatic massifs in Sudetes**.** Their thorough characteristics were given earlier. The descriptions of the Karkonosze massif were published by Borkowska (1966), Mierzejewski (2007) and Mikulski (2007), the Strzegom massif was characterized by Domańska-Siuda (2007) and the Strzelin massif – by Oberc-Dziedzic (2007).

Presently the massifs form a 140 km long west-east belt of intrusions (Fig. 1). Their degree of covering by the younger deposits is different, however, the accessibility to the fresh or relatively fresh rocks is good due to the exploitation of the granitoid raw material in quarries, which was (or is) periodically at in places very intensive.

All the massifs bear fractures and joints typical of the granitoid massifs (Cloos 1922, 1925). The post-magmatic activity in the massifs is usually closely related to these discontinuities and to the local stress, shearing and spreading zones in the massif rocks. The post-magmatic activity includes formation of pegmatites, veins and alteration (metasomatic) zones. This paper does not the presents the results of the studies origin of pegmatites, which have been discussed elsewhere (Kozłowski 1978, 2002b; Kozłowski, Sachanbiński 2007), however, the conditions of formation of the hydrothermal parageneses is one of the main problems shown here. Because the hydrothermal activity in the pegmatites and other bodies is frequently closely bound, the conclusions are given jointly.
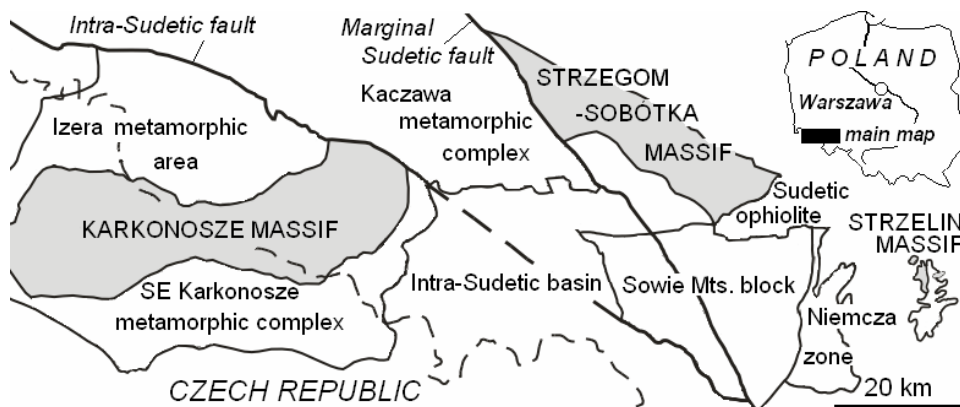
Fig. 1. Schematic geological map of location of the Karkonosze, Strzegom-Sobótka and Strzelin massifs (*after* Mazur *et al*. 2007, simplified)

METHODS

Fluid inclusions were investigated by routine microscope heating and freezing methods (*see e.g.* Roedder 1984) in double-side-polished 0.5 mm thick slices of quartz. The accuracy of measurements of the homogenisation temperatures (Th) of aqueous inclusions was ±1ºC and the accuracy of Th values of carbon dioxide inclusions was about ±0.05ºC. The *Fluid Co.* microscope cooling-heating stage was applied, calibrated on a set of artificial fluid inclusions, pure chemical compounds and on quartz inversion point. NaCl was identified in solution by eutectic point and salt concentration was determined by use of the Bodnar's (1978) data, the aqueous solution isochores were drawn according to the Potter's and Brown's (1977) tables and the isochores of CO_2 – on the basis of the Bulakh's and Bulakh's (1978) data. Pressure during quartz crystallization was determined by the crossed isochores method. The liquid CO_2 plus aqueous solution inclusions of heterogeneous trapping were applied as well to determine the P and T parameters of quartz crystallization with use of the appropriate experimental data (Gehrig 1980; Gehrig *et al*. 1986), when the shapes of the appropriate coeval inclusions allowed to calculate the phase proportions precisely enough. The composition of the solutions in fluid inclusions was recognized on the basis of the cryometric studies (Crawford 1981, Kozłowski 1984), by measurement temperatures of the eutectic points, temperatures of the passing the cotectic borders and temperatures of the last ice crystal melting.

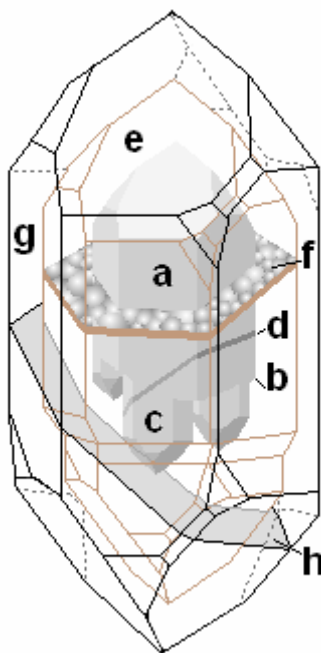## CONDITIONS OF THE HYDROTHERMAL MINERALIZATION

Karkonosze massif

The Karkonosze massif is a well-exposed intrusion with many quarries active in the past, though now only one at Szklarska Poręba Huta is in operation. This long period of exploitation yielded many interesting specimens of pegmatitic and vein minerals (Kozłowski, Sachanbiński 2007 and references therein).

The very good record of the evolution of the mineral-forming fluids and crushing phenomena of the minerals, apparently related to the massif cooling and jointing, was found in pegmatites. The samples for the present study came from the 27 pegmatites from the Karkonosze massif at Szklarska Poręba, Michałowice, Czarne, Staniszów, Marczyce and Karpniki. The selected 57 quartz crystals were investigated. The quartz crystals from 1 cm to 23 cm in length were thoroughly observed to distinguish their zoning,

regeneration and fissure healing peculiarities, then they were photographed and/or carefully drawn. Later preparations for fluid inclusion studies were made; for this study 930 inclusions from pegmatitic minerals and 1012 for the vein minerals, mostly quartz, were investigated. The temperatures for the crush events are given as homogenization temperatures (Th), which are lower than the crystallization temperatures – to calculate the latter, the addition of the temperature correction for pressure influence is necessary. However, for the studied specimens such correction could be calculated only exclusively.

Fig. 2. Euhedral quartz crystal from the pegmatite at Michałowice, Karkonosze massif, crushed, regenerated and healed many times; **a** – gray quartz with primary fluid inclusions (homogenisation temperatures *Th* 420–380ºC), **b** – surface of the crystal breaking, **c** – regene-ration of the broken end of the crystal *a* (*Th* 380–355ºC), **d** – healed fissure in the crystals *a* and *c* (*Th* 350ºC), **e** – smoky quartz zone of almost sceptre habit (*Th* 330–265ºC). **f** – healed fissure cutting the crystal zones *a* and *e* (*Th* 247ºC), **g** – rock crystal zone forming the perfect quartz habit (*Th* 233–137ºC), **h** – healed fissure cutting the growth zones *e* and *g* (*Th* 127ºC; other three such fissures in the same crystal yielded *Th* of fluid inclusions 123ºC, 115ºC and 109ºC).

In the pegmatites the earliest generation of quartz is gray and it formed before the main episode of crushing (Fig. 2); homogenization temperatures (*Th*) of fluid inclusions in this quartz ranges from 420 to 330ºC. This quartz always is broken into pieces, chipped out of the wall rock and fractured; the fractures or fissures from this quartz frequently continue in the wall rock. Probably this crush episode was caused by thermic contraction of the parent rock, which resulted also in origin of the joint fractures. Most of these damages was healed or regenerated by gray quartz (*Th* <380ºC).
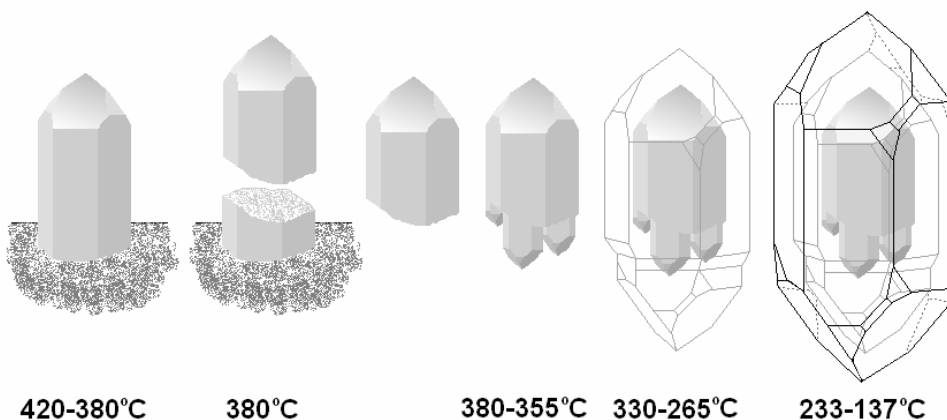

Fig. 3. Cycles of the quartz formation in pegmatites, from *left* to *right*: growth – crushing – healing and regeneration – growth, *etc*.; homogenization temperatures of the related inclusions are given.

The Karkonosze pegmatites bear quartz crystals, which after the main crushing episode recorded four distinct crush events. Temperature of homogenization (*Th*) of fluid inclusions in quartz healing the then formed fissures in quartz crystals had the following values: 350–330ºC (**d** in Fig. 2), 270–250ºC (**f** in Fig. 2), 210-180 ºC and 130-105ºC (**h** in Fig. 2). Other *Th* in healed fissures occur rarely, and such fissures were developed in limited ranges. Thus, the sequence of the quartz formation in pegmatites may be described as growth – crushing –healing and regeneration – growth – crushing, *etc*. (Fig. 3). Moreover, the sequence of the quartz varieties crystallisation is probably bound to distinct temperature ranges in all the studied pegmatites (Fig. 4), *see* Kozłowski (2002a).
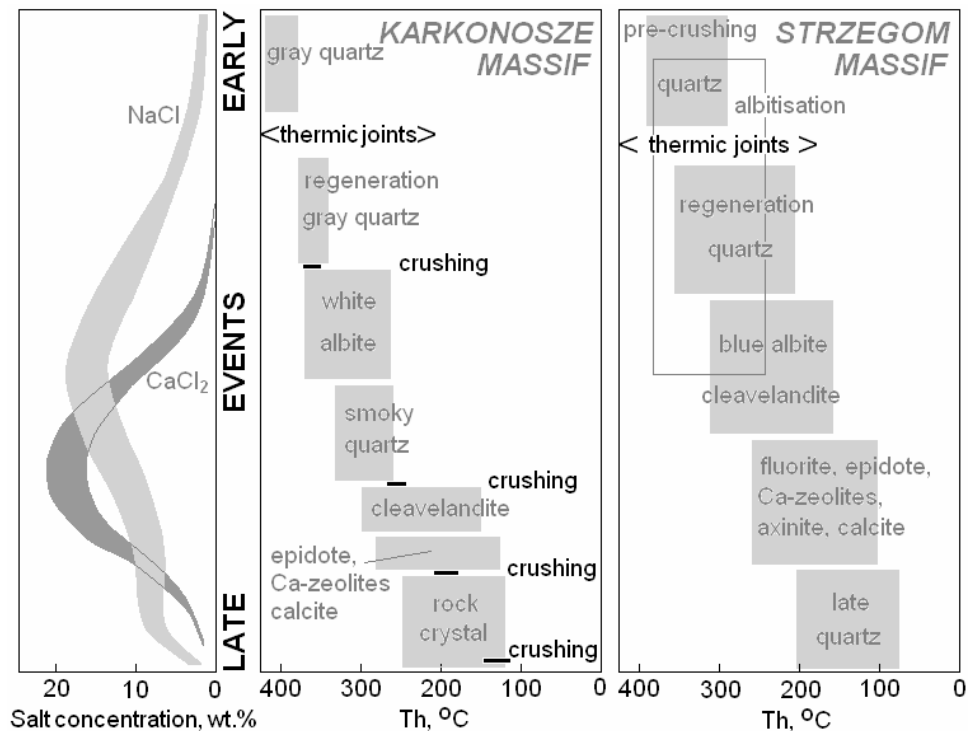

Fig. 4. Sequence of the pegmatite mineral crystallisation, crush events and changes of concentrations of the main salts dissolved in mineral-forming solutions. Potassium feldspar and mica formation not shown here.

In the pegmatitic quartz crystals the pneumatolytic inclusions are common, but, though generally bound to the early zones of quartz, they appear also at relatively low temperatures, having *Th* ca. 200ºC. This means, that after general gaseous state of the early post-magmatic fluids and after its condensation, locally decrease of pressure caused short-time boiling of liquid solutions and a limited presence of low-temperature pneumatolytic environment. However, at temperature below 420-400ºC the most common solution was the liquid one.

The concentrations of the parent fluids of the minerals (both in pegmatites and in veins) were not high, rarely approaching 30 wt. % (if a high content of calcium chloride occurred), the most common values are from 5 to 15 wt. %. The total salt concentrations, at high temperatures low, then increased with a maximum at 350-250ºC and then gradually decreased to very diluted solutions, bearing few percent of dissolved salts.

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Table 2. Crystallisation conditions of the post-magmatic minerals in the Karkonosze granite

Mineral	Fluid inclusion data (N – number of the studied inclusions)								
	Filling	Tcr, °C	P, kb	S, wt. %	NaCl	KCl	CaCl₂	CO₂	N
Gray quartz	G	*590*-410	*1.5*	?	?	?	?	+	55
	L	525-300	1.4-0.8	5-25	50-80	0-20	0–40	+	149
Morion, smoky	G	*470*-330	*1.4*-0.7	?	?	?	?	+	42
quartz	L	400-210	1.3-0.7	11-28	55-70	0-15	20–50	+	191
Rock crystal	L	270-90	0.9-0.6	1.7-16	70-95	0-5	5–30	+	211
Amethyst	L	290-200	0.7-0.6	4-9	75-100	0-5	0-25	+	101
Milky quartz	L	285-110	1.3-0.4	1.0-23	45-100	0-20	0-55	+	324
Topaz	L	430-400	1.2	6-11	80	10	10	+	4
Beryl	L	430-410	1.3	7-11	85	10	5	+	9
Tourmaline	L	460-390	1.5-1.3	8-19	75	20	5	+	12
Cleavelandite	L	320-160	1.1-1.0	9-16	60-75	5-10	15-30	+	41
Calcite	L	200-<90	0.6	1.0-16	60-80	5-10	10-35	+;–	21
Wolframite*	L	520-390	0.9	ca. 8	?	?	?	+	55
Cassiterite*	L	515-470	0.9	ca. 6	80?	20?	?	+	37
Magnetite*	L	525-465	1-0.9	ca. 6	90?	10?	?	+	15
Sphalerite*	L	420-390	*ca.* 0.7	7-15	60-65	0-15	20–30	+;–	18
Molybdenite*	L	455-390	0.8	6-11	70-75	0-10	15–25	+	38
Bismuthinite*	L	270-245	0.6	12-18	60-65	0-5	30-35	+	9
Bismuth*	L	265-135	0.5	15	85	0	15	+	9

*Note***: Tcr, P** crystallisation temperature and pressure, **S** total salinity, salt components in % of their total contents. Asterisks mark minerals, which occurred as inclusions in quartz in the same growth zones as fluid inclusions and the latter were the basis of their parent fluid characteristic; **G** mainly gas, **L** mainly liquid; **N** number of the inclusions measured; *italics* mean approximate values; "+" CO_2 present, "–" CO_2 absent; "?" determination impossible or very uncertain. Mineral identifications by the WDS method, the Cameca sx100 electron microprobe was used

The data from fluid inclusions in hydrothermal minerals the Karkonosze massif yielded typical conditions (Table 1), which are comparable to the formation parametres of the hydrothermal parageneses in the two other presented massifs (Fig. 4 and Table 2). The crystallization temperatures range from 525 to less than 100ºC, pressure – from 1.5 to 0.5 kbar, total salt concentrations in the mineral-forming solutions from 1 to 28 wt. % and the parts of the total salts (if all salts considered as 100%) were as follows: NaCl 50-100%, KCl 0-29%, CaCl₂ 0-50%. The initially diluted, high-temperature solutions are sodic with potassium addition, when temperature decreases, the total concentration increases with a sodium maximum preceding the calcium maximum, so that solutions may be even more calcic than sodic. Potassium content, though generally higher in the high-temperature solutions than in the low-temperature ones, varies rather without recognizable regularity. Low-temperature solutions are rather sodium rich, even "pure" sodic.

Strzegom-Sobótka massif

The post-magmatic assemblages of this massif were described by Lenkowski (1983) and Janeczek (1985, 2007). The investigated minerals, *i.e.* quartz (all varieties except for amethyst, which is absent in the Strzegom-Sobótka massif), topaz, beryl, tourmaline, cleavelandite and calcite, yielded fluid inclusion data similar to that obtained for the Karkonosze massif. Fluorite, quite common in the Strzegom hydrothermal assemblages, crystallized at temperatures from 280 to 130ºC, under pressure of 0.6-0.5 kbar, in part from calcium-rich (even to 65 % CaCl₂ in total salts) and relatively concentrated (to 30 wt. %). In general, the calcic maximum (Fig. 4) in the mineral-forming solutions in the Strzegom-Sobótka massif is better expressed then in the Karkonosze massif.

Strzelin massif

The Strzelin granitoids contain moderately abundant pegmatite pockets, veins and metasomatic zones. Till now, fluid inclusion data for the post-magmatic mineralization in the Strzelin granitoids were published by Stępisiewicz (1977), and the suggestions on the characteristics of fluids in Strzelin granite were proposed by Ciesielczuk and Janeczek (1999), Ciesielczuk (2001, 2007) and Kozłowski and Metz (2003). The chlorite geothermometry for the post-magmatic deposits in this granite was given by Ciesielczuk (2002).

Table 2. Crystallisation conditions of the post-magmatic minerals in the Strzelin granite

Mineral	Fluid inclusion data (*N* – number of the studied inclusions)								
	Filling	Tcr, °C	P, kb	S, wt. %	NaCl	KCl	CaCl₂	CO₂	N
Gray quartz	G	*570-430*	*1.4*	?	?	?	?	+	74
	L	460-290	1.4-0.9	7-12	50-80	0-20	0-40	+	127
Morion, smoky	G	*460-350*	*1.4*-0.8	?	?	?	?	+	39
quartz	L	390-230	1.2-0.8	10-17	50-70	0-15	20-50	+	179
Rock crystal	L	250-120	0.9-0.8	1.5-18	70-95	0-5	5-30	+	155
Garnet	L	450-430	1.4	7-8	80	15	*5*	+	9
Topaz	L	455-410	1.4	6-9	85	15	–	+	7
Beryl	L	440-410	1.4	7-9	85	15	–	+	11
Tourmaline	L	420-390	1.4-1.3	7-9	80	15	*5*	+	10
Apatite	L	430-320	1.3-0.9	8-9	80	10	10	+	12
Sphene	L	440-400	1.4	7-8	80	10	10	+	8
Zircon	L	450-420	1.4	7-10	70	20	10	+	9
Cleavelandite	L	340-190	1.1-1.0	10-15	60	10	30	+	41
Prehnite	L	*195-170*	*~1.0*	14-16	65	10	25	?	19
Apophyllite	L	200-160	0.9	14-15	65	10	25	+	23
Epidote	L	230-180	*0.9*	14-15	65	10	25	+?	17
Fluorite	L	240-140	0.9-0.8	14-18	50-65	0-10	25-40	+	59
Chlorite[*]	L	300-260	1.0-0.9	13-14	70	10	20	+	14
	L	210-180	0.8	14-15	50	15	35	+	11
	L	160-150	0.8	5.4	70	10	20	+	10
Calcite	L	190-<90	0.8	1.5-14	60-80	5-10	10-35	+;–	73
Stilbite[*]	L	210-140	0.8	5-14	60-80	5-10	10-35	+;–	10
Laumontite[*]	L	230-170	0.8	14-15	50-65	0-10	25-40	+;–	14
Chabasite[*]	L	200-140	0.8	5-14	60-80	5-10	10-35	+;–	8
Pyrrhotite[*]	L	340-280	1.1	9-16	50-70	10	20-50	?	6
Pyrite[*]	L	280-170	1.0-0.9	14-15	65	10	25	+;–	14
Chalcopyrite[*]	L	350-260	1.1-1.0	10-14	65	10	25	+;–	15
Sphalerite[*]	L	345-220	1.1-1.0	10-15	60-65	5-10	25-30	+;–	19
Molybdenite[*]	L	350-300	1.1-1.0	8-12	70-75	0-10	15-25	+;–	9
Galena[*]	L	190-140	0.8	3-13	70-80	5-10	10-35	+;–	5
Aikinite[*]	L	230	0.8	12	80	5	15	?	3
Emplectite[*]	L	220	0.8	12	80	5	15	?	5
Bismuth[*]	L	190	0.8	14	80	0	20	?	6

Note: **Tcr, P** crystallisation temperature and pressure, **S** total salinity, salt components in % of their total contents. Asterisks mark minerals, which occurred as inclusions in quartz, fluorite and calcite in the same growth zones as fluid inclusions and the latter were the basis of their parent fluid characteristic; **G** mainly gas, **L** mainly liquid; **N** number of the inclusions measured; *italics* mean approximate values; "+" CO₂ present, "–" CO₂ absent; "?" determination impossible. Mineral identifications by the WDS method, the Cameca sx100 electron microprobe was used.

The pegmatite parageneses, studied in the current project, consisted of the minerals listed in Table 2 and white albite, biotite and muscovite. Veins contained varieties of quartz, micas, K- and Na-feldspars, chlorite, laumontite, prehnite, fluorite and ore minerals. The sequence in Table 2 from garnet to calcite is the general crystallization sequence found by petrographic methods. Zeolites crystallized later than the earliest cleavelandite, and ore minerals essentially together with smoky and gray quartz, and chlorite; only bismuth was younger. The 56 samples of the post-magmatic assemblages (31 pegmatites and 25 veins) were used for the fluid inclusion investigations. The samples came from the biotite granite quarries at Strzelin and Mikoszów, and from the biotite-muscovite granite quarry at Gębczyce. The size of fluid inclusions ranged from *ca*. 50 μm in quartz, fluorite and calcite to less than 1 μm in zircon, epidote and garnet. The smallest investigated inclusions (in zircon and garnet) were 2.5 μm long and *ca*. 1 μm wide.
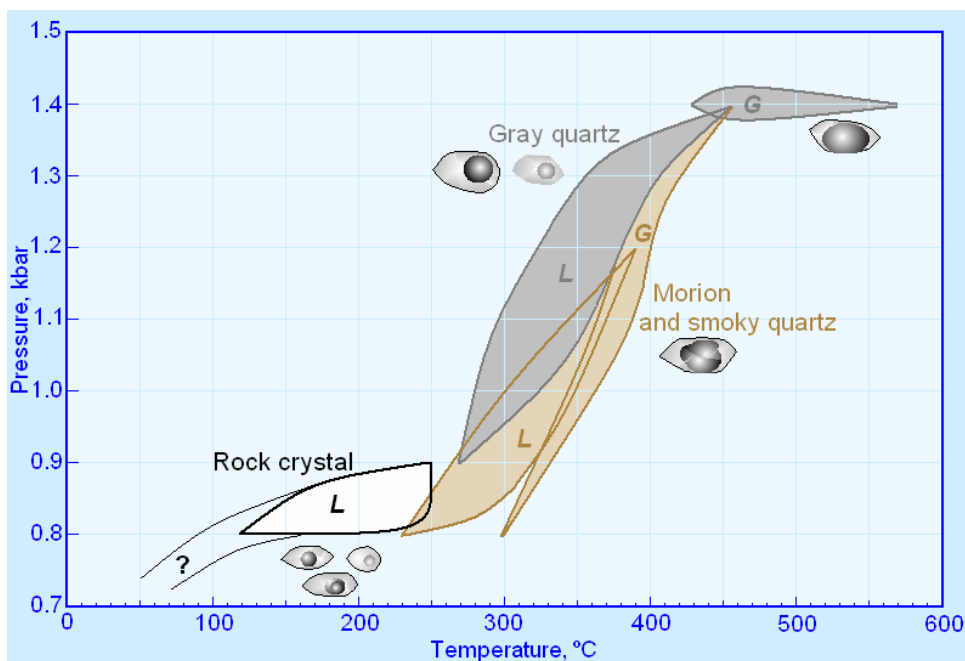

Fig. 5. Temperatures and pressures of crystallization of the post-magmatic quartz varieties in the Strzelin massif, and typical fluid inclusions; G – gaseous solutions, L – liquid solutions.

The results of the studies of fluid inclusions (Table 2) yielded temperature ranges of the post-magmatic mineralisation in the Strzelin granitoids from 570 to 100°C and pressure from 1.4 to 0.8 kbar The full range of the conditions was covered by several varieties of quartz (Fig. 5). The earliest solutions were pneumatolytic, and after condensation the hydrothermal ones had total concentrations 6–7 wt. % with dominating NaCl and appreciable content of KCl. During decrease of temperature to 250–200°C the total concentration of the mineral-forming solutions increased to 15–18 wt. %, with high contents of $CaCl_2$. Afterwards, concentrations decreased to 3–1.5 wt. % and the solutions became again of the NaCl type (Fig. 6.). The latter change was found earlier by Stępisiewicz (*op. cit.*), but the recent study did not confirm his statement on the very high concentration of Al in fluids. This author's rough determinations of decrepitation temperatures of sulphide minerals by methodic reasons cannot be compared to the values
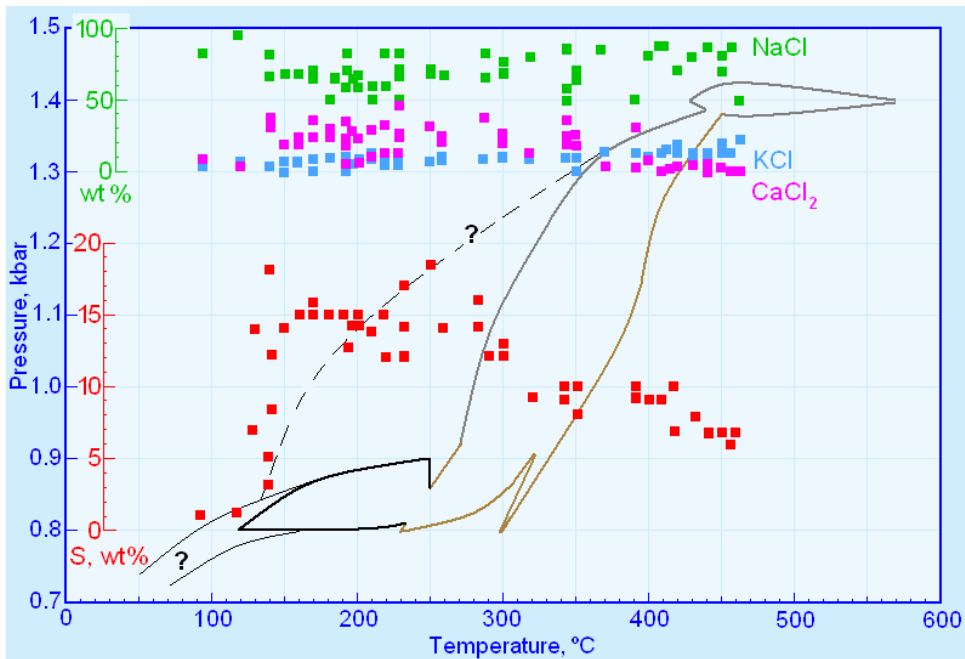
Fig. 6. Total concentrations of salts (S, wt. %) in solutions in fluid inclusions in quartz from the Strzelin massif and contents of the three main salts in the same inclusions, total of the salts assumed 100 %; the solid and dashed lines show the crystallization fields for quartz varieties (*see* Fig. 5), the temperature scale is common for the pressure and concentration axes.

determined for the respective minerals in this study. The conditions of formation of chlorites, zeolites and ore minerals were determined from fluid inclusions in the growth zones of quartz, fluorite and calcite, in which the included grains of the listed minerals were found, thus the obtained values may be extended to these minerals (for the examples *see* Fig. 7.).
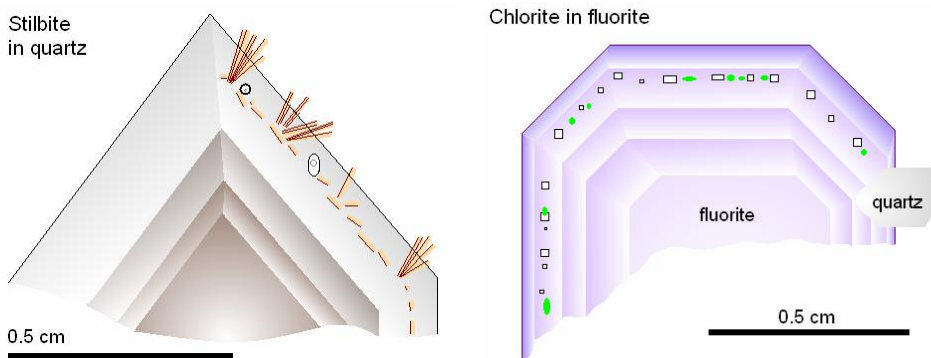

Fig. 7. Mineral inclusions occurring in the same growth zone as fluid inclusions, the examples from the Mikoszów quarry, stilbite (*left*) is orange-brown, chlorite inclusions (*right*) are green; the parametres determined from such fluid inclusions may be extended to mineral inclusions as their conditions of crystallization. For the obtained data *see* Table 2.

The presence of carbon dioxide in the mineral-forming fluids is common, what made possible to determine pressure of crystallisation of the minerals. The hydrothermal origin of the 0.5-1 mm zircon grains found in the quartz-chlorite assemblage, was recognised. Ciesielczuk (2002) obtained by chlorite thermometers 358 or 208°C as formation temperatures of this mineral, and she discarded these values. One her value meets the range 210-180°C obtained from inclusions.

FINAL REMARKS

Fluid inclusion studies in minerals of the hydrothermal (and partly pneumatolytic) intragranitic parageneses from the three granitoid massifs allowed to determine the temperatures of crushing events in pegmatites (the same is applicable to veins). The ranges of temperature for crystallization of minerals (or even their varieties) were similar in all the massifs. The same properties were pertinent to pressure of crystallization of the post-magmatic minerals. General pattern of the concentration change of the mineral-forming solutions and variation of the main salt proportions is also similar in all three massifs. However, the changes of the main salts proportions are less distinct in the Strzelin massif hydrothermal parageneses than in the other two massifs. This may be connected with multiple intruding of several magmatic stocks or dykes, which finally formed the Strzelin massif, thus with more variable conditions of formation and existenxce of the post-magmatic parageneses.

Acknowledgements

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