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TEMPERATURE, PRESSURE AND COMPOSITION OF THE PARENT SOLUTIONS OF QUARTZ FROM JEGŁOWA, LOWER SILESIA

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A b s t r a c t. The present paper is an attempt at elucidating the genesis of rock crystal occurring in the kaolinite rock at Jegłowa, Lower Silesia. The temperatures of quartz crystal formation vary in the range 350—120°C. Upon the determination of the chemical composition of the parent solutions it has been found that Na^+, Ca^{2+}, K^+, Al^{3+} and Cl^- were the principal ions. The mean concentration of the solutions was 18 weight per cent. The probable pressure during the crystallization of quartz from these solutions attained a value of 500—600 atm (for the temperature 220—160°C).

QUARTZ OCCURRENCE

Rock crystals at Jegłowa in Lower Silesia occur within the kaolinite rock associated with the series of quartzite rocks. The rock complex in the region of Jegłowa consists of quartzite schists, quartzites and sericite schists, regarded to be of Lower Devonian age. They are the elements of the metamorphic cover of the Strzelin granitoid massif. Kaolinite appears as lenses and beds up to 2 m thick, as well as in the form of nests and veins within the quartzite schists (Oberc 1966).

The kaolinite rock is made up of either kaolinite or mixed-layer kaolinite-smectite of hydrothermal origin (Szpila, Wiewióra, Gadomski 1972; Wiewióra 1973).

Quartz crystals grow on quartzite schist fragments or frequently form automorphic specimens, sometimes terminated at both ends of the c-axis. Occasionally, clusters of opaque and milky quartz crystals, commonly broken and regenerated, have been recorded. The size of crystals varies within a wide range, from some millimetres up to 25 cm. The bulk of crystals are small in size, their morphology being considerably diversified.

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The larger crystals have zonal structure. The crystals are often twinned according to Dauphiné, Brazil and Japanese laws. There are shallow cavities on the prism walls.

EXPERIMENTAL

The physico-chemical conditions of quartz crystallization have been determined using the following methods:

Temperature was determined by a) the method of homogenization of gaseous-liquid inclusions (Roedder 1967), b) decrepitation thermoacoustic method (Pawłowska 1971), c) decrepitation thermogravimetric method (Karwowski, Kozłowski 1972). The method of Naumov and Malinin (1968) was used to determine the *pressure*. The *chemical composition of the parent solutions* was defined by means of water extracts (Kalyuzhnyi 1960), whereas the *amount of inclusions* and the *solution concentrations* by calcination method (Karwowski, Kozłowski 1971).

The electron micrographs of the inclusion replicas were made by P. Dzierżanowski, M. Sc.

FLUID INCLUSIONS

Fluid inclusions in quartz from Jegłowa were first reported by Morawiecki (1953). The investigations performed by the present authors permitted to detect two-, three- and one-phase inclusions (Kozłowski, Karwowski 1972).

1. Two-phase inclusions are both primary and secondary. They contain mainly salt aqueous solution (80—95% of volume) and a gas bubble (20—5% of volume), and homogenize into liquid phase. The primary inclusions are associated with the zones of crystal growth or appear all alone; the secondary ones usually occur along healed fractures (Phot. 10).

2. Three-phase inclusions contain, besides aqueous solution and a gas bubble, a radial, loose or compact aggregate of lowbirefringent kaolinite-smectite *. The aggregates occupy different parts of volumes in the bubbles — from over 50% (Phot. 1), through 20—10% (Phots. 2, 3), down to single laths only (Phot. 4). Kaolinite-smectite fails to dissolve when heated to temperatures of the inclusion homogenization. The occurrence of various amounts of kaolinite-smectite in the inclusions with similar homogenization temperatures, as well as the presence of inclusions with the same homogenization temperatures that do or do not contain kaolinite-smectite (Phots. 4, 5) prove that kaolinite-smectite is the entrapped mineral, i.e. formed on the crystal surface or in fracture cutting crystal and then closed in the inclusion, but not a second-generation mineral, i.e. such that crystallized from the content of an already isolated inclusion. The fact that there are no disturbance in the orientation of the aggregates may testify to crystallization in the loci of the actual occurrence of the entrapped mineral, without the redeposition by hydrothermal solution.

* Identified on the basis of infrared absorption spectrum (Wiewióra 1973).

Morawiecki (1953) gives a drawing of an inclusion that contains a halite crystal (about 5—7% of volume) besides the gas bubble. The authors have failed, however, to find any similar inclusions; neither has the presence of liquid CO_2 been noted.

3. One-phase of fluid inclusions are not very numerous being the latest generation of the secondary inclusions.

TEMPERATURE

The determination of the temperature of quartz crystallization was based on 320 measurements of the homogenization temperature (T_h) of the inclusions (Fig. 1). The earliest parts of the crystals formed under relatively high-temperature hydrothermal conditions (350°C), the inclusions with T_h approximating 300°C being most amply represented in the high-temperature group. Subsequently crystals were broken and fractured, then ci-

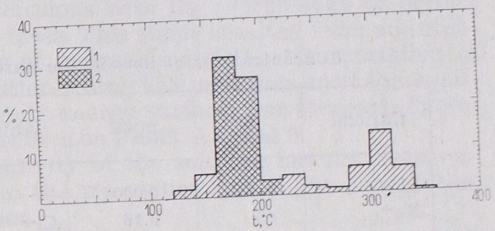

Fig. 1. A histogram of homogenization temperatures of inclusions in quartz

1 — two-phase inclusions, 2 — two- and three-phase inclusions (with kaolinite-smectite)

healed and regenerated. Regeneration as well as crystallization of the outer zones of crystals and of low-temperature specimens were most intensive in the temperature range 200—160°C, then terminated at about 120°C, giving rise in the final stage to transparent, almost inclusion-free crystals. Inclusions with kaolinite-smectite appeared at a temperature about 220°C, disappearing at 160°C. The temperature data obtained correspond to the temperature range determined by decrepitation methods (Kozłowski, Karwowski 1972).

PRESSURE

The determination of pressure on the basis of fluid inclusions is a far more complicated matter than temperature determination. The analysed quartz does not contain inclusions with liquid CO_2, which would permit a precise determination of pressure. Upon opening the individual inclusions it has been found that, under normal conditions, the gas bubble increases in volume, it therefore consists presumably of other gases besides H_2O vapour. However, the presence of the inclusions homogenizing into of fluid phase only makes it impossible to calculate the pressure from the difference in the volume of gaseous phase in a closed inclusion and under normal conditions (Kalyuzhnyi 1960). In consequence, the only applicable method for an approximate determination of pressure was that of Nau-

mov and Malinin (1968), based on the difference in the homogenization and decrepitation temperatures of the inclusions. The resultant data fall within the range 500—600 atm. This value should be presumably regarded as approximate and as characterizing rather the upper pressure limit during the crystallization of quartz. It should be mentioned here that it corresponds to a lithostatic pressure of a 2000-metre overburden.

THE COMPOSITION AND CONCENTRATION OF THE SOLUTION

The mean chemical composition of the parent solution of quartz (Tab. 1) shows that the rock crystal formed from a solution of the Na—Ca—K—Al—Cl type with the content of other cations not exceeding 0.1% and fluoride and bicarbonate anions occurring also in subordinate amounts. The presence of borate correlates well with small tourmaline aggregates

Table 1

Concentrations of ions in the parent solution of quartz

Cations	%	mval	Anions	%	mval
Li^+	0.004	0.0006	F^-	0.21 *	0.011
Na^+	4.2	0.18	Cl^-	11	0.305
K^+	0.83	0.021	BO_3^{3-}	0.007	
Mg^{2+}	0.02	0.002	HCO_3^-	0.15 **	0.002
Ca^{2+}	1.0	0.05			
Sr^{2+}	0.04	0.001			
Ba^{2+}	0.04	0.0006			
Al^{3+}	0.51	0.06			
Mn^{2+}	0.06	0.002			
Fe^{2+}	0.08	0.003			
Total	~6.8	~0.32		~11.4	~0.32

* Analyst: Z. Jońca, M. Sc.
** Analyst: Dr P. Zawidzki.

that appear in the quartz schists. Worthy of note, on the other hand, is the lack (up to the sensitivity limits of the method used) of titanium which appears in quartz (34 ppm) also as anatase inclusions, therefore must have been originally present in the solution.

In the analysed water extract the presence of silicon compounds was conspicuous; however this element has not been determined because of the unavoidable contamination of the solution with fine-dispersive silica formed during the grinding of quartz. It should be noted that $T = 200°C$ and $P = 500$ atm solubility of quartz in water is about 0.04% (Kennedy 1950).

The mean concentration of the solution was about 18 weight %.

The pH of the extract of the inclusion content in quartz tends to attain values lower than 7. Also the chemical composition of the inclusion fillings points to a weakly acid reaction of the solution.

The density of the solution present in the inclusions filled up to 92.5—93% and having a homogenization temperature of 164—167°C is 1.02 g/cm³ at the temperature of homogenization.

THE ACTIVITY OF THE SOLUTIONS

Examinations of the morphology of the inclusions prove that not in all the stages of their activity did the hydrothermal solutions affect quartz in the same degree. Three is a substantial amount of xenomorphic inclusions that have never attained the morphology of the minimum energy surface (Roedder 1971). This fact attests to a relatively weak intensity of recrystallization of the faces inclusion of after its isolation, and hence to a low activity of the inclusion filling (Phots. 2—5, 9). There is also a considerable number of inclusions with the morphology of perfect negative crystals enclosed by flat faces. This shape resulted from an intensive recrystallization of the faces of inclusions and the transportation of their substance by the active solution filling the inclusion until the equilibrium morphology, i.e. the minimum energy surface, was attained. Examples of such negative crystals are shown on Phots. 6, 7 and 8.

The nature of this variable activity of the solution has not been explained, though the differences in the pH values and in the composition seem to be the most probable reason.

THE INFRARED ABSORPTION SPECTRUM OF QUARTZ

Quartz from Jegłowa has a fairly rich infrared absorption spectrum in the range 3000—3700 cm^{-1}. The bands 3200 and about 3300 cm^{-1} refer to the vibrations of the quartz crystal lattice and are not connected with the

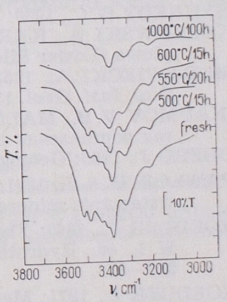

Fig. 2. Infrared absorption of quartz in the range 3000—3700 cm^{-1}; oriented preparation //Z, 1 mm thick, UR-20 spectrophotometer, LiF; determinations made by A. Pelc M. Sc.

lattice defects (Brunner, Wondratschek, Laves 1961). The absorption bands 3384, 3440, 3487 and 3520 cm^{-1} are due to the presence of OH groups in the association OH — Li in the vicinity of aluminium-oxygen tetrahedra that substitute the silicon-oxygen tetrahedra (Bukanov *et al.* 1969). It appears

therefore that quartz crystallization under the discussed conditions brought about the incorporation of lithium (10 ppm) and at least a part of aluminium present in quartz (280 ppm) in the structure of quartz.

The OH groups from the analysed quartz are relatively hard to remove (even when heated at 500—1000°C for 150 hours, in which at 1000°C for 100 h). Moreover, there is a difference in the rate of removal; while the band 3487 cm^{-1} disappears upon heating at 600°C for 15 h, the other ones are still visible after 100-hour heating at 1000°C (Fig. 2). It may be presumed then that this fact proves a different position of OH groups in the quartz structure.

FINAL REMARKS

The investigations performed and the resultant data permit to infer that both quartz and kaolinite-smectite occurring in a common paragenesis are minerals of hydrothermal origin. The first generation of quartz crystallized under high-temperature conditions, at about 300°C. It is separated from the following generation by a period of tectonic disturbances and the probable change in the chemical composition of the solution that led also to the crystallization of kaolinite-smectite besides quartz.

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TEMPERATURA, CIŚNIENIE I SKŁAD ROZTWORÓW MACIERZYSTYCH KWARCU Z JEGŁOWEJ, DOLNY ŚLĄSK

Streszczenie

W obrębie kwarcytów i łupków kwarcytowych, stanowiących osłonę metamorficzną masywu strzelińskiego, w miejscowości Jegłowa, w strefach wypełnionych minerałami ilastymi, występują automorficzne kryształy kwarcu. Minerał ilasty w którym występują kwarce jest mieszanopakietowym minerałem z grupy kaolinitu-smektytu.

Autorzy przebadali inkluzje gazowo-ciekłe (fot. 1 do 10), występujące w kryształach kwarcu. Na podstawie składu fazowego oraz temperatur homogenizacji ustalono, że kwarc jest pochodzenia hydrotermalnego. Początek krystalizacji kwarcu miał miejsce w temperaturze około 350°C z homogenicznego roztworu wodnego. Następnie doszło do silnego spękania i pokruszenia utworzonych kryształów. W temperaturze około 250°C nastąpił etap zabliźniania i regeneracji oraz ponownego wzrostu kryształów. Najsilniejszy rozwój tego zjawiska miał miejsce do temperatury 160°C. Działalność roztworów hydrotermalnych zaznaczyła się jeszcze do temperatury 120°C (fig. 1).

Skład fazowy inkluzji świadczy o niezbyt dużym stężeniu soli oraz podrzędnym udziale węglanów. Na podstawie analizy ekstraktów z inkluzji ustalono, że roztwór macierzysty zawierał jako główne kationy Na^+, Ca^{2+}, K^+, Al^{3+} oraz w podrzędnych ilościach Li^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+} i Fe^{2+}. Głównym anionem był jon chlorkowy, a podrzędnymi jon węglanowy i boranowy (Tab. 1).

Na podstawie metody Naumova i Malinina określono ciśnienie dla krystalizacji głównej masy kwarcu na około 500—600 atm. W przedstawionych wyżej warunkach zaistniały sprzyjające okoliczności do powstania w inkluzjach w kwarcu, a także w jego otoczeniu, minerału z grupy kaolinitu-smektytu. Dane te świadczą o hydrotermalnym pochodzeniu kwarcu jak i kaolinitu-smektytu.

OBJAŚNIENIA FIGUR

Fig. 1. Histogram temperatur homogenizacji inkluzji w kwarcu
1 — inkluzje dwufazowe; *2* — inkluzje dwu- i trójfazowe (z kaolinitem-smektytem)

Fig. 2. Absorpcja podczerwieni kwarcu w zakresie 3000—3700 cm^{-1}; preparat orientowany //Z, grubość 1 mm, spektrofotometr UR-20, LiF, oznaczenia wykonane przez mgr. A. Pelca

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Trójfazowa inkluzja w kwarcu z Jegłowej zawierająca uwięziony agregat kaolinitu-smektytu
g — faza gazowa, *k* — kaolinit-smektyt, pow. × 800

Fot. 2—4. Trójfazowe inkluzje zawierające zmienne ilości kaolinitu-smektytu (*k*), powiększenie × 600
Fot. 5. Dwufazowa inkluzja gazowo-ciekła, pow. × 600
Fot. 6. Automorficzna inkluzja „kubiczna", pow. × 12 200
Fot. 7. Automorficzna inkluzja „kubiczna", dwufazowa, pow. × 600
Fot. 8. Automorficzna inkluzja z symetrią trójkrotną, pow. × 12 200
Fot. 9. Ksenomorficzna inkluzja, pow. × 12 200
Fot. 10. Inkluzje ksenomorficzne na zaleczonej szczelinie, pow. × 12 200
Fot. 6, 8, 9, 10. Obrazy z mikroskopu elektronowego, repliki

Лукаш КАРВОВСКИ, Анджей КОЗЛОВСКИ

ТЕМПЕРАТУРА, ДАВЛЕНИЕ И СОСТАВ МАТЕРИНСКИХ РАСТВОРОВ КВАРЦА ИЗ ЕГЛОВОЙ В НИЖНЕЙ СИЛЕЗИИ

Резюме

В кварцитах и кварцитовых сланцах метаморфического комплекса, вмещающего Стшелинский массив, в местности Еглова, встречаются автоморфные кристаллы кварца, приуроченные к зонам, выполненным глинистыми минералами. Глинистые минералы представляют смешанные каолинит-смектитовые пакеты.

Авторы анализировали жидко-газовые включения в кристаллах кварца (фото 1—10). На основании фазового состава и температур гомогенизации определено гидротермальное происхождение кварца. Кристаллизация кварца в гомогенном водном растворе начиналась при 350°С. Далее происходило раздробление новообразованных кристаллов. При температуре порядка 250°С происходило залечивание, регенерация и новый рост кристаллов. Наиболее интенсивно этот процесс протекал до температуры около 160°С. Гидротермальная деятельность проявлялась вплоть до 120°С (фиг. 1).

Фазовый состав включений свидетельствует о довольно слабой концентрации солей и небольшой роли карбонатов. Анализ вытяжек из включений показал, что главными катионами в составе материнского раствора являлись Na^+, Ca^{2+}, K^+, Al^{3+} и в подчиненном количестве Li^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}. Главным анионом был хлоридный ион, подчиненными — карбонатный и боратный (табл. 1).

С помощью метода Наумова и Малинина было определено, что давление при кристаллизации основной массы кварца составляло 500—600 атм.

В описанных условиях в инклюзиях и в окружении кварца могло происходить образование минералов группы каолинита-смектита. Эти данные свидетельствуют о гидротермальном генезисе кварца и каолинита.

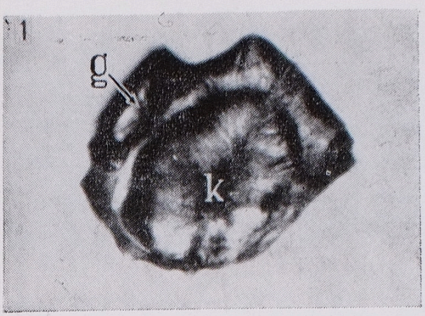
ОБЪЯСНЕНИЯ К ФИГУРАМ

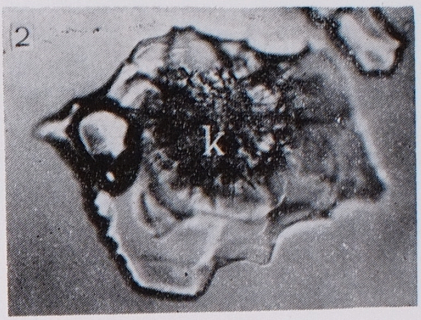
Фиг. 1. Гистограмма температур гомогенизации включений в кварце
1 — двухфазовые включения, *2* — двух- и трехфазовые включения (с каолинитом-смектитом)

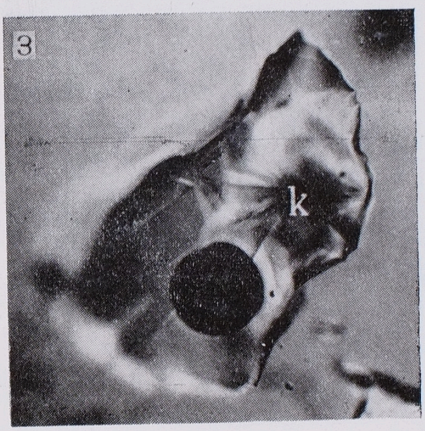
Фиг. 2. ИК-спектр поглощения кварца в области 3000—3700 $см^{-1}$; ориентированный препарат //Z, толщина 1 мм, спектрофотометр УР 20, LiF, анализ производил мгр. А. Пельц

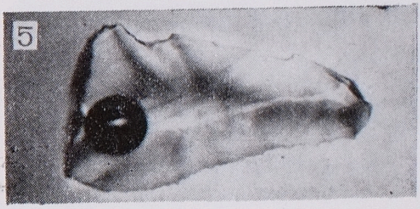
ОБЪЯСНЕНИЯ К ФОТОСНИМКАМ

Фото 1. Трехфазовое включение в кварце местности Еглова, содержащее каолинит-смектитовый агрегат
g — газовая фаза, *k* — каолинит-смектит; × 800
Фото 2—4. Трехфазовое включение, содержащее переменное количество каолинит-смектита (*k*); увел. × 600
Фото 5. Двихфазовое включения газово-жидкое; увел. × 600
Фото 6. Афтоморфное „кубическое" включение; увел. × 12 200
Фото 7. Автоморфное „кубическое" двухфазовое включение; увел. × 600
Фото 8. Автоморфное включение с треугольной симметрией; увел. × 12 200
Фото 9. Ксеноморфное включение; увел. × 12 200
Фото 10. Ксеноморфные включения на залеченной трещине; увел. × 12 200
Фото 6, 8, 9, 10. Образ под электронным микроскопом, реплики

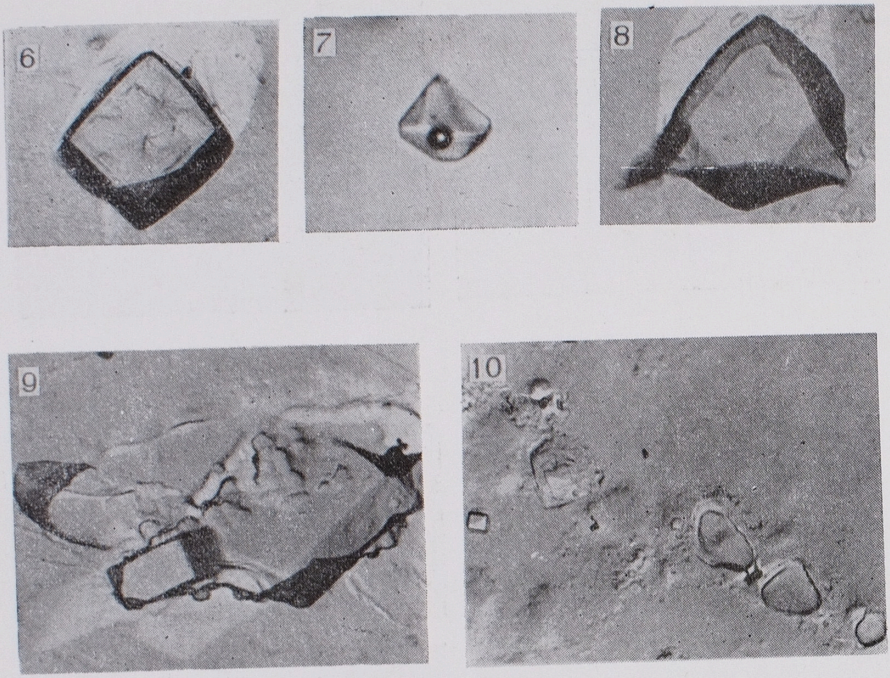








1. Three-phase inclusion in quartz from Jegłowa containing an entrapped kaolinite-smectite agregate; *g* — gaseous phase, *k* — kaolinite-smectite, × 800. 2—4. Three-phase inclusions containing variable amounts of kaolinite-smectite (*k*), × 600. 5. Two-phase inclusion, gaseous-liquid inclusion, × 600.



6. Automorphic "cubic" inclusion, × 12 200. 7. Automorphic "cubic", two-phase inclusion, × 600. 8. Automorphic inclusion with three-fold symmetry, × 12 200. 9. Xenomorphic inclusion, × 12 200. 10. Xenomorphic inclusions on a healed fracture, × 12 200. Phots. 6, 8, 9, 10. Images from the electron microscope, replicas