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**Author:** Łukasz Karwowski, Andrzej Kozłowski

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ŁUKASZ KARWOWSKI & ANDRZEJ KOZŁOWSKI

## Authigenic smoky quartz from the Famennian limestones at Łagów in the Holy Cross Mts

**ABSTRACT:** Inside smoky and black crystals of quartz from joint fractures in bituminous Famennian limestones at Łagów in the Holy Cross Mts, there occur inclusions containing variable amount of bituminous matter and aqueous solution of salts and gas. The occurrence of bitumen gives quartz its colour. The average temperatures of smoky quartz crystallization were c. 70°C, and of black quartz — c. 160—190°C. The veinlets of brown-black calcite, containing analogous inclusions, crystallized under similar conditions which revealed both minerals being connected with aqueous solutions containing dispersed droplets of bituminous matter.

### INTRODUCTION

Small crystals of smoky quartz, often in paragenesis with calcite occur in the bituminous Famennian limestones at the edges of the Łagowica stream, north of Łagów in the central part of the Holy Cross Mts. Usually, the crystals are strongly elongated (up to 2 cm) and flattened in the longer axis. They occur on the surface of joint fractures perpendicular to the bedding. The crystals form either rosette aggregates (Pl. 1, Fig. 1; cf. also Text-fig. 4) or parallel pattern in the bottom part of fractures in particular layers (Pl. 1, Fig. 2; cf. also Text-fig. 4). All the quartz crystals are euhedral. Locally, the individual crystals of quartz also appear in calcite druses (Fig. 1). The bituminous matter, which lost the volatile components was usually found inside fractures. The liquid bitumen (petroleum) occurs in druses.

Quartz from fractures is black or brown-black, whereas that from

druses is on the whole smoky<sup>1</sup>. Black, as well as smoky quartz are zoned: there occur dark-brown and light-brown or yellowish zones; the differences in colour are caused by various amount and kind of bitumen inclusions. Sometimes, calcite inclusions were found in quartz crystals (Pl. 2, Fig. 19).

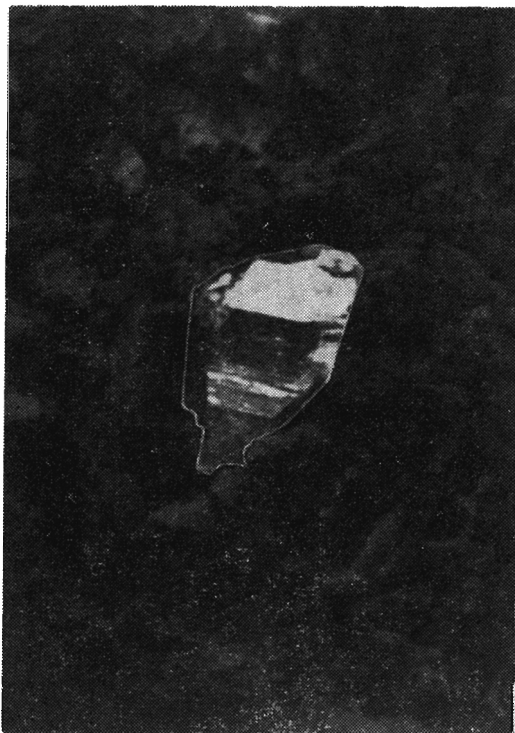


Fig. 1

Individual crystal of smoky quartz  
in a calcite druse,  $\times 2.5$   
Coll. Docent A. Radwański

Calcite concurring in fractures with quartz is colourless or brownish to brown-black. When crushed calcite emits a bituminous odour. Small aggregates of sulphides, usually pyrite, occur in calcite or limestone.

Similar exposures with bituminous calcite and quartz in the Famennian limestones were found at Górnó and Śluchowice in the western part of the Holy Cross Mts (for these localities — see Szulczewski 1971, Fig. 1); in the latter locality they are accompanied by insets of galenite, pyrite and chalcopryite. Although in the whole area of the Famennian, the deposits are rather monotonous and developed as bitumen-bearing marly limestones and marls (cf. Szulczewski 1971), the special variety of quartz was found only in the three localities discussed. Their crystallization took place due to fairly unfrequent mineral-forming conditions,

<sup>1</sup> Quartz crystals from the Famennian limestones are similar macroscopically to smoky quartz and morion of pegmatitic or hydrothermal, *i.e.* postmagmatic origin; the different nature of these very "morions" was ascertained during microscopic studies.

the reconstruction of which seems to be interesting to explain such a rare mineralogical curiosity as the authigenic smoky quartz. Czerwiński (1960) believed that quartz from the Famennian limestones at Łagów crystallized in the Tertiary as a rather remote result of the mineralization phase of the Alpine orogeny in the Carpathians. Recent studies proved (Kutek & Głazek 1972) that the Holy Cross Mts were beyond the control of this orogeny in the Carpathians, and therefore the Variscan orogeny should be regarded as a probable period of post-sedimentary processes leading to the formation of quartz crystals.

#### INVESTIGATION METHODS

Temperatures of inclusion homogenization were measured by means of a microscopic heating stage (Kalyuzhnyi 1960), as well as observations of individual inclusion decrepitation. Grained samples of minerals were investigated by the thermoacoustic decrepitation method.

Phenomena of luminescence were observed with the use of ultraviolet light. The bituminous matter was extracted from inclusions of a milled specimen by chloroform and a concentrated, chloroform-free bitumen was investigated by the infrared spectrophotometry method.

#### FLUID INCLUSIONS

Some varieties of fluid inclusions occur both in quartz and calcite. Gaseous-liquid inclusions in quartz contain small gas bubbles, which represent five per cent of inclusion volume. They are shaped as either negative crystals (Pl. 2, Fig. 1) or flat vacuoles, some of them with varying morphology (Pl. 2, Figs 2—10). Very intensive Brownian movements were observed inside small inclusions of this type (cf. Karwowski & Kozłowski 1971). No occurrence of crystal phase was observed. Neither CO<sub>2</sub>-bearing phases nor hydrated salt crystals (cf. Touray & Sabouraud 1970, Takenouchi 1971) originated during freezing. It was rather difficult to obtain a congealing point of inclusion filling. These facts indicate the occurrence of salt probably dissolved in aqueous solution as calcium hydrocarbonate, perhaps partly with calcium chloride.

In smoky quartz gaseous-liquid, inclusions homogenized at temperatures of 48—72°C and gave a liquid phase. Flat inclusions occurring on the borderline between smoky and brown-black quartz (Pl. 2, Figs 4—5 and 10) homogenized similarly.

Flat gaseous-liquid inclusions with varying morphology in brown-black quartz (Pl. 2, Figs 6—8) become homogenous at 106°C. Besides, gaseous-liquid inclusions, homogenizing at 160—190°C, have also been observed in that quartz (Pl. 2, Fig. 9).

Inclusions, containing bituminous matter are of another type. Those filled with bitumen and gas were often recorded. In brown-black quartz, inclusions usually contain dark-brown bitumen, sometimes with gas bubbles, indicating a high viscosity of this very bituminous matter. High viscosity of bitumen and their yellow lumines-

cence were found after opening an individual inclusion. More volatile components of bitumen boiled rapidly at 300–500°C. These inclusions (Pl. 2, Figs 11 and 13–14) yielded homogenization temperatures ranging from 250 to 300°C, but usually their earlier decrepitation did not permit to reach the homogenous liquid state of filling.

Bituminous inclusions of smoky quartz contain a light-yellow liquid bitumen (Pl. 2, Figs 17–18). Gas bubbles do not perform Brownian movements. Inclusions of this type homogenized at 48–74°C, reached a liquid phase, and then decrepitated at c. 150°C. During activating with ultraviolet light, bitumen contained in these inclusions emits a blue luminescence.

Beside those types of inclusions, three-phase inclusions may only rarely be observed; their filling consists of bitumen, aqueous solution and gas (Pl. 2, Figs 12 and 15–16). They contain both a light-yellowish and dark-brown bitumen. A gas bubble mostly occurred inside the bituminous phase, but in some cases the writers observed inclusions with their inner surface lined with bitumen, whereas a bubble occurred inside the aqueous phase. In small inclusions of this type the bubbles performed intensive Brownian movements (Fig. 2).

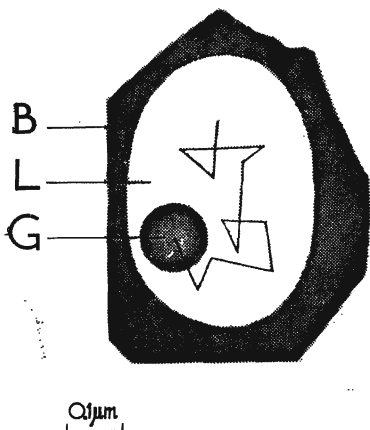


Fig. 2

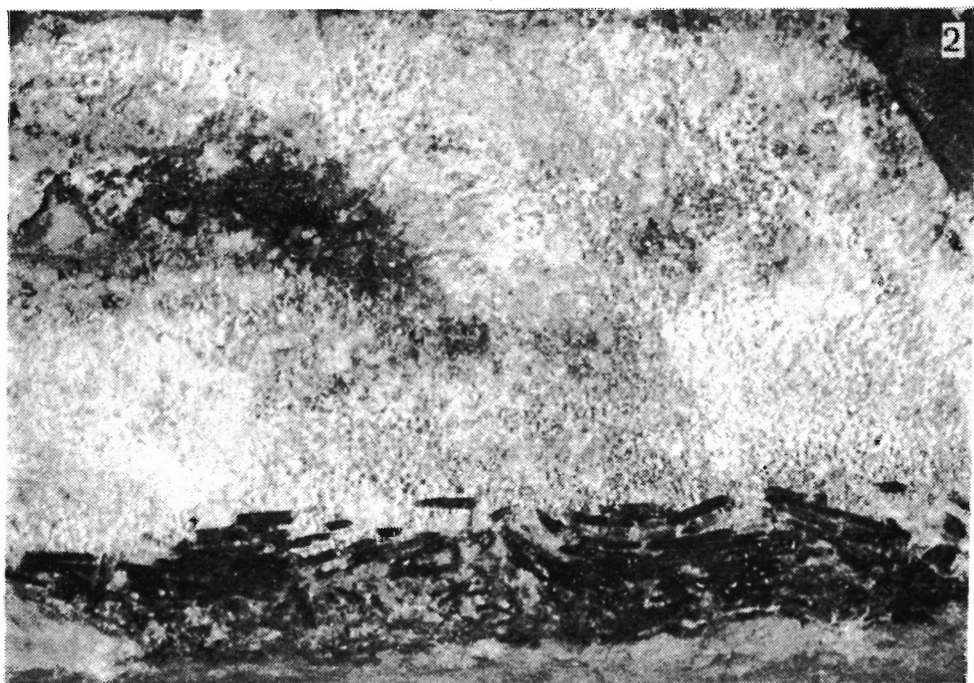
Inclusion in quartz, containing bitumen (B), aqueous solution (L) and gas bubble (G) performing intensive Brownian movements

Three-phase inclusions homogenized with difficulty. Temperatures of c. 500°C were necessary to evoke the state of aqueous emulsion(?) in a bitumen-bearing inclusion filling. Such inclusions usually decrepitated earlier, at c. 300°C.

Similar types of inclusions were found in calcite. The study of homogenization was not performed, since the inclusions in calcite were too small and, consequently, unsuitable (mostly some tenths of micrometer long). The decrepitation began at a temperature of c. 120°C. In calcite, bituminous matter often occurs in fissures of a rhombohedral cleavage or corresponds to the zones of crystal growth.

Because of a small amount of investigated quartz, bituminous matter was extracted only from calcite, containing c. 0.1 wt% of bitumen, if we assume its composition as representative of both minerals. On the other hand, the inclusions of calcite in quartz (Pl. 2, Fig. 19) are indicative of their synchronous crystallization.

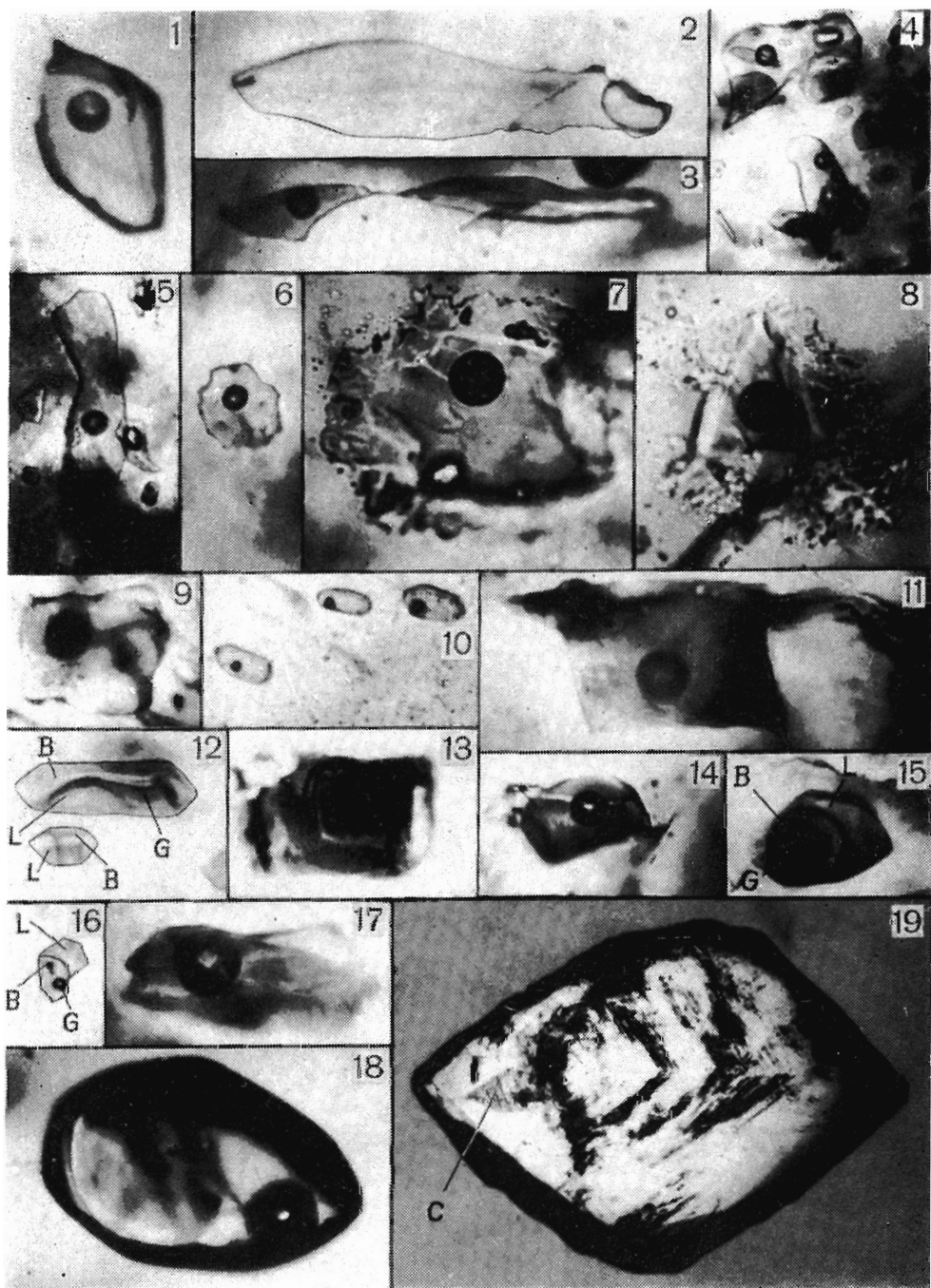
The infrared analysis reveals the following maxima of absorption bands (Fig. 3): 2,975, 2,928, 2,960, 1,475 and 1,385  $\text{cm}^{-1}$ . They indicate (cf. Gondek 1967) the occurrence of saturated hydrocarbons of the  $\text{CH}_3$  and  $\text{CH}_2$  groups. In addition, indistinct absorption bands recorded at: 3,060–3,080, 1,610, 1,280–1,300, 1,134, 1,080 and 745  $\text{cm}^{-1}$ , typical of a benzene ring, suggest the occurrence of aromatic compounds; in this case, the band 745  $\text{cm}^{-1}$  correspond to an *ortho*-substitution in the benzene ring.



1 — Flat quartz crystals on the joint-fracture surface;  $\times 2$ .

The specimen collected by Dr. J. Glazek

2 — Parallel quartz crystals on the joint-fracture surface in the bottom part of a limestone bed; nat. size.



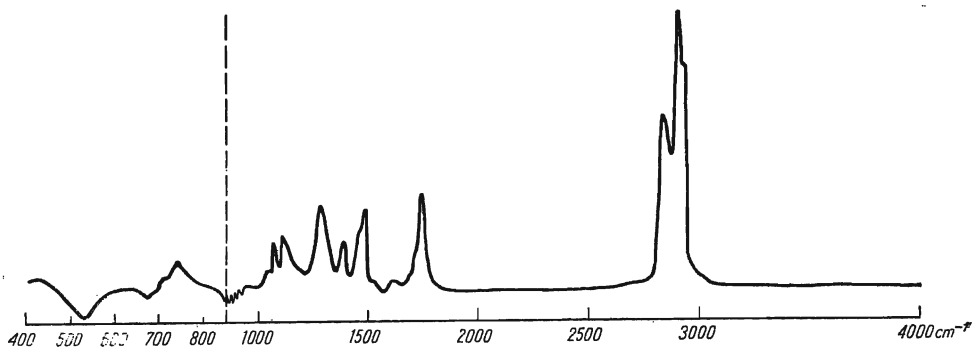


Fig. 3

## Infrared absorption curve for extract from calcite

The strong band  $1,745\text{ cm}^{-1}$  recorded seems to indicate the occurrence of oxygen either in ketone or cyclic compounds. The effect of band  $1,745\text{ cm}^{-1}$  (cf. references in Gondek 1967) results from the occurrence of oxidized compounds of the ether or acid type; such compounds are termed by the authors named above as resins washable by petrol ether. Hence, the substance in question may be regarded as a mixture of saturated hydrocarbons and their derivatives of the petrol ether type (or some other compounds with similar properties), as well as aromatic hydrocarbons.

## DISCUSSION

On the basis of the studies presented above one may conclude that quartz crystals have been formed from solutions of hydrothermal nature, with temperatures ranging between  $70$  and  $190^\circ\text{C}$ . Homogenization temperatures of bitumen-bearing inclusions cannot be a base for the determination of the host-mineral crystallization temperatures (Kven-

## PLATE 2

## Inclusions in quartz

- 1 — Gaseous-liquid in smoky quartz (Thom.  $72^\circ\text{C}$ );  $\times 60$ .
- 2 — Gaseous-liquid, flat, in smoky quartz;  $\times 200$ .
- 3 — Gaseous-liquid dividing into two daughter inclusions;  $\times 200$ .
- 4-5 — Gaseous-liquid, flat, on the boundary between smoky and black quartz (Thom.  $46$ — $72^\circ\text{C}$ );  $\times 200$ .
- 6-8 — Gaseous-liquid, flat, with varying morphology from black quartz (Thom.  $106^\circ\text{C}$ );  $\times 180$ .
- 9 — Gaseous-liquid from black quartz (Thom.  $180^\circ\text{C}$ );  $\times 220$ .
- 11, 13-14 — Gas-bituminous from black quartz bearing dark-brownish bitumen (Thom.  $250^\circ\text{C}$ );  $\times 220$ .
- 12, 15-16 — Gas(G)aqueous(L)-bituminous(B) from black quartz bearing brown-yellow bitumen (Thom. c.  $500^\circ\text{C}$ );  $\times 400$ .
- 17 — Gas-bituminous from smoky quartz bearing yellowish bitumen (Thom.  $74^\circ\text{C}$ );  $\times 300$ .
- 18 — Gas-bituminous from smoky quartz with yellow bitumen (Thom.  $53^\circ\text{C}$ ,  $T_{\text{decrep.}} 145^\circ\text{C}$ );  $\times 120$ .
- 19 — Slice of zoned smoky quartz crystal with an overgrown crystal of calcite (C);  $\times 9$ .



volden & Roedder 1971) because of the minute solubility of  $\text{SiO}_2$  in bituminous matter. Besides, the high compressibility of the organic fluids, considerably higher than that of the aqueous solutions, requires a correction of pressure, in the case of unknown and rather great value. Homogenization temperatures of the three-phase inclusions discussed (c.  $500^\circ\text{C}$ ) do not seem to be actual temperatures of crystallization, since there are no traces of effects of such a high-temperature fluid on the surrounding rocks. These temperatures are due to a nonhomogenous state of parent fluid. On the basis of these facts and the occurrence of various amounts and at least two kinds of bitumen entrapped in inclusion vacuoles, it may be stated that both quartz and calcite have been crystallized from a solution containing dispersed droplets of bituminous matter. These immiscible droplets came in contact with the surface of crystal, precluding its growth at the point of adhesion. A further growth of the surrounding parts of crystal has embraced the droplets.

Purely bituminous inclusions were formed when only droplets of bitumen were overgrown with the host mineral. Because of the bituminous and aqueous phases immiscibility, the most frequent are gas-aqueous or gas-bituminous inclusions, in contrast to three-phase inclusions.

The cause of the crystal zonation is as follows. Smoky crystals and zones, bearing inclusions with yellowish bitumen crystallized at lower temperatures ranging from  $48$  to  $72^\circ\text{C}$ . The brown-black parts of crystals originated from fluid as hot as  $106$  to  $190^\circ\text{C}$ , containing droplets of dense

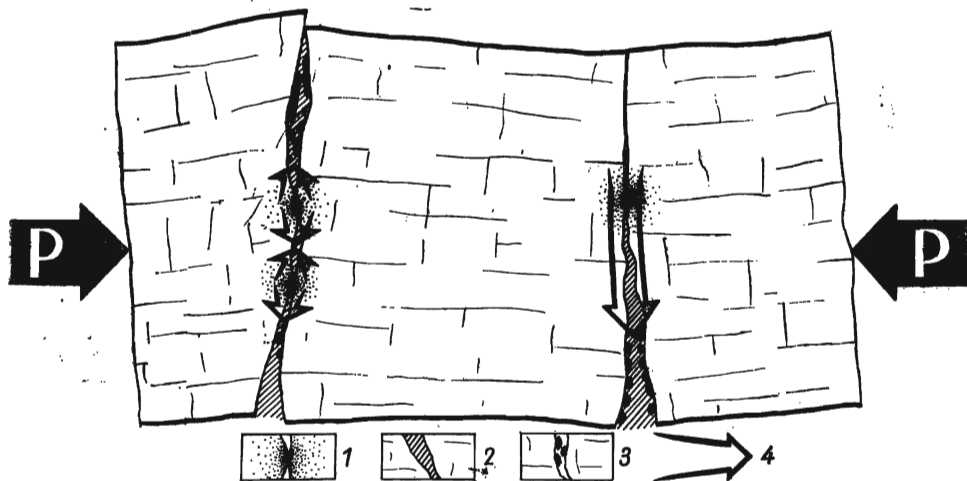


Fig. 4

Scheme of calcite and quartz crystallization along the joint fractures in the Famennian limestones at Łagów

1 places of rock dissolution, 2 calcite, 3 quartz, 4 migration routes of dissolved material; P direction of local pressure

brown bitumen. The lower-temperature fluid carried the light bituminous matter, whereas the higher-temperature one was able to carry the heavy matter. The zonation of crystals was caused by fluctuations in temperature and, consequently, by fluctuations in bitumen composition. The character of temperature fluctuations was probably connected with a changeable inflow of percolating waters<sup>2</sup>. The bituminous matter was extracted from the Famennian limestones which, being the rocks of reducing conditions, made also possible the crystallization of diagenetic sulphide inclusions.

The quartz here discussed probably originated from diagenetically dissolved admixture of detrital quartz or clay minerals in limestones. During the tectonic folding, the rocks were densely cracked, and in the vertical joint fractures the conditions, conducive to the local dissolving of limestone in water contained in the rock, arose as the result of pressure and higher temperature.

The solutions, bearing dissolved components of rock, migrated along the joint fractures. Inside the voids or in places of locally lesser pressure they became the parent fluids capable of mineralizing these surfaces with calcite and quartz (Fig. 4).

Considering the scheme presented, the writers suppose that quartz and calcite here studied are of authigenic origin and that they crystallized from a local material contained within the Famennian carbonate deposits.

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*Institute of Geochemistry, Mineralogy and Petrography  
of the Warsaw University  
Warszawa 22, Al. Zwirki i Wigury 93  
Warsaw, August 1972*

#### REFERENCES

- CZERMINSKI J. 1960. The lithologic development of the carbonate series of the Devonian in the southern part of the Holy Cross Mountains. — *Prace Inst. Geol.*, vol. 30, part II. Warszawa.
- GONDEK B. 1967. A quick method of determining the qualitative composition of bitumens for continuous profiling of rock samples from deep bore-holes. — *Bull. Geol. Inst.*, no. 213. Warszawa.
- GRINBERG I. V., KORZHINSKII A. F., MASLAKEVITCH Y. V. & SHVED N. A. 1964. K issledovanyu prirody novykh redkikh organicheskikh mineralov Zakarpatia. — *Dokl. Akad. Nauk SSSR*, vol. 158, no. 1. Moskva.
- KALYUZHNYI V. A. 1960. Metodi vivtchenia bagatofazovykh vklutchen u mineralakh. — *Vid. Akad. Nauk URSR. Kiiv.*

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<sup>2</sup> Similar temperatures were ascertained for so-called "Marmarosh diamonds", i.e. solitary, colorless crystals of quartz from the Carpathian flysch, also containing bitumen-bearing fluid inclusions (Grinberg & al. 1964, Maslakevitch 1967).

- KARWOWSKI Ł. & KOZŁOWSKI A. 1971. Brownian movements in microinclusions in minerals. — *Bull. Acad. Pol. Sci., Sér. Sci. de la Terre*, vol. 19, no. 4. Varsovie.
- KUTEK J. & GŁAZEK J. 1972. The Holy Cross area, Central Poland, in the Alpine cycle. — *Acta Geol. Pol.*, vol. 22, no. 4. Warszawa.
- KVENVOLDEN A. K. & ROEDDER E. 1971. Fluid inclusions in quartz crystals from South-West Africa. — *Geochim. Cosmochim. Acta*, vol. 35, pp. 1209—1229. Oxford.
- MASLAKEVITCH Y. V. 1967. Uglevodorodsoderzhashtchye vklutchenia v mineralakh postmagmatiticheskikh obrazovaniy. *In: Izutcheniye geokhimii glubinnykh rastvorov po uglevodorodsoderzhashtchim reliktam i paragenezisam mineralov*, no. 9. Kiev.
- SZULCZEWSKI M. 1971. Upper Devonian conodonts, stratigraphy and facial development in the Holy Cross Mts. — *Acta Geol. Pol.*, vol. 21, no. 1. Warszawa.
- TAKENOUCHI S. 1971. Study of CO<sub>2</sub>-bearing fluid inclusions by means of the freezing stage microscope. — *Kodzan Tisitsu (Mining Geol.)*, vol. 21, 108, pp. 286—300. Tokyo.
- TOURAY J. C. & SABOURAUD C. 1970. Metastable inclusion brines in fluorite from Ouezanne. — *Econ. Geol.*, vol. 65, no. 2. Lancaster.

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Ł. KARWOWSKI i A. KOZŁOWSKI

**AUTOGENICZNY KWARC Z WAPIENI BITUMICZNYCH  
FAMENU W ŁAGOWIE**

(Streszczenie)

W zadymionych i czarnych kryształach kwarcu ze szczelin ciosowych w bitumicznych wapieniach famenu z okolic Łagowa w Górach Świętokrzyskich (*vide* fig. 1 oraz pl. 1) stwierdzono obecność inkluzji zawierających zmienne ilości substancji bitumicznej (barwiącej owe kwarcy) oraz roztworu soli i gazu (fig. 2 oraz pl. 2). Metodą homogenizacji określono przybliżone temperatury krystalizacji kwarcu zadymionego na ok. 70°C, zaś kwarcu czarnego na 160—190°C. W podobnych warunkach krystalizował też brązowo-czarny kalcyt, zawierający analogiczne inkluzje, a tworzący wypełnienia szczelin ciosowych i kawern, w których niejednokrotnie występuje ciemny kwarc. Oba rozważane minerały krystalizowały z roztworów wodnych zawierających zawieszane krople bituminów o różnym składzie. Na podstawie analizy pasm absorpcji w podczerwieni (fig. 3) można stwierdzić, że substancja bitumiczna składa się głównie z węglowodorów nasyconych i aromatycznych.

Rozważane kwarcy należy zatem uznać za autogeniczne. Powstały one w czasie lub bezpośrednio po ruchach tektonicznych z roztworów węglanowych zawierających krzemionkę i bituminy, a pochodzących z lokalnego rozpuszczania (fig. 4) wapieni famenu oraz zawartych w nich domieszek.

*Instytut Geochemii, Mineralogii i Petrografii  
Uniwersytetu Warszawskiego  
Warszawa 22, Al. Zwirki i Wigury 93  
Warszawa, w sierpniu 1972 r.*

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