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Calcium-rich inclusion solutions in fluorite from the Strzegom pegmatites, Lower Silesia

ABSTRACT: Inclusions in fluorites from pegmatitic druses in the Strzegom massif bear aqueous solutions with calcium chloride as the main solute component. Homogenization temperatures were measured (165 to 180°C) and the physico--chemical analysis of inclusion fluid behavior during freezing down to —130°C was performed. This yields the following fluid composition: H_2O — 76 wt. %, $CaCl_2$ — 18 wt. %, NaCl — 6 wt. %. The discussion of possible presence of other salts is presented.

INTRODUCTION

The granitoid massif Strzegom-Sobótka of Variscan age in Lower Silesia bears numerous vein and world-famous drusy pegmatites with the extensive mineral association. The earliest observations on mineral assemblages of this massif were summarized by Traube (1888) and next by Michell (1941), Fersman (1960, pp. 135—137) and Kowalski (1967). The controversial problem of pegmatite genesis which has widely been discussed from various viewpoints in many countries (e. g. Andersen 1931; Hess 1933; Bjørlykke 1934; Fersman 1952, 1960; Jahns 1953; Rudenko 1972; Němec 1976; Kozłowski 1978) does not yield a definite bearing upon the role of hydrothermal solutions in formation of the medium- and late-stage mineral parageneses in pegmatites. The studies by means of the inclusion methods of hydrothermal fluids that formed minerals in the Strzegom pegmatites are still scarce and incomplete (Kozłowski 1973, 1981; Kozłowski & Karwowski 1973, 1974, 1976). This paper is a contribution to the knowledge of parent fluids of the late--stage fluorite-bearing parageneses in the pegmatite druses.

METHODS

The routine methods of the non-destructive inclusion studies were used. The homogenization temperatures (Th) of fluid inclusions were performed on the Author's construction microscope heating stage with the precision $\mp 2°C$. The freezing runs were made by the Author in the E. Roedder's laboratories, U.S. Geological Survey, National Center at Reston, Virginia. The used freezing/heating microscope gas-flow stage (Werre & al. 1979) yielded results with precision $0.1°C$ in temperature range from 0 to $-10°C$ and $\sim 1°C$ at -70 to $-100°C$. The preparations were made by double-side polishing of cleavage chips of fluorite crystals. Refractive indices of laboratory-prepared salt solutions were measured at temperature $20° \pm 0.1°C$ by refractometric method.

THE INVESTIGATED SPECIMENS

The fluorite specimens for inclusion studies were taken from typical pegmatite druses in the quarry No. 18 at Strzegom-Grabina. Fluorite--bearing paragenesis crystallized in the pegmatite zone consisting of gray and smoky quartz, albite, microcline, and biotite partly or completely altered in chlorite. Usually epidote, later than the previous minerals precedes here fluorite; it was however, also partly coeval with fluorite and partly younger. Other minerals paragenetic with fluorite are represented by rock crystal, chlorite (strzegomite = striegovite), tourmaline, and locally calcite. Strzegomite frequently forms zones of inclusions of 0.n mm size in fluorite crystals. Brownish-gray, blue-gray or pale blue, almost colorless tourmaline needles up to 1 cm long and 0.1 to 0.5 mm thick, either pierce fluorite crystals or occur as solid inclusions in the latter. Calcite and the zeolites are later than fluorite in all the studied druses.

Fluorite crystals are octahedral, more or less deformed, of light to very pale violet color with a greenish-blue tint, and with intensive violet zones outlining the octahedral habit. The deep violet zones are 0.1—0.5 mm thick and frequently are associated with primary inclusions of fluid or fluid plus trapped minerals.

FLUID INCLUSIONS

Fluid inclusions in the Strzegom fluorites have first been described over a century ago (von Lassaulx 1877), but tentative determination of the Th range (160—205°C) was performed about ten years ago (Kozłowski & Karwowski 1973). More detailed data on Th of fluid inclusions in the Strzegom fluorite are given by Lenkowski (1983), who extended the Th values range to 130—255°C for pegmatitic druse fluorites and 120—390°C for vein fluorites. Some Th values (130—185°C) are also submitted by Janeczek (1983), and they do not fall out the above limits.
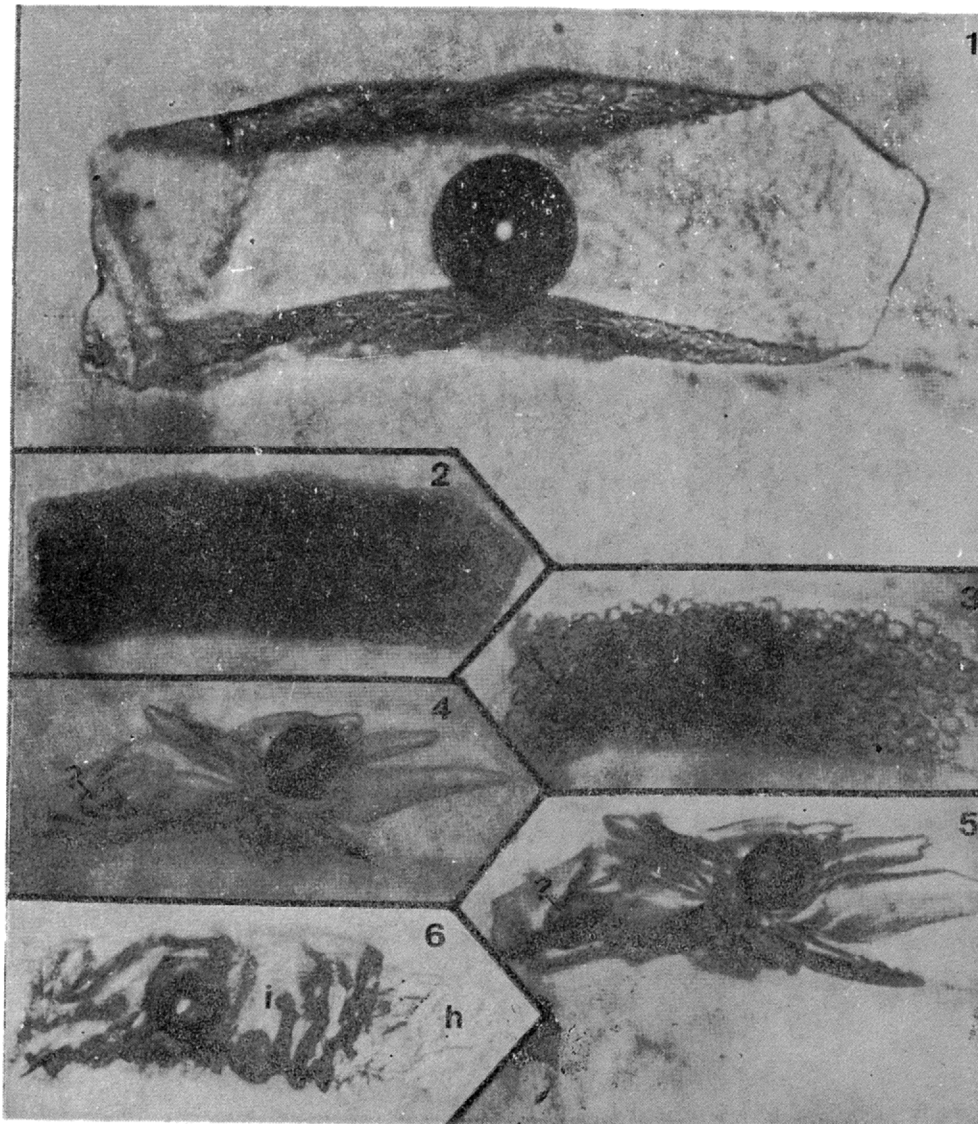
Fluid inclusion (0.38 mm long) in fluorite from the Strzegom pegmatite

1 — Room temperature

2 — frozen to —60°

3 — at —32°C, ice crystals only

4 — at —39.2°C, filling recrystallized to large crystals, ''?'' — marks   doubtful
liquid+gas CO_2

5 — at —72°C, boundary between host fluorite and liquid phase is invisible

6 — at —40°C, separation of ice (i) and hydrohalite (h) crystals

The studied fluorite crystals yielded Th from 165 to 180°C and the inclusions used for freezing runs had even a more narrow Th range, from 172 to 180°C. Hence, these Th values place the crystals under study in the middle of Th range hitherto known for the Strzegom pegmatite fluorites.

Freezing studies were performed on several large (0.1—0.4 mm) two-phase inclusions containing typical filling, i.e. gas $<$ liquid (Pl. 1, Fig. 1). The inclusions were undoubtedly primary and under the microscope they did not show visible traces of any kind of leakage or epigenetic alterations changing phase ratios. Unlike this description, most inclusions were first submitted to the freezing runs on heating, and two control ones were first homogenized and next frozen. No substantial differences were found.

During single rapid freezing down to —130°C the inclusion filling did not crystallize as it usually occurs in so large inclusions. Only a series of freezing--heating shocks caused break of metastable supercooling and crystallization at —60 to —62°C, rarely to —70°C (Pl. 1, Fig. 2). The crystallization front moved from one of the inclusion corners, usually with sharp edge or point, evidently stimulating crystallization.

The frozen inclusions started the eutectic melting at Te from —54 to —58°C, approximately. The low precision of Te determination was caused by difficult observation of first portion of liquid in opaque inclusions filled by aggregate of fine crystals. However, the Te value indicates that the inclusion filling is essentially $CaCl_2$—$NaCl$—H_2O solution, because Te in this system equals —52°C (Yanateva 1946; some sources give the value —55°C, e.g. Borisenko 1975). Thus, the inclusion was in the point E on the $CaCl_2$—$NaCl$—H_2O plot (Text-fig. 1), with theoretical eutectics in inclusion filling, consisting of 1.8 wt. % $NaCl$, 29.4 wt. % $CaCl_2$, 68.8 wt. % H_2O (Crawford 1981), plus excess $NaCl$ as $NaCl \cdot 2H_2O$ (hydrohalite) and H_2O ice. If $NaCl$ is more abundant in the solution, $CaCl_2 \cdot 6H_2O$ (antarcticite) melts first and during the T increase the system starts to follow the cotectic curve separating the hydrohalite+solution and ice+solution fields. Inclusion filling is now the mixture of ice and hydrohalite crystals floating in $NaCl$+ +$CaCl_2$ solution, with decreasing hydrohalite content. In the representative of the studied inclusions the last hydrohalite crystal melted at —32.3°C and the system left the cotectic curve in the point B (Text-fig. 1), starting to move across the field of ice+solution.

The point B may be used for determination of the $CaCl_2$ to $NaCl$ ratio by the lever method. For the studied inclusions this is 25 wt. % $CaCl_2$ in dry salts.

From this moment, ice is the only crystal phase in inclusion (Pl. 1, Fig. 3). However, the determination of the last melting hydrohalite crystal is not a trivial operation. In mixture of many crystals it is possible to miss it and to determine the point B erroneously. Recrystallization of the inclusion content from few small crystallization nuclei may be recommended (Pl. 1, Fig. 4), as well as a use of optical features: ice has low refractive indices (n_{ω} 1.3091, n_{ε} 1.3105 at —1°C) and parallel light extinction due hexagonal structure, but monoclinic hydrohalite has oblique light extinction. Properly made recrystallization causes quite good seperation fo hydrohalite and ice (Pl. 1, Fig. 6).

Melting of ice crystals occurs somewhere between the point B and the H_2O corner for solutions of various salt concentrations. In the studied material the last ice crystal melted at Tm 21.1°C (point A in Text-fig. 1). This helps to determine the total salt concentration $CaCl_2$+$NaCl$ in the solution filling inclusion,

equal here 24 wt. % (point *C* in Text-fig. 1). Thus, combining data from points *D* and *C*, the main components of inclusion filling are: H_2O — 76 wt. %/o $CaCl_2$ — 18 wt. %, and NaCl — 6 wt. %.

Some additional observations were made during freezing runs. During attempts of crystallization of the whole inclusion filling from few ice or/and hydrohalite crystals (*i. e.* on the path from *A* to *E* excluding start and final points) a part of the filling remained in metastable liquid state (Pl. 1, Fig. 5) even at temperature as low as —126°C, *i. e.* much below the eutectic temperature. This probably should be explained by strong tendency of many calcium salt solutions to metastability. At temperatures —72 to —126°C in such runs only 40—30 vol. % of inclusion was occupied by solution, containing almost exclusively all $CaCl_2$ solute present in the inclusion, *i.e.* very concentrated.

Concentration of $CaCl_2$ in that remnant solution caused the phenomenon of disappearance of the phase boundary between the solution and the crystal — fluorite, best visible at —70 to —80°C. This means that the remnant solution reached such concentration that its refactive index equals he refractive index of fluorite (1.434 at 20°C). Measurements of refractive indices of solutions of salts that are reasonable in hydrothermal solutions (Text-fig. 2) prove that only $CaCl_2$ is the
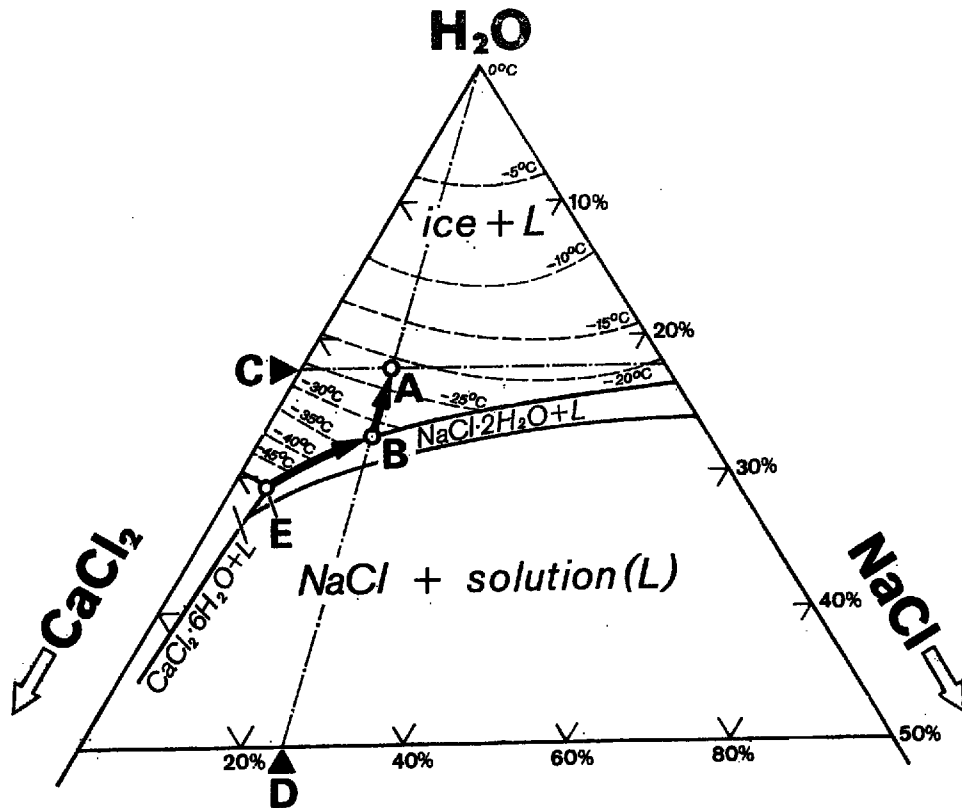

Fig. 1. Part of the plot of the $CaCl_2$—NaCl—H_2O system with the path of evolution of the studied inclusion fluids (*E-B-A*); weight percents, data from Yanateva (1946); see text for other explanations

appropriate salt: solution of 40 g $CaCl_2$ in 100 ml of solution has also refractive index 1.434 (at 20°C). Temperature variations change the refractive index value but not so essentially to made this evidence invalid.

During freezing runs the search for liquid CO_2 in inclusions was made and specific feature was observed which may be interpreted erroneously as rim of liquid CO_2 around gas bubble in a vacuole embedded in ice+hydrohalite, where salt solution from other part of inclusion was sucked or injected, forming liquid layer. However, the small "concentric" bubble in the left part of inclusion (Pl. 1, Figs 4 and 5; marked "?") cannot be explained satisfactorily, although it looks like liquid plus gas CO_2.
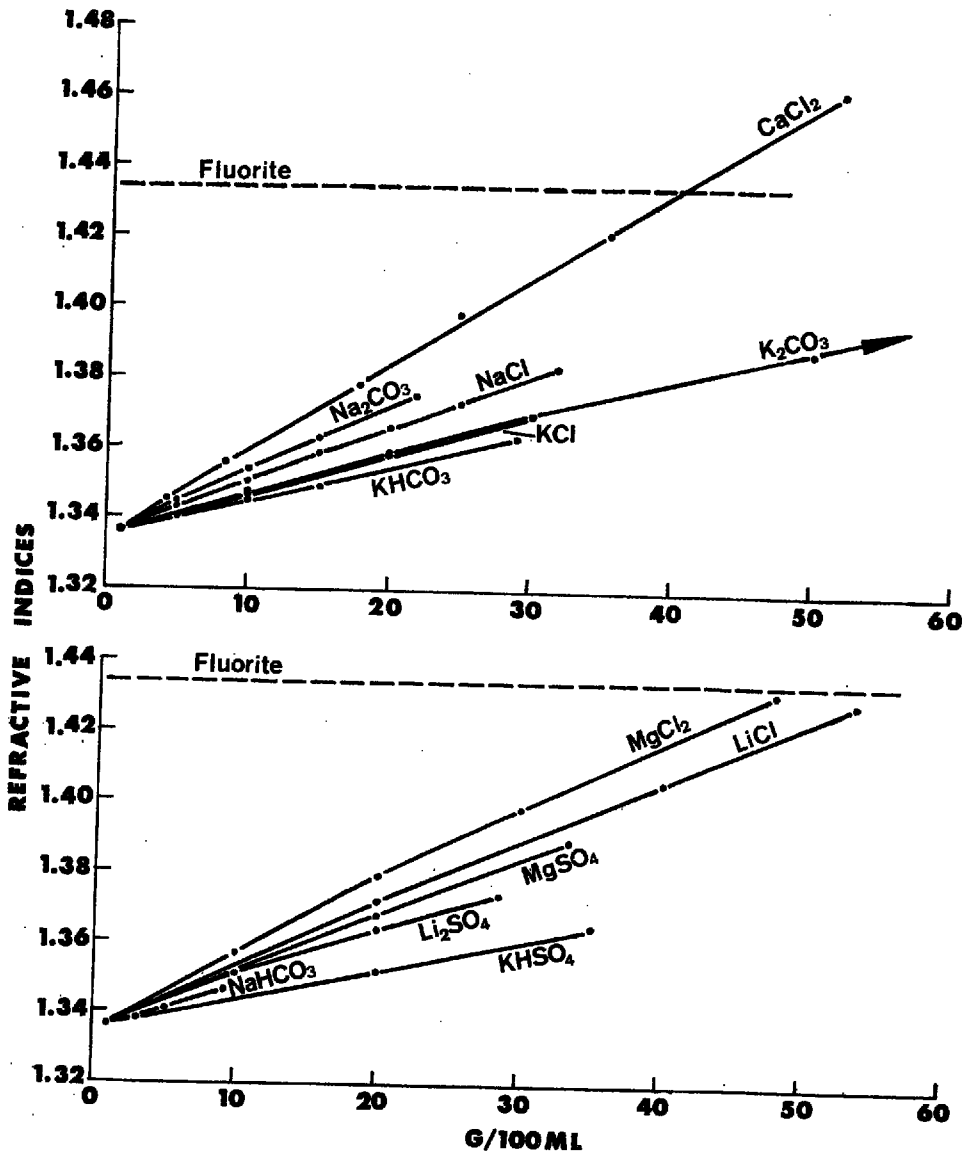

Fig. 2. Refractive indices of solutions of some selected salts

FINAL REMARKS

The presence of calcium-rich late-stage solutions in the Strzegom pegmatites might be also deduced from the abundant occurrence of other (than fluorite) calcium minerals: epidote, Ca-zeolites, calcite. The source of calcium may be expected in the extensive process of plagioclase (oligoclase) albitization (Kozłowski & Nowakowski 1981, Nowakowski & Kozłowski 1983), which precedes the fluorite formation. The fluorite crystallization from calcium-rich solution should be limited by the inflow of fluorine, immediately consumed for CaF_2 precipitation. Those solutions were supposedly low in magnesium, carbonate and sulfate ions, because otherwise sellaite MgF_2 (Schaefer & Strübel 1979), carbonates or sulfates would occur in inclusions as daughter minerals. The only cation, the presence of which is possible in limited amount in the inclusion fluid, is potassium.

Similar calcium-rich fluids are not extraordinary in various endogene geological environments and they have hitherto been recognized also in the scheelite deposits (Hing 1979), in metamorphic rocks (Crawford & al. 1979), and in present-day rift zones (Hardie 1978).

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ROZTWORY WAPNIOWE W INKLUZJACH WE FLUORYCIE Z PEGMATYTÓW STRZEGOMIA

(Streszczenie)

Przedmiotem pracy jest ustalenie składu roztworów macierzystych fluorytu z pegmatytów Strzegomia metodą badania inkluzji fluidalnych, których temperatury homogenizacji wynosiły od 165 do 180°C. Zastosowano zamrażanie inkluzji do temperatury —130°C (pl. 1), a następnie fizykochemiczną analizę przemian w inkluzjach podczas zmian temperatury (fig. 1) i porównanie własności optycznych roztworów w inkluzjach i roztworów syntetycznych (fig. 2). Stwierdzono, że badane fluoryty krystalizowały z roztworu o składzie 76% wag. H_2O, 18% wag. $CaCl_2$ i 6% wag. NaCl. Skład ten jest dość rzadki, ale nie wyjątkowy w rozmaitych środowiskach endogenicznych.