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FLUID INCLUSIONS AND CATHODOLUMINESCENCE OF FLUORITE FROM CARBONATITES OF THE TAJNO MASSIF, NE POLAND

Abstract: Tajno plutonic-volcanic complex in NE Poland consists of ultramafic and alkaline rocks with carbonatite-fluorite mineralization; the complex intruded into Precambrian gneissic-granitic basement. The cathodolumonescence studies of fluorite revealed mosaic zoning and presence of REE (mainly Ce, Gd, Er and Dy) in its structure. Two- and multiphase inclusions in fluorite (aqueous, with CO_2 and daughter minerals: halite, sylvite, calcite, brenkite, dawsonite, burbankite, parisite and synchysite) yielded homogenisation temperatures 440 to 190ºC (formation temperatures 450–244ºC). Pressure varied from 0.5 to 1.2 kbar. The REE carbonatite mineralisation formed under subvolcanic conditions during brecciation process with strong changes of the fluid temperature and pressure.

Keywords: carbonatite, fluorite, REE mineral, fluid inclusion, daughter mineral, carbon dioxide, cathodoluminescence, Tajno massif, NE Poland

INTRODUCTION

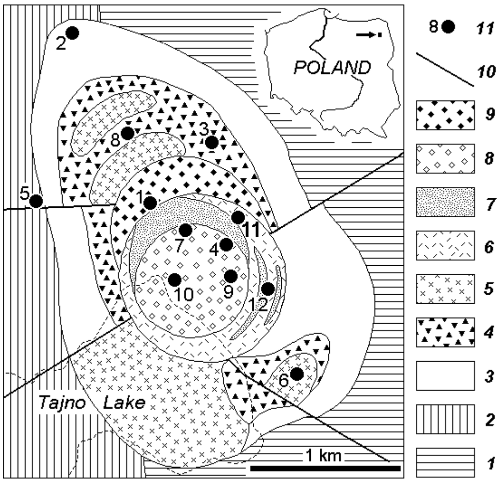

Fig.1 Tajno massif; Precambrian basement: *1* quartzites and schists, Biebrza complex, *2* granitoids, Mazowsze complex; Tajno complex: *3* syenite, *4* breccia, fenitised ijolite, *5* ijolite, *6* mixed tephra, *7* tuff, *8* vent breccia and carbonatite, *9* caldera breccia and carbonatite, *10* fault, *11* borehole.

The Tajno plutonic-volcanic carbonatite-bearing complex (327 Ma, K-Ar age; Depciuch *et al.* 1975) is localised in NE Poland, 15 km south of Augustów (Fig.1). This complex lies buried by a 600 m thick Meso-Cenozoic sedimentary cover (Ryka 1992). Twelve boreholes were drilled in 1970's–1980's to the maximum depths of about 1,800 m, to evaluate REE potential of the complex. The Tajno massif is a small (surface ca. 5 km^2) elliptical ultramafic, alkaline complex that intruded Precambrian gneissic-granitic crystalline basement. The main plutonic rocks are fenitized ijolites surrounded by microperthite syenite, malignite and shonkinite, and cut by dykes of various compositions. The most abundant plutonic rock is nepheline syenite that forms the outermost part of the complex. The central part of the massif is a diatreme breccia pipe 800 m in diameter that contains pyroclastic material

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as well as chimney polygenetic breccia cemented by carbonatites. Between central breccia and syenite there is an annular ijolite zone which has been extensively fractured and brecciated. Pyroxenites considered as cumulates and ultramafic foidites are cut by malignite, nepheline syenite and alkali feldspar syenite (Ryka 1992). The whole complex is crosscut by numerous dykes representing different magma composition and stage of intrusion, from foidites, phonolites, trachytes to tinguaites. Three stages of carbonatite formation have been documented (Gaczyński 1978; Ryka 1992). Most of the carbonatites from the Tajno massif are calciocarbonatites containing calcite and fluorite, and some of the carbonatites contain up to 65% fluorite. Ferrocarbonatites in part with manganoankerite and silicocarbonatites are less frequent.

Widespread fluorite mineralization accompanied each stage of the carbonatite origin. The veins of fluorite contain apatite and calcite crystals, and sometimes uranium minerals. REE-bearing minerals are common in Tajno carbonatites – burbankite, parisite, synchysite and bastnaesite are the most abundant ones. The average REE content for the complex, in terms of oxides, is estimated to be 0.33 wt.% (Ryka 1992). The main aim of our investigations was to estimate the composition, temperature and pressure of orthomagmatic, carbonatitic fluids precipitating REE- and Sr-rich fluorite and associated minerals.

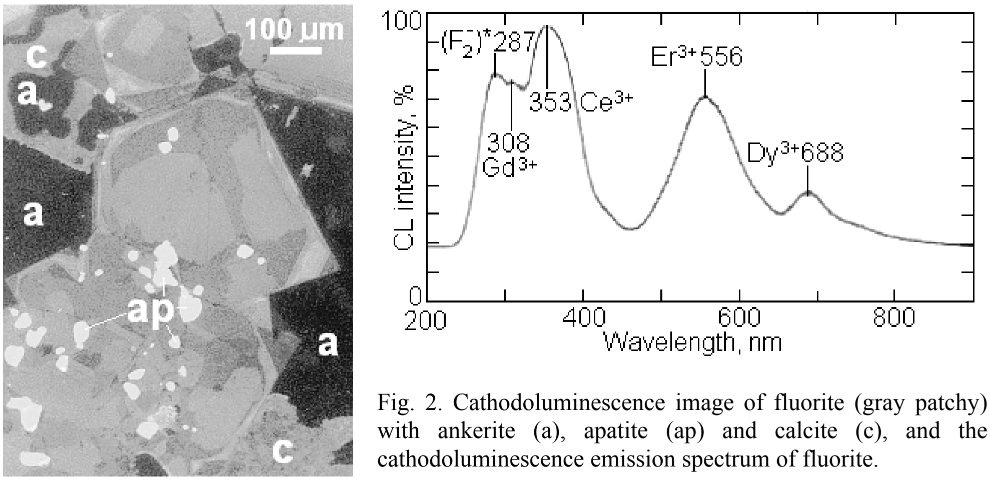

Fig. 2. Cathodoluminescence image of fluorite (gray patchy) with ankerite (a), apatite (ap) and calcite (c), and the cathodoluminescence emission spectrum of fluorite.

SAMPLES

Two samples of the investigated fluorite were taken from the drilling core (depths 1318.4 m – sample A, and 1306.4 m – sample B) of the borehole Tajno 11. The fluorite occurs with carbonates and REE minerals in brecciated magmatic rocks, being itself in part crushed and then cemented by next generation of fluorite. This resulted in patchy zoning revealed by cathodoluminescence (the photo in Fig. 2). The luminescence (the plot in Fig. 2) is connected with REE, in this case mainly Ce, Gd, Er and Dy diadochy in fluorite (Gorobets, Rogojine 2002). The size of the fluorite crystals was up to 5 mm.

METHODS

Cathodoluminescence investigations were performed on polished thin-sections by means of the CCL 8200 mk3 device (cold-cathode) mounted on polarising microscope. The SEM-CL analyses were obtained by the LEO scanning electron microscope (type 1430) with CL-image system (ASK-CL VIS Viev) and cathodoluminescence spectrometer (ASK SEM-CL).

Fluid inclusions were investigated in double polished slices 0.2-0.4 mm thick. The cooling and heating runs were performed in the *Fluid Co*. heating stage mounted on a Leitz Labor Lux S microscope. Accuracy of the freezing and warming determinations to +35ºC was ±0.05ºC (in the critical point region of CO_2 even better) and during heating the accuracy was ±1ºC to 300ºC and ±1.5ºC above this value. The calibrations were made on the *Fluid Co*. standards and on melting points of extra-pure salts and metals, and on pure CO_2 synthetic inclusions. The procedures of the calculations were made according to Roedder (1984), the isochors of the aqueous solutions were taken from Potter's and Brown's (1977) paper and those of CO_2 – from the Bulakh's and Bulakh's (1978) publication. The obtained data were verified by the use of the computer programs (Bakker, Brown 2003). The chemical compositions of the daughter minerals were checked in the inclusions opened by the crushing stage method, as first described by Krogh (1911). The chemical analyses were made by means of the Cameca sx100 electron microprobe in the Inter-Institution Laboratory for Microanalysis of Minerals and Synthetic Substances (Faculty of Geology, Warsaw University, the analysts L. Jeżak and Dr. P. Dzierżanowski). The natural minerals and synthetic oxides were used as the standards. The obtained chemical analyses are of low precision, because the analysed minerals were in their natural state, not polished, and the sizes of the grains or their clusters were in the ranges of few micrometers.

FLUID INCLUSIONS

Types of fluid inclusions. In the investigated fluorite fluid inclusions were found relatively frequently, however, only small fraction of them was suitable for studies. Many of the inclusions were either very small (<2 μm) or inconveniently located and oriented for the microscope studies. The perfect cleavage of fluorite caused additional troubles, because some inclusions were open by fractures when preparations were made. Only 103 inclusions were appropriate for heating and freezing runs, and 10 other inclusions were open in crushing stage after microscope investigations and analysed by means of electron microprobe. The size of the investigated inclusions ranged from 10 to 40 μm, their habits were single cuboids or their clusters (Fig. 3). The studied fluid inclusions comprised seven primary types. Secondary inclusions referred to the same kinds of fillings.

Type A. These inclusions filled by aqueous solution contained shrinkage bubble and 4-5 daughter minerals (Fig. 3a). Halite, sylvite and calcite were present in all inclusions of this type, moreover one or two of the following minerals: brenkite $Ca_2CO_3F_2$, dawsonite $NaAlCO_3(OH)_2$, burbankite $(Na,Ca)_3(Sr,Ba,Ce)_3(CO_3)_5$, parisite-(Ce) $Ca(Ce,La)_2(CO_3)_3F_2$ and synchysite-(Y) $Ca(Y,Ce)(CO_3)_2F$, were found in individual inclusions (Table 1). On durable heating all crystal phases dissolved in aqueous solution; the calculation of the total dissolved substances yielded concentration of the solution about 40 wt. %. Carbon dioxide was not observed in these inclusions. Homogenisation temperatures (*Th*; measured in 17 inclusions) ranged from 420 to 440ºC.

Type B. These inclusions contained aqueous solution, shrinkage bubble and halite daughter mineral (Fig. 3b). The total salt concentrations were between 25 and 30 wt. %, the second main cation (after sodium) was calcium. Homogenisation temperatures of the 12 found inclusions of this type were between 340 and 370ºC.

Type C. The fillings of these inclusions were relatively variable. Aqueous solution and

Table 1. Chemical composition of the daughter minerals in the *type A* fluid inclusions in fluorite from Tajno (excluding halite and sylvite).

Component	Calcite	Brenkite	Dawsonite	Burbankite	Parisite -Ce)	Synchysite -(Y)
Al_2O_2	–	–	35.2	–	–	–
Ce_2O_3	–	–	–	6.5	35.2	1.0
La_2O_3	–	–	–	–	25.5	–
Y_2O_3	–	–	–	–	–	41,0
CaO	56.0	62.9	–	6.1	10.3	20.5
SrO	–	–	–	26.2	–	–
BaO	–	–	–	19.4	–	–
Na_2O	–	–	21.3	9.4	–	–
CO_2	44.0	24.6	30.3	31.1	24.5	32.5
F	–	21.3	–	–	7.0	7.0
-O=2F	–	8.9	–	–	2.9	2.9
Total	100.0	99.9	*86.8	98.7	99.6	99.1

* Dawsonite contains theoretically 12.51 wt. % water.

liquid and gas carbon dioxide were the main components, but their ratios varied strongly in the nine studied inclusions (Fig. 3c). Thus these inclusions indicate heterogeneous state of the mineral-forming solution, probably local and shortly existing. Homogenisation runs did not yield reasonable and consistent results. This evidenced the incidental phase properties of the two-phase liquid during trapping of the inclusions, hence the experimental data on the state of such heterogeneous system (*e.g.* Gehrig 1980; Krüger, Diamond 2001) could not be used to find the crystallisation conditions of fluorite. Five inclusions contained halite daughter mineral and four of them – small clusters of daughter (or trapped) minerals. The electron microprobe analyses of three of them evidenced the presence of phosphorus, aluminium, silicon, calcium, yttrium, cerium, lanthanum, neodymium and sodium in the clusters, however, the exact determinations were not possible; this mineral probably is a complex phosphate.

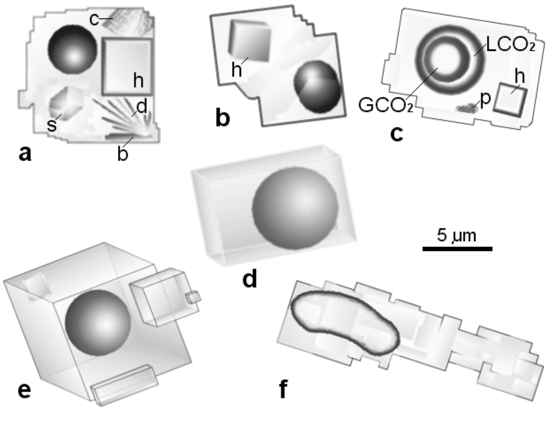

Fig. 3. Fluid inclusions in fluorite: **a** – type A, solution with shrinkage bubble and daughter minerals – burbankite (b), calcite (c), dawsonite (d), halite (h) and sylvite (s); **b** – type B, solution with shrinkage bubble and daughter halite (h); **c** – type C, solution with liquid (LCO_2) and gaseous (GCO_2) carbon dioxide, daughter halite (h) and trapped phosphate mineral (p); **d** – type D, filled with liquid and gaseous carbon dioxide; **e** – type E, aqueous solution with shrinkage bubble, **f** – type F, aqueous solution with shrinkage bubble.

Type D. Inclusions of pure or almost pure carbon dioxide (Fig. 3d) – the purity was evidenced by measurements of the triple point temperature. Homogenisation temperatures of 10 such inclusions were in a narrow range, from +27.6 to +29.7ºC, what yielded the CO_2 densities from 0.662 to 0.610 g/cm^3, since the inclusions homogenized in liquid phase.

Type E. The most common inclusions filled with liquid aqueous solution and shrinkage bubble (Fig. 3e) containing admixture of gaseous carbon dioxide. The solution has total salt concentration 11-19 wt. %; NaCl is the main component (70-85 wt. % of the total salts), the other component is $CaCl_2$. Homogenisation temperatures of 26 inclusions were from 280 to 330ºC. Soluble salt crystals were not found in these inclusions, 11 such inclusions contained tiny grains of apparently trapped minerals, which did not dissolve on heating. Crushing of these inclusions did not yield preparations suitable for electron microprobe analysis, thus even qualitative or approximate composition of these trapped minerals still remains unknown. Several these inclusions were almost coeval with the carbon dioxide *type D* inclusions, thus an attempt of determination of pressures of the fluorite crystallisation was made. Pressure, calculated by the crossed isochors method for the inclusions of the solution total concentration 11 wt. % NaCl equivalent, yielded 1.2 kbar, thus the formation temperatures for the type E inclusions were from ca. 390 to ca. 450ºC.

Type F. Inclusions of the last generation, relatively common (23 ones investigated), are flat, filled with aqueous solution with shrinkage bubble (Fig. 3f). Homogenisation temperatures ranged from 190 to 270ºC, total salt concentrations were about 10-11 wt. % and NaCl comprised 90-95 wt. % of the total salts; the remaining amount was $CaCl_2$.

Type G. Inclusions filled by carbon dioxide, coeval with the *type F* aqueous inclusions, thus belonging to the same last generation. Their *Th* ranged from +30,85ºC in liquid phase to +31.08ºC in gas phase (6 inclusions), thus the densities of CO_2 were from 0.525 to 0.427 g/cm^3, respectively. Inclusions with critical phenomena were not found. Pressures, calculated for the *type F* inclusions with Th 270 to 190ºC, were about 0.5 kbar, and formation temperatures from 244 to 322ºC.

Differences were found neither in the fluid inclusion types nor in the characteristic temperatures between the two investigated samples A and B.

DISCUSSION AND CONCLUSIONS

Carbonatites of the Tajno massif formed under unstable tectonic conditions, which were recorded by crushing of the fluorite grains. Subsequently the crushed grains were healed and enlarged to sub- or euhedral crystals, as evidenced by the cathodoluminescence images (Wiszniewska, Sikorska 2005). Such variable conditions are usually connected with changes of pressure, temperature and chemical composition of the mineral-forming medium. These changes were recognised due to both cathodoluminescence spectra, different for early and late fluorite, and fluid inclusion data. The parent fluid of the earliest found inclusions had very high total solved salt concentration and apparently high temperature, indicated by *Th* 440ºC; the formation temperature should not be drastically higher, because such dense fluid does not yield great pressure-related temperature corrections. Unfortunately, at present pressure estimations for this stage are not available. The concentration of the dissolved substances approaches to the saline melts found in some subvolcanic rocks (Kozłowski, Karwowski 1972). It is possible that denser fluids existed at the earlier stage of the carbonatite formation, like *e.g.* high-temperature saline melts found in inclusions in minerals of carbonatites from southern Mongolia (Andreeva *et al.* 2001). The inclusions rich in crystal phases were observed in fluorite from the Tajno carbonatites by Gaczyński (1978), however, he measured the *Th* values only for two-phase aqueous inclusions.

Fluid inclusions in carbonatite minerals containing numerous daughter crystal phases were found elsewhere (*cf. e.g.* Dorochkevich *et al.* 2001, Bühn *et al.* 2002, Fan *et al.* 2004b). The concentration of the fluid lowered along with temperature decrease, what apparently is a common feature of the carbonatite mineralisations. Intervals of the carbon dioxide inflows were found at least three times, the first one appeared, when salinity was relatively high (ca. 24 wt. %) and the conditions very unstable That resulted in heterogenisation of the parent fluid of carbonatite minerals – at that stage the fluid consisted of the aqueous and carbon dioxide liquid phases. Unstable conditions caused rapid growth of the minerals and trapping of the inclusions of two-phase fluid. Later carbon dioxide inflows were under more stable conditions and the growth of the minerals was slower, thus fluid inclusions embedded either aqueous or carbon dioxide phase (the latter either liquid or gaseous; generally densities of carbon dioxide were moderate to low). The non-aqueous liquid inclusions investigated till present contained relatively pure carbon dioxide. Nevertheless, elsewhere there are examples of the carbonatite-related mineralisation, that formed from methane-bearing fluids (*e.g.* Fan *et al.* 2004a), thus methane (and other hydrocarbons) may be expected in the Tajno massif.

Two contrasting values of pressure were obtained from fluid inclusions: 1.2 kbar and ca 0.5 kbar. Our interpretation is that the higher value is connected with a short increase of pressure in the volcano system (maybe accompanied by hydraulic crushing of minerals and rocks), generally the lower value may be accepted as typical of the whole mineral-forming process in the currently investigated ranges.

For the high-temperature solutions (ca. 500ºC or more) high concentrations of many elements are characteristic, as evidenced by daughter minerals in fluid inclusions. Calcium, sodium, potassium, chloride and carbonate ions are the main components, with appreciable addition of aluminium, strontium, barium, rare earth elements, phosphorus and fluorine. Later fluids contained mainly sodium, calcium, carbonate and chloride ions, other elements occurred in lower concentrations than earlier.

The problem whether carbonatites occurring in the Tajno massif formed from melt remains unsolved. The studies of the Grønnedal-Ika syenite massif with carbonatites from south Greenland revealed that carbonatites may form by melt immiscibility (Halama et al. 2005). The idea on magmatic origin of carbonatites is supported by studies of other occurrences (*cf. e.g.* Cooper, Reid 1998; Vuorinen 2005). Moreover, the experimental works (Keppler 2003) show that Ca-Na-Mg carbonatite melt may dissolve large amounts of water (*e.g.* at 900ºC, 0.5 kbar – ca. 4 wt% and at the same temperature, 1 kbar – ca. 8 wt. %). On cooling and along with crystallisation of the early carbonates from the melt, the gradual and continuous transition from melt to dense solution and next to diluted solution is possible. Hence, the future investigation of other samples from Tajno may yield an evidence of magmatic origin of the earliest carbonatite rocks. The present recognition of the origin of carbonatites in this massif resulted in defining the parent aqueous and carbon dioxide fluids as orthomagmatic ones.

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