

ANALYSIS OF TRACE ELEMENTS AND FLUID INCLUSIONS IN
FLUORITE FROM THE ARDENNES MASSIF (*)

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RÉSUMÉ

Des données nouvelles ont été obtenues sur la fluorine des Ardennes. Elles concernent les inclusions fluides d'une part et les oligo-éléments d'autre part. Elles confirment que les gisements dont provient le minéral appartiennent au type *Vallée du Mississippi*. Cependant le rapport Na/K est exceptionnellement faible dans les saumures qui remplissent les inclusions et la teneur en K y est élevée. Une comparaison est faite avec d'autres régions minéralisées, et en particulier le Derbyshire, en Angleterre.

ABSTRACT

Fluid inclusion and trace element data for fluorite from the Ardennes confirm that the mineral is from deposits of Mississippi Valley Type. Na/K ratios are, however, unusually low with high K concentration in the inclusion brines. Comparisons are made with other mineralized areas, particularly Derbyshire, England.

INTRODUCTION

Four samples of fluorite have been investigated, two from deposits in the Carboniferous of the Namur syncline between Liège and Charleroi (744 and 747) and two from deposits in the Devonian, near Givet on the Belgian-French border (745 and 746). All four fluorites are from deposits of telethermal type with no obvious igneous intrusives capable of providing the ore-forming fluids. According to de Magnée (1967) the economic mineralization of the Ardennes Massif is limited to the intersection of faults with limestones and dolomites of middle and upper Devonian age and with limestones of Carboniferous age, the latter only bearing mineralization where its lower part is dolomitized. In addition, irregular replacement deposits develop where cross-cutting veins intersect contact planes between Carboniferous limestones and shale. These are not true replacements, but are infillings of solution cavities in the limestone (palaeokarsts). Lead-zinc-fluorite-barite ores of the Derbyshire orefield, England, also occur chiefly as palaeokarst infillings, which are largely restricted to areas of limestone dolomitized by exposure to brines of the Zechstein Sea (Ford, 1969). These palaeokarsts were developed in two stages, an intra-Carboniferous stage related to the Viséan-Namurian boundary unconformity and a later Triassic stage.

Sample 744 is from Seilles. It occurs as discrete cubes, with variable colour from bright translucent blue to green, in association with material infilling a palaeokarst topography developed near the Viséan-Namurian boundary. Close by, at

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Hayes-Monet, a series of veins contain sphalerite (schalenblende), minor galena, marcasite and calcite. Sample 747 is purple fluorite from Engihoul. It occurs as discrete cubes disseminated as replacements in Viséan dolomitic limestone and is associated with spherulitic aragonite. Of the Devonian samples, 745 is from Foisches, (near Givet, northern France) occurring in a discontinuous stratiform deposit near the top of the Givetian limestone. It is associated with palaeokarst infillings and breccias which are heavily silicified. The fluorite varies from purple to colourless and occurs, generally, as dodecahedra. At Ave, about 30 km east of Givet, the same Givetian limestones contain a few cross-cutting PbS-BaSO₄ veins. Sample 746 comprises small colourless cubes of fluorite which occur at the contact between the veins and the country rock.

TABLE 1

Trace element and fluid inclusion data on fluorite

(a) *Homogenization temperatures; degrees C.*

Sample No	Locality	No of inclusions measured	Type	Mean T	Std. Devn.	Median
744	Seilles	25	P/PS	148.9	3.3	148.5
745	Foisches	19	P/PS	125	3.4	125.2
746	Ave	—	P Gas-less	< 70	—	—
747	Engihoul	17	P	108.8	10.8	106.9

(b) *Freezing data*

Sample No.	Locality	No of measurements	Melting point range °C	Mean	Salinity of mean; equivalent wt % NaCl	Na/K (atomic)
744	Seilles	9	—15.3 to —13.4	—14.2	18.2	9.4
745	Foisches	9	— 6.8 to — 6.3	— 6.6	10.8	3.4
746	Ave	40	—14.1 to — 6.3	— 9.1	13.0	—

(c) *Trace element data*

Sample No	Locality	Ba	Sr	Y	Ce	La	Mg
744	Seilles	6	15	9	< 9	< 7	20
745	Foisches	126	65	15	31	< 7	70 ± 10
746	Ave	4476	131	25	< 9	< 7	20
747	Engihoul	25	33	16	9	< 7	60 ± 10

P = Primary fluid inclusion

PS = Pseudosecondary fluid inclusion.

FLUID INCLUSION DATA

The filling temperatures recorded in Table I are in the epithermal range, with the possible exception of the sample from Ave whose gas-less inclusions indicate low temperatures which may be representative of a late phase of mineralization. The remaining temperatures are within the range shown by telethermal deposits of Mississippi Valley Type in Britain, Table II.

TABLE 2

Fluid Inclusion results from fluorites from some British deposits of Mississippi Valley Type

Orefield	Range of mean homogenization temps	N	Range of mean salinities, equivalent wt % NaCl	N
Derbyshire*	< 70 to 140° C		17.5 to 30.0	
Central Pennines	91 to 143° C	10	19.9 to 26.6	6
North Wales**	97 to 114° C	6	24.0 to 24.8	4
Mendip Hills	85° C	1	—	—
S. E. Durham***	104 to 108° C	3	22.4	1

N = No. of fluorite samples studied.

* Includes ranges of data by Roedder (in Ford, 1969) and Roedder (1967).

** From Smith (1973).

*** From Hirst and Smith (1974).

Freezing stage experiments have recorded mean ice-melting temperatures in the range — 14.2 to — 6.6° C for specimens 744, 745 and 746; no solid phases other than ice were observed. Specimen 745, from Foisches, contains a number of apparently primary fluid inclusions with anomalous ice-melting temperatures of 0° C. These do not seem to represent inclusions in which the original brine has been replaced at a late stage by groundwater, since they yield homogenization temperatures similar to those of the saline inclusions (Table I). Inclusions in the Engihoul fluorite were unsuitable for freezing experiments due to their very small size.

In accordance with general practice the ice-melting temperatures have been interpreted in terms of equivalent NaCl salinities. Flame photometric analysis of inclusion leachates, however, indicates the presence of unusually high concentrations of potassium, thus casting doubt upon the validity of this simple interpretation, which now appears to underestimate the total mixed chloride salinity. To the authors' knowledge there has been no data published regarding the freezing behaviour of mixed chloride brines.

The Na/K ratios are considerably lower than those found in inclusions from Mississippi Valley Type deposits (Sawkins, 1968). Low Na/K ratios may be attributed to a variety of mechanisms. They may be representative of high temperature, juvenile igneous hydrothermal fluids or may be achieved by reactions between connate or meteoric water and K-silicates at high temperatures. Involvement of connate or meteoric brine with evaporites may also result in a lowering of the Na/K ratio. This has been demonstrated, for example, in some connate brines associated

with evaporites by White (1963), to the extent evident here. Temperatures and, particularly rare earth analyses, suggest that the first two possibilities are unlikely and point to the possible involvement of evaporites in the evolution of the ore-forming brines. Deposition of Na and Ca evaporite minerals should result in the formation of residual interstitial brines which are relatively enriched in K. The record of evaporites in the Ardennes is not extensive, however several anhydrite beds have been revealed in the transgressive middle Devonian, by two boreholes sunk in 1960, one at Tournai (Van Tassel, 1960) and one at Leuze.

TRACE ELEMENT DATA

Trace element data are shown in Table I. The high Ba values in samples 745 and 746 can probably be attributed to contamination from barite, the same contaminant probably also being responsible for the relatively high Sr values. Yttrium contents are low, in the range 9 to 25 ppm. These values contrast markedly with the range from magmatic hydrothermal fluorites from Cornwall, England of 95 to 325 ppm, and are well outside the range of values recorded from the North Pennine orefield of Northern England, where the range is 120 to 815 ppm. The Y contents are, however, well within the range for telethermal deposits of Mississippi Valley Type, which have a general range of 0 to 60 ppm (Smith 1974). Specific comparisons could be made with the fluorite mineralization of Derbyshire where Y varies from 0 to 38 ppm (Smith 1974) or with fluorite from the Lower Magnesian Limestone of County Durham, England with a range of 22 to 53 ppm (Hirst and Smith, 1974). There is clearly a very strong similarity in the mode of occurrence, filling temperatures, salinities and Y contents between the Ardennes and Derbyshire fluorites.

CONCLUSIONS

We would suggest that the Ardennes fluorite, and by implication the associated Pb and Zn mineralization, is of Mississippi Valley Type with no obvious, or indeed necessary, contribution from igneous hydrothermal fluids, in agreement with the conclusions of de Magnée (1967). Both the Devonian and the Carboniferous mineral deposits probably result from movement of connate brines from thick sedimentary sequences in sedimentary basins adjacent to the mineralized areas. The brines have possibly been modified by contact with evaporites at some stage in their evolution.

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REFERENCES

- de MAGNÉE, I., 1967. — Contribution à l'étude génétique des gisements Belges de plomb, zinc et barytine. In: *Genesis of Stratiform Lead-Zinc-Baryte-Fluorite Deposits*. Ed. J. S. Brown. *Econ. Geol. Pub. Co.* 1967, 255-266.
- FORD, T. D., 1969. — The Stratiform ore deposits of Derbyshire. In *Sedimentary Ores*, James, C. H. ed. (Leicester: Department of Geology, University of Leicester) 73-93.

- HIRST, D. M. and SMITH, F. W., 1974. — Controls of Baryte Mineralization in the Lower Magnesian Limestone of the Ferryhill area, County Durham. *Trans. Instn. Min. Metall. (Sect. B. Appl. earth Sci)*, **83**, 844-55.
- ROEDDER, E., 1967. — Environment of deposition of stratiform (Mississippi Valley-type) ore deposits, from studies of fluid inclusions. In : *Genesis of Stratiform Lead-Zinc-Baryte-Fluorite Deposits*. Ed. J. S. Brown. *Econ. Geol. Pub. Co.* 1967, 349-362.
- SAWKINS, F. J., 1968. — The significance of Na/K and Cl/SO⁴ ratios in fluid inclusions and subsurface waters, with respect to the genesis of Mississippi Valley-type ore deposits. *Econ. Geol.*, **63**, 935-942.
- SMITH, F. W., 1973. — Fluid inclusion studies on fluorite from the North Wales ore field. *Trans. Instn. Min. Metall. (Sec. B. Appl. earth sci.)*, **82**, B 174-176.
- SMITH, F. W., 1974. — Regional variation of the yttrium content of fluorite. In preparation.
- VAN TASSEL, R., 1960. — Anhydrite, célestine et barytine du Givetien au sondage de Tournai. *Bull. Soc. belge Géol.*, **69**, 351-361.
- WHITE, D. E., 1963. — Saline waters of sedimentary rocks : Fluids in subsurface environments — a symposium. *Mem. N° 4, Am. Assoc. Petroleum Geologists*, 342-366.

