12th Biennial SGA Meeting
12–15 AUGUST 2013, UPPSALA, SWEDEN

Mineral deposit research for a high-tech world

SOCIETY for GEOLOGY APPLIED to MINERAL DEPOSITS

Proceedings

VOLUME 2

Stratiform fluorite deposits in the south-eastern part of the Paris basin (Morvan): paragenetic sequence, trace elements and Sr-Nd isotopes

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Abstract: In France, stratiform fluorite deposits occurred at the base of Mesozoic sedimentary units from the Paris Basin around the Morvan massif, and reserves are estimated to about 5Mt. Detailed paragenetic sequence, fluid nature and the timing of the mineralization are still poorly constrained. In this study we examine the petrographical properties, trace elements composition and isotopic signatures of the fluorite deposits. These investigations provide insights into the parameters controlling the mineralization stages. The petrographical observations revealed a distinct growth zonation of fluorite crystals and a mineral paragenesis composed of multiple fluorite stages associated with various minerals (barite, sphalerite, galena and others). Significant variations of U, Th, Sr, Ba, and especially U/Th ratios are recorded from all fluorite stages. Concerning Rare Earth Element (REE), a bell-shaped pattern is recognized for all fluorite stages. Sr isotopic data of fluorite ($^{87}Sr/^{86}Sr$= 0.7119 to 0.7134) are incompatible with a seawater signature. Available microthermometric data and the thermal history of the basin indicate hydrothermal fluid flow. A preliminary isochron data suggest a Lower Cretaceous age for the fluorite mineralization at the Pierre-Perthuis deposits.

Keywords: stratiform fluorite deposits, paragenesis, LA-ICP-MS, REE pattern, isotopes.

1 Introduction and geological settings

Fluorite is considered as a critical raw material by the European Commission Group working on defining critical raw materials in European Union with 13 other materials (Antimony, Beryllium, Cobalt, Gallium, Germanium, Graphite, Indium, Magnesium, Niobium, Platinum Group Metals, Rare Earth, Tantalum and Tungsten) (European commission, 2010, Nowakowska, 2012). In France, stratiform fluorite deposits occur at the base of Mesozoic sedimentary units in the Paris Basin around the Morvan Massif (Fig 1). Fluorite grades are between 30-40% and CaF_2 estimated reserve is more than 5Mt within six deposits (Soulé de Lafont and Lhégu, 1980). The Morvan area is composed of sedimentary formations corresponding to the south-eastern part of the Paris Basin and plutonic and metamorphic rocks forming a horst of Hercynian basement. The fluorite deposits are hosted in sandstones/conglomerates from Late Anisien/Early Ladinian at Antully, in limestones from Hettangian/Sinemurian at Courcelles-Fremoy and in dolomite from Carnian/Norian at the Pierre-Perthuis, Pontaubert, Marigny-sur-Yonne and Egreuil deposits.

The basement is composed of granitic, gneissic or rhyolitic rocks. The origin of the stratiform fluorite deposits from the Morvan region is poorly constrained. The aim of this study is to better constrain the origin and timing of fluorite deposits with a multi-disciplinary approach including (1) field work, (2) core descriptions, (3) petrographical investigations (optical, cathodoluminescence and electron microscopy), (4) trace element analyses (REE, Y, U, Th, Sr, Mg, Ba, Rb) and (5) Sr-Nd isotopic compositions.

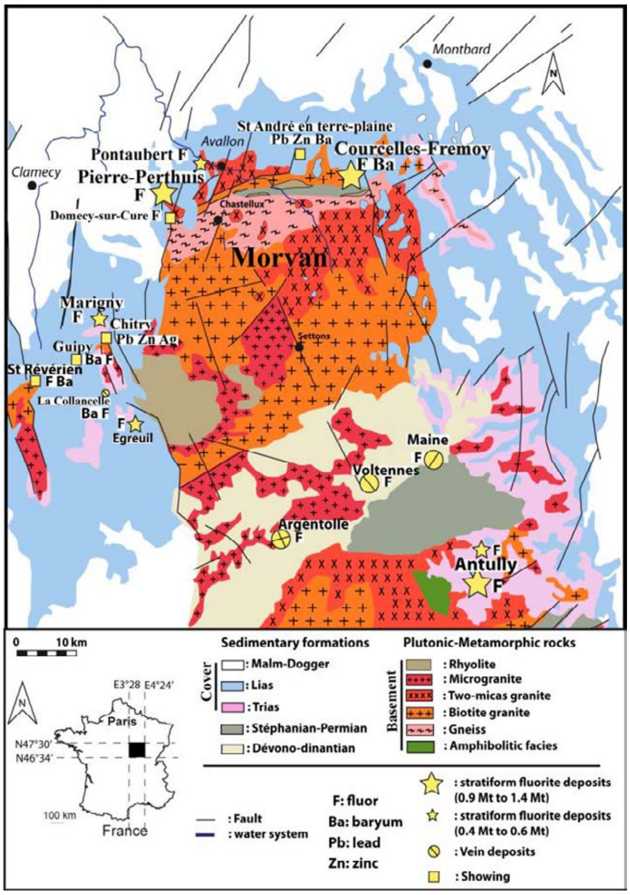

Figure 1. Location map of fluorite stratiform deposits around the Morvan Massif (modified after Soulé de Lafont and Lhégu, 1980).

2 Methods

Samples from four deposits (Pierre-Perthuis, Marigny-sur-Yonne, Antully and Courcelles-Frémoy) and three showings (Chitry, St André-en-Terre-Plaine, Guipy and Domecy-sur-Cure) were studied. Thin sections have been observed by optical, cathodoluminescence (CL) and using SEM-BSE-EDS study. Cubic fluorite crystals have been analyzed by Laser Ablation connected with an Induced Coupled Plasma-Mass Spectrometer (LA-ICP-MS) to determine trace elements (REE, Y, Mg, Rb, Ba, Sr, Th and U). Different crystals from the same samples were also analyzed by ICP-MS. REE data were normalized to the North American Shale Composite (NASC) after Gromet et al (1984). Rb-Sr and Sm-Nd isotopic analyses have been measured by Thermal Ionization Mass Spectrometry (TIMS) from the three deposits (Pierre-Perthuis, Marigny-sur-Yonne, Antully) and one showing (Domecy-sur-Cure).

3 Results

3.1 Paragenetic sequences

The paragenetic sequence in the different samples from the four fluorite deposits and the three showings display several fluorite stages coexisting with barite, pyrite, sphalerite, galena, azurite, malachite. The mineralogical successions between the different deposits show that all the sequences began by a sulfide stage (galena, sphalerite or pyrite). In addition, the north-western deposits or showings (Pierre-Perthuis, Marigny-sur-Yonne and Chitry-les-Mines) have similar paragenetic sequences (1) sulfides (2) fluorite 1/barite (3) quartz (4) sulfides (5) fluorite 2 and 3, (6) quartz and (7) azurite/malachite. At Pierre-Perthuis, there are two galena stages, three fluorite stages (Fl1, Fl2 and Fl3), two barite stages (Brt1 and Brt2) and four quartz stages (Qz1 to Qz4). The mineral paragenesis of all deposits is composed of Fl-Brt-sulfides assemblage type. However, there are variations of mineral concentrations according to their location.

Observations under CL microscopy revealed a well-defined CL pattern of fluorite from Pierre-Perthuis composed of two distinct growth zones between Fl1 and Fl2 stages (Fig. 2A, B). Fl1 stage consists mainly of 100-250µm isolated cubic crystals in matrix, and only rarely was observed in vein. Crystals are rich in inclusions and display a dark-blue luminescent core surrounded by a rim marked by succession of 3 subzones (1) fine light blue band (2) a relatively large dark-blue band and (3) light-blue band (Fig. 2B). Fl2 stage includes large inclusion-free cubic crystals (250µm to 1cm) mainly forming geodes or veins and rarely found in carbonate matrix. The natural colour of Fl2 is white, yellow and can be marked by a fine external purple band. The Fl2 stage is characterized by a concentric zoning with blue luminescent core and bright rims composed of 3 subzones (1) light-blue band (2) large dark-blue band and (3) dark-purple band (Fig. 2A).The Fl3 stage is characterized by a fine blue band (4) (Fig. 2A).

3.2 Trace element data

The results of the fluorite crystals analyzed with LA-ICP-MS method fit well with the solution ICP-MS results (Fig. 3). Fluorite crystals from four deposits show a difference in total REE concentrations with mean value of 57 ppm at Pierre-Perthuis, 99 ppm at Marigny-sur-

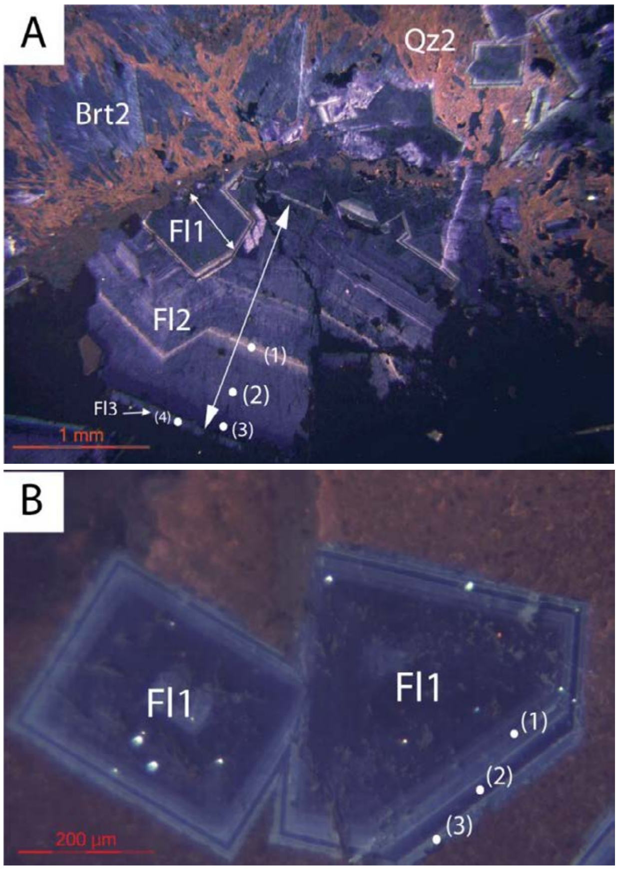

Figure 2. Cathodoluminescence microscopy image, **A**: Fl1, Fl2, Fl3 stages associated with quartz (Qz2) and barite (Brt2) stages from Pierre-Perthuis deposit; rims of Fl2: (1) light blue band (2) large dark blue band and (3) dark-purple band. (4) Fine blue band of Fl3 **B**: CL pattern of Fl1 stage from Pierre-Perthuis with a blue luminescent core and rim composed of 3 subzones (1: fine light blue band; 2: dark-blue band; 3: fine light blue band).

Yonne, 123 ppm at Domecy-sur-Cure (5km southward from Pierre-Perthuis) and 140 ppm at Antully. The distribution of normalized REE patterns displays a bell-shaped pattern in various fluorite stages (Fl1, Fl2 and Fl5) with a Mid-Rare Earth Element (MREE)-enrichment without europium (Eu) and cerium (Ce) anomalies. Significant variations of U (0.01 to 11 ppm), Th (0.01 to 12 ppm), Sr (33 to 283 ppm), Ba (0.4 to 278 ppm) and especially U/Th ratios (0.2 to 10.8) are recorded from the Fl1, Fl2 and Fl5 stages. REE patterns of fluorite can be related to the fluorite stage. In Pierre-Perthuis, for the first stage (Fl1) no variations from core to rim, and no Ce and Eu anomalies were observed. The Fl2 stage from Pierre-Perthuis displays different MREE and Heavy Rare Earth Element (HREE) content between the core (translucent white) and the rim (purple rim and yellow rim). The purple rim is enriched in Th whereas the yellow rim is enriched in U. A negative Eu anomaly is present in Fl2.

3.3 Sr-Nd isotopic data

The variations of the $^{87}Sr/^{86}Sr$ ratios range from 0.7119 to 0.7134. The $^{87}Rb/^{86}Sr$ ratios are very low (< 0.03) so whatever the "time corrected" initial $^{87}Sr/^{86}Sr$ ratios will not be very different from the measured one. For the

Pierre-Perthuis deposit, isotopic values range from 0.7119 to 0.7133 for 3 samples of Fl2. ε_{Nd} varies from -4.04 (Antully) to -6.38 (Pierre-Perthuis). Sm and Nd concentrations range from 6.29 to 10.60 ppm and from 10.84 to 20.63 ppm, respectively. The $^{147}Sm/^{144}Nd$ ratios range from 0.3083 to 0.43876.

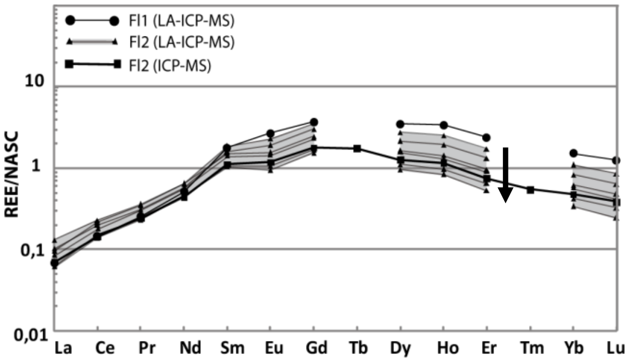

Figure 3. REE patterns for Fl1 and Fl2 stages in the Pierre-Perthuis deposit and comparison between LA-ICP-MS and ICP-MS methods for the same samples. The laser spots follow the crystal growth (the black arrow) for the Fl2 stage (LA-ICP-MS results in grey colour)

4 Discussion

4.1 Nature of mineralizing fluid

The bell-shaped REE patterns do not resemble the REE patterns of marine limestones or seawater (De Baar et al., 1985). For instance, they do not display significant anomalies in Ce and/or relative enrichment in HREE. The REE patterns in Pierre-Perthuis (Fl2) display a slight negative Eu anomaly, which could be interpreted as a geochemical fingerprint of fluid interaction inheritance from the source sedimentary or crystalline rocks. The fractionation between U and Th (U/Th>1) in fluorite crystals from most deposits could indicate an environment where redox potential (Eh) value favours a preferential transport of U over Th. On the contrary, the absence of fractionation between U and Th at Marigny-sur-Yonne suggests a lower Eh value.

The Sr isotopic data in fluorite do not display a seawater isotopic signature. However the $^{87}Sr/^{86}Sr$ ratios are similar to the $^{87}Sr/^{86}Sr$ ratios of the early diagenetic from Carnian/Norian dolomite formation (0.711; Spotl and Wright, 1992).

The reconstruction of the thermal history of the south-eastern part of the Paris Basin, and more precisely in the Pierre-Perthuis area indicates that the maximum temperature during burial reached 70°C at a depht of 1.25 km during the Late Cretaceous period (Uriarte, 1997). However the homogeneization temperatures deduced from fluid inclusions in fluorite crystals from Marigny-sur-Yonne deposit are hotter and range from 70°C to 120°C with 22 eq. wt.% NaCl (Nigon, 1988). A preliminary microthermometric study on Fl2 stage in Pierre-Perthuis also indicates warmer fluids with similar temperatures (90-120°C, 20 eq. wt. % NaCl). These higher temperatures indicate a hydrothermal fluid flow event.

4.3 Comparison with fluorite-vein deposits

Fluorite-vein deposits are known in the Morvan Hercynian basement (Voltennes, Maine and Argentolle; Joseph, 1974; Marchand et al., 1976; Valette, 1983; Jebrak, 1984 and Nigon, 1988). Some similarities exist between the last yellow-white fluorite stage (paragenesis, salinity, temperature) in Voltennes veins and yellow-white cubic fluorite stage in stratiform deposits. In fact the homogeneization temperatures range from 100 to 122°C with 16 eq. wt % NaCl which are similar with those at the Pierre-Perthuis and Marigny-sur-Yonne deposits. In terms of dating, at Voltennes, the ages determined by K-Ar dating on adularia (Fig. 4) associated to the first stage of purple/green fluorite crystallization range from 170-175 Ma (Baubron et al., 1980) to 185 ± 5Ma (Joseph et al., 1973), i.e contemporaneous to the first stage of purple fluorite. These ages correspond to a crystallization during the Early Jurassic period. The relation between stratiform deposits in Mesozoic sedimentary formation and veins in Hercynian basement will be further investigated: the adularia from Voltennes will be dated using the ^{40}Ar-^{39}Ar method and the possibility of Sm-Nd dating of the purple-green fluorite will be evaluated in order to compare the timing between vein and stratiform deposits in the Morvan.

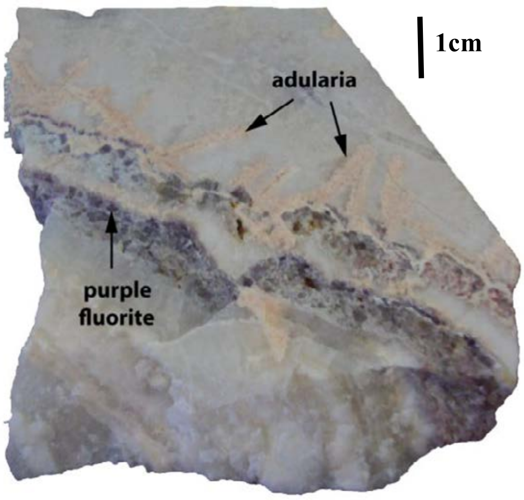

Figure 4. A sample from the Voltennes vein deposit composed of purple/green fluorite associated with adularia.

4.4 Timing of stratiform fluorite deposits

The preliminary Sm-Nd isotopic data of the Fl2 stage from Pierre-Perthuis may be interpreted as a crystallization age from the Lower Cretaceous period (Sm-Nd isochron at 135±18 Ma). In turn, these isotopic data may also reflect a mixing between fluids with different elemental and initial isotopic compositions. The analyses of new samples in the future will allow to carefully evaluate both hypotheses.

6 Conclusion

The ongoing study of stratiform fluorite deposits in the Morvan resulted in the following preliminary observations: 1) The north-western deposits or showings (Pierre-Perthuis, Marigny-sur-Yonne and Chitry-les-Mines) have similar paragenetic sequences: (1) sulfides (2) fluorite/barite (3) quartz (4) sulfides (5) fluorite, (6) quartz and (7) azurite/malachite. 2) The bell-shaped normalized REE pattern is typical for stratiform fluorite deposits in the Morvan. 3) The U/Th variation in fluorite between different deposits (Marigny-sur-Yonne and Pierre-Perthuis) suggests Eh variations in the fluid from which the fluorite crystallized the fluorite. 4) Fluid inclusions trapped in Fl2 crystals in Pierre-Perthuis and Marigny-sur-Yonne deposits revealed the presence of a warm and saline fluid (T= 90-120°C, up to 20 eq. wt % NaCl). 5) The $^{87}Sr/^{86}Sr$ ratios are different from a seawater isotopic signature but the data are consistent with the isotopic signature of the dolomitic host rocks. The timing of mineralization of the Fl2 stage at Pierre-Perthuis could indicate a Lower Cretaceous period.

Acknowledgements

This study is part of a PhD project funded by the BRGM and partially supported by INSU-CESSUR research project (Institut National des sciences de l'Univers Connaissance et Technologie du Sous-Sol pour son exploitation et Usage Durable). This paper is a contribution of the team "Relief et Basin" to the UMR-CNRS/ Université Paris-Sud 8148.

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