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## $\delta^{44}\text{Ca}$ of stratabound fluorite deposits in Burgundy (France): tracing fluid origin and/or fractionation processes

Morgane Gigoux<sup>a, b\*</sup>, Philippe Négrel<sup>b</sup>, Catherine Guerrot<sup>b</sup>, Benjamin Brigaud<sup>a</sup>,  
Guillaume Delpech<sup>a</sup>, Maurice Pagel<sup>a</sup>, Thierry Augé<sup>b</sup>,

<sup>a</sup>Université Paris-Sud, UMR CNRS/UPS Géosciences Paris Sud (GEOPS), Bât. 504, 91405 Orsay, France

<sup>b</sup>BRGM, 3 Avenue C. Guillemin, BP 36009, 45060 Orléans Cedex 02, FRANCE

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### Abstract

Combined Sr and Ca isotopic tracers have been applied to stratabound fluorite deposits in the central part of Burgundy (France). These deposits are spatially related to an unconformity between a Palaeozoic granitic and metamorphic basement and Late Triassic sediments. The aim of this work is to trace the origin of fluid(s) from which stratabound fluorite deposits formed. We suggest that the variations of the  $\delta^{44}\text{Ca}_{\text{sw}}$  in fluorite (-0.1 to +0.2‰ relative to seawater sw) could be explained by 1) precipitation from a fluid dominated by a Ca isotopic signature similar to that of seawater (calcite or dolomite dissolution from the host-rock) and a Sr isotopic ratio higher than seawater (granitic basement) and involves no fractionation, the preferred scenario or 2) cristallization from a fluid with a low  $\delta^{44}\text{Ca}_{\text{sw}}$  (carbonate and silicate sources) involving fractionation processes.

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### 1. Introduction

In France, stratabound fluorite deposits occur at the unconformity between crystalline basement of granites and metasediments and Mesozoic sandstone, conglomerate and carbonate rocks in the central part of Burgundy. They constitute a noticeable fluorite ( $\text{CaF}_2$ ) reserve (5.5 Mt) within six deposits around the Morvan Massif (Fig. 1). Recent studies suggest that stratabound barite-fluorite deposits in the Mesozoic sediments around the Northern Massif Central and in Poitou areas are probably formed by to fluid flow during Late Jurassic<sup>1</sup> and Early Cretaceous (Sm-Nd age of  $130 \pm 15 \text{ Ma}^2$ ). In this region, chemical, radiogenic (Nd, Sr)<sup>2,3</sup> and stable isotopic (C, O, S) tracers

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\* Corresponding author. Tel.: +33 (0)676497489; fax: +33 (0)169154880  
E-mail address: [morgane.gigoux@u-psud.fr](mailto:morgane.gigoux@u-psud.fr)

have been applied together with a detailed paragenetic sequence determination for tracing the origin of fluorite deposits and determine their age<sup>2</sup>. In the present study, Ca isotopes in fluorite were measured in order to provide an additional tool for deciphering the origin of fluids<sup>4</sup>.

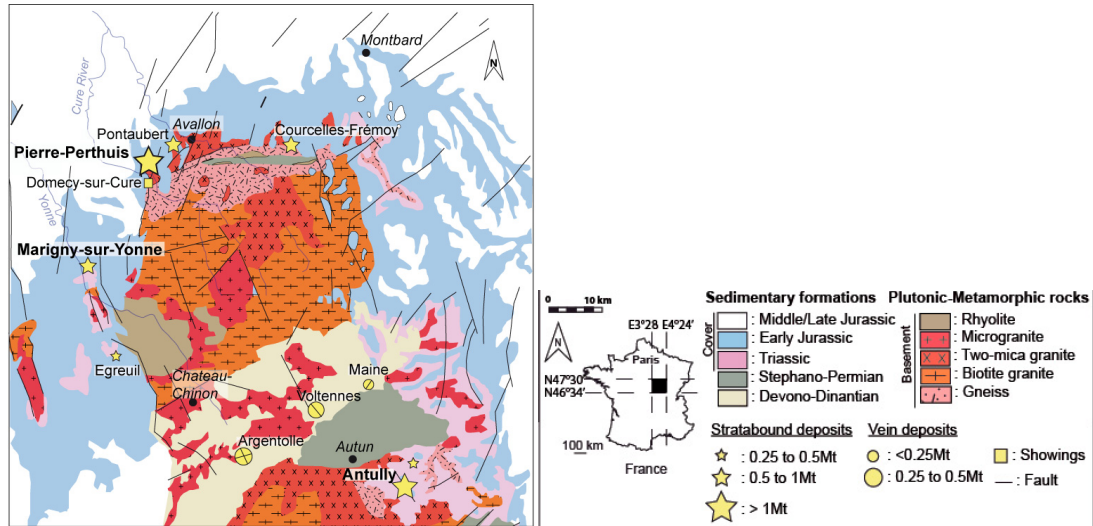


Fig. 1. Location map of stratabound fluorite deposits around the Morvan Massif (from ref. 2 and 3.).

## 2. Samples and analytical methods

Three fluorite deposits (Pierre-Perthuis, Marigny-sur-Yonne and Autully) and one showing (Doméc-sur-Cure), previously described in Gigoux et al.<sup>2,3</sup>, were investigated in this study (Fig. 1). These deposits are located around the crystalline Morvan Massif, which is bounded by Mesozoic sedimentary deposits. The fluorite deposits are hosted in Late Triassic dolomite at Pierre-Perthuis, Doméc-sur-Cure and Marigny-sur-Yonne and Late Triassic sandstone at Autully. These stratabound fluorite deposits or showing are spatially related to an unconformity between the basement and the Late Triassic sediments. Four fluorite samples (PP4, PP5, RP3A and RP3B) were collected at Pierre-Perthuis, along the Cure River, one at the Doméc-sur-Cure (1515), two at Marigny-sur-Yonne (LH164 and LH164a) and three at Autully (LM6b, LM6b' and LM6b'-1). In fluorite stratabound deposits, the general paragenetic sequence is (1) sulfides (2) euhedral fluorite /barite (3) quartz (4) sulfides (5) geodic fluorite/barite (6) quartz (7) azurite/malachite and (8) iron oxi-hydroxides. Sr and Ca isotopes were measured by Thermal Ionization Mass Spectrometry (TIMS) on the geodic fluorite stage from Pierre-Perthuis, Marigny-sur-Yonne and Autully deposits and from the Doméc-sur-Cure showing (BRGM Isotope laboratories). The fluorite samples were dissolved using ultrapure 12N HCl in Teflon beakers, after complete dissolution and evaporation, the dry residue was recollected in 8 to 10 ml of HNO<sub>3</sub>. One aliquot was used for trace element analyses and one for isotopic analyses. The Ca, Sr and Na contents were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Laboratoire des Sciences du Climat et de l'Environnement LCSE, Gif-sur-Yvette). For Ca isotope analyses, as fluorite is a calcium-bearing mineral, no further purification was done. A <sup>42-48</sup>Ca double spike was added to a sample aliquot of 2 µg Ca. External reproducibility is 0.04‰ (2σ<sub>m</sub>) based on replicate analysis of seawater and NBS915a. The <sup>44/40</sup>Ca isotopes ratios are represented as δ<sup>44</sup>Ca values and are reported compared to seawater (SW).

## 3. Major and trace elements

The fig. 2A displays the variation of Sr versus Na contents. A large range by a factor of variation of around 4 is observed for Na between the lowest value of 277 µg g<sup>-1</sup> observed in Pierre-Perthuis and the highest, close to 830 µg g<sup>-1</sup> observed in Autully fluorite crystals. The co-variation of these two elements in the 10 analyzed fluorite samples is significant, according to the 95% confidence interval (grayed area) and R<sup>2</sup> Pearson's coefficients close to 0.76. Fluorite from the Autully deposit has higher Na and Sr concentrations, while those from Pierre-Perthuis

deposit are lower. The concentrations of Sr and Na are fairly variable in Antully and Marigny-sur-Yonne deposits, they vary greater in the Pierre-Perthuis deposit. Na, as a classical tracer of silicate weathering in many environments, will be used in the following discussion as the Na/Sr or Na/Ca ratios.

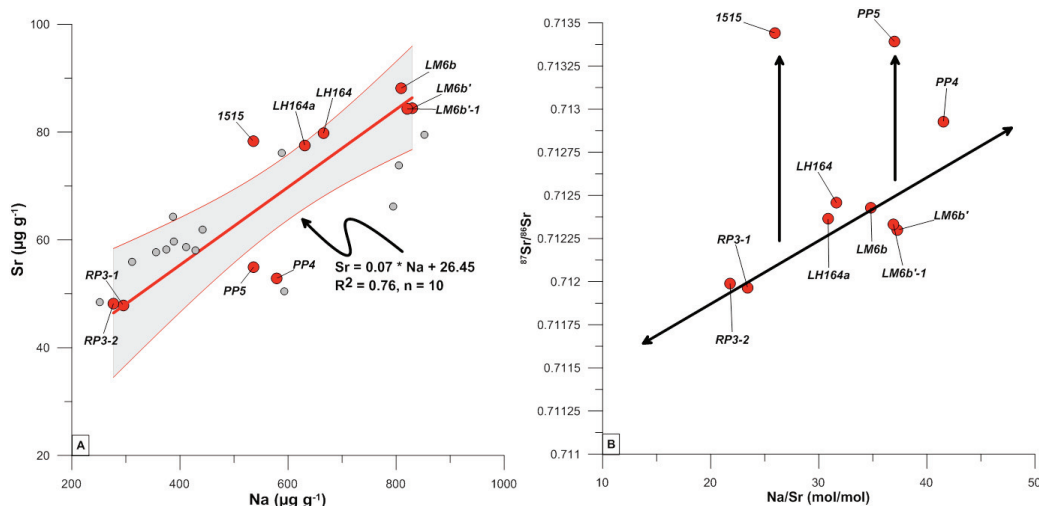


Fig. 2. (A) Plot of Sr vs. Na contents in the fluorite samples (contents in μg g<sup>-1</sup>). The red circles correspond to samples from this study. (B)  $^{87}Sr/^{86}Sr$  vs. Na/Sr ratios (from ref. 2 and 3).

#### 4. Strontium and calcium isotopes

Tracing Ca in the earth's systems (oceanic cycle, weathering, hydrothermal deposits) can be done using indirect proxies such as Sr isotopes since Sr and Ca behave similarly. However, Ca isotopes also directly trace Ca behavior<sup>4</sup>. The  $^{44}Ca$  ratio has the advantage to be a direct tracer of Ca sources but contrary to Sr isotopes, isotopic fractionation during crystallization may occur.

The  $^{87}Sr/^{86}Sr$  ratios in fluorite range from 0.71196 to 0.71344<sup>3</sup>, both extreme values being in the Pierre-Perthuis deposit and Domecy-sur-Cure showing. The range for other samples is very restricted (0.71236 to 0.71246 at Marigny-sur-Yonne and 0.71230 to 0.71243 at Antully). Since the  $^{87}Rb/^{86}Sr$  ratios of fluorite are very low, the measured Sr isotope ratios represent those of the fluids from which fluorite precipitated. Importantly,  $^{87}Sr/^{86}Sr$  ratios of fluorite never display a seawater isotopic signature ( $^{87}Sr/^{86}Sr > 0.712$ ). With the exception of two samples from the Pierre-Perthuis deposit that are shifted towards higher  $^{87}Sr/^{86}Sr$  ratios, the correlation between the  $^{87}Sr/^{86}Sr$  and Na/Sr ratios could be interpreted as a geochemical fingerprint of fluids from at least two sources (Fig. 2B). The first fluid source is characterized by a  $^{87}Sr/^{86}Sr$  ratios of at least 0.71175 and a Na/Sr ratio of around 20, whereas the second by higher  $^{87}Sr/^{86}Sr$  ratios of at least 0.7129 and Na/Sr ratios of around 50. The most radiogenic values would be mainly controlled by the Sr isotopic composition of fluids that interacted with a crustal source<sup>5</sup>. The radiogenic Sr, leached from Rb-rich rocks (e.g. siliciclastic, granitic rocks) could have been added to less radiogenic Sr derived from the fluorite-bearing Triassic carbonate sediments<sup>3</sup>. At Antully and Marigny-sur-Yonne, there are no significant differences in the  $^{87}Sr/^{86}Sr$  and Na/Sr ratios of fluorite, indicating that Sr in these fluorite crystals came from a similar source, which can be a mixing of the two different fluid sources. Contrary to that, the variations in fluorite at Pierre-Perthuis are important and may represent variable fluid sources in this deposit as shown by Soudry et al.<sup>4</sup> for carbonate fluorapatite formed during the Cretaceous-Eocene period.

The two extreme  $\delta^{44}Ca_{SW}$  values are -0.1‰ for fluorite at Antully and +0.2‰ for fluorite at Pierre-Perthuis (Fig. 3A). The  $\delta^{44}Ca_{SW}$  values of fluorite agree with a present day or a past seawater isotopic signature ( $\delta^{44}Ca_{SW} = \pm 0.0\%$ , Fig. 3B). When compared with fluids that could have interacted with different lithologies from the literature<sup>6-8</sup>, the  $\delta^{44}Ca_{SW}$  values of fluorite crystals are always higher. In Fig. 3A,  $\delta^{44}Ca_{SW}$  versus Na/Ca ratios display a significant

correlation ( $R^2 = 0.88$ ). As for Sr isotopes, this relationship can be interpreted as a fingerprint of fluid inheritance from at least two sources (e.g. end-members EM1 and EM2) if no fractionation processes occurred<sup>5</sup>. The increase in Na contents corresponds to lower  $\delta^{44}\text{Ca}_{\text{SW}}$  values and thus a predominant role of the EM1 source. Conversely, the higher  $\delta^{44}\text{Ca}_{\text{SW}}$  values and the lowest Na/Ca ratios would trace the EM2 source. We may postulate that EM1 interacted with silicate and EM2 interacted with carbonates but neither the  $\delta^{44}\text{Ca}_{\text{SW}}$  values, nor the Na/Ca and Na/Sr ratios agree with such sources, as shown in Fig. 3B. Another hypothesis relates to the Ca content and its variability in the fluid from which fluorite precipitated. A hydrothermal fluid circulation with typically  $\text{CaCl}_2$ -rich brines was identified by the microthermometric study of fluid inclusions in fluorite crystals, such brines have high and variable  $\text{CaCl}_2$  concentrations. Assuming that the  $\delta^{44}\text{Ca}_{\text{SW}}$  values of fluorite reflects that of the fluid (e.g. initial fluid A with a  $\delta^{44}\text{Ca}_{\text{SW}}$  between  $-0.1$  and  $+0.2\text{‰}$  = observed fluorite; no correction for mineral-fluid fractionation<sup>6</sup>), the  $\delta^{44}\text{Ca}_{\text{SW}}$  values of fluorite cannot be explained by the different lithology end-members. On the other hand, we may postulate that fractionation of  $^{44}\text{Ca}$  may account for the observed  $\delta^{44}\text{Ca}_{\text{SW}}$ , such as is observed during calcite precipitation<sup>9</sup>. However the fractionation during calcite precipitation<sup>6</sup> is opposite to the suggested fluorite fractionation. This is illustrated Fig. 3B by the vertical arrow joining the initial fluid B, where fluid B would result from the interaction between silicate and carbonate sources (e.g. the calcite or dolomite in the host-rocks). However, neither the origin and evolution of the fluid B is well constrained nor the processes leading to Ca isotopic fractionation.

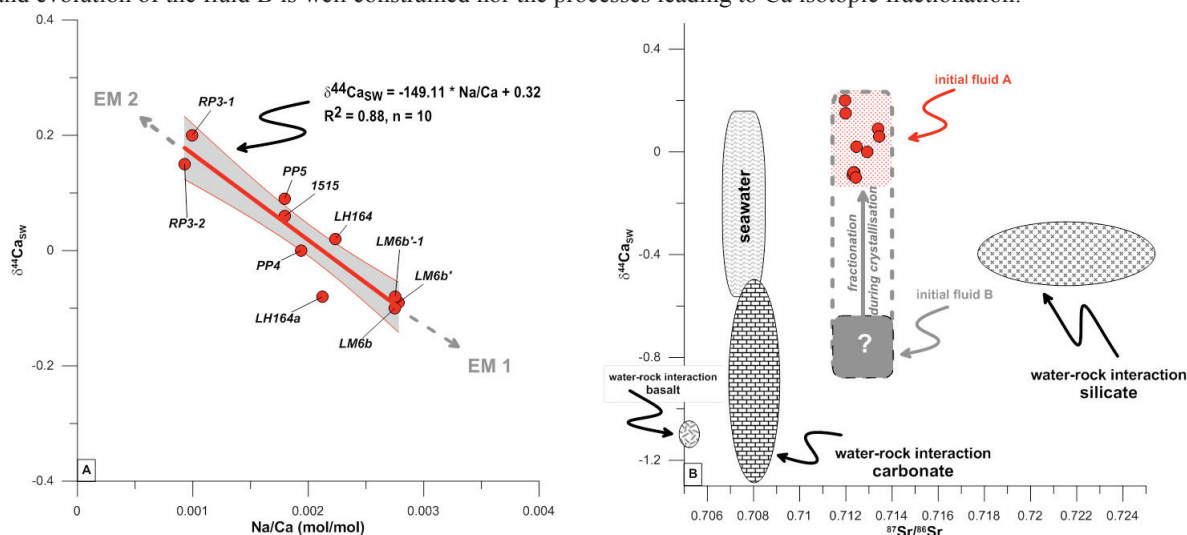


Fig. 3. (A)  $\delta^{44}\text{Ca}_{\text{SW}}$  vs. Na/Ca diagram; EM1 and EM2 are the two fluids end-members; the grayed area is the 95% confidence interval. (B)  $\delta^{44}\text{Ca}_{\text{SW}}$  vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  diagram ( $^{87}\text{Sr}/^{86}\text{Sr}$  from ref. 3), the fields of fluids having interacted with different lithologies are indicated (surface and groundwaters). SW: seawater (from Palaeozoic to modern compositions),  $\delta^{44}\text{Ca}$  modern seawater =  $0\text{‰}$ .

## 5. Summary

The values of  $^{44/40}\text{Ca}$  isotope ratios in fluorite from the Burgundy region could originate from two processes. The first involves the dissolution of calcite or dolomite from the host-rocks and suggests that fluorite crystals crystallized from a fluid dominated by a Ca isotopic signature similar to that of seawater and a Sr isotopic ratio higher than seawater (granitic basement), and involves no fractionation. The second involves crystallization from a fluid with a low  $\delta^{44}\text{Ca}_{\text{SW}}$  (carbonate and silicate sources) involving fractionation processes. Additional investigations are needed to confirm these preliminary results and explore the Ca isotopes as a useful tool for investigating mineral resources. For this purpose, these processes should be studied in more detail by analysing more fluorite deposits for Ca-Sr isotopes ratios in different geological contexts and through experimental fractionation models of fluid-fluorite crystallisation, under various temperatures, as crystallization of non-stoichiometric fluorite phases seems to be temperature dependant<sup>10</sup>.

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