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Genetic constraints on world-class carbonate- and siliciclastic-hosted stratabound fluorite deposits in Burgundy (France) inferred from mineral paragenetic sequence and fluid inclusion studies

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ABSTRACT

Stratabound fluorite deposits occur at the unconformity between the Variscan crystalline basement and the Mesozoic sandstone, conglomerate, limestone, and dolomite rocks of the Morvan Massif in central Burgundy. This study describes their petrographic characteristics in an attempt to determine the nature and temperature of mineralizing fluids in order to better understand the fluid migrations that led to massive stratabound fluorite deposition. The general paragenesis encompasses two major mineralizing events causing a succession of fluorite, barite, and quartz in all deposits. The two mineralizing events were preceded by two corrosion (dissolution or karstification) events affecting both the dolomite host rock at Pierre-Perthuis and Marigny-sur-Yonne and the limestone host rock at Courcelles-Frémoy with the creation of 1–10 m cavities and microscopic vugs. At Antully, the blocky calcite initially cementing the sandstone was partially dissolved. Microthermometric data on aqueous two-phase inclusions attest to $CaCl_2$-rich fluids giving rise to fluorite deposition in the Pierre-Perthuis, Courcelles-Frémoy, and Antully deposits. Homogenization temperatures range from 80 to 100 °C at Pierre-Perthuis and Courcelles-Frémoy, with sporadically higher temperatures. The range of $CaCl_2$ contents is 6.5–15 wt.% at Pierre-Perthuis, 1.7–9.4 wt.% at Courcelles-Frémoy, and 1.6–16.3 wt.% at Antully. The thermal history of the northwestern Morvan, compiled from organic matter, clay minerals and apatite fission track data indicates that the temperatures in fluorite and barite are higher than the maximum temperature recorded in sediments. This implies deep ascendant hydrothermal brine circulation during the Early Cretaceous. The impermeable cap rock retained the ascendant hydrothermal brine and allowed the deposition of massive fluorite stratabound mineralizations.

1. Introduction

Dill (2010) identified three main types of fluorite deposits: (1) fluorite deposits associated with magmatic rocks such as carbonatites; (2) structure-related including mineralization in breccias and veins or unconformity-related fluorite deposits; (3) sedimentary such as Mississippi Valley-type (MVT) deposits, forming stratabound fluorite associated with a major Pb–Zn sulfide stage. In France, stratabound fluorite deposits exhibit distinctive characteristics and occur at the unconformity between a Paleozoic basement and Mesozoic siliciclastic or carbonate rocks in the central part of Burgundy, around the Morvan Massif. In spite of their economic importance (5.5 million tons of fluorite), the fluid circulation and depositional processes controlling the formation of the stratabound fluorite deposits spatially associated with the unconformity around the Morvan Massif are poorly understood. Early investigations of these fluorite deposits including sedimentological and stratigraphic studies were synthetized by Soulé de Lafont and Lhégu (1980). This work highlighted (1) the different lithology of the host rocks associated with litho-stratigraphic control, (2) the position of the fluorite deposits along paleo-coastlines around a paleo-island at the onset of the Late Triassic and Early Jurassic, and (3) the association between fluorite mineralization, silicification, and the structural context. According to these authors, the fluorine and silica originated from leaching of various sedimentary formations in the basin, especially the clay formations, or leaching of granitic regoliths, as also suggested by Davaine (1980). The previous K–Ar ages obtained on adularia associated with the fluorite vein at Voltennes in the crystalline Morvan Massif are 172 ± 2.5 Ma (Baubron et al., 1980) and 178.3 ± 5 Ma (Joseph et al., 1973, recalculated using the decay constant of Steiger and Jäger, 1977). Soule de Lafont and Lhégu (1980) propose that the stratabound fluorite

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deposits hosted in Mesozoic carbonate or siliciclastic sediments were also formed during the Early Jurassic because of the occurrence of silicified pebbles in the Hettangian sediments. In the F–Ba Chaillac deposit, an Hettangian syngenetic model has also been suggested by the presence of barite pebbles in barite-cemented Hettangian sandstone (Sizaret et al. 2003). A connection was also proposed by Sizaret et al. (2003, 2004) between the Rossignol vein in the basement and the Redoutières stratiform deposit at Chaillac.

A recent Sm–Nd dating of the Pierre-Perthuis stratabound fluorite deposit indicates an Early Cretaceous age (Gigoux et al., 2015) prompting reconsideration of the syngenetic model suggested by previous studies (Soulé de Lafont and Lhégu, 1980; Davaine, 1980; Nigon, 1988; Sizaret et al., 2009). The nature of the mineralizing fluids and the changing nature of the fluid(s) related to the environmental system over time in the fluorite stratabound-type deposits associated with the unconformity are still poorly constrained, in contrast to the well-defined fluorite vein-type deposits of the French Massif Central. The F–Ba (Pb–Zn) vein-type deposits in the French Massif Central (Sizaret et al., 2004; Cathelineau et al., 2012), Germany (Meyer et al., 2000; Schwinn and Markl, 2005; Dill et al., 2012), Spain (Sanchez et al., 2010; Galindo et al., 1994; Piqué et al., 2008) and England (Gleeson et al., 2001) have been attributed to hydrothermal activity during Jurassic and Cretaceous extensional rift regimes related to the opening of the Tethyan or Atlantic Oceans and involve mineralizing fluids that have similar geochemical characteristics to MVT deposits (Leach et al., 2001). The origin of brines derived from seawater and/or meteoric water within the basement during deep circulation has often been considered as a mixing of two or more fluids leading to the formation of Pb–Zn–F–Ba–U deposits (Boiron et al., 2010). The mineralizing fluids responsible for the genesis of the fluorite vein deposits in western Europe are typically moderately to highly saline, $CaCl_2$–NaCl-rich brines at temperatures in the range of 70–200 °C (Sizaret et al., 2004; Boiron et al., 2010; Sanchez et al., 2010). In contrast to sulfide-rich Pb–Zn MVT deposits, the stratabound fluorite deposits are typically fluorite-rich and sulfide-poor and are hosted in different rock types such as dolomites, limestones, sandstones, and conglomerates. Genetic models for sulfide-rich Pb–Zn MVT deposits suggest that ore fluids were derived mainly from evaporated seawater and were driven within carbonate platforms by large-scale geodynamic events (Leach et al., 2010). The models suggest that low concentration of reduced sulfur sedimentary brines were capable of extracting metals from a variety of rock types, including basement rocks of various compositions, weathered regolith, basal sandstones, and/or carbonate aquifers (Leach et al., 2010). Dill et al. (2012) suggest that the ore fluids in the unconformity-related fluorite vein-type deposits were derived from granitic and gneissic brine sources. The precipitation of hypogene ore minerals, from sedimentary solutions and/or convectively circulating fluids near the unconformity, was due to steep hydraulic and chemical gradients between the basement and its overburden. The aim of this study is to (1) describe and compare the petrographic features of carbonate- and siliciclastic-hosted fluorite deposits in order to better understand stratabound fluorite deposition processes in relation to the nature of host rocks, and (2) determine the nature and temperature of mineralizing fluids in order to better understand the characteristics of fluid migrations leading to massive stratabound fluorite deposition. The comparison of detailed descriptions of mineral assemblages occurring within dolomite, limestone, sandstone, and conglomerate fluorite deposits allows us to highlight the similarities or differences in the replacement/precipitation processes and mineral sequences at the scale of deposits and/or at the regional scale. The microthermometric characterization study of fluid inclusions provides a better understanding of the temperature/salinity regime required for fluorite, barite, and quartz deposition in dolomite, limestone, sandstone, and conglomerate. The microthermometric data at the deposit scale will be included in the global thermal history of the Paris Basin (Uriarte, 1997; Barbarand et al., 2013) to better constrain the origin of the mineralizing fluids. Hence, the diagenetic changes in the type of mineralization in the different deposits over time will be discussed in light of the chemical factors and processes controlling fluorite deposition on the basis of temperature and salinity conditions.

2. Geological settings, stratigraphic and mineralizing framework

In the central part of Burgundy, the Paleozoic Morvan Massif, made of plutonic, metamorphic, sedimentary and volcano-sedimentary rocks, is bounded by Mesozoic sedimentary formations (Figs. 1 and 2). The Morvan Massif is composed of two main granitic batholiths (the Luzy and Settons batholiths). The Luzy batholith in the southern Morvan Massif comprises a granodiorite massif, biotite granite massifs, and two-mica granite massifs (Rolin and Stussi, 1991; Figs. 1 and 2). The Settons batholith is composed of biotite granites and the two-mica granite of Pierre-qui-Vire (Carrat, 1969).

These two batholiths are separated by a synclinal of (1) Tournaisian volcano-sedimentary deposits, (2) Visean lava flow deposits, and (3) microgranite veins (Fig. 1). A third granitic unit that crops out in the northern Morvan Massif is constituted by the two-mica granite of Avallon (Fig. 1). This unit is separated from the Settons batholith by Paleozoic gneisses forming the Chastellux-sur-Cure metamorphic complex (Caillère et al., 1968; Fig. 1). Around the Morvan Massif, six main stratabound fluorite deposits have been previously recognized and are spatially related to the unconformity between the Paleozoic crystalline basement and the Mesozoic sedimentary formation (Soulé de Lafont and Lhégu, 1980; Fig. 2).

In the northwestern part of the Morvan Massif, the Pierre-Perthuis fluorite deposit is located above the two-mica granite basement (Figs. 1, 2, and 3). The main fluorite mineralization forms geodic cavities hosted by the Late Triassic Assise de Chitry Formation, which is a 4–8 m-thick Carnian/Norian dolomite formation (Figs. 2 and 3). The Assise de Chitry Formation is entirely silicified (Fig. 3). The upper part of the well-preserved two-mica granite is overlain by altered granite varying from 50 cm to 3 m in thickness with decimeter-scale strata of black microquartz vein (Fig. 3). Core drills display numerous karstic cavities filled by fluorite and barite (Soulé de Lafont and Lhégu, 1980). The deposit is divided into two areas by the Cure river valley: (1) Bois de l'Epenay (0.23 km^2) and (2) Bois Dampierre (0.25 km^2; Fig. 4A). The Pierre-Perthuis fluorite reserves are estimated at 1.4 million tons (Soulé de Lafont and Lhégu, 1980). Adding the 0.6 million tons of fluorite of the Pontaubert deposit makes the northwestern part of the Morvan Massif the most important in terms of fluorite tonnage with 2 million tons. The Pierre-Perthuis fluorite deposit is located near the Fontaines Salées thermo-mineral springs (Fig. 4A), which emerge along a NE–SW transverse fault that intersects the N–S Pierre-Perthuis fault (Fig. 4A, Risler, 1974).

The Marigny-sur-Yonne fluorite deposit, 20 km south of the Pierre-Perthuis deposit, has been studied in detail with samples from the Toyot quarry (Fig. 4B). In terms of fluorite tonnage, the Marigny-sur-Yonne deposit is one of the major fluorite deposits (0.5 million tons) along the western edge of the Morvan Massif with the Egreuil deposits (0.4 million tons; Soulé de Lafont and Lhégu, 1980). It is located near a N–S fault where the Paleozoic basement to the west and the Pliensbachian sedimentary formations are in contact (Soulé de Lafont and Lhégu, 1980, Fig. 4B). The fault offset is about 50 m (Soulé de Lafont and Lhégu, 1980). In the ancient Toyot quarry, the 3–4 m-thick Assise de Chitry Formation exhibits intense silicification and mineralization in fluorite, filling geodic and karstic cavities up to several meters in size (Lhégu, 1978; Soulé de Lafont and Lhégu, 1980). The fluorite contents can reach about 60% in these large cavities. The Toyot quarry produced about 10,000 tons of fluorite during the twentieth century (Soulé de Lafont and Lhégu, 1980; Gourault, 1999). The basement is composed mainly of rhyolitic rocks (Fig. 2). Some 4 km south of the Marigny-sur-Yonne deposit, the Chitry-les-Mines deposit has also been studied with samples taken from the Mézière-Chaumot quarry. This deposit produced 30,000 tons of galena and sphalerite and tens of tons of silver during the