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# Mesozoic fluorite veins in NE Spain record regional base metal-rich brine circulation through basin and basement during extensional events

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#### ABSTRACT

Basinal brines are commonly involved in the formation of hydrothermal base metal ore deposits in sedimentary basins, although in many instances, the source of metals is often thought to be the underlying basement rocks. The evidence of brine infiltration through the basement is sometimes directly found in vein systems in fracture zones crosscutting the basement. That is the case of the fluorite-barite-base metal veins found throughout the Hercynian basement of Europe, North Africa and the Appalachians. A geochemical study of brines trapped in these veins can reveal their origin and evolution, but also their mineralizing potential, and coupled with the timing of fluid circulation, can give clues to elucidate the role of these, or similar brines in the genesis of base metal mineralizations, together with their possible links to tectonic events. The Sm-Nd dating of fluorite samples from one of these veins in NE Spain, the Rigròs fluorite vein, has yielded an age of  $137 \pm 25$  Ma  $(2\sigma)$  (MSWD=0.40). The vein formation took place during the Late Jurassic-Early Cretaceous rifting event in the western European basins, which is related to the opening of the Atlantic. Inclusion fluids in samples from Rigros and another vein system from the same region, the Berta fluorite vein, have been studied with microthermometry, crush-leach and LA-ICP-MS. The brines trapped in the two studied vein systems are Na-Ca-Cl-(K-Mg) brines, with homogenization temperatures ~120 °C and salinities up to 25 equiv. mass % NaCl. The source of this salinity is related to evaporated seawater, at least in the halite precipitation field, and to the leaching of Mesozoic halite and gypsum sequences by seawater and/ or meteoric water. The basinal brines later evolved through water-rock interaction with the crystalline basement, resulting in some sodium loss and potassium, calcium, strontium (the latter inferred from isotope data) and barium enrichment. The analyzed brines have concentrations of Zn between 3 and 790 ppm, of Pb between 3 and 995 ppm and of Fe between 27 and 2639 ppm, which are similar to those reported in comparable hydrothermal veins and Mississippi Valley-type deposits, but higher than in most present-day sedimentary brines. Despite the fact they were able to transport large amounts of metals, no significant precipitation of sulfides occurred in the veins and, consequently, the mineralizing potential of these brines was still preserved after fluorite vein formation.

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#### 1. Introduction

During extensional events, the downward penetration of surface fluids into basement rocks may occur along fault zones (e.g. Oliver et al., 2006). These fluids can leach metals from the basement and transport them, leading later to the formation of hydrothermal ore deposits in the basement and/or the overlying cover sequences. In fact, many hydrothermal ore deposits from sedimentary basins have isotopic and geochemical signatures that point to an involvement of basement rocks, particularly as a source of metals (e.g. Shelton et al., 1995). However, few data exist on base metal content in brines after leaching the basement. One example of ore deposit genetically related to the basement fluid flow is the low temperature fluorite–barite-base metal vein type, widespread throughout the Paleozoic basement of Western and Central Europe, North Africa and the Appalachians (e.g. Jébrak, 1984; Behr et al., 1987; Jébrak et al., 1988; Lhégu et al., 1988; Cardellach et al., 1990; Tornos et al., 1991, 2000; Zák et al., 1991; Boni et al., 1992; Carignan et al., 1997). The genesis of these ores, despite being mainly hosted in Paleozoic materials, has been generally related to the circulation of fluids during Mesozoic extensional events (e.g. Canals and Cardellach, 1993; Galindo et al., 1994; Meyer et al., 2000; Munoz et al., 2005), which are in turn related to the opening of the Atlantic (Ziegler, 1988; Hiscott et al., 1990).

This paper deals with two outstanding fluorite vein systems from NE Spain (Rigròs and Berta), which recorded this regional fluid event during the opening of the Atlantic. Although they are enclosed within

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Paleozoic granitic materials, their genesis has been linked to the circulation of basinal brines (e.g. Cardellach et al., 1990, 2002). The geochemistry of the fluids trapped in these veins can give valuable information regarding the origin of the solutes, circulation paths, water–rock interaction processes and mineralizing potential of basinal brines, evolved during the circulation through the Paleozoic basement. Furthermore, the flow of base metal-bearing fluids can be linked to tectonic events and can help to elucidate the fluid evolution of basins and their relationship with mineralizing processes. The aim of this paper is to shed some light on these processes, by means of a detailed geochemical study of the fluids trapped in the Rigròs and Berta vein systems, which includes microthermometry, crush-leach and LA-ICP-MS analysis of fluid inclusions, together with Sr isotope analysis of ore phases and a Sm–Nd dating of the Rigròs vein system.

Rigròs and Berta fluorite vein systems were selected for this study because: (1) they belong to a type of vein which is widespread throughout Western and Central Europe; (2) they are both hosted in Paleozoic crystalline rocks (Canals, 1989a,b; Cardellach et al., 2002), therefore, the fluids involved in the formation of both veins had some interaction with the basement; (3) at the time of vein formation (Mesozoic; Canals and Cardellach, 1993), a sedimentary basin was developing over the basement (Salas et al., 2001); and (4) they share similar vein mineralogy, microthermometric and isotopic (S, Sr, Pb) data (Canals, 1989a,b; Canals and Cardellach 1993, 1997; Cardellach et al., 2002), which makes them comparable to each other. Although these vein systems are relatively small, their study can provide clues to understanding other economically more important ores. These veins are located in the Catalan Coastal Ranges (CCR; Fig. 1), which host many deposits of this type (e.g. Cardellach et al., 1990). The Rigròs fluorite-(barite) vein system is located in the Montseny-Guilleries Massif (northern CCR), together with other veins such as Osor, Espinelves and Tagamanent (Fig. 1). The Rigròs mineralogy was first reported by Font (1983) and Canals (1989a,b) and the fluid chemistry by Canals (1989a,b) and Canals and Cardellach (1993, 1997). The original fluorite stock was estimated at 3.5 to 4 Mt at 40-50% CaF<sub>2</sub> (Font, 1983) and fluorite mining in the area was active until the late

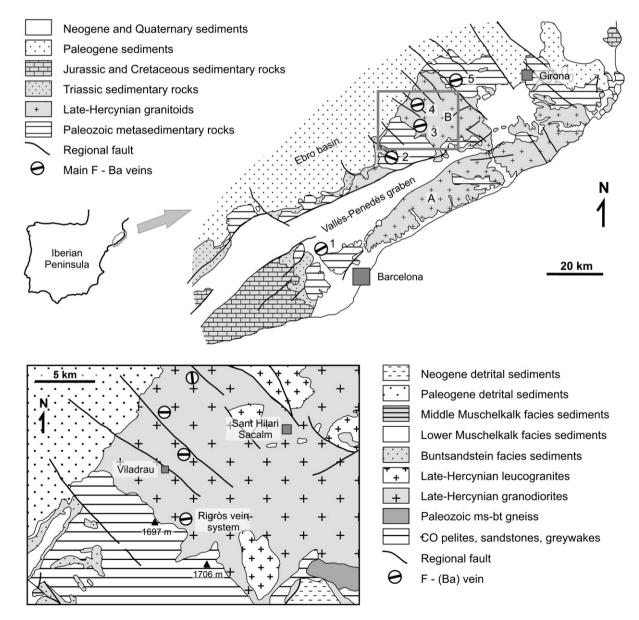


Fig. 1. Geological map of northern and central Catalan Coastal Ranges (NE Spain), together with locations of the main fluorite-barite vein systems. (A) Montnegre Massif. (B) Montseny-Guilleries Massif. (1) Berta; (2) Tagamanent; (3) Rigròs; (4) Espinelves; and (5) Osor vein systems. The enlargement shows the local geology of the area where the Rigròs vein system is located.

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