



## Variability in fluid sources in the fluorite deposits from Asturias (N Spain): Further evidences from REE, radiogenic (Sr, Sm, Nd) and stable (S, C, O) isotope data

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### ABSTRACT

Fluorite deposits in Asturias (Iberian Peninsula, N Spain) are hosted in Permo-Triassic and Paleozoic rocks. The three main districts of Berbes, La Collada and Villabona preferentially occur along the margins of a Mesozoic basin and comprise veins and stratabound mineralization composed of fluorite, barite, calcite, dolomite, quartz and sulphides. Although the geological framework is similar and fluorite dominates in all deposits, variability in sources and processes has led to each area having its own distinctive characteristics. Sr isotope data of fluorite, calcite and barite ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7080$  to  $0.7105$ ) are compatible with a mixing between seawater and an evolved groundwater that interacted with basement rocks. Sm/Nd ratios in fluorites from Villabona district provide an isochron age of  $185 \pm 28$  Ma (Late Triassic–Late Jurassic), consistent with other hydrothermal events in the Iberian Peninsula and Europe. The total REE content of fluorite increases from Berbes to Villabona by an order of magnitude (0.4 to 9.3). The La/Lu ratio in fluorites decreases from a mean value of 0.36 in Berbes, 0.17 in La Collada to 0.09 in Villabona indicating a strong fractionation between LREE and HREE.

Calculated  $\delta^{18}\text{O}$  of fluids ranges from 0.3 to +7.4‰ during barite precipitation, from +0.8 to +4‰ during quartz formation and around +3‰ during carbonate deposition. The  $\delta^{34}\text{S}$  of barite (+17 to +56‰), is explained by sulphate reduction processes (either thermochemically or bacterially mediated) in a system closed with respect to sulphate. The  $\delta^{34}\text{S}$  of sulphide (+0.6 to –32‰) is compatible with these processes although bacterial processes must have dominated at Villabona. Organic matter was an important source of C in the fluids especially in Villabona ( $\delta^{13}\text{C} = -14.8$  to  $-2.5$ ‰ in calcites and from  $-7.9$  to  $-2.2$ ‰ in dolomites). Differences in host rock and position within the basin, and the lithology of the basement, seem to have exerted a strong control on the chemistry of mineralizing fluids providing each district with distinctive characteristics.

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### 1. Introduction

Asturias is one of the most important fluorite producing regions in Europe. Mining started in the 1930's, with the most important activity in the 1960's. More than 15 Mt. of ore has been produced and mining continues today. The most important active deposits are found in three districts: Berbes, La Collada and Villabona (Fig. 1). Mineralization is typically fluorite-rich and sulphide-poor and shares characteristics with MVT deposits. Similar examples are found widespread in Europe, e.g., the Massif Central of France (Sizaret et al., 2004; Munoz et al., 2005), the Hercynian massifs of Germany (Behr et al., 1987; Behr and Gerler, 1987; Lüders and Möller, 1992; Schwinn et al., 2006),

Spain (Canals and Cardellach, 1993; Galindo et al., 1994; Tornos et al., 2000; Cardellach et al., 2007; Piqué et al., 2008) and the Northern Pennines in England (Sawkins, 1966; Dunham, 1988; Cann and Banks, 2001).

The deposits preferentially occur along the margins of a Mesozoic basin which unconformably overlies Paleozoic and Precambrian basement rocks. Fluorite mineralization occurs as vein and stratabound bodies in highly silicified Permo-Triassic red-bed sediments (marls and sandstones) and carbonates, and as veins within limestones of the Paleozoic basement. Previous studies focused on the geological, mineralogical and geochemical (fluid inclusion studies) aspects of these mineralizations (García Iglesias and Touray, 1976, 1977; García Iglesias, 1978; Loredó and García Iglesias, 1984; García Iglesias and Loredó, 1992, 1994). García Iglesias and Loredó (1994) suggested that a possible source of F is the volcanic rocks (trachyandesites) outcropping in the depocenter of the Permo-

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