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## Temporal constraints on genesis of the Caravia-Berbes fluorite deposits of Asturias, Spain, from paleomagnetism



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#### ABSTRACT

The Caravia-Berbes district is a major fluorite producing area in Europe. The fluorite occurs as mantos replacing breccio-conglomerates of the Middle Permian Caravia Formation and as veins and irregular replacive bodies in the unconformably underlying limestone of the Late Carboniferous Caliza de Montaña Formation. Paleomagnetic analyses were done using alternating field and thermal step demagnetization and saturation remanence methods. Ten sites (82 specimens) in massive and disseminated fluorite ore from the Emilio manto yielded a stable chemical remanent magnetization (CRM) in hematite inclusions with a direction of Decl. 20.1°. Incl. 67.3°  $(\alpha_{95} = 6.1^{\circ})$ . After correction for Neogene Pyrenean tilt, the manto's paleoinclination gives a CRM acquisition age of 206  $\pm$  8 Ma that dates a major hydrothermal and ore emplacement event. The age is coeval with the onset of Pangea's break up as the Iberian microplate began to split from the Armorican terrane of Eurasia as part of the ocean-forming CAMP (Central Atlantic Magmatic Province) event. Another 11 sites (109 specimens) of silicified dolostone of the Caliza de Montaña Formation just below the Cueto L'Aspa manto yielded a stable CRM that resides in single and pseudosingle domain magnetite inclusions that has a direction of Decl. 328.7°, Incl. 76.6° ( $\alpha_{95} = 4.9^{\circ}$ ). After Neogene tilt correction, the altered zone's paleopole gives a CRM acquisition age of 115  $\pm$  3 Ma. This age shows that the western Cantabrian basin also underwent a major hydrothermal alteration and remagnetization event by fluid flow through steep re-activated faults when Iberia rotated  $35 \pm 2^\circ$ away from Eurasia during Aptian-Albian time.

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#### 1. Introduction

Asturias is a major region of fluorite production in Europe, yielding > 140000 t/yr (Fig. 1). Its three main mining districts are Caravia-Berbes, La Collada and Villabona that have yielded >15 Mt of ore (Martínez García, 1983; Sánchez et al., 2009). Most of this ore has been stratabound in Permian calcareous breccio-conglomerates that rest either unconformably on the underlying Carboniferous basement or a few meters stratigraphically above the basement (Fig. 2A, B). Minor amounts of fluorite have also been mined from veins in faults that cross-cut both the unconformity surface and ore horizon (Fig. 2C). Here we report paleomagnetic results from the large stratabound Emilio deposit being mined by MINERSA and a fluorite-bearing dolomitic alteration zone in the mid-Carboniferous Caliza de Montaña limestone basement of the Caravia-Berbes district (Fig. 2).

In general, fluorite deposits can be formed by a variety of genetic processes in a range of tectonic settings. However, two styles of

\* Corresponding author. *E-mail address:* kkawasak@sci.u-toyama.ac.jp (K. Kawasaki). mineralization are most common: 1) deposits in sedimentary rocks, mostly carbonates, with characteristics akin to Mississippi Valley-type (MVT) Zn-Pb-Ba deposits; and, 2) deposits in veins associated with alkaline-peralkaline igneous activity. Early geological studies of the Caravia-Berbes deposits led to both syngenetic and epigenetic origins being suggested for their genesis (Tejerina and Zorrilla, 1980; Fernández, 1995). Recently Sánchez et al. (2010), based on geochemical evidence from the ore minerals and fluid inclusions, suggested that the ores were formed when ascending hot reduced Paleozoic connate brines mixed with descending oxygenated Mesozoic meteoric seawater. This model is similar to that proposed for other fluorite deposits in Iberia's Variscan belt (Tornos et al., 1991; Galindo et al., 1994; Johnson et al., 1996). Based on a Sm/Nd fluorite isochron age of 185  $\pm$  28 Ma from Villabona some 50 km to the west (Fig. 1), Sánchez et al. (2010) speculated that the Caravia-Berbes fluorite deposits were Late Triassic-Late Jurassic in age because none of these deposits have been dated radiometrically although they tried to do so using the Sm/Nd method. This paleomagnetic study was undertaken to try to date the genesis of these fluorite deposits and to tie them more closely to the post-Carboniferous tectonic evolution of the region.



Fig. 1. Generalized geological map of the Cantabrian Zone of northern Spain (modified from Julivert, 1971, Pérez-Estaún et al., 1988, Alonso et al., 1992). The Caravia-Berbes fluorite deposits occur at the contact between the Stephanian and overlying Permian strata.

Paleomagnetic methods have proven to be an effective tool for studying the genesis of fluorite mineralization. In the Illinois-Kentucky (Cave-in-Rock) district, geological relationships show that both the strataform manto and vein ores postdate both deformation of the Mississippian host rocks and intrusion of Early Permian (285-250 Ma) alkali ultramafic dikes, sills and plugs (Grogan and Bradbury, 1968). Curiously, Sm/Nd fluorite dating gives an inconsistent age of 272  $\pm$ 17 Ma (Chesley et al., 1994), whereas both fluorite fission-track dating and paleomagnetism give consistent earliest Cretaceous and Late Jurassic ages, respectively (Symons, 1994). At St. Lawrence, Newfoundland, fluorite occurs in two intersecting vein sets in the 374 + 2 Ma St. Lawrence granite. The fluorite failed to give a tenable Sm/Nd fluorite age. However, paleomagnetic methods have dated fluorite emplacement at  $316 \pm 8$  Ma during the Acadian orogeny (Kawasaki and Symons, 2008). Further, a score of MVT and sedimentary exhalative (SEDEX) ore deposits that are kindred geologically to the Caravia-Berbes fluorite deposits have been successfully dated using paleomagnetic methods (Leach et al., 2001, 2010; Kawasaki et al., 2010).

#### 2. Geology

#### 2.1. Pre-Permian basement

The Caravia-Berbes fluorite district is located on Iberia's northern coastline in the Cantabrian Zone (Figs. 1, 2). This zone bounds the Variscan Orogen in northern Spain that forms the core of the Iberian-Armorican Arc. This orogen was born when Gondwana and Laurasia closed the Rheic Ocean during the Devonian-Carboniferous and then collided (Merino-Tomé et al., 2009; Pastor-Galán et al., 2014). The Cantabrian Zone contains Lower Cambrian to Lower Ordovician and Late Devonian to Late Carboniferous strata (Zamarreño and Julivert, 1967; Alvarez-Marrón and Perez-Estaún, 1988). These strata were intensely deformed during the latest Carboniferous-earliest Permian Variscan orogeny by thrust faulting and nappe folding. The deformation caused imbrication, very low-grade metamorphism and complex oroclinal rotation of the originally linear collisional belt (Colmenero et al., 2008; Weil et al., 2010, 2013; Pastor-Galán et al., 2013, 2014,

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