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Rare earth elements (REE)—Minerals in the Silius fluorite vein system (Sardinia, Italy)

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ABSTRACT

The Silius vein system, located in SE Sardinia (Italy) is analogous to other late- to post-Hercynian mineral systems of this type in Europe. The Silius system consists of two main veins, characterized by several generations of fluorite, calcite and quartz, with initial ribbon-like geometries, followed by breccias and cockade-like textures. In this study, aimed at investigating the REE concentrations in the Silius vein system, a REE average of ~800 ppm (locally ΣREE > 1500 ppm) has been observed in the carbonate gangue of the fluorite orebody. These amounts are related to the presence of the REE-bearing minerals synchysite-(Ce) and xenotime-(Y). The chemical composition of synchysite-(Ce) has been obtained by wavelength dispersive spectrometry (WDS). The average synchysite-(Ce) formula, built on the basis of $(CO_3)_2F$ and 5 negative charges, is $Ca_{1.07}(La_{0.19},Ce_{0.36},Pr_{0.04},Nd_{0.15},Sm_{0.03},Gd_{0.03},Y_{0.13})(CO_3)_2F$. From their geochemical characteristics, and their textural relationships with other gangue phases, it is likely that synchysite-(Ce) and xenotime-(Y) formed at the same P-T-*X* conditions as the other minerals of the Silius fluorite mineralization. Synchysite-(Ce) and xenotime-(Y) at Silius could be related to a local circulation phenomenon, where the REE are derived from a REE-bearing source rock in the basement of southeastern Sardinia, which has been leached by the same fluids precipitating the fluorite/calcite mineralization. REE concentrations contained in the carbonate gangue of still unexploited parts of the Silius vein deposit, as well as in dumps and tailings accumulated during past fluorite processing, could possibly represent a sub-economic by-product of the fluorite exploitation.

1. Introduction

Rare Earth Element (REE)-bearing minerals occur in many igneous, sedimentary, and metamorphic rocks, where they may be concentrated in ore deposits both related to igneous and hydrothermal processes, or associated with sedimentary environments and weathering (Chakhmouradian and Wall, 2012). REE-rich ores in carbonatites and peralkaline igneous rocks can be directly derived from magmatic processes, but also from metasomatism and hydrothermal remobilization of magmatic REE minerals (Chakhmouradian and Zaitsev, 2012; Gysi and Williams-Jones, 2013). Other REE-bearing mineral deposits can be associated with hydrothermal quartz- and fluorite-bearing veins of orthomagmatic derivation (Samson et al., 2004; Williams-Jones et al., 2000). Typical weathering-related REE-mineral concentrations occur in placers, and in laterite caps and ion-absorption clay deposits (Chakhmouradian and Wall, 2012).

REE concentrations have been also detected in several fluorite vein systems, not directly related to magmatism, occurring in the Hercynian basement of Europe. Hercynian fluorite vein systems were emplaced in the basement rocks between late Paleozoic and early Mesozoic, as a consequence of far-field tectonics (e.g. continental extension) associated with the initial opening of the Atlantic Ocean, and circulation of brines within the basement (Muchez et al., 2005; Muñoz et al., 1999, 2005). To date, REE analyses of these Paleozoic-Mesozoic systems have largely focused at defining their occurrence and content in fluorite, caused by ion-substitution processes (Dill et al., 2011; Möller, 1991; Möller et al., 1976, 1994; Möller and Giese, 1997; Schwinn and Markl, 2005). Several studies, carried out on fluorite veins in south Germany (e.g. Harz Mountains, Schwarzwald, Bohemian Massif), revealed that the measured REE concentrations are associated with the occurrence of specific REE minerals (e.g. Dill et al., 2011; Gieré, 1996, and references therein; Haack et al., 1987; von Gehlen et al., 1986). Comparable research was also carried out on Triassic-Jurassic fluorite deposits in the Hercynian terrains of northern Africa (Bouabdellah et al., 2010; Cheilletz et al., 2010).

We present here the results of an investigation aimed at evaluating the REE behavior and fractionation in the Silius fluorite vein system, located in SE Sardinia, Italy. The Silius system is analogous to other

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late- to post-Hercynian mineralization of this type in Europe (Boni et al., 2009; Natale, 1969). Fluorite and galena reserves were evaluated at 2 million tons of raw material in 2006 (Castorina et al., 2008), when mining operations ceased, but a new exploration campaign has been recently carried out, to find new fluorite resources. The REE contents in the Silius fluorite ore had been already reported by Castorina et al. (2008), in relation to a more general study on the different types of fluorite deposits in Sardinia. These authors used the REE content in fluorite to distinguish between the different hydrothermal F-ore deposits in Sardinia, and compared their data with the REE contents of other Hercynian fluorite mineralizations in Europe.

As for other classical studies on European fluorite deposits (e.g. Dill et al., 2011), we have re-evaluated the REE amounts contained in both fluorite and host rock. Moreover, we have also carried out a thorough mineralogical research on the various gangue components of the vein system. The results of this study, aside from obtaining new data on the nature of the REE minerals in the Silius veins, have shed new light on the characteristics of this kind of fluorite ore and its gangue.

2. Geological setting

2.1. Regional geology

The Sardinia-Corsica Paleozoic basement represents a fragment of the Hercynian orogen (Arthaud and Matte, 1977; Carmignani et al., 1994; Crowley et al., 2000) that can be subdivided into three tectono-metamorphic zones (Fig. 1A): i) a "foreland zone", outcropping in southwestern Sardinia, with low-grade or no metamorphism, ii) a "nappe-zone", in southeastern and central parts of Sardinia, affected by low- to medium-grade metamorphism, and iii) an "inner zone", in northern Sardinia, characterized by medium- to high-grade metamorphic signatures (Carmignani et al., 2001).

The "external zone" successions (SW Sardinia), spanning in age from early Cambrian to Devonian and Carboniferous, are represented by clastic and carbonate, mainly shallow water sedimentary rocks (Bechstädt and Boni, 1994; Carmignani et al., 2001).

The "nappe-zone" area, where the Silius mineralization is located, is characterized by various lithotypes (Fig. 1B). The upper Cambrian-Ordovician successions mostly consist of siliciclastics (metasandstones, phyllites and quartzites), collectively grouped in the "Arenarie di San Vito" (Fig. 1B) and "Solanas" Formations (not outcropping in the study area). These Formations are overlain by the so-called "Ordovician magmatic and volcano-sedimentary complex" (Carmignani et al., 2001), which consists of both effusive and intrusive igneous products, displaying an almost complete arc-related calc-alkaline suite of middle to late Ordovician age (Gaggero et al., 2012; Oggiano et al., 2010). In the Silius area the Ordovician volcano-sedimentary complex, named "Porfiroidi" Formation (Fig. 1B), is represented by rare andesitic lavas and abundant metasediments derived from the reworking of the former, overlain by metarhyolites and metarhyodacites (Carmignani et al., 1994). The Ordovician magmatic and volcano-sedimentary complex is unconformably overlain by siliciclastic continental to neritic sediments, which were deposited during a period of active intraplate magmatism, resulting in alkali basalt flows, sills and dykes (late Ordovician-Silurian) (Gaggero et al., 2012; Oggiano et al., 2010) (Fig. 1B). In the Silurian to Devonian period, the magmatic activity stopped and pelagic sediments (Graptolitic Shales, or "Formazione degli Scisti a Graptoliti") were deposited (Fig. 1B). These consist of

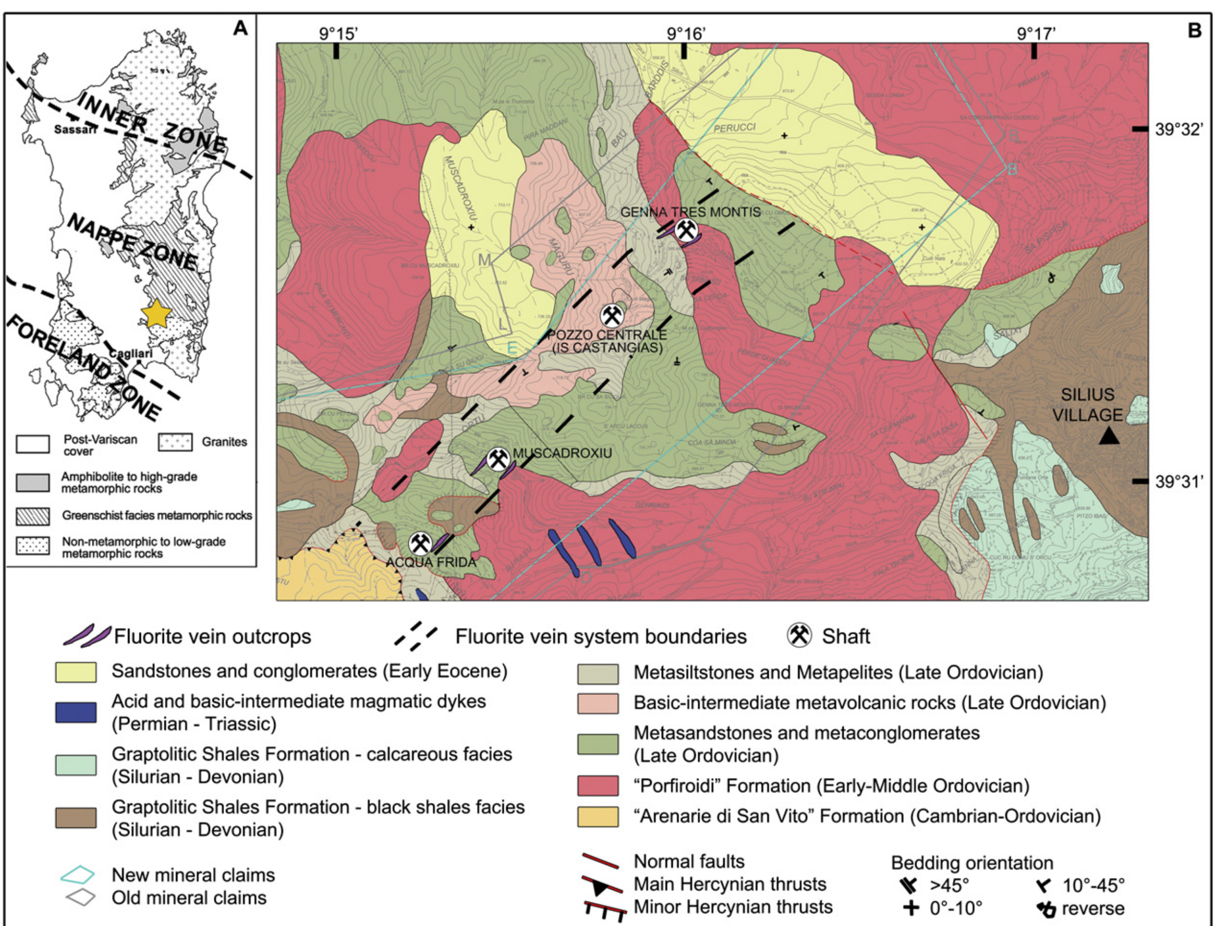

Fig. 1. A) Major tectonic and metamorphic zones of the Hercynian basement in Sardinia (Italy) (Carmignani et al., 2001, modified); yellow star = Silius area. B) Geological sketch map of the Silius area (Nuova Mineraria Silius s.p.a., modified).