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Rare earth elements, S and Sr isotopes and origin of barite from Bahariya Oasis, Egypt: Implication for the origin of host iron ores

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ABSTRACT

Based on their occurrences and relation to the host iron ores, barites are classified into: (1) fragmented barite occurs as pebble to sand-size white to yellowish white barite along the unconformity between the Bahariya Formation and iron ores, (2) interstitial barite is present as pockets and lenses of large and pure crystals inside the iron ores interstitial barite inside the iron ores, and (3) disseminated barite occurs at the top of the iron ores of relatively large crystals of barite embedded in hematite and goethite matrix. In the current study, these barites have been analyzed for their rare earth elements (REE) as well as strontium and sulfur isotopes to assess their source and origin as well as the origin of host iron ores.

Barite samples from the three types are characterized by low ΣREE contents ranging between 12 and 21 ppm. Disseminated barite shows relatively lower ΣREE contents (12 ppm) compared to the fragmented (19 ppm) and interstitial (21 ppm) barites. This is probably due to the relatively higher Fe_2O_3 in the disseminated barite that might dilute its ΣREE content. Chondrite-normalized REE patterns for the three barite mineralizations exhibit enrichment of light rare earth elements (LREE) relative to heavy rare earth elements (HREE) as shown by the high $(La/Yb)_N$ ratios that range between 14 and 45 as well as pronounced negative Ce anomalies varying between 0.03 and 0.18. The $^{87}Sr/^{86}Sr$ ratios in the analyzed samples vary between 0.707422 and 0.712237. These $^{87}Sr/^{86}Sr$ values are higher than the $^{87}Sr/^{86}Sr$ ratios of the seawater at the time of barite formation (Middle Eocene with $^{87}Sr/^{86}Sr$ ratios of 0.70773 to 0.70778) suggesting a contribution of hydrothermal fluid of high Sr isotope ratios. The $\delta^{34}S$ values in the analyzed barites range between 14.39‰ and 18.92‰. The lower $\delta^{34}S$ ratios in the studied barites compared with those of the seawater at the time of barite formation (Middle Eocene with $\delta^{34}S$ ratios of 20–22‰) is attributed to a possible contribution of hydrothermal fluid of low $\delta^{34}S$ values that lowered the $\delta^{34}S$ values in the studied barites.

Rare earth elements distribution and patterns, as well as strontium and sulfur isotopes suggest a mixing of seawater and a hydrothermal fluid as possible sources for barite mineralizations in the Bahariya Oasis. The seawater source is suggested from the low Ce/La ratios, "V" shape of the rare earth patterns and pronounced negative Ce anomalies. On the other hand, the hydrothermal fluid contribution is evident from the low concentrations of rare earth and the deviation in both S and Sr isotopic compositions from those of the seawater during the time of barites formation (Middle Eocene). The relatively heterogeneous Sr and S isotope ratios among the studied barites suggest the Bahariya Formation and Basement Complex as possible sources of the hydrothermal fluids. The similarity in the REE as well as S and Sr isotopic compositions of the three types of barite suggest that they form simultaneously.

As the geology and occurrence of the barites suggest a genetic relationship between these barites and the host iron ores, the mixed seawater and hydrothermal sources model of the barites is still applicable for the source of the host iron ores.

1. Introduction

Barite is widespread in hydrothermal deposits of diverse geological settings and fluid sources, including magmatic (Williams-Jones et al., 2000), metamorphic (Hanor, 2000), or sedimentary basinal hydrothermal fluids (Kontak et al., 2006), as well as ancient and modern oceanic water (Monnin and Cividini, 2006). Barite-bearing deposits form in a variety of ways: fluid-cooling (Pfaff et al., 2010), mixing of two or more fluids (Valenza et al., 2000), intense fluid–rock interaction (Marchev et al., 2002), or bacterial processes (Pfaff et al., 2010).

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Strontium and sulfur isotopes have been widely used to examine the source and origin of barite and differentiate between barites of different origins (e.g., Valenza et al., 2000; Marchev et al., 2002; Scotney et al., 2005; Wagner et al., 2005; Marchev and Moritz, 2006; Schwinn et al., 2006). Using the two isotopes systems (Sr and S isotopes) should help to distinguish between different fluid sources, and obtain information about changes in the fluid composition, transport and precipitation mechanisms. Fluid inclusions analysis (e.g., Luders et al., 2001; Gültekin et al., 2003; Bozkaya, 2009) and rare earth elements geochemistry (e.g., Guichard et al., 1979) were also used to examine the source and origin of barite but in less extensive compared to the strontium and sulfur isotopes.

Several deposits of iron ores are located in Bahariya Oasis, Egypt, in El Harra, El Heiz, Ghorabi, El Gedida, and Nasser areas. Nakhla and Shehata (1967) classified these iron ores into four types; (i) pisolitic ores, (ii) hard goethitic ores, (iii) soft ores with relatively high Mn contents, and (iv) ochreous ore. Due to their geological and economic importance, the genesis of these ores has been a matter of scientific discussions for a long time. The origin of these ores is controversial and includes epigenetic-supergene (e.g. El Shazly, 1962; Dabous, 2002), to epigenetic-hypogene (e.g. Nakhla, 1961; Basta and Amer, 1969), volcanogenic (e.g. Tosson and Saad, 1974), hydrothermal-metasomatic (e.g. El Sharkawi et al. (1984), karstification of the pre-existing limestone (e.g., El Aref and Lotfy, 1985), hydrogeneous (e.g., Baioumy et al., 2013), and mixed hydrogeneous and hydrothermal (e.g., Baioumy et al., 2014) origins.

Origin of barite in these iron ores is also the debatable due to its occurrence in some ores (e.g., El Gedida ores) and absence from other ores as well as a source of high barium and sulfur required to precipitate barite in these ores. In addition, no systematic investigations have been performed to examine the origin of these barite mineralizations and their genetic relationship with the host iron ores. Therefore, this work was designed to utilize the geology, rare earth elements geochemistry and S and Sr isotopic signatures of the barite mineralizations from the iron ores of the Bahariya Oasis to examine their source and origin. The origin and source of these barite mineralizations were also used to discuss the possible origin of the host iron ores.

2. Geology and stratigraphy of the barite-bearing iron ores

The Bahariya Oasis is a large depression in the Western Desert of Egypt located about 270 km SW of Cairo (Fig. 1A). Within the depression, the Lower Cenomanian fluviomarine sandstone of the Sabaya Formation (Morsy, 1987) is covered by the sandstone, shales and glauconite of the Lower Cenomanian Bahariya Formation (Soliman and El Badry, 1980). The Bahariya Formation is unconformably overlain by the Upper Cenomanian fluviomarine shale, dolomitic limestone and calcareous sandstone of El the Heiz Formation as well as by the Campanian cherty dolostone, cross-bedded sandstone and phosphatic limestone of the El Haufhuf Formation (Morsy, 1987). The succeeding chalk of the Maastrichtian Khoman Formation overlies conformably El Haufhuf Formation and extends southward with increasing thickness. The Eocene rocks are represented by the limestone of the Lower Eocene Qalamoun Formation (El Shazly, 1962), and the gray and pink crystalline limestone of the Middle Eocene Naqb Qazzun Formation (El Bassyony, 2005). The sandstone, quartzites, shale and silt of the Oligocene Qatrani Formation cover the Bahariya Formation at the top of the conical hills (Morsy, 1987). North of Gebel El Haufhuf, the Oligo-Miocene basaltic and doleritic extrusions are recorded (Meneisy and El Kaleubi, 1975).

Economic sedimentary iron ores with an average of 47.6 wt.% Fe (Said, 1990) occur in the northern part of the Bahariya depression

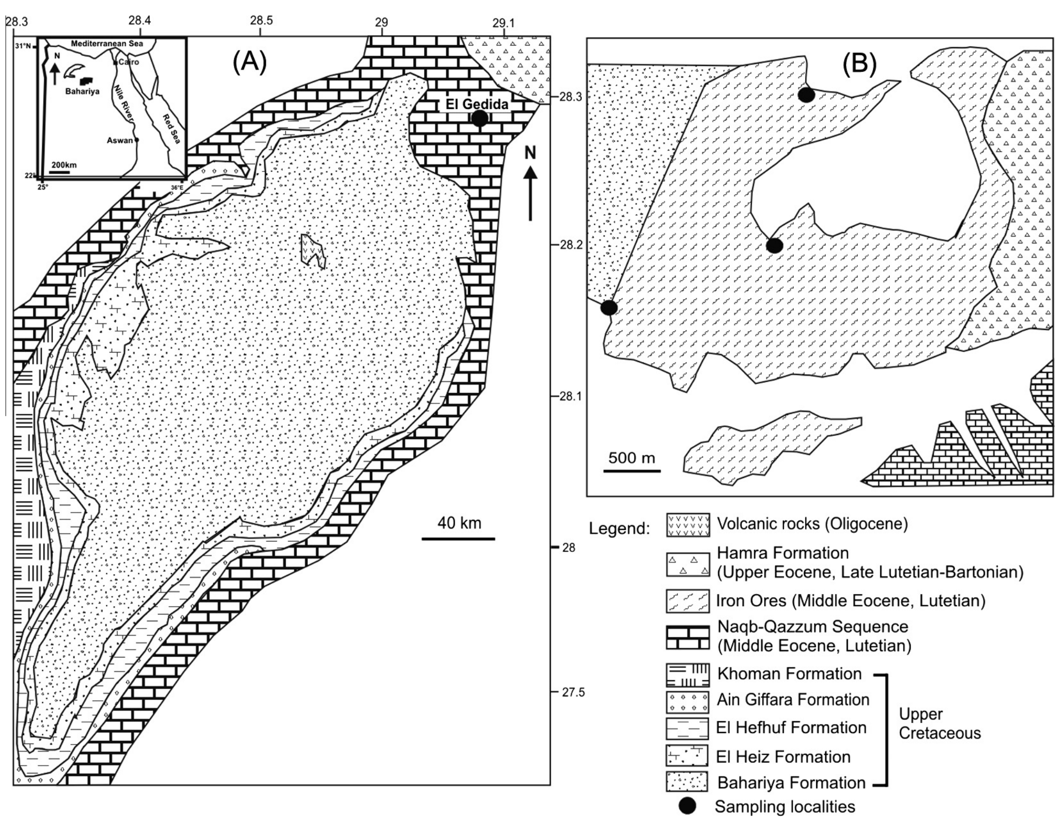

Fig. 1. (A) Generalized geological map of the Bahariya Oasis, Western Desert, Egypt with the location of the studied iron ores (from Catuneanu et al., 2006). (B) Detailed geological map of El Gedida iron ores mine (from El Aref et al., 1999).