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Trace Element Geochemistry of Devonian Strata in the Shizhuyuan Ore District, Hunan Province

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1 Introduction

Both the Qiziqiao Formation and Shetianqiao Formation, which controls the occurrence and distribution of a great deal of metal mineral resources, are extensively developed in southern Hunan province (Liu et al., 1998), showing quite important indicative significance to deep concealed metal mineral resources (Yu et al., 2003).

The geochemistry characteristics of Devonian strata could not affect the spatial occurrence shape of orebody (Wang et al., 2014; Zhai et al., 2014), but also determined the reserve of W-Sn-Mo-Bi polymetallic mineral resources (Li et al., 2011; Zaw et al., 2014). Especially，the surrounding rock is one of the important clues to the deep geological prospecting, and it is essential to study the geochemistry of the Qiziqiao Formation and Shetianqiao Formation.

In southern Hunan province, the Qiziqiao Formation can be divided into four types of lithological association sequences (Lu et al., 2003), including limestone-dolomite, argillaceous limestone-marl, dolomite and limestone, among which the limestone-dolomite lithological association is most widely distributed, such as Daoxian and Linwu. And, the argillaceous limestone-marl lithological association mainly occurred in Xintian and Lingling with zonal distribution; the dolomite distributed in the border between Hunan and Guangxi; the limestone distributed in the border between Hunan and Jiangxi (Cheng et al., 2012; Cheng et al., 2014).

The basal boundary of Qiziqiao Formation is clear that is characterized by the disappearing of siltstone, quartz sandstone and the occurrence of marl, limestone, or dolomite; yet the top boundary is different in different places, including the siliceous rock, brachiopod and coral.

The Shetianqiao Formation mainly occurred in the north and northeast of Shexingping-Tangzhashui area, and the southwest of Yejiwei-Niujiaolong area, with an exposed area of 5.5 km^2.

2 Geochemistry Characteristics

2.1 Trace element composition

The trace elements are mainly composed of Li, V, Cr, Co, Ni, As, Rb, Sr, Y, Zr, Ba, La, Ce and Nd. It is rich in Sr, ranging from 102×10^{-6} to 582×10^{-6}, with an average value of 318.57×10^{-6}. The Ba content has a large scope from 17.3×10^{-6} to 171×10^{-6} with an average value of 75.67×10^{-6}. The Zr content is from 9.74×10^{-6} to 79.1×10^{-6} (averaged, 43.41×10^{-6}), and the Rb content ranges from 6.8×10^{-6} to 81.5×10^{-6} with an average value of 38.61×10^{-6}. The As content is from 14.8×10^{-6} to 34.7×10^{-6} with an average value of 23.61×10^{-6}, and the Ni content ranges from 8.54×10^{-6} to 22.5×10^{-6} (averaged, 14.22×10^{-6}).

The trace element shows an enrichment of U and Sr, yet Ba, Nb and Nd weak loss. The primitive mantle normalized spider diagrams have a good consistency, and decline slightly to the right.

2.2 Rare earth element composition

The geochemistry characteristics of rare earth elements are the tracer to explore the formation and evolution of various geological bodies in nature. Usually, it can supply a few clues by comparing REE distribution characteristics of ore minerals, magmatic rock and strata.

According to the chondrite normalized, the contents of ΣREE show a great difference, ranging from 18.86×10^{-6} to 49.21×10^{-6} with an average value of 31.34×10^{-6}; the value of LREE ranges from 17.35×10^{-6} to 44.43×10^{-6}

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with an average value of 28.15×10^{-6}; and the content of HREE ranges from 1.51×10^{-6} to 4.82×10^{-6} (averaged, 3.19×10^{-6}). The ratio of LREE/HREE and La_N/Yb_N is from 7.39 to 11.49 and from 5.64 to 15.71 with an average value of 9.01 and 10.55, respectively; and the value of δEu and δCe ranges from 0.36 to 0.98 (averaged, 0.66) and from 0.97 to 1.09 (averaged, 1.04), respectively.

The chondrite normalized distribution shows obvious right-dipping curve with weak Eu anomaly; and there is an excellent similarity between the different samples, possibly indicating the consistent characteristics and genetic mechanism.

3 Metallogenic Significance

There is a certain negative correlation between Mo and REE, but the positive correlation between Zn and REE. Except a sample, there is an obvious positive correlation between Bi and REE. In contrast, it is very difficult to find a clear relationship between W and REE.

It shows a certain positive correlation between Zn and LREE, and most samples have a positive correlation between Bi and LREE. The linear positive correlation between W and Bi is significant, followed by W and Zn.

The Qiziqiao Formation and Shetianqiao Formation are the main protolith of skarn rock and the dominant surrounding rock of W-polymetallic deposit (Cheng et al., 2013). Che et al (2005) suggested that the carbonate contributed to constitute a kind of geophysical and geochemical barrier that was favorable to the location of orebody.

About the concealed ore prospecting, the Devonian stratum is an important factor to be considered, especially the contact zone between the strata and intrusive body (Cai et al., 2006). And, the deep characteristics of Devonian stratum should be critical, including the petrology, dynamics, occurrence and spatial morphology.

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