Carbon, oxygen and boron isotopic studies of Huangbai-shuwan witherite deposit at Ziyang and Wenyuhe witherite deposit at Zhushan

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Abstract Being stratiform or stratoid, the Huangbaishuwan witherite deposit at Ziyang and the Wenyuhe witherite-barite deposit at Zhushan occur in the lower Lower Cambrian siliceous rocks and the orebodies are remarkably controlled by lithological character and petrography. Boron, carbon and oxygen isotopic studies of witherite, barytocalcite and calcite have shown that the carbon, involved in the formation of these minerals, was derived mainly from hydrocarbons and biogenetic gases resulting from degradation, polycondensation and dehydroxylation of bio-organic matter in sediments at the early stage of diagenesis; the boron was a mixture of boron in pore water and that released in the process of degradation of organic matter, with a minor amount of boron from cycling brines in the deep interior of the basin. Boron, carbon and oxygen isotopic studies unanimously demonstrated that witherite was precipitated in this sort of organic carbon-rich pore water medium during the early stage of diagenesis. Extensive occurrence of biodetritus and clastic texture in witherite ores strongly evidenced that Ba2+ was concentrated and settled down in the form of bio-barite on the seafloor as a result of biological processes, thereafter forming the initially enriched orebodies of barium deposits. Biological processes in seawater and early diagenesis in sediments are the major ore-forming mechanisms of witherite deposits in the region studied.

Keywords: witherite deposit, boron isotope, carbon and oxygen isotopes, early diagenesis, bio-barite.

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Since the 1980’s, with the improvement and sophistication of the methods of boron isotopic analysis, boron isotopes have been widely applied in the study of ore deposits. The research results available have shown that boron isotopes are of great significance in constraining the genesis of ore deposits, ore-forming temperature, metallogenic geotectonic setting, and the origin and evolution of ore-forming fluids[1–3]. But, even up to now, research on boron isotopes in the known deposits is only restricted to the deposits with B-bearing minerals (e.g. tourmaline) and boron deposits. Little has been reported both at home and abroad on the boron isotope geochemistry of carbonates in ore deposits, especially that of carbonates deposits (e.g. witherite deposits). Boron is
high in content in carbonates, even up to $11 \times 10^{-6}$—$71 \times 10^{-6}$\(^4\). Boron in carbonates stems principally from their crystallization parental liquid (e.g. seawater or ore-forming hydrothermal solution) and can indicate the pH conditions during their precipitation\(^5\). So studies on boron isotopes in carbonates deposits, in conjunction with the application of carbon and oxygen isotopes, can serve as a direct approach to a better understanding of the genesis of this type of ore deposits. In this study boron isotopes in combination with carbon and oxygen isotopes are applied on a trial basis to the investigation of witherite deposits.

Witherite deposits are extensively developed in the Lower Cambrian black rock series of north Daba Mountain at the boundary of Sichuan, Shaanxi and Hubei provinces, which constitute the only large-sized witherite ore zone in China. The entire witherite ore zone is exposed on the northern side of the Daba Mountain arc fault (fig. 1), and it measures more than 300 km in whole length, extending from the Fushui River at Xixiang, Shaanxi in the north, southwards into the areas around Zhuxi and Zhushan of Hubei Province via Ziyang of Shaanxi, Wanyuan and Chengkou of Sichuan and Zhenping of Shaanxi. At present, more than 40 witherite deposits or witherite-barite deposits (occurrences) have been discovered in this ore zone. These ore deposits, being stratiform or stratoid in form, are hosted in the lower Lower Cambrian siliceous rocks, and they are characterized by persisting ore beds, synsedimentation, and control over orebodies by lithological character and petrography. Although witherite as the product of alteration of barite at the late stage may appear in barite-bearing or barite deposits, witherite deposits can hardly be found in the world, and the north Daba Mountain large-sized witherite ore zone of commercial significance, being located at the boundary of Sichuan, Shaanxi and Hubei provinces, is rarely

![Fig. 1. Sketch map showing the distribution of the north Daba Mountain Lower Cambrian witherite ore zone, modified after ref. [11].](image-url)