1 Introduction

China reserves about world’s 40% barite and has been the largest barite-producing country since 1980s (U.S. Geological Survey, 2013). The Qinling-Daba (QD) region on the passive continental margin of the Yangtze Platform hosts more than seventy sediment-hosted stratiform barite (BaSO₄) and witherite (BaCO₃) deposits, making this region one of the economically most important Ba provinces of the world (Wang and Li, 1991; Clark et al., 2004; Lü et al., 2005; Liu et al., 2010). These Ba deposits are widely distributed in the Lower Cambrian strata and generally occur in dark-gray or black cherts, and carbon-rich black shale. Barite and witherite ores generally occur as lenticular bodies, dark, gray or white in color, laminated or massive, and locally containing rosettes and nodules. Stratigraphic study reveals a transition from dominantly chemical (chert) to clastic (shale) sedimentation with decreasing purity of Ba mineralization upwards. Some Ba deposits occur as independent stratiform witherite layers whereas in most cases witherite ore beds also contain some barite. Such a mineralization style has been scarcely reported from other parts of the world. Two metallogenic belts have been identified according to the mineral assemblages in the QD region: the southern and the northern belt. In general, a metallogenic zonation has been recognized, with witherite dominant in the southern belt (e.g. Huangbaishuwan, Miaozi, Bashan, Wamiao, and Wangjiashan) and grading into barite mineralization in the northern belt (e.g. Shiti, Chiyang, Shuping, Zhangziping, Shenhe, Zengjia, Shexiantai, and Shuping). However, the northern belt is not exclusively dominated by barite; some exceptions such as the large-scale Wenyuhe witherite deposit also occur in the northern belt (Fig. 1).

Many studies have focused on the tectonic evolution, stratigraphic correlation, and paleo-environment of the Ba deposits in the QD region (e.g. Wang and Li, 1991; Clark et al., 2004; Lü et al., 2005; Liu et al., 2010; Pi et al., 2013). With respect to regional geological setting and detailed studies of specific deposits, however, the QD region is still among the most poorly documented of all barite provinces of the world. In particular, the metallogenic zonation from barite to witherite is still poorly understood.

2 Geological Setting

Several NW-trending deep thrust faults as well as a number of roughly parallel shallow faults cross the QD region, making this area a large-scale nappe system (Fig. 1). The QD region has been divided into the northern and the southern belt by the Hongchunba fault, with the northern belt dominated by barite deposits and the southern belt dominated by witherite deposits. Low-grade metamorphic rocks (e.g. slate and meta-phyllyte) formed by regional metamorphism are widespread in the region, whereas high-grade metamorphic rocks only exist within or near the fracture zones of the deep thrust faults. Three main epochs have been identified with respect to the tectonic evolution of the QD region: 1) the formation of the basement from Neoarchean to Neoproterozoic, 2) the deposition of marine sediments from Neoproterozoic to Silurian, and 3) the orogenic event from Devonian to Middle Triassic.

Ba ores occur as multiple layers in black shales and cherts locally enriched in pyrite and phosphatic nodules.
Ore bodies are lenses and beds in shape, with thickness varying from tens of centimeters to tens of meters. Ba ores can be divided into four textural types: massive, laminated, banded, and nodular ores. Among them the massive and laminated ores are dominant. The massive ore consists of nearly pure Ba minerals (over 60 wt.% BaO), with organic matter, clay minerals and quartz as impurities. The massive ores are generally located at the base of the ore beds and overlain by the laminated ores. Thickness of laminae is variable, generally ranging from several millimeters to tens of centimeters. Due to the variable content of organic carbon, barite is pure white, gray and black in color. The chemical composition of the gray to black laminae is similar to the white barite, except that dark laminae contain more organic carbon. In addition, the organic-poor white barite ores are characterized by coarse grain and are sometimes intergrown with witherite. Banded barite ores have normally lower grade than the massive and laminated ores because of thicker interbeds of black shales and cherts. Fine-grained quartz occurs as thin interlayers with coarse-grained barite. Ore minerals include barite, witherite, and barytocalcite. Gangue minerals include quartz, calcite, chernykhite, cymrite, gypsum, organic matter and pyrite, as well as rutile as accessory minerals.

### 3 Oxygen Isotopes

We collected oxygen isotope data of both barite deposits (Shenxiantai and Chiyan) and witherite deposits (Wenyuhe, Huangbaishuwan, Chengkou, Wamiao, Bashan, and Miaozi) of the QD region. Oxygen isotopes of the barites and witherites shows statistically variable, with barites have more positive $\delta^{18}O$ values (22.1 ±1.34‰ on average) than the witherites (17.2 ±2.06‰ on average) (Fig. 2). Goldberg et al. (2005) suggested that a higher contribution of $^{18}O$ enriched atmospheric O$_2$ during sulfide oxidation would result in higher $\delta^{18}O$ in the seawater sulfate. This can be applied to explain why Early Cambrian sulfates have lighter $\delta^{18}O$ values than Neoproterozoic sulfates. During the Early Cambrian, $^{18}O$ depleted oxygen would have been the major oxidant for sulfide, resulting in lighter $\delta^{18}O$ values in sulfates. With respect to the barites and witherites in the QD region, redox conditions during witherite deposition may be more anoxic than that of the barite. This is consistent with recent study by Pi et al. (2013), who suggested that witherites were deposited in reducing environments.

To precipitate witherites from seawater, severe depletion...
of $\text{SO}_4^{2-}$ is necessary. A restricted basinal situation may meet the requirement, where replenishment of sulfate from open seawater could not keep pace with removal by bacterial sulfate reduction (BSR). In addition, abundant organic matter possibly promoted the conversion from barite to witherite during early diagenesis. For a basin with very high Ba contents, barite could be diagenetically converted to witherite by sulfate reduction coupled with formation of $\text{CO}_3^{2-}$ from bacterial decomposition of organic matter (Maynard et al., 1991). The BSR process consumes the $\text{SO}_4^{2-}$ and release $\text{CO}_2$, which was isotopically light and subsequently incorporated in the witherite. The metallogenic zonation indicates that generally the southern belt was under more restricted situation and reducing environment, where connection with open seawater was limited. In contrast, the sedimentary basins in the northern belt may have been well connected with open oceans, resulting in sufficient sulfate replenishment.

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References


