Ore Geology Reviews 59 (2014) 73–82

Contents lists available at ScienceDirect

Ore Geology Reviews

journal homepage: www.elsevier.com/locate/oregeorev

New understandings of Ni–Mo mineralization in early Cambrian black shales of South China: Constraints from variations in organic matter in metallic and non-metallic intervals

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ARTICLE INFO

Article history:
Received 10 May 2013
Received in revised form 9 December 2013
Accepted 10 December 2013
Available online 18 December 2013

Keywords:
Nickel–molybdenum (Ni–Mo) polymetallic deposit
Black shale
Bioorganic matter
Biotic impacts on mineralization
early Cambrian Terraneuvian Series
Zunyi City of northern Guizhou Province
South China

ABSTRACT

The well-known Ni–Mo ores hosted in early Cambrian black shales of South China are one of the research highlights in economic geology for the past few decades; however, their origin is complex and still debated. Here, based on a case study in the Huangjiawan ore of Zunyi City, Guizhou Province, we generate several new understandings regarding Ni–Mo mineralization through a comparative investigation of organic matter in metallic and non-metallic stratigraphic intervals, including abundance, type, maturity and relationship to mineralization. We find new direct evidence for biotic impacts on mineralization. Organic matter, and rhodophyte cystocarps (red algae) in particular, may be significantly correlated to mineralization, as it accumulates mineralized Ni and Mo. However, this organic material, as well as disseminated and amorphous organic matters, is not the sole and predominant factor controlling mineralization as implied from the nonlinear correlation between organic matter abundance/maturation and mineralization. Other fluid sources (e.g., hydrothermal and/or seawater) also contribute to mineralization, which may be influenced by hydrothermal activity. Ni and Mo may have mineralized independently, as suggested by their differential accumulation in different structures of the cystocarps, different relationships between organic matter abundance and thermal maturation and mineralized element concentration, as well as the large variation in element accumulation coefficients. The history of mineralization is complex, as Ni and Mo may be or not be deposited together during the same stage of mineralization. These results might also have broader implications for understanding the origin of sediment-hosted ores worldwide.

1. Introduction

An early Cambrian black shale sequence found in several sites in South China is well known for containing various kinds of ores; for example, the nickel–molybdenum (Ni–Mo) polymetallic deposits of Hunan and Guizhou provinces (Fig. 1) (Chen et al., 1982; Fan et al., 1973, 1984, 2004; Zeng, 1998). These polymetallic deposits have been of research interest since their discovery in the 1970s, for two main reasons. First, the Hunan and Guizhou deposit locations are among the few black shale sites that can accommodate Ni–Mo mining worldwide, and thus they have economic value (Chen et al., 1982; Coveney and Chen, 1991; Coveney et al., 1992; Fan et al., 1973, 1984, 2004; Zeng, 1998). Second, these unusual deposits occur at, or close to, the Precambrian–Cambrian (Pc/C) boundary. Therefore, the study of these black shale-hosted deposits can provide information on the Pc/C transition, which is a critical interval in Earth's history characterized by global environmental and biological changes, such as major plate tectonic reconfiguration, mass extinction, and accelerated diversification of metazoans (Banerjee et al., 1997; Brasier, 1992; Kimura and Watanabe, 2001; Schröder and Grotzinger, 2007; Slack et al., 2009; Wille et al., 2008).

Many petrological, mineralogical, geochronological, paleontological, geochemical, and metallogenic studies have been conducted either on the sulfide ores or on the host black shales (Coveney et al., 1992; Fan et al., 1984; Horan et al., 1994; Jiang et al., 2006, 2007a, 2007b, 2009; Kao et al., 2001; Lehmann et al., 2003, 2007; Lott et al., 1999; Mao et al., 2002; Pan et al., 2005; Pašava et al., 2008; Steiner et al., 2001; Xu et al., 2011, 2012, 2013). However, due to the complexity of the mineralization, the origin of the metal enrichment is still strongly debated with three main proposed models: sedimentary exhalative (SEDEX) (Jiang et al., 2003, 2007a, 2007b, 2009; Lott et al., 1999; Steiner et al., 2001); seawater precipitation (Lehmann et al., 2003, 2004, 2007; Mao et al., 2002; Wille et al., 2008; Xu et al., 2012, 2013); and derivation from multiple sources, including hydrothermal, seawater, and terrestrial inputs (Pašava et al., 2008; and references therein). In addition, some studies have noted the biotic involvement in ore formation, since the mineralization is hosted in organic-rich black shales whose total organic carbon (TOC) content is generally >1.0% (Cao et al., 2013; Coveney and Pašava, 2004; Kříbek et al., 2007; Orberger et al., 2007; Pašava et al., 2008; Steiner et al., 2001).

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http://dx.doi.org/10.1016/j.oregeorev.2013.12.007

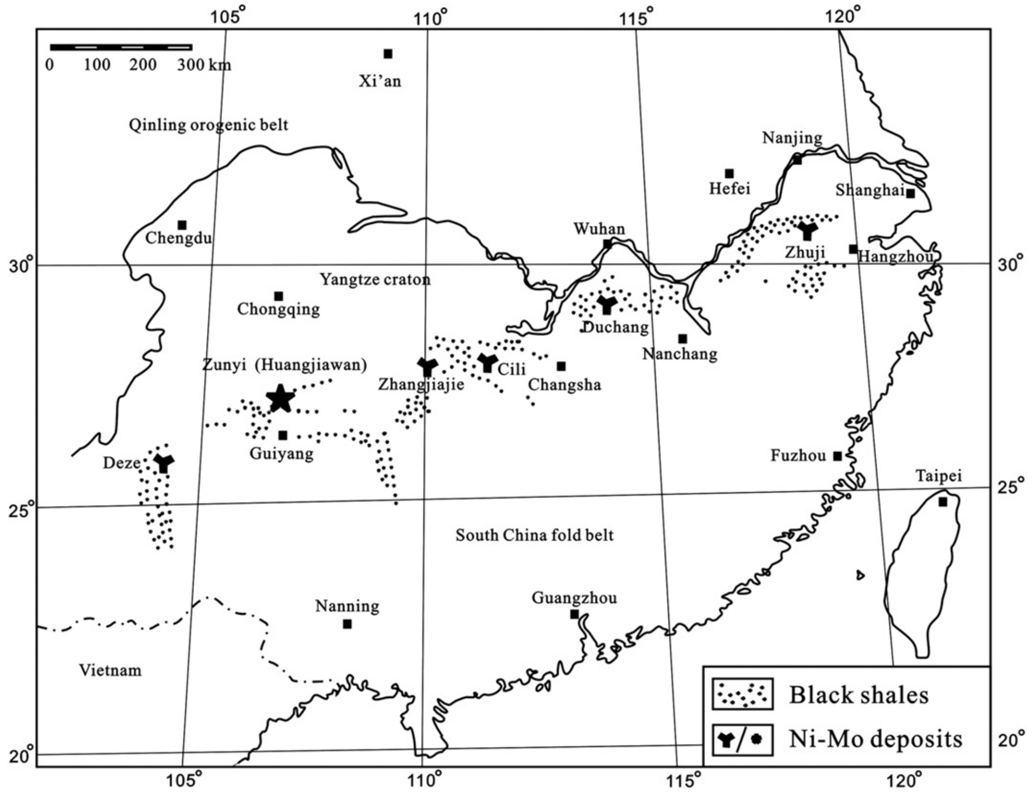

Fig. 1. Occurrence of early Cambrian black shale sequences containing Ni–Mo polymetallic deposits in South China (background map based on Mao et al., 2001).

To provide new constraints on the complex mineralization, we conducted a case study of the Huangjiawan Ni–Mo ore of Zunyi City, southwestern China. We report new data on the characteristics of organic matters, in particular their differences between metallic and nonmetallic stratigraphic intervals, followed by a discussion of the relationship and implications for mineralization.

2. Geological setting

The well-known early Cambrian black shale sequences in South China extend approximately 1600 km in a NE–SW direction (Fig. 1). These sequences culminate in ore (e.g., Ni–Mo polymetallic) deposits in several sites, such as the Tian'eshan–Huangjiawan Ni–Mo deposit belt, which is located in Zunyi City of Guizhou Province, and the Daping–Dahu Ni–Mo deposit belt, which is located in Zhangjiajie City of Hunan Province (Fig. 1). Although the sulfide ore layer is only several centimeters thick, it shows extreme metal enrichment with Ni and Mo contents reaching up to ~10 wt.%, and PGE + Au concentrations of ~1 ppm (Chen et al., 1990; Coveney et al., 1992, 1994; Fan et al., 1984; Lehmann et al., 2007; Xu et al., 2011; Xu et al., 2013), making this layer a target for widespread and small-scale mining in both Hunan and Guizhou provinces (Fan et al., 1984; Mao et al., 2002). Besides the extreme enrichment in Ni, Mo, PGE and Au, the sulfide ore layer is also strongly enriched with $>10^4$ times average continental crust in elements Se, Re, Os, As, Hg and Sb (Coveney et al., 1994; Fan et al., 1984; Jiang et al., 2006; Lehmann et al., 2007). Zn, Cu and Pb are locally enriched to concentrations in the percent range (Xu et al., 2013).

The Ni–Mo polymetallic mineral systems studied here are located in the counties of Zunyi City, northern Guizhou Province and are exposed at the base of the early Cambrian Niutitang Formation (Mao et al., 2001) (Figs. 1 and 2). Here, we focus on the Tian'eshan–Huangjiawan Ni–Mo ore belt. Located in the northeastern and southwestern sectors of the Songlin dome structure, the Tian'eshan–Huangjiawan Ni–Mo ore belt is composed primarily of three mining areas: Huangjiawan, Tian'eshan, and Xintugou (Zeng, 1998) (Fig. 2). The dome structure is located in the northern Songlin–Yankong NE-trending arc structure. Locally, the ore trend is within the Loushan fold belt, situated in the northeastern side of the Qianzhong uplift in the eastern Upper Yangtze craton (Zeng, 1998; Zhang, 1987).

As shown in Fig. 3, the black shale sequences of the Niutitang Formation in the Huangjiawan area consist mainly of carbonaceous shale, chert, and carbonaceous phosphate-nodule-bearing mudstone. These beds unconformably overlie the dolomite of the Neoproterozoic (Sinian) Dengying Formation. The interface contains a weathered layer that is 5–10 cm thick, and above this layer, the black shale sequences generally contain six segments (from lower to upper): carbonaceous shale (0.3 m thick), black siliceous rocks (0.25 m thick), carbonaceous shale (0.3 m thick), carbonaceous shale with phosphate nodules that are lined with banded pyrite (approximately 1 m thick), a Ni–Mo enrichment layer (5–30 cm thick), and black shale (>9 m thick). In general, above the ore layer the lithology is relatively simple, being composed of black shale that is dark-gray to black in color, fine grained, laminated, and containing both framboidal and euhedral pyrite grains. However, the lithology below the ore layer is variable and complex, including carbonaceous shale, black siliceous rock (chert) and phosphate. The phosphate-rich horizon is up to several centimeters thick with abundant chalcedony, vivianite and bitumen pseudomorphs. The Ni–Mo mineralization layer is confined to a sulfide- and phosphate-rich stratiform breccia body 5 to 30 cm thick. The highly porous matrix of the ore body is composed of laminae that are rich in organic matters or silicates or of lenticular bodies that intercalate with phosphate- or sulfide-rich lenses. Sulfide and phosphate laminae of the mineralized rock matrix are commonly distorted by rounded, elongate or angular rip-up clasts.

3. Samples and methods

A systematic sampling of the metallic layer and surrounding nonmetallic strata was conducted in the Huangjiawan mining area of Zunyi City, Guizhou Province. One ore sample and 16 samples from