Journal of Asian Earth Sciences 62 (2013) 531–536

Contents lists available at SciVerse ScienceDirect

Journal of Asian Earth Sciences

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

Organic clots and their differential accumulation of Ni and Mo within early Cambrian black-shale-hosted polymetallic Ni–Mo deposits, Zunyi, South China

Jian Cao [a,*], Kai Hu [a], Jie Zhou [a,b], Chunhua Shi [a], Lizeng Bian [a], Suping Yao [a]

[a] State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing, Jiangsu 210093, PR China
[b] Nanjing Institute of Geology and Mineral Resources of China's Ministry of Land Resources, Nanjing, Jiangsu 210016, PR China

ARTICLE INFO

Article history:
Received 3 March 2012
Received in revised form 30 October 2012
Accepted 1 November 2012
Available online 10 November 2012

Keywords:
Ni–Mo polymetallic deposits
Rhodophyta
Cystocarp
Black shale
Early Cambrian Terraneuvian Series
South China

ABSTRACT

The celebrated early Cambrian Ni–Mo deposits that occur near Zunyi City of Guizhou Province, South China, are hosted in shales. The ore formation has been widely accepted to be related to biotic impact, but direct evidence is still lacking. In the present study of the Huangjiawan ore deposit, organic clots are found to occur widely in the Ni–Mo ore beds, but not in the barren layers. The clots are generally elliptic, with sizes ranging from 200 to 600 μm. The clot morphology is similar to that of modern rhodophyta as reported in the literature. We tentatively interpret the clots as rhodophyte cystocarps. Electron microprobe analysis revealed that the clots have a differential accumulation of Ni and Mo, with Ni in the inner part and Mo in the outer part (of the cystocarp). Our study seems to have provided direct evidence for the biotic impact on the ore mineralization.

1. Introduction

The black-shale-hosted early Cambrian Terraneuvian Ni–Mo polymetallic deposits of South China (Fig. 1a) have been the subject of much research and are one of the few examples of this style of mineralization known worldwide. These deposits contain both Ni and Mo, with both of these metals present at ore grades (Fan et al., 1973, 2004; Zeng, 1998), and are enriched in a number of other elements, including the platinum-group elements (PGE), Cu, Se, As, Hg, Sb, Ag, and Au (Fan et al., 1973; Zeng, 1998); these enrichments are the reason these deposits are termed Ni–Mo polymetallic deposits. These deposits can yield a significant amount of information on both the Precambrian and Cambrian periods, as the ore interval is located approximately at the Precambrian–Cambrian boundary (Lehmann et al., 2007; Jiang et al., 2009). These factors have led to these deposits being the focus of many studies in recent decades (Coveney et al., 1992; Horan et al., 1994; Murowchick et al., 1994; Mao et al., 2002; Kříbek et al., 2007; Xu et al., 2012; Wang et al., 2012), with the Zunyi and Zhangjiajie deposits (Fig. 1a) being the focus of particularly intense research because they are the only two large Ni–Mo deposits to have been exploited within this sedimentary package (Fan et al., 1973).

Although these unusual ore deposits have been extensively studied, their origin is still debatable, reflecting the complexity of ore formation. A number of models for the formation of these deposits have been proposed, include sedimentary exhalative (SEDEX) (Lott et al., 1999; Jiang et al., 2009), seawater precipitation (Lehmann et al., 2007), and derivation from multiple sources, including hydrothermal, seawater, and terrestrial inputs (Pašava et al., 2008; and references therein). Even given these differing potential formation models, a number of authors have noted biotic involvement in ore formation (Coveney and Pašava, 2004; Parcha and Pandey, 2011; Sun et al., 2012). For instance, Lott et al. (1999) identified microscopic organisms and bacterial structures, and suggested that algae and bacteria caused precipitation of V and Mo from seawater. Furthermore, Kao et al. (2001) used transmission electron microscopy (TEM) to image circular MoSC structures, a type of amorphous material containing variable proportions of Mo, S, and C. This material has a striking resemblance to bacterial cells, with two bounding circles likely corresponding to inner and outer cell walls, and therefore strongly suggesting that the formation of MoSC is related to biological activity.

However, previous studies have only postulated or indirectly deduced potential biotic influences on ore formation, without providing any direct evidence. Here, we present a case study of the Huangjiawan mine, Zunyi, South China (Fig. 1a), where organic clots have previously been described (e.g., Kříbek et al., 2007; Pašava et al., 2008) and are thought to be rhodophyte cystocarps with analogues to modern rhodophyta, as reported elsewhere (Zhang et al., 2004, 2007; Bian et al., 2005; Ji and Xu, 2007; Cao et al.,

* Corresponding author.
E-mail address: jcao@nju.edu.cn (J. Cao).

1367-9120/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.jseaes.2012.11.002

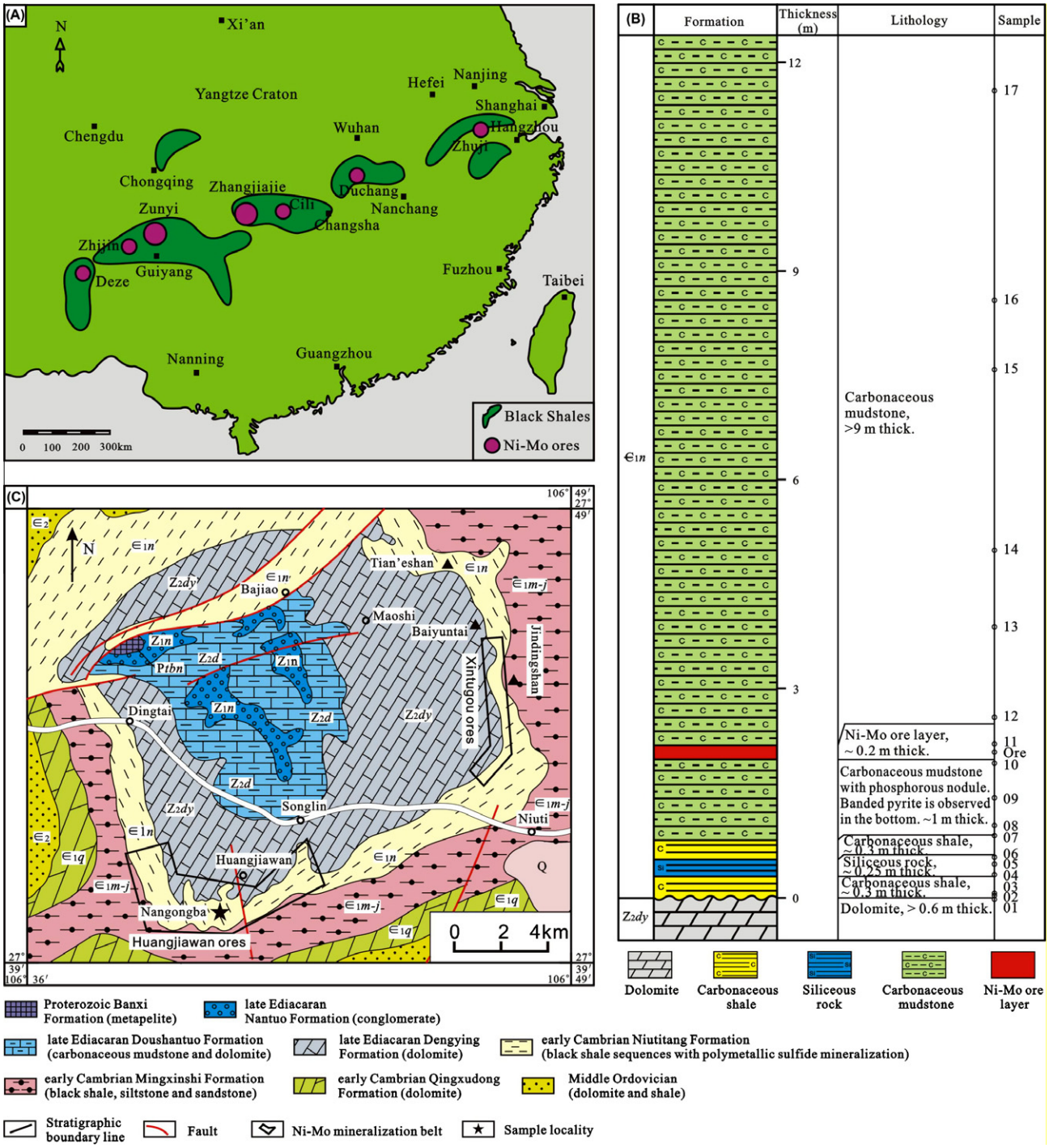

Fig. 1. (a) Sketch map showing the distribution of early Cambrian black shale sequences and related Ni–Mo polymetallic deposits in South China (adapted from Mao et al. (2002)). (b) Generalized stratigraphic column for Ni–Mo polymetallic deposits in the Huangjiawan mine area, showing sample locations. (c) Geological sketch map of the Songlin dome, showing the location of the Huangjiawan mine area (modified after Zeng (1998) and Mao et al. (2002)).

2009; Jiang et al., 2011). We also present the first evidence of the differential accumulation of Ni and Mo in these clots. The aim of this paper is to present new information and to enable a better understanding of the formation of these highly unusual ore deposits, with a particular focus on biotic impacts during ore formation.

2. Geological setting

The black shale sequences that host Ni–Mo polymetallic deposits in the Zunyi area are dominated by shales, mudstones, and siliceous rocks (Fig. 1b). The lowermost section of the sequence contains a thin layer of sulfide mineralization with an apparently unique and extreme metal enrichment (Fan et al., 1973; Murowchick et al., 1994; Lott et al., 1999; Li et al., 2002; Mao et al., 2002; Fig. 1b). These black shale sequences and associated Late Ediacaran Dengying Formation dolomites are exposed in the cores of anticlines (Mao et al., 2001; Fig. 1c). Economic mineralization is primarily located in the Tian'eshan and Huangjiawan mineralization belts in the northeast and southwest of the Songlin dome structure, respectively (Fig. 1c). This structure is located in the