

# Submarine hydrothermal contribution for the extreme element accumulation during the early Cambrian, South China



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## ABSTRACT

Throughout the geological history of the Earth, submarine hydrothermal activity has played an important role in seawater chemistry, biological evolution and enrichment of metals in the Earth crust. However, the prospect of hydrothermal activity for extreme element accumulation during the early Cambrian, a key geological period, in South China has not been well-constrained. This study reports geochemical (e.g. REE and Sr isotope) investigations of a coarse-grained limestone layer and associated calcite veins in Zunyi and Nayong areas, Guizhou Province, to constrain the hydrothermal activity and evaluate the significance of hydrothermal contribution to extreme element accumulation during the early Cambrian, South China. Our results reveal positive Eu anomalies and higher initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7083–0.7150) for carbonate samples than those of early Cambrian seawater, indicating the presence of hydrothermal processes. Combined with constraints from the spatial relationships and coincidence with adjacent mineralization, these hydrothermal processes provide the most probable contribution for polymetallic Ni–Mo–PGE mineralization. Furthermore, there are abundant hydrothermal dolomite and barite–calcite veins in the dolostone of the Dengying Formation, indicating the occurrence of a variety of hydrothermal fluids. Overall, multi-stage hydrothermal pulses with different fluid compositions spanned the Ediacaran–Cambrian transition in South China. In particular, these hydrothermal fluids with positive Eu anomalies and enriched radiogenic Sr, originating from Proterozoic mafic/ultramafic rocks, may have flowed through the underlying Precambrian silicate clastic rocks (e.g., Xiajiang, Banxi and Lengjiaxi Groups) and may have been crucial for the marine environment, biological diversity and extreme element accumulation during the early Cambrian, South China.

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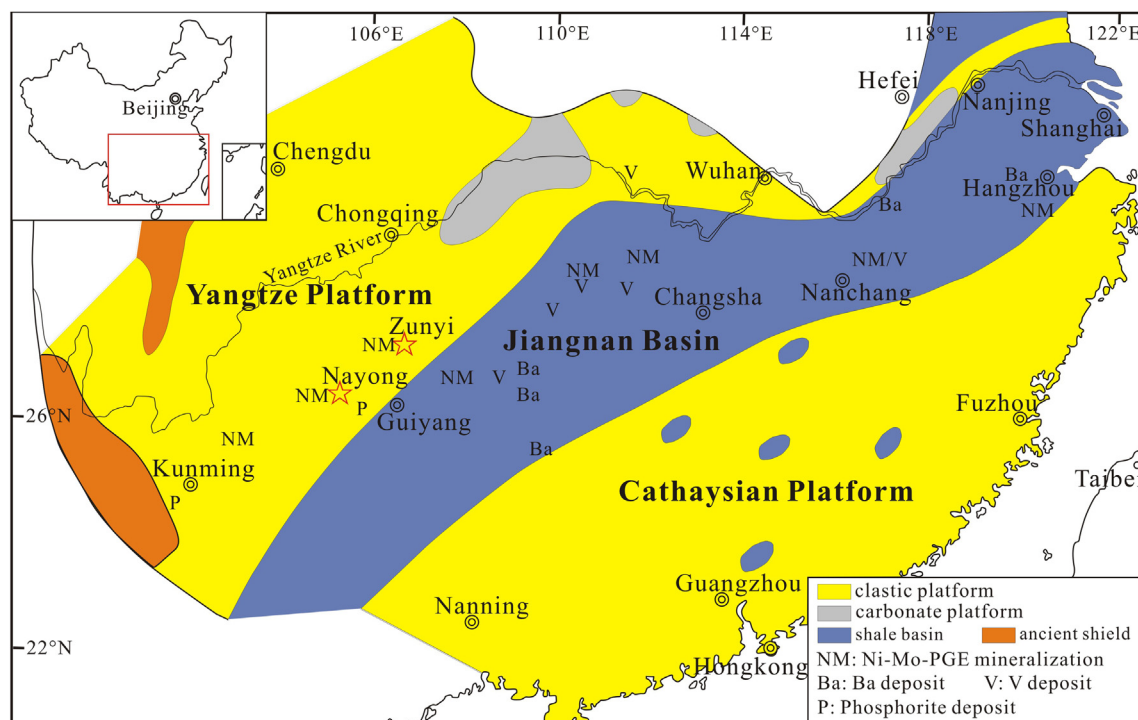
## 1. Introduction

Submarine hydrothermal activity may provide a perspective for understanding the geological processes, geochemical cycling, and the origin and evolution of life throughout the Earth's history (Baross and Hoffman, 1985 and references therein). Hydrothermal activity with hot, volatile-rich hydrothermal solutions may have changed the redox and chemical conditions of seawater, and even resulted in mineralization on and/or below the seafloor (e.g., Baross and Hoffman, 1985; Zierenberg et al., 1998, 2000; Perner et al., 2013). Moreover, the discovery of hydrothermal communities living in hydrothermal venting system also provides a possibility for investigating the origin of early life (e.g. Baross and Hoffman, 1985; Russell and Hall, 1997; Nisbet and Sleep, 2001; Mcdermott et al., 2015 and references therein).

In South China, submarine hydrothermal processes have been suggested to explain extreme element accumulations (e.g., Ni, Mo, Se, PGE, Ba, Si) within the widespread chert (e.g., Li, 1997; Chen et al., 2009; Wang et al., 2012; Fan et al., 2013; Liu et al., 2015), the bedded polymetallic Ni–Mo–PGE mineralization (e.g., Coveney and Chen, 1991; Murowchick et al., 1994; Lott et al., 1999; Li and Gao, 2000; Jiang et al., 2006, 2007) and the super-large barite deposits (e.g., Wang and Li, 1991; Xia et al., 2004; Žák et al., 2003; Pašava et al., 2008; Han et al., 2015a) during the early Cambrian (Fig. 1). However, the hydrothermal contribution for extreme element accumulation has not been well constrained, although marine redox conditions and biological evolution were studied intensively across this crucial Ediacaran–Cambrian transition (e.g., Zhou and Jiang, 2009; Xu et al., 2012a; Pi et al., 2013; Feng et al., 2014; Och et al., 2015; Cai et al., 2015; Wang et al., 2015a; Wen et al., 2015; Cheng et al., 2016; Jin et al., 2016; Zhang et al., 2016). For instance, the polymetallic Ni–Mo–PGE mineralization, has been studied for four decades (Fig. 1), however, entirely different arguments were proposed, such as asteroid

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**Fig. 1.** Lithofacies palaeogeography map and distribution of several mineralization/deposits in the lower Cambrian sedimentary strata along the southern margin of Yangtze Platform (modified from Wang and Li, 1991; Feng et al., 2002; Mao et al., 2002; Coveney and Pašava, 2005; Xu et al., 2014). Note: the provincial capitals here represent different provinces.

impact (Fan, 1983), seawater scavenging (Mao et al., 2002; Lehmann et al., 2007, 2016; Xu et al., 2012b), submarine hydrothermal exhalative origin (Coveney and Chen, 1991; Murowchick et al., 1994; Lott et al., 1999; Li and Gao, 2000; Jiang et al., 2006, 2007; Fan et al., 2011; Wen and Carignan, 2011; Cao et al., 2013; Shi et al., 2014; Han et al., 2014; Guo et al., 2016) and multiple sources (Pašava et al., 2008; Han et al., 2015b). Furthermore, it has been proposed that metazoans may have already existed in deep-sea hydrothermal systems during the Precambrian, later migrating from these hydrothermal vents to shallow water in the early Cambrian, according to the mass occurrences of arthropods, sponges and undetermined shells which appear linked to the hydrothermal vents (Steiner et al., 2001). Consequently, hydrothermal activity may have played a crucial role in the extreme enrichment of elements, marine chemical conditions and biological diversity during the early Cambrian, South China.

To constrain the hydrothermal contribution to extreme enrichment of elements during the early Cambrian in South China, a coarse-grained limestone layer closely underlain the polymetallic Ni–Mo–PGE sulfides layer, coupled with nearby geological features across the Ediacaran–Cambrian transition in Zunyi and Nayong areas of Guizhou Province were investigated through the geological, petrographic and geochemical (e.g., REE and Sr isotope) studies. Especially, the characteristics of Eu anomaly and the scope of Sr isotopic signature can effectively identify hydrothermal involvement for extreme metal accumulation.

## 2. Geological background

The lower Cambrian black shale sequence is well-preserved and widely distributed along the southern margin of Yangtze Platform, which is known as the Niutitang Formation in Guizhou and is equivalent to the Qiongzhusi/Guojiaba Formation in Yunnan and Sichuan, the Muchang/Xiaoyanxi Formation in Hunan, and the

Hetang Formation in Zhejiang Province (Fig. 1). The Ediacaran–Cambrian boundary was constrained by SIMS U–Pb zircon ages of  $542.1 \pm 5.0$  Ma and/or  $542.6 \pm 3.7$  Ma in South China where the lower Cambrian black shale is underlain unconformably by the Ediacaran dolostone of the Dengying Formation and/or chert of the Liuchapo Formation (Chen et al., 2015). However, a SHRIMP U–Pb zircon age of  $532.3 \pm 0.7$  Ma from a volcanic ash bed just below the polymetallic Ni–Mo–PGE sulfides layer in the lowermost Niutitang Formation in Zunyi area was also proposed (Jiang et al., 2009).

Several types of significant ore deposits are hosted in these lower Cambrian sedimentary strata of South China (e.g., Emsbo et al., 2005; Xu et al., 2014; Fig. 1). First, the polymetallic Ni–Mo–PGE mineralization, with a few to tens of centimeters thickness, occurs in Yunnan, Guizhou, Hunan, Jiangxi and Zhejiang Provinces contains extremely high Ni, Mo, Zn, TOC (total organic carbon) and total PGE concentrations, which can reach up to 7 wt.%, 8 wt.%, 12 wt.%, 12 wt.% and 943 ppb, respectively (e.g., Xu et al., 2012b; Han et al., 2015b). Second, the phosphorite deposits have been mainly explored in Kunyang of Yunnan and Zhijin of Guizhou. In particular, the Zhijin phosphorite deposit is a uniquely associated REE deposit, with the concentration of total rare earth oxides up to 0.17 wt.% (Jin et al., 2007; Chen et al., 2013). Third, the barium mineralization usually occurs as sediment-hosted stratiform barite deposit, with thicknesses ranging from 3 m to 10 m and content of  $\text{BaSO}_4$  up to 95 wt.% in Tianzhu of Guizhou, Xinhuang of Hunan, Dongzhi of Anhui and Linan of Zhejiang (Wang and Li, 1991; Fang et al., 2002; Han et al., 2015a). Finally, vanadium deposits are mainly distributed in Tongren of Guizhou, Jishou, Zhangjiajie and Changde of Hunan, Yichang of Hubei and Duchang of Jiangxi. This vanadium-bearing black shale sequence commonly starts from the base of the Niutitang Formation and has a thickness of 7–40 m with the  $\text{V}_2\text{O}_5$  concentrations of up to 2 wt.% (Hu et al., 2010; Shu et al., 2014).

In Zunyi and Nayong areas of Guizhou Province, South China, the lower Cambrian Niutitang Formation exhibits a similar

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