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Reconstructing marine redox conditions for the transition between Cambrian Series 2 and Cambrian Series 3, Kaili area, Yangtze Platform: Evidence from biogenic sulfur and degree of pyritization

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ABSTRACT

The transition between Series 2 and Series 3 of the Cambrian Period was a time of environmental perturbations and biological innovations. A generally positive sulfur isotopic composition of sedimentary pyrite with $\delta^{34}S_{pyrite}$ values between +1.7 and +37.3‰ is consistent with a biological origin via reduction of strongly ^{34}S enriched seawater sulfate. No substantial changes in the redox conditions of the water column are discernible from the DOP record, and the sulfide sulfur isotopic composition is independent of DOP, in particular an excursion towards less ^{34}S enriched values immediately preceding the proposed level of the Cambrian Series 2 to Cambrian Series 3 transition. This level is also characterized by a negative carbonate carbon isotope excursion, believed to reflect the transgressive flooding of the shelf with basinal anoxic waters. Low DOP values would suggest that these might have been ferruginous rather than sulfidic.

1. Introduction

The stratigraphic interval representing the Cambrian Series 2 and Cambrian Series 3 transition was a time of environmental perturbations and biological innovations (Sundberg et al., 1999; Zhao et al., 2001a,b; Guo et al., 2005; Zhao et al., 2008; Guo et al., 2010a; Sundberg et al., 2011). This transition is marked by a globally recognizable negative carbon isotope excursion (the ROECE event) that records the transgressive flooding of the shelf areas with ^{13}C depleted basinal and previously anoxic bottom water. Respective changes have been archived in the sedimentary rocks from this time interval and are reflected, among others, in the temporal evolution of the carbon isotopic composition of carbonate and organic carbon in the Wuliu-Zengjiayan and Jianshan sections of southern China (e.g., Guo et al., 2010a).

This study aims at further reconstructing the environmental conditions by investigating temporal fluctuations in the sulfur isotopic composition of sedimentary pyrite ($\delta^{34}S_{pyrite}$) and potential changes in redox conditions in these two sedimentary successions that were deposited on the Yangtze Platform, South China. As a side aspect, the global correlation potential of $\delta^{34}S_{pyrite}$ for this transition will be evaluated.

In the modern marine realm, dissolved sulfate represents the most important sulfur compound. In fact, for the past 2.3 Ga, the input of sulfate into the oceanic reservoir resulted primarily from the riverine delivery of sulfate resulting from oxidative continental weathering with a minor contribution from hydrothermal activity (e.g., Strauss, 2004; Reuschel et al., 2012; Strauss et al., 2013). The principal output functions of sulfate from the ocean into the rock record have been the precipitation of evaporitic sulfate (including the incorporation of sulfate into carbonates; cf. Takano, 1985; Calvert et al., 1996; Staudt et al., 1999; Strauss, 1999; Kampschulte et al., 2001; Lyons et al., 2003; Kampschulte and Strauss, 2004; Goldberg et al., 2007), and the process of bacterial sulfate reduction and the formation and subsequent burial of iron sulfide into marine sediments (e.g., Canfield, 2001). While the former process is not associated with any substantial sulfur isotope effect (e.g., Holser and Kaplan, 1966; Claypool et al., 1980), the biological sulfur cycling, most notably the microbial reduction of sulfate, is associated with a substantial fractionation of the sulfur isotopic composition, discriminating against the heavy ^{34}S isotope and resulting in variable but generally negative $\delta^{34}S$ values archived in the sedimentary pyrite (for a review, see e.g., Canfield, 2001, and Johnston, 2011). Frequently, $\delta^{34}S$ values of biogenic pyrite vary between −40 and 20‰ (Clark and Fritz, 1997). Most recently, Sim et al. (2011) reported a large isotopic fractionation between oceanic sulfate and sedimentary sulfide of 66‰ for sulfate reducing bacteria, both from a natural setting as well as from laboratory culture. In general, the sulfur isotopic composition of sedimentary sulfur can be utilized to monitor perturbations of the global sulfur cycle (e.g., Strauss et al., 2013). But caution has to be exerted as the development of sulfate-limiting conditions in the water column and or the pore water realm due to intense microbial sulfate reduction will result in the progressive enrichment of ^{34}S yielding progressively more positive $\delta^{34}S$ values.

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In addition to the abundances and isotopic compositions of carbon and sulfur, iron abundances/speciation and related geochemical parameters such as the degree of pyritization (DOP: Raiswell et al., 1988) have been utilized for evaluating the geochemical conditions during pyrite formation within a given sedimentary environment. The DOP quantifies iron availability but has been related to the redox condition of the bottom water. Specifically, DOP values <0.45 and >0.75, respectively, reflect deposition from an oxic or an anoxic to euxinic bottom water (Raiswell et al., 1988).

The present study examines the sulfur isotope geochemistry and DOP across the Cambrian Series 2 to Cambrian Series 3 transition in the Wuliu-Zengjiayan and Jianshan sections, Guizhou Province, South China.

2. Stratigraphy and sampling

A succession of carbonates and siliciclastic sediments spanning the Cambrian Series 2 to Cambrian Series 3 transition is exposed at the Wuliu-Zengjiayan section near Balang village (Taijiang County, Guizhou Province, South China; Fig. 1), and this section has been proposed as a potential Global Stratotype Section and Point (GSSP) for this boundary (Sundberg et al., 1999; Zhao et al., 2001a,b, 2007, 2008, 2012). Correlative strata are exposed in the Jianshan section which is located along a ridge of Jianshan Mountain, ca. 1.5 km west of Chuandong Village (Zhao et al., 2008) and ca. 8 km NE away from the Wuliu-Zengjiayan section. The Jianshan section represents an additional candidate section in support of the stratotype for the Cambrian Series 2 and Cambrian Series 3 transition (Zhao et al., 2008) (Fig. 1).

During Cambrian times, these sections were located in a low latitude position (Scotese and McKerrow, 1990; Saltzman et al., 2000). Both sections straddle the Cambrian Series 2 to Cambrian Series 3 transition. In terms of stratigraphic units, the studied sections comprise the upper part of the Qingxudong Formation, the Kaili Formation, and the lower part of the Jialao Formation (Fig. 2). Lithologies include limestone, dolostone, and silty calcareous mudstone, with abundant fossils preserved in the Kaili Formation. Sediments of the Kaili Formation were deposited in a shelf environment presumably in a water depth between 90 and 300 m (Zhang et al., 1996).

The Kaili Formation at the Wuliu-Zengjiayan section is more than 200 m thick, and is composed of gray silty mudstone, calcareous mudstone and limestone (Zhao et al., 2001a,b; Guo et al., 2005; Zhao et al., 2007). Interbeds of marl are common in the lower and middle parts of the formation, containing abundant trilobite fossils, such as *Oryctocephalus*, *Bathynotus* and *Ovatoryctocara*. The FAD of *Oryctocephalus indicus* occurs at 52.8 m above the base of the Kaili Formation (Zhao et al., 2007; Guo et al., 2010a,b; Sundberg et al., 2011). The part of the Kaili Formation lying below this horizon belongs to the *Ovatoryctocara* cf. *granulata*–*Bathynotus keichouensis* assemblage zone (Zhao et al., 2012), and that above 52.8 m belongs to the *O. indicus* zone and *Peronopsis taijiangensis* zone (Zhao et al., 2012).

The Kaili Formation at the Jianshan section is also more than 200 m thick, and is composed of calcareous mudstone, silty mudstone and limestone (Zhao et al., 2008; Guo et al., 2010a). There are abundant trilobite fossils in Kaili Formation, such as *Oryctocephalus*, *Bathynotus*, *Peronopsis* and *Olenoides*. The FAD of *Oryctocephalus indicus* of the Cambrian Series, Stage 5 occurs at 44.25 m above the base of the Kaili Formation (Zhao et al., 2008). The portion of the Kaili Formation lying below this horizon belongs to the *Ovatoryctocara* cf. *granulata*–*Bathynotus keichouensis* assemblage zone, and that above 44.25 m belongs to the *O. indicus* zone and *Peronopsis taijiangensis* zone (Zhao et al., 2012).

According to a revised measurement of this section (Zhao et al., 2008, 2012), the transition from Cambrian Series 2 to Cambrian Series 3 is located at 52.8 m above the boundary between the Qingxudong and Kaili formations in the Wuliu-Zengjiayan section and at 44.25 m above the boundary between the Qingxudong and Kaili formations in

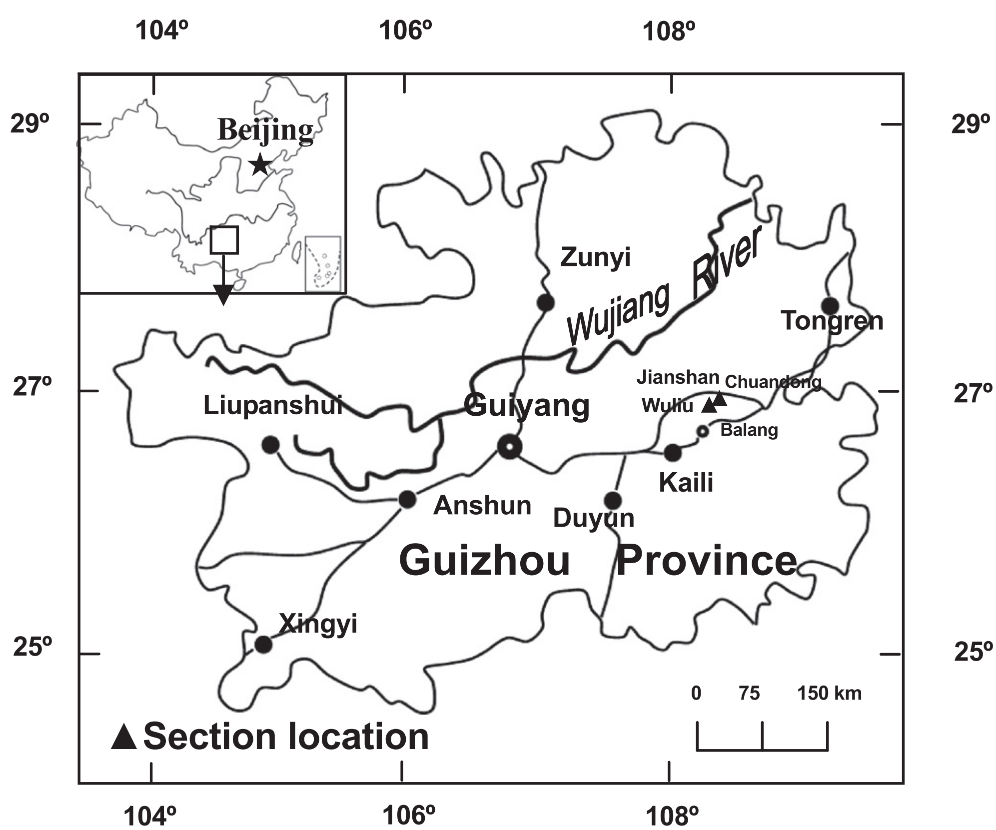

Fig. 1. Map showing the location of the Wuliu-Zengjiayan and Jianshan sections at Balang and Chuandong villages, Guizhou Province, South China.