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Carbon and sulfur isotopic fluctuations associated with the end-Guadalupian mass extinction in South China

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ABSTRACT

Concentrations of total organic matter (TOC), carbon isotopic compositions of carbonate and organic matter ($\delta^{13}C_{carb}$, $\delta^{13}C_{org}$), and sulfur isotopic compositions of carbonate associated sulfate ($\delta^{34}S_{sulfate}$) across the Guadalupian–Lopingian (G–L) boundary were analyzed from identical samples of Tieqiao section, Laibin, Guangxi province, South China. The $\delta^{13}C_{carb}$ values show a positive excursion from −0.45‰ to the peak of 3.80‰ in the Laibin limestone member of the Maokou Formation, followed by a drastic drop to −2.60‰ in the lowest Heshan formation, then returned to about 1.58‰. Similar to the trends of the $\delta^{13}C_{carb}$ values, $\Delta^{13}C_{carb-org}$ values also show a positive excursion followed by a sharp negative shift. The onset of a major negative carbon isotope excursion postdates the end Guadalupian extinction that indicates subsequent severe disturbance of the ocean–atmosphere carbon cycle. The first biostratigraphic $\delta^{34}S_{sulfate}$ values during the G–L transition exhibit a remarkable fluctuation: a dramatic negative shift followed by a rapid positive shift, ranging from 36.88‰ to −37.41‰. These sulfate isotopic records suggest that the ocean during the G–L transition was strongly stratified, forming an unstable chemocline separating oxic shallow water from anoxic/euxinic deep water. Chemocline excursions, together with subsequent rapid transgression and oceanic anoxia, were likely responsible for the massive diversity decline of the G–L biotic crisis.

1. Introduction

The Guadalupian–Lopingian (G–L) (Middle–Late Permian) transition was a critical interval in geological history, during which dramatic climatic, oceanic, and biological changes occurred (Jin et al., 1994; He et al., 2003; Isozaki et al., 2007a). In particular, a mass extinction coinciding with the end Guadalupian global regression, was identified (Jin et al., 1994; Stanley and Yang, 1994; Wang and Sugiyama, 2000; Clapham et al., 2009). Numerous hypotheses, including global regression (Jin et al., 1994; Hallam and Wignall, 1999; Wang and Jin, 2000), oceanic anoxia (Isozaki, 1997; Weidlich, 2002), Emeishan flood basalt eruptions (Sephton et al., 2002; Zhou et al., 2002; Wignall et al., 2009a), climate cooling (Isozaki et al., 2007a; Lai et al., 2008) and catastrophic methane outburst (Retallack et al., 2006; Retallack and Jahren, 2008), have been proposed as the cause of this particular geologic event. The ultimate cause, however, is still highly controversial.

Some studies have revealed a large-magnitude negative carbon excursion, associated with the mass extinction, implying an abrupt and global change in the carbon cycle (Wang et al., 2004; Isozaki et al., 2007b; Lai et al., 2008). However, the cause of the $\delta^{13}C$ shift and its relationship to the extinction has been a matter of debate. By analogy to carbon cycles, sulfur reservoir sizes and redox variations within the sedimentary sulfur cycle account for the observed variations in $\delta^{34}S$ values (Burdett et al., 1989; Strauss, 1997). Until now, few comparable sulfur isotopic studies across this critical boundary have been conducted. In this paper, we present new carbon and sulfur isotopic chemostratigraphic data across the G–L boundary that provides useful clues to understand the tremendous environmental, oceanographic changes and relevant biotic crisis during this critical transition.

2. Geological setting

Marine sections recording continuous deposition across the G–L boundary are particularly rare because the end Guadalupian global regression tends to produce an unconformity. However, the Laibin area of Guangxi Province, South China is exceptional and records the complete G–L succession of pelagic biozones. The Global Stratotype Section and Point (GSSP) for the G–L boundary is located at the Penglaitan section, east of Laibin, which has well-constrained biostratigratigraphic resolution for this interval (Jin et al., 2006). The well-preserved Tieqiao section, ~25 km from the classic Penglaitan section, was selected for the chemostratigraphic study because it shows the same depositional sequence (Fig. 1).

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The Laibin area is located in the Jiangnan Basin and lies between the Yangtze and Cathaysian cratons throughout the Late Palaeozoic–early Triassic interval (Wang and Jin, 2000). The rapid change between the end Guadalupian regression and the quick transgression during the early Lopingian drastically changed the geography of the entire South China block (Wang and Jin, 2000). The Guadalupian–Lopingian boundary succession, in ascending order, includes the Maokou (Laibin limestone member), and Heshan Formations. At the Tieqiao section, the Laibin limestone Member, 11 m thick, consists of massive pale-gray slope debris and mound limestone. The overlying Heshan Formation, 150 m thick, is mainly composed of thin-bedded cherty limestone and biogenic limestone. Details of the biostratigraphy and other relevant information were provided previously (Mei et al., 1998; Jin et al., 2006). Some studies suggested that mass biotic extinctions occurred in the base of the *J. granti* zone, considerably below the Guadalupian–Lopingian boundary (Sun and Xia, 2006). However, Chen et al. (2009) indicated that the potential extinction horizon is ~30 cm above the G/L boundary at the Tieqiao section.

3. Analytical methods

Systematic analyses for $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$ and $\delta^{34}S_{sulfate}$ were conducted in the G–L boundary succession at the Tieqiao section. Diagenetic influences on the carbonate samples for isotopic analyses were first evaluated by petrographic examination; only homogeneous micritic carbonates were selected for isotopic analyses. The total organic carbon (TOC) content was measured by High TOC II analyzer and the analytical precision is better than $\pm 0.05‰$.

Sample splits (~5 mg) for inorganic carbon and oxygen analysis were reacted with 100% phosphoric acid at 50 °C for 24 h; isotopic ratios were measured on a Finnigan MAT-251 mass-spectrometer. Analytical precision is better than $\pm 0.05‰$ both for $\delta^{13}C_{carb}$ and $\delta^{18}O$. Sample splits (300 mg to 1.5 g) for $\delta^{13}C_{org}$ analysis were first dissolved with 5 N HCl in a centrifuge beaker to remove carbonates through multiple acidifications (at least two times) and subsequent drying in the heating oven, and repeatedly rinsed with deionized water to neutrality. The decalcified samples (30 to 110 mg) + CuO wire (1 g) were added to a quartz tube, and combusted at 500 °C for 1 h and 850 °C for

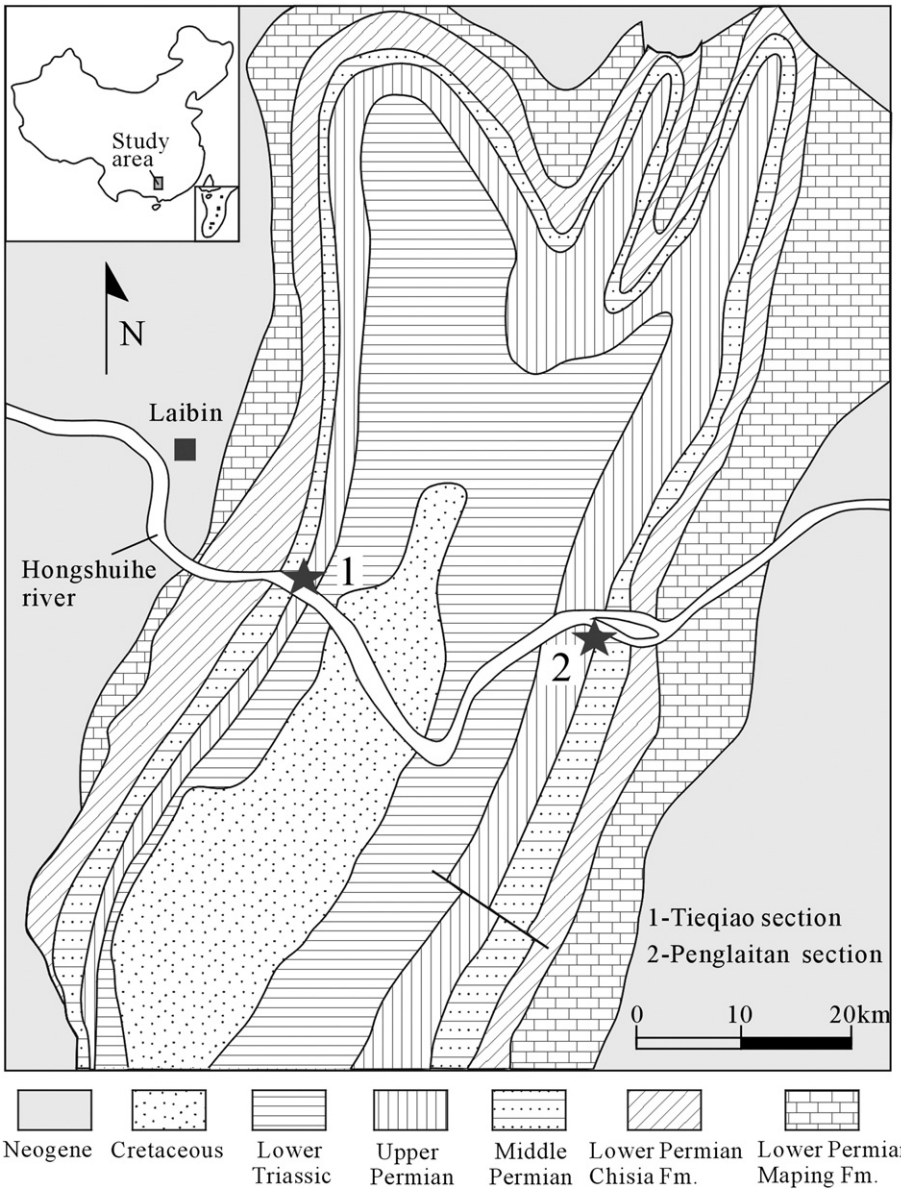

Fig. 1. Location and geological map for Tieqiao section, Laibin, Guangxi Province, South China (after Wang et al., 2004).