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The Late Devonian Frasnian–Famennian (F/F) biotic crisis: Insights from $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic systematics

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Abstract

A severe biotic crisis occurred during the Late Devonian Frasnian–Famennian (F/F) transition (± 367 Myr). Here we present $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic systematics, from identical samples of two sections across F/F boundary in South China, which directly demonstrate large and frequent climatic fluctuations (~ 200 kyr) from warming to cooling during the F/F transition. These climate fluctuations are interpreted to have been induced initially by increased volcanic outgassing, and subsequent enhanced chemical weathering linked to the rapid expansion of vascular plants on land, which would have increased riverine delivery to oceans and primary bioproductivity, and subsequent burial of organic matter, thereby resulting in climate cooling. Such large and frequent climatic fluctuations, together with volcanic-induced increases in nutrient (e.g., biolimiting Fe), toxin (sulfide) and anoxic water supply, and subsequent enhanced riverine fluxes and microbial bloom, were likely responsible for the stepwise faunal demise of F/F biotic crisis.

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1. Introduction

The severe F/F biotic crisis, one of the greatest five in the Phanerozoic times, was characterized by stepwise massive demises by $\sim 80\%$ of marine fauna, particularly shallow-water tropical species

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[1]. Numerous hypotheses, including bolide impacts [2], marine anoxia [3] or land plant-induced marine anoxia [4,5], eutrophication [6], and climate warming [7] or cooling [8], have been proposed as the cause of this event. The ultimate cause of this extinction event, however, is still highly controversial.

A prominent feature of this event is the greatly increased $^{13}\text{C}/^{12}\text{C}$ ratios of marine carbonates ($\delta^{13}\text{C}_{\text{carb}}$) [3,9–11] and organic matter ($\delta^{13}\text{C}_{\text{org}}$) [6,9,10,12], indicating an increased burial rate of ^{13}C -depleted organic carbon (C_{org}) in response to the oceanic anoxia [3,10], and/or enhanced primary productivity [6]. Enhanced burial of organic matter would have, in turn, led to a significant drop in atmospheric CO_2 concentrations (or P_{CO_2}) [13], which may explain the apparent, transient climatic cooling, associated with the Late Kellwasser Event in the earliest Famennian [8]. Accordingly, the peak of $\delta^{13}\text{C}_{\text{org}}$ excursion should be larger in magnitude and later in time compared to $\delta^{13}\text{C}_{\text{carb}}$ values, as a result of a drop in the isotope fractionation effect (ϵ_{p})—isotopic difference between aqueous dissolved CO_2 ($[\text{CO}_{2\text{aq}}]$) and biomass of marine phytoplankton [14,15]. However, such a pattern of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ pairs has not been established yet in the marine carbonates of Late Devonian in the global data set [3,6,9–12]; this has greatly limited our understanding of the oceanic and climatic changes over the F/F transition.

The Sr isotopic composition of seawater at any time represents the balance between continental weathering (radiogenic ^{87}Sr -enriched) and hydrothermal fluxes (^{87}Sr -depleted) to the oceans due to a short mixing time (~1500 years) and a long residence time (2–3 Myr.) of dissolved Sr in the oceans [16]. Increased continental weathering would increase the flux of both dissolved Sr with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and nutrients to the oceans [17,18], causing an increase in oceanic primary productivity. Alternatively, increased sea-floor spreading, submarine volcanism, and hydrothermal activity would increase the flux of Sr with low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios [19], as well as the flux of iron and reducing sulfide, thereby decreasing the oxygen content in bottom water. Therefore, the temporal variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of marine carbonates can reflect the signature and magnitude of interactions between tectonics, weath-

ering rate and climate. Nevertheless, $^{87}\text{Sr}/^{86}\text{Sr}$ data across the F/F interval are extremely rare except for the low-resolution $^{87}\text{Sr}/^{86}\text{Sr}$ data sets presented by Veizer et al. [20].

In order to better constrain the tectonic, oceanic and climatic changes, and their biogeochemical responses during the F/F event, $\delta^{13}\text{C}_{\text{carb}}-\delta^{13}\text{C}_{\text{org}}-^{87}\text{Sr}/^{86}\text{Sr}$ isotopic systematics from identical sample sets of two sections across the F/F boundary in South China were analysed in this research; these combined isotopic data will provide more realistic information, greatly improving and refining our understanding of the causes of the F/F biotic crisis.

2. Geological setting

The Late Devonian carbonates were widely deposited on platforms and interplatform basins in the South China transtensional rift basin (Fig. 1A) [21]. The studied sections are located at Fuhe and Baisha between Guilin and Yangshuo, Guangxi province, South China. Palaeogeographically, they were located within the offshore spindle-shaped Yangshuo Basin, which was surrounded by shallow-water carbonate platforms and isolated from significant continental siliciclastic influxes (Fig. 1B). Such a basin configuration was interpreted as having been formed through strike-slip faulting [21]. The carbonates at these two localities are mainly composed of pelagic nodular limestones intercalated with subordinate calcareous gravity-flow deposits (calciturbidites and pebbly conglomerates), which are well dated through conodont zonation and high-resolution cyclostratigraphic approaches on the basis of Milankovitch orbital-forcing cyclicity (see Figs. 2 and 3) [22].

3. Materials and methods

Combined $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values were measured from identical samples from two sections (Fuhe and Baisha) (Fig. 1B) across the F/F boundary in South China. The analysed samples are micritic carbonates collected from basal successions generally with a low

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