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### Global and regional controls on marine redox changes across the Ordovician-Silurian boundary in South China

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### ABSTRACT

The Ordovician-Silurian (O-S) transition coincided with significant environmental and biological changes. In South China, the Yangtze Platform experienced both global and regional events at this time, including sea-level fluctuations, tectonic movements, volcanic eruptions, mass extinction, and widespread anoxia. The O-S transitional strata of the Yangtze Platform comprise organic-rich black shales that are an important oil source rock. To explore the evolution of watermass chemistry and its relationship to organic matter accumulation, we conducted an integrated Fe-S-C geochemical study (i.e., Fe-speciation,  $\delta^{13}C_{org}$ ,  $\delta^{34}S_{py}$ , pyrite-S and TOC) of the O-S boundary sections at Datianba (Chongqing Municipality) and Shuanghe (Sichuan Province). These sections were located in the restricted inner Yangtze Sea, in contrast to the previously studied Wangjiawan section, which was deposited in a more open setting of the outer Yangtze Sea. In contrast to the well-oxygenated conditions during the Hirnantian, which can be explained by the unique paleogeography and restricted hydrography of the inner Yangtze Sea. We propose that the regional Kwangsian Orogeny, which was driven by collision of the Yangtze and Cathaysia blocks, played a key role in basin development, watermass chemistry changes, and accumulation of Wufeng Formation black shales within the Yangtze Sea. The more widespread black shales of the Lower Silurian Lungmachi Formation were linked to the post-Hirnantian global marine transgression.

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#### 1. Introduction

The Late Ordovician (Katian-Hirnantian) to Early Silurian (Rhuddanian) (~453–441 Ma, referred to herein as the 'O-S transition') was an important interval in Earth history, during which a series of events of global consequence took place. These events included the Hirnantian glaciation and deglaciation, one of the 'Big Five' mass extinctions and a post-extinction faunal recovery, large sea-level changes, and the widespread deposition of organic-rich shales (see review in Algeo et al., 2016). The relationships among these events are still not fully understood. For example, some authors have proposed that the biological extinction was caused directly by cooling associated with the Hirnantian glaciation (Stanley, 2010; McGhee et al., 2012), whereas others have linked it to glacially induced changes in oceanic redox conditions (e.g., Harper et al., 2014). The latter hypothesis involves two different views

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http://dx.doi.org/10.1016/j.palaeo.2016.10.006 0031-0182/© 2016 Elsevier B.V. All rights reserved. of ocean-redox changes during the Hirnantian glaciation: (1) increasingly oxic conditions (e.g., Sheehan, 1988; Melchin and Mitchell, 1991; Skelton, 1994; Brenchley et al., 2001; Yan et al., 2012), or (2) increasingly reducing conditions (e.g., Zhang et al., 2009; Hammarlund et al., 2012).

The causes of widespread deposition of black shales in the aftermath of the Hirnantian glaciation are under debate also (Lüning et al., 2005; Armstrong et al., 2006; Le Heron et al., 2009; Loydell et al., 2009). One theory contends that glaciation enhanced physical weathering on the continents, generating rock flour with a high surface-to-volume ratio (Saltzman, 2005). Intensified chemical weathering during the subsequent deglaciation then released large amounts of nutrients such as phosphorus, silica and ferrous iron that were transported to the ocean, leading to algal blooms. Generally high primary productivity and organic carbon sinking fluxes led to the development of black shales. However, in South China, black shale formation began much earlier than elsewhere, during the Katian (i.e., pre-glaciation), and continued for longer, into the Telychian (mid-Silurian) (Chen et al., 2004; Yan et al., 2012; Gorjan et al., 2012).

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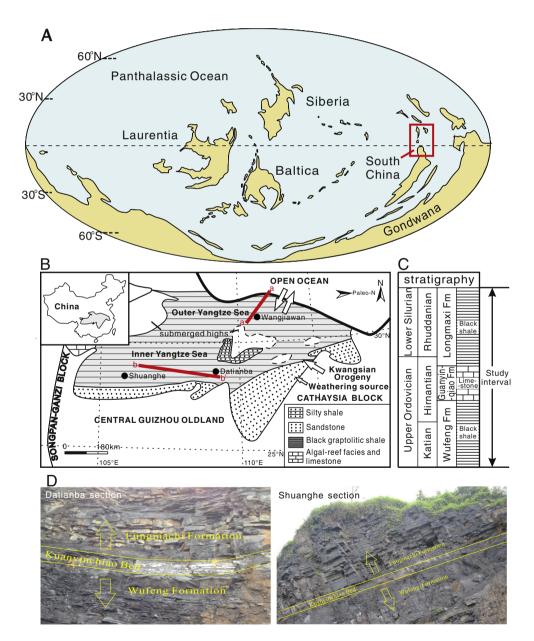
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The protracted deposition of black shales on the South China Craton may have been due to unusual paleogeographic boundary conditions (Chen et al., 2004; Melchin et al., 2013). During the Early Paleozoic, South China was largely isolated from other continents (Fig. 1A). This craton consisted of the Yangtze and Cathaysia blocks, which were separated by the Neoproterozoic-early Paleozoic Nanhua Basin and welded together during the Ordovician-Silurian Kwangsian Orogeny (Chen et al., 2014). The Yangtze Platform, which comprised the central part of the Yangtze Block, was surrounded by emergent uplifts on three sides and connected to the open ocean to the north (note: all orientations given are modern compass directions), generating the mostly enclosed epeiric Yangtze Sea (Fig. 1B). Owing to this distinct paleogeographic pattern, the Yangtze Sea exhibited weak to no watermass restriction in its outer regions (to the north-northeast) and strong watermass restriction in its inner regions (to the south-southwest). Owing to its relative restriction, regional tectonic events strongly influenced the

evolution of water redox conditions in the inner Yangtze Sea during the Late Ordovician to Early Silurian.

The O-S transition interval in South China was marked by major regional volcanic and tectonic events, including frequent volcanic eruptions (Su et al., 2003, 2007, 2009) and the Kwangsian Orogeny (Chen et al., 2012, 2014). The composition of K-bentonites in the O-S black shale succession indicates a source related to subduction-zone volcanism, possibly associated with convergence of the Cathaysia and Yangtze blocks (Su et al., 2003, 2006). The Kwangsian Orogeny, first proposed by Ting (1929), was a major tectonic event that produced an angular unconformity between O-S strata and overlying Devonian strata in South China. However, the influence of these two important regional events on the evolution of environmental and watermass redox conditions in the Yangtze Sea are not well understood.

In order to explore the combined effects of global and regional events on the evolution of watermass redox conditions and the



**Fig. 1.** Geological background. (A) Late Ordovician global paleogeography (modified from Melchin et al., 2013). (B) Paleogeographic map of the Yangtze Platform during the Late Ordovician (modified from Chen et al., 2004). Note that the Yangtze Platform was rotated ~90° counter-clockwise relative to its modern orientation. (C) General stratigraphy of the Upper Ordovician to Lower Silurian in South China. The red lines a-a' and b-b' represent the transects shown in Fig. 5. (D) Photographs of Datianba (left) and Shuanghe (right) sections. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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