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## Palaeoenvironmental change across the Guadalupian-Wuchiapingian boundary in Sichuan, South China

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The Guadalupian-Lopingian (Middle-Late Permian) transition was a critical interval in geological history, during which dramatic climatic, oceanic, and biological changes occurred (Banner and Hanson, 1990; Chen et al., 2009). Numerous hypotheses have been proposed as the cause of this particular geologic event, including changes in sea level, in temperature, and in paleoceanography, reduction in habitata, and any of the above combinations (Burdett et al., 1989; Hallam and Wignall, 1999; Clapham et al., 2009). The ultimate cause of this event, however, is still highly controversial. Although a catastrophic event of some type appears to have occurred at the Guadalupian-Lopingian boundary, long-term changes in environmental conditions appear to have played a role as well(Freeman and Hayes, 1992; Jin et al., 2006; Wignall et al., 2009a,2009b). There is strong evidence for environmental deterioration throughout the Guadalupian-Lopingian boundary, which may have stressed marine ecosystems prior to the main extinction event. In this study, we present the results of chemostratigraphic analyses of one Guadalupian-Lopingian boundary section with a complete biostratigraphy sequence from the South China plate. The present high-resolution analysis of this section using

multiple chemostratigraphic proxies provides evidence of large, high-frequency changes in seawater chemistry, and the significance of these changes for understanding the origin of the catastrophic event will be considered in this contribution.

Thirty-five samples collected from a ca. 21.2m thick sequence in the Rongcun section have been provided for the present trace element study. Samples were analyzed on a VG PQ2 Turbo inductively coupled plasma source mass spectrometer (ICP-MS) at the Institute of Geology and Geophysics, Chinese Academy of Sciences. Analytical precision for elemental concentrations was generally better than 4%. Cerium ( $Ce/Ce^*$ ) and europium anomalies ( $Eu/Eu^*$ ) were calculated from:  $Ce/Ce^*=Cen/(Lan\times Prn)^{1/2}$ ,  $Eu/Eu^*=Eun/(Smn\times Gdn)^{1/2}$ , using shale-normalized abundances. Normalization value is the North American shale composite (NASC). Shale-normalized Lan/Ybn ratios are assigned to reflect the relative enrichment of light REE (LREE) vs. heavy REE (HREE). Ce/La ratios are also used in this study to differentiate the depositional environment.

Trace elements generally show systematic enrichment throughout the sequence. A comparison of the average

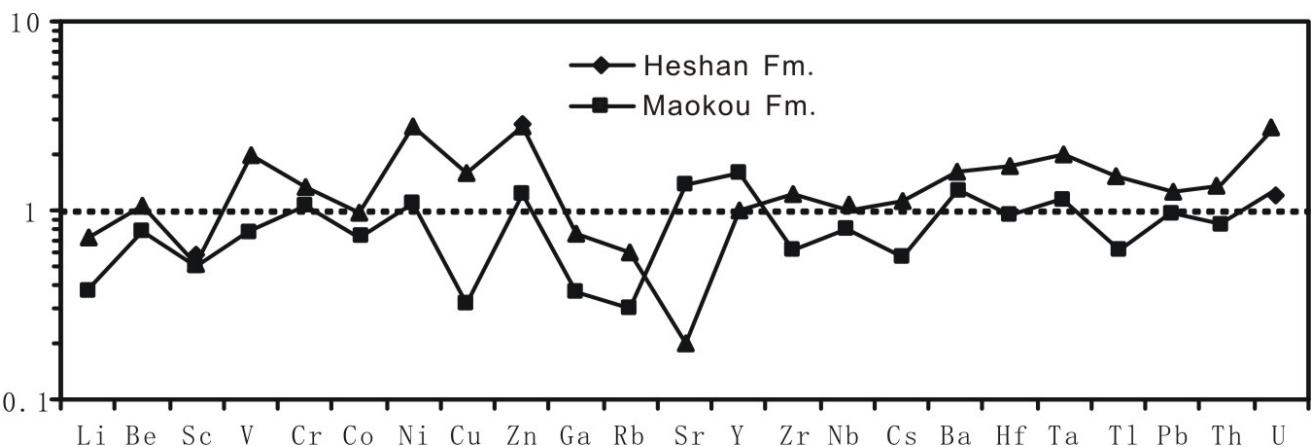


Fig.1. Trace element enrichment factors relative to average shale in sedimentary rocks of the Rongcun section.

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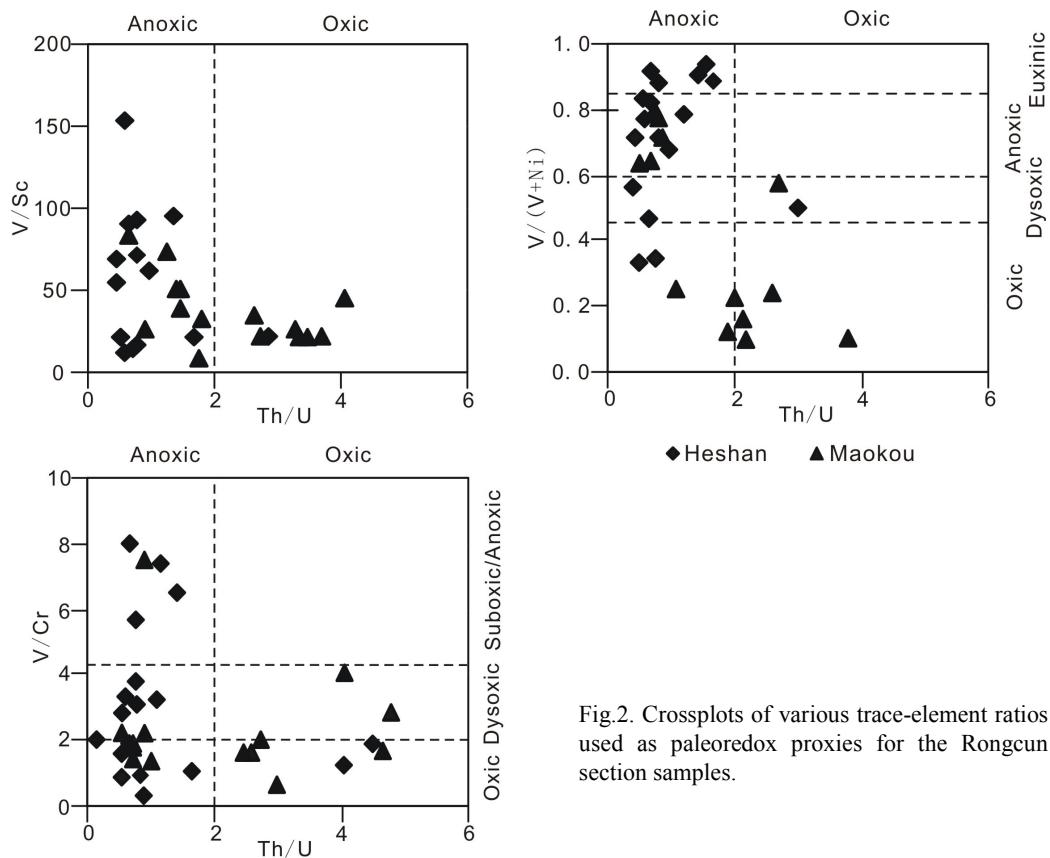


Fig.2. Crossplots of various trace-element ratios used as paleoredox proxies for the Rongcun section samples.

compositions by stratigraphic position with NASC on multi-element plots shows that many elements such as Cr, Ni, Cu, Zn, Nb, Tl and Pb fluctuate in their abundance through time (Fig. 1). Ni, Cu and Zn are enriched relatively to NASC in these formations, whereas other compatible elements such as Sc, Co and Sr show depletion. Fluctuations in the suite seem to be greatest along these grouping, with prominent changes in V, Zn and U. The total REE abundances show a large variation, with the Rongcun section from 27.03 to 357.65 ppm (averaging 159.98 ppm). Compared to NASC,  $\Sigma$ REE in Rongcun section are high in regimes greatly influenced by continental input, owing to the low sedimentation rate, which increases exposure time to seawater and, thus, the adsorption of REE. The La/Ybn ratios are mostly greater than 1.00 in the two lithologic types except for two low values (0.76 and 0.87, respectively). A remarkable and noteworthy stratigraphic change of Ce anomaly is recognized in this section. Secular variation of whole-rock Ce anomalies of the Rongcun section fluctuates between 0.67 and 0.95. The Ce negative spans without any relation to the lithological change from Limestone to mudstone.

Previous studies show that fine-grained sediments deposited near ocean spreading ridges have the lowest Ce/Ce\* values (avg. 0.29), while those deposited on the ocean basin floor have the intermediate Ce/Ce\* values (avg. 0.60), and those deposited on continental margins have the

highest Ce/Ce\* values (avg. 1.03). Our Ce/Ce\* values (0.67-0.95) from shale and limestone are generally consistent with those of an ocean basin environment as stated above, suggesting that the shale and limestone was deposited in an environment far from terrigenous sources, i.e., in an marine basin. The Ce negative excursion which occur independent of lithological change from limestone to mudstone and shale also suggests marine basin environemnt. Therefore, we interpret the Ce negative excursion to be the change in sea water chemistry. Ce anomalies have been found exclusively in ocean basins, with seawater being typically depleted in Ce with respect to its REE neighbours La and Pr. It is suggested that the extent of Ce anomaly in seawater is mainly controlled by the redox conditions and has been used as a tracer to distinguish between anoxic and oxic water bodies in the geological past. A depletion of Ce relative to its neighboring elements give rise to a negative Ce-anomaly and may result from the presence of calcareous and siliceous organisms, phillipsites, phosphorite and smectite. A positive Ce-anomaly results where Ce is enriched relative to its neighbors and might resulted from the presence of Fe-Mn oxyhydroxides.

Based on previously established thresholds, geochemical ratios, including Th/U, Ni/Co, V/Cr, and V/(V+Ni), together with sedimentary facies and fossils, indicate that the Guadalupian ocean was strongly stratified

(Fig. 2). The oxic bottom waters predominated over the Rongcun area, but the redox environment may have changed due to chemocline instability. During the lower Heshan intervals, an anoxic environment predominated during rapid transgression. An upward chemocline excursion led to significant amounts of  $H_2S$  gases being released into the photic zone and even atmosphere, resulting in photic zone euxinia (Kaiho et al., 2005); this scenario would have been very harmful, both for the benthic and planktonic fauna (Isozaki et al., 2007). The subsequent rapid transgression resulted in oceanic anoxia, expelling the benthos from their previous ecologic niches, thereby leading to their significant decline. Therefore, chemocline excursions, together with subsequent rapid transgression and oceanic anoxia, may account for the massive demises during the Guadalupian-Lopingian transition.

**Key words:** Trace elements; Paleoredox proxies; Guadalupian-Lopingian boundary; South China

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