

# Calcium isotope evidence for an episode of ocean acidification across the Early Triassic Smithian-Spathian boundary recorded in the Shitouzai section, South China

He Zhao<sup>1</sup>, Feifei Zhang<sup>2</sup>, Zhong-Qiang Chen<sup>3</sup>, Yongsheng Liu<sup>1</sup>, Zhaochu Hu<sup>1</sup>, Zihao Hu<sup>1</sup>

<sup>1</sup> *State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan 430074, China*

<sup>2</sup> *Department of Geology and Geophysics, Yale University, New Haven, CT 06511, U.S.A.*

<sup>3</sup> *State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China*

The Smithian-Spathian boundary (SSB) is marked by a global positive carbon isotope ( $\delta^{13}\text{C}$ ) shift, climatic cooling from a middle/late Smithian boundary hyperthermal condition, and a major marine biotic crisis on the road of marine ecosystem recovery from the end-Permian mass extinction. Several scenarios, including ocean acidification, have been proposed to account for the positive  $\delta^{13}\text{C}$  shift in and the marine biotic crisis. Secular variation in the calcium isotope ( $\delta^{44/40}\text{Ca}$ ) composition of marine carbonate sediments provides a tool for examining changes in marine Ca chemistry and a potential ocean acidification event across the SSB. In this study, we constructed high-resolution  $\delta^{13}\text{C}$  and  $\delta^{44/40}\text{Ca}$  profiles for a shallow platform carbonate section (the Shitouzai section in the Ziyun County, Guizhou Province, South China) that captured the SSB to track changes in marine Ca chemistry and potential acidification across the SSB. Our  $\delta^{44/40}\text{Ca}$  profile exhibits a transient positive shift from  $\sim+0.14\text{‰}$  in the early late Smithian to  $\sim+0.49\text{‰}$  at the SSB, which is followed by a negative shift to  $\sim+0.24\text{‰}$  in the earliest Spathian. Traditional carbonate diagenetic indicators suggest that our  $\delta^{44/40}\text{Ca}$  record was not systematically altered by post-depositional diagenesis, we thus tentatively interpret our  $\delta^{44/40}\text{Ca}$  record as a primary oceanographic signal that recorded secular variations in seawater Ca chemistry across the SSB. During the late Smithian, the increase of seawater  $\text{Ca}^{2+}$  concentrations coincide with the Smithian Thermal Maximum, reflecting episodic marine acidification that contributed to the loss of marine biodiversity losses at the end of the Smithian.