

Constraining diagenetic barium cycling with pore-water stable barium isotopes

Z. CAO^{1*}, X. RAO¹, Q. HONG¹, E. C. HATHORNE², C. SIEBERT², C. EHLERT³, S. KASTEN^{4,5} AND M. FRANK²

¹State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361102, China
(*correspondence: zmcao@xmu.edu.cn)

²GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel 24148, Germany

³Max Planck Research Group for Marine Isotope Geochemistry, Institute for Chemistry and Biology of the Marine Environment, University of Oldenburg, Oldenburg 26111, Germany

⁴Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Bremerhaven 27570, Germany

⁵Faculty of Geosciences, University of Bremen, Bremen 28359, Germany

Recent success in the determination of stable barium (Ba) isotopic compositions provides a novel tool to study the diagenetic cycling of Ba and evaluate the reliability of the Ba proxy for reconstruction of paleosalinity and paleoproductivity. Here we present a new set of pore-water profiles of dissolved Ba isotopes ($\delta^{138/134}\text{Ba}$) in surface sediments from the upper reaches to the lower seaside of the Pearl River Estuary (PRE) in Southern China. We find pronounced depth-dependent $\delta^{138/134}\text{Ba}$ variations generally showing a shift to lighter values from the topmost layer down to 15 cm depth. These gradients, primarily resulting from Ba isotope fractionation caused by various solution-solid phase interactions, confirm that Ba isotopes are a powerful tracer for Ba dynamics during sediment diagenesis. Both formation of authigenic barite and Ba precipitation associated with the redox cycling of manganese preferentially remove light Ba isotopes from the pore-water. These processes induce the heaviest $\delta^{138/134}\text{Ba}$ (0.5-0.7‰) in the topmost pore-water, which, however, does not significantly contribute to the bottom waters of the PRE characterized by lighter $\delta^{138/134}\text{Ba}$ (0.1-0.3‰). This contrast suggests that Ba isotopes in sediments are potentially a more robust proxy of paleosalinity than Ba concentrations because even considerable benthic fluxes of Ba would not significantly influence the conservative $\delta^{138/134}\text{Ba}$ -salinity relationship in the water column of estuaries. On the other hand, barite dissolution in sulfate-depleted sediments and subsequent precipitation of authigenic barite most likely alter the original sedimentary Ba isotopic compositions, implying that in this case the Ba isotope proxy data need to be considered with caution.