



Reconstruction of pH and partial pressure of carbon dioxide during the Mesozoic era period using boron and oxygen isotopic compositions of fresh ammonoids & nautiloids

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The increase of partial pressure of carbon dioxide ($p\text{CO}_2$) in the atmosphere induces global warming and ocean acidification at the modern condition. The reconstruction of $p\text{CO}_2$ during the geological time is required together with proxy calibration by laboratory experiments to predict the future environments. Boron isotopic ratio is an excellent proxy for pH and the relevant partial pressure of carbon dioxide in the seawater (PCO_2). This study is the first to quantify pH dependence of $\delta^{11}\text{B}$ of the ammonoids and nautiloids mainly in the Cretaceous and in Jurassic (70-162 Ma), which are expected to be much warmer due to higher PCO_2 . However, no reliable reconstruction data using foraminiferal $\delta^{11}\text{B}$ before Cenozoic era has been reported. We used the very fresh aragonite shells of ammonoids and nautiloids by big advantages. Since aragonite changes into secondary calcite by diagenesis, it is easy and effective to identify the degree of alteration at each sample by measuring calcite/aragonite ratio. Also we carefully conducted the assessment of secondary alteration from three perspectives: 1) Determination of calcite/aragonite ratio by X-ray diffraction (XRD), 2) Observation of microstructures of the nacreous layers by scanning electron microscope (SEM), and 3) Measurement of trace element contents and stable isotope ratios. We conducted high precision boron isotope analysis of biogenic carbonates with ± 0.1 per mil reproducibility by adopting positive thermal ionization mass spectrometry (P-TIMS) methods. Also we analyzed $\delta^{18}\text{O}$ to estimate paleo-temperature, at which biogenic aragonite was formed. Combination of $\delta^{11}\text{B}$ and $\delta^{18}\text{O}$ of biogenic aragonite in 80 Ma and 86 Ma revealed that deeper dwellers showed lower $\delta^{11}\text{B}$ values, which corresponded to lower pH. This feature is consistent with those observed in the modern vertical water column. The respective shallow water temperature was 19.7 and 19.1 centigrade. Based on these results, the reconstructed maximum PCO_2 levels at late Cretaceous (80 Ma and 86 Ma) were estimated to be 1750 and 1540 ppm, respectively. This coincides with the suggestion by Breecker et al. (2010) that $p\text{CO}_2$ for the last 400 millions was usually at below 2000 ppm by reassessing the $\delta^{13}\text{C}$ proxy in soils.