Reconstruction of pH and PCO2 by boron isotopes of unaltered ammonoids & nautiloids and the expected high alkalinity during the Cretaceous

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The reconstruction of pCO2 during the geological time is required in order 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 (PCO2). By using P-TIMS method, we conducted the high precision analysis of delta 11B (+/- 0.1 per mil reproducibility) of unaltered aragonite shells of ammonoids and nautiloids mainly in the Cretaceous and in Jurassic (70-162 Ma), which were expected to be much warmer due to higher PCO2. So far, difficulty of fresh biogenic carbonate during these periods has produced no reliable reconstruction data using foraminiferal delta 11B before Cenozoic era. Our careful assessment of secondary alteration was conducted by 1) Determination by X-ray diffraction (XRD), 2) Observation of microstructures of the nacreous layers by SEM, and 3) Measurement of trace element contents. Positive correlation between delta 11B and delta 18O (temperature) of biogenic aragonites in 80 and 86 Ma revealed that relatively deeper dwellers within the surface ocean showed lower delta 11B values, which corresponded to lower pH. It is observed in the modern vertical water column. The reconstructed maximum PCO2 levels at late Cretaceous (80 Ma and 86 Ma) are 1,750 and 1,540 ppm, respectively. This is moderately high, coinciding with the suggestion by Breecker *et al*. (2010). Abundant deposition of biogenic carbonate during the Cretaceous requires the enhancement of alkalinity, which could be raised by 20% relative to modern value. This is indirectly supported by seawater-rock interaction in Oman ophiolite around 100Ma. Both terrestrial and ocean environments have strong buffering mechanism for pH and PCO2 levels in moderate time scale.

Supercontinent cycle and 2nd continents

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It has been thought that granitic crust, having been formed on the surface, must have survived through the Earth's evolution because of its buoyancy. Recent geological studies have suggested that a significant amount of crustal material has been lost from the surface due to delamination, continental collision, and subduction at oceanic–continental convergent margins (von Huene and Scholl 1991; Yamamoto *et al*. 2009; Ichikawa *et al*. 2013a). If so, then the subducted crustal materials are expected to be trapped in the mid-mantle due to the density difference from peridotitic materials induced by the phase transition from coesite to stishovite (Kawai *et al*. 2013). In order to study the effect of the subducted granitic materials floating around the mantle transition zone, we conducted two-dimensional numerical experiments of mantle convection incorporating a continental drift with a heat source placed around the bottom of the mantle transition zone. We found that the addition of heat source in the mantle transition zone considerably enhances the onset of upwelling plumes in the upper mantle, which further reduces the time scale of continental drift. The heat source also causes massive mechanical mixing, especially in the upper mantle. The results suggest that the heat source floating around the mantle transition zone can be a possible candidate for inducing the supercontinent cycle (Ichikawa *et al*. 2013b).

www.minersoc.org
DOI:10.1180/minmag.2013.077.5.11