Reconstruction of seawater pH and atmospheric CO₂ concentration based on boron isotopic composition of biogenic calcium carbonate

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A lot variety of environmental information is recorded in marine biogenic calcium carbonate that is represented by reef building coral skeletons and foraminifera shells. Among these, **boron isotope** (δ^{11} B) proxy is of great importance in the realm of paleoclimatology and paleoceanography, since it can record seawater pH and CO₂ concentration of the overlying atmosphere. Along with the growing interest to recent environmental problems such as global warming and ocean acidification due to anthropogenic CO , emission, past carbon cycle research has been actively conducted, and boron isotope proxy is priceless tool to study it. In 1980s, applicability of this proxy was foreseen, but high precision boron isotope measurement with small sample requirement was difficult at that time. As boron exist abundantly around us (the most representative one is borosilicate grass), analytical technique has evolved as the boron-free clean environment improved. Thermal ionization mass spectrometry (TIMS) was first developed, and nowadays multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), secondary ionization mass spectrometry (SIMS), and laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) (and others) is now available. Measurable minimum sample amount, achievable analytical precision, and spatial resolution of the analysis are largely different among methods, and efforts to measure boron isotope composition more precisely with smaller amount of samples has continued at research institutes around the world. In Kochi Institute for Core Sample Research, Japan Agency for Marine-Earth Science and Technology, boron isotope measurements by using TIMS and MC-ICPMS are available: the former realizes the most precise measurement in the world, and the latter realizes analytical precision and required sample amount that is comparable with major overseas laboratory. In this presentation, I will explain theoretical background why boron isotope of marine biogenic calcium carbonate becomes seawater pH proxy and characteristics of two different mass spectrometry, and then overview already-done research and ongoing research topics. Recent development of visualization technology of pH of calcifying fluid of reef building coral and foraminifera has enabled deeper understandings of boron incorporation systematics. On the one hand, boron isotopes of reef building coral is most-likely a direct indicator of pH of calcifying fluid; on the other hand, those of foraminifera is likely influenced by microenvironment pH gradient surrounding foraminifera. Whatever the mechanism is, a clear relationship between boron isotopes and seawater pH is observed in various samples such as cultured, recently live-collected, and fossil samples, thus many studies use this proxy in paleoclimatology and paleoceanography by understanding empirical relationship collectly ("calibration").

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