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Li/Ca in multiple species of planktonic foraminifera: Observed millennial to glacial-interglacial variations

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Lithium and calcium are both conservative elements in ocean, with similar residence time of one million years. With such long residence time, lithium to calcium ratio (Li/Ca) in seawater is not expected to have changed over recent glacial-interglacial cycles. Like many other dissolved metals in ocean, Li is incorporated in foraminiferal calcite shell. Previous studies suggested that Li/Ca in planktonic foraminiferal shell was largely elevated during the last glacial period. This implies that Li/Ca change may be related to some kind of glacial-interglacial changes in the ocean. However, culture experiments show that Li/Ca in planktonic foraminifera is not driven by any key physico-chemical parameters, such as ion carbonate concentration ($[CO_3^{2-}]$), dissolved inorganic carbon (DIC), temperature or salinity. Thus, the underlying mechanisms that lead to the elevated foraminifer Li/Ca during the last glacial period and Li/Ca glacial-interglacial changes remain unknown.

In order to test whether planktonic foraminifer Li/Ca ratios had been high during each past glacial period and check for glacial/interglacial variations, we measured Li/Ca changes from planktonic foraminifera *Globigerinoides ruber* and *Pulleniatina obliquiloculata* through the last 270 ka in a sediment core located in the eastern tropical Indian Ocean. Li/Ca values were systematically higher in *G. ruber* than in *P. obliquiloculata* during the interval of ~270 to 19 ka; however, from 19 to 5 ka, Li/Ca ratios became comparable between the two species, implying a noticeable change in hydrographic and/or physico-chemical conditions. In both species, Li/Ca varies independently from Mg/Ca, clearly indicating that Li/Ca is not mainly controlled by growth temperature. Both records show precession (23ka) and obliquity (41ka) periodic components, which appear to co-vary with atmospheric pCO_2 variations, suggesting a possible link of Li/Ca with seawater carbonate chemistry. However, Li/Ca ratios in *G. ruber* and *P. obliquiloculata* show anomalously high values between ~ 37 to 19 ka, which do not compare with either benthic $\delta^{18}O$ or pCO_2, suggesting that other environmental or diagenetic influences are at play.