Ph. D. Thesis Abstract

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Title: CO₂ Ventilation, Hydrological Cycle over Southern Ocean and Clumped Isotope Thermometry in Biogenic Carbonates

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Abstract: The thesis presents observations on the CO_2 concentration and carbon isotopes in air CO_2 ($\delta^{13}C$) to constrain the inter-annual variability of carbon inventory over the Southern Ocean between the years 2011-2013. Based on the observation, the region of CO_2 venting was identified over the Southern Ocean. Further, isotopic characterization allowed inferring about the possible sources of CO_2 degassing and contribution from the dissolved inorganic carbon (DIC) that exsolved to generate CO_2 . It is concluded that the origin CO_2 is mainly from the degassing of CO_2 available from the dissociation of DIC or organic degradation.

Live Foraminiferal samples of *Globigerina bulloides* from towing were captured, separated and analysed for δ^{18} O and δ^{13} C from various locations across the Southern Ocean between 10°N-60°S. A large similarities in the estimated values (deduced from simultaneous composition of ocean water δ^{18} O, δ^{13} C in DIC and temperature i.e. SST under equilibrium condition) and measured δ^{18} O and δ^{13} C values were observed until 40°S from the equator, and hence it was concluded that the calcification depth of G. bulloides is confined to a depth of ~75-200m till 40°S latitude. However, further south (>40°S) disequilibrium from the estimates was detected. A number of possible reasons were cited for the observed disequilibrium such as (1) Deeper depth habitat (2) Partial dissolution (3) Non-equilibrium calcification (4) Oceanic Suess Effect and (5) Genetic Variability. A box model of isotopic mass balance was presented in this study to explain the pattern of enrichment in the ¹³C values of sea water DIC with latitude (up to about 43°S). The model shows that a steady state of the carbon isotope ratio of water is achieved in a relatively short time of ~5000 days. Rainwater isotope in the open marine condition across the latitudinal transects over Southern Ocean marking zone of precipitation and evaporation is another element of this thesis. A variation with excess lighter isotopes in rainwater was observed in high latitude rain in this study. Observed isotopic depletion is attributed to rainout process over the ocean. The average rainout fraction over the Southern Ocean in the region of zone of precipitation is ~44%, while it drops to \sim 25% in the zone of evaporation. Second part of the thesis presents a novel method of isotope thermometry which is called "clumped isotope (13C18O16O16O-2 in the calcite structure) thermometry". A revision in the thermometry equation relating Δ_{47} vs T in synthetic carbonates precipitates and otoliths was proposed. The revised calibration was used on fish otoliths from the modern and past environment to estimate the temperatures. Together with the clumped isotope, conventional stable isotopes in the shell carbonates were measured to effectively reconstruct the seasonal fresh water fraction at seasonal time scales.