

Benthic foraminiferal I/Ca ratios as redox proxy in the Peruvian OMZ: Q-ICP-MS and SIMS Systematics

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The decline in ocean oxygenation induced by anthropogenic global warming is a matter of growing concern. The most important areas of oxygen depletion in today's oceans are tropical oxygen minimum zones (OMZs). An increase in the magnitude of oxygen depletion and OMZ extension might endanger habitats, currently rich in pelagic fish. Indeed, tropical OMZs have expanded over the last 60 years [1]. Thus, a quantitative oxygen proxy in OMZs is highly desirable.

Iodine/calcium (I/Ca) ratios in marine carbonates have been shown to be a valuable proxy for oxygen concentrations in the ambient water masses [2]. We explored the correlation between I/Ca ratios in four benthic foraminiferal species from the Peruvian OMZ to bottom water oxygen concentrations ($[O_2]_{BW}$) using quadrupole ICP-MS [3]. All species showed a positive trend in the I/Ca ratios correlated to $[O_2]_{BW}$. The highest significance has been found for the shallow infaunal species *Uvigerina striata* ($I/Ca = 0.032(\pm 0.004)[O_2]_{BW} + 0.29(\pm 0.03)$, $R^2 = 0.61$, $F = 75$, $P < 0.0001$). Although benthic foraminiferal I/Ca ratios are a promising redox proxy some methodical issues need to be considered: (a) the iodine volatility in acidic solutions, (b) a species dependency of the I/Ca- $[O_2]_{BW}$ correlation, and (c) the inter-test variability of I/Ca between specimens from the same species and habitat.

To assess also the intra-test heterogeneity, I/Ca ratios have been measured with secondary ion mass spectrometry (SIMS) on cross-sections of single foraminiferal specimens. Furthermore, cleaned and uncleaned specimens have been compared. Specimens treated with oxidative cleaning before embedding showed an iodine depletion compared to uncleaned specimens. Our results show that I/Ca ratios in benthic foraminifera are a valuable quantitative $[O_2]_{BW}$ proxy in the Peruvian OMZ which can be extended to calibrations for other OMZs as well, if methodological issues are carefully considered.

[1] Stramma *et al.* (2008) *Science*, **320**, 655-658. [2] Lu *et al.* (2010) *Geology*, **38**, 1107-1110. [3] Glock *et al.* (2014) *Biogeosciences*, **11**, 7077-7095.