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High resolution I/Ca ratios of benthic foraminifera from the Peruvian oxygen-minimum-zone: A SIMS derived assessment of a potential redox proxy

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ABSTRACT

Oceanic oxygen decline due to anthropogenic climate change is a matter of growing concern. Tropical oxygen minimum zones (OMZs) are the most important areas of oxygen depletion in the modern oceans. A quantitative oxygen proxy in OMZs is highly desirable in order to identify and monitor recent dynamics as well as to reconstruct pre-Anthropocene changes in amplitude and extension of oxygen depletion.

A previous study revealed that there are significant correlations between I/Ca ratios of foraminiferal bulk samples for different benthic foraminiferal species from the Peruvian OMZ. Nevertheless, species for which less specimens were available showed a higher variability between I/Ca ratios in different badges. To test if this might be related to intra- or inter-shell heterogeneity we focused on microanalyses of I/Ca ratios within these species in our present study. We developed a method for measuring benthic foraminiferal I/Ca ratios, a potential proxy for the reconstruction of marine oxygen concentrations. We applied 92 spot analyses in individual foraminiferal specimens from the Peruvian OMZ using secondary ion mass-spectrometry (SIMS). The I/Ca ratios on 8 of 11 cleaned *Uvigerina striata* and *Planulina limbata* specimens determined with SIMS showed no significant difference to previous ICP-MS measurements on bulk samples from the same species. This indicates that both techniques are suited to the analysis and that the applied cleaning protocols efficiently removed the strong iodine contaminations.

Nevertheless, despite the highly significant correlation between bulk ICP-MS I/Ca ratios and bottom water oxygen concentrations for *U. striata*, no significant correlation was observed for the SIMS derived individual I/Ca ratios. This indicates that ICP-MS bulk analyses on pooled bulk samples might be more suitable for reliable oxygen reconstructions using I/Ca ratios. On the contrary, the strong intra-test (e.g. -shell) variations could be induced by the oxygen variability in the habitats of foraminifera. Therefore, the high resolution findings provide the perspective for tracking relative short term oxygen fluctuations by measuring ontogenetic changes in I/Ca ratios within individual foraminiferal tests.

Measurements on cross-sections of uncleaned *U. striata* specimens revealed a strong contaminant iodine phase within the massive centre of the foraminiferal test walls which usually would be considered to be free of contamination. The contaminant iodine is probably associated to organic matter and located inside a microporous framework within the foraminiferal calcite. This might be related to microtubular structures which have been revealed in previous studies during early dissolution states of foraminiferal test walls.

1. Introduction

Tropical oxygen minimum zones (OMZs) are important areas of oxygen depletion in the modern oceans. Oxygen-dependent nutrient recycling within these regions has a large socio-economic impact because they account for ~17% of global commercial fish catches (source: FAO FishStat, 2013). Potential increases in the area and magnitude of seawater oxygen depletion in these regions might, in the future, endanger rich fisheries, threatening global marine food supply. Through use of a quantitative geochemical proxy for seawater oxygen in OMZs it should be possible to reconstruct temporal variation in OMZ extent to provide information about past changes in seawater oxygenation. This is of high interest considering the recent trend of expanding OMZs (Stramma et al., 2008).

Abbreviations: ICP-MS, inductively coupled plasma mass spectrometry; $[O_2]_{BW}$, bottom water oxygen concentration; OMZ, oxygen minimum zone; SIMS, secondary ion mass spectrometry.

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For such paleoceanographic perspectives a geochemical proxy for quantitative reconstruction of oxygen concentrations ($[O_2]$) in OMZs is highly desirable. The tests (e.g. shells) of benthic foraminifera are important geochemical proxy archives for reconstructing past chemical and physical seawater properties. Benthic foraminifera inhabit the seafloor. While epifaunal foraminiferal species live on the sediment surface, infaunal species exist, which are able to migrate vertically in the sediment column to where food availability and the oxygen level meets their individual requirements up to a depth of ~10 cm ((Jorissen et al., 1995; Duijnstee, 2003). Due to the overexcess in food and the low oxygen concentrations at the Peruvian OMZ most of the living benthic foraminifera can be found in the first few millimeters of the sediment column (Mallon et al., 2012; Glock et al., 2013). Most suitable for geochemical paleoreconstructions are foraminiferal species which build their tests out of calcium carbonate. Several elemental ratios have been studied as possible proxies for past seawater oxygenation. These proxies include V/Ca and U/Ca ratios (V/Ca: Hastings et al., 1996a, b, c; U/Ca: Russell et al., 1994) as well as Mn/Ca ratios that have become of more and more interest in several recent studies (Fhlaitheartha et al., 2010; Munsel et al., 2010; Glock et al., 2012; Groeneveld and Filipsson, 2013; McKay et al., 2015; Koho et al., 2015).

The most common microanalytical techniques to study foraminiferal element and isotope ratios amongst secondary ion mass spectrometry (SIMS) are laser ablation ICP-MS (Wu and Hillaire-Marcel, 1995; Hathorne et al., 2003; Reichart et al., 2003; Pena, 2005; Munsel et al., 2010; Raitzsch et al., 2011; Jonkers et al., 2012; Vetter et al., 2013a; Mewes et al., 2014; Fehrenbacher et al., 2015; Kaczmarek et al., 2015; Koho et al., 2015; Mewes et al., 2015; Spero et al., 2015) and electron-microprobe (EMP) (Nürnberg, 1995; Nürnberg et al., 1996; Eggins et al., 2003, 2004; Sadekov, 2005; Toyofuko and Kitazato, 2005; Pena et al., 2007; Kozdon et al., 2013; Fehrenbacher and Martin, 2014). Secondary ion mass spectrometry itself has also become more widespread within the last years with the advantages of a lower spot size than laser ablation techniques and a higher sensitivity than EMP (Allison and Austin, 2003; Sano et al., 2005; Bice et al., 2005; Kunioka et al., 2006; Rollion-Bard et al., 2008; Kasemann et al., 2009; Rollion-Bard and Erez, 2010; Glock et al., 2012; Nehrke et al., 2013; Kozdon et al., 2013; Vetter et al., 2013b; Vetter et al., 2014; McKay et al., 2015). Nevertheless, the effort of sample preparation and measurement for SIMS typically exceeds other techniques, which prevents it becoming widely-applicable.

Iodine is a redox sensitive element, such that the iodide (I^-) to iodate (IO_3^-) system has a reduction potential close to O_2/H_2O. Thus, the speciation of iodine is very sensitive to seawater $[O_2]$ (Rue et al., 1997; Brewer and Peltzer, 2009, Lu et al., 2010). The anions I^- and IO_3^- are the two most thermodynamically stable inorganic forms of dissolved iodine (Küpper et al., 2011). From these two forms of dissolved inorganic iodine, (Wong and Brewer, 1977) only IO_3^- (not I^-) is incorporated into carbonate materials (Lu et al., 2010). Only few studies have been focused on iodine speciation in pore waters but it has been shown that iodate reduction occurs during early diagenisis before MnO_2 reduction but after denitrification (Kennedy and Elderfield, 1987). An iodate reducing *Pseudomonas* species has been isolated from marine sediments at Sagami Bay, Japan (Amachi et al., 2007).

Inorganic precipitation experiments show that I/Ca ratios in synthetic calcite are a linear function of IO_3^- concentrations in the ambient water, while variable I^- concentrations did not affect the I/Ca ratios (Lu et al., 2010). Thus, it has been proposed that the IO_3^- anion partially substitutes for carbonate anions within the calcite lattice. More dissolved IO_3^- occurs at higher $[O_2]$ and thus higher I/Ca ratios in foraminiferal tests are supposed to be precipitated within those waters. Several modern benthic foraminiferal species show a positive covariation of test calcite I/Ca ratios with bottom water oxygen concentrations ($[O_2]_{BW}$) (Glock et al., 2014). Similarly, fossil planktonic foraminiferal I/Ca ratios decrease during mid-Cretaceous Oceanic Anoxic Events (OAE), times in the geological record when global oceans experienced stagnation and low $[O_2]$, as evidenced by the preservation of organic-rich sediments (Zhou et al., 2015).

Monospecific bulk analyses with ICP-MS revealed a lower reproducibility on I/Ca ratios in benthic foraminiferal species of which only a limited amount of specimens are available (Glock et al., 2014). In the present study we test the inter- and intra-test variability of benthic foraminiferal I/Ca ratios from the Peruvian OMZ to assess if indeed strong heterogeneity is causing this low reproducibility. Furthermore, it will be tested if I/Ca ratios from single foraminiferal specimens are already sufficient to reconstruct past oxygenation or if indeed bulk analyses are necessary to get a significant statistical average. Finally, I/Ca ratios of cleaned and uncleaned foraminiferal specimens are compared to study the impact of cleaning on SIMS derived I/Ca ratios. We focus on the shallow infaunal species *Uvigerina striata* because it showed the most significant correlation between I/Ca ratios and $[O_2]_{BW}$ (Glock et al., 2014). Due to its infaunal living environment *U. striata* is exposed to the chemical environment of the sediment pore waters.

2. Material and methods

2.1. Sampling procedure

Six sediment cores from the Peruvian OMZ were recovered using a video-guided multiple corer in October and November 2008 during the R.V. Meteor Cruises M77/1 and M77/2 (Table 1). The water depth at the sampling locations ranged from 465 m to 878 m with a range of bottom water oxygen concentrations ($[O_2]_{BW}$) from 2 to 34 μmol/kg). This transition zone from hypoxic to suboxic conditions suites perfectly to study the switch from microxic to anaerobic processes (like the reduction of IO_3^- to I^-). The inner diameter of the coring tubes was 100 mm. The multicorer tubes were transferred to a constant temperature (4 °C) laboratory immediately after retrieval. Supernatant water of the core was carefully removed. The core was then gently pushed out of the multicorer tube and cut into 10-mm-thick slices. Finally, the sediment samples were transferred either to plastic bottles or Whirl-Pak™ plastic bags, transported to and stored at GEOMAR, Kiel, Germany at a temperature of 4 °C.

2.2. Foraminiferal studies

The sediment samples were washed through a 63 μm mesh sieve. Water was removed from the residue >63 μm through a 63 μm filter stone using a waterjet pump. The residue was taken up in a small amount of ethanol to prevent sample-dissolution and dried overnight at 50 °C. The dried residues were further subdivided into 63–125, 125–250, 250–315, 315–355, 355–400, and >400 μm fractions. All specimens from the species *Uvigerina striata*, *Planulina limbata* and *Hoeglundina elegans* were sampled from the size fraction >400-μm. Light micrographs of chosen specimens from the different species can be found in Glock et al. (2014). While foraminifera from

Table 1
Sampling sites. $[O_2]_{BW}$ are taken from Glock et al. (2011 & 2014).

Site	Longitude (W)	Latitude (S)	Water depth (m)	$[O_2]_{BW}$ (μmol/kg)
M77/1-455/MUC-21	78°19.23′	11°00.00′	465	2.4
M77/1-487/MUC-38	78°23.17′	11°00.00′	579	3.7
M77/1-565/MUC-60	78°21.40′	11°08.00′	640	8.2
M77/1-604/MUC-74	78°22.42′	11°17.96′	878	34.2
M77/1-459/MUC-25	78°25.60′	11°00.03′	697	12.6
M77/1 553/MUC-54	78°54.70′	10°26.38′	521	3.0