Late inception of a resiliently oxygenated upper ocean

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Rising oceanic and atmospheric oxygen levels through time have been crucial to the habitability of surface Earth environments. Few redox proxies can track secular variations in dissolved oxygen concentrations ([O_2]) around threshold levels for metazoan survival in the upper ocean. We present a compilation of iodine to calcium ratios (I/Ca) in marine carbonates. Our record supports a major rise in atmospheric pO_2 at ~400 million years ago (Ma), and reveals a step-change in the oxygenation of the upper ocean to relatively sustainable near-modern conditions at ~200 Ma. An Earth system model demonstrates that a shift in organic matter remineralization to greater depths, which may have been due to increasing size and biomineralization of eukaryotic plankton, likely drove the I/Ca signals at ~200 Ma.

The survival of animals depends on oxygen availability, particularly in upper ocean waters – ranging from the sea surface to the thermocline – during early Earth history (*1*). The [O_2] in the upper ocean commonly decreases from the well-mixed surface ocean (top few tens of meters) into deeper subsurface waters, at a few hundred meters. This [O_2] gradient is controlled by two key factors: (i) the partial pressure of oxygen in the atmosphere (pO_2) together with the intensity of upper ocean mixing and (ii) oxidation of organic matter in the water column, which consumes dissolved oxygen (*2*). Atmospheric pO_2 changes through time have been estimated via geochemical proxy data and box models (*3*). Oceanic paleo-redox proxies typically track the areal extent of euxinic waters (containing H_2S) and the presence/absence of anoxia (positive/zero $[O_2]$) (*4, 5*). For subsurface $[O_2]$ values in the range lethal for most modern marine animals – ca. 10 and 100 μmol/kg (*2*), long-term proxy reconstructions may help elucidate when and how oceanic oxygenation evolved to accommodate the modern ecological landscape.

Carbonate I/Ca is one of the novel proxies developed for the oxic–hypoxic window with the potential to reconstruct secular trends in upper-ocean oxygenation (*6, 7*). The long residence time of iodine (~300 kyr) leads to generally uniform total iodine concentrations in the modern ocean, but speciation changes of iodine between iodate (IO_3^-) and iodide (I^-) are controlled locally (*8, 9*). IO_3^- is completely reduced to I^- in waters at low $[O_2]$ (*8, 9*) and re-oxidized under well-oxygenated conditions. Since IO_3^- is the only chemical form of iodine incorporated into the calcite structure (*7*) by replacing the CO_3^{2-} ion (*10*), carbonate I/Ca records of local seawater $[IO_3^-]$ through time are an indicator for changes in $[O_2]$. Carbonate I/Ca has been shown to be a reliable tracer responding primarily to $[O_2]$ variations in marine environments over a wide range of geological periods (*6, 11-16*).

We measured I/Ca in an extensive collection of carbonate samples through the Phanerozoic and compiled them with published data (Table S1 and Fig. 1A). These Phanerozoic carbonates most likely formed within the top 200 m of the water column (Table S1). The boxes defining the 25th to 75th percentile values show the ranges of most data points at each geological section. Key observations in this new record are: 1) an excursion to high I/Ca values around 400 Ma and 2) a step change to persistent occurrence of high I/Ca after ~ 200 Ma (Fig. 1A).

Maximum I/Ca values for individual localities were generally low in the Proterozoic, except for periods which have been associated with potential atmospheric pO_2 rises [e.g., the Great Oxidation Event (*12*) and the Bitter Springs Anomaly (*15*)], when maximum values temporarily increased to Cenozoic levels (3-4 μmol/mol) (Fig. 1A). Paleozoic maximum values are comparable to those of the Proterozoic, despite a relatively short spike during the Devonian, at approximately 400 Ma, when the 75th percentile values reached Cenozoic levels. Since ~200 Ma (Early Jurassic), maximum values have remained above 4 μmol/mol, with 75th percentile values mostly higher than 3 μmol/mol, representing locally well-oxygenated conditions in upper-ocean waters (*6, 13*).

The stark contrast between predominantly low Paleozoic values and high Meso-Cenozoic values (excluding the Triassic, i.e., <200 Ma) cannot be explained by sampling biases. The sample size for the Paleozoic (n = 894) is comparable to that for the Proterozoic (n = 1078) and the Meso-Cenozoic (n = 926). The sampling density (number of samples per unit time) is similar in the Paleozoic and Meso-Cenozoic, although lower in the Proterozoic (Fig. 1B). For Paleozoic samples, we targeted carbonate- and fossil-rich (shallow) continental-shelf locations, i.e., relatively well-oxygenated settings, which are prone to record high I/Ca values. By contrast, many Mesozoic data were generated from sections recording well-established global oceanic anoxic events (OAEs), which, if anything, would bias that dataset toward low values. Therefore, the low Paleozoic values relative to the Mesozoic are not likely the result of sampling bias towards poorly oxygenated regions. The current data set has better sample coverage across shorter-term perturbations (e.g. $\delta^{13}C$ excursions and extinctions) than over background time intervals, but this should not the influence main features of the data compilation.

I/Ca values could be lowered during subaerial exposure, marine burial and dolomitization, but no post-depositional alterations are known to increase I/Ca (*11*). A variety of diagenetic indicators have been considered in studies of individual sections (*7, 16-18*). In all these studies, the number of potentially altered samples is limited and does not influence the central trend of the majority of the data through time statistically, as plotted by 25th and 75th percentile values (Fig. 1A). However, secular trends in maximum and minimum values are more prone to both sampling and diagenetic issues. High I/Ca values throughout the record (Fig. 1A) are not consistently tied to a specific inferred primary carbonate mineralogy (e.g., calcite *vs* aragonite seas, Fig. S1A). The distinct behaviors of I/Ca before and after ~200 Ma (Fig. 1A) cannot be explained by secular changes in seawater [Ca^{2+}] (Fig. S1B). No evidence suggests that Paleozoic samples are uniformly and significantly more altered than the Mesozoic samples to explain the difference in their I/Ca distributions (Fig. S2). Lower relative standard deviations (RSD) of neighboring samples in each section (i.e., smoother I/Ca profiles; Fig. S3) may reflect better preservation of the Paleozoic than the Proterozoic samples (Fig. S3). Thus, the similarity and distinction among the Proterozoic, Paleozoic and Meso-Cenozoic (Fig. 1C) are unlikely to have been driven mainly by preservational factors.

We interpret I/Ca in marine carbonates primarily as a qualitative indicator for the depth of the oxycline (Fig. 2), i.e., that part of water column where the [O_2] decreases relatively abruptly. Carbonate rocks formed in the upper ocean record surface or near-surface seawater [IO_3^-], which is strongly affected by the presence/absence of a proximal oxygen minimum zone (OMZ) or a shallow oxycline. Due to the relatively slow oxidation kinetics of I^- on the order of decades (*19*), surface waters may retain a low iodate signal despite *in situ* high [O_2] levels. For instance, core-top (modern) planktonic foraminiferal shells exhibit low I/Ca values (~0.5 μmol/mol) in waters above a shallow OMZ in the equatorial Pacific, but record higher values (>3 μmol/mol) at other well-oxygenated locations (*6*).

The large I/Ca excursion during the Devonian (Fig. 3) most likely reflects deepening of the oxycline and development of better oxygenated conditions in the upper ocean, consistent with published proxy data and modeling results (*4, 5, 20, 21*). Although different box models yield somewhat divergent interpretations of atmospheric pO_2 variation through the Phanerozoic (*22-25*), a Devonian rise in pO_2 levels seems possible, based on the COPSE model and charcoal proxy reconstructions (Fig. 3A), and was most likely due to increased abundance of vascular land plants (*20, 21*). Compilations of δ^{98}Mo, iron-speciation and biological data (Fig. 3C) were interpreted to reflect oceanic redox changes and similarly support the idea of atmospheric pO_2 rise during the Devonian (*4, 5*). The combination of these independent proxies indicates that the Devonian atmospheric pO_2 rise impacted the whole atmosphere-ocean system, across the entire redox spectrum (Fig. 3).

I/Ca values returned to Proterozoic-like levels following the transient Devonian excursion, but there is no evidence for a pO_2 decrease to pre-Devonian levels between the Carboniferous and the Triassic. Instead, the post-Devonian atmosphere was probably relatively O_2-rich (Fig. 3A). High atmospheric pO_2 likely altered terrestrial weathering feedbacks and enhanced nutrient delivery to the ocean (*26, 27*), leading to intensified O_2 consumption in the upper ocean, a generally shallow oxycline, and low I/Ca values between ~400 and 200 Ma (Fig. 3B). Under such conditions, carbonates formed in surface-oceans rapidly equilibrated with the high-pO_2 atmosphere, and would record *in situ* low [IO_3^-] due to the slow oxidation of I^- during the mixing between surface and subsurface waters (Fig. 2B). If the oxycline was indeed shallow, marine animals on continental shelves at that time (~ 200-400 Ma) would have been living in a thin layer of well-oxygenated surface water directly underlain by an OMZ (Fig. 2B). Our dataset (Fig. 1A) shows that well-oxygenated upper-ocean conditions (i.e., elevated surface water [O_2] without widespread shallow oxyclines) became persistent and resilient only by the early middle Mesozoic (Jurassic, ~200 Ma), much later than previously inferred (*28*). The prerequisites for achieving such well-oxygenated upper-ocean conditions are a combination of high atmospheric pO_2 and a generally deep oxycline (Fig. 2C). The position of the oxycline is strongly controlled by the depth of organic-matter remineralization, which is dependent on the efficiency of organic-matter export from the photic zone, and has been proposed as a governing parameter for OMZs during the Phanerozoic (*29*).

We hypothesize that changes in remineralization of organic matter strongly influenced the upper-ocean I/Ca signature (Fig. 2) and test this hypothesis by simulating the marine iodine cycle in the 'cGENIE' Earth system model (see Methods, Fig. S4) (*30*). We aim to identify possible causes for low I/Ca during the Paleozoic through ensembles of model runs using a range of values for atmospheric pO_2, the depth of organic-matter remineralization in the water column, and the mean concentrations of iodine and phosphate in seawater. For each Paleozoic model run, surface-water $[IO_3^-]$ values along continental margins were extracted to calculate a relative frequency distribution (Fig. S5). The modeled IO_3^- distributions were compared with observed Paleozoic I/Ca distributions (Fig. 1C) to obtain the residual sum of squares (RSS) (see Materials and Methods, Fig. 4A and Fig. S6). We found that the lowest RSS values (<0.05), representing the best data-model fits, were achieved at shallow remineralization depths [i.e., <0.5 present oceanic level (POL)]. In the same set of cGENIE runs (Fig. 4B), lower RSS values correlated with lower average $[O_2]$ in the subsurface layer (80-176 m), which is consistent with a shallower oxycline. Even as Paleozoic oceans experienced transitions between greenhouse and icehouse climate conditions, pCO_2 levels appear to have had minimal influence on IO_3^- distributions (Fig. S7), and the effects of remineralization depth remain dominant. The RSS contours were altered only slightly when the Paleozoic I/Ca distribution was compared with modeled $[IO_3^-]$ distributions in the top four layers in the upper ocean (from 0 to 410 m, Fig. S8). Thus, a lack of precise constraints on the paleo-depths of carbonate formation is unlikely to have affected the main conclusions of our data–model comparison. Additional model runs also suggest that oceanic nutrient levels and total iodine concentrations are unlikely to dominate the temporal trends in proxy data (Fig. S9-10). Our data-model comparison (Fig. 4A) should not be viewed as a precise estimate on the atmospheric pO_2 for any single time slice, since the data were compiled over the entire Paleozoic under varying pO_2 levels. Thus, the lower RSS values at pO_2 below 1 PAL suggest that some portion of the Paleozoic might have had pO_2 levels lower than today, consistent with recent literatures (*5, 24*).

Based on our data compilation and model analyses, we interpret the transition at ~200 Ma from Proterozoic-like low I/Ca values in the Paleozoic (except for the mid-Devonian) to modern-like high values in the Meso-Cenozoic, as a profound increase in the average remineralization depth of organic matter in the water column. The timing of this transition is consistent with the proliferation of eukaryotic phyto- and zooplankton after the Permian-Triassic extinction (Fig. 3A)(*31, 32*), which eventually shaped the ecological landscape of the modern ocean (*33*). The larger size of primary producers (*34*), grazing/repackaging of organic matter into fecal pellets (*35*), and/or the advent of mineralized plankton (*33*) may have led to faster sinking of organic matter, which reduced O_2 utilization in the upper water column and caused a pervasive deepening of the oxycline (*29*).

The rise of oxygen levels over geological time has been linked to increases in animal body size (*25, 36*). A comprehensive compilation of Phanerozoic marine animal body-size data (*37*) shows that maximum bio-volume probably to some extent co-varied with I/Ca (Fig. 3B), indicating that O_2 availability in the global upper ocean might have been an important factor in Phanerozoic metazoan evolution. New forms of organisms (e.g., mineralized plankton, larger animals) fundamentally influenced oceanic environments, which in turn affected the evolving biosphere, representing a prime example of the co-evolution of life and planet.

Figure captions

Figure 1. Carbonate I/Ca through time. A. Candlestick plot showing ranges of I/Ca values for Proterozoic (red), Paleozoic (blue) and Meso–Cenozoic (purple). Boxes mark the 25th and 75th percentiles of values at each locality, and the whiskers show the maximum and minimum. Note that the Proterozoic values from dolostones are I/(Mg+Ca). **B.** Number of samples measured at each section. **C.** Relative frequency distributions of I/Ca.

Figure 2. Schematic illustrations for the evolution of oxygenation conditions.

Figure 3. Phanerozoic I/Ca compared with atmospheric pO_2, oceanic oxygenation and animal evolution trends. A. Modeled atmospheric pO_2 curves (*5, 22, 24, 25*) in comparison with the charcoal proxy record (*21*). Dashed lines (*5*) mark a broadly defined ocean-atmospheric O_2 level, not atmospheric pO_2. **B.** I/Ca records through Phanerozoic. Blue boxes for bulk carbonate rock, gray boxes for bulk coarse fraction of Ocean Drilling Project samples (>63 µm). **C**. Marine animal body size record (*37*). Thickness of green bars indicates relative generic diversity modified from literature (*32, 33*). The red *vs* blue bars mark greenhouse *vs* icehouse climate conditions, respectively.

Figure 4. Residual sum of squares (RSS) and subsurface $[O_2]$ at different pO_2 levels and remineralization depths. A. Shallow remineralization depths (POL for present oceanic level) produce the best model fit (the smallest RSS < 0.05) to Paleozoic I/Ca distribution, at 1× CO_2 condition. White dots represent 45 cGENIE simulations defining the contours. **B.** Averaged $[O_2]$ in the shallowest subsurface layer in each cGENIE run as an indicator of oxycline depth correlating with the RSS.

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