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Redox stratification and anoxia of the early Precambrian oceans: Implications for carbon isotope excursions and oxidation events

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Abstract

An updated compendium of $\delta^{13}C$ data offer compelling evidence that $\delta^{13}C$ positive excursions of unsurpassed magnitude in the recorded Earth history (>8‰, and up to 18‰ PDB) occurred in the early Proterozoic (the Lomagundi event). Questions whether or not these unprecedented positive $\delta^{13}C$ shifts were contemporaneous in various basins and represent local or global events remain unresolved. The framework of major geologic events that occurred in the Paleoproterozoic argues against a Snowball Earth scenario as a backdrop to these exceptional ^{13}C-enrichments. Substantial increases of carbon flux ratio (F_o/F_c, eight times the Phanerozoic average) and organic carbon burial rate (F_o, three times the Phanerozoic average) are required to account for the observed ^{13}C-enrichments under steady-state and dynamic equilibrium modes, respectively. These enhanced ratios and rates are conditional on the availability of a flux of nutrients to the contemporaneous biota producers in excess of the riverine flux, and a decoupling of the P and C cycles. It is argued that these two conditions were met between 2.25 and 2.11 Ga in a redox-stratified ocean with weak upwelling and sluggish meridional surface circulation. The alternative, that the major disturbance in the terrestrial carbon cycle occurred in a rapidly ventilated ocean, is assessed as being unlikely. A large pulse of O_2 equivalent to six to seven times the present terrestrial oxygen budget was rapidly scavenged and spent in the oxidation of reduced Fe and S transported to the shelves by rivers. This contention is consistent with data inferring low oxygen levels (10^{-5} to 10^{-2} PAL) in the Paleoproterozoic atmosphere and the occurrence of ocean anoxia until the late Precambrian.

Keywords: Redox stratification; Anoxia; Carbon isotopes; Precambrian oceans

1. Introduction

The question of how and when the Earth acquired its oxygen presently stored in the atmosphere–ocean–crust system has long engaged the geologists because of the intimate link between the emergence of life and the evolution of photosynthesis-derived oxygen. However, with few notable exceptions (e.g., air bubbles locked in late Pleistocene ice cores and possibly in amber imbedded in Cretaceous and Tertiary sediments) atmospheric oxygen left no direct imprint in the rock record.

Broecker (1970) suggested that in the absence of a paleo-oxygen geologic archive the $\delta^{13}C$ composition of marine carbonates, ubiquitous from around 2.7 Ga

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to the present (Grotzinger, 1989), may offer a reliable proxy of oxygen that was released into the Earth environment on account of (i) the stoichiometry of photosynthesis that dictates a release of one mole of free oxygen for every mole of organic matter buried in the sediments, and (ii) relative constancy of biological fractionation of $^{13}C/^{12}C$ isotopes between the organic-derived carbon and inorganic carbon pools at about −25‰ PDB. Viewed this way, modern oxygen levels released into the environment were attained when $\delta^{13}C$ values of marine carbonates leveled off at about 0‰ PDB and the partition of sedimentary carbon between the organic (F_o) and inorganic (F_c) fluxes (Ronov ratio, F_o/F_c) reached a ratio of 1/4.

In order to test Broecker's (1970) model, a comprehensive $\delta^{13}C$ dataset of Precambrian carbonates was required. An influential study by Schidlowski et al. (1975) played a prominent role in the endeavor to reconstruct the terrestrial oxygen evolution on the basis of $\delta^{13}C$ records from marine carbonates of Precambrian age. A $\delta^{13}C$ dataset of Precambrian limestones and dolomites, yielding a mean value of +0.40± 2.7‰ PDB ($n = 260$), formed the basis for the observed "constancy" of $\delta^{13}C$ values around 0‰ from the start of the sedimentary record. The $\delta^{13}C$ dataset also provided the necessary constraints for a numerical model indicating that close to 80% of the oxygen locked in the present atmosphere–ocean–crust system has been released before 3 Ga (Schidlowski et al., 1975; Schidlowski and Eichmann, 1977).

Among the 260 samples listed by Schidlowski et al. (1975), the dolomites from the ca. 2.15 Ga old Lomagundi carbonate province in Zimbabwe stood out because of their unusually high ^{13}C enrichment ($\delta^{13}C = 9.4 \pm 2.0$‰ PDB). Initially, the exceptional Lomagundi values were explained in terms of an enhanced burial spike of F_o into the sediments (Schidlowski et al., 1975) temporarily altering the Ronov ratio. Further analyses of the Lomagundi dolomites (Schidlowski et al., 1976) confirmed their exceptional ^{13}C enrichments ($\delta^{13}C = 8.2 \pm 2.6$‰ PDB, for $n = 67$, with values spread between a minimum of 2.6‰ and a maximum of 13.6‰). However, the absence of contemporaneous carbonates with similar ^{13}C enrichments compelled Schidlowski et al. (1976) to conclude that the anomalous carbonates may represent a regional event confined to a closed basin as opposed to a global event. Interestingly enough, positive $\delta^{13}C$ excursions documented earlier by Galimov et al. (1968, 1975) in Karelia and Kola Peninsula, Russia, were not correlated by Schidlowski et al. (1975) with the Lomagundi $\delta^{13}C$ excursion because of poor age constraints.

Over the past two decades a number of studies have augmented the pioneering work of the Mainz group. First, the global distribution of the Lomagundi ^{13}C-high anomaly was corroborated by Baker and Fallick (1989a,b) from studies of limestones and marbles in Scotland and Norway, respectively. Second, compilation of more recent $\delta^{13}C$ data on limestones and dolomites from Scandinavia, South Africa, North America and Australia by Karhu and Holland (1996) substantiated the unusual ^{13}C enrichments in the Lomagundi carbonates, and led to the conclusion that the Lomagundi anomaly likely represents a worldwide early Precambrian event. The $\delta^{13}C$ of carbonates, however, may serve as an integrated signal reflecting the state of the carbon cycle only if the $\delta^{13}C$ difference between the burial fluxes of organic carbon and carbonate-carbon is known or assumed over the time interval of interest. An improved history of oxidation during the Proterozoic eon was achieved by determining the trend in the $\delta^{13}C$ difference between the organic and inorganic carbon fluxes which likely varied through time (Des Marais et al., 1992; Hayes et al., 1999).

Interpretation of the carbonate $\delta^{13}C$ record in the Paleoproterozoic time (2.5–1.6 Ga, containing the Lomagundi event) as an indicator of processes within the global carbon cycle is hindered by a number of quandaries. First, most of the Paleoproterozoic-age carbonates underwent mild (diagenesis) to severe (metamorphism) post-depositional alterations that may have offset their initial isotope compositions. Although the general paradigm maintains that such alterations are primarily sensed by the oxygen isotopes during fluid–rock interaction while the carbon isotopes likely remain unchanged on account of carbon mass balance considerations (Aharon and Liew, 1992), and screening procedures have been devised to select the "least altered" samples (Veizer, 1983; Knoll et al., 1986), nevertheless the potential offset by postdepositional effects is of concern. Second, many of the Paleoproterozoic sequences underwent post-depositional tectonic disturbances that make stratigraphic correlations difficult even within the same tectonic province (e.g., the Transvaal Supergroup; Buick et al., 1998;