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Total organic carbon, organic phosphorus, and biogenic barium fluxes as proxies for paleomarine productivity

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ABSTRACT

Although marine productivity is a key parameter in the global carbon cycle, reliable estimation of productivity in ancient marine systems has proven difficult. In this study, we evaluate the accumulation rates of three commonly used proxies for productivity from a set of primarily Quaternary sediment cores at 94 marine sites, compiled from 37 published sources. For each core, mass accumulation rates were calculated for total organic carbon (TOC), organic phosphorus (P_{org}), and biogenic barium (Ba_{bio}). Calculated mass accumulation rates were compared to two independent estimates of modern regional primary productivity and export productivity, as well as to two potential controlling variables, bulk accumulation rate (BAR) and redox environment. BAR was found to exercise a strong control on the preservation of organic carbon. The linear regression equations relating preservation factor to BAR can be transformed to yield equations for primary and export production as a function of TOC and BAR, two variables that can be readily measured or estimated in paleomarine systems. Paleoproductivity can also be estimated from empirical relationships between elemental proxy fluxes and modern productivity rates. Although these equations do not attempt to correct for preservation, organic carbon and phosphorus (but not barium) accumulations rates were found to exhibit a systematic relationship to primary and export production. All of the paleoproductivity equations developed here have a large associated uncertainty and, so, must be regarded as yielding order-of-magnitude estimates.

Relationships between proxy fluxes and BAR provide insights regarding the dominant influences on each elemental proxy. Increasing BAR exerts (1) a strong preservational effect on organic carbon that is substantially larger in oxic facies than in suboxic/anoxic facies, (2) a weak clastic-dilution effect that is observable for organic phosphorus (but not for organic carbon or biogenic barium, owing to other dominant influences on these proxies), and (3) a large negative effect on biogenic barium that is probably due to reduced uptake of barium at the sediment–water interface. These effects became evident through analysis of our globally integrated dataset; analysis of individual marine sedimentary units most commonly reveals autocorrelations between elemental proxy fluxes and BAR as a result of the latter being a factor in the calculation of the former. We conclude that organic carbon and phosphorus fluxes have considerable potential as widely useful paleoproductivity proxies, but that the applicability of biogenic barium fluxes may be limited to specific oceanic settings.

Contents

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1. Introduction

Organic productivity is a fundamental parameter of all marine ecosystems, playing a pivotal role in ecological dynamics, environmental redox conditions, and the cycling of carbon, nitrogen, phosphorus, and other nutrient elements. In the modern open ocean, the main primary producers are single-celled phytoplankton in the surface mixed layer (Levinton, 2008). Some phytoplankton, e.g., calcareous coccolithophores and siliceous diatoms, produce mineralized tests whose fluxes to the sediment can be used as productivity proxies (e.g., Kinkel et al., 2000; Rageneau et al., 2000). Although biogenic sediments are common in the Paleozoic and early Mesozoic pelagic ocean, mainly as radiolarites (e.g., Hori, 1992; Algeo et al., 2010), mineralized phytoplankton did not become common until the Triassic, and phytoplankton tests did not become a dominant component of marine sediments until the Cretaceous (Martin, 1995; Ridgwell, 2005). Even in the modern ocean, many marine algae lack mineralized tests (Tomas, 1997) and contribute only amorphous organic matter (AOM) to the sediment (Taylor et al., 1998). In regions dominated by non-mineralized algae, productivity has been estimated on the basis of geochemical proxies such as total organic carbon (TOC), organic phosphorus (P_{org}), and biogenic barium (Ba_{bio}) (Tribovillard et al., 2006; Calvert and Pedersen, 2007).

The utility of TOC, P_{org}, and Ba_{bio} as paleomarine productivity proxies depends on a dominantly marine source of organic matter and favorable conditions for preservation in the sediment. Carbon and phosphorus have the advantages of being major components of marine algal biomass and having few other sources in open-ocean settings. The only other significant source of either component to marine sediments is terrestrial organic matter, which is prevalent mainly in coastal areas (Hedges and Parker, 1976; Showers and Angle, 1986). Preservation factors (PFs) for organic carbon (i.e., the fraction of primary production preserved in the sediment) can be as high as 30% in reducing facies but are commonly far lower (≤1%) in oxic facies (Canfield, 1994; Tyson, 2005). On the other hand, burial efficiencies (BE; i.e., the fraction of the organic carbon sinking flux preserved in the sediment) are typically in the range of 10–50% (Canfield, 1994; Tyson, 2005) and, thus, can be more reliably estimated for paleomarine systems (Algeo et al., 2013). P_{org} is preferentially recycled back into the water column under reducing conditions (Van Cappellen and Ingall, 1994) but can be effectively retained within the sediment under oxic to suboxic conditions (Föllmi, 1996; Algeo and Ingall, 2007). The utility of Ba_{bio} as a productivity proxy is ascribed to the close relationship between the production of authigenic barite and the decay of organic matter in contact with seawater, which is the source of Ba_{bio} (Paytan and Griffith, 2007). An advantage of this proxy is that the mineral barite is relatively resistant to dissolution under oxic to suboxic conditions, providing a means of estimating export production in non-reducing paleomarine systems. Because of the incomplete preservation of all of these components in marine sediments, estimates based on measured concentrations represent minimum values of both primary productivity (i.e., the flux of carbon fixed from the atmosphere into the surface ocean) and export productivity (i.e., the flux of carbon from the surface mixed layer to the thermocline region of the ocean).

In this contribution, we undertake an analysis of TOC, P_{org}, and Ba_{bio} fluxes in modern marine settings with the goal of evaluating their utility as paleoproductivity proxies. To this end, we (1) calculated the fluxes of TOC, P_{org}, and Ba_{bio} in a range of modern marine settings, (2) compared these data with estimates of primary and export productivity for each setting, and (3) evaluated the relative influences of productivity versus preservation (which is closely related to sediment bulk accumulation rates) on the accumulation of TOC, P_{org}, and Ba_{bio}.

In a companion paper in this volume by Shen et al. (in review), the findings of the present study are applied to an analysis of productivity variations during the Permian–Triassic transition, the most severe biodiversity crisis of the Phanerozoic (Erwin et al., 2002). While marine anoxia is widely agreed to have played a major role in the extinction (Isozaki, 1997; Wignall and Newton, 2003), models suggest that this could not have occurred without a substantial increase in marine export production (Hotinski et al., 2001; Winguth and Winguth, 2012).

2. Paleoproductivity proxies

2.1. General considerations

A variety of geochemical proxies have been used to reconstruct past changes in biological productivity, including methods based on C and N isotopes, organic biomarkers, and trace metal (Cu, Ni, Cd, Zn) abundances (see reviews in Tribovillard et al., 2006; Calvert and Pedersen, 2007). Each proxy is affected by a host of environmental factors such as temperature, redox conditions, and ocean circulation, in addition to