

## **Contrasting the response of marine calcifiers and silicifiers during carbon cycle catastrophes**

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An important control on the relative abundance of marine calcifying and silicifying plankton is the mineral saturation of their shell material in seawater: properties typically described by the concentration of dissolved silica (DSi, which is undersaturated with respect to opal throughout the oceans) for silicifiers, and the saturation state of calcite ( $\Omega$ , which is several times oversaturated in most of the surface ocean) for calcifiers. We argue, using a novel model of the coupled carbon and silica cycles (LOSiCAR), that during many of the coupled climate-carbon cycle catastrophes known from Earth history (e.g. Phanerozoic mass extinctions and Paleogene hyperthermal events), Earth system responses and feedbacks operated to drastically shift the influence of seawater chemistry on the competition between silicifiers and calcifiers. Immediately following C release, dissolution of CO<sub>2</sub> into seawater causes ocean acidification, lowering  $\Omega$  over ocean mixing timescales. Subsequently, elevated atmospheric *p*CO<sub>2</sub> accelerates continental silicate weathering, which quickly (over millennial timescales, due to the short residence time of Si) elevates DSi, and restores  $\Omega$  over significantly longer timescales. The lowered  $\Omega$  and elevated DSi during the thousands of years following C release would shift the seawater chemistry advantage from calcifiers to silicifiers. Our LOSiCAR results predict a several-fold increase in the pelagic export of biosilica relative to carbonate during this period. Evidence for this phenomenon from the sedimentary record includes elevated silica burial (chert layers and other siliceous facies) coincident with reduced %CaCO<sub>3</sub> during the PETM and later hyperthermals, and the “sponge takeover” of the Triassic-Jurassic extinction, although the latter competition played out in a neritic setting. Results suggests that the magnitude of the relative DSi/ $\Omega$  response (and hence the relative advantage imparted to silicifiers) is a function of both carbon release magnitude and rate: a faster C release results in a greater the degree of acidification and more rapid dissolved [Si] rise, accentuating the siliceous advantage.