An end to the "rain ratio" reign?

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[1] One of the most elegant mechanisms forwarded for late Quaternary atmospheric CO_2 variability concerns the sensitivity of calcium carbonate preservation in deep ocean sediments to the relative delivery rates of calcium carbonate and particulate organic carbon (the $CaCO_3$:POC "rain ratio"). It was implicitly assumed that any change in the $CaCO_3$:POC rain ratio of biogenic material produced in the surface ocean will be communicated directly to the sediments. This would allow relatively subtle shifts in ecosystem composition to affect sedimentary $CaCO_3$ preservation (and thus atmospheric CO_2). However, recent research into the controls on the transport of POC to depth suggests that the rain ratio "seen" by the sediments may instead be buffered against any perturbation occurring at the surface. This casts doubt on the viability of hypotheses envisaging ecological changes as a means of accounting for the observed glacial-interglacial CO_2 signal.

[2] Ice cores recovered from the Antarctic ice cap and analyzed for air bubble gas composition reveal that the atmospheric mixing ratio of CO_2 ($x CO_2$) at the height of the last glacial was only about 190 ppm, compared with 260–270 ppm at the start of the Holocene [*Delmas et al.*, 1980; *Neftel et al.*, 1982]. Although numerous different possible biogeochemical mechanisms for controlling CO_2 have been identified, an accepted explanation for an increase of this magnitude has proved surprisingly elusive [*Archer et al.*, 2000]. Arguably the most elegant candidate mechanism involves the influence that the ratio of biogenic calcium carbonate to particulate organic carbon (the $CaCO_3$ to POC

flux (or "rain") ratio) has on the preservation of $CaCO_3$ in deep sea sediments [*Archer*, 1991]. In order to maintain steady state (weathering inputs balanced by loss through $CaCO_3$ burial in sediments) in the ocean carbon cycle, the effect of any perturbation able to drive an initial decrease in $CaCO_3$ burial is ultimately compensated for by an increase in the carbonate ion concentration ($[CO_3^{2-}]$) of the deep sea (which, in turn, equates to a reduction in atmospheric $x CO_2$). A reduction in the production and export rate (relative to POC) of $CaCO_3$ is one possible means of initiating such a chain of events, and forms of the basis of the "rain ratio" hypothesis [*Archer and Maier-Reimer*,

1994]. The operation of this is shown schematically in Figure 1a.

[3] Coupled ocean-sediment models have confirmed the plausibility of this mechanism, and indicate that a mean global reduction of 40% in the $CaCO_3$:POC rain ratio at the sediment surface is sufficient to drive atmospheric xCO_2 down by about 70–90 ppm [*Archer and Maier-Reimer*, 1994; *Ridgwell et al.*, 2002]. This is equivalent to the entire amplitude of observed glacial-interglacial CO_2 change, making this mechanism potentially key to resolving the "glacial CO_2" question. How might a glacial decrease in rain ratio have arisen? While the remains of all phytoplankton species contribute toward the settling flux of POC leaving the base of the euphotic zone, it is primarily only coccolithophorids (together with their zooplankton equivalent – foraminifera) that contribute to $CaCO_3$ export. Thus a change in the $CaCO_3$:POC export ratio can, in theory, be brought about simply through a shift in ecosystem composition [*Dymond and Lyle*, 1985] - one involving a change in the relative contribution made by coccolithophorids to total ecosystem productivity. Probably the most powerful means of achieving this is via the "silicate switch" [*Ridgwell et al.*, 2002], whereby increased silicic acid (H_4SiO_4) availability enables diatoms to further "out compete" smaller and more tightly grazing-controlled phytoplankton species (such as the coccolithophorids) for limiting nutrients common to all phytoplankton species (such as nitrate and iron). Just such a control has been expounded in a number of recent studies, in which lower atmospheric xCO_2 is (at least partly) explained as a consequence of greater H_4SiO_4 availability. The larger oceanic H_4SiO_4 inventory necessary to achieve this could arise due to either increased Si supply rates to the ocean derived from aeolian dust [*Harrison*, 2000] or continental rock weathering [*Tréguer and Pondaven*, 2000], or due to decreased rates of Si removal by opal burial on continental shelves [*Ridgwell et al.*, 2002]. Other modeling work has highlighted the possibility that rather than a whole-ocean change in H_4SiO_4 inventory, a meridonal redistribution of nutrients might have occurred. In this hypothesis, enhanced dust deposition to the Southern Ocean during glacial times enables greater (iron-driven) utilization efficiency of H_4SiO_4 by diatoms [*Watson et al.*, 2000]. The result of this is an increase in the northward transport of "left over" (unutilized) H_4SiO_4 to the subtropics where it was previously in insufficient supply and limiting to diatom growth [*Brzezinski et al.*, 2002; *Ganeshram*, 2002; *Matsumoto et al.*, 2002].

[4] In each of these scenarios atmospheric xCO_2 will be affected directly as a result of changes in $CaCO_3$ export – lower $CaCO_3$ export fluxes producing a reduction in the alkalinity gradient between surface and deep, and thus a lower partial pressure of CO_2 in the surface ocean [*Dymond and Lyle*, 1985]. An analogous effect could also arise should POC originating from diatoms be transferred to the deep ocean more efficiently than POC originating from pico- and nano-plankton [*Ganeshram*, 2002], although in this case it is an increase in the dissolved inorganic carbon gradient that causes lower atmospheric xCO_2. The dominant CO_2 control in each glacial scenario, through, was assumed to be mediated indirectly via the "rain ratio" mechanism [*Archer and Maier-Reimer*, 1994]. However, research just recently published by *Klaas and Archer* [2002] now casts doubt on the effectiveness of the "rain ratio" mechanism, and with it, the importance of this particular control on CO_2.

[5] Critical to a correct understanding of the "rain ratio" mechanism is the distinction between the $CaCO_3$:POC export ratio (i.e., that measured at the base of the euphotic zone or stratified ocean surface) and the ratio measured at the sediment surface – it is not the export rain ratio that is the critical variable in determining preservation of $CaCO_3$ in deep sea sediments, per se, but the sediment rain ratio. Any process that affects the efficiency (relative to $CaCO_3$) with which POC is transferred from the surface to the deep sea will therefore impact on the operation of the "rain ratio" mechanism. It seems that "ballast" minerals play such a role – by increasing mean particulate density, the presence of $CaCO_3$, opal, and dust (terrigenous silicate minerals) in aggregates with organic matter enhance the settling rate of particles
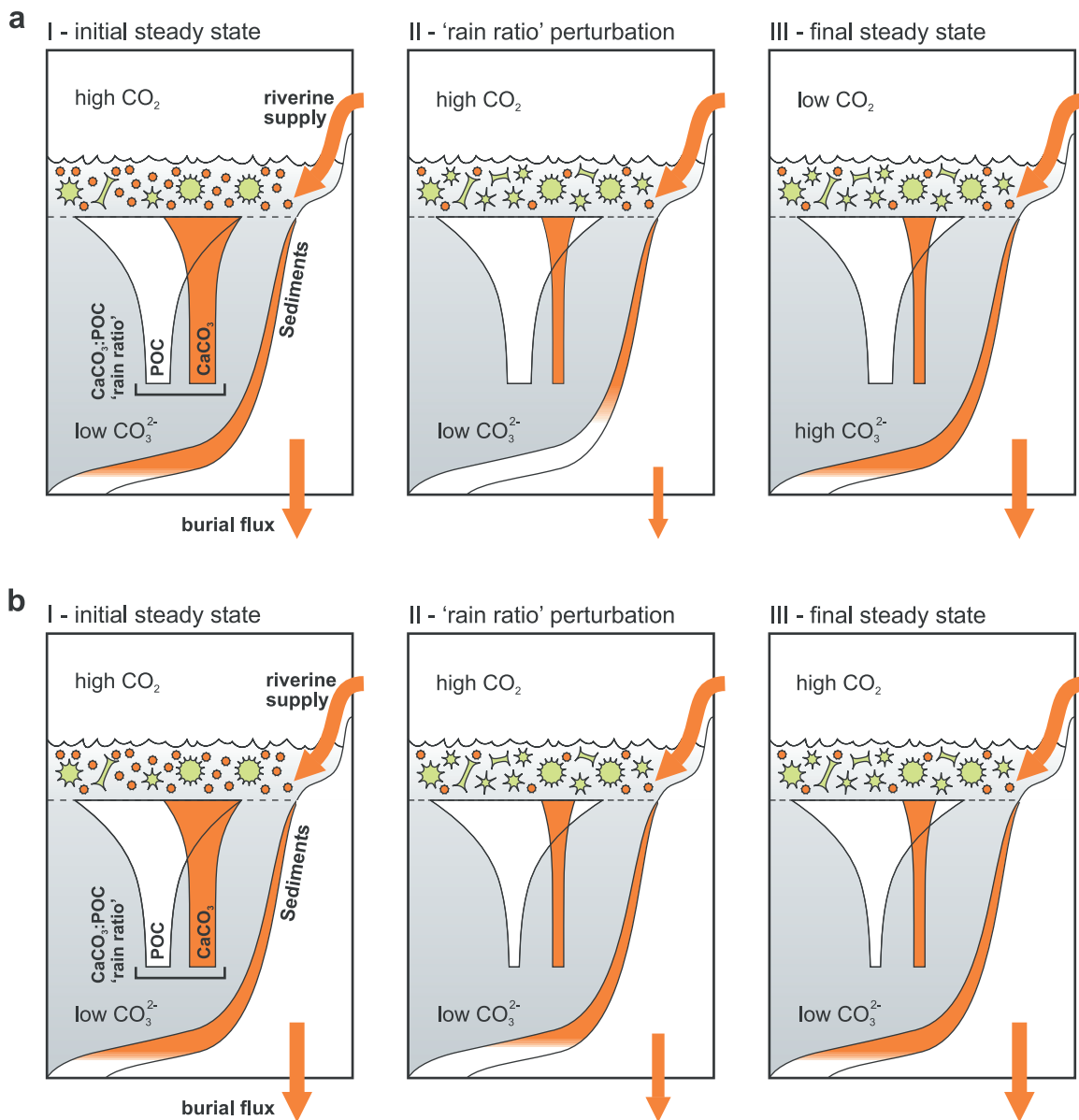
Figure 1. Conceptual operation of the "rain ratio" mechanism [*Archer and Maier-Reimer*, 1994]. (a) Sequence of events assuming no change in the efficiency of POC export to the deep sea. (I) Initial system steady state, with (riverine) influx of Ca^{2+} and CO_3^{2-} to the ocean balanced by the burial of $CaCO_3$ in deep sea sediments. (II) Perturbation of ecosystem composition resulting in a decrease in the surface ocean $CaCO_3$:POC export ratio. The reduction in the $CaCO_3$:POC rain ratio is communicated proportionally to the sediments, resulting in decreased carbonate preservation and a significantly lower global burial rate of $CaCO_3$ (manifested in a shoaling of the lysocline). Inputs of Ca^{2+} and CO_3^{2-} to the ocean now exceed losses. (III) Deep sea $[CO_3^{2-}]$ rises, driving an increase in the preservation of $CaCO_3$ in the sediments, until the point is reached where the global burial flux once again balances input. Higher oceanic $[CO_3^{2-}]$ equates to lower atmospheric xCO_2 (other things being equal). (b) Sequence of events assuming a reduction in the efficiency of POC export through a decrease in $CaCO_3$ ballasting. (I) Initial steady state. (II) Perturbation of ecosystem composition resulting in a decrease in the $CaCO_3$:POC export ratio from the surface ocean (as before). However, because there is less $CaCO_3$ available for ballasting organic matter, there is a reduction in the efficiency of POC export to the deep sea. The result of this is that the $CaCO_3$:POC rain ratio at the sediment surface and net burial flux changes much less than before (i.e., Figure 1a, above). (III) With only a relatively small increase in oceanic $[CO_3^{2-}]$ required to restore steady state, atmospheric xCO_2 is ultimately little affected by the surface ocean ecosystem perturbation.

through the water column [*Armstrong et al.*, 2002; *Klaas and Archer*, 2002]. Mineral surfaces and clay inter-layer sites can also help protect (primarily dissolved) organic material from bacterial attack [*Kennedy et al.*, 2002]. Either way, the presence of mineral particles will enhance the proportion of organic matter exported from the surface that reaches deep ocean depths [*Armstrong et al.*, 2002]. Of the three candidate ballast minerals, analysis of sediment trap data suggests that $CaCO_3$ is by far the most important, and on a global basis is responsible for 83% of the POC flux to the ocean floor [*Klaas and Archer*, 2002]. If the analysis of *Klaas and Archer* [2002] is correct (with opal and dust, the other possible ballast minerals, playing only a minor role) any perturbation of surface ocean ecosystem composition that results in a decrease in $CaCO_3$ export will also drive a reduction in the efficiency with which POC is transported to depth. Thus the $CaCO_3$:POC rain ratio seen at the sediment surface is "buffered" against changes in the export ratio, and the effectiveness of the "rain ratio" mechanism diminished (shown schematically in Figure 1b). For instance, assuming that $CaCO_3$ is responsible for 83% of the POC flux to the ocean floor [*Klaas and Archer*, 2002], a 40% reduction in export $CaCO_3$:POC would result in only a 10% decrease in rain ratio at depth. This is sufficient to account for no more than 20–25% of the total glacial drawdown in CO_2 – just a quarter of the magnitude previously assumed.

[6] There are also implications of this "ballast buffer" in the interpretation of certain paleoceanographic proxies. The search for a reliable proxy for past changes in deep ocean $[CO_3^{2-}]$ has assumed something of "Holy Grail" status in paleoceanography research in recent years. Such a proxy would be invaluable in deciphering the mechanisms responsible for the observed glacial-interglacial changes in atmospheric xCO_2 (A. J. Ridgwell et al., Implications of coral reef buildup for the late Quaternary carbon cycle, manuscript submitted to *Paleoceanography*, 2003). Applied over timescales beyond the current ~400 ka limit of ice core records [*Petit et al.*, 1999], it would also greatly help in reducing uncertainty in reconstructions of past surface ocean pCO_2 (and thus atmospheric

xCO_2) [*Pearson and Palmer*, 2000], which can rely heavily on assumptions regarding past ocean chemistry. One of the leading contenders for such a $[CO_3^{2-}]$ proxy involves the analysis of foraminiferal shell weight [*Broecker and Clark*, 2001]. Although interpretation is complicated by a number of currently poorly understood factors [*Bijma et al.*, 2002], correction for arguably the most important variable, that of the dependence of initial shell weight on surface environmental conditions, is now possible [*Barker and Elderfield*, 2002]. However, the findings of *Klaas and Archer* [2002] suggests that an additional correction will be required, and the effect of changes in ballasting (thinner, lighter shells, for instance, being able to "ballast" less organic matter to the sediments, with the result that dissolution loss of $CaCO_3$ by organic carbon metabolism will be less) be taken into account. While this does not necessarily present an insurmountable problem for this proxy, it does add a further dimension to the interpretation.

[7] Considerable advances have been made over the past decade in how complex biological processes in the ocean surface and diagenetic transformation in deep-sea sediments are represented and coupled together in carbon cycle models [e.g., *Archer and Maier-Reimer*, 1994; *Heinze et al.*, 1999]. However, the representation of ocean interior biogeochemical processes has tended to lag behind, and the simple exponential and power law functions, previously standard in describing the transfer of biogenic material from the ocean surface to the sediments, are now no longer sufficient in many current model applications. For instance, even when ambient water column conditions of temperature and silicic acid are used to calculate a depth-specific opal dissolution rate, model predictions still perform poorly against sediment trap observations [*Ridgwell et al.*, 2002]. In this example, it is likely that still further factors such as microbial degradation of protective organic coatings [*Bidle and Azam*, 1999] are important and need to be taken into account. For $CaCO_3$, the existence of microenvironments within individual "marine snow" aggregates may be critical in determining the overall degree of dissolution that takes place in the water column [*Jansen et al.*,

2002]. Clearly, improved understanding of how the global carbon cycle responds to perturbation and the nature of its relationship to both past and future climatic change requires further focused research effort in this area. There may be further "regime change" to come in our view of how the global carbon cycle operates.

Acknowledgments

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