

Role of river-suspended material in the global carbon cycle: Comment and Reply

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Gislason et al. (2006) make a claim that would significantly change our understanding of the long-term carbon cycle. They argue that reaction of basalt glass in seawater (especially in what they call the “fluidized bed reactors” in the delta environment) constitutes a significant, heretofore unrecognized, carbon sink, because dissolved Ca from this reaction ends up precipitating in the ocean as calcium carbonate. This conclusion is derived from experimental results given in their cited paper (Stefánsdóttir and Gislason, 2005). However, these same experiments demonstrate that the uptake of Mg from seawater in this reaction exceeds the supply of Ca by a factor of ~1.3 (molar ratio), with a large uncertainty. The Mg is reported to probably end up in calcite or a clay mineral (Stefánsdóttir and Gislason, 2005). The authors acknowledge that dissolved Mg supply to the ocean contributes to the carbon sink. The change in amount of divalent cations available to precipitate as carbonate minerals as a result of this process would be the amount of Ca released minus the amount of Mg removed. Because the amount of Mg removed may be greater than the amount of Ca released, this process may represent a reduction in cations available to the marine sedimentary carbonate sink, which effectively would be a carbon source with respect to the ocean/atmosphere pool. It is unclear whether the possible movement of seawater Mg into calcite in these experiments is by a precipitation reaction with dissolved bicarbonate. What fraction of this Mg goes into clay is also uncertain. Assuming such Mg goes into clay, if a sufficient amount is subsequently replaced by the exchange of seawater Na and/or K, then there may be a net carbon sink from the authors’ proposed reaction [neglecting any change in dissolved inorganic compound (DIC) in the proposed reaction; DIC concentrations are not reported in their results]. Given these uncertainties, it is not possible to estimate the primary alkalinity flux to the ocean for the proposed reaction. Therefore, the authors’ claim of a new carbon sink is not robustly supported by the reported experimental results from their cited paper (Stefánsdóttir and Gislason, 2005).

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REPLY doi: 10.1130/G23146Y.1

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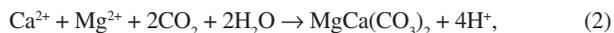
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The main point made by Schwartzman in his Comment is that because the interaction of suspended basalt material and seawater in deltas

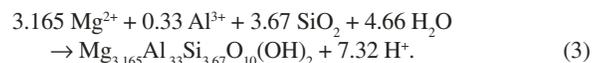
leads to the consumption of Mg concurrent with the release of Ca, the overall effect of suspended material transport from the continents and volcanic islands to the oceans on long-term global climate moderation may be small. This assertion is based on the common perception that both Ca and Mg have similar roles in the carbon fixation process in the oceans. The validity of this assertion is unclear. The efficiency of carbonate precipitation in the ocean for these two elements is very different. Calcium in the ocean draws down CO₂ directly via the formation of calcite in accord with



Although magnesium could draw down CO₂ in the ancient oceans (>100 m.y. ago) via dolomite precipitation in accord with



this process is no longer important in the present-day ocean (i.e., Hardie, 1996; Stanley and Hardie, 1999; Berner, 2004; Holland, 2005). In the current ocean, the majority of dissolved Mg is removed via Mg-silicate precipitation, such as the formation of Mg-saponite:



Because Equation 2 is not important in the present-day ocean, the link between Mg flux into the ocean and CO₂ drawdown at present is indirect. The formation of Mg-silicate secondary minerals has been observed to be coupled to Ca liberation originating from the dissolution of the Ca-rich minerals and glasses present in the mid-oceanic-ridge basalts (i.e., Mottle, 1983). This coupling between Mg precipitation and Ca silicate dissolution is likely via both 1) the production of protons, and 2) by the consumption of Al and Si during the Mg-silicate precipitation. The link between “Mg-clay” mineral precipitation and Ca liberation in the mid-ocean rifts is so efficient that this process has been referred to as a “huge rock-fluid ion-exchange systems for Ca²⁺ and Mg²⁺” (e.g., Stanley and Hardie, 1999, p. 3). This exchange is probably analogous to the processes that occur when Ca-Mg-rich basaltic river suspended material interacts with the ocean. Recent experimental work reported by Stefánsdóttir and Gislason (2005) and referred to by Schwartzman in his Comment, suggests that, like the alteration of mid-ocean ridges, Ca liberation from basalt and basaltic glass is concurrent with Mg consumption. The degree to which Mg consumption is required for the liberation of Ca from either the basaltic suspended material or the mid-ocean ridges is unclear. Ca release from basalt in either the mid-ocean ridges or suspended material in deltas is due to the dissolution of Ca-bearing minerals and glasses. These Ca-bearing minerals and glasses are undersaturated, and their dissolution reactions have been demonstrated to proceed in natural seawater, meteoric waters, and experimental solutions regardless of the aqueous Mg concentration (e.g., Mottle, 1983; Oelkers and Gislason, 2001; Stefánsdóttir and Gislason, 2005). These observations demonstrate that the presence of aqueous Mg is not necessary for the liberation of silicate-bound Ca. Moreover, although Mg precipitation may promote Ca-silicate dissolution via proton production and/or Si and Al consumption, this enhancement may be balanced by the slowing of these dissolution reactions by either blocking reactive surfaces (e.g., Cubillas et al., 2005) or by clogging fluid flow paths by Mg-rich secondary phases. It is, therefore, unclear if dissolved Mg either enhances or inhibits the liberation of Ca from mid-oceanic-ridge and river suspended basalts.

We showed that (1) the flux of Ca to the ocean originating from silicate minerals transported via suspended material is of same order of magnitude as that transported by aqueous transport in river water, and (2) the suspended Ca flux is far more climate dependent than the aqueous river Ca flux and therefore has a stronger negative feedback for Earth's climate through the greenhouse effect. As evidenced by the arguments presented above, Ca liberated from suspended material undoubtedly has a greater effect on carbon fixation in the present-day ocean than that of Mg consumed by the diagenesis of these sediments. The degree to which this Mg may have effected carbon fixation in the ancient (>100 m.y. ago) oceans is related to the relative efficiency of Mg carbonate versus Mg silicate precipitation in these waters.

The critical Comment of Schwartzman does, however, open up an interesting question: Could the Mg-for-Ca exchange in deltas play a role in the historic seawater Mg/Ca ratio evolution? Until now only two processes have been suggested: 1) changing ocean floor spreading rates (Hardie, 1996) and 2) dolomitisation rates (Holland, 2005). Schwartzman's Comment suggests that the weathering of volcanogenic material in deltas, such as those of volcanic islands and North and South America, could play a role in seawater Mg/Ca ratio evolution and perhaps, most interestingly, provide a link between climate and this ratio.

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