

# THE POTENTIAL OF UPPER OCEAN ALKALINITY CONTROLS FOR ATMOSPHERIC CARBON DIOXIDE CHANGES

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## ABSTRACT

Extreme global model scenarios of complete preservation and degradation of biogenic particulate CaCO<sub>3</sub> (calcium carbonate) in open ocean waters which are supersaturated with respect to CaCO<sub>3</sub> were carried out. According to these experiments, the theoretical potential of upper ocean alkalinity controls for changing the atmospheric pCO<sub>2</sub> (CO<sub>2</sub> partial pressure) amounts to several hundred  $\mu\text{atm}$  on time scales of several 10<sup>4</sup> years. Up to a timescale of 10<sup>3</sup> years, however, the respective influence is minor as compared to an expected anthropogenic increase of the atmospheric pCO<sub>2</sub> in the order of 500-1000  $\mu\text{atm}$ .

## BACKGROUND

Marine buffering of carbon dioxide from the atmosphere is based on the transformation of dissolved carbon dioxide to carbonic acid and its subsequent dissociation into bicarbonate and carbonate. The ability of seawater to dissociate carbonic acid is quantified through "alkalinity." Short term alkalinity variations are primarily controlled by production and degradation of biogenic particulate matter, especially of calcium carbonate. Though the upper ocean is oversaturated with respect to calcium carbonate, sinking calcium carbonate particles are subject to degradation. The reasons for this "apparent paradox" are not yet identified conclusively. Some possible explanations are based on: microenvironments on the particles during remineralization of organic carbon, semi-stable or contaminated forms of calcium carbonate, physical/mechanical degradation of particles, and digestion of calcium carbonate in organism guts.

## MODEL METHODOLOGY

The global BOGCM (biogeochemical ocean general circulation model) HAMOCC (Hamburg ocean carbon cycle model, Maier-Reimer, 1993; version 2, annually averaged, see Heinze et al., 2003) was employed to quantify (1) the extent of calcium carbonate degradation in supersaturated waters, (2) the potential impact in changes of this process on the atmospheric carbon dioxide concentration. The HAMOCC-BOGCM considers the reservoirs atmosphere, ocean water column, and sediment. The velocity field is derived from a dynamical ocean circulation model. The BOGCM includes export production of organic carbon, calcium carbonate, and biogenic silica. The sediment is simulated through a diagenetic model, so that the mode of particle flux can be additionally checked through the reproduction of correct sediment coverage. The model is computationally economic, so that multiple integrations including the sediment water column equilibration are feasible.

## MODEL RESULTS - STANDARD CASE

The model was integrated over 40,000 years for pre-industrial conditions in order to fully equilibrate water column and sediment tracers. At first, the model parameters governing the calcium carbonate degradation in the water column were adjusted so that the simulated carbonate ion distribution approximately reproduces the observations. The resulting integrated calcium carbonate degradation rate in the upper ocean was diagnosed and amounts to 65% of the modeled CaCO<sub>3</sub> export production. This value compares well with evidence based on observations [Milliman et al., 1999]. The atmospheric pCO<sub>2</sub> in the standard run is 282.6  $\mu\text{atm}$ .

## MODEL RESULTS – PERTURBED CASES

Then the model ocean system was perturbed for cases of (a) strongly enhanced calcium degradation in the water column and (b) complete preservation of calcium carbonate in supersaturated waters. In case (a) the CaCO<sub>3</sub> re-dissolution rate constant was increased by a factor of 100% so that nearly all biogenic calcareous material was re-dissolved almost immediately. In case (b) no CaCO<sub>3</sub> degradation was allowed at grid cells where formal CaCO<sub>3</sub> super-saturation had been diagnosed in the control run. The results are summarized in Table 1.

## CONCLUSION

Independently from any changes in CaCO<sub>3</sub> production due to ecological or environmental changes a drastic change in upper ocean CaCO<sub>3</sub> re-dissolution in open ocean areas is of only minor quantitative importance as compared to a doubling or quadrupling of the atmospheric pCO<sub>2</sub> due to additional greenhouse gas emissions within the next 100-1000 years.

**Table 1.** Results for atmospheric CO<sub>2</sub> partial pressure for the standard and sensitivity runs.

Run	pCO <sub>2</sub> after 100 years [μatm]	pCO <sub>2</sub> after 1000 years [μatm]	pCO <sub>2</sub> after 10000 years [μatm]	pCO <sub>2</sub> after 40000 years [μatm]
standard	-	-	-	282.6 (quasi-equilibrium)
complete degradation	265.4	243.7	197.0	122.9
complete preservation	287.2	321.7	463.2	590.5

## ACKNOWLEDGMENT

This work was in part supported through contract 511176-2 (CARBOOCEAN Integrated Project) by the European Commission.

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