

## Sources and sinks of carbon dioxide in the surface oceans

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The ocean plays an important role in the global carbon cycle as it contains a vast reservoir of carbon, rapidly exchanges carbon with the atmosphere, and takes up from the atmosphere an amount equivalent to approximately 30% of anthropogenically-released carbon. Over the past four decades, we have collected an extensive database of surface water pCO<sub>2</sub> measured from research ships and other volunteer observing ships. This data set has been used to determine the primary source and sink regions for CO<sub>2</sub> in the oceans. The results show that Atlantic Ocean as a whole, which has 23.5% of the global ocean area, is the strongest CO<sub>2</sub> sink (41%). The high latitude northern North Atlantic region including the Greenland-Iceland-Norwegian Seas is a major sink. This is probably due to a combination of two factors: (1) the intense summer time photosynthesis; and (2) low CO<sub>2</sub> concentrations in subsurface waters resulting from recent ventilation of the North Atlantic subsurface waters. The Pacific Ocean as a whole has the smallest sink flux (18% of the total) in spite of its larger oceanic area (49%). This is because the mid-latitude sink flux (about 1.1 Pg C yr<sup>-1</sup>) is nearly compensated by the large equatorial source flux of about 0.7 Pg C yr<sup>-1</sup>. If the equatorial source flux were totally eliminated, as occurs during strong El Niño events, the Pacific would become a major CO<sub>2</sub> sink, comparable to the entire North and South Atlantic Oceans. The southern Indian Ocean is one of the most intense sink areas in spite of its small area (15% of the total). This may be attributed primarily to the cooling of tropical waters flowing southward in the western South Indian Ocean. The annual net sea-air CO<sub>2</sub> flux has been computed using the NCEP/NCAR 41-year mean monthly wind speeds. An annual net uptake flux of CO<sub>2</sub> by the global oceans has been estimated to be 1.6 ± 0.4 Pg C yr<sup>-1</sup> using the wind speed dependence of the CO<sub>2</sub> gas transfer velocity of Wanninkhof (1992). Time-series measurements of CO<sub>2</sub> fluxes in the equatorial Pacific over the past three decades suggest that decadal changes in CO<sub>2</sub> out-gassing of CO<sub>2</sub> may be related to decadal changes in shallow meridional overturning circulation.

## How the coupling of the C, N and O cycles determines atmospheric CO<sub>2</sub> and O<sub>2</sub> concentrations

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Geochemical evidence suggests that the deep ocean remained anoxic for several hundred million years after the establishment of oxygenic photosynthesis. In this paper we examine the possibility that this extraordinary delay was caused by a geochemical "bottleneck" imposed by feedbacks between carbon burial, net oxygen evolution, and the evolution of the nitrogen cycle in the Proterozoic oceans. Whereas under anoxic conditions oceanic ammonium would have been relatively stable, as oxygen concentrations rose, nitrification and subsequent denitrification would have rapidly removed fixed inorganic nitrogen from the oceans. Denitrification would have imposed a strong constraint on the further rise of free oxygen by depriving oxygenic photoautotrophs of an essential nutrient. To examine the dynamic interactions between oxygen and nitrogen cycling, we developed a simple box model that incorporates the basic features of oxygen, nitrogen and carbon biogeochemistry, ocean circulation and ocean-atmosphere gas-exchange.

Model simulations, initiated under anaerobic conditions with no free oxygen in the atmosphere or ocean, are characterized by an initially reduced deep ocean with abundant ammonium, followed by a low-nitrogen phase where neither form of fixed nitrogen is stable, and a fully oxidized phase with abundant nitrate. We infer that, in the process of oxidizing the early Proterozoic ocean, the system had to go through an extended nitrogen-limited phase during which time export production was severely attenuated. Our studies suggest that the presence of shallow seas with increased organic matter burial was a critical factor determining the concentration of oxygen in the ocean and atmosphere, while the phosphate concentration played a key role in determining the rate of oxygenation of the deep ocean.

## Fossil fuel CO<sub>2</sub> in geologic time

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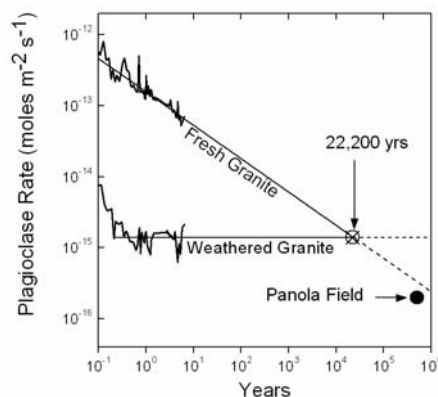
I will present a series of model calculations to forecast the geologic timescale impact of fossil fuel CO<sub>2</sub> release to the atmosphere / ocean carbon pools. Fossil fuel CO<sub>2</sub> release perturbs atmospheric pCO<sub>2</sub> for hundreds of thousands of years, with roughly 10% of the CO<sub>2</sub> release remaining in the atmosphere until it is neutralized by the silicate weathering feedback. I'll show how fossil fuel CO<sub>2</sub> may trigger further release of carbon from the clathrate reservoir. A model of the methane clathrate reservoir in deep sea sediments gets the present-day methane inventory about right, and predicts a strong temperature dependence of the steady state inventory. Finally, I'll show an analysis of the onset of glaciation as a function of orbital forcing and atmospheric pCO<sub>2</sub>, to demonstrate the capacity of anthropogenic CO<sub>2</sub> to prevent the onset of the next ice age for up to 500 kyr into the future.

## Extrinsic versus intrinsic controls on rates of silicate weathering and CO<sub>2</sub> drawdown

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Estimating atmospheric CO<sub>2</sub> uptake over the earth's history by the surficial weathering of silicate rocks requires quantifying reaction rates over a range of chemical and physical conditions. These controls are summarized as intrinsic and extrinsic weathering properties (White and Brantley, 2003). Intrinsic properties are physical or chemical characteristics, such as mineral composition, surface area and defect densities. If intrinsic properties dominate weathering, such characteristics should be transferable between environments, e.g., laboratory and field rates of the same mineral should be comparable. Extrinsic features reflect conditions external to the silicate phase that impact chemical weathering such as solution composition, climate and biological activity. These processes are dependent on the external environmental conditions which are difficult to fully recreate under laboratory simulations. Intrinsic effects on rates are shown below by the difference in experimental dissolution of fresh and naturally weathering plagioclase in Panola Granite. The intrinsic effects are predicted to be neutralized after 22 kyrs. of experimental weathering. Extrinsic controls on natural weathering, which are dominantly saturation-controlled and transport-limited, is shown by the difference in the extrapolated experimental rate and the actual field rate.



### Reference

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## **Cenozoic carbon cycling and climate change**

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A new box model for carbon cycling over the Cenozoic is presented showing that the evolution of pCO<sub>2</sub> values closely follows the trends in Cenozoic climate change. According to the model, the partial pressure of CO<sub>2</sub> in the atmosphere (pCO<sub>2</sub>) is high (up to 1000 μatm) during the early Eocene climate optimum and strongly decrease towards the late Eocene/early Oligocene boundary. Oligocene to Pleistocene pCO<sub>2</sub> values are rather constant ranging in between 200 and 300 μatm. Simulated pCO<sub>2</sub> changes are mainly driven by rates of volcanic and metamorphic degassing, silicate weathering and organic carbon burial. The rather good correspondence between Cenozoic pCO<sub>2</sub> and climate suggests that carbon cycling processes had a strong effect on Cenozoic climate change.

## **The role of continental erosion and river transports in the global carbon cycle**

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The chemical and physical erosion of land materials released into the rivers organic (dissolved (DOC) and particulate (POC)), and inorganic (dissolved (DIC) and particulate (PIC)) carbon which is subsequently discharged into the oceans: about 1 GtC.y<sup>-1</sup> (DIC, PIC, DOC and POC represent respectively 38%, 17%, 25% and 20%). Most of the carbon transported by the rivers originates from the atmospheric CO<sub>2</sub>, except PIC and half of the DIC which are supplied respectively by the physical and chemical erosion of carbonates.

The chemical erosion of inorganic materials which consists in dissolving or hydrolyzing primary minerals of rocks and soils requires CO<sub>2</sub> and releases DIC. The flux of CO<sub>2</sub> consumed by weathering processes is mainly produced by soil organic matter oxydation. Nevertheless, on a geological time scale, it is only the fluxes of CO<sub>2</sub> consumed by silicate rock weathering which represent a non-negligible sink of CO<sub>2</sub>. Runoff and lithology are the major factors controlling rock weathering and atmospheric/soil CO<sub>2</sub> consumption. Among all silicate rocks, shales and basalts appear to have a significant influence on the amount of CO<sub>2</sub> uptake by chemical weathering. Moreover, soil cover plays an important role: the CO<sub>2</sub> flux is lower for lateritic river basins than for non-lateritic ones.

DOC and POC riverine fluxes are respectively dependent on the soil organic carbon contents and on the river sediment transports.

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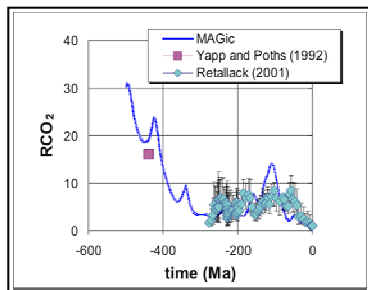
## How tightly coupled are seafloor spreading rates and seawater-atmosphere composition?

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Although many current models of the geologic history of atmosphere and seawater composition assume that seafloor spreading and volcanic degassing rates have varied over the Phanerozoic Eon, the mechanism and role of these variations are poorly understood. Although spreading rate was an important forcing function in the earlier BLAG model, GEOCARB's paleo-CO<sub>2</sub> curve is relatively insensitive to degassing rate variations, and the current version suggests that degassing has played a minor role in CO<sub>2</sub> regulation compared to that of vascular plants, paleocontinental organization, shifts in skeletal carbonate deposition, and other factors (e.g., Berner and Kothavala 2001).



Variations in spreading rate have played a much more central role in models that compute seawater compositions from marine evaporite and carbonate mineral proxies (e.g., Stanley and Hardie 1998;

Lowenstein et al. 2001). However, the relationship between seawater chemistry and spreading/degassing rates has been complicated by the controversy over whether the production of new oceanic lithosphere has varied significantly over the past 180 Ma (Rowley 2002). This argument questions the relationships between seafloor spreading rate, volatile fluxes, and eustatic changes assumed in previous shallow earth system models. As a means of resolving whether these divergent views are necessarily incompatible, we have modified our MAGic model to accommodate isotopic constraints. By integrating critical Earth system processes over time, this detailed model offers insight into how tectono-physical, chemical, and biological driving forces have interacted to produce the stable hothouse/greenhouse modes that characterize Phanerozoic climate.

## $\delta^{13}\text{C}$ tracing of dissolved inorganic carbon sources in major world rivers

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The significance of rock weathering and river transport in the global carbon cycle has already been discussed by many authors. Rivers discharge into the oceans on average 1 GtC.y<sup>-1</sup> of which 40% as Dissolved Inorganic Carbon (DIC). DIC originates mainly from atmospheric CO<sub>2</sub>, soil organic matter oxidation and carbonate dissolution. Only geochemical modeling and geochemical tracers have been used until now to distinguish DIC sources. Nevertheless each DIC sources have different  $\delta^{13}\text{C}$  isotopic signatures (-26‰ to -9‰ for soil organic matter according to C3 or C4 plants, -8‰ to -6‰ for the atmospheric CO<sub>2</sub> and around 0‰ for carbonate rocks) but few studies have been devoted to the use of carbon isotopes to trace the different DIC sources and their behaviour in the river water. This study presents the results obtained for some large rivers in South America, in India, in Africa and in Europe.  $\delta^{13}\text{C}_{\text{DIC}}$  values are greatly variable from one river to another, going from very negative values as for the Amazon river (until -27‰) to less negative values as for the Patagonian rivers (until -2‰ for the Chico). All these results are also compared with literature values which are not yet very abundant. These variations show that the average isotopic signature of the DIC fluxes discharged into the world ocean (-10‰ to -12‰) which is used in the oceanic carbon cycle modeling needs to be revised, at least regionally. The major result of this study concerns the negative relationship between  $\delta^{13}\text{C}_{\text{DIC}}$  and the dissolved organic carbon (DOC) content, showing that the organic carbon oxidation greatly contributes to decrease the riverine  $\delta^{13}\text{C}_{\text{DIC}}$ .