## 4.1.47

## Ocean sources and sinks for natural and anthropogenic CO<sub>2</sub>

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One of the most robust constraints on the spatial distribution of carbon sources and sinks at the earth surface is the observed north-south gradient of atmospheric  $CO_2$ , which is smaller than expected given the predominantly northern hemisphere emission of anthropogenic  $CO_2$ . This observation can be explained either by a strong uptake of anthropogenic  $CO_2$  in the northern hemispheric driven by oceanic or terrestrial biosphere processes, or by a north-south transport of carbon by the ocean with  $CO_2$  uptake at high northern latitudes and outgassing at high southern latitudes. This transport must have existed already during preindustrial times and would have caused a preindustrial south-north gradient of atmospheric  $CO_2$ .

We will present new results from an ocean inverse modeling study where we use a global data set of interior ocean carbon observations to estimate natural and anthropogenic  $CO_2$  fluxes across the air-sea interface. Relative to previously reported results [1], the new estimates are based on an extended oceanic carbon data set, a wide range of new ocean circulation models and an improved consideration of errors and biases.

The inversely estimated natural air-sea fluxes reveal the expected pattern with CO<sub>2</sub> outgassing in the tropics and CO<sub>2</sub> uptake at mid to high latitudes. The contemporay air-sea fluxes agree reasonably well with flux estimates derived from  $\Delta pCO_2$  observations [2], with the exception of the subpolar regions in the Southern hemisphere where our estimates are three to five times smaller, and an equatorward shift of the main oceanic sink regions.

Our results imply a substantial interhemispheric gradient in atmospheric CO<sub>2</sub>. This gradient is mainly forded by an interhemispheric asymmetry in the oceanic CO<sub>2</sub> source-sink distribution where all oceanic regions north of 13°N are sinks, whereas most of the oceanic regions south of 36°S are sources of CO<sub>2</sub>. Our results support the existence of substantial sink for anthropogenic CO<sub>2</sub> in the northern hemisphere terrestrial biosphere.

#### References

[1] Gloor et al. (2003).GRL 30 (1).

[2] Takahashi et al. (2002) DSRII 49, 1601-1621.

## 4.1.51

# Further evaluation of flow-through as a method for cleaning and dissolving shells of planktonic foraminifera for Mg/Ca paleothermometry

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The primary Mg/Ca ratio of foram shells is a potentially valuable paleoproxy for sea surface temperature (SST) reconstructions. However, the reliable extraction of this ratio from sedimentary calcite assumes that we can overcome artifacts related to foram ecology and partial dissolution, as well as contamination by secondary calcite and clay. The standard batch method for Mg/Ca analysis involves cracking, sonicating and rinsing the tests to remove clay followed by chemical cleaning and finally single-point measurement. This extensive procedure often results in substantial loss of sample (typically 30-60%). We find that even the earliest steps in this procedure can fractionate Mg from Ca, biasing the batch result toward a lower ratio. Moreover, the more rigorous the cleaning, the more calcite is lost, and the more likely it becomes that any residual clay will move the ratio higher. These potentially significant sources of error can be overcome with a flow-through (FT) leaching method that makes timeand labor-intensive pretreatment unnecessary. When combined with time-resolved analysis (FT-TRA), flowthrough produces continuous records of Mg, Sr, Al, and Ca concentrations sorted by susceptibility of the reacting material. These "dissolution curves" can be used to correct the shell Mg/Ca ratio for clay using Al. However, the separation of calcite from clay is so good in FT that this correction is typically <1%, even in clay-rich sediments. Flow-through not only separates the more susceptible secondary calcite from the more resistant biogenic calcite, but also sorts biogenic calcite into more- and less-susceptible fractions. We find that the most susceptible fraction of biogenic calcite gives the most accurate value for SST and is therefore primary calcite. Unlike hands-on batch methods, flow-through lends itself to automation. The "Haleyomatic" automated flow-through system can process 22 samples, 2 system blanks, and 48 mixed standards in 11 hours of unattended operation. Flowthrough thus represents a faster, cheaper, and better way to determine Mg/Ca ratios in foraminiferal calcite.