

## STABLE ISOTOPE GEOCHEMISTRY APPLIED TO PALEOCLIMATOLOGICAL AND GREENHOUSE GAS PROBLEMS

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The stable isotope ratios of hydrogen and oxygen in ice cores from glaciers and polar ice sheets have been used as an empiric surface "paleothermometer", and for age dating through the use of "annual isotope variations". It will be pointed out that in several cases short term variations of H and O isotopes in ice cores cannot be interpreted as "annual cycles", and that such variations are obliterated in old ice. This is due to a number of physico-chemical processes including melting, sublimation, freezing, and condensation operating in situ and in the ice cores leading to redistribution of H and O stable isotopes when the sample cannot be considered a closed system (see Jaworowski, Segalstad & Ono 1992: Do glaciers tell a true atmospheric CO<sub>2</sub> story? *Science of the Total Environment* 114, 227-284).

An assumption of a closed system with respect to H and O isotopes does not hold for the firn strata. The release of vapor by sublimation of the ice in an open system will leave the remaining ice enriched in D and <sup>18</sup>O isotopes. Artifacts from H<sub>2</sub>O state changes due to thermal gradients, both natural and during core drilling, may be falsely interpreted as changes in the paleotemperature of snow precipitation. H and O stable isotope data from glacier and polar ice cannot be regarded as a reliable basis for estimation of past climate changes. Core samples reportedly stored for 16 years before isotope analysis, which had lost 30% of their mass through sublimation, will, if also the condensed vapor is considered, have changed the H and O stable isotope ratios of the remaining ice vs. the condensed vapor to a level corresponding to the whole "paleotemperature" range in the Vostok (Antarctica) core. H and O isotope fractionation processes, starting immediately after precipitation of snow and occurring until analysis of ice cores, will change the stable isotope composition in ice. The isotopic changes may be of the same magnitude, or even larger, than the range reported from deep ice cores. Such changes contain no quantitative information on surface paleotemperatures or paleoclimates, but are rather due to a combination of paleotemperature variations and later physico-chemical processes.

Carbon isotopes in CO<sub>2</sub> gas in ice have been shown to be negatively correlated with the CO<sub>2</sub> concentration, ascribed to the release of carbon into the atmosphere from man's burning of fossil fuel. Such a negative correlation will, however, be expected through a combination of solubility and isotope fractionation as a function of the temperature gradient in ice sheets. The oxygen isotopes of CO<sub>2</sub> in gas inclusions in ice show that there has been equilibration between the gas and the bubble wall. Hence the assertion, that the CO<sub>2</sub> variations found from analyses of ice cores reflect exclusively an atmospheric change, mainly due to man's burning of fossil fuels, does not hold.

Stable  $^{13}\text{C}/^{12}\text{C}$  isotope ratios (expressed as  $\delta^{13}\text{C}_{\text{PDB}}$ ) can be used to compute the composition of atmospheric  $\text{CO}_2$ . The natural atmospheric  $\text{CO}_2$  reservoir has  $\delta^{13}\text{C} \approx -7\text{‰}$  when in isotopic equilibrium with marine  $\text{HCO}_3^-$  and  $\text{CaCO}_3$ .  $\text{CO}_2$  from burning of fossil-fuel and biogenic materials has  $\delta^{13}\text{C} \approx -26\text{‰}$ .

$\delta^{13}\text{C}$  reported for atmospheric  $\text{CO}_2$  was  $-7.489\text{‰}$  in Dec. 1978, decreasing to  $-7.807\text{‰}$  in Dec. 1988 (Keeling et al. 1989; *AGU Geophys. Mono.* 55, 165-236). In  $\sim 300$  years old Antarctic ice  $\delta^{13}\text{C} = -6.31$  of trapped  $\text{CO}_2$  (Friedli et al. 1986; *Nature* 324, 237-238).

If the decreasing  $\delta^{13}\text{C}$  was only caused by mixing natural  $\text{CO}_2$  with  $\text{CO}_2$  from burning of fossil fuels or plants (current  $\sim 79\%/ \sim 21\%$   $\text{CO}_2$  mix; lifetime 50-200 years; *IPCC* 1989), the current atmospheric  $\text{CO}_2$   $\delta^{13}\text{C}$  should be much lower than reported.

The December 1988 atmospheric  $\text{CO}_2$  composition was computed for its 748 GT C (GT =  $10^{15}$  g) total mass and  $\delta^{13}\text{C} = -7.807\text{‰}$  for 3 components: (1) natural fraction remaining from the pre-industrial atmosphere; (2) cumulative fraction remaining from all annual fossil-fuel  $\text{CO}_2$  emissions; (3) carbon isotope mass-balanced natural fraction. The masses of component (1) and (2) were computed for different atmospheric lifetimes of  $\text{CO}_2$ .

The result fits a lifetime of  $\sim 5$  (5.4) years, in agreement with  $^{14}\text{C}$  studies. The mass of all past fossil-fuel and biogenic emissions remaining in the current atmosphere was  $\sim 30$  GT C or less, i.e. maximum  $\sim 4\%$ , corresponding to an atmospheric concentration of  $\sim 14$  ppmv.

The implication of the  $\sim 5$  year lifetime is that  $\sim 135$  GT C ( $\sim 18\%$ ) of the atmospheric  $\text{CO}_2$  is exchanged each year. The isotopic mass balance calculations show that at least 96% of the current atmospheric  $\text{CO}_2$  is isotopically indistinguishable from non-fossil-fuel sources, i.e. natural marine and juvenile sources. Hence for the atmospheric  $\text{CO}_2$  budget marine equilibration and degassing and juvenile degassing from e.g. volcanic sources must be much more important, and burning of fossil-fuel and biogenic materials much less important, than hitherto assumed.

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