On the Carbon Isotope Fractionation Between Silicate Melts and Gaseous CO_2

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The understanding of $\delta^{13}C$ changes as a result of CO_2 loss from degassing magmas requires knowledge of the melt-CO_2 carbon isotope fractionation. In order to assess the magnitude of the effect that the interaction of melt cations with the carbonate group in melts could have on this fractionation, ^{13}C reduced partition functions were computed for carbonates of varying bond strengths. We find that the reduced partition function for the carbonate ion in combination with different cations can be represented by:

$$1000\ln\hat{a} = \left(0.0324 - 0.0726\frac{10^3}{T} - 0.01073\frac{10^6}{T^2}\right)$$
$$-14.00 + 29.953\frac{10^3}{T} + 9.461\frac{10^6}{T^2}$$

where μ is the reduced mass of the cation-carbonate group combination, and T is in K. Published experimental CO_2-silicate melt ^{13}C fractionations also suggest a cation dependence. At 1200°C the relationship between melt-CO_2 ^{13}C fractionation as a function of melt composition, in terms of molecular proportions of the cations Mg, Fe, Mn, Ca, Na, K and Si and Al, can be expressed as:

$$1000\ln(\hat{a}_{Melt-CO_2}) = 5.14\frac{Mg + Fe + Mn + Ca + Na + K}{Si + Al} + 0.86$$

For a given carbonate structure the tendency to concentrate ^{13}C increases with pressure. The effect of pressure on the size of the reduced partition function of aragonite varies with temperature. In the pressure range 1 to 10^5 bar the pressure effect (permil change for a 10 kbar increase in pressure) is:

$$\ddot{A}^{13}C_P = -0.01796 + 0.06635\frac{10^3}{T} + 0.006875\frac{10^6}{T^2}$$

Similar size pressure effects can be expected for melt-CO_2 fractionations. A conceptual model, expressing melt-vapour fractionations as a function of C speciation, is presented.

Sensitivity of the Atmospheric Carbon-14 Content in a Climate Model

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The last deglaciation was interrupted in the northern hemisphere by a cold period, the Younger Dryas, best explained by a marked reduction of the oceanic thermohaline circulation. A rapid increase in the atmospheric carbon-14 content observed at the beginning of this event supports this explanation. Still, the dynamical oceanic models have failed to reproduce quantitatively both the amplitude and timing of this carbon-14 increase (Broecker, 1998; Marchal et al., 2001).

Here we use the Stocker et al. (1992) coupled model to show that changing some model parameters and parameterizations helps to come closer to the observed carbon-14 variations. This zonally averaged model couples a dynamical oceanic model to an energy balance model of the atmosphere. It is forced by a meltwater discharge in the North Atlantic to produce a temporary collapse of the deep water formation.

We discuss the following model parameters and parameterizations:

* The oceanic vertical diffusivity: a weaker diffusivity enables a stronger decoupling between the surface and the deep ocean when the North Atlantic deep water formation weakens, and thus a stronger carbon-14 response in the atmosphere (by 5 to 10 permil in our case).

* The shape of the meltwater discharge and the freshwater forcing (E-P) at the surface of the oceans control the rate at which the north Atlantic deep water formation decreases, and thus the increase rate of the carbon-14 in the atmosphere (lead of at least 100 to 200 years).

* The wind stress, allowed to change according to the simulated climatic variations. It influences the atmospheric carbon-14 content both directly by the ventilation of the upper ocean (Ekman cells) and indirectly through the formation of North Atlantic deep water. Halving the wind stress in the Tropics increases both the atmospheric carbon-14 content (by 20 permil) and its rate of increase (shifted ahead by ~500 years).

References
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