

Isotopic fingerprints of mass transport processes

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I will discuss three types of mass transport related isotope fractionations. 1. Isotope fractionation by evaporation of silicate liquids. 2. Isotope fractionation by chemical diffusion in liquids. 3. Isotope fractionation by thermal diffusion in molten basalt.

We (Richter *et al.*, 2002 and work in progress) have carried out a large number of experiments on isotope fractionation during evaporation and find that it follows a Rayleigh fractionation law of the form $R_{ij}/R_{i0} = f_j^{\alpha-1}$ where R_{ij} is the ratio of isotopes i and j when a fraction f_j of isotope j remains in the condensed phase and R_{i0} is the original isotope ratio of the of the condensed phase. The fractionation parameter α is the ratio of the isotopic composition of the evaporation flux to that of the substrate. In the case of magnesium evaporating from silicate liquid at 1400°C, (relevant to the evaporation history of Ca-Al-rich inclusions found in primitive meteorites), we find $\alpha=0.9910$, which is significantly different from the often assumed value of $\alpha=(24/25)^{1/2}=0.9798$ for the fractionation of $^{25}\text{Mg}/^{24}\text{Mg}$ in the evaporation residue.

We (Richter *et al.*, 1999, 2003) reported the results of experiments for the isotopic fractionation of Li, Ca, and Ge (used as a Si analogue) during diffusion between molten basalt and rhyolite, and now have new data on the isotopic fractionation of Mg in this system. We have also carried out experiments on the isotopic fractionation of Li, Mg, and Cl during diffusion in water (Richter *et al.*, 2006). The results are reported in terms of the exponent β in $D_i/D_j = (m_i/m_j)^\beta$, where the D_k is the self diffusion coefficients of isotope k and m_k is its atomic mass. For molten silicate we found $\beta_{\text{Li}/6\text{Li}} \approx 0.215$, $\beta_{44\text{Ca}/40\text{Ca}} \approx 0.075$, $\beta_{26\text{Mg}/24\text{Mg}} \approx 0.05$, $\beta_{76\text{Ge}/70\text{Ge}} \approx 0$. In water $\beta_{7\text{Li}/6\text{Li}} \approx 0.015$, $\beta_{37\text{Cl}/35\text{Cl}} \approx 0.025$, $\beta_{26\text{Mg}/24\text{Mg}} \approx 0$. Note the very much smaller fractionations in water.

Our most recent experiments involve isotopic fractionations by thermal diffusion (often also called Soret diffusion). We are finding surprisingly large isotopic fractionations ($\sim 8\%$ for $^{26}\text{Mg}/^{24}\text{Mg}$) associated with a change of only about 150°C across molten basalt. We are in the process of determining the thermal isotopic fractionation factors of the other major elements in molten basalt.

References

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Deglacial rearrangement of carbon and nutrients in surface and intermediate depth waters

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Changes in the pattern of conveyor circulation, reconstructed from the combined nutrient proxies Cd/Ca and $\delta^{13}\text{C}$, have been implicated in abrupt climatic events of the last deglaciation. But, the assumption that characteristic endmember water mass signatures derived from southern nutrient rich surface waters close to sea ice, and northern nutrient depleted ice free surface waters, have remained invariant in time, has recently been called into question. We contrast new deglacial planktonic and benthic foraminiferal histories from intermediate depths in the high latitude North and Equatorial Atlantic with records from the South Atlantic and Pacific. The timing and amplitude of the deglacial minimum in $\delta^{13}\text{C}$ of atmospheric CO_2 from Taylor Dome, is captured by the surface $\delta^{13}\text{C}$ records. The surface $\delta^{13}\text{C}$

minimum is paralleled at intermediate depths in the high northern latitudes throughout the early deglacial. This may indicate continued northern sourced ventilation with an altered endmember $\delta^{13}\text{C}$ signature, which can account for the early deglacial warming documented in the North Atlantic. Globally, intermediate depth signatures converge to the same value at the start of the deglaciation. Our data are consistent with vertical fractionation of carbon and nutrients into a poorly mixed deep reservoir during the last glacial, which is reventilated at the deglaciation and the sequestered carbon mixed via the intermediate waters to the surface and atmosphere. Divergence between the surface and intermediate depth chemical signatures occur only during the Younger Dryas. Our results confirm that endmember water mass signatures change significantly on a glacial-interglacial cycle.