

## Kinetic fractionation of gases by deep air convection in polar firn

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A previously unrecognized type of gas fractionation occurs in firn air columns subjected to intense convection. It is a form of kinetic fractionation that depends on the fact that different gases have different molecular diffusivities. Convective mixing continually disturbs diffusive equilibrium, and gases diffuse back toward diffusive equilibrium under the influence of gravity and thermal gradients. In near-surface firn where convection and diffusion compete as gas transport mechanisms, slow-diffusing gases such as krypton and xenon are more heavily impacted by convection than fast diffusing gases such as nitrogen and argon, and the signals are preserved in deep firn and ice. We show a simple theory that predicts this kinetic effect, and the theory is confirmed by observations of stable gas isotopes from the Megadunes field site on the East Antarctic plateau. Numerical simulations confirm the effect's magnitude at this site. A main purpose of this work is to support the development of a proxy indicator of past convection in firn, for use in ice-core gas records. To this aim, we also show with the simulations that the magnitude of kinetic effect is fairly insensitive to the exact profile of convective strength, if the overall thickness of convective zone is kept constant.