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Kinetic gas fractionation by air convection in polar firn: An ice core paleoconvection proxy

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Recent firn air studies at the Megadunes site in central Antarctica (80.78 S, 124.5 E) show the existence of a 25-m deep zone of intense air convection, enabled by large cracks or fissures in the firn. The fissures appear to be due to near-zero accumulation rate, intense weathering, thermal-contraction cracking, and sublimation (Courville et al., 2007). Measured xenon and krypton isotopes are less gravitationally enriched than argon and nitrogen isotopes, and the xenon-nitrogen isotope difference has been explored as a possible paleo-convective zone thickness indicator for use in ice cores (Kawamura et al., 2006). Here we show from first principles that this phenomenon is a type of kinetic gas fractionation. Convective mixing continually disturbs gravitational equilibrium, and gases diffuse back toward equilibrium, with heavier gases diffusing more slowly, causing a steady state depletion of heavy gases. Maximum fractionation occurs when convective (turbulent) mixing and diffusive gravitational unmixing are in competition with each other, such that the effective eddy diffusivity and molecular diffusivity are similar (Péclet number near 1). The effect on deep firn gases (and hence bubble air) increases with the thickness of the layer in which the Péclet number is near 1. At Megadunes the magnitude of the effect is 143 per meg for ^{136}Xe/^{129}Xe, 61 per meg for ^{86}Kr/^{82}Kr, and 12 per meg for ^{40}Ar/^{36}Ar. The effect may be safely neglected in ice core studies for most trace gases, but offers a novel means to estimate past convective zone thickness from measurements of noble gas isotopes. Such a paleo-convection proxy would be useful for establishing the phasing of climate and greenhouse gases.