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Molecular size dependent gas fractionation in firn air derived from noble gases, oxygen, and nitrogen measurements

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Air withdrawn from the firn of Devon Island (Canada), North GRIP(Greenland), South Pole and Siple Dome (Antarctica) is enriched in He and Ne, $O_2$and Ar compared to N_2 near the bubble close-off depth, reaching the maximum values in the deepest samples just above the zone of impermeable ice where no free air can be extracted anymore. In contrast isotopic ratios of $^{15}N/^{14}N$, $^{18}O/^{16}O$, and $^{36}Ar/^{40}Ar$ show no extraordinary enrichment near the close-off depth. The observed isotopic ratios in the firn air column can be explained within the uncertainty ranges by the well-known processes of gravitational enrichment and thermal diffusion. To explain the elemental ratios, however, an additional fractionation process during bubble inclusion has to be considered. We implemented this additional process into the firn air model. Empirical fractionation factors are found by fitting model profiles to the data. For smaller gas species (mainly He and Ne) the fractionation factors are linearly correlated to the molecule size, whereas for diameters greater than about 3.6 Å the fractionation seems to be significantly smaller or even negligible. However, these empirical fractionation factors are not thought to be fundamental constants, but rather are expected to vary with site temperature and accumulation rate. A minimally-complex physical model of the bubble close-off fractionation and lock-in zone enrichment provides a more

realistic alternative to the empirical fractionation factor model. The model presumes that fractionation is caused by selective permeation of gas through the ice lattice from slightly overpressured bubbles. The adequate fit of this model to data in the open firn air column at sites with differing temperature provides tentative support for the view that gas permeation through the ice lattice is responsible for the fractionation.