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Diffusive smoothing of isotopic signals in ice cores: the grain-scale signature of excess diffusion as a testable prediction

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Diffusion limits the survival of climate signals on ice-core isotope records. Diffusive smoothing acts not only on annual signals near the surface, but also on millennial signals in deep ice where they shorten to decimetres or centimetres. Short-circuiting of the slow diffusion in crystal grains by fast diffusion along liquid veins can explain the accelerated or "excess" diffusion found on some isotope records. But direct experimental evidence is lacking whether the short-circuiting mechanism really operates as theorised; current theories of it also neglect diffusion along grain boundaries. The pattern of isotope concentrations across crystal grains caused by short-circuiting provides a testable prediction of the mechanism. Here, we extend the theory for grain boundaries and calculate the pattern for different assumptions of grain-boundary diffusivity and thickness, and different temperature, vein and grain sizes, and vein-water flow velocity. Two isotopic patterns prevail in ice of millimetre grain sizes: (i) an axisymmetric pattern with isotopic excursions centred on triple junctions in the case of thin, low-diffusivity grain boundaries; (ii) a three-spoke pattern of excursions around triple junctions in the case of thick, highly-diffusive grain boundaries. Because these signatures have excursions potentially reaching several per mil and as thick as 10–25% of the mean grain radius, they should be detectable by LA-ICP-MS mapping on ice affected by excess diffusion. We further examine how the predicted patterns vary with depth (through a wavelength of the bulk isotopic signal) to formulate the procedure of testing for the occurrence of short-circuiting, such as applicable to ice-core samples from the EPICA Dome C and Beyond EPICA Oldest Ice projects. Because our model accounts for grain boundaries and veins, it also characterises the bulk-ice isotopic diffusivity more comprehensively than past studies.