

LOCATION, MOVEMENT AND REACTIONS OF IMPURITIES IN SOLID ICE

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1. Introduction

The aim of drilling ice cores is to obtain paleoatmospheric information of wide significance. However, the concentrations of chemicals found in the ice are determined both by the atmospheric concentrations, and by depositional and post-depositional processes. Other papers in this volume discuss the depositional processes, and the processes that subsequently alter the concentrations in near-surface (up to a metre or so depth) snow. However, there are a number of documented cases where further changes occur below the surface snow. Additionally, there is the possibility that chemical changes can occur, at least to more complex species, over the long timescales that are relevant for ice. Diffusion is bound to take place to some extent, affecting the apparent rate of temporal change inferred from ice core profiles. Discussion of all these factors requires an understanding of the way in which impurities are held in the ice. This paper discusses all these items, concentrating on processes in solid ice, and in firn below the top metre or two.

2. Known examples of changes within the firn and ice

Most ice core researchers assume that the profiles they look at are locked firmly in place by a snow depth of about 2 metres (I exclude here the gases trapped in air bubbles, which form only at the pore close-off, and are discussed by Schwander (1996)). However, a number of examples have been presented in the literature where this is clearly not the case. These are summarised below without any deep exploration of the causes, which will be discussed in later sections. Naturally, the list includes only examples that have been observed and reported: it is conceivable that other important cases await discovery.

2.1. H₂O₂ losses

Hydrogen peroxide is the clearest example of a species that suffers diffusive smoothing throughout the firn layer (Neftel 1991; Sigg and Neftel 1991). The original strong seasonal signals are almost completely lost (at Summit, Greenland, an original max/min ratio of about 10 is reduced to <2 by 70 m (Neftel 1991)) (Fig. 1A). This is caused by movement of H₂O₂ in the vapour phase through the pore space, and implies that most of the H₂O₂ is at some time available at the grain surfaces. Oxygen isotope ratio seasonal signals are attenuated in an apparently similar way to this (Johnsen 1977), and one can assume that other molecules with a relatively high volatility would behave similarly.

While diffusion will destroy the seasonality of signals, long-term average concentrations will not be affected. However, other processes seem to destroy H₂O₂ completely. In alpine glaciers, H₂O₂ is lost rapidly, probably by a light-enhanced catalytic destruction on dust particles (Neftel 1991). In ice from the polar regions, H₂O₂ is also lost, but much more slowly. Nonetheless, H₂O₂ is completely absent from the very dusty, alkaline ice of the last ice age at Summit (Fuhrer et al. 1993) (Fig. 1B). H₂O₂ "holes" are also seen in shallower ice, and cannot have been due to a decrease in atmospheric deposition, because diffusion would have smoothed out the sharp edges of the holes. Again, the holes seem to be associated with the presence of alkaline dust. Other holes are associated with sulphate from volcanic eruptions, and it is unclear whether they are of atmospheric or post-depositional origin (Laj et al. 1990; Sigg and Neftel 1991).

In summary, it is clear that H₂O₂ suffers disintegration, probably on dust particles, even in the dark, and this makes it currently impossible to deduce the atmospheric concentrations of H₂O₂, at least in Greenland, from any period earlier than the Holocene.

2.2. MSA movement

Methanesulphonic acid (MSA) is an oxidation product of dimethylsulphide, which is produced by marine organisms. It is generally considered to be deposited as part of the primary aerosol, and its concentrations in Antarctic air and snow always peak in summer (eg (Prospero et al. 1991; Wagenbach 1996)), more or less in phase with excess sulphate (also largely a DMS oxidation product).

However, at a site in the Antarctic Peninsula (Dolleman Island), it has been observed that, although most MSA peaks in the top 10 m occur in summer, in phase with excess sulphate peaks, by 50 m the peaks are clearly out of phase, and by 120 m the MSA peaks are centred in the winter trough of excess sulphate, while the excess sulphate peaks remain at the isotopic summers (Mulvaney et al. 1992) (Fig. 2). Similar, but less extreme, behaviour was seen in another Antarctic Peninsula core. It is extremely unlikely that MSA deposited in