Continuous chemistry in ice cores - Phosphorus, pH and the photolysis of humic like substances

By Helle Kjær

Abstract
Ice cores provide high resolution records of past climate and environment. In recent years the use of continuous flow analysis (CFA) systems has increased the measurement throughput, while simultaneously decreasing the risk of contaminating the ice samples. CFA measurements of high temporal resolution increase our knowledge on fast climate variations and cover a wide range of proxies informing on a variety of components such as atmospheric transport, volcanic eruptions, forest fires and many more. New CFA methods for the determination of dissolved reactive phosphorus (DRP) and pH are presented as part of this thesis.

Phosphorus is an essential nutrient for the biosphere. To investigate if atmospheric deposition of P has changed over time a CFA method was developed for the continuous determination of dissolved reactive phosphorus (DRP) by means of a reaction with molybdenum blue. The concentration of DRP in polar ice is low and thus the method relies on enhancing the limit of detection by increasing the absorption length by means of a 2.5 metre LiquidWaveguide Capillary Cell. The method was applied to a firn core from the North East Greenland Ice Stream (NEGIS) and to glacial sections of the Greenland NEEM ice core. In the NEGIS firn core concentrations were about 2.7 nM PO_4^{3-} and there was no evidence of any recent anthropogenic impact during the past 300 years. Sources of DRP to the NEGIS site were found to be dust as well as a secondary source-likely of biological origin. The DRP deposited at the NEEM site during the last glacial maximum was 14 times higher than the DRP deposited at present at the NEGIS site. The study of the NEEM ice core sections also included determination of total P. The ratio between DRP and total P reveal large changes in the soluble fraction of P over time, with low solubility in cold glacial periods.

The second part of the thesis continues in the track of CFA ice core measurements: A high resolution optical method has been developed using the dyes chlorophenol red and bromophenol blue for the determination of pH in ice cores. pH controls many chemical processes and equilibria. The method includes a heat bath to minimize the acidifying effect of CO_2 both from the laboratory and from the ice itself. While for acidic ice the method finds similar concentrations of H^+ as are deduced from the ionic budget, for more alkaline ice there seems to be an acidifying effect of the CO_2, causing the indicator method to error towards lower pH. The pH method was applied on the NEGIS firn core where it proved an improvement over both conventional ECM and DEP, which require density corrections. Further the method successfully identified volcanic eruptions as well as the underlying anthropogenic signal related to the industrial pollution peaking in the 1970's. The pH method was also applied on the Antarctic RICE ice core and proved useful, contrary to both the ECM and melt water conductivity obtained for the ice ore, to determine a volcanic eruption record.

The third part of the thesis is a theoretical review to determine if photolysis of pyruvic acid is a likely source of in situ production of CO_2 in ice cores. While CO_2 records from Antarctica show similar trends with decreased CO_2 concentrations during the glacial, excess peaks of CO_2 are observed in parts of the Greenland CO_2 records as a result of in situ production of CO_2. The source of the in situ production is debated. One proposed source is the photolysis of pyruvic acid or other carboxylic acids.

As part of this thesis the penetration of light on surface layers of snow at NEEM was determined and the 1/e depth was found as a function of wavelength. Further, by computational chemistry hybrid density functional methods (DFT), the four most common conformers of pyruvic acid were investigated in both gas, water and ice using the DFT model CAM-B3LYP with dielectric medium methods. A decrease of the energy difference between the second and third most common conformers of pyruvic acid was found. The study serves as a basis of future studies of the photolytic production of CO_2 from pyruvic acid and other β-carbonyl humic-like substances found in glacial ice.