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SCAVENGING OF GASES DURING GROWTH OF ICE CRYSTALS

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ABSTRACT

Scavenging of HCl and SO_2 during snow-crystal growth by water vapour from supercooled liquid droplets is studied. The mean sulfur (as sulfate) in crystals was independent of the SO_2 gaseous phase concentration in the tested 1.2-7.4 ppm range. The results with HCl indicate that for a Cl^- concentration in the liquid phase of less than 20 ppm, all the HCl goes from the droplets into ice and enhance knowledge of the acidification precipitation.

1.EXPERIMENTAL METHODS AND RESULTS

The chemical composition of precipitation is determined by the interactions of numerous processes , e.g. scavenging processes of aerosol particles and gases within and below clouds, chemical transformation in liquid or gas phase, mechanism of precipitation formation and so forth.

As in many climates precipitation forms by processes that include the ice-phase, it is important to study scavenging processes of gases during snow crystal growth by sublimation of water vapour or by accretion of cloud droplets (riming) .These processes influence precipitation pH.

As to riming, previous laboratory experiments have measured different values of the SO_2 retention coefficient (Γ) , depending on the operating configuration (Lamb et al., 1987; Iribarne et al., 1990). With highly water-soluble gases (HCL, HNO_3, H_2O_2) , Iribarne and Pyshnov (1990) measured Γ as equal to about unity.

Experiments on scavenging of gases during crystal growth from water vapour have mainly concerned SO_2 and HNO_3. Hydrogen chloride also plays an important role in the acidification of precipitation. In laboratory experiments we studied the sorption of SO_2 and HCl during growth of crystals by water vapour. Droplets produced by spraying Super-Q water were introduced at the bottom of a cylindrical chamber housed in a cold room (T=-13 °C). Crystals grow via vapour diffusion from supercooled droplets in the presence of SO_2 or HCl. Collected ice crystal were analyzed after melting for ionic species ($SO_4^{=}$, Cl^-) by ion chromatography. SO_2 concentration in the gas phase was in the 1.2-7.4 ppmv range. The mean crystal concentration of sulfur (as sulfate) was independent of the SO_2 gaseous concentration.

HCl test data indicate that for a Cl^- concentration in the liquid phase of less than 20 ppm, HCl goes entirely into the ice phase. This finding can be explained by assuming the existence of a liquid-like surface layer during crystal growth in which HCl and SO_2 dissolve and ionize.

The existence of a liquid-layer at $T < 0\,^{\circ}C$ during crystal growth is confirmed by further experiment. Finnegan and Pitter (1988) and Finnegan et al. (1991) demonstrated that differential ion incorporation during the growth of ice crystals from supercooled water containing halide or ammonium salts leads to charge separation in the ice that affects the ice crystal shape. In addition, both oxidation and reduction reactions occur in growing ice crystals at T=-16 °C. Both these phenomenon require the existence at the growing interface of a liquid layer which is sufficient to dissolve and ionize the included ionic salt.

Given our data and the fact that the HCl retention coefficient during riming is about one, there is an almost complete transfer of HCl from liquid to solid phase, whether crystal growth occurs via vapour diffusion from supercooled droplets containing dissolved HCl or by riming. This result has important consequences in the acidification of precipitation.

2. REFERENCES

1.D.Lamb and R. Blumenstein, Atmos.Env. 21 (1987) 1765
2 J.V.Iribarne, T.Pyshnov and B.Naik, Atmos.Env. 24A (1990) 389
3 J.V.Iribarne and T.Pyshnov, Atmos.Env. 24A (1990) 383
4 W.G.Finnegan and R.L. Pitter, Atmos.Res., 22 (1988) 235
5 W.G.Finnegan, R.L.Pitter and L.G.Young, Atmos.Env., 25A (1991) 2531