



The influence of monolayer amounts of HNO₃ on the evaporation rate of H₂O over ice in the temperature range 179-208K: a quartz crystal microbalance study.

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We present new experimental results concerning the evaporation flux, J_{ev} , of H₂O from ice that is doped with monolayer amounts of HNO₃.

The experiments have been performed in a new multiple diagnostic (mass spectrometry, absolute pressure monitoring, FTIR, quartz crystal microbalance) experimental apparatus whose validation has been published in PCCP in 2004¹. Using this device we have been able to investigate the impact of the doping parameters such as the rate of deposition and the absolute number of molecules of the dopant on the change in J_{ev} of H₂O during film evaporation of HNO₃-doped ice.

The flux of evaporation J_{ev} in molec cm⁻² s⁻¹ of H₂O from thin ice films containing between 0.5 and 7 monolayers of HNO₃ has been measured in the range 179 to 208 K under both molecular and stirred flow conditions. The kinetics of evaporation of H₂O was measured using both residual gas mass spectrometry as well as the quartz crystal microbalance as thickness or mass monitor using a known technique^{??}.

Subsequent to the end of the HNO₃ doping process of an approximately 1 μm thick ice film performed at deposition times in the range 16 to 80 s and at a rate in the range (6-60)·10¹² molec cm⁻² s⁻¹ J_{ev} was always that of pure ice. Subsequently, J_{ev} gradually decreased upon the evaporation of H₂O. Concomitantly with the increase of the average concentration of HNO₃ the final values of J_{ev} were smaller by factors varying from 2.7 to 65 relative to pure ice.

¹Delval, C.; Rossi, M. J. *Phys. Chem. Chem. Phys.* 2004, 6,4665-4676.

In addition, under atmospherically relevant conditions the FTIR absorption in transmission of the condensate systematically revealed the formation of the metastable crystalline α -NAT which converted under certain conditions to the stable β -NAT at approximately 205 K.

We conclude that there exist three different types of H₂O molecules under the present experimental conditions, namely (a) free H₂O corresponding to pure ice, (b) complexed H₂O we have called c-ice and (c) H₂O molecules originating from the break-up of NAT. The equilibrium vapour pressure for (a) and (b) correspond to that of pure ice.

The significant decrease of J_{ev} with the increase of the average mole fraction of HNO₃ leads to an increase of the evaporative lifetime of atmospheric ice particles in the presence of HNO₃ and may help explain the occurrence of persistent and/or large contaminated ice particles under certain atmospheric conditions.