

# Thin Water and Ice Films on Minerals: *A Molecular Level Study*

**Merve Yeşilbaş**

Akademisk avhandling

som med vederbörligt tillstånd av Rektor vid Umeå universitet för  
avläggande av filosofie doktorsexamen framläggs till offentligt försvar i

KBC-huset, Stora hörsalen KB.E3.03

Fredag den 13 April, kl. 09:30.

Avhandlingen kommer att försvaras på engelska.

Fakultetsopponent: Dr. Grégory Lefèvre,  
PSL Research University, Chimie ParisTech – CNRS, Institut de  
Recherche de Chimie Paris, France



**Department of Chemistry**

Umeå University

Umeå, 2018

**Organization**  
Umeå University  
Department of Chemistry

**Document type**  
Doctoral thesis

**Date of publication**  
April 13<sup>th</sup>, 2018

**Author**

Merve Yeşilbaş

**Title**

Thin Water and Ice Films on Minerals: *A Molecular Level Study*

**Abstract**

Minerals in Earth's crust and suspended in the atmosphere form water or ice films as thin as a few nanometers to as thick as a few micrometers, and beyond. Mineral-bound water and ice films in terrestrial systems (e.g. vadose zones, permafrosts) can impact the bio(geo)chemistry of nutrients and contaminants, water cycling, as well as possible land-air exchanges in terrestrial environments. In the atmosphere, films are tied to clouds and rain formation, and can influence the absorption and scattering of solar radiation of dust mineral aerosols. Water films are, at the same time, of interest to technology. They are even of interest in the study of asteroids, comets, and planet Mars. Still, their formation on the various types of minerals common to the environment is misunderstood.

The aim of this thesis is to gain fundamental insight on the roles that minerals play on forming and stabilising thin water and ice films. This work is separated in two parts, with Part A associated with Papers I-II and Part B with Papers III-V of the appendix of this thesis.

In *Part A* of this work (Papers I-II), water loadings and vibrational signatures of thin water films were collected on 21 different minerals (metal oxides, silicates, carbonates) relevant to terrestrial environments, atmosphere and perhaps outer-space. Measurements were made on minerals of varied (i) composition, (ii) structure, (iii) morphology, (iv) particle size and (v) surface roughness. Loadings, measured by a microgravimetric Dynamic Vapour Sorption technique, were of a few monolayers in sub-micrometer-sized particles but of several hundreds to thousands of water layers in micrometer-sized particles (Paper I). This was seen in the Fourier Transform Infrared (FTIR) spectra of sub-micrometer-sized particles with different hydrogen bonding environments than liquid water. Micrometer-sized particles formed liquid-like films regardless of the mineral. Similar observations were made in the spectra of the thinnest water films remaining on these minerals after long periods of sublimation of ice overcoatings at sub-freezing temperatures (Paper II). In *Part B* of this work (Papers III-V), focus on the expandable clay mineral montmorillonite was made to study (i) intercalated water, (ii) ice and cryosalt formation inside microporous gels, and (iii) its interactions with intercalated CO<sub>2</sub>. FTIR extracted spectral components reflecting interlayer hydration states of ~0W, 1W and 2W monolayers of water (Paper III). Thermal dehydration/dehydroxylation experiments showed that the driest forms of montmorillonite strongly retained low levels of crystalline water in its structure. FTIR also showed that frozen wet gels of montmorillonite form ice and the cryosalt mineral hydrohalite. Ice was seen in rigid gels and aggregated compact particles, as well as low particle density with low salt content. In contrast, concentrated (>> 10 g/L) saline gels host hydrohalite, probably between and/or near aggregated clay particle walls. Field-Emission Cryogenic Scanning Electron Microscopy showed that ice microcrystals form in micropores of the gels (Paper IV). Finally, release rates of CO<sub>2</sub> trapped in interlayers of montmorillonite, monitored by FTIR spectroscopy, were larger in the presence of 1-2W. The activation energy of CO<sub>2</sub> release from ~0W montmorillonite (34 kJ/mol) is comparable to other mineral surfaces. This study highlights that the most stabilised CO<sub>2</sub> occur in of dry and cold conditions.

This thesis will hopefully serve as a springboard for further work exploring the chemistry and physics of water and ice films at minerals surfaces. It should contribute to improve our understanding of the geochemistry of Earth's soils, processes in the atmosphere, and even of space chemistry.

**Keywords**

water, ice, cryosalt, minerals, rocks, Dynamic Vapour Sorption, FTIR, cryo-FESEM

**Language**  
English

**ISBN**  
978-91-7601-868-2

**Number of pages**  
67 + 8 papers