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

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“It is the time that you spend on your rose that makes your rose so important!”

– Antoine de Saint-Exupéry, Little Prince
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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, permafrost) 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 CO₂. 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 CO₂ trapped in interlayers of montmorillonite, monitored by FTIR spectroscopy, were larger in the presence of 1-2W. The activation energy of CO₂ release from ~0W montmorillonite (34 kJ/mol) is comparable to other mineral surfaces. This study highlights that the most stabilised CO₂ 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.
Abbreviations

ATD  Arizona Test Dust

ATR  Attenuated Total Reflectance

Cryo-FESEM  Field Emission Cryogenic Scanning Electron Microscopy

DVS  Dynamic Vapour Sorption

IR  Infrared

FWHM  Full Width at Half Maximum

FTIR  Fourier Transform Infrared Spectroscopy

MCR  Multivariate Curve Resolution

MMT  Montmorillonite

QCM  Quartz Crystal Microbalance

SEM  Scanning Electron Microscopy

SVD  Singular Value Decomposition

TEM  Transmission Electron Microscopy

TGA  Thermal Gravimetric Analysis

XRD  X-ray Diffraction

XPS  X-ray Photoelectron Spectroscopy
List of Publications

I. Particle Size Controls on Water Adsorption and Condensation Regimes at Mineral Surfaces

Yeşilbaş, M., Boily, J.-F.

II. Thin Ice Films at Mineral Surfaces

Yeşilbaş, M., Boily, J.-F.

III. A Cohesive Vibrational and Structural Depiction of Intercalated Water in Montmorillonite

Yeşilbaş, M., Holmboe, M., Boily, J.-F.

IV. Ice and Cryosalt Formation in Saline Microporous Clay Gels

Yeşilbaş, M., Lee, C.C., Boily, J.-F.
ACS Earth and Space Chemistry (in press)

V. Trapping and Release of Atmospheric Carbon Dioxide by Clays

Yeşilbaş, M. Holmboe, M., Boily, J.-F.
Manuscript
Author’s contributions

I. The author helped design, developed and carried out all surface microgravimetry and vibration spectroscopy experiments. She also performed all specific surface area determination and experiments. The author interpreted the experimental data, carried out chemometric analyses, and co-wrote the paper and was involved in the submission and revision. She also helped set the paper in the context of geochemical and atmospheric research.

II. The author carried out all freezing experiments using vibration spectroscopy, and all chemometric analyses. She helped interpret the experimental data, co-wrote the paper, and assisted in the submission and revision. She also helped set the paper in the context of geochemical and atmospheric research.

III. The author performed all water vapour binding and clay thermal dehydroxylation, as well as microgravimetric experiments. She carried out all chemometric analyses. The author was involved in scientific discussions with co-authors, co-wrote the paper and was involved in the submission and revision processes.

IV. The author helped initiate the research and design of the experiment. She led the collaboration with Umeå Core Facility for Electron Microscopy and assisted all cryo-imaging for this paper. She performed all vibration spectroscopy measurements and all chemometric analyses. She co-wrote the paper, and helped submit and revise the paper.

V. The author initiated this project through exploratory work and drove the project. She helped design the experimental set-up, performed all vibration spectroscopy experiments, and assisted in the extraction of rate constants/half-lives from experimental data. She helped interpreting the data, co-wrote the paper, and is the corresponding author.
Other publications by the same author:

I. *Thin Water Films at Multifaceted Hematite Particle Surfaces*

Boily, J.-F., Yeşilbaş, M., Uddin, M.M., Baiqing, L., Trushkina, Y., Salazar-Alvarez, G.

II. *Fullerene Films with Suppressed Polymerizing Ability*

Yeşilbaş, M., Makarova, T.L., Zakharova, I.
1. Introduction

Water plays essential roles in a wide range of chemical and biological reactions on Earth\textsuperscript{1-3}, as well as in Space\textsuperscript{4,5}. Although water appears to be a simple and ubiquitous compound, many standing questions remain on the nature and reactivity of water in its different phases – solid (ice), liquid and gas (vapour)\textsuperscript{1,6-7}. The Greek philosopher Aristotle had, as early as \textasciitilde340 B.C., already thought about the roles and behaviours of water vapour on Earth\textsuperscript{8-10}, yet even today much remains to be learned on water chemistry and physics\textsuperscript{1,11-12}.

Understanding water condensation from air and its subsequent freezing is important to predict the behaviour of atmospheric ice, and how atmospheric clouds absorb/scatter sunlight in relation to Earth’s radiation budget\textsuperscript{13-20}. It is, at the same time, equally important to understand how water vapour condenses and freezes in soils of the Cryosphere. This is especially needed to explain nutrient cycling in Arctic ecosystems, the energy budget of Earth’s surface, water cycling, as well as sea level and exchange of surface gases with the atmosphere\textsuperscript{12,21-22}. Knowledge of such interactions also have a great impact to our understanding of ice in outer-space, and especially planet Mars.

Looking into the role of water in nature cannot be done without studying its interactions with minerals, such as those of Earth’s crust or those blown by wind from terrestrial environments to the atmosphere\textsuperscript{23-24}. Silicates (e.g. quartz, olivine) and aluminosilicates (e.g. clays) constitute a large part of the Earth’s crust\textsuperscript{25-27}, yet nanosized aluminium and iron oxides are also strongly reactive minerals\textsuperscript{28}. Minerals in soils and suspended in the atmosphere (a.k.a ‘atmospheric dust’) can be seeds for the condensation of water vapour\textsuperscript{12,29} and form thin water and thin ice films\textsuperscript{29-31}, ranging from a new nanometers to a few microns in thickness\textsuperscript{32-33}.

This thesis aims to improve our fundamental understanding of thin water and thin ice films formed on minerals in these various settings. The main findings are organised in two parts:
• Part A. Water Adsorption and Condensation on Mineral Surfaces
• Part B. Montmorillonite Interactions with Water, Ice, Hydrohalite and CO₂

In Part A (Section 6), thin water (Paper I) and ice (Paper II) films formed on 21 different types of minerals were mainly studied by vibration spectroscopy. Minerals that play major roles on the chemistry of Earth and planet Mars were chosen for this work. These minerals were of different bulk and surface composition and structures, shape particle size (a few nm to several µm) and surface roughness. They include (i) iron and aluminium (oxy)hydroxides, (ii) clays (phyllosilicates), (iii) orthosilicates, (iv) tectosilicates, as well as (v) volcanic ash and (vi) the widely-used Arizona Test Dust (ATD).

Part B (Section 7) is specifically focused on the mineral montmorillonite, a representative clay mineral of widespread occurrence and technological uses on Earth, and potentially present on the planet Mars. Paper III is focused on the detection of thin water films intercalated between nanometer-thick layers of this expandable minerals using vibration spectroscopy. This work was followed by a cryo-imaging and vibration spectroscopy study of ice and cryosalt formed in the micropores of montmorillonite gels. Finally, Paper V details the uptake and rates of release of CO₂ intercalated in dry and hydrated montmorillonite from cold (-50°C) to hotter (60°C) conditions.

This Ph.D. thesis is organised as follows. A brief overview on research in water and ice film chemistry is first given in Section 2. The ‘Background’ (Section 3) section then provides information on the development of infrared spectroscopy, the major technique of this thesis, and on the properties of water and the minerals used in this work. The ‘Methods’ (Section 4) section details all main experimental and numerical analysis techniques used by the author of this thesis. Other experimental and theoretical methods used by the authors’ collaborators are presented in Papers I-V. Section 5 provides basic information on the properties of water and minerals used in this work. This is then followed by Section 6, focusing on general aspects of thin water and ice films in Papers I-II, and Section 7 on water and ice formation in montmorillonite (Papers III-V). Finally, conclusions and an outlook for the future are presented in Section 8.
2. Thin Water and Ice Film Research

The study of thin water and ice films on minerals in nature are of central interest for atmospheric chemistry (e.g. cloud formation, reactivity of trace gas molecules) and bio(geo)chemistry (e.g. cycling of elements, contaminant and nutrient transport), and how land-air exchanges occur, especially as the global climate is changing\textsuperscript{12, 19, 21, 34-36}. It is also very important for understanding space chemistry\textsuperscript{37}, including that of planet Mars\textsuperscript{4, 38-39}, as well as technology (e.g. lubrication)\textsuperscript{11, 40}. Each of these disciplines is connected by a common search for a molecular level understanding of water and ice films. A comprehensive review on water at several surfaces, including important characterisation techniques, was recently published in a collaborative paper by fifteen authors\textsuperscript{11}.

At a molecular level, active sites responsible for binding water at most environmental mineral surfaces are hydrophilic (hydr)oxo groups\textsuperscript{33, 41-42}. Hydrogen bonding of water molecules on low-solubility and hydrophilic mineral surfaces can be described in two key stages. The first stage, 'adsorption', involves hydrogen binding of water molecules directly onto (hydr)oxo groups at mineral surfaces\textsuperscript{29}. The thinnest water and ice films during the 'adsorption' stage can be affected by the physical and chemical properties of the host minerals\textsuperscript{29-30, 40}. A representation for very thin water and ice films is shown in Figure 2.1. The second stage, 'condensation', involves growth of water layers by water-water interactions and is less affected by the property of the mineral. Ice surfaces can also be terminated by a ‘quasi-liquid layer’, first described by Michael Faraday in 1859\textsuperscript{43}. This layer is believed to have a lower melting point, and continues to be an active research topic comprising both experimental and theoretical studies\textsuperscript{44-49}. One example is in the study of atmospheric heterogeneous ice nucleation, where thin water films formed at mineral dust are nucleation environments triggering ice formation\textsuperscript{32, 41, 47, 50}.

![Figure 2.1 An illustration for (left) thin water and (right) ice films.](image)

Research on thin water and ice films on minerals has originally been especially active in the atmospheric chemistry community, and dates easily back to the 1940s. Mineral dust particles blown from terrestrial environments into the atmosphere are immediately covered with water and/or ice. Atmospheric clouds, such as mixed-phase or ice clouds, may even depend on the type of mineral dust present. Processes of how water vapour binds onto environmentally and atmospherically relevant minerals (e.g. clays, quartz, feldspars, carbonates, Arizona Test Dust, volcanic ash) have been the object of extensive field and laboratory investigations, yet they are still not well understood.

The atmospheric chemistry literature shows that water-ice or ice particles form by homogeneous and heterogeneous freezing. Homogeneous freezing, from pure water vapour, takes place below -38°C and cannot, therefore, alone explain the formation of atmospheric ice. Heterogeneous freezing is triggered by atmospheric ice nuclei, for example grown onto mineral dust, soots, polens, bacteria particles. This process is responsible for initiating ice formation at higher temperatures and lower vapour saturations than homogeneous freezing. Heterogeneous freezing is also divided into four sub-processes: condensation, contact, immersion and deposition modes, requiring specific conditions for nucleating ice. A comprehensive, yet not so recent, review by Hoose and Möhler highlights the main differences between these different freezing modes. Another review by Tang et al. describes the ice nucleation efficiency of environmentally and atmospherically relevant minerals, in the presence of atmospheric gases including SO\textsubscript{x}, NO\textsubscript{x} and O\textsubscript{3}. These gases can change the hydrophilicity of mineral surfaces, and decrease their ability to form ice. There are also published papers examining the impact of salts and particle size on water film formation. Some of these studies have already suggested that larger particles are better ice nucleation agents. Paper I deals with this topic.

Atmospheric cloud chamber experiments revealed that clay minerals (kaolinite, illite and montmorillonite) and quartz can be successful nucleating agents for ice. This type of work also revealed the necessity of improving our molecular-level understanding of water condensation and ice formation. In recent years, more attention was focused on the roles of mineral surfaces on water and ice formation.
Techniques that have contributed to recent advances in this area include Sum-Frequency Generation\(^{45}\)\(^{60-61}\), Raman and Infrared spectroscopies, X-ray techniques (e.g. X-ray Diffraction\(^{62}\), X-ray photoelectron spectroscopy\(^{49}\) and Near Edge X-ray absorption fine structure).\(^{48-49}\) Environmental Scanning Electron Microscopy (ESEM)\(^{63-64}\) is now allowing imaging of ice particle growth in real time. Additionally, Environmental Molecular Beam\(^{65}\) allows determination of growth kinetics. Molecular modelling methods\(^{44,66-67}\), including Density Functional Theory and Molecular Dynamics, have contributed to our understanding of molecular-level processes responsible for thin water and ice film growth.

Recent works on water film and ice growth on minerals include the following examples. Kaolinite, one of the major mineral dusts in the atmosphere, was suggested to be a very efficient ice nuclei because its dominant basal (001) plane exhibits a hexagonal pattern that could serve as a template to ice growth, in the same way that silver iodide (AgI) famously triggers ice formation.\(^{50}\) More recent simulation work by Hu and Michaelides\(^{66,68}\) suggests that ice formation depends on the population of surface hydroxyl groups, and is not favoured by the basal plane but rather by the prismatic plane. At the same time, ESEM work highlights the importance of surface defects and edges on ice formation at kaolinite surfaces.\(^{50}\) Another important paper from Atkinson et al.\(^{69}\) revealed that feldspar, specifically K-feldspar, has a strong efficiency for ice formation by immersion freezing. This efficiency was confirmed later by Zolles et al.\(^{70}\) by Scanning Electron Microscopy (SEM), X-ray powder diffraction and infrared (IR) spectroscopy. Furthermore, Kiselev et al.\(^{71}\) recently determined the high ice formation efficiency of K-rich feldspars with electron microscopy and computer simulations, revealing that surface defects (or referred as 'active sites') initiate ice formation. Work from this thesis (Papers I&II) however also shows that thin water and ice films on K-feldspar are not so different from those on other silicate minerals. Also, because it can be argued that their surfaces are terminated by (hydr)oxo groups that are not very different than other minerals, special forms of (structural, roughness) defects on K-feldspar could be more responsible for ice nucleation, as in Kiselev et al.\(^{71}\). It should also be noted that this thesis (Papers I&II) highlights illite (a non-expandable clay mineral) as another potentially successful ice stabilising agent for ice.
The interest in water and ice films is not limited to the atmosphere. Asteroids and comets, for example, contain ice and water-ice as well as some signatures of rock. Water-ice is also present on the rings of Saturn and on Enceladus, the moon of planet Saturn. Additionally, the search for water in outer-space is one the most important clues for environments that can sustain life.\textsuperscript{39} \textsuperscript{72} Research on planet Mars, the 'Red Planet', and its polar ice caps is especially relevant. Recent work\textsuperscript{39} using vibrational spectroscopy investigated the presence of minerals on Mars including several type of iron oxy(hydr)oxides (goethite, hematite and akaganéite, phyllosilicates), olivine, carbonates and sulphates as well as water-ice. Understanding the (past) aqueous environments of Mars also helps understand environments responsible for forming phyllosilicates. This is important knowledge that is especially needed as new missions to Mars, including ExoMars of the European Space Agency and Mars 2020 of NASA, will explore the climate, geology and possible signatures of life.

Finally, in this thesis, the topic of thin water and ice films is presented in the context of terrestrial environments. The principle is very similar to what is known about atmospheric condensation, because water vapour flowing through unsaturated soils can also condense and freeze at mineral surfaces. These films are hydration environments, and even habitats for microorganisms, in which important geochemical reactions can occur. The emphasis on montmorillonite in Part B of this thesis represents a step towards setting this research theme more in the context of terrestrial environments.
3. Background

This section is divided in three parts. The first and second parts respectively provide a brief overview of the properties of water, and of the minerals under study. A third and last part covers the development and application of IR spectroscopy to water and minerals.

3.1 The Nature of Water and Ice

Water can coexist as ice (solid), liquid and vapour (gas) at Earth’s surface. Water (H₂O) is a simple polar molecule (O-H bond length of 0.96 Å, H-O-H angle of 104.5°, dipole moment of 1.83 D (~ 0.21 eÅ)) with four orbitals. Two orbitals are two covalent (sigma) O-H bonds acting as hydrogen bond donors, and the remaining four electrons on the oxygen atoms form two lone pairs, called ‘non-bonding’ orbitals, that act as hydrogen bond acceptors. These four orbitals are responsible for the ‘tetrahedral’ hydrogen bond environment of water. A dense and closely interacting hydrogen bond network can therefore be formed in water. This hydrogen bond network promotes the same number of hydrogen and covalent bonds that can be observed in both liquid water and ice phases. Ice possesses a more strongly ordered, yet distorted hydrogen bond network, than in liquid water, where the angle between H-O-H of each water molecules are broadened to 106° from 104.5°. Additionally, the hydrogen bond network of water is responsible for many of its anomalous properties. Some of these include (i) a complex phase diagram, (ii) a density maximum at 4°C, (iii) a high boiling point and (iv) a high dielectric constant.

Ice formed below 0 °C under ambient pressure is called hexagonal ice (Ih). Ih is the phase of ice occurring in snowflakes, glaciers and even the ice cubes formed in freezers. Ih is hexagonal because O atom are positioned on the top of nonplanar hexagonal chains, and linked to a neighbouring oxygen atom by one hydrogen atom, one through a covalent bond and the other through a hydrogen bond. The coordination of ice within the neighbouring molecules will be in form of O-H...O or O...H-O, but it is the oxygen atom that controls the ordering of hydrogen atom. Thus, hydrogen atom is randomly ordered and situated closer to one of the oxygen atom than the other one. The random and fast ordering hydrogen bonding environment is required for following the
(Bernal-Fowler) ‘ice rule’, where each oxygen form covalent bonds to two hydrogen atoms, and two hydrogen bonds with two other oxygens.'

3.2 The Minerals of This Study

Figure 3.1 provides an overview of the contrasting bulk structures and composition of some of the main minerals used for this study. Some minerals, and mineral assemblages, of interest are described in the following sections.

3.2.1 Metal Oxy(hydr)oxides

The oxy(hydr)oxides of this work differ in the organisation of their iron and aluminium building blocks. For example, goethite (α-FeOOH) consists of double chains of edge-sharing octahedra that form diagonally crossed H-bonds in the form of ‘pseudo tunnel’ structure. In lepidocrocite (γ-FeOOH) sheets of the same type of double chains are held together by zig-zagging H-bonds. In akaganéite (β-FeOOH) these double chains form 0.4 nm x 0.4 nm wide tunnels containing chloride ions and capable of absorbing water molecules. Hematite (α-Fe₂O₃), the most stable iron oxide, contains both edge and face sharing octahedral is of high density (~ 5.26 g/cm³). Finally, gibbsite is the only pure aluminium hydroxide (α-Al(OH)₃) considered in this work. It consists of sheets of aluminium octahedral connected by H-bonding.
3.2.2 Phyllosilicates

Kaolinite, illite and montmorillonite are aluminosilicates belonging to phyllosilicates. These are layer-type minerals consisting of continuous sheets (1) of Si\(^{4+}\), Al\(^{3+}\), or Fe\(^{3+}\) tetrahedra forming an 'hexagonal pattern', stacked with (2) with Al\(^{3+}\), Fe\(^{3+}\), Mg\(^{2+}\) or Fe\(^{2+}\) edge-sharing octahedra forming hexagonal or pseudohexagonal symmetry. One unshared ‘apical oxygen’ connects the tetrahedral and octahedral layers.

Kaolinite has one tetrahedral layer linked to only one octahedral layer and is a 1:1 layer (‘TO’) clay. Illite and montmorillonite are ‘dioctahedral’ type clays because they consist of one octahedral layer with two capping tetrahedral layers (2:1 layer structure, or TOT). Isomorphous substitution of Si\(^{4+}\) (e.g. Al\(^{3+}\)) and Al\(^{3+}\) (e.g. Mg\(^{2+}\)) in the TOT layers causes a charge imbalance that can be compensated by cations (e.g. Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\) and Ca\(^{2+}\)) in the interlayer region. Illite is an interlayer deficient mica. Most importantly, while kaolinite and illite are of non-swelling type, montmorillonite can swell and even delaminate when hydrated. The extent of swelling is governed by the nature of the exchangeable cation in the interlayer space, as will be explained further in Part B (Section 7).

3.2.3 Silicates

Silicate minerals compose nearly 90% of Earth's crust, and are important rock-forming minerals. This large class of minerals is subdivided in categories according to their Si/O ratios. The three silicates used in this thesis are quartz and microcline, which belong to ‘tectosilicates’, and olivine, which belongs to neso(ortho)silicates.

Tectosilicates, or ‘framework silicates’, are composed of Si atoms surrounded by four O-atoms three-dimensional network (O/Si=2). In quartz (SiO\(_2\)), continuous coordination of each SiO\(_2\) tetrahedral units gives the framework of SiO\(_2\). Microcline (KAlSi\(_3\)O\(_8\)) is part of the ‘feldspar group’ of tectosilicates, also referred as one of K-feldspars (e.g., sanidine, orthoclase). Olivine ((Mg,Fe)SiO\(_4\)) is a member of neso(ortho)silicates in which isolated [SiO\(_4\)]\(^4-\) tetrahedral units are coordinated with divalent metal ions. Any oxygen atoms in the [SiO\(_4\)]\(^4-\) tetrahedra is linked to three metal ions. As olivine is highly responsive to
weathering on the surface of Earth, it has been the object of many laboratory and field experiments.

**3.2.4. Carbonates**

Anhydrous Calcium carbonate (CaCO$_3$) was of interest for this thesis because it is soluble and can exchange CO$_2$. CaCO$_3$ can be a very important actor in environmental aquatic and atmospheric processes. Calcium carbonate has polymorphs that can be induced by heating, such as calcite, aragonite and vaterite minerals, of which the most stable one is calcite.

**3.2.5 Natural samples**

Arizona Test Dust (ATD) is a widely used mineral assemblage in atmospheric ice studies. ATD is obtained from topsoil of Salt River Valley that was blown by wind after some screening and blending processes. Volcanic ash collected from Eyjafjallajökull (Iceland) is a second natural sample used for this work. ATD and volcanic ash are composed of varied composition of ions (e.g. Na, Ca, Mg, Fe, Al, Si) indicating a complex mixture of minerals.

**3.3 Infrared (IR) Spectroscopy**

**3.3.1 The History of IR Spectroscopy**

The colours of rainbow have astonished mankind for thousands of years. In the 17$^{th}$ century, the rainbow effect was observed as colour fringes on early telescopes, but remained an unsolved problem. To overcome this issue, Sir Isaac Newton studied the nature of light by passing sunlight through a glass prism in 1666. He observed that sunlight, or the white light from sun, contains a regular series of colours, which he referred to as ‘spectrum’. He also checked the reversibility of his experiment by passing the formed colours into a glass prism and obtained white light again. These basic experiments of Newton led to beginning of the science of ‘spectroscopy’.

Building from the early discoveries of Sir Isaac Newton in the 17$^{th}$ century, much progress has been made by several scientists. In 1800, Sir Friedrich Wilhelm Herschel$^{25}$ made a significant breakthrough by
discovering infrared light (IR). Herschel used a glass prism with blackened thermometers to split light into colours. Herschel determined the radiant heat released by near to the red end of the spectrum. Herschel was an astronomer, who also discovered the planet Uranus in 1781 and the moon of Saturn, Enceladus. At the end of 19th century, IR absorbance drew attention again to characterise organic and inorganic compounds and their corresponding functional groups at specific wavelengths. From 1905 to 1908, William W. Coblentz published studies compared the infrared reflection, transmission and emission spectra of organic and inorganic compounds and minerals. His work was however challenged by a number of shortcomings of the technique: (i) requirement of a specific material size to obtain sufficient reflective surfaces; (ii) unsteady light source caused by magnetic disturbances required frequent repeating of experiments and calibration of the spectrometer. Coblentz and his colleagues had to design and construct their own optical components and calibrate their own instruments. Furthermore, spectra were taken at night to reduce effects of vibrations on the sensitive spectrometers, and each spectrum generally took 3-4 hours. These challenges limited the use of IR spectroscopy until the invention of the first commercial IR-spectrometers in 1940’s. Some of the first models include Model 12 by Perkin-Elmer and Model IR-1 by Beckman. After the release of these and other successful commercial IR spectrometers, IR-spectroscopy gained attention as a technique to obtain a 'fingerprint' for molecules. With the arrival of Fourier Transform Infrared (FTIR) spectroscopy, spectra over a wide spectral range could be collected simultaneously. The first FTIR instruments were released in commercial form (Model FTS-14) in 1969.

The infrared analysis of minerals has been studied throughout the 20th century. Despite the challenges of using IR, there have been still many scientific developments were acquired for characterisation of compounds. For instance, Heinrich Kayser, a German physicist and spectroscopist discovered, in 1903, specific IR bands for –OH (~ 3330-3450 cm⁻¹) and –CH₃ (~2915 cm⁻¹) groups in the mid infrared region. He also demonstrated that Kundt’s Law (index of refraction does not change continuously with wavelength in absorption bands) is not sufficient to explain the nature of –OH groups. Coblentz also published infrared reflection spectra of carbonates (e.g dolomite, calcite), sulphides, oxides (e.g. magnetite, hematite, rutile and corundum) and
aluminium silicates (e.g. topaz, sodium silicate), and even the infrared transmission spectra of quartz. Starting in the 1960s, a series of papers by Farmer, V. C. and Russell, J. D. reported infrared spectra of various minerals, including kaolinite, montmorillonite, beidellite, lepidolite, hectorite, saponite and biotite. An example of the spectrum montmorillonite collected for this thesis is shown in Figure 3.1. In the 1970s a growing number of infrared studies on metal (oxy)(hydr)oxide minerals involved goethite ($\alpha$-FeOOH), hematite ($\alpha$-Fe$_2$O$_3$) and gibbsite ($\gamma$-Al(OH)$_3$), lepidocrocite ($\gamma$-FeOOH), ferrihydrite, boehmite ($\gamma$-AlOOH),

![Figure 3.2 Typical FTIR spectrum of dried Na-montmorillonite, collected by the author of this thesis.](image)

The sensitivity of the O-H stretching region to interfacial reactions (e.g. protonation, desorption, ligand exchange) with water, gases ($\text{CO}_2$, $\text{SO}_x$, $\text{NO}_x$) and ions also opened new possibilities. This may have started with the study of Anderson and Wickersheim in 1964 on surface hydroxyl groups and sorbed water on silica gel surfaces in the near infrared region (3333 cm$^{-1}$ - 10000 cm$^{-1}$). In the same year, Fripiat J. J. et al. detected hydroxyl groups and adsorbed water on aluminosilicates with IR. List led to many other efforts in the literature since those original studies.
**3.3.2 The Theory of IR Spectroscopy**

**3.3.2.1 Fundamental Aspects of the Technique**

Spectroscopy is a scientific discipline determining how matter (or samples) interacts with electromagnetic radiation. Electromagnetic radiation can be described by two theories. The *classical theory* treats electromagnetic radiation as continuous waves, where their frequencies \( \nu \) and wavelengths \( \lambda \) are synchronised in relation the speed of light \( c \) in vacuum \( (\lambda \nu = c) \). Refraction, diffraction and polarisation of light are all explained by classical theory. The second theory, *quantum theory*, describes electromagnetic radiation in terms of a stream of particles with discrete energy levels (e.g. \( E_0, E_1 \)). Interactions between molecules and electromagnetic radiation results in the absorption or emission of photons. The energy of the photon relates to the energy difference \( (\Delta E) \) between two distinct levels (e.g. \( E_0 \) to \( E_1 \)), and to the frequency of radiation through the relation:

\[
\Delta E = h\Delta \nu = \frac{hc}{\lambda} = h\bar{\nu}
\]

where \( h \) is Planck’s constant \( (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) \), and \( \bar{\nu} \) indicates the wavenumber which is the reciprocal of the wavelength in the units of \( \text{(cm}^{-1}) \). Electromagnetic radiation covers a wide spectral range from \( 10^5 \text{ s}^{-1} \) (radiofrequency region) to \( 10^{21} \text{ s}^{-1} \) (gamma-rays). Different energy levels of the electromagnetic spectrum impact specific molecular processes (e.g. vibration, rotation, changing the spin direction of nucleus or electron), and these molecular processes are detected through different techniques.

Infrared spectroscopy, the main technique used in this thesis, covers the 14000 cm\(^{-1}\) to 10 cm\(^{-1}\) range, and is classified into three sub-regions:

(i) Near-infrared (NIR, 14000 cm\(^{-1}\) to 4000 cm\(^{-1}\)) is the region that covers the first overtone and combination vibrational band of C-H, N-H and O-H functional groups;

(ii) Mid-infrared (MIR, 4000 cm\(^{-1}\) to 400 cm\(^{-1}\)) is the region mainly covering fundamental vibrations, and rotations of gaseous molecules.
Far-infrared (FIR, 400 cm$^{-1}$– 10 cm$^{-1}$) is mainly for excitation of lattice vibrations, and for metal-ion vibrations and rotations.

Infrared spectroscopy measures the absorbed infrared light by sample. Light transmitted through a sample carries the characteristic vibrational signatures of the sample. Using Beer-Lambert law, the transmitted light intensity ($A$) can be calculated with an equation:

$$A = A_0 \exp (-\varepsilon C l)$$  \hspace{1cm} (3.2)

Equation (3.2) shows the incident light as ($A_0$), and ($\varepsilon$) is the molar absorption coefficient of the sample, concentration of absorbed species is ($C$) and the length ($l$) of path that light passes through. The square root of IR absorption intensity is nearly correlated with the dipole moment change in a molecule. Most importantly, IR active vibrations occur if the dipole moment changes in case of IR absorption, which gives ‘stretching and bending’ IR active modes. This will be explained in detail in the next section.

3.3.2.2 Normal Modes of Vibration and IR Active Modes

When a molecule absorbs infrared light, the atoms in the molecule start to vibrate in relation to the centre of mass of the molecule. This type of vibration is similar as described in Hooke’s Law. The ‘normal mode’ is the collective in phase motion of atoms in the molecule. The normal mode of vibrations is related to number of atoms in a molecule (N) vibrating at a characteristic frequency. Each molecule has a total of 3N possible translational motions. Non-linear molecules have motions in three dimensions (x,y,z), but linear molecules cannot rotate around their principal axis. The remaining motions from a total 3N degrees of freedom gives the total number of molecular vibrations. Linear molecules vibrate with 3N-5 and non-linear molecules with 3N-6 degrees of motion. For instance, the CO$_2$ is a linear molecule with four vibrational modes, while the non-linear water molecule has three vibrational modes. Figure 3.3 presents the infrared spectrum of water, consisting of one symmetric ($\nu_1$) and one antisymmetric ($\nu_3$) O-H stretching modes and one bending mode ($\delta_{\text{H-O-H}}$).
The IR spectra of liquid water and ice have greater similarities than that of water vapour, because their H-bond network of water and ice are more similar. Applying thermal energy provokes the phase transformation of ice to water, so do their H-bond network. Therefore, vibrations of the H-bond network (including librations) can affect the spectra of water and ice. This also explains the difference in the spectra of water and ice (at -10°C and -100°C). Furthermore, the stretching broadband of liquid water is shifted to lower frequencies in ice due to the formation of stronger H-bonds. The intensified and narrower band is caused by hydrogen bonding between O atoms placed closely each other, as already described in the work of Bragg. In the case of bending motions, ice has a broader spectrum centred around ~ 1600 cm⁻¹, which corresponds to the distribution of its ordered hydrogen bonding environment. Liquid water possess a weaker hydrogen bonding environment, and therefore a narrower band at ~ 1640 cm⁻¹. Additionally, a broad band for water and ice is shown around ~2200 cm⁻¹. This band is the first overtone of δH-O-H and ρH₂O, resulting from Fermi resonance.

**Figure 3.3.** The comparison for the vibrational spectra of hexagonal ice (-10 °C and -100 °C), liquid water (25 °C) and water vapour (25 °C) at ambient conditions. Spectra collected by the author of this Ph.D. thesis.

From a classical point of view, the moment of inertia (I) of a molecular bond is related to mass (m) and the distance through the principal axis (r) by I=mr². Recalling that the moment of inertia is quite small due to the light mass of hydrogen, this provides a rich combination of vibrational-rotational spectra. This can especially be seen in the
spectrum of water vapour (Figure 3.3, red) which carries traces of the rotational spectrum within several thousands of absorption lines, arise from free rotations of isolated gaseous water molecules. Actually, water vapour also has rotational transitions in the far infrared spectral region ~ 10 - 200 cm$^{-1}$ (not shown in Figure 3.3). In contrast, the rich hydrogen bonding environments of liquid water and ice hinder rotations, and this is expressed through broader spectral bands as well as librations (\(\rho_{\text{H}_2\text{O}}\)) in the spectral region of ~ 900-40 cm$^{-1}$. In fact, the librations of water are caused by the establishment of hydrogen bonds between relative rotations of isolated water molecules in relation to their neighbouring water molecules. As a result, the study of the shifts of band positions in water can provide information on the changes undergone in the hydrogen bonding environment of water. For example, the redshift (towards lower frequencies) of an IR spectral band results from stronger H-bonds, while a blueshift (towards higher frequencies) to a weakening of H-bond environment, and therefore of a stronger, and more covalent, O-H bond. Band shifts scale in the order of 150-175 cm$^{-1}$ per pm change in O-H bond length.
4. Methods

4.1 Minerals & Characterisation

All metal (oxyhydr)oxides, including several types of iron (oxyhydr)oxides- goethite (α-FeOOH), rod- and lath-shaped lepidocrocite (γ-FeOOH), akaganéite (β-FeOOH), ferrirhydrite (e.g. Fe₈.₂O₈.₅(OH)₇.₄ + 3H₂O) and hematite (α-Fe₂O₃) in nano-sized and micron-sized- forms as well as gibbsite (γ-Al(OH₃)) were synthetised in our laboratory using well-established methods. All other minerals in this study were obtained from our providers. Quartz and olivine were taken from the mineral collection of Umeå University and ground to a fine powder within help of an agate mortar and pestle. Mineral particles in powder form of microcline (KAlSi₃O₈) were obtained from Technical University Darmstadt, and kaolinite minerals (Al₂Si₂O₅(OH)₄) were obtained from Fluka (Sigma Aldrich) and from the Clay Mineral Society (KGa-1b). Illite-rich (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,[(H₂O)]] powder was obtained from Arginotec (B + M Nottenkämper), while montmorillonite was obtained from the Clay Mineral Repository, a portion of Na- was Ca-exchanged. Calcium carbonate is from KEBO Lab AB as well as the natural samples ATD is from (Ultrafine Test Dust, Powder Technology Inc.) and volcanic ash is from Eyjafjallajökull (Iceland).

The structures of the minerals synthesised in our laboratory were confirmed by powder X-ray diffraction (Bruker d8 Advance working in θ - θ mode with CuKα radiation). Phase purity and the crystallinity of minerals acquired for this work had already been independently verified. X-ray photoelectron spectroscopy (Kratos Axis Ultra DLD electron spectrophotometer) was used to identify the surface elemental composition of all the minerals in this study. XPS revealed that mineral surfaces are mostly representative bulk compositions of minerals and contain negligible organic contaminations.

Particle sizes were estimated by imaging using Scanning Electron Microscopy (SEM; Zeiss Merlin, GmbH) or Transmission Electron Microscopy (TEM; JE-1230 (JEOL)). Distribution of particle sizes were
calculated using up to 5 different particles for each of minerals at several different images from 3 to 7 and at various magnified images where needed. B.E.T specific surface area and B.J.H micropore volume were obtained from 90-point N₂(g) gas adsorption/desorption isotherms (Micromiretics) at LN2. Using these values, maximal levels of pore water for minerals were estimated. As a final characterisation method, electrophoresis (Zetasizer, Malvern) method was used to examine the surface potentials of minerals particles at their natural pH of suspension in 2 g/L, at 25 °C.

4.2 FTIR Spectroscopy

FTIR spectroscopy makes use of the Michelson interferometer. This interferometer gives interference where a light beam is split into two parts with help of two plane mirrors situated perpendicular to one another. While one of these plane mirrors are fixed, the other mirror is movable. Light split from these mirrors follows varied path lengths. Reflected beams of varied path lengths join together, forming an interference pattern. FTIR transforms the information in interference pattern into the spectrum. This thesis covers the interactions of mineral/water/ice/gas interfaces monitored by FTIR spectroscopy, details of which can be found in the next sections.

FTIR spectroscopy provides a sensitive, non-destructive and rapid characterisation of minerals. In this study, two FTIR cells were used: (1) reflectance light measured with Attenuated Total Reflectance (ATR), and (2) transmittance. Note that care was taken to thoroughly grind, yet not damage, micron-sized particles prior analysis to minimise the ‘Christiansen effect’, whereby large particles can scatter IR radiation and generate broadened bands.

4.2.1 ATR-FTIR Spectroscopy

4.2.1.1 Water Vapour Adsorption by (ATR)-FTIR

For water vapour adsorption experiments, aqueous suspensions of minerals were prepared with deionised water (18.2 MΩ.cm). These suspensions were centrifuged at their natural pH and then dried on the single-bound diamond Attenuated Total Reflectance (ATR) cell covered with a flow-through cell under dry N₂(g). A 200 standard cubic
centimeters per minute (sccm) stream of N₂(g)+H₂O(g) prepared in the 0-18 Torr H₂O range was then titrated to the dried films on the ATR cell (Fig. 4.1). Water vapour pressure was generated by mixing streams of dry and water-saturated N₂(g) and the constant total flow rate was controlled with mass flow controllers (MKS, 179A). The total pressure on the system was monitored with a calibrated Non Dispersible Infrared device (LI-7000, Licor Inc.) that also used to ensure that the gases were free of CO₂(g) (Paper I).

Montmorillonites gels were prepared by equilibration in deionised water (18.2 MΩ.cm) for least 30 min in polyethylene test tube, following by a 10 min sonication period. Montmorillonite films were deposited on the ATR cell and dried over 24 h under N₂(g) prior titration with water vapour (Paper III).

Spectra were collected with a Bruker Vertex 70/V FTIR spectrometer in a room kept at 25 °C. The instrument is equipped with a deuterated L-alanine doped triglycine sulphate (DLaTGS) detector. Measurements for water vapour adsorption experiments were carried out between 4000-600 cm⁻¹ spectral range at a spectral resolution of 4 cm⁻¹, and with a forward/reverse scanning rate of 10 Hz.

4.2.1.2 Ice and Hydrohalite Formation by Cryogenic-FTIR

Mineral-ice interactions were resolved with help of cryogenic-FTIR spectroscopy by focusing on the O-H stretching and bending regions of frozen water/mineral mixtures. Prior all type of ice experiments, background measurements were always taken at desired working temperature, most of case at -10°C. Cryogenic-FTIR spectroscopy in this study is presented as Figure 4.2.
A first set of experiments was performed to characterise pure ice formation at from -10°C to -100 °C. A 0.1 mL aliquot of pure water (Trace SELECT, Fluka) was applied directly to precooled cold ATR stage and the spectra of frozen droplets were monitored. *Paper II*

![Figure 4.2](image)

**Figure 4.2** Experimental set-up for used Cryogenic-FTIR spectroscopy.

Freezing in the presence of mineral was made from centrifuged wet pastes of thin mineral films deposited on the ATR stage. Minerals were first mixed with deionised water (18.2 MΩ.cm) for 5-20 min, then centrifuged for 10 min at 5000 rpm. The centrifuged wet pastes were then applied on a thermostated ATR accessory for cryogenic measurements (Golden Gate, Serial Number N29328 by Specac) and dried under a stream of dry N\(_2\)(g). The drying process of wet pastes were tracked by FTIR. A 0.1 mL aliquot of pure water (Trace SELECT, Fluka) was then added to these thin mineral films, and allowed to equilibrate for ~10-30 min (Paper II). For the study of hydrohalite (Paper IV), 5 µL of 0.01, 0.1, 1 and 5 M NaCl solutions were applied onto thin montmorillonite films and equilibrated for 30 min. The temperature was then dropped to a sub-freezing temperature (e.g. -10°C, -90°C) over a 20 min period. Water was evaporated or sublimated during this period, ultimately leaving a metastable thin water-ice film in the sample. The spectra of these films were monitored for at least 15 min, and up to ~1-1.5 h.
4.2.2 Transmission-FTIR Spectroscopy

4.2.2.1 Temperature Programmed Desorption (TPD) and Carbon dioxide uptake and release by Transmittance-FTIR

Transmission-FTIR was used for TPD (Paper III) and CO$_2$(g) uptake/release (Paper V) experiments for montmorillonite suspensions. Aqueous solutions of 20 g/L montmorillonites equilibrated under N$_2$(g) environment for 2 h. Equilibrated samples were centrifuged at 5000 rpm for 10 min and the top part of the suspensions was applied onto a fine tungsten mesh (Unique wire weaving, 0.002” mesh diameter). The prepared mesh was dried under N$_2$(g) overnight to form a dried thin film of montmorillonite. The mesh was squeezed into a copper heating shaft, and inserted in a vacuum cell (AABSPEC #2000-A) equipped with CaF$_2$ optical windows. The wet paste was dried under vacuum environment for 40 min below < 0.7 Torr, the detection limit of the pressure sensor (MKS, Barathon). For CO$_2$(g) experiments with varied temperature range (Paper V), the dried sample on the mesh were either heated/ cooled in a temperature range from (-50°C to 60°C). The dried mineral film was then exposed to ~20,000 ppm CO$_2$(g), and the FTIR spectra collected in the same resolution as in Section 4.2.1.1. An experimental diagram for describing the experiments on Paper V is presented in Figure 4.3. Furthermore, the spectra of water absorbed Na-montmorillonite films at cold temperatures (-10°C and -50°C) were obtained by freezing the sample directly on the cold probe.

The same experimental setup and procedures were used for TPD-FTIR experiments. Mineral pastes dried on the tungsten mesh were heated at a constant rate of 10 °C /min from 25 to 700 °C, while the effluent gases (e.g H$_2$O, CO$_2$, CO, NO, H$_2$) were measured with a quadrupole mass spectrometer (Preiffer Vacuum, PrismaPlus). The resolution and data acquisition of FTIR spectra were also same as described in section 4.2.1.1.
4.2.3 FTIR Spectral Analysis

All of the FTIR spectra were first offset at negligible absorbance close zero absorbance at 1800–2000 cm$^{-1}$ or 3800–4000 cm$^{-1}$. When needed, the raw spectra were baseline-corrected with a polynomial function or an asymmetric least squares function. The data was thereafter analysed by means of chemometrics analyses. Using single-value decomposition (SVD)–matrix scaling method- and evolving factor analysis function helped to evaluation and calculation of the number of chemically relevant factors. Then, the calculated chemical factors were treated by Multivariate Curve Resolution Alternating Least Squares (MCR) analysis$^{109}$, which produces the pure spectral components ($\varepsilon$) with their correlated concentration ($C$) profile using the absorbance ($A=\varepsilon C$) data from FTIR. All of these analyses were performed in MATLAB 8.0 (The Mathworks, Inc.).

4.3 Dynamic Vapour Sorption (DVS)

Water vapour uptake of minerals was determined by DVS$^{110}$ method at 25$^\circ$C with using an Quartz Crystal Microbalance (QCM; eQCM 10M, Gamry Instruments Inc.). These microgravimetric measurements were performed at the same time as water vapour adsorption experiments by FTIR, using the same gas mixture described in section 4.2.1.1 (Fig. 4.1). The serial resonance frequency of ($f_s$) of a 10 MHz gold-coated quartz resonator was first determined by measurements under a constant total flow rate of 200 sccm of dry $N_2(g)$ with help of a mass-flow controller (MKS, 179A) to determine a correct baseline of the empty cell. This
crystal was then coated either by pipetting or spraying a dilute aqueous mineral suspension over the gold area, and dried under dry N\(_2\) (g). After that, the crystal was emplaced back onto the measurement cell and equilibrated under 200 sccm N\(_2\) (g) for at least 1 h in order to obtain a dry, time-independent weight of the sample. Montmorillonite samples were, in contrast, dried at least 24 h to evacuate removable interlayer waters. Each sample was equilibrated with different partial pressure of water for 30 min minerals and 1 h for montmorillonites, using an automated water vapour titration system.

Figure 4.5 A typical example of a QCM-based DVS experiment with a homogeneously coated Ca-MMT film. The mass of deposited mineral is calculated using Sauerbrey equation given in below (Equation 4.1), and is here systematically changed as water loadings are increased during DVS.

\(f_s\) values were used to calculate the water vapour uptake of minerals, the parallel resonance frequency \(f_p\) was used to track the viscosity of the mineral films on quartz resonator. Uncorrelated \(f_s\) and \(f_p\) values were seen in thick heterogeneous films produced by pipetting of micron-sized particles, a result also further confirmed by optical microscopy. To overcome the heterogeneous coating issue, an especially with large particles, minerals were instead sprayed from an aqueous suspension on the electrode. This produced more homogeneous films on the quartz crystal electrode, and therefore more correlated \(f_s\) and \(f_p\)
values, as shown in Figure 4.4. This figure shows a typical example of the response of the QCM to changes in water vapour pressure during a DVS experiment.

The variation of frequency (Δf) was converted into the variation of mass (Δm) on the quartz crystal using the Sauerbrey equation:

\[
\Delta f = -\frac{2f_0^2}{A}\sqrt{\frac{\rho_q\mu_q}{\epsilon}} \Delta m
\]

(4.1)

where \(f_0\) is the resonant frequency of empty cell, using \(A=0.205\) cm\(^2\) for the area of the gold-coated quartz crystal, \(\rho_q=2.648\) g/cm\(^3\) for the density quartz and \(\mu_q=2.947 \times 10^{11}\) g/cm.s\(^2\) for the shear modulus.

### 4.4 Field Emission Cryogenic Scanning Electron Microscopy

Field Emission Cryogenic Scanning Electron Microscopy (cryo-FESEM) was used to image drop of frozen MMT gels. Gels were first plunged into liquid nitrogen, then transferred to a cryo preparation chamber where a cold knife was used to expose the sample’s cross-section. Imaging was performed on a Carl Zeiss Merlin field-emission cryogenic scanning electron microscope, fitted with a Quorum Technologies PP3000T cryo preparation system. Images were taken at temperatures at -90 °C using in-chamber secondary electron detector at accelerating voltage of 4 kV. Elemental mapping was conducted using an Oxford Instruments X-Max 80 mm\(^2\) energy dispersive X-ray spectrometer.
5. Mineral Characterisation

Minerals in this study were characterised with several methods, the results of which are summarised in Table 5.1. Particle size was calculated using the images of SEM and TEM (Figure 5.1), and ranged from several nanometers (10 nm) to micrometers (~15 µm). Accordingly, N₂(g)-based B.E.T specific surface area (sₘ) were in the 0.4-155 m²/g range. These values form the empirical linear relationship shown in Figure 5.2 and fitted with the following equation:

\[
\log(sₘ) = -0.76 \log(D_d) - 3.62
\] (5.1)

where \(D_d\) is in m (Note that that \(D_d\) and \(sₘ\) terms of Equation 6 of Paper I were erroneously swapped, and that Equation 5.1 is the correct equation). Blue and red lines of Figure 5.2 refer to theoretical predictions of \(sₘ\) based on the low (2.6 g/cm³) and high density (5.3 g/cm³) minerals if particles were perfect cubes with no surface defects. These predictions underestimate the measured experimental N₂-BET values. This could be caused by (i) a bias in the sampling of larger-sized particles, and (ii) micro-/meso-pore surface area.

![Figure 5.1 SEM and TEM images of minerals under this thesis.](image-url)
Table 5.1 Chemical and physical characteristics of minerals used in this thesis

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>Atomic Ratio (XPS)</th>
<th>Particle Size*</th>
<th>Average Size*</th>
<th>Area (m²/g)*</th>
<th>Micropore volume (cm³/g)*</th>
<th>Max pore H₂O (sites/nm²)*</th>
<th>ζ-potential (mV)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>Fe:O:OH = 1.35:1.0:1.43</td>
<td>75-100 nm</td>
<td>75 ± 9.4 nm</td>
<td>55.6</td>
<td>0.085*</td>
<td>158</td>
<td>47.5</td>
</tr>
<tr>
<td>Lath-Lepidocrocite</td>
<td>Fe:O:OH = 1.4:1.0:1.2</td>
<td>70-210 nm</td>
<td>70 ± 9 nm</td>
<td>81.3</td>
<td>0.124*</td>
<td>230.4</td>
<td>10</td>
</tr>
<tr>
<td>Rod-Lepidocrocite</td>
<td>Fe:O:OH = 1.3:1.0:1.2</td>
<td>60-250 nm</td>
<td>60 ± 7.1 nm</td>
<td>64.4</td>
<td>0.204*</td>
<td>379</td>
<td>7</td>
</tr>
<tr>
<td>Akaganéite</td>
<td>Fe:O:OH:Cl = 1.0:0.82:1.2:2.0:17</td>
<td>100 nm</td>
<td>102 ± 11 nm</td>
<td>111.2</td>
<td>0.22</td>
<td>408.7</td>
<td>43</td>
</tr>
<tr>
<td>Ferrhydrite</td>
<td>Fe:O:OH = 1.5:1.3:1.0</td>
<td>- 25-50 nm</td>
<td>34 ± 5.4 nm</td>
<td>155</td>
<td>0.051*</td>
<td>95</td>
<td>10.5</td>
</tr>
<tr>
<td>Hematite (10 nm)</td>
<td>Fe:O:OH = 4.1:4.5:1.0</td>
<td>10 nm</td>
<td>10 ± 0.01 nm</td>
<td>50</td>
<td>0.182*</td>
<td>338.2</td>
<td>32.1</td>
</tr>
<tr>
<td>Hematite (50 nm)</td>
<td>Fe:O:OH = 2.8:3:8:1:0</td>
<td>50 nm</td>
<td>50 ± 6 nm</td>
<td>20.4</td>
<td>0.093*</td>
<td>172.8</td>
<td>38.4</td>
</tr>
<tr>
<td>Hematite (4µm)</td>
<td>Fe:O:OH = 1.5:1.9:1.0</td>
<td>1-4 µm</td>
<td>3.66 ± 0.82 µm</td>
<td>2</td>
<td>0.064*</td>
<td>118.9</td>
<td>10.1</td>
</tr>
<tr>
<td>Hematite (5µm)</td>
<td>Fe:O:OH = 1.7:2.0:1.1</td>
<td>0.95-5 µm</td>
<td>4.5 ± 0.6 µm</td>
<td>1.6</td>
<td>0.048*</td>
<td>89.2</td>
<td>37.4</td>
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<tr>
<td>Gibbsite</td>
<td>Al:OH = 1:0:3:0</td>
<td>100-290 nm</td>
<td>255 ± 35 nm</td>
<td>44</td>
<td>0.26</td>
<td>483.1</td>
<td>40.3</td>
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<tr>
<td>Kaolinite (CMS)</td>
<td>K:Al:Si:O = 0.0:2:0.2:8.2</td>
<td>100-900 nm</td>
<td>600 ± 110 nm</td>
<td>12</td>
<td>0.126*</td>
<td>234.1</td>
<td>-11</td>
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<tr>
<td>Kaolinite (Fluka)</td>
<td>K:Al:Si:O = 0.2:2:0.6:9.3</td>
<td>0.1-1 µm</td>
<td>745 ± 15 nm</td>
<td>8.6</td>
<td>0.121*</td>
<td>225</td>
<td>-22.4</td>
</tr>
<tr>
<td>Illite</td>
<td>K:Al:Si:O = 0.3:1:0.2:5.7:6</td>
<td>25-100 nm</td>
<td>50 ± 15 µm</td>
<td>121.7</td>
<td>0.228*</td>
<td>424</td>
<td>-11.2</td>
</tr>
<tr>
<td>Na-Montmorillonite</td>
<td>Na:Fe:Mg:Al:Si:O = 0.1:0.1:1:1:0:2:3:7:8</td>
<td>20-550 nm</td>
<td>520 ± 110 nm</td>
<td>25.3</td>
<td>0.138*</td>
<td>256.4</td>
<td>-12.3</td>
</tr>
<tr>
<td>Ca-Montmorillonite</td>
<td>Ca:Fe:Mg:Al:Si:O = 0.13:0.1:1:1:0:2:3:8:2</td>
<td>40-300 nm</td>
<td>230 ± 40 nm</td>
<td>39.8</td>
<td>0.191*</td>
<td>355</td>
<td>-18.3</td>
</tr>
<tr>
<td>Quartz</td>
<td>Si:O = 1.0:2.0</td>
<td>0.3-14 µm</td>
<td>14 ± 0.7 µm</td>
<td>0.4</td>
<td>0.024*</td>
<td>45</td>
<td>-32.7</td>
</tr>
<tr>
<td>Microcline</td>
<td>Na:K:Al:Si:O = 0.2:0.8:1:0:2:8:7:2</td>
<td>0.2-11 µm</td>
<td>11 ± 0.5 µm</td>
<td>1</td>
<td>0.041*</td>
<td>76.2</td>
<td>-45.2</td>
</tr>
<tr>
<td>Olivine</td>
<td>Fe:Ca:Mg:Si:O = 0.1:0.95:1.0:4:0</td>
<td>0.35-13.7</td>
<td>13.7 ± 0.7 µm</td>
<td>0.4</td>
<td>0.005*</td>
<td>9.3</td>
<td>-20.9</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>Mg:Ca:Si:O = 0.3 : 0.7 : 1.1 : 3.6</td>
<td>0.25-1.5 µm</td>
<td>1.2 ± 0.12 µm</td>
<td>11</td>
<td>0.057*</td>
<td>106</td>
<td>12.7</td>
</tr>
<tr>
<td>Volcanic ash</td>
<td>Na:K:Ca:Fe:Al:Si:O = 0.40:1.0:3:0:1:0:3:4:12:5</td>
<td>2 0.2-12 µm</td>
<td>11 ± 1.6 µm</td>
<td>2.9</td>
<td>0.011*</td>
<td>20.4</td>
<td>-24.3</td>
</tr>
<tr>
<td>Arizona Test Dust</td>
<td>Na:K:Ca:Fe:Al:Si:O = 0.2:3.0:1.1:0:1:0:2:3:19:3</td>
<td>0.25-6.4 µm</td>
<td>16.5 ± 1.5 µm</td>
<td>4.6</td>
<td>0.06*</td>
<td>111.5</td>
<td>-24.1</td>
</tr>
</tbody>
</table>

a. in vacuo XPS measurements; b. Size range obtained by SEM or TEM imaging; c. From B.E.T. analysis of 90-point N2(g) adsorption/desorption isotherms at LN2; d. From B.J.H. analysis of 90-point N2(g) adsorption/desorption isotherms at LN2; e. Derived from B.J.H. pore volume. f. Obtained from electrophoretic mobility of 2g/L suspensions of particles in distilled deionized water at 298 K.
IR spectroscopy monitored possible hydrocarbons, carbonates and carboxyls in minerals, which were generally absent in the samples used for this study. It also helped confirm the identity and phase purity of the synthetic and acquired minerals. Figure 5.3 shows the FTIR spectra of thin mineral films deposited on the ATR cells before thin water and ice film formation in Papers I and II. The left part of Figure 5.3 shows spectra of metal (oxy)(hydr)oxides. Those of iron contain bulk O-H stretching modes in the spectral range of 3000-3800 cm\(^{-1}\), while the surface O-H groups are in the range ~ 3550 – 3700 cm\(^{-1}\). The IR bands of these minerals can depend on the particle shape, and also the predominant crystallographic planes of the hydroxyl groups. For instance, the spectrum of rod-shaped lepidocrocite contains a band centered at 3060 cm\(^{-1}\), while that of lath-shaped lepidocrocite a doublet at 2855 and 3115 cm\(^{-1}\). The doublet bands of lath-shaped lepidocrocite caused induced by the preferential alignment of (010) plane making the vibration of O-H stretching groups perpendicular to the propagated infrared light at 2855 cm\(^{-1}\).78 The bulk O-H stretching mode of goethite is at 3130 cm\(^{-1}\) whereas O-H bending modes are situated at 896 and 794 cm\(^{-1}\). Akaganéite has O-H stretching bands at 3490/3320 cm\(^{-1}\) and O-H bending bands at 805, 680 and 615 cm\(^{-1}\). Because hematite has an O-H stretching band at ~ 3400 and as water bending band at ~ 1639 cm\(^{-1}\), and that was made hydrothermally, it is rather a ‘hydrohematite’ (Fe\(_2\)O\(_3\).xH\(_2\)O). Finally, the 2-line ferrihydrite used for this work\(^{112}\) has O-H stretching and water bending modes.

Gibbsite contains a series of 6 distinct bands between 3300 and 3700 cm\(^{-1}\).\(^{113}\) Although O-H bending region of iron oxy(hydr)oxides reveals less distinct bands, gibbsite generates more vibrational bands in this region. This is mainly due to the symmetrical structure of gibbsite, producing several degenerate Raman and IR active bands. Just like

![Figure 5.2](image_url) Relationship between N\(_2\)-BET specific surface area and particle size estimated by scanning and transmission electron imaging.
lepidocrocite, the IR spectrum of gibbsite relates to the shape of the particles (e.g. sphere, plate)\(^{14}\) and the way it is deposited on the ATR cell. This is due to differences in the sampling of (longitudinal vs. transversal) O-H stretches.\(^{78}\)

The middle part of Figure 5.3 shows the IR spectra of phyllosilicates, including 1:1 (kaolinite) and 2:1 non-swelling (illite) and swelling (Na- and Ca-montmorillonites) minerals. Kaolinite has four distinct O-H stretching bands (~3692, 3667, 3653 (CMS)/3651 (Fluka), and 3620 (CMS)/3618 (Fluka) cm\(^{-1}\)). Other typical crucial bands for kaolinite are at ~938 cm\(^{-1}\) and 913 cm\(^{-1}\) referring the vibrations of inner OH deformation and the inner surface OH deformation. In the case of illite, dominant O-H stretching bands are shown ~3620 and 3697 cm\(^{-1}\). The vibrations in the spectral region of 1150 - 960 cm\(^{-1}\) are the indicator of Si-O stretching region whereas the several vibrations in the 960-550 cm\(^{-1}\) spectral region implies the interactions of hydroxyl groups with octahedral cations and their corresponding Si-O framework vibrations. Other important characteristic vibrational bands of illite are doublets at 825 and 750 cm\(^{-1}\). *The IR spectra of the montmorillonites will be described in detail in Part B (Section 6).*

Finally, the right part of Figure 5.3 shows IR spectra of silicate-bearing minerals. No distinct bulk/structural water stretching and bending bands could be seen. Quartz has an asymmetric Si-O stretching band at 1200 - 950 cm\(^{-1}\) (maximum at 1060 cm\(^{-1}\), a shoulder at 1080 cm\(^{-1}\).
The doublet at 780 and 800 cm\(^{-1}\) are from symmetric Si-O stretches, and the intense band at 695 cm\(^{-1}\) is a fingerprint vibrational mode of quartz. Microcline, olivine, quartz, volcanic ash and ATD all contain significant amounts of silicates (as also seen by XPS in Table 5.1), as seen in the Si-O stretching bands at 1200 - 950 cm\(^{-1}\). The doublet bands at ~ 700 – 800 cm\(^{-1}\) reveals the characteristic signatures of Si-O stretch and the 600 – 800 cm\(^{-1}\) is the Si-O bending. Finally, calcium carbonate is recognised by the asymmetric stretching CO\(_3\) band at 1454 cm\(^{-1}\) and CO\(_3\) asymmetric bending mode at 872 cm\(^{-1}\), as well as 715 cm\(^{-1}\) symmetric mode (\(\nu_4\)) of CO\(_3\).
6. Part A. Water Adsorption & Condensation on Mineral Surfaces

6.1 Water Condensation on Minerals

In this section, water vapour binding and condensation reactions were explored on 21 minerals samples of contrasting (i) mineral structure, (ii) composition, (iii) solubility, (iv) particle morphology/crystal habit (v) surface charge and, (vi) particle size/specific surface area (Table 5.1; Figure 5.1). This was carried out by measuring the water-binding capabilities of these different minerals under ambient conditions using the DVS technique. The water loadings of minerals at 25°C was measured by QCM, revealing the water vapour pressure ($p_w$) dependence of minerals (Figure 6.1).

Figure 6.1 DVS (25 °C) results of minerals under study. (a) Do-Do modelling showing concurrent adsorption and condensation regimes of Gibbsite. (a-c) DVS results for sub-micron-sized minerals, including expandable montmorillonites (c). (d-f) DVS results for micron-sized minerals.

Figure 6.1 shows strong differences in water loadings achieved in sub-micron and micron-sized particles. Sub-micron sized particles develop a low adsorption maximum below a water partial pressure of $p_w$ ~ 12 Torr H$_2$O, falling in the ~ 5 – 15 H$_2$O/nm$^2$ range (Figure 6.1 (a-c)). This range of loadings corresponds to about one monolayer of water (~
0.28 nm thick layer), which is close to the density of reactive (hydr)oxo groups at oxide surfaces (i.e. 13 – 15 H₂O/nm²). At higher p_w, these minerals stabilise 5-70 H₂O/nm² as water condenses at surfaces. As a note, greater maximum condensable water loadings occur in (i) ferrihydrite, because of possible condensation in pores of its aggregated high specific surface area, (ii) akaganéite, because of water diffusion withing tunnels of its nano-sized channels (0.4 x 0.4 nm), and (iii) montmorillonites because of the intercalation of water between its sheets, as will be explained in greater detail in Part B (Section 7).

Water loadings on larger particle show greater variations corresponding to 120-2300 monolayers (Figure 6.1, (d-f)). According to the micropore sizes of minerals in this study (Table 5.1), even saturating all the micropores is still not enough to explain these large water loadings. Excess water must therefore be at mineral surfaces and in the pores between particles. Additionally, DVS experiments with pure hematite of strongly contrasting particle size (Fig. 6.2) suggest that particle size has a strong role to play on these results.

![Figure 6.2](image_url) **Figure 6.2** DVS results of hematite particles with varied particle size.

![Figure 6.3](image_url) **Figure 6.3** DVS experiments of (a) kaolinites and (b) ATD with spray deposition.

It should be noted that minerals deposited by spraying accumulate less water than those by pipetting (Figures 6.1 (d-e), 6.3 b). Interestingly, the difference is seen in the condensation regime, not in the adsorption regime, as shown for the case of kaolinites (Figure 6.3 (a)). The method of deposition could therefore affect more the condensation of water in pores between particles. Still, we note that differences in deposition methods are not enough to explain differences between the low water
loadings in sub-micrometer-sized and larger water loadings in micrometer-sized particles.

All adsorption isotherm data can be accounted for with the Do and Do$^{115}$ model, which predicts water binding in terms of ‘adsorption’ and ‘condensation’ regimes. Although it was originally intended to predict water vapour uptake in microporous carbon, it can be applicable for minerals with:

$$C_\mu = S_0 \frac{K_1 \sum \alpha^{n+1} P_w^n}{1 + K_1 \sum \alpha^{n+1} P_w^n} + C_{\mu s} \frac{K_\mu \sum \alpha^{n+1} P_w^n}{\sum \alpha^{n+1} P_w^n + K_\mu \sum \alpha^{n+1} P_w^n}$$  \hspace{1cm} (6.1)

with (i) adsorption (left-hand) and (ii) condensation (right-hand) terms for water-binding sites densities ($S_0$, $C_{\mu s}$), association constant ($K_1$, $K_\mu$) and hydration numbers ($\alpha$, $\beta$). As shown for the case of gibbsite in Figure 6.1 (a), this model accounts for the Type II adsorption isotherms of sub-micron sized minerals. It also accounts for the dominance of the ‘condensation’ regime in larger particles.

**Figure 6.4** Condensation saturation densities obtained by fitting of DVS data (Figure 6.1) with the Do-Do model (Eq. 6.1) as a function specific surface area. The dashed lines show the model predictions within ~1σ. ’aka’ and 'ferri' are the abbreviations for 'akaganéite' and 'ferrihydrite'. These two FeOOH-like minerals have slightly larger water loadings due to the incorporation of water in the bulk structure of akaganéite and possible condensation in aggregated nanosized ferrihydrite particles.
The condensable water loadings \( (C_s) \) derived from the Do-Do model reveal an interesting correlation with the specific B.E.T surface area of the minerals (Figure 6.4). This relationship shows that (i) micron-sized particles with specific surface area less than \(~10 \, \text{m}^2/\text{g}\) promote water condensation, while (ii) submicron-sized particles stabilise water films formed by adsorption. Submicron-sized particles cannot promote condensation reactions probably because they do not have meso-/micro-scale surface defects/pores that can promote condensation, and also because of the high curvature of their surfaces (Kelvin effect) requires higher partial pressures of water for condensation than on flatter surfaces. These experimental data can be predicted with the empirical formula

\[
\log(C_s) = -0.29 \log(s_{2}) - 0.76 \log(s_{s}) + 4.36 \quad (6.2)
\]

From this correlation, water loadings of hydrophilic minerals measured by DVS are not majorly driven by (i) mineral structure, (ii) composition, (iii) particle morphology/crystal habit and (iv) surface potential (namely \( \zeta \)-potential in aqueous media) (Table 5.1). They are mostly driven by particle size.

![Diagram of mineral water loadings](image)

**Figure 6.5** Schematic representation of cooling/freezing and evaporation/sublimation of water bind to wet mineral pastes, providing the mineral-bound thin ice films under the temperature range (25 to -10 and -50 °C in \( \text{N}_2(\text{g}) \)). Diagram partially developed after Freedman.\(^4\)
6.2 Thin Water/Ice Films on Minerals

Mineral particle surfaces can form ice by freezing of aqueous solutions or by direct deposition of water vapour. As the mineral surfaces expose (hydr)oxo groups, mineral-ice bound films could be expected to be controlled by the hydrogen bonding between the water molecules. The formed few monolayers of ice formed at mineral surfaces could exhibit different features of hexagonal (Ih) ice.

Figure 6.6 Schematic representation of cooling/freezing and evaporation/sublimation of water bind to wet mineral pastes, providing the mineral-bound thin ice films under the temperature range (25 to -10 and -50 °C in N2(g)). Diagram partially developed after Freedman.

The previous section highlighted details on processes through which water vapour condensed at mineral surface at 25°C. This section presents information on the vibrational signatures of hydrogen-bonding environment of mineral-bound water/ice films. FTIR spectra of these water films contain a dominant band at ~3400 cm⁻¹ with a relatively smaller band at ~3200 cm⁻¹. These results show the formation of smaller number and weaker hydrogen bonds in comparison of liquid water (Figure 6.5). In fact, these are the signatures of relatively thin water films (e.g. ~1.4 nm for 5 and ~280 nm for 1000 evenly spread monolayers), in which water-water interactions are less important than in liquid water. Intercalated thin water (1-3 monolayer) films on montmorillonite also reveal these features. Additionally, the water symmetric bending region (~1610-1640 cm⁻¹) can be responsive to these changes. When water-water interactions increase in thick water films, the bending region is blue-shifted towards that of liquid water (~1637 cm⁻¹). Because of that, the spectral signatures of large-sized particles are more similar to those of liquid water and ice. On the other hand, the spectra of sub-micron sized particles are more characteristic of distinct hydrogen bonding environments induced by interactions with surface (hydr)oxo groups (Figure 6.5)
Figure 6.7 Example for vibrational spectroscopic response for illite corresponding to (a) The O-H stretching region upon cooling from 25°C to -10°C. The asterisks show peaks from bulk O-H stretches of illite. (b) Spectral components MCR I-III extracted from a Multivariate Curve Resolution (MCR) analysis of spectra of (a) giving three representative hydrogen bonding states. Spectra are shown alongside those of liquid water at 25°C, hexagonal ice (Ih) at -10°C as well as dry and humid illite (82% relative humidity, R.H.) at 25°C. (c) MCR concentration profiles of MCR I-III of (a).

Figure 6.8 Relative MCR concentration profiles of the spectral components in Figure 6.7. Left: Concentration profiles show the evolution of MCR components corresponding to temperature, which MCR I (blue), II (green) and III (red) as a wet mineral paste is frozen from 25°C to -10°C. Right: MCR components of ice films at -10 °C.
Initial attempts at freezing these condensed water films, during the course of this work, showed that ice was readily evaporated/sublimated to the atmosphere. This motivated a changed strategy, whereby a thick overlayer of ice on wet mineral pastes was first formed, then sublimated until thin ice-like films were formed (Fig. 6.6). An example of such cooling events in shown in Figure 6.7 for the case of illite (\((\text{K, H}_3\text{O})(\text{Al, Mg, Fe})_2(\text{Si, Al})_4\text{O}_{10}[\text{(OH)}_2, (\text{H}_2\text{O})])\), a nanosized (50 ± 15 nm) non-expandable clay of high specific surface area (121.7 m²/g) that has recently gained significant attention in atmospheric ice nucleation studies. Figure 6.7(b) shows MCR (Section 4.2.3) spectral components (MCR I-III) extracted from these data, in relation to spectra of liquid water (25°C), ice (-10°C), and dry (0% RH) and wet illite (82% RH at 25°C). O-H stretching region of wet illite paste at 25°C is dominated by liquid water. Cooling wet illite paste to -10°C induces the hydrogen bonding environment leading to an attenuation of O-H stretching bond strength (red-shift). This resulted in the growth and intensification of bands at lower wavenumber. Further cooling attenuated of the band O-H stretching band intensities because of the loss of water through evaporation. Freezing induced the red-shift of the ~3400 cm⁻¹ region to ~3230 and ~3150 cm⁻¹. Finally, the stability of the mineral-bound ice films were probed by FTIR over time at a constant temperature under dry N₂(g) atmosphere. The variations can be easily captured by a MCR analysis of the freezing data (Figure 6.8 (a)).
Figure 6.9: Three left panels: MCR III spectral components of thin water/ice films on mineral surfaces at -10°C (red and turquoise) and -50°C (purple). Red lines are for the thick ice layers upon the first minutes of exposure -10°C, while red dashed line is the difference spectra subtracted by from the mineral bulk. Blue lines are for the thinner water/ice overlayers formed due to prolonged exposure at -10°C, many of which denote the loss of the 3200 cm⁻¹ region upon sublimation/evaporation of excess ice. Blue dashed lines give the resulting difference spectra contributions from the mineral bulk. Representative spectra at -50°C for thin water/ice films are shown in purple. The asterisk presents intensities (absolute or loss) of surface hydroxo groups. Far right panel denotes the spectra of ice and ice + illite.

The same procedure for cooling was also applied to the other minerals of this thesis (Figure 6.8). The spectra of the thin ice films were decomposed in relation to their corresponding concentration profiles with the help of MCR (red ‘mineral+ice (time 0)’), shown in Figure 6.8. Continuous exposure of dry N₂(g) to ice overlayers during 10-70 min at -10°C resulted the progressive sublimation of these formed ice overlayers leaving the thinnest ice films at mineral surfaces. The resulting spectra
are shown in Figure 6.9. This case was manifested in nine minerals including ferrihydrite kaolinite, Ca-montmorillonite, quartz, microcline, olivine, lath-shaped lepidocrocite and calcium carbonate. The resulting thin ice films contained weakly hydrogen bonded water molecules. Ten other minerals (goethite, rod lepidocrocite, akaganéite, both hematites, gibbsite, Na-montmorillonite, illite, volcanic ash and ATD) kept stable thin water films upon further exposure of dry N₂(g) at -10°C. This is highlighted in MCR analyses of the experimental data in Figure 6.8 (right). This work shows that the thinnest forms of mineral-bound ices (Figure 6.9) could be compared to thin water films formed by vapour deposition at mineral surfaces. The hydrogen bonding environments of films on the majority of minerals considered in this study reveals strong similarities. Even so, illite is a noteworthy mineral regarding to its ability to stabilise ice while it sublimated more readily on other minerals.
7. Part B. Montmorillonite interactions with water, ice, hydrohalite and CO2

Montmorillonite (MMT) is the second major clay (~40 %) component in Earth’s troposphere\(^{20}\), and can intervene in atmospheric cloud formation by triggering heterogeneous water condensation and ice nucleation reactions.\(^{12}\) Its widespread occurrence in terrestrial environments of the Cryosphere, and even possibly on the planet Mars,\(^{120}\) also opens the question of the geochemical reactions it can host under thawed and frozen conditions\(^{62, 121}\).

MMT is a negatively-charged swelling type clay mineral (smectite) (Figures 7.1 and 7.2). It can expand by intercalation with water and even by more complex molecules (e.g. organics, polymers), as well as by gas molecules, for instance CO\(_2\) and N\(_2\). When exposed to water vapour, MMT particles can form water films between individual aluminosilicate layers. Water can be bound to interlayer cations (e.g. Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\)), with the siloxane groups exposed at the layer surfaces, and with other ‘free’ water molecules.

![Figure 7.1 Montmorillonite with different interlayer water populations.](image1)

![Figure 7.2 Zeta potentials of Na- and Ca-MMT suspensions of 2 g/L prepared in solutions of NaCl.](image2)
7.1 Thin water films formed in montmorillonite

Water diffused in the interlayer region of MMT occurs in a stepwise fashion. First *crystalline* swelling stage mostly proceeds when MMT is exposed to water vapour, and involves the formation of integral water layers (nW),\(^{122}\) and increases interlayer \(d\)-spacings from 9.5-10.0 Å at 0 W to 18.4-19.0 Å at 3 W.\(^{122}\) An *osmotic* swelling stage takes place mostly in liquid water and can even lead to the delamination of individual MMT particles in weakly-held layers (*e.g.* Li-, Na-).\(^{123,124}\) In this section, FTIR spectroscopy was used to extract the spectral signatures of sodium- and calcium-exchanged MMT with 0-2 W.

MMT was first outgassed at 25 °C by prolonged exposure to \(\text{N}_2\) and in high vacuum (< 0.7 Torr). Removal of original populations of water with bending frequencies \((\nu_2)\) at 1637 cm\(^{-1}\) left crystalline water molecules at 1624 cm\(^{-1}\) (Na-MMT) and 1628 cm\(^{-1}\) (Ca-MMT). These lower frequencies, even lower than those achieved in Johnston *et al.*\(^89\) in Na-MMT (1630 cm\(^{-1}\) for \(2\text{H}_2\text{O}/\text{Na}^+\)), represent the intrinsic values of the most resilient forms of Na\(^+\)- and Ca\(^{2+}\)-bound water molecules at 25 °C, shown in Figure 7.3.

![Figure 7.3](image1)

**Figure 7.3** Water-bending region of Na-MMT under drying dried with \(\text{N}_2\) for 25 h on ATR diamond cell (a), under vacuum for up to 40 min (b). Asterisks (*) denote MMT bands unaffected by dehydration.

![Figure 7.4](image2)

**Figure 7.4** TGA of Na- and Ca-MMT.

Thermogravimetric analysis (TGA; *cf.* Paper III for details on methods) was used to evaluate the amounts of water that can be removed from MMT (Figure 7.4). These experiments revealed an initial ~5.0-5.5 % weight loss of free water molecules below ~100-150 °C, an
additional ~1.5-2.0 % weight loss in the ~150-550 °C from water bound to interlayer cations, and a final ~4 % in weight at greater temperatures resulted from the dehydroxylation of the MMT bulk.

Finally, TPD-FTIR experiments provided more detailed information on the temperature-resolved loss of water and bulk hydroxyls. These events were decomposed by three MCR components (Figure 7.5 (b, e)). MCR II is particularly interesting as it corresponds to a mostly dehydrated clay with residual water molecules that we can see in the water bending region. The conversion of MCR II to MCR III in both Na- and Ca-MMT those that the loss of interlayer water bound to Na\(^+\) and Ca\(^{2+}\) cations occurs at least at 200-250 °C.

Figure 7.5 TPD-FTIR data (a,d) and MCR analysis (b,c,e,f) of Na-MMT. TPD-FTIR data of the O-H stretching (a) and water bending (d) regions were decomposed into MCR spectral (b,e) and concentration (c,f) profiles. See paper IV for Ca-MMT data.

Thin water film formation in the interlayer spacing of the dry Na- and Ca-MMT was then investigated by exposing the clays to water vapour pressures of up to ~17 Torr. QCM measurement from Paper I (Figure 7.5) already showed that water loadings did not exceed ~200-250 mg H\(_2\)O/g clay, which corresponds to about two water layers (2W). FTIR spectra (Figure 7.6 (a)) revealed the appearance of clay-bound water through the (i) stretching (ν\(_{\text{O-H}}\)), (ii) bending (ν\(_2\)) and the (iii) Si-O stretching (δ\(_{\text{Si-O}}\)) regions. MCR analysis of these data generated three
components for 0W, 1W and 2W (Figure 7.6 (b)), showing the water vapour pressure-dependent concentration profiles and their spectral components.

Intensities of O-H stretching bands are represented in MCR components C₀, C₁ and C₂. Those of C₀ contain only those of the driest form of MMT achieved under an atmosphere of N₂(g), and with a bulk O-H a stretching band at ~3622 cm⁻¹. Intercalation of water produces the fundamental O-H stretch of water (ν₁) at 3391 cm⁻¹ and the Fermi resonance (2·ν₂) of the bending mode (ν₂) at 3227 cm⁻¹.¹⁸⁴ These are well-represented in MCR components C₁ and C₂. A third water band at ~3622 cm⁻¹ is also intensified upon exposure to water vapour. Recent studies¹²⁵-¹²⁶ show that this band predominantly arises from a monodentally-bound water to siloxane groups of the interlayer (H₂O-Si₂O). In the water-bending region, we see that crystalline water bound to Na⁺ and Ca²⁺. Ca-MMT is at a lower water bending frequency (1620 cm⁻¹) than Na-MMT, because of its greater valence charge/ionic radius. At larger water loadings, C₁ is replaced by C₂ where the lower bending frequencies (~4 cm⁻¹ in both Na- and Ca-MMT) possibly indicates the presence of a greater number of ‘free’ water-water interactions. Finally, the Si-O stretching region undergoes a reduction in the full width at half maximum (FWHM), and a slight blue shift. This slight blue-shift is explained by the displacement of Na⁺ and Ca²⁺ from (siloxane-terminated) ditrigonal cavities upon hydration, and becomes only important in liquid water.⁹⁰ We also note that the OH deformation bands from the octahedral layers (cf. 820 cm⁻¹ from Fe³⁺Fe³⁺-OH; 840 cm⁻¹ from AlMgOH; 845-890 cm⁻¹ from Al³⁺Fe³⁺-OH; 915-920 cm⁻¹ from Al³⁺Al³⁺-OH; 950 cm⁻¹ from SiOH deformation), are only slightly affected by water loadings.⁷⁷, ⁸⁰, ⁸³, ⁹⁰. Knowledge of the response of the Si-O stretching region will become essential in our interpretation of the conditions under which hydrohalite forms in saline MMT gels (Paper IV).
Figure 7.6 (a) FTIR spectra of Na- and Ca-MMT exposed to 0-17 torr water at 25°C. (b) MCR components extracted from FTIR spectra (corresponding concentration profiles are in Figure 7.1). For comparison the spectra of hexagonal ice (Ih) at -10 °C and liquid water at 25 °C, taken from Yeşilbaş and Boily \[32\], are included.

Figure 7.7 Concentration profiles obtained by MCR analysis of FTIR spectra (left column) and new MD-assisted analysis of XRD data (right column; Paper IV) for (a) Na-MMT and (b) Ca-MMT.
MCR concentration profiles of each of these components show the partial pressures under which 0W, 1W and 2W dominate in Na- and Ca-MMT (Figure 7.7). We note that exposure of water consumes C<sub>0</sub> at lower water vapour pressures in Ca- than in Na-MMT. The C<sub>1</sub> component dominates over a narrow range of water vapour pressures in Ca-MMT (~4-6 Torr), and in Na-MMT (~6-8 Torr) favours the appearance of C<sub>2</sub>. Comparison of these profiles with those that were independently determined by modelling d-spacing data by X-ray diffraction, as explained in greater detail in Paper III, confirms the validity of these assignments.

7.2 Ice and Hydrohalite formation in saline gels of montmorillonite

As highlighted in the first part of this section, MMT hydration includes a crystalline and osmotic swelling. Crystalline swelling, from 0W to 2W, in Na- and Ca-MMT was addressed in the previous section. In this section osmotically-swollen MMT gels were studied to understand how ice and salt-bearing ice form in the gels. There has been recent cryogenic scanning electron microscope imaging work showing that MMT forms 3D honeycomb networks. In the work of Paper IV, NaCl-bearing MMT gels were imaged in vacuo by Field-Emission Cryogenic Scanning Electron Microscopy (cryo-FESEM). Freshly cut samples also showed ice in honeycomb-like internal structure of the gels. The walls of these gels are composed of aggregated clay nanoparticles stacked in face-to-face configuration. At low NaCl concentration repulsive electric double layer forces disperse clay particles but at high attractive van der Waals interactions facilitate clay particle aggregation. Under these conditions, the clay pores increase in size. Chemical mapping by Energy Dispersive X-ray Spectrometry of the cut frozen gels (Paper IV) showed that ice was localised in the pores, and that NaCl was pushed onto walls of the gels where hydrohalite forms.
Figure 7.8 Hydration and freezing of clay minerals across scales. Top: Schematic representation of clays under hydration and freezing, summarizing the experimental work of this study. Middle: Cryo-FESEM images Na-MMT (a), Ca-MMT (b) and (d) 1 M NaCl and (c) EDS mapping of Ca-MMT in 1 M NaCl. Samples were initially flash-frozen in liquid nitrogen cut with a cold knife then imaged at -90 °C after exposure to vacuum for 10 min. Bottom: Schematic representation of clay particles across scales, from aggregated layers to the scale tetrahedra-octahedra-tetrahedra layers with interlamellar water (MMT+nW; where n is the number of water layers) and cations sitting in the ditrigonal cavities formed by siloxanes.

Slow freezing of saline MMT gels showed that hydrohalite only forms in Na-MMT clay gels of stronger salinity (>> 0.1 M NaCl) than in aqueous droplets (Fig. 7.9), and a transient phase that effloresces to NaCl over time. These also show that the more rigid gels of Ca-MMT completely suppress hydrohalite formation, even in solutions as high as 5 M NaCl (Figures 7.9 and 7.10).

The Si-O stretching region (Figure 7.10) during slow freezing also showed that Na-MMT pastes that do form hydrohalite have mostly unoccupied ditrigonal cavities characteristic of particles submerged in
aqueous solutions. Pastes that do not form hydrohalite have mostly occupied ditrigonal cavities, which is characteristic of clays with only interlamellar water. From these results, hydrohalite formation could be related to the availability of free interparticle water in MMT gels.

Figure 7.9 Selected ATR-FTIR spectra of 5 µL gel droplets of MMT in 1 M NaCl droplet cooled from 25 to -10 °C under an atmosphere of dry N₂(g). The data sequence were decomposed into their spectral components and correlated concentration profiles by MCR¹⁰⁹.

Figure 7.10 Selected ATR-FTIR spectra of 5 µL gel droplets of (a) Na-MMT and (b) Ca-MMT (νO-H ~3400 and ~3250 cm⁻¹; δO-H ~1626) in 1 M NaCl droplet cooled from 25 to -10 °C under an atmosphere of dry N₂(g) over a ~ 20 min period. The data sequence were decomposed into their spectral components and correlated concentration profiles by MCR¹⁰⁹ as in Figure 7.9.
This work shows that MMT gels formed from rigid and compact particle aggregates, such as those of Ca-MMT, or of low particle density and salt content are not favourable to hydrohalite formation. Gels with densities of >> 10 g/L of Na-MMT a high ionic strength are capable of growing hydrohalite. Although the detection of hydrohalite in nature is challenging, this work shows that it can be an important transient mineral during ice formation. These results could even be extendable to other expandable gel-forming clays found in terrestrial environments and the atmosphere. They are probably not extendable to non-expandable type, such as illite. Laboratory tests using this mineral showed that in the only few occasions that hydrohalite formed, its lifetimes were very short.

7.3 Trapping and Release of CO₂ from MMT

The intercalation of CO₂ in clay minerals has come into prominence by scientific community, as CO₂ is main greenhouse gas contributing to climate change. CO₂ storage in geological structures, such as deep saline formations, organic-rich shales and basalts under supercritical CO₂ (e.g. $P_{sc} \sim 73$ bars, $T_{sc} \sim 31°C$) has been studied extensively in recent years. These conditions also enable to interact of CO₂ with basalts and other type of rocks as well as some amounts of H₂O. Taking this into account, there have been several experimental and theoretical studies conducted to develop an understanding of clays/CO₂/H₂O interactions. At the same time, there is a strong need to develop this understanding for contrasting settings, such as in the mesosphere of Mars ($P_m$ up to $\sim 1$ mbar, $T_m \sim -173 °C$) where minerals might play important roles in the formation of CO₂ ice clouds. Although clay/CO₂ interactions also play very important role to control the release of CO₂ in nature, few molecular level studies are dedicated to environmental conditions. In this section, the intercalation of CO₂ in MMT is especially studied in the context of Earth’s warming soils of the cryosphere. This work is motivated by concerns that MMT-bound and biorespired CO₂ could be released to the atmosphere in the forthcoming decades.

As interlayer cations have a greater impact to control the dynamics, the structural environment and swelling feature of montmorillonites corresponding to the hydration energy and polarisability of cations, intercalation of CO₂ into the interlayer space will be also depend on
interlayer cations. Previous studies on Na⁺, Mg²⁺ and Ca²⁺ montmorillonite/CO₂/H₂O system with XRD, IR, and QCM techniques revealed that Na-montmorillonite has a strong response to H₂O because of Na⁺ has larger hydration energy. Also, greater levels of CO₂ are stored in 1W environments than at larger hydration levels. Under 1 W, CO₂ molecules lies at the center of the interlayer space, with its O-C-O axis parallel to the basal clay surface. Formation of 2W-layer disturbs the orientation and position of CO₂ molecule, which remains close to basal surfaces rather than the center of interlayer space. CO₂ can enter the hydration shell of Na⁺ and, at higher loadings, can form clusters (e.g. dimers).

In this work, rates of CO₂ released from dry MMT were measured by FTIR spectroscopy. CO₂ was first trapped in the interlayer region of dry Na-MMT by exposure to an atmosphere of 20,000 ppm CO₂. Intercalated CO₂ was detected in a single asymmetric band of the stretching mode (ν₃) at 2349 cm⁻¹ once excess free gaseous and sorbed CO₂ were evacuated from the system (Figure 7.11). Although previous studies assigned the ν₃ band at 2349 cm⁻¹, we conclude that the organisation of CO₂ molecules through varied temperature and also using transmission IR may affect the vibrations of C-O molecules leading to shift of spectrum to lower wavenumbers. This band is also very similar to that reported by Romanov after depressurisation of CO₂(g) from SWy-2. The position and width of the ~ 2343 cm⁻¹ band is very similar to the asymmetric C-O stretching band of CO₂ dissolved in water.

![Figure 7.11](image.png)

**Figure 7.11** Asymmetric O-C=O stretching region of CO₂ of MMT (~0W) originally exposure to CO₂(g) at -30 °C. (a) Free and MMT-intercalated CO₂ and (b) only MMT-intercalated CO₂ during 160 min of evacuation at -30 °C.
Figure 7.12 (a) Examples of loss of normalized band area of the 2345 cm\(^{-1}\) region during evacuation of MMT originally exposed to 20,000 ppm CO\(_2\). Lines are generated from a first-order kinetic model. (b) Arrhenius plot of the first-order rate constants for the release of CO\(_2\) from the interlayer region of MMT-0W. The release rate of CO\(_2\) resulting by evacuation with 760 Torr N\(_2\)(g) is shown through the pink data point at -30 °C. Enhanced release rates with ~1 W and 2W at -50 °C are shown in turquoise.

Intercalated CO\(_2\) was removed from MMT by prolonged exposure to vacuum (< 0.7 Torr) (Figure 7.12). The rates of release of CO\(_2\), seen in the decrease in area (a) of the ~2345 cm\(^{-1}\) band, were larger at higher temperatures and mostly follow first order-reaction kinetics:

\[
\ln(a) = \ln(a_0) - k t \tag{7.1}
\]

where with slope \(k\) (min\(^{-1}\)) and intercept \(a_0\). Rates of CO\(_2\) released from MMT greatly varied from half-lives \(t_{1/2} = \ln(2)/k\) ranging from \(t_{1/2}(CO_2) = \sim 1120\) min at -50 °C to \(t_{1/2}(CO_2) = \sim 4\) min at 60 °C. Values of \(a_0\) were mostly temperature dependent, with \(a_0\) larger at lower temperatures, but more work is needed to see whether exposure time, the thickness and/or roughness of the MMT samples played a role on this matter. Preliminary QCM measurements are pointing to loadings of 4-6 mg CO\(_2\)/g clay.

The rate constants follow the Arrhenius equation:

\[
\ln k = \ln A + E_a/RT \tag{7.2}
\]
with an activation energy of \( E_a = 34 \text{ kJ/mol} \) and a pre-exponential factor \( A = 3.8 \times 10^4 \text{ min}^{-1} \). Similar sets of experiments for Ca-MMT showed that this mineral did not intercalate \( \text{CO}_2 \). Release rates were also tested upon displacement of \( \text{CO}_2 \) by 200 sccm \( \text{N}_2 \)(g) (Figure 7.13). A MCR analysis of the data was needed to separate the gaseous from the intercalated \( \text{CO}_2 \) (Figure 7.13). The rate calculated from the concentration profile was highly comparable to those obtained by displacement of \( \text{CO}_2 \) in vacuum (Figure 7.12(b)).

**Figure 7.13.** Evacuation of \( \text{CO}_2 \) upon flushing of 200 sccm \( \text{N}_2 \)(g) to \( \text{CO}_2 \)-loaded MMT (~0 W) at -30°C (0 W). (a) Asymmetric stretching region \( (\nu_3) \) of \( \text{CO}_2 \) during the ~200 min evacuation period. (b) Spectral components for \( \text{CO}_2 \)(g)+\( \text{CO}_2 \)(MMT) and \( \text{CO}_2 \)(MMT) extracted by MCR-ALS analysis of the data from (a). The spectrum of \( \text{CO}_2 \)(g) is shown for references. (c) Concentration profiles of MCR-ALS components of (b). The values of \( \text{CO}_2 \)(MMT) were used to estimate the first-order rate constant the evacuation of \( \text{CO}_2 \) from MMT by \( \text{N}_2 \)(g).

Finally, repeated experiments with MMT 1-2 W, discussed in greater detail in Paper V, show effects only at sub-freezing temperatures because water removal rates in vacuum were too high at higher temperatures. Evacuating \( \text{CO}_2 \)+\( \text{H}_2\text{O} \) intercalated MMT at -10°C and below only partially removed water during the course of the experiments. Most remarkably, at -50°C, initial loadings of ~1.5-2W only decreased ~1-1.5W, yet rate constants for \( \text{CO}_2 \) increased by 2-3 orders of magnitude. It can therefore be concluded that cold conditions stabilise thick interlayer water over longer periods, and therefore trigger large \( \text{CO}_2 \) release rates. Dry and cold conditions should therefore stabilise \( \text{CO}_2 \) in the interlayer region MMT of thawing soils.
8. Conclusions and Outlook

This thesis helped develop a fundamental insight into the nature of thin water and ice films on minerals. This insight is central for understanding the chemistry and physics of terrestrial environments, the atmosphere and even the planet Mars, where a variety of minerals are present.

• **Paper I** shows that water loadings on minerals are strongly dependent on particle size. While sub-micron sized particles stabilise water films mainly by ‘adsorption’, micron sized particles mostly accumulate water by condensation. ‘Condensation’ on sub-micron sized particles is inhibited by lack of meso-/micro-porosity and likely by the Kelvin effect.

• In **Paper II**, the vibrational spectra of the thinnest water films that could be formed at mineral surfaces under sub-freezing conditions showed that they were highly comparable to those acquired by water vapour deposition. They could be even the attachment of the so-called quasi-liquid layer\(^5\). These are therefore the films on which ice nucleation and growth are likely to occur on minerals.

• In **Paper III**, the vibration spectral signatures of 0W, 1W and 2W water layers in the interlayer region of MMT were derived by chemometric analysis, and comparison with \(d\)-spacing data. Even after extensive sessions of degassing, 0W at room temperature is associated with residual crystalline water bound to interlayer cations. 1W and 2W interlayer waters consist of ‘free’ and siloxane-bound water molecules.

• **Paper IV** cryo-FESEM revealed micrometer-sized ice crystals within gel pores of frozen saline gels of MMT. Gels of rigid and compact particle aggregates, or of low particle density and salt content, mostly formed hexagonal ice, \(I_h\). Those of concentrated (\(>>10\) g/L) and saline gels were also capable of growing hydrohalite, probably between and/or near aggregated clay particle walls.
• **In Paper V**, the rates of CO$_2$ released from MMT varied from half-lives ranging from $t_{1/2}$(CO$_2$) = ~1120 min at -50 °C to $t_{1/2}$(CO$_2$) = ~4 min at 60 °C. The activation energy for this release is of 34 kJ/mol. Release rates are increased by 2-3 orders of magnitude in 1 – 2 W under sub-freezing conditions. These findings suggest that dry and cold conditions should mostly stabilise CO$_2$ in the interlayer region MMT of thawing soils.

Additionally, this thesis helped define future paths of exploration for its two main themes:

• **Part A** of this thesis could be easily expanded to future studies on the impact of co-existing solids (e.g. sea sprays), overcoatings (e.g. salts) as well as reactive gases (e.g. NO$_x$, SO$_x$, CO$_2$) both in the context of terrestrial environments (e.g. vadose zone and permafrost geochemistry) and the atmosphere (cloud formation). It can even help address how atmospheric mineral aerosols act as cloud condensation nuclei in the condensation of cloud droplets $^{138-140}$. These findings already fall in line with several laboratory and field studies$^{139-141}$ supporting the idea that particle size and surface defects (e.g pores, roughness)$^{54, 141}$ could strongly affect the activation of cloud condensation nuclei. This work also revealed that water condensation can also be strongly affected by particle aggregation. Additional studies are therefore needed to address how aggregation patterns can impact water adsorption, condensation, and freezing.

• **Part B**, opens future possibilities for exploring water adsorption, freezing and their impact on gaseous exchanges of clay minerals that are of central importance to terrestrial environments, atmosphere, even for the planet Mars. By having (i) identified the vibrational spectroscopic profiles of interlayer water and ice, (ii) the conditions under which water freezes within pores of clay gels, and (iii) CO$_2$ exchanges, this work will facilitate further molecular-level studies dedicated to the geochemistry and atmospheric chemistry of clays. Exploring different intercalation of common ions, and the impact of pore water freezing/thawing on CO$_2$ release are examples of important themes that should be explored in the future.
Exploration of some these paths were under way during the course of this Ph.D. study but could not be included here. They will be communicated in the near future.
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References


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132. Schaef, H. T.; Ilton, E. S.; Qafoku, O.; Martin, P. F.; Felmy, A. R.; Rosso, K. M., In Situ Xrd Study of Ca2+ Saturated Montmorillonite (STX-1) Exposed to
Anhydrous and Wet Supercritical Carbon Dioxide. *Int. J. Greenhouse Gas Cont* 2012, 6, 220-229.


