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Hydrolysis Reactions of Inverted 1:1 and Layered 2:1 Silicates

presented by

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Ph.D. degree in <u>Chemistry</u>

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HYDROLYSIS REACTIONS OF INVERTED 1:1 AND LAYERED 2:1 SILICATES

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Hemamali D. Kaviratna

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

HYDROLYSIS REACTIONS OF INVERTED 1:1 AND LAYERED 2:1 SILICATES

By Hemamali D. Kaviratna

Crystalline porous materials find wide-spread use as catalysts, ionexchangers and adsorbents. They also are potentially useful as composites and materials for the design of electronic, optical or magnetic devices. The nanoporous regime (1-10 nm) spans the mid-micropore region characteristic of traditional crystalline porous materials (< 2.0 nm) and the lower mesopore size range (2.0-50 nm) typical of amorphous oxides. Regularly ordered nanoporous materials would represent new arenas for chemistry in constrained environments.

The present work reports a new approach for synthesizing nanoporous materials. The approach makes use of a layered nonporous material as a template for the formation of a new nanoporous derivative that can not be obtained by using direct crystallization. The viability of this concept is demonstrated for the topochemical acid hydrolysis of antigorite, a silicate with an inverted wave structure. Approximately 70% of the octahedral Mg can be depleted by acid hydrolysis without dramatically changing the crystallographic order of the antigorite. A BET surface area of more than 300 m² g⁻¹ was obtained. This is a very large increase compared to 6 m² g⁻¹ for the starting clay. The mechanism for acid hydrolysis of antigorite is considered to have three main steps: (i) Initial acid attack of the octahedral Mg sheet through the eight membered rings of the basal plane of antigorite; (ii) Secondary lateral hydrolysis of the octahedral Mg of already hydrolyzed 001 planes; (iii) A relatively slow, compared to the steps i and ii, edge hydrolysis process. A regular



Hemamali D. Kaviratna

nanoporous magnesium silicate was synthesized by topochemical hydrolysis of antigorite. The nanopore size varied from a diameter ~ 8 Å to ~ 39 Å depending on the Mg^{2+} depletion and the rearrangement of the SiO₂ sheet.

The acid hydrolysis reactions of kaolinite, phlogophite and fluorohectorite also were studied. Kaolinite with aluminum in octahedral sites is not a good candidate for acid hydrolysis reactions as judged by the insignificant change in surface area upon hydrolysis. Acid hydrolysis of phlogophite increases the surface area from 2 m² g⁻¹ to a maximum value of 77m² g⁻¹ at 87% Mg depletion. The acid hydrolysis of phlogophite was found to involve an edge hydrolysis diffusional mechanism. Fluorohectorite is more sensitive towards acid hydrolysis than all other silicates studied. The final product exhibits a substantially higher surface area (208 m² g⁻¹) compared to the starting surface area (3 m² g⁻¹). Acid attack most likely occurs both through the basal surface (hexagonal cavities) and the edge sites of the layer. Depletion of octahedral Mg occurs starting from edges of the clav particles as it would be expected to occur in talc and mica clays. But fluorohectorite, unlike mica or talc, affords an exceptionally high surface area comparable to those of acid hydrolyzed palygorskite, sepiolite and other smectites.

According to the present work and the early work done in area of acid hydrolysis of clay minerals, three different categories of minerals can be identified depending on their behavior towards the acids: (1) Swellable clay minerals including vermiculite give high BET surface areas upon acid treatment; (2) Nonswellable clays afford little or no surface area increase upon acid treatment (e.g. talc, phlogophite); (3) Nonswellable clays with special structural features give high surface areas (e.g. sepiolite, palygorskite, antigorite).

TO MY TEACHERS

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ABBREVIATIONS

- BET: Brunauer, Emmett and Teller
- BJH: Barrett, Joyer and Halenda
- CEC: Cation Exchange Capacity
- DCP: Direct Current Plasma
- FTIR: Fourier Transformed Infra Red
- GC: Gas Chromatography
- ICP: Inductively Coupled Plasma
- MAS: Magic Angle Spinning
- NMR: Nuclear Magnetic Resonance
- TCD Thermo Conductivity Detector
- TEM: Transmission Electron Microscopy
- TPD: Temperature Programmed Desorption
- XRD: X-ray Diffraction

Chapter I

Introduction

I.a Objective and rationale

Nanoporous Materials

The economy of the United States, indeed the economy of the entire world, depends critically on nanoporous materials. Consider, for instance, the fact that almost all of the petroleum-derived fuels are processed over catalysts that contained a class of aluminosilicates known as zeolites. These open framework structures can adsorb a wide variety of organic molecules on their intracrystal surfaces. Once constrained in the nanoporous space of zeolites, organic reagents can be transformed with unique efficiency into specific reaction products. Thus, many of the fine chemicals that support large volume manufacturing technologies are produced using nanoporous zeolites and related shape-selective materials as catalysts.¹⁻⁴ In addition to their use as shape selective catalysts, nanoporous solids exhibit adsorption and ion exchange properties useful for a wide variety of advanced technological processes including environmental pollution control, the design of new structural composites and novel electronic, optical and magnetic devices.⁵⁻⁸

In general terms, nanoporous materials are solids with an accessible open space of 1.0-10 nm range.⁹ In describing porous materials, the IUPAC

has defined three size domains: micropore, <2 nm; mesopore, 2-50 nm; and macropore, >50 nm. Thus, the nanoporous regime spans the traditional midmicropore to lower -mesopore range. Meso- and macropores are associated with the materials that are either finely divided or structurally highly disordered (amorphous). That is, meso- and macro porosity often are consequences of the texture of a material. Figure I.1 illustrates the "textural pores" arising, for example, from the random aggregation of platy particles and from the voids formed within the grains in an amorphous solid, such as silica gel. Micropores can also result from the textural properties of materials (e.g., carbon molecular sieves), but, more commonly, micropores are associated with crystalline materials with open framework structures. In zeolites and other molecular sieves, for example, the oxide framework defines open channels and cavities that can accommodate guest molecules. As illustrated in Figure I.a, these "crystallographic" pores are rigorously regular on an atomic scale. In contrast, textural pores normally exhibit broad size distributions, some over hundreds of nanometers.

Until recently, relatively few microporous materials approached the nanoscopic regime. For instance, the faujasitic zeolites used for cracking petroleum are accessed through 12-membered oxygen rings of approximately 0.74 nm diameter.¹⁰ Molecules with kinetic diameter substantially larger than 0.74 nm are unable to access the intracrystal surface of these zeolites. Zeolites, VPI-5 and cloverite have 18- and 20- ring apertures, respectively.^{11,12} In the case of VPI-5, the pore opening is ~1.2 nm in diameter, but in the case of cloverite the ring is not symmetrical.

Crystalline materials with regular pores in the 1-10 nm regime are of considerable current interest because they offer exiting new arenas for

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a. "Textural Pores"



b. "Crystallographic Pores"

Figure I.1 Frequently observed pore types.
molecular assembly and chemical reactions. Early in 1992, Kresge and his co-workers at Mobil disclosed in the patent literature¹³ the synthesis of nanoporous zeolites with channel size of 6.0 nm or more by using liquid crystal templates to direct the crystallization of the aluminosilicate framework.^{13b}, 13c

Silica

Silica, "SiO₂" is an almost universally present and is a frequent constituent of clays. It exists in three different basic structural types as amorphous silicon dioxide, quasicrystalline layered silicic acids and crystalline three-dimensional silica

Silicon dioxide, especially the amorphous form which can be fabricated in the purest state, is a material of very considerable technological importance. It is used in microelectronics devices containing metal-oxidesemiconductor transistors, optical fibers, etc. It also forms the basis of the glass matrix used for stocking radioactive waste materials.¹⁴ Furthermore, silica is used in various other applications such as ceramics and cement industries. Silica supported transition metal complexes serve as heterogeneous catalysts with high stability, good dispersion. Moreover, these catalysts are free of contamination and have high reaction rates.¹⁵

Silica exists in many crystalline forms, the better known being quartz, cristobalite and tridymite. Quartz, cristobalite, tridymite and amorphous silicon dioxide are all built of SiO₄ tetrahedra linked together so that each oxygen atom is common to two tetrahedra giving the composition SiO₂. However, the spatial arrangement of the tetrahedral links are quite different in these different forms. In these structures some, often about one -half, of

the tetrahedral positions are occupied by aluminum, and rarely, by beryllium. Other positive ions such as Na⁺, K⁺ and Ca²⁺ are present to neutralize the negative charge of the (Si, Al)O₂ framework. These framework structures and some of their physical properties are more easily understood if they are subdivided based on whether or not they contain polyhedral cavities or tunnels in their structures. Examples of these are feldspars, zeolites and ultramarines. The feldspar structure is relatively compact, but polyhedral cavities or tunnels are found in the other two groups. These cavities or tunnels are filled with water molecules (in zeolites) or finite anions (Cl⁻, SO4²⁻, S²⁻ etc. in the marines), in addition to the necessary number of cations.¹⁶ Zeolites are potentially useful in industrial applications because of their capability to adsorb gases, vapors and liquids and to act as cation exchangers. Nowadays zeolites are widely used as catalysts in photochemistry and in organic synthesis.¹⁷

Due to their layered structure, lamellar silicic acids show properties similar to those found in some layered silicates. Some of the interesting properties of the layered silicic acids are interlamellar sorption of water and other polar molecules and their ion exchange capacity. Owing to the presence of interlamellar SiOH groups, which are capable of ligating metal ions, the layered silicic acids are excellent hosts for the immobilization of metal complexes.¹⁸ A naturally occurring crystalline silicic acid, silhydrite, was discovered in Trinity county (CA) magadiite deposit.^{19, 20} Many of the silicic acids are synthesized via the acid treatment of alkaline layered silicates. A large number of naturally occurring alkali metal silicate minerals with layered structures have been discovered in alkaline lakes

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around the world over the last five decades.²¹ Also synthetic forms of silicic acids and other alkali metal silicates are readily obtainable.¹⁸

Established Approaches to the Synthesis of Crystallographically Regular Nanoporous Materials.

Materials with silicate frameworks, such as zeolites, are known to be good adsorbents and catalysts due to their porous structure. The direct crystallization method promises to be a fruitful approach to the synthesis of nanoporous solids, at least for frameworks based on corner-shared SiO₄ and AlO₄ tetrahedra. In addition, there recently has been developed a conceptionally complementary synthetic strategy for the design of nanoporous solids based on the structural modification of layered solids by pillaring reactions.

Pillared layered materials also play such an important role in this aspect but not as good as Zeolites.^{22, 23} The porous materials derived from the pillaring of lamellar solids are cationic smectite clays²⁴⁻²⁸, anionic layered double hydroxides²⁹⁻³², and many other cationic structures, including layered titanates,³³ phosphates and phosphonates,³⁴⁻⁴⁰ silicates,⁴¹ niobates,⁴²

Pillaring of these materials can be achieved by different experimental methods. In the case of smectite clays and layered double hydroxides, ion exchange intercalation procedures are preferable (Figure I.2). The metal phosphates are particularly interesting because, unlike smectite clays, the gallery surfaces are chemically functional. Figure I.3 shows the structure of

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Figure I.2 Schematic representation of pillaring or intercalation of layered materials.



Figure I.3 Cross-linking of layered materials via functional groups.

pillared material obtained by replacing some of the P-OH groups with rigid difunctional phosphate groups to form crosslinking bridges between adjacent layers.⁴³

Another recent approach for designing nanoporous layered materials is to form the pillaring species directly within the galleries of the host (Figure I.4). This concept was first demonstrated for the hydrolysis and polymerization of tetraethylorthosilicate (TEOS) in the galleries of layered titanates and silicates interlayered by alkyl ammonium ions.⁴⁴

New Approach to Synthesis of Nanoporous Materials

The main objective of this work is the synthesis of new layered silicic acids from clay precursors. The significance of this work would be the synthesis of new nanoporous structural types not achievable by direct crystallization. Novel reactivity for catalysis and adsorption would also be advantages. The general strategy is to utilize clay as templates and convert these materials to new layered silicic acids by topotactic acid hydrolysis. The use of concentrated acids to selectively dissolve clay minerals was developed in the early part of the twentieth century as a means for obtaining aluminum solution for the production of aluminum metal. Octahedral cations, such as Al^{3+} , Fe^{3+} , 2^+ , Mg^{2+} can be depleted by treating the clay minerals with concentrated acid solutions at elevated temperatures.⁴⁵⁻⁴⁷ In addition to strong acids (e.g. hydrochloric, nitric and sulfuric) weak acids(e.g. acetic), strong bases(e.g. sodium hydroxide), neutral solutions(e.g. sodium chloride) as well as natural sea water have also been used to examine the selective extraction of cations from clay minerals.⁴⁸ Our approach is the examination of the acid hydrolysis of 1:1 and 2:1 layered silicates and the



Figure I.4 Stepwise *in-situ* pillar formation of layered materials.^{44b}.



characterization of products by using various analytical techniques (e.g. MAS NMR, IR, XRD, physical sorption of molecules, elemental analysis and TEM).

Topotactic Reactions

According to Gunter and Oswald⁴⁹ the term "topochemistry" was first used by V. Kohlschutter to describe reactions occurring in or at the surface of a solid, which often show specific influences of the substrate on the kinetics and mechanism of the reaction as well as on the properties of the The porosity, particle size, shape, surface structure, crystal product. structure or even chemical composition of the solid substrate can influence topochemically.50 Such reactions have been studied extensively by Kohlschutter and later by Feitknecht.⁵¹,⁵² The growing field of applications of X-ray and electron diffraction revealed a great number of topochemical reactions, in which the property influenced most strikingly by the substrate is the product crystal structure. The necessity of introducing a special term for this type of reaction was first recognized by Lotgering in 1959.53 He proposed the term "topotaxy" for all the solid state chemical reactions that lead to a material with crystal orientations correlated with the crystal orientations of the starting material. At about the same time, Bernal introduced the term "metataxy" for the same reaction, but Lotgering's expression gained the general acceptance. Bernal reduced the wide range of Lotgering's definition in 1960 by requiring a three dimensional accord between original and product crystals for a reaction to be called topotactic.⁵⁴ He stated that in general the main directions of symmetry of the reacting crystal remain intact in topotactic reactions. This definition was expanded by Mackay to include structural transformations.⁵⁵ Furthermore, according

to Mackay the term should only be applied if the majority of the atomic positions remain fixed. This was again altered by Dent-Glasser and coworkers⁵⁶ who adopted an intermediate position with respect to the requirements of structural accord between the strict requests of Bernal and Mackay and the rather diffuse statement of Lotgering. In 1964, Bernal and Mackay again stressed the importance of dimensional and structural correspondence in the three axial directions.⁵⁷ Shannon and Rossi attempted a new definition of topotaxy by reducing the requirement of Bernal and Mackay by introducing different degrees of topotaxy, corresponding to the extent of perfection of the preferred orientation found in the product crystallites.⁵⁸ A clear separation of topotaxy from epitaxy was suggested, the latter term being used for oriented overgrowth and not for transformations. Kleber pointed out that most topotactic reactions do not yield single crystal products, but "topotactic reaction fabrics", assuming only "a structural relation" between parent and product crystals, which may be one-, two- or three dimensional.⁵⁹ In a review of topotactic reactions, Deschanvres and Raveau cover only phenomena included in Bernal and Mackay's concept, treating phase transformations as well.⁶⁰ Their classification is according to supposed reaction mechanisms (homogeneous, heterogeneous and others), which, however, are often not established The most recent paper on questions of terminology for definitely. crystallographic orientation relations by Bonev defines topotactic reactions as chemical reactions of a solid leading to a product with defined crystallographic orientation with respect to the original crystal.⁶¹ This orientation need not be three-dimensional, but may be only two- or even one-dimensional. An additional requirement is the exchange of components with the surrounding, separating topotaxy from endotaxy (in Bonev's

terminology), in which only energy, but no components may be exchanged. This definition is supported by a number of observations by Kleber and mainly based on work of Oswald and Gunter who expressed similar views earlier.^{62,63,49}

In 1975 Gunter and Oswald⁴⁹ concluded that a chemical reaction of a solid may be called topotactic if the product is formed in one or several crystallographically equivalent orientations relative to the parent crystal, if there has been an exchange of components with the surroundings, and if the reaction can proceed through out the entire volume of the parent crystal.⁶⁴ It can be concluded that a topochemical reaction is a solid state chemical reaction in which a product is formed with a structure that reflects the structure of the original crystal.

If the product is formed in a small number of defined, but not equivalent orientations, the reaction is treated as a case of several different topotactic reactions occurring simultaneously.

I.b Structure and Properties of Clays

The hydrous layer silicates commonly known as clay minerals are part of a larger family called phyllosilicates. The layer silicates considered in this work contain a continuos two-dimensional tetrahedral sheets of composition M_2O_5 (M=tetrahedral cation, generally Si, Al, Fe³⁺) in which individual tetrahedra are linked with neighboring tetrahedra by sharing three corners each (the basal oxygens) to form a hexagonal mesh pattern (Figure I.5a). The fourth tetrahedral corner (the apical oxygen) points in a direction normal to the sheet and at the same time forms a part of an immediately adjacent octahedral sheet in which individual octahedra are linked laterally



Figure I.5 The formation of composite silicon-aluminum-oxygen or siliconmagnesium-oxygen layers.¹⁶

by sharing octahedral edges (Figure I.5b). The common plane of junction between the tetrahedral and the octahedral sheets consists of the shared apical oxygen and unshared OH groups that lie at the center of each tetrahedral six-fold ring at the same z-level as the apical oxygen. F may substitute for OH in some species. The octahedral cations normally are Mg^{2+} , Al^{3+} , Fe^{2+} and Fe^{3+} . The assemblage formed by linking one tetrahedral sheet with one octahedral sheet is known as a 1:1 layer. In such layers the uppermost, unshared plane of anions in the octahedral sheet consists entirely of OH groups. A 2:1 layer links two tetrahedral sheets with one octahedral sheet. In order to accomplish this linkage, the upper tetrahedral sheet must be inverted so that its apical oxygen points down and can be shared with the octahedral sheet below (Figure I.5c and d).^{16, 65, 66}

2:1 Clays

The idealized oxygen framework of a 2:1 clay is shown in Figure I.6. In a unit cell formed from twenty oxygen and four hydroxyl groups, there are eight tetrahedral sites and six octahedral sites along with four cavities surrounded by a six-membered oxygen ring on the surface. When two thirds of the octahedral sites are occupied by cations, the mineral is classified as a dioctahedral 2:1 phyllosilicate. A trioctahedral 2:1 phyllosilicate has all the octahedral sites filled with cations. Based on the magnitude of the layer charge per unit cell, 2:1 phyllosilicates are divided into five groups; talc-pyrophillite, smectite, vermiculite, mica and brittle mica (Table I.1)^{65, 67}. The members of each group are distinguished by the type and location of cations in the oxygen framework.



Figure I.6 Idealized oxygen framework of clay minerals.

Mineral group	Dioctahedral	Trioctahedral
Pyrophyllite-Talc	Pyrophyllite [Al4](Si8)O ₂₀ (OH)4	Talc [Mg6](Si8)O ₂₀ (OH)4
Smectite (x = 0.4 - 1.2)	Montmorillonite ^X Mn ⁺ yH ₂ O[Al _{4-X} Mg _X] (Sig)O ₂₀ (OH) ₄	Hectorite ^X Mn+ yH2O[Mg _{6-x} Li _x] (Sig)O ₂₀ (OH́)4

Table I.1 Idealized Structural Formulae for representative 2:1 Phyllosilicates. In each Formula the Parentheses and Bracket Define Metal Ions in Tetrahedral and Octahedral Sites Respectively.

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Beidellite	Saponite
$\frac{x}{n}$ Mn+ yH ₂ O[Al ₄] (Si _{8-x} Al _x) O ₂₀ (OH) ₄	$\frac{x}{n}$ M ⁿ⁺ yH ₂ O[Mg ₆] (Si _{8-x} Al _x)O ₂₀ (OH) ₄

Nontronite

 $\frac{x}{n}$ Mn+ yH₂O[Fe₄] (Si₈)O₂₀(OH)₄

Laponite

^{<u>x</u>}Mⁿ⁺ yH2O[Mg_{6-x}Li_x] (Si₈)O₂₀(OH)₄

Fluorohectorite

^x/_nMⁿ⁺ yH₂O[Mg_{6-x}] (Si₈)O₂₀(F)₄

Table II.1 Cont'd.		
Vermiculite	·	Vermiculite
(x = 1.2 - 1.8)		^x Mn+ yH2O[Mg6] (Si _{8-x} Al _x)O
Mica	Muscovite	Phlogopite
	K2[Al4] (Si ₆ Al2)O ₂₀ (OH)4	K2[Mg6] (Si ₆ Al2)O20(OH)4
Brittle Mica	Margarite	Clintonite
	Ca ₂ [Al ₄] (Si ₄ Al ₄)O ₂₀ (OH) ₄	Ca2[Mg4Al2] (Si2Al6)O20(OH)

 $(Si_{8-x}Al_x)O_{20}(OH)_4$

Al6)020(0H)4

TableII.1 Cont'd.

Trioctahedral types only

Sepiolite-Palygoskite Palygoskite (x = variable) [Mg5_{-y-z}Ry³⁺ z](Si_{8-x}F

 $[Mg_{5-y-z}Ry^{3+} z](Si_{8-x}R_x^{3+})O_{20}(OH)_2(OH2)4R^{2+}(x-y+2z)/2.(H_{20})4$

Sepiolite

 $[Mg_{8-y-z}R_y^{3+}z](Si_{12-x}R_x^{3+})O_{30}(OH)_4(OH2)_4R^{2+}(x-y+2z)/2.(H_2O)_8$

In talc, all the tetrahedral and octahedral sites are filled by Si⁴⁺ and Mg²⁺ respectively, and the layers are electrically neutral. In pyrophyllite only two thirds of the octahedral sites are occupied by Al³⁺ ions leaving a neutral aluminosilicate layer. Therefore, in crystals of these minerals the layers are coupled through relatively weak dipolar and van der Waals forces.⁶⁸ In contrast to talc and pyrophyllite, the layers in muscovite and phlogopite bear a net charge of 2 e⁻ per Si₈O₂₀ unit due to a positive charge deficiency which results from the substitution of Si⁴⁺ by Al³⁺ in tetrahedral positions. The charge deficiency is balanced by interlayer potassium ions which are coordinated to the hexagonal arrays of oxygen atoms at the layer surface.⁶⁵ Among the 2:1 layered phyllosilicates, the brittle mica group has the highest layer charge, 4 e⁻ per Si₈O₂₀ unit cell. The layer charge in vermiculite arises from the substitution of Al³⁺ for Si⁴⁺ in the tetrahedral layer. Vermiculite has a varying layer charge depending on the amount of substitution, 1.2 - 1.8 e⁻ per Si₈O₂₀ unit.

The charge on the layers of smectite is intermediate and varies from 0.4-1.2 e⁻ per Si₈O₂₀ unit.⁶⁹ To balance the layer charge, layers of hydrated cations are intercalated between the clay layers. The moderate layer charge in smectite clays gives physical and chemical properties that are not found in the end members. In montmorillonite, the most familiar and common member of the smectite group, the layer charge originates from the substitution of octahedral Al³⁺ by Mg²⁺. Hectorite is also octahedrally charged with Li⁺ substituting for Mg²⁺ in the octahedral sheet. Nontronite is a tetrahedrally charged smectite with Al³⁺ replacing Si⁴⁺ in the tetrahedral sheet and Fe³⁺ replacing Al³⁺ in the octahedral sheet. Laponite and fluorohectorite are synthetic hectorites and they represent two extremes in

particle size and layer charge within the smectite group. Fluorohectorite has a particle size of up to about 2000 Å with a layer charge of $1.2 e^{-}$ per Si₈O₂₀ unit and originates from the substitution of Li⁺ for Mg²⁺ in the octahedral layer while laponite has a particle size of 200 Å with a layer charge of 0.4 e⁻ per Si₈O₂₀ unit as a results of substitution of Li⁺ for Mg²⁺ in the octahedral layer. In fluorohectorite, all the OH groups have been replaced by F. The layer charge in octahedrally charged clays is distributed over all oxygen in the framework. These clays tend to be turbostratic, that is the layers are randomly stacked with respect to the a-b planes of adjoining layers. The negative charge on the layers of the tetrahedrally charged smectites is more localized, and these derivatives tend to exhibit greater three dimensional order.^{66,70}

The sixth group of 2:1 type silicates is sepiolite-palygorskite (Table I.1). The structures of these minerals can be regarded as containing ribbons of the 2:1 phyllosilicates structure, one ribbon being linked to the next by inversion of SiO₄ tetrahedra along a set of Si-O-Si bonds. Ribbons extend parallel to the x-axis, and they have an average width along Y. The tetrahedral sheet is continuous across ribbons but with apices pointing in different directions in adjacent ribbons, where the octahedral sheet is discontinued. Consequently, with this framework rectangular channels also run parallel to the x-axis between opposing 2:1 ribbons. As the octahedral sheet is discontinuous at each inversion of the tetrahedra, oxygen atoms of the octahedra at the edge of the ribbon are coordinated to cations of the ribbon side only, and coordination and charge balance are completed along the channel by H⁺, H₂O (bound), and a small number of exchangeable



Figure I.7 Schematic structures of palygorskite and sepiolite.⁷¹

cations. In addition, a variable amount of zeolitic water is contained in the channels (Figure I.7a and b).⁷¹

1:1 Clays

All the regular structures of the 1:1 layer types are included in the serpentine-kaolin group (Table I.2). Almost all the 1:1 layer structures have been studied in detail, the position of adjacent layers is determined by the pairing of each oxygen of the basal tetrahedral surface of one layer with an OH of the upper octahedral surface of the layer below (Figure I.8). This O---OH pairing results in the formation of long and relatively weak hydrogen bonds, approximately 2.9-3.0 Å between anion centers, that bond the layers together. The O--OH pairing can be obtained by several different ways of superimposing one layer on top of another, this variable represents the second degree of freedom in 1:1 layer structures. Additional electrostatic attraction between layer surfaces may also exist as a result of tetrahedral and octahedral substitutions. Although a 1:1 layer ideally must be electrochemically neutral, coupled substitutions can create balanced negative and positive charges on the tetrahedral and the octahedral sheets, respectively.⁶⁵ In a unit cell formed from ten oxygen and eight hydroxyl groups, there are four tetrahedral sites and six octahedral sites along with two cavities surrounded by a six-membered oxygen ring on the surface. The dioctahedral, trioctahedral classification is the same as that in 2:1 structure types.

The kaolin minerals include all the dioctahedral 1:1 layer silicates. The common unit cell formula for the kaolin group is $Al_4Si_4O_{10}(OH)_8$.⁷²

The serpentine minerals, lizardite, chrysotile, and antigorite represent the trioctahedral 1:1 layer silicates. The crystal morphologies and structures of

Table I.2 Idealized Structural Formulae for representative 1:1Phyllosilicates. In each Formula the Parentheses and Bracket Define MetalIons in Tetrahedral and Octahedral Sites Respectively.

Mineral group	Dioctahedral	Trioctahedral	
Kaolin-Serpentine	Kaolinite	Antigorite	
	[Al ₄](Si ₄)O ₁₀ (OH) ₈	Lizardite	
		Crysotile	
		[Mg ₆](Si ₄)O ₁₀ (OH) ₈	

the serpentines range from planar (lizardite) to alternating waves (antigorite) to cylindrical rolls (chrysotile).⁶⁵ These three serpentine minerals have similar chemical compositions, with the occupancies at the octahedral sites dominated by magnesium. The lateral dimensions of an ideal magnesium occupied octahedral sheet (b= 9.43 A), are larger than those of an ideal silicon occupied tetrahedral sheet (b= 9.1 A). The misfit between sheets is significant, and leads to the three serpentine structures (Figure I.9). Each has different solution to the misfit problem. In lizardite, the misfit is accommodated within the normal, planar 1:1 layer structure. In chrysotile, the misfit is partly overcome by the cylindrical curvature of the layer. In antigorite, the misfit is one of the few examples in layer silicates in which three different structures occur in a material of the same or similar chemical composition.⁷³ Since most of the work in this thesis is based on antigorite,



Figure I.8 Pairing of tetrahedral oxygen atoms (stippled) at the base of an upper 1:1 layer with the octahedral OH groups (large double circles) on the upper surface of the layer below.⁶⁵



Antigorite

Figure I.9 Schematic [010] projections of the three species of serpentine minerals.^{65b}

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it is appropriate to discuss the antigorite structure in detail.

Antigorite

Antigorite is generally some shade of medium to pale green, but can be pale buff or gray. Antigorite serpentines are usually tougher and less porous than lizardite or chrysotile serpentines. The color of rocks composed of antigorite, as well as other serpentine minerals, is determined by the distribution of accessory minerals, principally magnetite. Antigorite occurs as fine to coarse, interpenetrating anhedral blades that give the rock a toughness not found in other serpentines. Some of the coarse blades have been used for single crystal studies. The first single-crystal study of antigorite was done by Aruja (1945).⁷⁴ The structure given in Figure I.10 (From Kunze, 1956)⁷⁵ is in the form of an alternating wave extending along the x axis, the super structure direction. Kunze proposed the superstructure A= 43.3 Å and other cell dimensions, b=9.23 Å c= 7.27 Å, similar to the other serpentine minerals.⁷⁵⁻⁷⁸ The tetrahedral sheet is continuous through the structure, but reverses polarity at the midpoint where the wave changes its direction of curvature. The octahedral sheet is also continuous, but it too reverses at the midpoint and is bonded to different tetrahedral sheets in each half of the structure. The antigorite structure A is not fixed at 43.3 Å, but varies among certain preferred values. The most commonly occurring values are A = 33.7-43.31 Å (Zussman et al., 1957)^{79,80}, A = 25.7-51.5 Å (Kunze, 1961)²⁸ and A = 32.8-51.4 Å (Uehara and Shirozu).⁸¹ Kunzu defined the superstructure period in terms of m, the number of tetrahedra in the super period. When m is odd, the reversal in the tetrahedral sheet at PP' and RR' (Figure I.11) occur in normal 6-fold tetrahedral rings, but the reversals at



Figure I.10 [010] projection of the structure of antigorite; the structure reverses polarity at PP', QQ; and RR'.⁶⁵

QQ' occur in unusual 8- and 4-fold rings. Under these conditions, the Mgoctahedra at all inversion points are only slightly distorted.²³ There are 17 tetrahedra and 16 octahedra within one super period.⁶⁵

I.c Early Studies

A number of natural silicates yield a residue of hydrated silica when acted on by acid. Rinne⁸² concluded that the hydrated silica residue constituted a well ordered remnant of the biotite structure and suggested the name baueritization for the natural hydrolysis of biotite. A few years later (Rinne, 1924) he reported that "X-ray crystallograms are no longer obtainable for the residual silica of zeolite and mica.⁸³ Wyart examined hydrolyzed single crystals of zeolite by the rotating crystal X-ray method and obtained only characteristics of amorphous silica.⁸⁴ Mehmel⁸⁵ made an extensive study of the hydrolysis of biotite by acids. In those cases in which he studied the product by the powder X-ray diffraction method; only amorphous silica was indicated. Pabst found that Gillespite, a tetragonal sheet silicate, BaFeSi₄O₁₀ is hydrolyzed by hydrochloric acid leaving flakes of hydrated silica. These flakes retained the main features of the sheet structure to X-ray precession patterns. Gradual distraction of this structure has seen upon thermal dehydration to an unoriented structure.⁸³ In 1959 Lopez-Gonzalez and Cano-Ruiz reported that the surface area of the acid treated vermiculite increased with increasing concentration of acid. They noticed that the hydrolyzed structure lost its surface area upon calcination.⁸⁶ Luce and coworkers reported that the diffusion coefficient of magnesium is greater than that of silicon for some magnesium silicates towards acid hydrolysis and hence the rate of extraction of magnesium was greater than that of silicon.⁸⁷ According to Rice and Strong, the dissolution of Mg^{2+} is



Figure I.11 [001] projection of the tetrahedral sheet of antigorite structure.



caused by the rupture of weak Mg-O bonds.⁸⁸ Any acid treatment depleted some silicon, but the rates were very small. Girgis and Mourad⁸⁹ in 1976 have reported the same observation as Lopez-Gonzalez and Cano-Ruiz with serpentine upon acid hydrolysis. Both groups described the higher surface area obtained as a result of the formation of some kind of silica called "free silica". Suguet and coworkers⁹⁰ recently obtained a porous, less crystalline hydrated silica material with original platy morphology upon acid hydrolysis of vermiculite. Harkonen and Keiski studied the conditions for the acid extraction of cations from phlogophite and obtained a porous material comparable to the porosity of active coal.⁹¹ Corma and coworkers (1987) have reported that the hydrolysis order of $Mg^{2+} > Fe^{3+} > Al^{3+}$, fo palygorskite indicates that most of the octahedral positions at the edges are occupied by Mg^{2+} , some by Fe^{3+} , and partially or none by Al^{3+} in palygorskite.⁹² Corma and coworkers also reported in 1987 that the acid hydrolysis of up to 60% of the octahedral cations in palygorskite minerals does not provoke any structural changes or amorphization. Gonzalez and coworkers (1989) reported that the acid activation is much higher in the magnesium-rich palygorskite, which undergoes a greater dissolution of its octahedral sheet as well as a more extensive alteration of its structure and a greater increase of microporosity.93 They indicated that as the acid hydrolysis progressed, the octahedral sheet increasingly dissolved, creating microporosity between the tetrahedral silicate sheets. In a third stage, increasing acid concentration and/or reaction time condensed silanol groups. and the microporosity decreased. No microporosity was observed for the acid activated sample after silica extraction. The fibrous morphology of the samples was preserved throughout the acid treatment, both before and after silica extraction.94 Corma and coworkers (1990) concluded that acid attack of palygorskite does not obey a purely diffusional controlled process According to them diffusion is the controlling factor at low levels of hydrolysis, while at high levels the chemical reaction (hydrolysis) can be the rate determining step. The table below shows the activation energies for the extraction of three different octahedral cations as reported by Corma and coworkers.⁹⁵

The dissolution of Mg^{2+} from sepiolites using acids was firs attempted by Abdu-Latif and Weaver (1969) who found that the dissolution of palygorskite and sepiolite in excess hydrochloric acid was a first order reaction in terms of concentration of Al, Fe and Mg.⁹⁶ In several studies the

 Table I.3
 Activation energies of octahedral cations.

	Mg ²⁺	A1 ³⁺	Fe ³⁺
∆E (kcal/mol)	3.05	9.01	4.2

acid activation of sepiolite has been carried out to determine the structural changes in sepiolite [Shimosaka et al.(1973)⁹⁷; Corma et al.,(1986)⁹⁸], to improve the surface area and porosity [Jimenez-Lopez et al. (1978)⁹⁹; Rodriguez-Reinoso et al. (1981)]¹⁰⁰, the amount of surface acidity [Bonilla et al. (1981)]¹⁰¹ and to obtain good quality products to use as adsorbents [Gonzalez et al. (1984)]¹⁰², filling materials [Gonzalez et al. (1982)¹⁰³. Acosta et al. (1984)]¹⁰⁴] and catalysts [Dandyn & Nadiye-Tabbiruka (1982)¹⁰⁵, Corma et al. (1984)]¹⁰⁶, Corma & Perez-pariente (1987)]¹⁰⁷]. Jimenez-Lopez et al. reported a maximum of 391 m²g⁻¹ BET surface area for acid hydrolyzed sepiolite after a series of acid reactions under different

conditions.⁹⁹ Gonzalez et al. reported a fibrous silica gel with an acceptable purity level and a high specific surface area of 505 m²g.⁻¹ ¹⁰² Cetisli and Gedikbey (1990) concluded that the dissolution of Mg from sepiolite is a first order reaction in terms of acid concentration and Mg content of the The reaction rate constants were proportional to the acid solid.108 concentrations, and inversely proportional to the square-root of the initia particle radii of the sepiolite. In 1987 Mendioroz and coworkers acid treated bentonite and revealed an evolution in the hysteresis loops of the corresponding nitrogen adsorption-desorption isotherms.¹⁰⁹ They concluded that in the first stage of the attack, an opening of the bentonite lamella was produced by the abstraction of interlayer cations and corresponding water molecules. Thus accessibility, otherwise impossible, or nitrogen to the internal surface of the samples with subsequent increase in nitrogen adsorption occurred. A second stage was produced when the octahedral aluminum sheet was dissolved as the acid attack progressed. A higher levels of acid concentrations, the partial distraction of the tetrahedra sheet leads to the changes in the structure. Jovanovic and Janackocvic (1991) observed a similar pore structure and adsorption properties upon acid hydrolysis of bentonite.¹¹⁰ Bremner et al. (1984) calcined various kaolir samples from 500 to 900 °C and found only little difference in alumina solubility with 26% HCl.¹¹¹ Lussier (1991) found that narrow calcinatior windows give acid-reactive calcined kaolin which develops high surface areas.¹¹² He also found that little or no Al^{3+} is depleted from the solid during the hydrolysis process.

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Chapter II

Acid Hydrolysis of 1:1 Layered Silicate Structure

II.a Introduction

The serpentine-kaolin subgroup of silicates is the only group of minerals under the category of 1:1 clays. On the basis of the earlier work summarized in section I.c it can be seen that the octahedral magnesium in 1:1 clay minerals is selectively dissolved under acid conditions at elevated temperatures. Aluminum in the octahedral sites of kaolinite is much more difficult to deplete under acid hydrolysis .^{1,2} Girgis and Mourad in 1976 reported obtaining a high surface area silica upon acid hydrolysis of octahedral magnesium in antigorite serpentine minerals.³ Results obtained for the acid hydrolysis of kaolinite and antigorite are discussed in this chapter with appropriate conclusions.

II.b Acid Hydrolysis of Serpentine

II.b.1. Experimental

Starting Material

The starting material was a greenish black antigorite serpentine rock from Lancaster county Pennsylvania. The major mineralogical component was antigorite and an appreciable amount of a magnetic impurities (magnetite). Large rock particles (about 5 cm diameter) were manually crushed to smaller particles (1 mm inch diameter) and the magnetic impurities were separated by using a magnet. The light green material obtained after the above separation was mechanically ground and the desired mesh fractions were obtained by sieving. The purified antigorite was characterized by elemental analysis, XRD, TEM, ²⁹Si MAS NMR and by FTIR.

Acid Hydrolysis

After mechanical grinding and separation through sieves the desired particle size fractions were obtained. Acid hydrolysis was carried out by placing the sample in contact with 20 wt% HCl at room temperature and then heating the mixture to the desired temperature (60 °C, 80 °C or 105 °C) with constant stirring. The liquid/solid ratio was 100 cm³/5g. Moles of H⁺ per mole of octahedral M²⁺ (M= Mg, Fe) in antigorite were 5 times stoichiometric ratio. After the desired reaction time at above temperatures, the mixture was filtered, washed until chloride free, and air dried.



Physical Measurements

The percentage of Mg depleted from the antigorite structure upon acid hydrolysis was determined base on chemical analysis. Chemical analysis was performed by the ICP (Inductively Coupled Plasma) method by using a lithium metaborate flux for preparing the solutions suitable for analysis.⁹ XRD patterns were obtained by using a Rigaku rotaflex diffractometer equipped with DMAXB software and Ni-filtered Cu K_{α} X-ray radiation. ²⁷Al and ²⁹Si MAS NMR experiments were performed on a Varian 400 VXR solid state NMR spectrometer. A Bruker multinuclear MAS probe equipped with zirconia rotors was used for all the measurements. The ²⁹Si spin-lattice relaxation times (T₁) were determined by the inversion recovery method. A total of 12 scans were accumulated for each sample. The spinning rate was 4.2 kHz and the delay time was 600 sec which was 5 times as large as the largest T₁ of ²⁹Si MAS NMR signals. Cross polarization experiments were carried out with delay times of 10 sec and contact times of 1000 ms. The delay time used with ²⁷Al MAS NMR was 10 seconds.

Adsorption and desorption measurements were carried out on an Ominisorb 360cx Coulter instrument with nitrogen as the adsorbate at 77K except the surface area measurements reported in section II.b.4 which were carried out on a Quantasorb Jr. surface area analyzer . Surface areas were calculated according to the BET (Brunauer, Emmett and Teller) method. t-Plots were constructed according to either the Boer, Lippens and Osinga^{10,11} (for samples with C_{BET} constant >70) or Lecloux and Pirard method¹² (for samples with C_{BET} constant < 70). Because it has been demonstrated that the standard isotherm has to be chosen according to C_{BET} constant, which

depends on the adsorbent-adsorbate interactions. Adsorption desorption isotherms constructed by using the data obtained from the continuous sorption measurements correspond to the selected p/p_0 values. The samples were outgassed at 150 °C under a vacuum. The adsorption of othe adsorbates was determined by using a McBain balance equipped with quarts glass springs and buckets. Pore size distribution curves were obtained from the nitrogen adsorption isotherms by the BJH (Barrett, Joyer and Halenda method¹³ by using a Coulter Ominisorb Beta 0.05 Analysis softward program. Derivative uptake plots were obtained with the same softward program used for the pore size distribution curves. Pore diameters tha correspond to the log p/p_0 values were obtained according to the equation proposed by Kresge et al¹⁴ by using nitrogen adsorption data. Micropore volume values were determined by plotting the following equation of Dubinin and-Radusikevich¹⁵:

Log V = Log V_{mic} - D(
$$\log \frac{P_0}{P}$$
)²,

the intercept of which will give the derived value of $(V_{mic} \text{ in } mlg^{-1})$.

FTIR spectra were obtained on an IBM IR44 spectrometer by the KB pressed pellet technique. TEM photographs were obtained on a JEOL 100cx II transmission electron microscope operated at 100kV. Samples were embedded in polymerized epoxy resin and sectioned to 90nm thick films.

Temperature programmed desorption (TPD) of ammonia was carried out as follows. A sample was outgassed at 300 °C in a flow of Ar gas for 4 hours and then cooled to 100 °C. Anhydrous ammonia gas was passed over the sample for 30 minutes and then flushed with pure Ar gas for another 30 minutes. Then the sample was switched to an on line GC system and the



temperature ramped at a rate of 10 °C/minute up to 300 °C. TCD (therm conductivity detector) was used to detect the amount of ammonia desorber as a function of temperature.

The *in situ* FT-IR spectroscopy of adsorbed pyridine was followed order to characterize the acid strength and Lewis acid and Bronsted acid si distributions of the samples. A thin film of sample was prepared by using 1 mg of the sample. The sample was heated under helium in the IR cell to 35 °C over a period of 2 hours by using a programmable temperature controlle and then evacuated for 1 hour, and finally cooled to 200 °C. The reference spectra were recorded at this temperature on a Nicolet FT-IR 4 spectrometer. Pyridine then was introduced at its vapor pressure level a room temperature for 20 minutes. The pyridine adsorption spectra were recorded after 10 hour evacuation at 200 °C. The difference between the tw spectra was used to determine the acid strength and Lewis-Bronsted acid sit distribution.

Alumination Experiments

Alumination reaction of acid hydrolyzed antigorite and startin antigorite were carried out according to the method presented by Fripiat an coworkers for alumination of sepiolite.¹⁶ A 5 g quantity of the sample wa allowed to react at 90 °C for 6 hours with 0.5M NaAlO₂ in 6N NaOH i such a way that the Al/Si ratio was between 3 and 14. After the reaction th solid was separated by centrifugation, washed five times with 100 ml of diluted NaOH (pH=12.8), and rinsed with 200 ml of water. Finally, th product was stirred for 1 hour in 1.25 L of a 1N NH₃ solution at root temperature three times and rinsed again with water. The conversion of th product into the ammonium exchanged form was completed by rinsing wit a 1M NH₄+-acetate solution, the excess salt being removed by washing with deionized water. A blank experiment was done without any antigorite present.

The cation exchange capacity (CEC) of the aluminated product was determined by the ammonia exchanged method.¹⁷

Determination of Crystallinity

Crystallinity is represented as a crystallinity ratio with respect to the starting material. Two methods were used to determine the crystallinity ratio.

Method I

This method is an extension of the procedure of Wims and coworkers for determining the crystallinity of polymers.¹⁸ We used the following equation to calculate the C% (percentage of crystallinity).

$$C \% = \frac{\int I_S dq - [\int I_A dq][k]}{\int I_S dq} \times 100$$

where I_S and I_A are the scattering intensities of the crystalline sample and the amorphous derivative. The scaling factor k is the ratio of the intensities at a particular 2Θ value outside of the crystalline peak region. All the intensities were baseline corrected. The biggest advantage of this method is that the percent crystallinity is independent of the absolute areas of the sample or the amorphous diffraction patterns. Thus it is not necessary to be concerned about measurement and normalization of the incident X-ray intensity I, sample thickness, size, shape or the electronic structure. A crystallinity index was obtained with respect to the starting material.



The scattering intensities for the amorphous reference were obtained by using a totally amorphous antigorite sample, which was obtained by hydrolysis with 20% HCl at reflux temperature for 24 hrs. Oriented film samples were used for all the XRD measurements.

Method II

In this method phlogopite was used as an internal standard. A 1:1 by weight mixture of phlogopite and sample, each <325 mesh, was prepared by grinding with a motor and pestle. Powder XRD patterns were taken for three different mixtures for each sample to average random errors due to mixing. The average integrated area of the 001 peak of the three different mixtures was obtained with respect to the internal standard. A crystallinity index with respect to starting material was calculated based on this intensity.

II.b.2. Results and Discussion

Characterization of Starting Material

The approximate structural formula calculated from the elemental analysis results was $(Si_2)[Mg_{2.9} Fe_{0.1}] O_5 (OH)_4$. XRD results obtained were very similar to the XRD results reported by Brindley and Santos (Figure II.1).⁴ TEM photographs agree well with the early work (Figure II.2).⁴⁻⁶ ²⁹Si MAS NMR showed a single peak at -94.1 ppm relative to TMS. The same results were reported by Lippama and coworkers for serpentine from Sharum, Norway (Figure II.3).⁷ FTIR peaks perfectly match the IR peaks reported for antigorite, but not any other



Figure II.1 X-ray powder diffraction of antigorite. Inset: X-ray diffra of antigorite reported by Brindley and Santos, 1971.



Figure II.2 TEM pictures of antigorite. Top: From Brindley and Santos, 1971. Bottom: From present work.



Figure II.3 ²⁹Si MAS NMR of starting antigorite.

serpentine group minerals (Figure I.4).⁸ The BET surface area of the non porous antigorite was $6 \text{ m}^2 \text{ g}^{-1}$.

Highly Active Material from Acid Leaching of Antigorite

Girgis and Mourad showed that an increase in HCl concentration beyond 20 wt% does not increase the weight loss, surface area or porvolume (Table II.1)³ of silica prepared by acid hydrolysis of 1:1 layered silicates at 75 °C. On the basis of these results by Girgis and Mourad, 204 HCl acid was used in the present study of antigorite with a particle size <100 mesh. Variable reaction times and temperatures have been studied in the work. The fraction of Mg depleted as a function of hydrolysis time a various temperatures is plotted in Figure II.5. It is very clear that the rate of acid hydrolysis depends on the reaction temperature. 100% depletion of M was reached faster at 105 °C (refluxing temperature) than 80 °C and 60 °C In addition, the Mg depletion rate at 80 °C is higher than that at 69 °C a indicated by the slopes of the curves at lower reaction times.

Tables II.2-4 show that there is agreement between the crystallinit ratios obtained for acid hydrolyzed antigorite by methods I and II. Eve though the method I was developed for determining the crystallinity of polymers where there are no compositional changes of the polymer durin the polymerization process, it is reasonable to use the same methodology t obtain the crystallinity of acid hydrolyzed clays where there is a loss of octahedral metal atoms. The mechanism for depletion of octahedral cation by H⁺ will be discussed later in detail.



Figure II.4a Top: IR spectra of antigorite from 3000 cm⁻¹ to 4000 cm⁻¹ (Vander and Beutelspacher, 1976). Bottom: FTIR spectra of antigorite (present work).



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Figure II.4b Top: IR spectra of antigorite from 700 cm⁻¹ to 1800 cm⁻¹ (Vander and Beutelspacher, 1976). Bottom: FTIR spectra of antigorite (present work).





Figure II.4c Top: IR spectra of antigorite from 400 cm⁻¹ to 700 cm⁻¹ (Vander and Beutelspacher, 1976). Bottom: FTIR spectra of antigorite (present work).





Figure II.5 Percent of depletion of magnesium from antigorite (>100 m verses the reaction time at different temperatures. The initial l concentration was 20 wt%. The H⁺/Mg²⁺ was 5/1.



Table 1	I.1	Effect	of	various	HCl	concentrations	on	the	physical	and
chemica	l char	acterist	ics	of serper	ntine ((acid treatment f	or 7	h at	75 °C)	

	Acid concentration						
	10%	20%	25%	30%	35%	40%	
Weight loss (%)	36.80	46.10	46.80	49.50	50.6	-	
Surface area (m ² g ⁻¹)	124	199	236	196	227	229	
Pore volume (mlg ⁻¹)	0.123	0.165	0.165	0.169	0.177	0.224	

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Figure II.6 shows the relationship between the amount of octahedral Mg depleted and the crystallinity ratio obtained according to method I. It is obvious that the change in the crystallinity with the removal of octahedral Mg at these three different temperatures is more or less the same. In other words, the pattern of crystallinity changes depends on the amount of Mg depleted. Up to 70% Mg removal the rate of change in crystallinity is very low compared to the change that occurs beyond 70% Mg depletion. The initial change in the crystallinity ratio below 70% Mg hydrolysis most likely reflects the decrease in the number of Mg atoms available for x-ray diffraction, but the oxygen frame work of the hydrolyzed structure remains the same as that of the starting clay. Relatively rapid loss in the crystallinity ratio above 70% Mg depletion can be explained in term of loss of framework oxygen. From this observation we can conclude that a well crystallized

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layered silicate can be obtained with only 30% of the original octahedra. Mg remaining in the octahedral layer.

Table II.2 Crystallinity and magnesium depletion with respect to reaction time for antigorite samples hydrolyzed at 60 °C

Reaction time (hr)	Mg% depleted	Crystallinity ratio		
		Mtd 1	Mtd 2	
1	27	.88	.93	
3	39	.88	.94	
9	41	.88	.92	
15	52	.86	.89	
24	56	.84	.96	
48	69	.81	.83	
72	79	.74	.56	

Figure II.7 shows a typical X-ray powder diffraction pattern for acid hydrolyzed antigorite at different levels of Mg depletion. Broadening of the 001 XRD peaks was not observed with these oriented peaks as one would



Table II.3 Crystallinity and magnesium depletion with respect to reactiotime for antigorite samples hydrolyzed at 80 °C

Reaction time	Mg% depleted	Crystallinity ratio	
		Mtd 1	Mtd 2
1	43	.86	.92
3	52	.85	.85
6	57	.85	.76
9	68	.79	.74
15	75	.54	.55
24	94	.32	.18
48	97	.6	.1
72	96	.1	.11

expect with structural alterations (depletion of Mg). Figure II.8 shows the XRD peaks observed in the region of 50-70 2Θ for the transparent powde samples run at transmission mode (reflected beam of X-ray was detected). The in-plan 24 3 0, 0 6 0. and 0 6 1 reflections can be observed. With the increasing depletion of Mg there is little modification in these in-plan XRI peaks. Modifications to a reflections other than 001 peaks suggests that there
Table II.4 Crystallinity and magnesium depletion with respect to reactiotime for antigorite samples hydrolyzed at 105 °C

Reaction time (hr)	Mg% depleted	Crystallinity ratio	
		Mtd 1	Mtd 2
.25	-	-	.92
1	52	.86	.89
3	78	.45	.43
6	87	.38	.24
9	93	.4	.24
15	98	.05	.06
24	99	<.05	~0

may be some rearrangement of layers.

Figures II.9, II.10 and II.11 show the relationships between the percentage of Mg depleted, BET surface area, and the reaction time at 60 °C, 80 °C and 105 °C respectively. In all these cases a continuous increase in the amount of Mg hydrolyzed was observed. However, the surface area showed a maximum at about 60-80% Mg depletion and then started to decrease as Mg depletion become more complete. Similar behavior was observed by Girgis and Mourad for acid hydrolysis of antigorite serpentine





Figure II.6 Relationship between the amount of magnesium depleted and the crystallinity, as determined by method I.





Figure II.7 Typical X-ray powder diffraction patterns of acid hydrolyz antigorite at different levels of octahedral Mg depletion.





Figure II.8 24 3 0; 0 6 0 and 0 6 1 diffraction peaks of antigorite and Mgdepleted antigorite.





Figure II.9 Percentage of Mg depleted from antigorite and the BET surface areas of hydrolyzed products plotted versus reaction time at 60 °C.





Figure II.10 Percentage of Mg depleted from antigorite and the BET surface areas of hydrolyzed products plotted versus reaction time at 80 °C.





Figure II.11 Percentage of Mg depleted from antigorite and the BET surface areas of hydrolyzed products plotted versus reaction time at 105 °C.



(See Table II.5). A maximum of BET surface area of $326 \text{ m}^2\text{g}^{-1}$ has been observed for Mg depleted antigorite serpentine. But the authors were unable to comment further on the origin of the maximum.³ It is very surprising to notice that from our results the maximum surface area values (312 - 35 m²g⁻¹) obtained at all three reaction temperatures correspond to the

Table II.5 Effect of various duration of treatment on the physical characteristics of serpentine (acid treatment at 75 °C)^a

	Duration of treatment			
	3h	5h	7h	12h
Surface area (m ² g ⁻¹)	186	219	236	211
Pore volume (mlg ⁻¹)	0.146	0.159	0.185	0.216

^a Data obtained from Girgis, B. S.; Mourad, W. E. Chem. Biotechnol 197
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condition in which about 70% of the Mg is hydrolyzed. This observation agrees perfectly with the effect we observed for the crystallinity change with Mg depletion. This proves again that hydrolysis of more than 70% of the octahedral Mg leads to the almost complete collapse of the crystallinic structure. The decrease in the BET surface area beyond ~70% Mg depletion suggests that there is a formation of less active material such as an inactive form of silica. The crystallinity ratios clearly indicate that the materia formed at the early stages of Mg depletion rapidly undergoes transformation to an amorphous material with further Mg removal.

highest BET surface area we obtained was $353 \text{ m}^2 \text{ g}^{-1}$ (see Table II.6). W also obtained BET surface area of $300 \text{ m}^2 \text{ g}^{-1}$ or more for all thre hydrolysis temperatures, compared

Table II.6 BET (m^2/g) surface area and MAS NMR curve fitting result with respect to Mg depletion for antigorite samples hydrolyzed at 60 °C

Mg% depleted	BET (m ² /g)	Relative intensities of ²⁹ Si MAS NMR peaks			
		Q ³ (-92.4 ppm)	Q ³ HOSiO ₃ (-103 ppm)	Q ⁴ (-112.0 ppm)	
27	97	47	6	47	
39	117	30	15	55	
41	181	27	18	55	
52	195	17	16	67	
56	217	11	33	56	
69	353	12	19	69	
79	339	1	24	75	

to 6 m² g⁻¹ for the starting antigorite (see Tables II.7 and 8). These values above $300 \text{ m}^2 \text{ g}^{-1}$, agree with the highest BET surface area value reported set

far for acid hydrolyzed antigorite. Girgis and Mourad reported a BE surface area of $326 \text{ m}^2 \text{ g}^{-1}$ for acid hydrolyzed antigorite.³

Table II.7 BET (m^2/g) surface area and MAS NMR curve fitting result with respect to Mg depletion for antigorite samples hydrolyzed at 80 °C

Mg% depleted	BET (m ² /g)	Relative intensities of ²⁹ Si MAS NMR peaks			
		Q ³ (-92.4 ppm)	Q ³ HOSiO ₃ (-103 ppm)	Q ⁴ (-112.0 ppm)	
43	161	21	19	60	
52	205	22	19	59	
57	270	10	30	60	
68	307	14	27	59	
75	312	5	23	72	
94	300	-	17	83	
97	225	-	15	85	
96	200	-	20	80	

Even under the mildest conditions used to hydrolyze the octahedra Mg from antigorite (20% HCl, 1 hr. and 60 °C - see Table II.2) thre different ²⁹Si MAS NMR signals were observed in contrast to a single peal observed at -94.0 ppm for the starting antigorite. The peaks observed for hydrolyzed samples occurred near -92.4 ppm, -103.0 ppm and -112.0 ppm.

Table II.8 BET (m²/g) surface area and MAS NMR curve fitting result with respect to Mg depletion for antigorite samples hydrolyzed at $105 \text{ }^{\circ}\text{C}$

Mg% depleted	BET (m ² /g)	Relative intensities of ²⁹ Si MAS NMR peaks			
		Q ³ (-92.4 ppm)	Q ³ HOSiO ₃ (-103 ppm)	Q ⁴ (-92.4 ppm)	
-	207	28	19	53	
52	300	20	13	67	
78	320	5	35	60	
87	307	-	34	66	
93	277	-	32	68	
98	230	-	32	68	
99	127	-	20	80	



The peak near -92.4 ppm can be assigned to Q³ tetrahedral Si still bonded the remaining octahedral Mg through Si-O-Mg type bonds. The 2 pp down field shift of this peak relative to the Q³ resonance parent antigori may be due to the initial changes in the octahedral sites such as weakening of O-Mg bonds caused by the acid attack. The results of curve fitting of the ²⁹Si MAS NMR spectra are shown in Tables II. 6, 7 and 8 of the peak ne -94.2 ppm (peak 1) fit well with the above assignment. Once more than 94 of octahedral Mg is hydrolyzed out, there is no detectable peak near -92 Figure II.12 shows changes in ²⁹Si NMR peaks for sample ppm. hydrolyzed at 80 °C. ²⁹Si CP/MAS NMR of hydrolyzed samples shows a enhancement of the peak near -92.4 ppm (Figure II.13). This enhancement may be due to the Q^3 Si nuclei like Si_a indicated in Figure II.14. The ²⁹ MAS NMR peak near -103 ppm (peak 2) can be assigned to Q³ sites which are more accurately specified as HOSi(OSi)3. The enhancement of the pea near -103 ppm in ²⁹Si CP/MAS spectra confirms this assignment. The pea near -112 ppm (peak 3) can be assigned to Q⁴ sites. Peaks near -103 pp (peak 2) and -112 ppm (peak 3) may respectively be due to Q³ Sib and Q Sic type nuclei as shown in Figure II.14. This Q⁴ site formation can occu within layers. According to Engelhardt and Michel Q⁴ peaks around -11 ppm correspond to an Si-O-Si angle of 151 ° (Table II.9).¹⁹ This chemica shift value is bigger than most of the commonly known silica types such a quartz (-107.4 ppm), crystobalite (-109.9 ppm) and silica gel (-109.3 ppm This higher Si-O-Si bond angle supports Sic type arrangement. The broa Q^4 band suggests that there may be several overlapping peaks with th highest intensity at -112 ppm, possibly a result of a range of Si-O-Si bon angles.



Figure II.12 ²⁹Si MAS NMR spectra of acid hydrolyzed antigorite samples with different reaction time at 80 °C.





Figure II.13 ²⁹Si MAS NMR and ²⁹Si CP/MAS NMR spectra for Mg depleted antigorite at 80 °C. A. 50% Mg depletion, B. 96% Mg depletion.





Figure II.14 Scheme for the Mg hydrolysis of octahedral Mg in 1:1 layered silicate lattice.



-5					
–δ(ppm)	n _{Si} a	α(o)p	–δ(ppm)	n _{Si} a	α(⁰) ^b
109.87	1	146.1	113.79	1	152.2
111.76	1	148.9	113.97	5	152.6
112.04	1	149.3	114.32	1	153.2
112.55	1	150.1	114.54	1	153.6
112.70	1	150.4	114.83	1	154.2
112.83	1	150.6	115.16	1	154.8
113.44	3	151.6	115.90	1	156.3
113.55	2	151.8	115.99	1	156.5
			117.00	1	158.8

Table II. 9 ²⁹Si chemical shifts, δ (ppm), relative intensities, $n_{Si}^a a$ calculated mean SiOSi bond angles, α , of highly dealuminated zeolite ZS

^a Relative to a total of 24 Si atoms.

b Calculated from the shifts according to the equation, $\delta = -247.0 \cos \alpha/(\cos \alpha - 1) + 2.19$

Engelhardt, G.; Michel, D. "High-Resolution Solid-State NMR of Silicate and Zeolites" John Wiley & Sons 1987, 304.



This can be explained by the presence of both Q^3 and Q^4 sites in the silicate layer as shown in Figure II.14. With this kind of a layer (a) which contains both Q3 and Q4 with variable Si-O-Si bond angles), possible to keep the initial templates parallel to each other and then retain long range order. But it is also possible for the resulting hydr silicon tetrahedra to become distorted, resulting in poor crystallinity Figure II.15). It is very unrealistic to conclude that all the newly formed sites are edge shared as shown in the Figure II.14. as there is only silicate structure with edge shared tetrahedra reported in the literatum Upon 70% depletion of the Mg there might be a delamination of structure that gives a compacted arrangement without much void space.

Figure II.16 shows the FTIR bands in the region 2000 to 400 cm⁻¹ acid hydrolyzed antigorite samples with different amounts of Mg depleti According to Farmer²¹ the IR bands near 1076 cm⁻¹, 980 cm⁻¹ and 448 cm for the starting clay are assigned to perpendicular vibrations of the pseu hexagonal layer, and Si-O stretching and bending vibrations, respective The bands near 625 cm⁻¹ and 565 cm⁻¹ involve Mg-O vibrations. The FI band near 1076 cm⁻¹ gradually shifts to a shoulder near 1200 cm⁻¹ w increasing amounts of octahedral Mg depletion. Similarly, the band ne 988 cm⁻¹ shifts to a band at 1095 cm⁻¹ and the band near 448 cm⁻¹ shifts a band near 467 cm⁻¹. The Mg-O associated bands near 621 cm⁻¹ and 5 cm⁻¹ diminished as the percentage of Mg depletion increased. Comparal modifications in the FTIR spectra of acid hydrolyzed palygorskites we reported by Gonzalez and coworkers in 1989.²²

Figure II.17 shows the FTIR bands between 4000 cm⁻¹ and 2500 cm for acid hydrolyzed antigorite samples with different amounts of M depletion. If the guide lines given by Ledoux and White²³ are followed





x = Leached out octahedra

Note : Clay layers are drawn straight

Figure II.15 Schematic representation of antigorite showing disordered structure ⁴Q on acid hydrolysis





Figure II.16 FTIR bands in the region 2000 cm^{-1} -400 cm⁻¹ for antigorite and acid hydrolyzed antigorite at different levels of Mg depletion.





Figure II.17 FTIR bands of antigorite and acid hydrolyzed antigorite at different levels of Mg depletion between 4000 cm⁻¹ and 2500 cm⁻¹.


classify -OH groups, the following assignments can be made for the starting clay. The strong sharp peak near 3679 cm⁻¹ is assigned to inner-surface hydroxyls located at the surface of the octahedral sheet opposite of the tetrahedral oxygens of the adjacent clay layer and is indicated with an X in Figure II.14. The broad band near 3443 cm⁻¹ is assigned to inner -OH groups (indicated with a Y in Figure II.14). The very weak FTIR bands between the above two -OH bands can be assigned to outer -OH groups at the surface, including both -OH at broken edges and at the octahedral sheet found at upper surface. Upon acid hydrolysis of octahedral Mg all -OH bands observed for the starting clay gradually are replaced by a single broad SiO-H band with its maximum near 3432 cm⁻¹. These changes in hydroxyl group vibrations clearly agree with the structural hydroxyl changes shown in Figure II.14. Similar changes in hydroxyl bands have been observed for acid hydrolyzed palygorskites.²¹

Micro and Meso Porous Materials Obtained from Acid Hydrolysis of Antigorite.

Earlier in previous section it was discussed that a crystallinity index of 0.70 could be retained, upon 70% removal of magnesium, when the particle size of the starting material is <100 mesh. Table II.10 shows the relationship between the crystallinity index and the percentage of magnesium depleted with different reaction times where the starting material was <325mesh (45 microns). These data indicate that the 0.70 crystallinity index limit can be reached with 50% of the magnesium depleted. This observation suggests that there may be a particle size dependence of crystallinity upon hydrolysis could be a diffusional controlled process. However, the results recorded in Table II.11 give us a very surprising fact about the initial hydrolysis phenomenon. For three different particle

Table II.10 Crystallinity, BET surface area, MAS NMR and percentage of magnesium depletion with respect to hydrolysis time for 325 mesh antigorite samples hydrolyzed at 80 °C. (NOTE: Different batches of starting clay were used in samples with reaction time 3, 4 and 6-12 hours)

Reaction time	Mg% depleted	Crystallinity ratio	CBET	BET surface	Total pore volume
(nound)					(iiiig)
3	39	.99	135	135	.078
4	41	.99	87	130	.096
6	50	.76	43	140	.096
9	61	.64	50	169	.130
12	70	-	46	178	.160

* Total pore volumes estimated at $P/P_0 = 0.95$ from nitrogen adsorption isotherms.

sizes, namely particles with <150 -75 μ m, <75 -45 μ m, <45 μ m there is no appreciable difference in BET surface area, crystallinity ratio or percentage of magnesium depleted after acid hydrolysis for 3 hrs (or when 40% of the magnesium is depleted out). This observation clearly suggests that the initial acid hydrolysis mechanism is not diffusional control.



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Considering both facts we can suggest a two step hydrolysis mechanism, namely, an initial non diffusional control process and a secondary diffusional control process. Mechanistic possibilities for the two processes will be discussed in further detail later.

Figure II.18 shows the 29 Si MAS NMR of samples with different amount of Mg depletion. The same peaks as reported previously were observed. The Q³ peak observed at -92.4 ppm has a higher intensity compared to other peaks especially for samples with less than 50% Mg depletion. This observation suggests minimal structural alteration of the starting material.

Table II.11 Dependence of the surface area, crystallinity and the percentageof magnesium depleted on the particle size for acid hydrolyzed antigorite.

Particle Size(<u>µ)</u>	% Mg depleted	Surface Area(m ² g ⁻¹)	Crystallinity Index
<150-75	41	119	.98
<75-45	42	134	.90
<45	39	130	.99

Figure II.19 shows t-plots obtained according to the Boar, Lippens and Osinga 10,11 method for samples with 39%, 50% and 60% Mg depletion. Since the t-curves for samples a and b are overlapped the total





Figure II.18 ²⁹Si MAS NMR spectra of acid hydrolyzed antigorite (325 mesh).





Figure II.19 (parts a and b) t-plots of antigorite hydrolyzed at 80 °C (325 mesh).





Figure II.19 (part c) t-plots of antigorite hydrolyzed at 80 °C (325 mesh).



surface area of samples with 39% and 50% Mg depletion can be obtained from the slope 1 drawn in Figure II.19 (139 m^2g^{-1}). This total surface area agrees with the BET surface areas of both samples (135 m^2g^{-1} and 140 m^2g^{-1} 1). The difference between these two samples, See Table II.10, is in their CBET constants and total pore volume. This suggests the presence of some structural differences in pore volumes. And also we see a difference between slope 2 and slope 3 in Figure II.19 which are the second slopes drawn for sample a and b respectively. In other words these two slopes give different microporous surface areas. The microporous surface area obtained from slope 2 for sample a is $131 \text{ m}^2\text{g}^{-1}$ and that of sample b from slope 3 is $65 \text{ m}^2\text{g}^{-1}$. This difference in microporousity and total pore volume hint at the difference in the Mg depleting process. This new process can be correlated with the secondary diffusional controlled mechanism already discussed in the earlier part of this section. Part c of Figure II.19 shows the t-plot for the sample with 60% Mg depletion. It is very clear that the choice of reference (aluminum oxide) used in this t-plot was not suitable. The same phenomenon was observed with all other samples with higher percentages of magnesium depletion. The CBET values in Table II.10 show that they decrease with increasing percentage of magnesium depleted. Figure II.20 shows the t-plot for sample c according to the Pirard and Lecloux method with the same volume adsorbed as that used in Figure II.19. Numerical values of the standard data n= v/v_m for $100 \ge C_{BET} \ge 40$ reported by Pirard and Lecloux were used to match the CBET constants reported in Table II.10. These standard values have been correctly fitted (within 5% up to $p/p_0=0.6$) by the n-layers of the BET equation. Slope in Figure II.20 gives the total surface area of 172 m²g⁻¹. The BET surface area of 169 m²g⁻¹ of the sample c agrees well with the total surface area obtained. Even though





Figure II.20 Lecloux-Pirad plot of the nitrogen adsorption data for acid hydrolyzed antigorite with 60% Mg depletion, illustrating the absence of microporosity in the sample.



there is a negative deviation in the t-plot, the partial pressure correspond to the deviation point is too high to consider the system to be micropord No upward deviation due to capillary condensation was noted either.

Figure II.21 shows the pore size distribution for samples with differ amounts of Mg depletion according to the BJH (Barrett, Joyer and Halen method¹³ obtained by using desorbed nitrogen volumes. The sample v 39% Mg depletion has a very small amount of pores with radii around 19 but the contribution of these pores to the surface area is negligible. T result confirms that the total surface area of this sample mostly comes fr micropores below 15 Å diameter. The micropore volume calculated plotting the Dubinin-Radusikevich equation¹⁵ for the same sample is 0.0 mlg⁻¹ (Figure II.22). This value shows very good agreement with the to pore volume of 0.078 mlg⁻¹ reported in Table II. 10. Two kinds of po were found in samples with higher amount of Mg depletion. Pore ra corresponding to these values agree with the literature values of 14 Å-22 reported by Girgis and Mourad³ for a serpentine compost that predominantly antigorite. Figure II.23 shows the nitrogen adsorpt desorption isotherms of samples with Mg depletions of 39% and 60%. sample with 39% Mg depletion has only one hysteresis loop whereas that the sample with 60% Mg depletion has two distinguishable hysteresis loc This observation agrees well with the pore size distribution curv Moreover, the isotherm for 39% Mg depletion shows the basic typ isotherm related to its microporosity. The isotherm for 60% Mg deplet shows nonmicroporous behavior at low relative pressures.

Figure II.24 shows the derivative of the nitrogen uptake obtained using omnisorb software. Pore diameters obtained according to the meth





Figure II.21 Pore size distribution of acid hydrolyzed antigorite sam obtained by BJH method.¹³





Figure II. 22 Dubinin-Radusikerich plot of hydrolyzed antigorite with : Mg depletion.



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Figure II.23 Nitrogen adsorption-desorption isotherms for acid hydrolyzed antigorite with 39% and 60% Mg depletion



Figure II. 24 (parts a and b)Derivative of nitrogen adsorption versus log partial pressure.



Figure II. 24 (parts c and d)Derivative of nitrogen adsorption versus log partial pressure.

of Kresge and coworkers¹⁵ are reported in the same figure. These values suggest a micropore diameter of 8 Å and a mesopore diameter of 39 Å. When the system goes from the microporous to the mesoporous region there is an intermediate pore diameter of about 25 Å can be seen in the derivative uptake curves which was not observed with the t-plots or pore size distribution curves. As discussed above, the derivative of the desorption curves gives the mesopore diameter of 35 Å and derivative of the uptake curves gives the mesopore diameter about 39 Å. The similar results shown in adsorption and desorption modes suggest that the nanopores formed are regular.

Derivative data also explain the hysteresis loops observed in the adsorption-desorption isotherms. Figure II. 24 gives the derivative uptake vs p/p_0 plot for an amorphous sample at 99% Mg depletion in which we do not observe any porosity. absence of porosity suggests that the mesoporous structure formed at 60% Mg depletion disappears with further magnesium depletion. Table II.12 shows the physical adsorption volumes of some adsorbates with different effective kinetic diameters at saturated vapor pressures for samples with different amounts of Mg depletion. The kinetic diameters and the calculated cross sectional areas of the adsorbates used are given in Table II.13. The amounts of ethanol and benzene adsorbed for all the samples were very similar. However, the adsorption of nitrogen was always highest. The high nitrogen adsorption capacity may be because the small cross sectional area of nitrogen allows a higher packing density. But the amounts of 1,3,5 trimethylbenzene and perfluorotributylamine adsorbed were much lower compared to those of the rest of the adsorbates used because of the larger kinetic diameter of the adsorbates. The mesopore radii



obtained from the distribution curves (Figure II.21) and the amount of any of these adsorbates adsorbed, (with the kinetic diameters given in Table II.13), agree very well.

Table II.	12	Adsorption	of	different	molecules	by	acid	hydrolyzed
antigorite (mmo	oles g ⁻¹).						

	Adsorbate (Kinetic diameter)					
Mg% depleted	Nitrogen (3.64 Å)	Ethanol (-)	Benzene (5.85 Å)	1, 3, 5 Trimethyl- benzene (7.50 Å)	Perfluoro- tributyl- amine (10.2 Å)	
					(
39	3.05	1.60	1.62	0.77	0.35	
41	4.97	1.62	1.45	0.85	0.37	
61	5.97	3.60	2.63	1.77	0.78	
70	6.63	4.30	4.35	1.90	0.91	

To propose a better explanation for this behavior the unique structural characteristics of antigorite must be considered. Figure I.10 shows an edgeon view inverted array of tetrahedral and octahedral sheets of the antigorite layer, whereas Figure I. 11 shows the 001 projection of the layer. At every other inverting point in the structure there are eight-membered rings and



Molecule	Kinetic Diameter (nm) ⁹	Cross sectional area (nm ²) ¹⁰
Nitrogen	0.364	162
Ethanol	-	0.230
Benzene	0.585	0.323
1,2,3-trimethylbenzene	0.750	0.442
Perfluorotributyl-amine	1.02	-

 Table II.13
 Molecular parameters of the adsorbates used

four-membered oxygen rings instead of only hexagonal rings as in most other clay structures. Earlier we discussed the lack of a particle size dependence for the initial acid attack up to 40% magnesium depletion (-see Table II.10). At this point we can conclude that the initial acid attack of the Mg octahedral sheet is through the z direction (hence no particle size dependence), specifically via the so-called eight-membered rings. It also has been known for several decades that any acid will selectively deplete by edge attack the octahedral cations (especially magnesium).^{3,22} It is reasonable to expect a very rapid Mg depletion process at the 8-membered ring inversion points in the octahedral sheet along the z direction perpendicular to the antigorite layer. Inverted octahedral sheets with the six



and the four-membered ring inversion points, as in palygorskite could not be attacked by the acid through the z direction. Thus the mechanism for acid hydrolysis of clay is mostly reported as edge hydrolysis or diffusion control.^{3,25} Because of the depletion through the 8-membered ring channels, a structural topochemical magnesium removal can take place in antigorite. At about 40% of Mg depletion a completely nanoporous structure is generated. The higher the depletion the lower the microporosity (Figure II.19). However, a new kind of mesopore formation (Figure II.21 and 23) and an increase in the BET surface area were observed. These mesopores may be generated because of lateral hydrolysis starting from already hydrolyzed octahedral sites. The lateral hydrolysis process which generates smaller mesopores around 17 Å radii supports the secondary diffusional control process. Growth of this lateral hydrolysis may propagate from outside to inside of the particle. At the same time a slow edge hydrolysis process (compared to the above-discussed process) can be expected. The cartoon in Figure II.25 below depicts the zones expected in the process.

Hydrolysis of layered silicates also removes some of the silicon atoms from the tetrahedral sites of clay minerals, but the quantities are very small.^{24, 25, 26} According to the our proposed mechanism for hydrolysis of antigorite most accessible silicon for hydrolysis is that around the eightmembered ring outside the clay particle. This hydrolysis of tetrahedral silicon will tend to make the pores bigger and hence facilitate the lateral hydrolysis. This argument explains the adsorption of nitrogen, ethanol and benzene in reasonable amounts. If the pore openings were just the same size as those of the eight membered rings of the silica sheet there would not be any physical adsorption of the above adsorbates simply because the





of layered structure

Figure II.25 Edge view of acid hydrolysis of the octahedral sheets of an antigorite clay particle



adsorption would be controlled by the narrowest opening of the tetrahedral sheet. Therefore, there should be a rearrangement of Si tetrahedra in such a way that the original layered oxygen framework structure is preserved. A more detailed illustration of the hydrolysis steps are shown in Figure II.26.

Electron Micrographic Evidence for Acid Hydrolysis of Antigorite

Severe experimental difficulties were encountered in electron microscopy studies of serpentine minerals due to the poor stability of the minerals under the electron beam (Mellini, et al 1986, 1987).^{27,28} We also experienced difficulty in obtaining good quality TEM images. Figure II.27 shown a HRTEM picture of antigorite reported by Mellini.²⁸ In this picture twin planes (010) appear due to stacking disorders and run from top to bottom. Figure II.28 illustrates the origin of the disorders.²⁹ Figure II.29 explains the so called lattice fringes.³⁰ In figure II.27 the lattice fringes (100) run from left to right. Figure II.30 shows a transmission electron micrograph of the starting antigorite clay used in the present work and Figure II.31 shows a acid hydrolyzed sample with 39% octahedral Mg depletion (Table II.10). Resolution and the magnification of these images were good enough to see twin (001) planes.

Spinnler systematically analyzed effects of specimen thickness, defocusing (Figure II.32) and tilting (Figure II.33) on calculated HRTEM images.²⁹ Since the quality of the images of antigorite depend on these factors as shown by Spinnler, the poor HRTEM images were obtained in the present work. The acid hydrolyzed antigorite showed no appreciable structural alteration compared to the starting material. This also supports the most of the observations discussed above. Moreover we



Figure II.26 Stepwise acid hydrolysis of antigorite.




Figure II.27 HRTEM of antigorite (Mellini, reference 28). Twin planes (001) run from top to bottom, lattice fringes (100) run from left to right.

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Figure II.28 Schematic drawing of (001) faults. The curved solid line represents the tetrahedral and octahedral layers, and the 6 and 8 refer to the types of reversals. In (a), a mirror perpendicular to c*, and in (b), two-fold axes parallel to b, the types of reversal that do not change across the fault. In (c) an a-glide perpendicular to c* produces a change in the type of reversal across the fault.



Figure II.29 Lattice fringes of antigorite.

Figure II.30 A TEM image of the starting antigorite used in this work.



Figure II.31 A TEM picture of an acid hydrolyzed sample a (acid hydrolyzed for 3 hours at 80 °C).

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Figure II.32 Calculated HRTEM images of antigorite as viewed down (010).

THICKNESS 138.0 Å

108

....

220.8 Å

303.6 Å

DEFOCUS		
-750 Å		
-850 Å		
-950 Å		
-1050 Å		
-1150 Å		
-1250 Å		
-1350 Å		
-1450 Å		
-1550 Å		
-1650 Å		
-1750 Å		
-1850 Å		



Figure II.33 Calculated HRTEM images of antigorite as a function of crystal tilt.



observe the same morphology as in the starting materials upon acid hydrolysis of up to 40% of the octahedral magnesium. Moya and coworkers (1984) reported the same results as this work with TEM studies of acid hydrolyzed sepiolite.²⁹

Figure II.34 and Figure II.35 show TEM images of antigorite with 70% Mg depletion (Section II.b.1). In Figure II.34 the layered structure can be seen in areas labeled L. Light color bands running from top to bottom are so called lattice fringers. Areas labeled A could be either improperly focused or thicker regions. Figure II.36 is an image of an antigorite clay from Spinnler given for comparison with the same magnification as the other images. The existence of lattice fringes with white colored paths at this higher magnesium depleted state supports the hydrolysis through the eightmembered inverted points discussed in Section II.b 4 (compare with Figure II.27). Figure II.35 shows a 001 view of an acid hydrolyzed antigorite. Light colored areas may represent the pores in the clay particle that exist because of depletion of octahedral magnesium.

Acidity of Acid Hydrolyzed Antigorite

Neither Bronsted nor Lewis acidity was observed for acid-hydrolyzed antigorite by FT-IR spectroscopic studies of the pyridine adsorption. No pyridine adsorption was observed at the 150 °C outgassing temperature, only physically adsorbed pyridine. A peak in the temperature programmed desorption (TPD) of adsorbed ammonia was observed at 150 °C (Figure II.37) for samples with 39%, 60% and 70% Mg depletion. This peak also may be due to ammonia physically adsorbed in the pores. Furthermore, since the peak was observed at fairly low temperature it could not be due to Figure II.34 A TEM image of acid hydrolyzed sample with 70% Mg depletion (acid hydrolyzed 12 hours at 80 $^\circ$ C).





Figure II.35 A 001 TEM view of antigorite with 70% Mg depletion (acid hydrolyzed 12 hours at 80 $^{\circ}$ C).





Figure II.36 An HRTEM picture of antigorite from Spinnler, 1985.





Figure II.37 Temperature Programmed Desorption of ammonia for acid hydrolyzed 325 mesh antigorite with different levels of Mg depletion. Outgassing temperature was 400 °C.

any acid sites. The amount of ammonia released increases with the total pore volume (Table II.10). This fact confirms that the peaks shown in Figure II.37 are in fact due to ammonia trapped in the pores.

Thermal Stability of Acid Hydrolyzed Antigorite

Table II. 14 shows the effects of outgassing temperature on the BET surface area of acid hydrolyzed samples with different amounts of Mg depleted. For samples with 60% Mg and 70% Mg depletion there is little temperature effect on the BET surface area. In fact, there is a slight increase in BET surface area with degassing temperature for samples at higher Mg depletion. This confirms that the mesoporous structure discussed above is stable towards thermal effects and differ from the data that Girgis and Mourad.³ Antigorite samples hydrolyzed with 25% HCl for 7 hours show thermal instability in the BET surface area. (Table II.15). But on the other hand samples treated with 40% HCl for 7 hours show a BET surface area increment when the degassing temperature is changed from 100 °C to 200 ^oC (Table II.15). According to the BET surface area values reported for the nanoporous samples at 39% and 41% Mg depletion there is a thermal instability of the material that depends upon the degassing temperature. The hydrolysis mechanism and the structures of samples with lower Mg depletion are different from those of highly Mg depleted samples as discussed in previous sections.

Alumination of Acid Hydrolyzed Antigorite

In all the alumination experiments including the blank experiment a white fine powder was obtained. Alumination was done by reacting samples with NaAlO₂/NaOH solution at 90 °C according to Fripiat and coworker.¹⁶



Table II.14 Effect of the outgassing temperature on the BET surface area (m^2g^{-1}) of acid hydrolyzed Antigorite.

Mg% depletion	Degassed at 150 °C	Degassed at 250 °C	Degassed at 350 °C
39	135	82	80
41	130	81	81
60	110	120	128
75	178	184	195

Table II.15 Variation of BET surface area of antigorite hydrolyzed with 25and 40% HCl, according to Girgis and Mourad³.

Temperature (°C)	BET Surface area (m ² g ⁻¹)		
	25% HCl (7h)	40% HCl (24h)	
100	236	263	
200	210	326	
280	168	244	

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The blank experiment was an NaAlO₂/NaOH solution cooked without any antigorite present.

Figure II.38 shows ²⁹Si MAS NMR of aluminated antigorite, 39% Mg depleted antigorite, and 70% Mg depleted antigorite. The aluminated acid hydrolyzed samples give a single peak at about -87.6 ppm. Figure II.39 shows the ²⁹Si MAS NMR of acid hydrolyzed samples with 39% Mg depletion and 70% Mg depletion. According to the prior assignments given in Section II. b.3 acid hydrolyzed samples had Q³ (-92.4 ppm), Q³ with -OH groups (-103.0 ppm) and Q⁴ sites (-112.0 ppm). There is no appearance of Q^4 or Q^3 with Si-OH groups for the aluminated sample shown in Figure II.38. This could be due to the dissolution of silicon in the strongly basic media used. But the resonance for the aluminated sample was shifted about 5 ppm downward from Q^3 sites reported for acid hydrolyzed samples (shifted from -92.4 ppm to -87.6 ppm). This shift could be easily explained by the tetrahedral substitution of silicon by aluminum. Each AlO₄ tetrahedron that is connected to a SiO₄ tetrahedron shifts the ²⁹Si signal by about 5-6 ppm to low field.³¹ This is further supported by the fact that the ²⁷Al MAS NMR of aluminated resonance of the 39% and 70% Mg depleted antigorite (Figure II.40) shows only tetrahedral aluminum. However, the blank experiment also showed the tetrahedral alumina. The resulting solid may be a mixture of tetrahedrally aluminum substituted antigorite and the aluminum salt as in the blank experiment. For aluminated antigorite that has not been subject to acid hydrolysis, a single peak at -92.86 ppm was observed. This is a noticeable shift from pure antigorite which gives a single peak at -94.1 ppm (Figure II.3). In the ²⁷Al MAS NMR only octahedral aluminum is present in the aluminated antigorite. The shift in the





Figure II.38 ²⁹Si MAS NMR of aluminated antigorite and acid hydrolyzed samples.



Figure II.39 ²⁹Si MAS NMR of acid hydrolyzed samples.



Figure II.40 ²⁷Al MAS NMR of, 1. Blank, 2. Aluminated antigorite, 3. Aluminated sample with 39% Mg depletion, 4. Aluminated sample 70% Mg depletion.



²⁹Si NMR peak could also be due to aluminum substitution for Mg in octahedral sites, because the value of -92.8 ppm lies between the values for the ²⁹Si NMR shift for antigorite, -94.1 ppm (trioctahedral clay) and kaolinite, -91.5 ppm (dioctahedral clay). Figure II.41 shows the X-ray diffractograms of the blank, the aluminated antigorite and the aluminated acid hydrolyzed samples. Both aluminated versions of the acid hydrolyzed samples show relevant peaks for antigorite (Figure II.1). There also exists in the antigorite sample a new phase whose peaks exactly match the XRD peaks of the blank. This clearly shows that there are two phases present in the aluminated acid hydrolyzed samples. The two different phases are tetrahedrally aluminum substituted antigorite and an unidentified aluminum phase which is different from the starting sodium aluminated, gibbcite [Al(OH)₃] or alumina (Al₂O₃). The XRD of aluminated antigorite exhibits only the antigorite phase. This agrees well with the MAS NMR results and prove that only one reaction has taken place in the system, namely substitution of Mg by Al at octahedral positions of antigorite.

Table II. 16 shows the cation exchange capacity (CEC) and the BET surface area of the two aluminated acid hydrolyzed samples. Both acid hydrolyzed samples show a very high CEC after alumination. This confirms the tetrahedral substitution of aluminum suggested by ²⁹Si MAS NMR. Low surface areas can be explained by the dissolution of amorphous silica containing Q³ Si-OH groups and Q⁴ Si groups in the strong basic medium used for the reaction. For future studies it would be worthwhile to do the same reaction in either neutral or a slightly acidic medium in order to maintain the high surface area.



Figure II.41 X-Ray Diffraction pattern of aluminated samples.



Table II.16 Cation Exchange Capacities and BET surface Area ofaluminated acid hydrolyzed samples and antigorite.

Sample	Cation E	BET Surface Area $(m^{2}g^{-1})$	
	Before alumination	After alumination	surface area before alumination
39% Mg depleted antigorite	0.42	46	10
70% Mg depleted antigorite	0.39	53	7
Antigorite	0.30	Ъ	6

^a The CEC were measured by the ammonia desorption method¹⁷

^b Not measured


II.c Acid Hydrolysis of Kaolinite

II.c.1 Experimental

Acid hydrolysis of kaolin was carried out by placing the sample in contact with 50 wt% HNO3 at room temperature and then heating the mixture to reflux with constant stirring. The liquid/solid ratio was 80 cm³/5g or 5 moles H⁺ per mole of Al. After the desired reaction time the mixture was filtered, washed until chloride free, and air dried. The percentage of Al depleted was calculated based on the results obtained from chemical analysis. Chemical analysis was performed by the ICP method by using the lithium metaborate flux method for preparing solutions suitable for analysis.⁹ The BET surface area measurements were carried out on a Quantasorb Jr. surface area analyzer with nitrogen as the adsorbate at 77 K.

II.c.2 Results and Discussion

Table II.17 shows the percent of aluminum depleted, the Si/Al ratio and the BET surface area of the resulting residues after the acid hydrolysis reaction. No hydrolysis of octahedral aluminum was observed upon acid hydrolysis at elevated temperatures. The stability of aluminum in clay minerals toward acids has been observed before.³²⁻³³ Present work with out precalcination we find very low surface area.



 Table II.17 Comparison of percentage Al depleted and BET surface area to reaction time of kaolinite.

Reaction time (hours)	2	4
Al% depleted	2.5	2.7
Si/Al ratio	1.0	1.1
BET surface area (m ² g ⁻¹)	18.27	19.51

II.d Conclusions

1. Based on the changes in the crystallinity index and the BET surface areas with the percentage of octahedral Mg depleted by hydrolysis with 20% HCl acid, it can be concluded that up to 70% of the octahedral Mg can be depleted without dramatically changing the structure of 100 mesh antigorite. The Si Q⁴ SiO₄ sites formed upon the acid hydrolysis process help maintain the layered structure during the acid attack.

A BET surface area of more than $300 \text{ m}^2 \text{ g}^{-1}$ was obtained. This is a very large increase compared to the $6 \text{ m}^2 \text{ g}^{-1}$ for the starting clay.

The prolonged attack (removal of octahedral Mg beyond 75%) leads to the disappearance of the layered structure and the formation of an amorphous, low surface area silica.

2. The mechanism for acid hydrolysis of antigorite is considered to have three main steps:



i. Initial acid attack of the octahedral Mg sheet through the eight membered rings located at the inversion points in the basal plane of the silica sheet.

ii. Secondary lateral hydrolysis of the octahedral Mg sheet starting from the already hydrolyzed 001 planes that correspond to the eight membered rings.

iii. A relatively slow, compared to the steps i and ii, edge hydrolysis process.

A microporous material with an average pore diameter ~8 Å can be obtained from the selective removal of 40% of the octahedral magnesium from antigorite. The hydrolysis of magnesium beyond 40% leads to the secondary hydrolysis discussed above with the formation of a mesoporous material with an average pore diameter of 39 Å. Mg²⁺ is depleted from the wave structure by H⁺/Mg²⁺ migration through the 8-membered ring of the basal surface.

A regular nanoporous magnesium silicate was synthesized by topochemical hydrolysis of Antigorite. The nanopore can have two forms one with a diameter of ~ 8 Å and the other with ~ 39 Å form depending on the Mg²⁺ depletion and the rearrangement of the SiO₂ sheet.

3. The TEM images show clear evidence for the topochemical acid hydrolysis of antigorite and evidence for rapid acid hydrolysis through the eight membered ring channels.

4. No acid sites were found by pyridine chemisorption in acid hydrolyzed antigorite.



5. Aluminum could be tetrahedrally substituted in acid hydrolyzed samples to obtain material with a higher cation exchange capacity. Also aluminum could be substituted for octahedral Mg in antigorite.

6. Owing to the eight-membered openings in the inverted silica sheet of antigorite, the acid depletion of octahedral Mg could be carried out to provide resulting materials with good physical properties. Topotactic hydrolysis has not been observed with 1:1 and 1:2 clays bearing only hexagonal cavities in the 001 plane. But as mentioned in the section I.c clays with ribbon structures (palygorskite and sepiolite) and hence bigger cavities in the silica sheet have shown special behavior towards mineral acids.^{32,34-48} Silicates with cavities bigger than the hexagonal cavities in the 001 plane of the tetrahedral layer would be the perfect candidates for manganpyrosmalite, similar studies. Silicates such as Mn8[Si₆O₁₅](OH,Cl)₁₀⁴⁹, bementite, Mn7[Si₆O₁₅](OH)₈⁵⁰ and apophyllite, KCa4[Si4O₁₀]₂(F,OH).8H₂O^{51,52} would be good candidates in this aspect (Figure II.42). Carlosturanite⁵³ and Greenalite⁵⁴ (Figure II.43) also should be especially suitable candidates to be examined. Both of these minerals are as serpentine group minerals. Even though, for simplicity they are not included in clay mineral classification given in Table I.2. Figure II.44 shows two other layered silicates which have modulated tetrahedral sheets with continuos octahedral sheets as do the other examples given above, namely zussmanite and stilpnomelane.55

7. Kaolinite with aluminum in the octahedral sites would not be a good candidates for acid hydrolysis reactions without thermal pretreatment.



Figure II.42 Sructures I Suggested for future leaching experiments. a. Manganpyrosmalite, b. Bementite, c. apophyllite, d. Hypothetical structure.



Figure II.43 Structures II Suggested for future leaching experiments (001 view is shown). a. Greenalite, b. Carlosturanite.



R - Tetrahedra, coordinate to D of the next 2:1 layer



b

a

- D Tetrahedra, coordinate to octahedra
- R Tetrahedra, coordinate to inverted R of the next 2:1 layer



Figure II.44 Sructures III Suggested for future leaching experiments (001 and 100 views) a. Zussmanite, b. Stilpnomelane.



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Chapter III

Acid Hydrolysis of 2:1 Layered Silicate Structure

III.a Introduction.

As discussed in Section I.c, the acid hydrolysis of 2:1 clay minerals such as phlogopite¹, vermiculite^{2,3}, montmorillonite (bentonite)^{4,5}, sepiolite⁶⁻¹⁸ and palygorskite¹⁹⁻²² has been investigated to a certain extent. The clay minerals used in this study were phlogopite and fluorohectorite. Minerals containing a predominance of Mg²⁺ in the octahedral sheet were chosen because of the instability of Mg²⁺ towards acids compared to other common cations in octahedral sites.

II.b Acid hydrolysis of phlogopite

II.b 1 Experimental

Starting Material and Chemical Reactions

The idealized structure of a 2:1 layered clay is shown in Figure I.6. Phlogopite has a mica type oxygen framework. Two tetrahedral layers are fused with an octahedral layer to form a three layer sheet. The central octahedral layer consists of Fe²⁺ and Mg²⁺ cations while the tetrahedral layers consist of Si⁴⁺ and Al³⁺ cations. Since the layer charge is very high, the gallery cations, K⁺, are tightly bound to the negatively charged layers. These gallery cations do not bear any water of hydration. This causes a close contact of the K⁺ to the adjacent layer units. Thus it is extremely difficult to achieve interlayer separation or expansion of phlogopite galleries. The close stacking of layer units make the material less porous and inaccessible for guest molecules. Therefore, only a very small external surface area is available for reaction in phlogopite clay minerals (2 m²g⁻¹).

Phlogopite from North Burgess, Ontario, Canada was ground to obtain <100 mesh particles. Of the many different methods available for the selective dissolution of clay minerals, three acid procedures were used in this work. Exact concentrations and type of acid used are given wherever applicable. Five times the stoichiometric amount of acids was used to facilitate the swift and complete dissolution of the Mg²⁺ cations.

The following experiments were carried out to determine the significance of different variables such as temperature, reaction time and acid strength on the hydrolysis process.

1. Phlogopite samples were refluxed with 20 wt% HCl , 50 wt% HNO₃ or 40 wt% H₂SO₄ and the length of treatment was varied to determine the optimal treatment time. The residues were washed with 1N solutions of the respective acids then by distilled-deionized water until free from Cl⁻ and air dried. Both the solid residues and the filtrates were analyzed for Mg²⁺ by using a Direct Current Plasma (DCP) analyzer.



2. The following solvents were used to wash phlogopite samples which had been treated with 20% HCl for six hours in order to determine the effect of washing agents upon the surface area of the residues.

a. distilled-deionized water.

b. pH 10 (CH₃)₄NOH solution.

c. 1N HCl solution.

3. Phlogopite samples were treated with 20% HCl at two different temperatures (40 °C and 70 °C) and dried at two different temperatures (room temperature (25 °C, and at 110 °C) to determine the significance of the reaction and drying temperatures.

4. A 0.1N hexadecyltrimethylammonium bromide salt was added to a mixture of phlogopite and 20% HCl to elucidate the structural changes that occur during the acid treatment. The reaction temperature was maintained at 80 °C for six hours.

5. Phlogopite was pretreated with NaF and Na₂SiF₆ at 600 °C to replace -OH groups with -F groups and the resulting residue was acid hydrolyzed with 20% HCl at 80 °C.

The following experiments were performed to understand the structure and the reactivity of residues obtained from acid treatments.

I. Intercalation of n-decylamine and pillaring with $AlCl_3/OH^-$ or Al_{13} oligomer were carried out with phlogopite residues obtained by treatment with 20% HCl for six hours at room temperature.

II. Determination of free silica content in the residues was carried out as follows. One gram of the acid treated material was boiled for ten minutes in 100 ml of 5% sodium carbonate solution. Subsequently, the reaction mixture was filtered, washed, dried and weighed. The dissolved material was considered "free" silica^{23,24}. The same experiment was carried out with an acid hydrolyzed highly active sample of antigorite as a reference.

Physical Measurements

XRD patterns were obtained by using a Rigaku rotaflex diffractometer equipped with DMAXB software and Ni-filtered Cu K_{α} radiation. ²⁷Al and ²⁹Si MAS NMR experiments were performed on a Varian 400 VXR solid state NMR spectrometer. A Bruker multinuclear MAS probe equipped with zirconia rotors was used for all the measurements. The ²⁹Si spin-lattice relaxation times (T₁) were determined by the inversion recovery method. A total of 12 scans were accumulated for each sample. The spinning rate was 4.2 kHz. The delay time was 600 sec which was 5 times as large as the largest T₁ of the ²⁹Si MAS NMR signals. Cross polarization experiments were carried out with delay times of 10 sec and contact times of 1000 ms. The delay time used for ²⁷Al MAS NMR was 10 seconds. Adsorption measurements were carried out on an Ominisorb 360cx Coulter instrument with nitrogen as the adsorbate at 77K. Surface areas were calculated according to the BET method. FTIR spectra were obtained on an IBM IR44 spectrometer by the KBr pressed pellet technique.

II.b.2 Results and Discussion

The HCl 20 wt% treatment was the more effective than either 40 wt% H₂SO₄ or the 50 wt% HNO₃ method for removing Mg²⁺ from phlogopite





Figure III.1 Percentage of magnesium depleted from phlogophite by reaction with different acids at 105 °C. The H+/Mg²⁺ ratio in each case was 5/1



samples (Figure III.1). The amount of Mg^{2+} depleted increased with treatment time. Table III.1 shows the correlation between the amount of Mg^{2+} released and the amount remaining in the residues when the clays were treated with 20% HCl. As shown in Figure III.1 almost all of the Mg^{2+} ions have been depleted in the first 4-6 hours of the treatment. Therefore, a prolonged treatment does not have much affect on the final product.

Table III.2 summarizes the surface areas of the phlogopite hydrolysis products. Owing to the acid treatment, the surface area of phlogopite was increased from 2 m²g⁻¹ to a maximum value of ~77 m²g⁻¹. The acid concentration, the treatment time and the reaction temperature have some effects on the surface area of the final product. The observed values of the surface area do not show a systematic trend for any variable studied. Keiski and Harkonen have reported the formation of a porous structure with a surface area of 620 m²g⁻¹ for phlogopite obtained as a hydrolysis byproduct in processing done at apatite mines in Siilinjarvi, Finland.¹ However the surface areas obtained in the present work were low when compared to Keiski and Harkonen. In our attempt to reproduce the work of Keiski and Harkonen with phlogopite from North Burgess, Ontario, Canada we obtained a surface area of only 32 m²g⁻¹ instead of the reported 620 m²g⁻¹.

The method of washing and drying the acid hydrolyzed product has no effect on the surface area of the final product (values are not shown in the table). This indicates that the low surface areas of acid hydrolyzed phlogopite is not a result of post treatments. The surface area of phlogopite residues obtained from 20 wt% HCl in the presence of hexadecyltrimethyl ammonium bromide was increased to ~ 50 m²g⁻¹



Table III.1 Percentage of Mg^{2+} depleted by 20 w% HCl and the Percentage retained in the phlogopite residues.^a

Reaction time (hours)	Mg ²⁺ depleted (%)	Mg ²⁺ retained (%)	
1	53	46	
2	66	29	
3	69	26	
4	87	9	
6	87	5	
7	88	. 2	
9	91	0.9	
11	94	0.4	
13	98	<0.06	
15	~100	~0	

^a Reaction was carried out at 105 °C, at a molar ratio of H⁺/Mg²⁺ of 5/1. The amounts of Mg²⁺ depleted were determined by chemical analysis of the filtrate and solid product, respectively.



compared to the value of $18 \text{ m}^2\text{g}^{-1}$ without the organic cation. This confirms that the lower surface area of phlogopite residues is due to a structure formed during the acid treatment.

Table III.2	BET surface	area of acid	hydrolyzed	phlogopite	samples	under
different con	ditions.(H+/N	$1g^{2+} = 5/1$				

Reaction time	S _{BET} (m ² g ⁻¹)			
(hours)	30%	20% HC1		
	At 80 °C	At boiling	At boiling	
		(105 °C)	(105 °C)	
0.25	-	7	-	
1.00	38	49	18	
3.00	30	30	-	
4.50	78	28	16	
6.00	12	57	14	
7.50	25	-	16	
12.00	45	-	14	
48.00	29	-	-	
72.00		18	11	


The X-ray diffraction pattern of hydrolyzed phlogopite varies as a function of the acid hydrolysis time; the longer the treatment time the lower the crystallinity of the final product. The products obtained after reaction times of fifteen hours were largely amorphous (Figure III.2).

The X-ray diffractograms of phlogopite residues obtained by treating at 105 °C with 20% HCl for six hours in the presence of n-alkylammonium ions indicated a higher degree of crystallinity than those obtained in the absence of n-alkylammonium cations. This can be explained by considering a better orientation of clay particles with the help of interactions with intercalated cations. Even though the d-spacing is very high (36.8 Å) for the residues obtained in the presence of n-alkylammonium cations, upon washing with deionized water the spacing returns to values comparable to that of the original sample (~9.6 Å). This suggest that the alkylammonium cations exist as ion pairs, not electrostatically bound within the clay layers.

However, the X-ray diffractograms of phlogopite residues after reaction with the AlCl₃/OH, Al₁₃ oligomer or n-decylamine did not show any increase in d-spacing, indicating a failure of intercalation. This again proves that the cation exchange capacities of the product are extremely low or zero.

The FTIR spectra of acid-hydrolyzed phlogopite residues were virtually indistinguishable from each other. Bands at ~535 cm⁻¹ due to the stretching vibration of Mg-O, ²⁵ were not found, an indication of the complete removal of Mg²⁺ from the octahedral sheets (Figure III.3). Bands at ~1168, ~1094, ~800 and ~470 cm⁻¹ were feature typical of four-coordinated silica^{25,26}. Bands near 800 cm⁻¹ can be due to either Si-O or





Figure III.2 XRD spectra showing the change in crystallinity upon acid hydrolysis of phlogophite with 20% HCl.





Figure III.3 FTIR spectra of, Top: Untreated phlogophite, Bottom: Acid hydrolyzed phlogophite formed by reaction with 20% HCl for 6 hours at boiling (105 °C).



Al-O bonds. The OH stretching vibrations of Si-OH and H₂O was observed near 3400 cm⁻¹ and H₂O bending was found near 1630 cm⁻¹. There was a shift in the IR SiO bands of acid hydrolyzed products compared to those of untreated samples. This may be due to the structural changes in the basic silicate unit, such as the condensation of Si-OH groups to form Si-O-Si bonds²⁵.

Figure III. 4 shows the 29 Si MAS NMR spectra of acid hydrolyzed phlogopite formed by reaction with 5%, 10% and 30% nitric acid for 1 hour at 80 °C. NMR peak assignments are very similar to those for acid treated antigorite. The first peak at -86 ppm is assigned to Q³ Si sites of the parental clay. The peak at -103 ppm can be assigned to Q³ HOSiO₃ groups and the peak at -112 ppm is indicative of Q⁴ Si. The Q³ assignment can be verified by CP- 29 Si MAS NMR as shown in Figure III.5. There is a reasonable enhancement in intensity of the -103 ppm resonance under cross polarization conditions. The Q⁴ SiO₄ sites could be either in the layer or in the amorphous form.

Figure III.6 shows the ²⁹Si MAS NMR spectrum of a 20% HCl acid hydrolyzed phlogopite sample after 1 hour at the boiling temperature. Figure III.7 shows the ²⁷Al MAS NMR of the same sample. The ²⁷Al spectrum shows only tetrahedral sites, suggesting that the tetrahedral sites in the starting material are still intact after acid hydrolysis. This sample shows predominantly Q⁴ SiO₄ sites and a shoulder due to Q³ HOSiO₃ sites that is not well resolved from the peak due to Q³ HOSiO₃ groups. But this sample is X-ray crystalline. Also, it retained ~47% of octahedral magnesium. From the presence of a FTIR band at 535 cm⁻¹ it is clear that Mg ions are still in the octahedral sites. The BET surface area of this sample is 18 m²g⁻¹. At



Figure III. 4 ²⁹Si MAS NMR spectra of phlogophite acid hydrolyzed for 1 hour at 80 °C. a. 5% HCl, b. 10% HCl, c. 30% HCl.





Figure III.5 ²⁹Si CP/MAS NMR spectrum of acid hydrolyzed phlogophite formed reaction with 20% HCl for 1 hour at boiling temperature (top), ²⁹Si MAS NMR spectrum of acid hydrolyzed phlogophite formed by reaction with 20% HCl for 1 hour at boiling temperature (bottom).





Figure III.6 ²⁹Si MAS NMR spectrum of acid hydrolyzed phlogophite formed by reaction with 20% HCl for 1 hour at boiling temperature.





Figure III.7 ²⁷Al MAS NMR spectrum of phlogophite acid hydrolyzed with 20% HCl for 1 hour at boiling temperature.



this point it is very hard to explain why the sample does not exhibit a Q^3 resonance indicative of the unhydrolyzed fraction of phlogopite with Mg in octahedral sites. Protons may affect most of Mg cations still present in the octahedral sites of clay with weakened Mg-O bonds, may shift the parent NMR peak to a more negative value. It is also difficult to explain the crystalline structure of the product when the NMR exhibits predominantly Q^4 Si sites. There is no question that Q^4 Si is derived from the dehydroxylation of the two -OH groups of Q^3 . This dehydroxylation could happen either in the same tetrahedral layer or with the tetrahedral layer formed, because of the octahedral hydrolysis. This latter process should take place in selected areas because the inter layer cations (protons at this stage of hydrolysis instead of potassium cations in the starting clay) bind to the tetrahedral layers of each sheet of clay (see product 3 in Figure III.8). The dehydroxylation by condensation of SiOH groups in the same layer is unlikely to occur for reasons already discussed in section II.d. However, there is a remote possibility of a condensation reaction(see product 2 in Figure III.8). In this situation voids formed between the tetrahedral sheets would not let nitrogen penetrate. Limited surface area can be expected for either condensation process.

Product 1 shown in Figure III.8 is an amorphous silica with a random arrangement of distorted clay fragments. The small increase in the surface area could be due to the formation of this amorphous silica. The mixed structures proposed in Figure III.8 would afford a totally amorphous structure upon prolonged acid treatment.

Table III.3 shows the free silica content (as determine by dissolution with Na_2CO_3 solution^{23,24}) and the cation exchange capacities for both acid





Figure III.8 Proposed mechanism for acid hydrolysis of phlogophite.



hydrolyzed phlogopite and antigorite. Although both mineral products contain the same amount of free silica, they show completely different surface areas. Therefore, the "free" silica argument used by many early workers to explain the higher surface area in acid treated clays is not really accurate.

Table III.3 Free silica content and BET surface area for different acidhydrolyzed reaction products.

Acid hydrolyzed sample ^a	wt% of free silica	BET surface area
Phlogopite	80.7	14
Antigorite	80.7	270

^a Hydrolyzed with 20 wt% HCl for 6 hours at boiling temperature $(H^+/Mg^{2+}=5)$. Antigorite product treated with the same experimental conditions is included for comparison

IR, NMR and elemental analysis for acid treated phlogopite show the disappearance of Mg^{2+} ions in the octahedral sheet and the formation of Q^4 units. The formation of Q^4 units arises from the condensation of Si-OH groups. When 100% removal of Mg^{2+} occurs mostly Q^4 units are formed and result is an amorphous SiO₂ structure. Other 2:1 clays (Smectites, Vermiculite) are known to yield active materials upon acid hydrolysis.²⁻²² Micas do not exhibit any swellable properties as a result of a high negative



layer charge because the layers are bound tightly to each other via positive cations, giving no access to acid protons. Mica does not bear any special structural features like eight membered rings with inverted tetrahedra as does antigorite. It is clear that the only possible acid attack is through edges. As soon as the octahedral cations become hydrolyzed, the remaining silicon tetrahedra rearrange to give the silica structures discussed above through the dehydroxylation of two -OH groups (Figure III.8). In an effort to prevent this dehydroxylation, acid hydrolysis was carried out in the presence of nalkylammonium cations. But this approach was unsuccessful . Another option was to substitute -OH groups with F to obtained F-phlogopite and carry out the acid hydrolysis. This approach also was not successful in forming high surface area products.

III.c Acid Hydrolysis of Fluorohectorite and Pillared Fluorohectorite

III.c.1 Experimental

Starting Material

The idealized structure of a fluorohectorite clay is the same as that shown in Figure I.6. The octahedral layer consists of Mg²⁺ and Li⁺ cations while the tetrahedral layers consist of only Si⁴⁺ cations. Since the layer charge is 1.2e⁻ per Si₈O₂₀F₄ unit the gallery cations are less tightly bound to the negatively charged layers compared to mica clays. These cations could bear a layer or two of hydrated water and possess layer expanding capability. The larger particle size (2000 Å) and the large aspect ratio of fluorohectorite make the material degassed at 150 °C under vacuum non porous. The external BET surface area is only 3 m²/g. As shown in Table I.1 the chemical formula is Na⁺1.2 H₂O[Mg_{4.8}Li_{1.2}] (Si₈)O₂₀(F)₄.



The starting material was obtained from Corning, Inc. as a 10% suspension. The concentration of this dense liquid was determined by air drying a known quantity of suspension and weighing the residue. All the calculations for acid treatments are based on this concentration. Acid hydrolysis was carried out using 0.5M hydrochloric acid at 60 °C. Five times the stoichiometric amounts of acids were used to facilitate dissolution of the Mg²⁺ and Li⁺ cations. Pillaring of fluorohectorite was done according to Pinnavaia and coworkers with Chlorhydrol[®] as the pillaring agent.²⁷

Physical Measurements

XRD patterns were obtained by using a Rigaku rotaflex diffractometer equipped with DMAXB software and Ni-filtered Cu k_{α} X-ray radiation. ²⁷Al and ²⁹Si MAS NMR experiments were performed on a Varian 400 VXR solid state NMR spectrometer. A Bruker multinuclear MAS probe equipped with zirconia rotors was used for all the measurements. The ²⁹Si spin-lattice relaxation times (T₁) were determined by the inversion recovery method. A total of 12 scans were accumulated for each sample. The spinning rate was 4.2 kHz. The delay time was 600 sec, 5 times as large as the largest T₁ of ²⁹Si MAS NMR signals. Adsorption measurements were carried out on an Ominisorb 360cx Coulter instrument by using nitrogen as the adsorbate at 77K. Surface areas were calculated according to the BET method.



III.c. 2 Results and Discussion

Acid Hydrolysis of Fluorohectorite

Figure III.9 shows the X-ray diffraction powder patterns of acid treated fluorohectorite samples. It is clear that no crystallinity retained after a 2 hour acid treatment. But the samples treated for only 0.5 hour and 1 hour show a reasonable crystallinity in their residues. Table III.4 shows the Mg% depleted and the BET surface areas of the different acid treated samples examined. The BET surface area of fluorohectorite increased dramatically from the parent clay value of $3 \text{ m}^2\text{g}^{-1}$ to $111-208 \text{ m}^2\text{g}^{-1}$ upon acid treatment that depleted 36%-83% of the octahedral Mg, respectively. Analogous observations were reported for bentonite^{4,5} and vermiculites^{2,3} with acids at elevated temperatures. In all these literature reports as well as in the present study, the crystallinity of smectite clays decreases with the acid treatment while the BET surface area increases.

This relationship between crystallinity and surface area for smectite clays is completely different from what we observed with all the other types of clays examined. Acid treatment of antigorite shows a maximum value of surface area with retention of same crystallinity (Chapter II). For phlogopite the surface area never increased substantially with the decrease of crystallinity (Section III.b). Very recently Brown and Rhodes reported a maximum in surface area of $325 \text{ m}^2\text{g}^{-1}$ with the acid treatment of montmorillonite (bentonite) (Figure III. 10 and 11).²⁸ No explanation for the observation of an unusually high surface area was provided in their report. The maximum value of surface area and the XRD given suggest that





Figure III.9 XRD spectra of fluorohectorite acid hydrolyzed with 0.5M HCl at 60 °C.





Reaction time (hours)	Mg% depleted	BET surface area (m ² g ⁻¹)	
	(for unpillared samples)	Fluorohectorite	Pillared fluorohectorite
0.0	0	3	250
0.0	, i i i i i i i i i i i i i i i i i i i		
0.5	36	111	124
1.0	62	201	83
2.0	83	208	-

Table III. 4 BET surface area of acid hydrolyzed fluorohectorite (0.5MHCl at 60 °C)

a new porous crystalline structure is formed, but disappears upon prolonged hydrolyzing. The difference between Brown and Rhodes acid treatment and that of others is that their treatment is shorter because a higher acid concentration and higher hydrolysis temperature are used. The concept of free silica formation upon acid hydrolysis as proposed by many earlier workers has to be ruled out because in any of these acid treatments the ultimate product is amorphous silica. In other words the very large surface area observed suggests that surface area depends on the silica structure formed. Since the acid reaction is fast, there is limited time for clays to undergo side reactions such as dehydroxylation. Figure III. 12 shows the ²⁹Si MAS NMR spectra of acid hydrolyzed fluorohectorite. Very similar spectra were obtained by Brown and Rhodes for acid hydrolyzed bentonite III.13).28(Figure NMR peak assignments very are





Figure III.10 Dependence of BET surface area and CEC of montmorillonite on time of acid hydrolyzing.²⁸

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Figure III.11 XRD patterns of montmorillonite, following progressive acid treatment. (a) 0, (b) 1, (c) 5 and (d) 15 min.²⁸




Figure III.12 ²⁹Si MAS NMR spectra of fluorohectorite acid hydrolyzed with 0.5M HCl at 60 °C.





Figure III.13 ²⁹Si MAS NMR spectra of (a) untreated and progressively acid-treated [(b) 15 min., (c) 20 hours] montmorillonite.²⁸



similar to those of acid treated antigorite and acid treated phlogopite. The first peak at -93.3 ppm is characteristic of the O^3 Si sites of the parent clay. The peak at -103 ppm can be assigned to Q^3 Si with -OH groups and the peak at -112 ppm assigned to Q⁴ Si. These Q⁴ Si could be either in the clay layer or in an amorphous form. The structure and the properties of these products varied with the starting clay and its properties. It is clear that hydrolysis of fluorohectorite requires very mild acid conditions compared to antigorite and phlogopite. In other words F-hectorite is less stable towards acid than other clays. Neither mica (phlogopite) nor serpentines (antigorite) has swellable galleries in aqueous media, but smectites (fluorohectorite) are swellable. This expanded gallery in both sides of the clay layer enhances the acid attack through hexagonal cavities of the clay layer (Figure III.14). Since every single sheet is attack in fluorohectorite it is less stable towards acids. In other words, in fluorohectorite the acid depletion mechanism takes place simultaneously through out the whole clay particle whereas in phlogopite the hydrolysis occurs by an edge-hydrolyzing mechanism. This difference in swelling properties results in a higher surface area for acid hydrolyzed fluorohectorite but not for acid hydrolyzed phlogopite.

¹⁹F MAS NMR spectroscopy provides further important insights into the structural consequences of fluorohectorite hydrolysis. Spectra for representative reaction products are shown in Figure III.15. The presence of two resonances agrees with earlier studies of fluorinated 2:1 structures (Butruille *et al.*, 1993; Huve *et al.*, 1992)^{29,30}. The upfield line at -16 ppm arises from fluorine atoms triply bridging a positively charged triad of edge shared octahedra occupied two Mg²⁺ ions and one Li⁺ ion. The lower field resonance (-11 ppm) is assigned to fluorine atoms bridging a neutral triad of





Figure III.14 A cartoon showing the possible acid attacking sides of fluorohectorite.



Figure III. 15 19 F MAS NMR spectra of acid hydrolyzed fluorohectorites at different levels of Mg²⁺ depletion.



octahedra filled by three Mg²⁺ ions. In the pristine mineral the two lines are of nearly equal intensity, in accord with the unit composition Li+12 $[Mg_4 gLi_{1,2}]Si_8O_{20}F_4$. Upon depletion of Mg^{2+} from the octahedral sheet the intensities of the two 19F resonances decrease due to HF formation, but the relative intensities remain unchanged up to a Mg²⁺ depletion level of 62%. That is, fluorine and magnesium hydrolysis occur concomitantly, and the rates of Mg²⁺ depletion from charged and neutral octahedral triads are equal. However, as the extent of Mg²⁺ hydrolysis nears the 80% level, the charged triads are preferentially hydrolyzed, as judged by the unequal intensities of the fluorine lines (cf., Figure III.15). Depending on the extent of hydrolysis, BET surface areas up to 208 m^2/g are found for fluorohectorite reaction products, whereas values less than 20 m²/g are observed for products derived from phlogopite. These differences cannot be attributed to differences in the acid concentrations used in the hydrolysis reactions. Low surface area products also are formed from phlogopite upon reaction with 0.5 M HCl Moreover, these important differences cannot be attributed to differences in reaction mechanism.

For the structural reasons already discussed, non-swelling phlogopite should hydrolyze primarily by an edge attack mechanism, whereas swelling fluorohectorite is potentially capable of undergoing hydrolysis by proton edge attack and/or gallery access mechanisms. However, the ¹⁹F NMR results provide strong evidence for acid hydrolysis occurring primarily, though not exclusively, through an edge attack mechanism even in the case of the smectite clay. Butruille et al. (1993)²⁹ have shown in ¹⁹F NMR studies of pillared fluorohectorites that the fluorine atoms bridging positively charged Mg2Li triads in the octahedral sheet react with gallery water



molecules through the dioctahedral cavities and become replaced by hydroxyl groups. In contrast, the fluorines bridging neutral Mg3 triads are stable toward displacement by hydroxyl groups. Thus, if Mg^{2+} hydrolysis occurred by a gallery access mechanism, we should expect the NMR lines for the two types of fluorine environments to decrease at different rates. Instead, we find that the two resonances decrease at essentially equal rates up to a Mg^{2+} depletion level of 62% (cf., Figure III, 15). This result is in complete accord with proton attack at edge - site oxygen atoms of the octahedral sheet. At a Mg^{2+} depletion of 83%, however, the -16 ppm resonance for the fluorines bridging Mg2Li triads decreases more rapidly than the -11 ppm line, thus signaling the participation of a gallery access mechanism. However, edge attack remains the primary Mg2+ depletion mechanism with at least two-thirds of the total structural Mg^{2+} being replaced by this pathway. It is not clear why the gallery access is manifested at the later stages of Mg^{2+} depletion. Perhaps the gallery access path is facilitated by the structural disorder and reduction in layer charge density caused by proton edge attack.

Since the hydrolysis reactions of fluorohectorite and phlogopite occur primarily through equivalent pathways, one is unable to attribute the differences in surface areas to structural effects caused by different reaction mechanisms. Instead, the swelling properties of the starting 2:1 structure most likely plays a central role in establishing the textural properties of the amorphous hydrolysis products. Hydration of the protonated fluorohectorite galleries separates the 2:1 layers during hydrolysis. We propose that the gallery water and protons serve in part to lower the bulk density of the silicate phase formed by the crosslinking of the residual tetrahedral sheets.

The second

As shown schematically in Figure III. 16, both surfaces of the evolving silicate layer can be efficiently solvated during the hydrolysis reaction. In contrast, the non-swelling phlogopite is relatively limited in its ability to mediate the texture of the hydrolysis product through solvation (cf., Figure III. 16). Consequently, the surface areas of the phlogopite hydrolysis products are much lower than those formed from fluorohectorite.

Acid Hydrolysis of Pillared Fluorohectorite

In order to monitor the rapid Mg depletion process from fluorohectorite, alumna pillared fluorohectorite calcined at 350 °C was hydrolyzed under the same reaction conditions. The main idea behind the experiment was to limit the acid attack on clay layers since there are tightly bound pillars in between clay sheets. As shown in Table III.4 the BET surface areas reported for acid hydrolyzed pillared fluorohectorite are 124 and 83 m²g⁻¹ for samples hydrolyzed for 0.5 hour and 1.0 hour respectively. These values are substantially from the ~250 m²g⁻¹ BET surface area of the starting pillared fluorohectorite. The reason the surface area is lower than that of the pillared clay becomes clear when the 001 d-spacing reported in Table III.5 is considered. The lowered-spacing between sheets in pillared hydrolyzed samples explains the lower surface area. This surface area decrease could result from hydrolysis of the pillar before the clay sheets hydrolyze. A lower surface area for the hydrolyzed pillared acid hydrolyzed samples than for unpillared hydrolyzed samples confirms that the pillars inhibit the acid attack from the galleries and clearly confirms the acid hydrolysis mechanism proposed for the smectite clays.





Figure III. 16 Schematic illustration of solvation effects on the textures of silicate products formed in the acid hydrolysis of swelling and non - swelling 2:1 structures. Open circles represent water molecules.



The idealized structure for highly active fluorohectorite should be very similar or the same as that of montmorillonite postulated by Thomas, Hickey and Stecker (Figure III.17).³¹

 Table III. 5 Basal spacing for different F-hectorite samples.

Sample	001 d-spacing (Å)
F-hectorite	14.7
Al pillared F-hectorite	18.5
F-hectorite acid treated for 0.5 h*	17.0
F-hectorite acid treated for 1.0 h*	16.0

* 0.5M HCl treated at 60 °C





Figure III.17 The idealized structure of acid activated montmorillonite as postulated by Thomas, Hickey and Stecker.³¹



Conclusions

1. Acid hydrolysis of phlogopite increases the surface area from 2 m^2 g⁻¹ to a maximum value of 77 m² g⁻¹ at 87% Mg depletion. Acid hydrolysis is truly an edge hydrolysis diffusional mechanism.

2. Fluorohectorite is more sensitive towards acid hydrolysis than other silicates studied. The final product exhibits a substantially higher surface area (208 m² g⁻¹) compared to the starting surface area of F-hectorite (3 m² g⁻¹). Acid attack occurs both through the basal surface (hexagonal cavities) and the edge sites of the layer.

3. The general mechanism for the depletion of metal ions from the octahedral sheet of 2:1 layered structures involves proton attack at the edges of the layers. Evidence for edge attack is provided in part by the dependence of hydrolysis rates on the particle size of a non-swelling clay. However, the possibility of hydrolysis occurring by proton attack through the ditrigonal cavities of the basal surfaces also has been recognized in the case of swelling smectite clays, wherein protons can easily occupy the gallery surfaces by ion exchange. Figure III. 18 schematically illustrates these two available pathways for Mg²⁺ hydrolysis from trioctahedral 2:1 structures.

Depletion of octahedral Mg occurs starting from edges of the clay particle as it would expect in talc and mica clays. But fluorohectorite gives a high surface area comparable to palygorskite, sepiolite and smectites unlike mica or talc. According to the present work and the early work done in area of acid hydrolysis of clay minerals, three different categories of minerals can be identified depending on their behavior towards the acids. 1) Swellable clay minerals including vermiculite give high surface area upon acid treatment, 2) Nonswelllable clays give no or little surface area with acid treatment (talc, phlogopite), 3. Nonswellable clays with special porous structures give higher surface areas (sepiolite, palygorskite).







Figure III.18 Schematic illustration of the depletion of octahedral Mg²⁺ from 2:1 layered silicates by proton edge attack and gallery access mechanisms.



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