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Department of Economic Geology and Geochemistry

***Thesis: Bentonite as an industrial mineral
and comparison between Greek and
Northern American Bentonite***

Author:
Dimitriou Aikaterini
1114201500024

Supervisor:
Stamatakis Michael



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Abstract

The aim of the study is to compare two different bentonite types, one from Kimolos, Greece and one from Wyoming, USA, in order to determine their similarities or differences.

Kimolian bentonite appears to be usually white or very light gray than Wyoming one, which is dark gray. Furthermore, Kimolian is a Ca/Mg bentonite and Wyoming one is a natural Na bentonite.

Both of them have the same genetic type which is the alteration of volcanic ash by heating the water of shallow basins in alkaline marine or lacustrine environments, but it took place in Cretaceous times (Late Albian to early Cenomanian), in Wyoming and in Lower Pleistocene, in Kimolos. In Wyoming the bentonite beds occur in the same cyclic sedimentary sequence which, from bottom to top, comprises shale, coal, bentonite, and finally shale grading to sandstone and conglomerate (*Slaughter and Earley, 1965*). While in Kimolos, bentonite is formed from the unwelded Prassa ignimbrite, the alteration (hydrothermal activity) being structurally controlled.

In the framework of the research for the characterization of the bentonite deposit of Kimolos and Wyoming, FT-IR, Atomic Absorption, Ion chromatography, Thermal analysis, Loss of Ignition (LOI), X-ray fluorescence (XRF), X-ray diffractometer (XRD) – Rietveld, Methylene Blue Test - CEC and Percentage of Carbon and Sulfur presence analysis were executed for specific samples.

Περίληψη

Σκοπός της συγκεκριμένης πτυχιακής εργασίας είναι η σύγκριση δύο διαφορετικών τύπων μπεντονίτη, ενός από την Κίμωλο, Ελλάδα και ενός από το Γουαϊόμινγκ, ΗΠΑ, με στόχο την εύρεση ομοιοτήτων και διαφορών.

Ο μπεντονίτης της Κιμώλου εμφανίζεται κυρίως λευκός ή σε αποχρώσεις πολύ απαλού γκρι, ενώ αντιθέτως του Γουαϊόμινγκ, σκούρο γκρι. Επιπλέον, ο μπεντονίτης της Κιμώλου είναι ασβεστομαγνησιούχος, ενώ του Γουαϊόμινγκ, νατρούχος.

Και οι δύο μπεντονίτες παρουσιάζουν τον ίδιο γενετικό τύπο, που χαρακτηρίζεται από την εξαλλοίωση της ηφαιστειακής τέφρας, λόγω θέρμανσης του νερού των ρηχών λεκανών σε αλκαλικά θαλάσσια ή λιμναία περιβάλλοντα. Όμως αυτό το γεγονός έλαβε χώρα στο Γουαϊόμινγκ στο Κρητιδικό (Κατώτερο Άλβιο – Ανώτερο Κενομάνιο), ενώ στην Κίμωλο στο Κατώτερο Πλειστόκαινο. Στο Γουαϊόμινγκ, τα στρώματα μπεντονίτη εμφανίζουν την ίδια κυκλική ακολουθία ιζηματογένεσης, η οποία, από κάτω προς τα πάνω, περιλαμβάνει σχιστόλιθο, γαιάνθρακα, μπεντονίτη και τελικά σχιστόλιθο που μεταπίπτει σε ψαμμίτη και κροκαλοπαγές. (*Slaughter and Earley, 1965*) Ενώ στην Κίμωλο, ο μπεντονίτης σχηματίζεται από την δομικά ελεγχόμενη υδροθερμική εξαλλοίωση του Ιγνιμβρίτη Πρασσών.

Στα πλαίσια της έρευνας για τον χαρακτηρισμό του μπεντονίτη της Κιμώλου και του Γουαϊόμινγκ ήταν απαραίτητες οι εξής αναλύσεις, Φασματοσκοπία FT-IR, Ατομική απορρόφηση, Χρωματογραφία ιοντοανταλλαγής, Θερμική ανάλυση, απώλεια πύρωσης (LOI), φθορισμός ακτινών X (XRF), Περίθλαση ακτινών X (XRD) – Rietveld, Δοκιμή ιοντοανταλλακτικής ικανότητας με Κυανό του Μεθυλενίου και ποσοστό Άνθρακα - θείου.

Introduction

Bentonite is an absorbent aluminum phyllosilicate clay consisting mostly of montmorillonite $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot v\text{H}_2\text{O}$ (in percentage greater than 80%). This term was proposed by Wilbur C. Knight in 1898 after the Benton Shale near Rock River, Wyoming.

Bentonite defined by its origin as a rock composed essentially of a crystalline clay-like mineral formed by devitrification and the accompanying chemical alterations of a glassy igneous rock material, usually a tuff or volcanic ash. It often contains variable proportions of accessory crystal grains that were originally phenocrystals in the volcanic glass. These are feldspar (commonly orthoclase and oligoclase), biotite, quartz, pyroxenes, zircon, and various other minerals typical of volcanic rocks. The characteristic clay-like mineral has a micaceous habit and facile cleavage, high birefringence and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite, but less often beidellite (*Ross and Shannon 1926*).

However, many deposits that don't have volcanic origin such as montmorillonite-rich deposits are mined and sold as bentonite. Therefore, commercially, bentonites are defined exclusively on a mineralogical basis.

If the content of montmorillonite is low, the material is called bentonitic clay. In order to have commercial value, the percentage of montmorillonite should be greater than 50%.

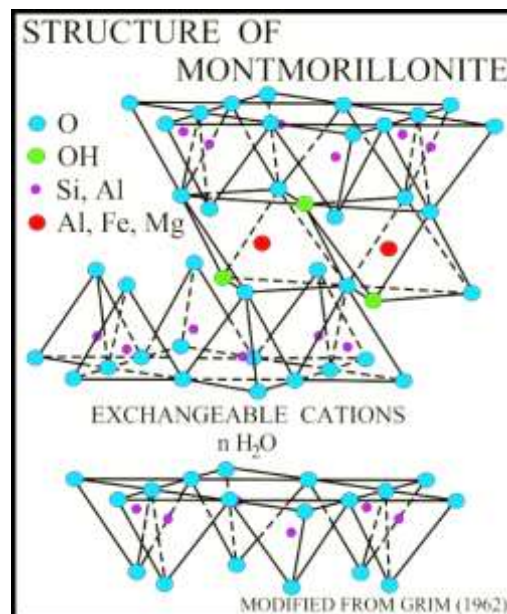
Bentonite, has many different types which are named after the respective dominant element and categorized as potassium (K), sodium (Na), calcium (Ca), magnesium (Mg) and hydrogen (H^+).

Bentonites are also classified, based on their interlayer cations and corresponding ability to swell in water, as high swelling (sodium), non-swelling (calcium) and medium swelling.

Mineralogy

Bentonite's predominant mineral component is smectite. It consists mainly of one or more members of the smectite group minerals (montmorillonite, beidellite, hectorite, nontronite, saponite, pyrophyllite, talc, sauconite). Montmorillonite is the dominant smectite mineral in bentonite. The structure is similar for all the minerals in the smectite group but the chemical composition is different for each mineral.

The structure of the smectite minerals is composed of two silica tetrahedral layers, enclosing an octahedrally coordinated aluminum oxide layer. These layers are separated by an interlayer space containing exchangeable ions and water molecules.



General formula of smectite group: $X_{(0,7)} Y_{(4-6)} Z_{(8)} O_{(20)} (OH)_4 nH_2O$

The smectite group-minerals are divided into two subgroups, dioctahedral $\{X^{u+v+z} [(Al_x Fe_y Mg_z)_2 (Si_{4-(u+v)} Fe_v Al_u) O_{10} (OH)_2] nH_2O\}$ when two octahedral sites are occupied and trioctahedral $\{X^{z+u} [(Mg_{3-z} Li_z)_2 (Si_{4-u} Al_u) O_{10} (OH)_2] nH_2O\}$ when three are occupied.

{ X^+ : exchangeable cations}

Mineral	Z tetrahedral	Y octahedral	X interlayer
Dioctahedral			
Pyrophyllite	Si ₈	Al ₄	
Montmorillonite	Si ₈	Al _{3,3} Mg _{0,7}	(1/2Ca,Na) _{0,7}
Beidellite	Si _{7,3} Al _{0,7}	Al ₄	(1/2Ca,Na) _{0,7}
Nontronite	Si _{7,3} Al _{0,7}	Fe ³⁺ ₄	(1/2Ca,Na) _{0,7}
Trioctahedral			
Talc	Si ₈	Mg ₆	
Saponite	Si _{7,2} Al _{0,8}	Mg ₆	(1/2Ca,Na) _{0,8}
Hectorite	Si ₈	Mg _{5,3} Al _{0,7}	(1/2Ca,Na) _{0,7}
Sauconite	Si _{6,7} Al _{1,3}	Zn ₄₋₆ (Mg,Al,Fe ³⁺) ₂₋₀	(1/2Ca,Na) _{0,7}

Table 1: Compositional variation in the smectite family of minerals
Source: D.A.C Manning, *Introduction to Industrial Minerals*, 1995, pg 64.

The substitution of elements within the sheets is responsible for the unique physical and chemical properties. The number and type of the substitutions are responsible for the magnitude and distribution of surface charge. A substitution between a higher charged cation with a lower one creates a negative layer charge net, which has loosely held surface cations, which are easily exchangeable.

The prevalent exchangeable cations in smectite are sodium (Na), calcium (Ca), magnesium (Mg), potassium (K) and hydrogen (H⁺). This ability to exchange cations is called Cation Exchange Capacity (CEC) and the unit of measurement is milliequivalents per 100g of clay (meq/100g). Smectite's CEC varies between 60 and 170 meq/100g and the most common values vary between 100 and 120 meq/100g.

CEC of bentonite is affected by these factors: pH, iron presence and Eh, which is responsible for changes in iron's oxidation state.

Other minerals that can be found in bentonite are divided into three categories:

1. **minerals with volcanic origin:** feldspars, biotite, quartz, apatite, zircon, magnetite, amphibolites and volcanic glass.
2. **secondary minerals that form in situ as a result of diagenesis and weathering:** opaline silica, zeolites, calcite, gypsum, iron, sulfate and oxide minerals. Also clay minerals like kaolinite and illite.
3. **minerals with detrital origin:** rock-forming minerals that are found in sedimentary environments. They are rarely greater than 10% of a high profitable deposit.

Properties

Smectites have a minor crystal size, usually less than 1 μm. They have high exchange ability of cations and they are swelling, when they are mixed with water or other fluids. This happens because the bentonite is dispersed into colloid particles with minor size (1-100 μm) and it swells up to about 15-30 times the original dry bulk volume without agitation. Therefore, the liquid develops higher viscosity, suspending power and thixotropy.

Bentonitic clays have high adsorption (the ability to attract and hold ions or molecules of gas and liquid) and absorption (the ability to assimilate or incorporate material). When calcined, all clays have a large pore volume and surface area and can take up liquids rapidly to 200% or more of their own weight. (*Mayhew et al.1979*)

The original adsorbent was fuller's earth – either calcium montmorillonite or attapulgite.

Hectorite presents higher ability of shrinking and swelling, once the surface area gets bigger or the cation exchange ability gets higher.

Saponite presents mediocre cation exchange ability but very high catalytic and infiltrative properties.

Properties of bentonite depending on the respective dominant element

Potassium: or Metabentonite (low grade metamorphosis) which appears at Ordovician or Paleozoic rocks. It is composed mainly of illite and mixed clays. Smectite minerals are found in minor amounts.

Sodium: - high swelling capability
- stable at temperatures above 400 °C
- excellent plasticity, dry-bonding strength
- high shear and compressive durability
- impermeability
- low grade compressibility and consolidation
- pH=8-10

Calcium: - low swelling capability
- decomposed at temperatures above 400 °C
- calcium bentonite is treated with sodium carbonate (Na_2CO_3) in order to be transformed into Sodium Bentonite, who has higher swelling capability
- also calcium bentonite is treated with H_2SO_4 to transform its crystalline structure into a porous Al-Si material, in order to increase the surface area of the granules and the volume of the gaps. This treatment increases the absorbent capability of the bentonite.
- pH=8-10

Magnesium: - non-swelling in their natural form

Hydrogen: - near-surface exposures
- non-swelling
- when dissolved in water, they produce pH=4

Occurrence

Most of the bentonites are created by tuff and volcanic ash alteration. Although some deposits are created by hydrothermal alteration of volcanic or igneous rocks, and some other consisting from pure smectite that has been transferred. The parent rock type is mostly siliceous and ranged from dacitic and rhyolitic composition.

Bentonites can occur in both marine and nonmarine environments. The age range is between Jurassic and Pleistocene. They are found as beds that can have an extensively geographic range and are usually parallel with the overlay and the underlay bed. These beds can have different thickness from several centimeters to tens of meters. Also they are developed as small lens with diameter only a few tens of meters.

They are found in a variety of colors, the most common are gray, yellow, olive green, brown, gray-blue and white when they have high levels of humidity and get lighter when they are dry. The change of color near the surface happens due to oxidization of iron. Furthermore they have

a soapy texture and wavy appearance, but the texture changes depending on the type of the bentonite. Weathered calcium one display an “alligator skin” texture and sodium one, a “pop-corn” texture, this is particularly because of the repeated swelling and drying of the bentonite.

Distribution of deposits

<i>Deposits</i>	Locations	Type/ Characteristics
<i>United States</i>		
<i>Western/ Wyoming Bentonite</i>	Wyoming, Montana, South Dakota	Sodium
<i>Southern/ Calcium Bentonite</i>	Texas, Mississippi, Alabama, Gulf coast	Calcium
<i>Fuller’s Earth</i>	Mississippi Embayment, Missouri, San Joaquin Valley near Taft (California), Monterey Formation, Hawthorne Formation near Ocala (Florida) and the Twiggs Clay Member of Barnwell Formation near Wrens (Georgia)	Minerals: Calcium-magnesium smectite, opal C-T, kaolinite, illite and trace of halloysite and clinoptilolite
<i>Hectorite</i>	Hector (California), Amargosa Valley (Nevada), West of McDermitt (Nevada)	<u>Hector</u> : altered alkaline lake sediments <u>Amargosa Valley</u> : 25% hectorite and 75% calcium carbonate <u>West of McDermitt</u> : pure to impure hectorite beds and lenses that contain volcanic sediments, zeolites and carbonates
<i>Other</i>	Near Chambers (Arizona), near Vici (Oklahoma), near Adrian (Oregon), Utah	Chambers and Vici: desiccant bentonites Adrian: sodium
<i>Canada</i>	Alberta, Manitoba, British Columbia, Saskatchewan, Northwest Territories	Calcium (Saskatchewan: Sodium)
<i>Mexico</i>		Hildago: Calcium Durango: Sodium
<i>South America</i>		
<i>Brazil</i>	Minas Gerais, Rio Grande Sul, Santa Catarina, Pariba, Parana, Sao Paulo	Not commercially viable because of high percentage of non-clay minerals
<i>Argentina</i>	La Pampa, San Juan, Mendoza, Neuquen, Rio Negro	Sodium
<i>Peru</i>	Callao, Ica, Piura	Dominant: Calcium Piura: natural Sodium
<i>Chile</i>	Bocanegra	Calcium Acid-activated: Lima
<i>Europe</i>		
<i>United Kingdom</i>	Bedfordshire, Oxfordshire, Surrey	Calcium
<i>Germany</i>	Bavaria, Mainburg, Mossburg, Lanshut	Calcium
<i>Greece</i>	Milos, Kimolos, Lesvos, Chios, Mesti-Sikorachi Evrou	

<i>Italy</i>	Sardinia	Hydrothermal alteration of trachytes and trachytic tuffs
<i>Spain</i>	Madrid, Almeria	Calcium, natural Sodium and Sodium exchanged bentonites
<i>Turkey</i>		White, desiccant-grade calcium
<i>Africa</i>	Morocco (southwest Nador) Koppies district of the Free State and the Heidelberg area of Western Cape, KwaZulu-Natal Province.	
<i>Australia</i>	Queensland and Gurulumundi (New South Wales)	Queensland: Calcium Gurulumundi: Sodium
<i>Asia</i>		
<i>India</i>	Rajasthan and Gujarat	Sodium and calcium (high at structural iron)
<i>Japan</i>		Sodium, Calcium, Acid and Hydrogen
<i>China</i>	Shandong, Sichuan, Liaoning	Sodium (rare and low quality) and Calcium

Table 2: Source: *Industrial Minerals & Rocks: Commodities, Markets and Uses*, 7th Edition, Kogel J.E., Trivedi N.C., Barker J.M, Krukowski S.T., Society for Mining, Metallurgy and Exploration Inc., 2006, pg 362-364

Genetic types of deposits

The formation and survival of bentonite deposits depends on a combination of parent rock type, alteration environment and geologic history. Bentonite deposit's genetic processes are distinguished in:

1. The alteration of volcanic ash by heating the water of shallow basins in alkaline marine or lacustrine environments (Wyoming, Milos-Greece).
2. The abiding action of groundwater on deeply buried tuff layers with the liberated silica conceivably constructing a silicified zone underneath the bentonite.
3. The autochthonous weathering of basic tuffs, basalt and ultramafic rocks resulting in smectite-rich soil. The parent rock can be separated from the:
 - angular non-clay minerals
 - chip-like relics of volcanic glass
 - argillation that causes decrease in SiO₂ and alkalis
 - large aerial extent, which is similar one with a layer of volcanic ash
4. The hydrothermal alteration, either at depth or in a small alkaline lake with hot springs on the bottom (seawater convection at half-submerged felsic volcanoes- Milos, Greece).
5. The rewashing of bentonite in an alkaline environment gives rise to montmorillonite clays, which cannot be inferred from the residual bentonite. The term bentonite is usually given to the montmorillonite clay as well.

Bentonite deposits tend to occur as:

- continuous stratigraphic horizons, layers, or lenses having an abrupt top and bottom contacts (**genetic types 1 & 2**).

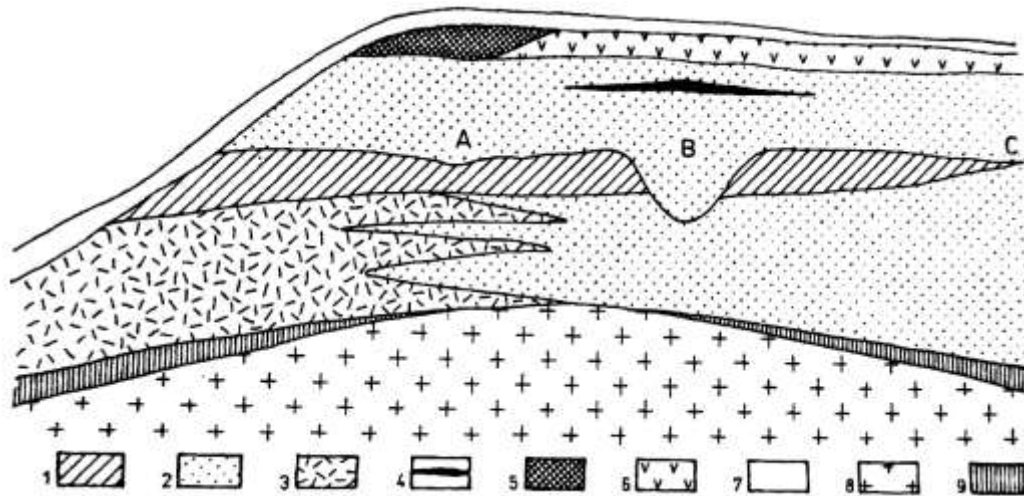


Figure 1: Schematic general section across a generic bentonite deposit

Source: Harben P.W. and Kûzvar M., *Industrial Minerals, A Global Geology*, pg 130

1. high quality bentonite
2. low quality bentonite
3. argillized tuff
4. carbonaceous clay
5. volcanic rock
6. tuff
7. quaternary loams
8. basement complex (granite or gneiss or old sediments, often kaolinized)
9. oldest member of the transgressive complex with bentonite

Volcanic tuff is the parent rock of all types of bentonite

- (A) thinning of bentonite layer due to its squeezing out valleywards by the height at the overlying beds
 (B) erosion furrow
 (C) sedimentary wedging out of bentonite, that is of the original tuff layer.

- gradational contacts with the underlying beds and abrupt ones with the upper beds (**genetic type 3**).
- Montmorillonite and zeolites are created from volcanic ash or hydrothermally action, but since zeolites are developed under more alkaline conditions (*Minato and Aoki, 1979*), they generally form in the deeper parts of the deposit (**genetic type 4**).
- abrupt contacts with the underlying beds and gradational ones with the upper beds (**genetic type 5**).

Geology of deposits

▪ In situ deposits

In situ deposits of smectite clays, that have been formed by hydrothermal alteration of the parent rock, even though they are small, they can present economic significance.

Figures 2 and 3 present the conditions that must prevail in hydrothermal alteration in order to form smectite minerals. These requirements are:

- High temperatures
- Fluid composition must have high cation/ hydrogen ratios in order to stabilize smectite
- Fluid's silica contents > quartz saturation
- Parent rock must be rich in Ca and Na, in order to form Ca- or Na-smectite
- Potential parent rocks of hydrothermal bentonites: basic or intermediate igneous rocks, because the alteration of calcic plagioclase produces the Ca and Na cations needed.

Furthermore, bentonites are composed of minerals which are either formed during bentonization or residual ones that have stayed unaffected. Most of the times, cristobalite is the silica mineral, which represents higher solubility than quartz and provide stabilization to smectite by restricting the fluid composition such that $\log(a\text{SiO}_2)$ is in excess of that required for quartz saturation.

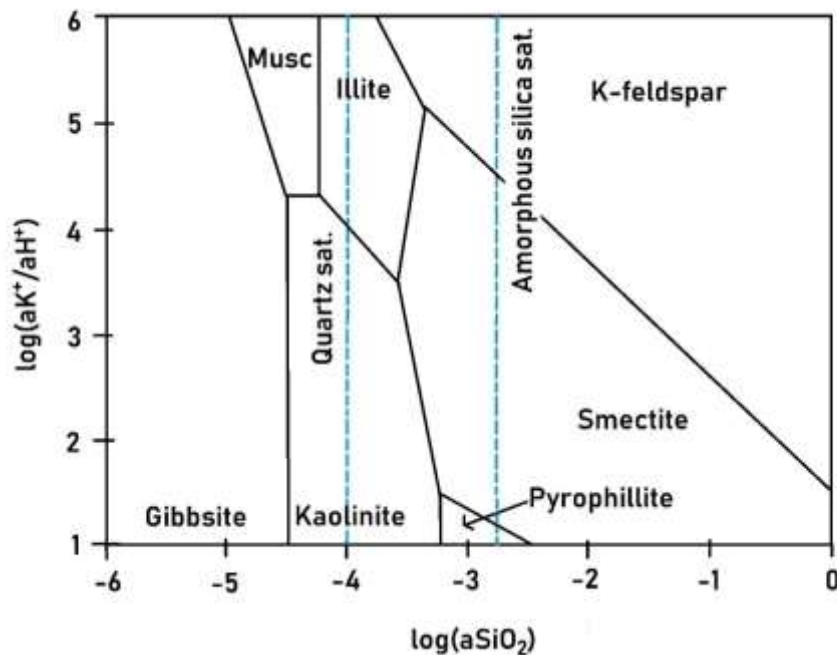


Figure 2: Relative stabilities of clay minerals as a function of fluid composition, showing fluid silica contents which correspond to saturation with respect to quartz or amorphous silica (Garrels, 1984)

Source: D.A.C Manning, *Introduction to Industrial Minerals*, 1995, pg 64.

As seen in figure 3, clays with interlayer cations are stable under conditions with higher proportions of cations to hydrogen, or conversely that kaolinite stability is favored by low cation content relative to hydrogen. Compared with illite or smectite, kaolinite is also low temperature phase. These phase relationships allow the origin of smectite within the bentonites to be placed in a relatively well constrained physicochemical framework. (D.A.C Manning, 1995)

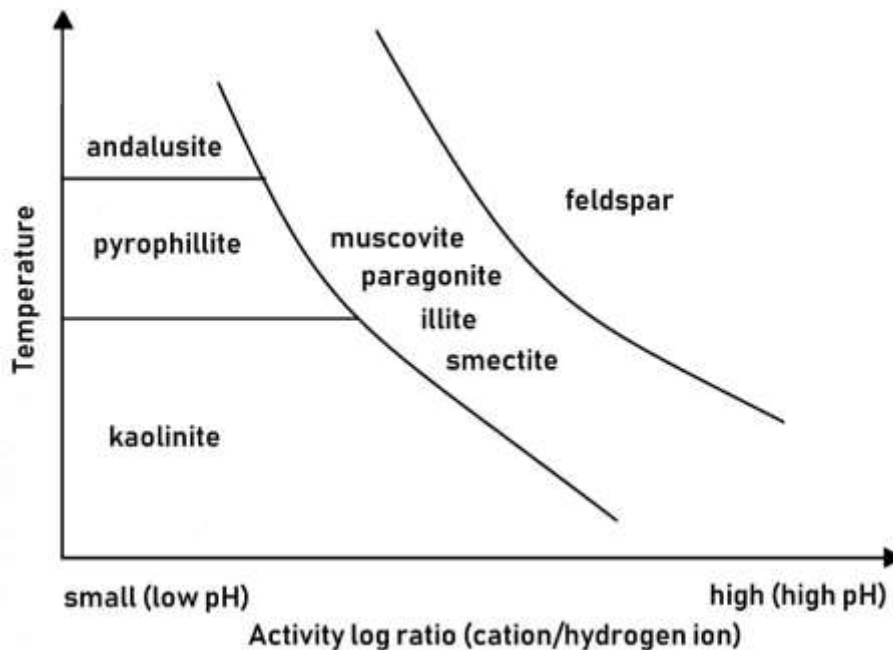


Figure 3: Relative stabilities of clay minerals as a function of temperature and fluid composition. Note that the position of the field boundaries, the size of the stability fields and the nature of the phases which are stable will depend in detail on the compositions used.

Source: D.A.C Manning, *Introduction to Industrial Minerals*, 1995, pg 64.

- **Sedimentary bentonites**

The majority of bentonites are sedimentary, and they mostly formed at Mesozoic or Tertiary sequences. The most important production of bentonite derives from Wyoming deposits which they consist of natural sodium bentonite known as “Wyoming Bentonite”. These deposits occur as individual beds that have formed during the Upper Cretaceous and present an extensively geographic range (several kilometers) and thickness up to 3 meters (D.A.C Manning, 1995) All of them have been interstratified with marine sediments, except for the Newcastle bed mined in the Black Hills District, which is limited geographically and probably deposited in fresh water. Wyoming bentonites have probably formed from erupted rhyolitic volcanic ash, altered and settled through a marine water column. Individual beds are consisting of many clay layers and have sharp, often silicified, bases. Although, the grade changes at the upper strata and we have bentonitic schist.

Wyoming Bentonites are composed of montmorillonite, mica (illite, muscovite), feldspar, quartz, zeolites and kaolinite (not always). If iron occurs, it cannot be used at many applications.

After USA, Greece is the one of the countries in biggest production of bentonite. Deposits form irregular bodies in pyroclastics that may be several tens of meters thick. The most important deposits are the ones in Milos with beds greater than 30 meters thick (*Don Eisenhour and Franz Reisch, 2006*) and Kimolos, where white bentonite occurs, forming a commercial grade deposit (*Harben P.W. & Kûzvar M., 1996*). These deposits have occurred by hydrothermal alteration of acidic igneous rocks and tuffs into marine environments, but also with fresh water, in Lower Pleistocene. Bentonite used to form at deeper levels because the environment is more alkaline. On the other hand, kaolin is formed in shallow levels, in which the oxygen-rich surface water is mixed with the solutions, resulting kaolin to develop over the bentonite.

The degree of alteration is variable and the smectite usually contain, variable amounts of quartz, potassium feldspar, plagioclase and minor quantities of opal, zeolites, alunite, jarosite, barite, gypsum, sulfides, iron oxides and titanium oxides. (*Stamatakis et al., 1996*). In some beds it may be fairly complete, with only a few perlitic glassy particles disseminated in the clay, whereas in others unaltered tuffaceous material is present or pure clay forms pockets within the glass. Overall, the bentonite is primarily of calcium type, with some magnesium as exchangeable cations, and quartz, feldspar, mica and kaolinite as the main impurities (*Grim and Güven, 1978*).

The formation of sedimentary bentonite deposits demands some requirements/geological factors:

- a source of volcanic ash
- a depositional basin where the ash can accumulate and be concentrated by natural processes of sediment sorting
- the ash reacting with the seawater must produce yield smectite clays
- the deposit must be protected from erosion
- no further change in the clay minerals assemblage

Smectite can be gradually transformed into mixed layer smectite-illite clays, when the burial is increasing. Illite proportion is increased even to 80% at ~3700 meters depth. The reason that bentonites are instable during burial, is that they likely don't form at Paleozoic sequences, except from potassium ones, that develop under mild metamorphism.

Deposit Evaluation - Mining – Processing

- **Exploration – Appraisal of field**

Exploration of bentonite requires geological knowledge and field investigations. The first step includes the examination of the geological environment. As already mentioned, bentonite is formed by post-depositional alteration of volcanic ash, in marine environments, at Cretaceous and Tertiary age. Bearing in mind the above, a typical environment will be an area of past volcanic activity, which was located near a substantial body of water.

The second step is to investigate the field, in order to discover the presence of the bentonite. After it is confirmed, surface mapping and drilling are necessary in order to determine the nature, the possible reserve volume and quality of the deposit. When a deposit is characterized viable after mineralogical and laboratory results, more factors are taken into consideration such as, thickness of the overburden, grades, distance to processing facilities, transportation routes and markets and governmental permission. All of the above must be accounted before mining can begin.

- **Mineralogical Evaluation**

This part includes the examination of mineralogical components, the physical and chemical properties of the containing minerals, allowing for proper economic utilization and to design optimum utilization. The analytical methods include, X-ray diffraction, differential scanning calorimetry, infrared spectroscopy, zeta potential measurements, GTA, DTA and other ones in order to identify particle size distribution, surface area and interlayer cation chemistry.

- **Laboratory results**

This step includes laboratory tests that are standard like, rheology testing (API), foundry bond testing, swelling, liquid absorbance and water permeability, or customer-specified tests. Also, these tests are depending on specialized markets, such as bleaching oil procedures and purity requirements.

- **Mining**

The most common mining method for the bentonite is an open-pit method. Overburden is removed in panels, to expose the desired commodity, by bulldozers, scrapers and excavators and the bentonite is mined with draglines or end loaders. The topsoil and subsoil from different parts of the pit or from different pits, are removed and stockpiled separately for redistribution during pit closure and land reclamation. So, after bentonite is removed in the first area, the overburden from the adjacent area is placed in the void left and the process moves to the next area. Bentonite is placed into trucks for transport to the processing facility. Overburden thickness usually varies from 0 to 10 meters, but in Wyoming is 9-12 meters.

In order bentonite to be economic viable, requires that the ratio of overburden to clay thickness be less than 10:1. Although this ratio could be exceeded if other logistic or markets factors are in favor.

Furthermore, underground mining methods are used in New Discovery Mine, near Beatty, Nevada, at Comb Hay, UK, in Durango, Mexico and in many locations in China.

- **Processing**

Processing of bentonites requires field and plant drying in order to reduce their moisture from 25 to 35 wt% to say 7 to 12 wt%. The temperature of the dryers is about 800°C at inlet, 400-500°C in the main drying zone and 100-200°C at the outlet. Precautions must be taken so the bentonite won't be overdried, because this can result in reduced performance.

Next step is grinding. This step requires roll crushers, screens, roller mills and hammer mills. When extremely fine particles are necessitated, air classification is used either during milling or as a separate stage in the process. Improvement in viscosity and fluid loss can be achieved by adding polymers, 0,1 to 0,7 kg per ton of clay, either directly before or after milling. Also, long-chain water soluble polymers are most commonly used to enhance the performance of bentonites.

Bentonites may be further processed or treated. They can be treated with soda ash either in the field or at the plant before drying. Field operations contain addition of soda ash as stockpiles are built or on clay that has been spayed out to dry. On the other hand, plant additions of soda ash include wetting the clay using a paddle mixer to mix thoroughly the components. Sometimes right amounts of water may be added to improve the reaction between the soda ash and clay, without over affecting the dryness. Mixing of soda ash and clay can be helped with pug mills and extruders, improving clay's performance through mechanical delamination.

For example, sodium bentonite (swelling) may be produced by treating calcium bentonite (nonswelling) with soda ash. Acid-activated bentonites, are manufactured through the reaction of inorganic acids like sulfuric or hydrochloric acid with the bentonite (slurry).

Pressure filtration removes residual acid. Sometimes the formation of “noodles” is been used, which are acid leached and washed without filter presses. Then they are dried and ground to the desired particle size. Acid activation causes Brunauer Emmett Teller (BET) surface areas to increase from less than 10 m²/g to more than 250 m²/g, and this measurement is based on the physisorption and desorption of nitrogen.

The desirable result is to enhance the mineral’s physical and chemical properties while maintaining the crystal lattice. The physical effects contain, opening up the edges of the platelets, increasing pore diameters and enlarging surface area. The acid helps impurities to dissolve such as calcite and replaces exchangeable divalent calcium ions with monovalent hydrogen ions, it also dissolves some aluminum ions contained in the tetrahedral layers and some ferric, ferrous, aluminum and magnesium ions from the octahedral layers. The intensity of the reaction is based on the montmorillonite, the type of acid, temperature and contact time. The outcoming product has excellent absorbent and catalytic properties.

High-end cosmetic and pharmaceutical products include impurity removal and brightness improvement by water washing. Therefore, low solid slurries are subjected to a series of wet screening, hydrocyclones and centrifugation. Soda ash is added in wet clays either on rotary drums to produce flake products or sprayed to produce powdered products. After that, mills are used to reduce particle size to less than 20 μm.

Uses of bentonite

The commercial value of bentonite arises from its mineralogical, ion exchange and sorptive properties. So, it is common procedure to test the bentonite according to the anticipated end use, and so to match it with a particular market.

The cation exchange capacity and surface area can be found with chemical tests. The surface area can provide the estimation of the maximum smectite content of clay. Bentonites are used in numerous applications but in some of them, bentonite must be treated with many processes in order to be suitable for specific applications. For example, Wyoming bentonites are sodium bentonites and because of their natural swelling they can be used instantly. On the other hand, calcium bentonites must be activated with sodium (exchange Ca with Na) in order to produce sodium bentonites. There are more treatments including, acid activation (Ca-bentonite is treated with acid to improve its sorptive properties) and organic activation (interlayer cations are exchanged for positively charged organic species). Some of the uses are analyzed below.

Drilling Fluids

Bentonite is used in drilling muds to keep the cutting tools cool, to remove cuttings, to lubricate the drill bit, to confine fluids by building an impervious coating on the wall of the drill hole, and to help prevent blowouts (*Larsen, 1955*). Generally, a high viscosity and a low yield stress and a thixotropic behavior are required from bentonites. Rheological properties are optimized by use of suitable additives. For instance, addition of activated lignite improves the rheological properties (*Kelessidis et al, 2007*).

Foundry-sand bond

Bentonites are used since 1920 in iron and steel foundries, because they provide bonding strength and plasticity to sand-clay mixtures and in that way, the shape of the mold, before and after pouring of the molten metal, is maintained. The majority of foundry sands contain silica sand and 5-10% bentonite. In foundry sand preparation, a small amount of bentonite is added to the sand and mixed. Then a small amount of water is added and after it is mixed until the mixture is turned to mold. Green process is used when the molten metal is poured into wet mold. On the other hand, when the molten metal is poured into dry mold, it is called dry process. Both, sodium and calcium bentonites are used in foundry industry, but they have different bonding properties. Therefore, sodium bentonites have medium-low green strength and a very high dry compression strength, whereas calcium bentonites have medium green strength and a low compression strength. Nevertheless, sand molds that demand intermediate (green and dry) strengths, can be produced by mixing Ca-bentonite, Na-bentonite and sand.

Iron ore pelletizer

Taconite iron ore (siliceous low grade iron ore) is processed in order to increase the iron content by eliminating the impurities. The purified powder is mixed with bentonite and pressed into pellets with diameter about 25mm, for use as basic oxygen furnace feed. The green iron ore pellets must present sufficient strength to resist handling, compaction, and drying, and the dry pellets must be even stronger to maintain their shape during transportation and furnace charging. The properties for evaluating mixtures of bentonite, taconite ore and water are wet-drop strength, wet compression strength, plastic deformation and dry compression strength. The amount of bentonite used is less than 9kg/t of iron ore. Therefore, the type of bentonite used must have a very high dry strength. The sodium bentonite meets this demand. Although bentonite is unsurpassed as a pellet bond, it adds undesirable impurities to the iron ore (*Hosterman and Patterson, 1992*)

Bleaching clay

Some bentonites are utilized in decolorizing various mineral, vegetable, and animal oils. They are also used for clarifying wines, beer, liquors, cider and vinegar. Bentonites are used together with alum in water clarification. With acid activation process, the filtration properties of some bentonites, is enhanced. More than 6% of the bentonite and almost 1% of fullers earth are used in filtering, decolorizing, and clarifying purposes (*Ampian, 1988*).

Absorbent

Bentonites are used to form absorbent granules, 10-20 mesh in size, by calcining them at 400-1000°C, in order to increase the absorbent capacity and by crushing and screening the calcined product, the desired particle size granules is produced. Some of the uses are as pet waste absorbent and oil and grease absorbent.

Carrier

Is important in attaining uniform dispersion, retaining, and preserving of pesticides and fertilizers.

Filler

Bentonite is used as a filler, stabilizer and extender in materials such as adhesives, greases, medicines, cosmetics, paint, rubber, soaps and as a bond animal feed. Almost 6% of bentonite and more than 1% of the fuller's earth production is used as a filler (*Ampian, 1988*).

Sealant and waterproofing

Bentonite is used as sealant, to reduce water seepage from ponds and irrigation ditches. It is also used to waterproof the outside basement walls of homes and other structures (*Mielenz and King, 1955*). The best bentonite in these procedures is sodium bentonite, because of its swelling capacity. Nonetheless, a small amount of calcium bentonite is also used.

The table below it includes the majority of bentonite uses:

Drilling muds	De-inking newsprint	Paper
Foundry Sands	Desiccants	Pencil leads
Iron ore pelletizing	Deodorizers	Pharmaceuticals
Cat litter	Detergents	Pillared clays
Absorbents	Emulsion stabilizers	Plasticizers
Adhesives	Fertilizer carrier	Rubber filler
Aerosols	Food additive	Sealants
Animal feed bonds	Fulling wool	Seed growth
Barrier clays	Herbicide carrier	Soil stabilization
Bleaching earths	Industrial oil absorbent	Slurry trench stabilization
Catalysts	Insecticide and pesticide carrier	Suspension aids
Cement	Medicines	Tape joint compounds
Ceramic and refractories	Nanoclays	Water clarification
Cosmetics	Organoclays	
Crayons	Paint	

Table 3: Applications of smectite rich clays (adapted from Murray,2007)

Source: Christidis G.E., *Advances in the characterization of Industrial Minerals*, 2011, pp 388

Competitive Products

- **Pet waste absorbents:**

- Attapulgite or sepiolite
- Gypsum
- Diatomite
- Zeolites
- Sawdust

- **Distillation:**

- Activated Bauxite
- Mg-Silica Compounds

- **Excipients:**

- Atapulgitite or sepiolite
- Vermiculite
- Diatomite
- Zeolites
- Talc
- Kaolinite
- Peat
- Pumice
- Pyrophillite

- **Desiccants:**

- Attapulgite or sepiolite
- Activated alumina
- Activated carbon
- Activated lime
- Zeolites
- Silica gel
- CaSO₄
- CaCl₂
- LiCl
- LiBr

- **Drilling Muds:**

- Attapulgitite or Sepiolite
- Polymers

- **Iron Pelletizing:**

- Polymers

Production - Prices

▪ World Bentonite Production and Reserves

Country	2001	2002	2003	2004	2005	2006	2007	2008
United States	4290	3970	3940	4060	4710	4940	4820	4900
Brazil (beneficiated)		175	175	200	227	221	240	32
China	250							
Czechia	500	174	175	175	200	220	220	174
Germany		500	500	405	410	350	365	414
Greece	1150	1150	950	950	950	950	950	950
Italy		500	500	500	500	470	600	599
Mexico		400	425	470	426	450	435	375
Spain				150	150	110	105	150
Turkey		559	600	850	925	950	930	900
Ukraine								300
Commonwealth of Independent States		750	750	750	750	750	750	750
Former Soviet Union	750							
Other Countries	3560	1820	2220	1990	2450	2290	2490	2900
World Total	10500	10000	10200	10500	11700	11700	11900	11700

Table 4

Source: U.S. Geological Survey, Mineral Commodity Summaries

Country	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019 ^e
United States	3650	4630	4810	4980	4350	4800	4320	3600	4300 ^e	4670	4700
Brazil (beneficiated)	239	265	532	567	513	440	440	405	450	520	520
China						3500	3500	5600	5600	5600	5600
Czechia	116	183	160	221	226	230	310	369	369	280	280
Germany	350	350	350	375	375	360	360	395	395	395	390
Greece	845	850	850	800	1000	1010	1300	808	1100	1360	1400
India						1080	1080	802	800	800	810
Italy	146	111	110	110	110						
Iran						430	430	436	436	360	360
Mexico	511	591	54	54	618	600	600	470	470	470	470
Spain	155	155	155	115	115	115	115	113	113	175	180
Turkey	1000	1200	1000	400	1100	650	700	3135	3140	1500	1500
Ukraine	300	200	185	210	210	220	220	210	210	110	110
Uzbekistan				15	25						
Other Countries	2350	2100	2100	2100	3360	2660	2660	2700	3300	2230	2200
World Total	9660	10600	10300	9950	12000	16100	16100	19000	20600	18500	18500

Table 5

Source: U.S. Geological Survey, Mineral Commodity Summaries

e: estimated

Note: Data in thousand metric tons

World Estimated Reserves 2018

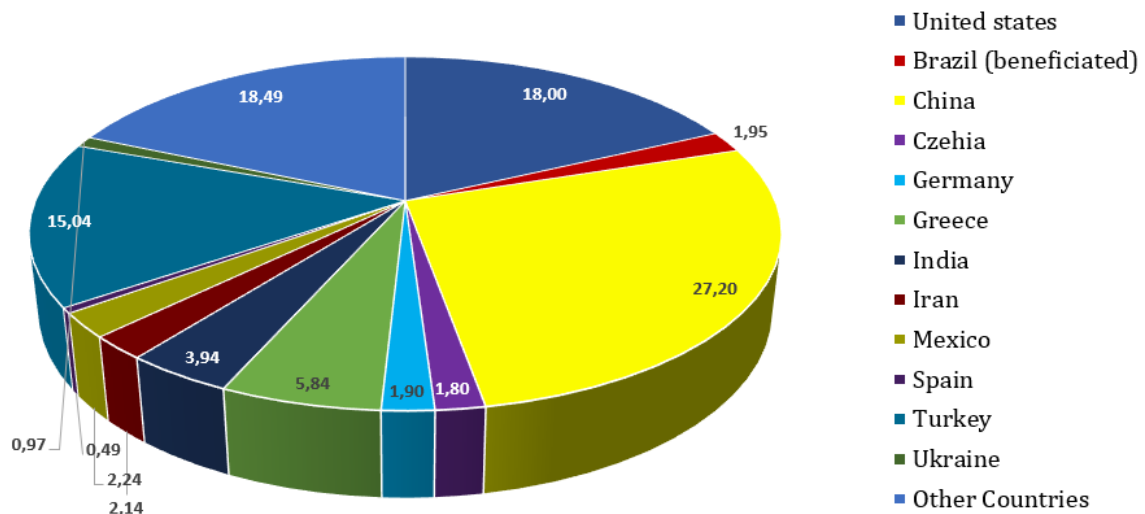


Figure 4: (Source: U.S. Geological Survey, Mineral Commodity Summaries, February 2019)

■ **USA Domestic Production and Use:**

- Production of clays (sold or used) in the United States was estimated to be 26 million tons valued at \$1.8 billion in 2019, while in 2018 there were estimated to be 27 million tons valued at \$1.6 billion, with about 145 companies operating clay and shale mines in 40 States. The leading 20 firms produced approximately 50% of the U.S. tonnage and 85% of the value for all types of clay.
- Principal uses for bentonite were estimated as 52% pet waste absorbents and 31% drilling mud
- In 2018 the United States accounted for 15% to 25% of the global production of refined clays, excluding common clay and shale.
- U.S. exports of bentonite decreased by an estimated 3% in 2018 relative to the prior year.
- Canada, Japan, and Mexico were, in decreasing order by tonnage, the leading destinations for United States bentonite and accounted for 67% of exports.
- Exports of clay and shale were estimated to have increased by 4% in 2019 after remaining essentially unchanged in 2018.
- In 2019, the United States exported 820,000 tons of bentonite mainly for pet waste absorbent, drilling mud, foundry sand bond, and iron ore pelletizing applications, with again Canada, Japan, and Mexico being the leading destinations.
- Total U.S. sales of clays decreased slightly in 2018 and again in 2019 compared with those of the previous year. Over the past 2 years, other industrial minerals associated with construction activity have been estimated to have increased. Sales of bentonite increased in 2018 and were essentially unchanged in 2019.

(Source: U.S. Geological Survey, Mineral Commodity Summaries, February 2019 and January 2020)

- **Average bentonite price in the U.S. from 2007 to 2018 (in U.S. dollars per ton)**

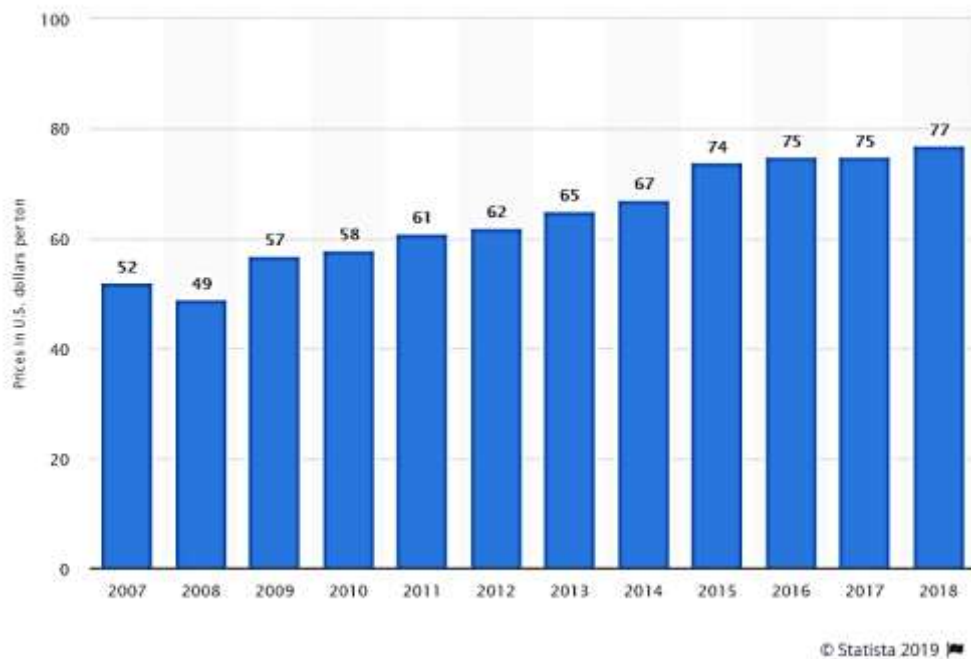


Figure 5: Source: Statista 2019

- **Greece: Domestic Production and Sales**



Figure 6: Source: www.sme.gr - Modified

Kimolos bentonite production (*Bentomine Kimolian Enterprises*) per year is 250.000 tons. The half of the production is Na-bentonite with 20% montmorillonite and is the white bentonite which is unique in Europe and provides high whiteness in the final product. The other half is, lower quality, Ca and K-bentonite and bentonitic clay with 60% montmorillonite.

Geology of Kimolos



Figure 7: Location map of Milos and Kimolos
 Source: Christidis G.E., P.W. Scott (1997) *The origin and control of color of white bentonites from the Aegean islands of Milos and Kimolos, Greece*

Kimolos is a Greek island of the Aegean Sea. It lies on the southwest of the island group of Cyclades, near Milos. Kimolos lies on the outer zone of the volcanic arc of the Aegean, therefore is a product of intense volcano activity. Kimolos is consisted mainly of acidic volcanic rocks, mostly rhyolitic type and granite occurrences. Furthermore pre-volcanic bedrock can be observed in very few places, while large areas of tuffs and tuffites, are presented too. The island is also rich in minerals of the silica group. The erosion of the volcanic minerals, caused by the water from the hot springs, the rain and the sea, enriched the island with significant industrial minerals, mostly bentonite, pozzolana (white cement), perlite, kaoline (porcelain), ferromanganese barite, zeolite and some sulphur. Additionally, semi-precious minerals, mainly quartz variations, like amethyst, agate, chalcedony, jasper, opal can be found on the island. Many colored crystal and microcrystal variations can exist in masses of minerals.

(Source: gokimolos.gr and kimolos.gr)

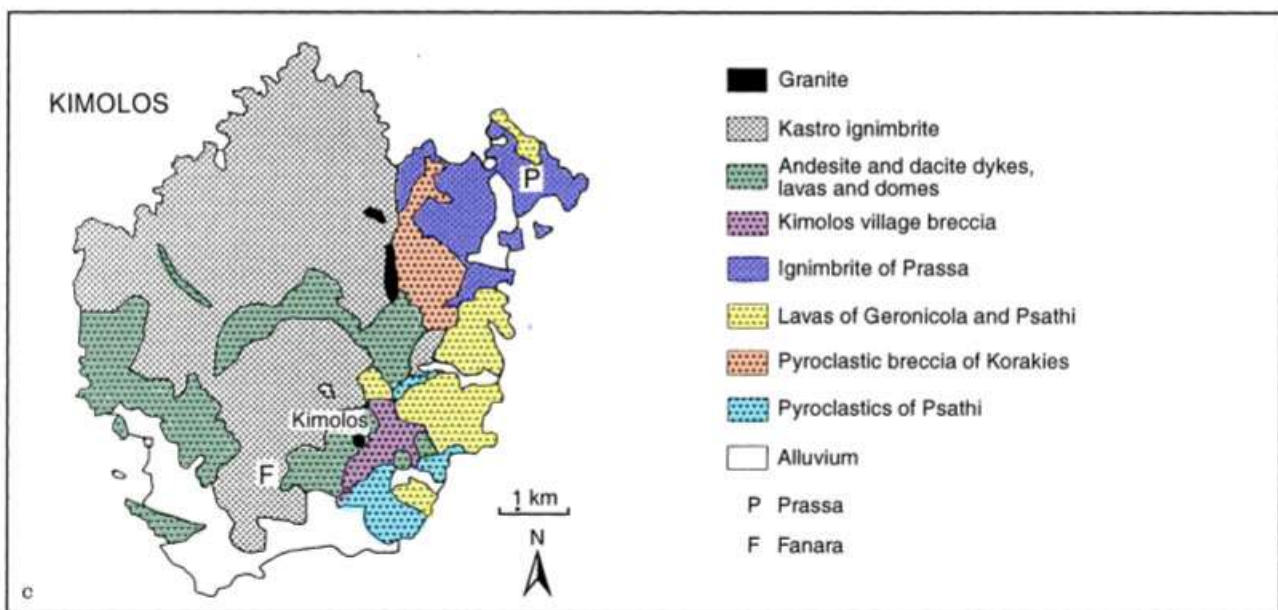


Figure 8: simplified map of Kimolos, modified after Fyticas and Vougioukalakis (1992)- Source: Christidis G.E., P.W. Scott (1997) *The origin and control of color of white bentonites from the Aegean islands of Milos and Kimolos, Greece* (Modified)

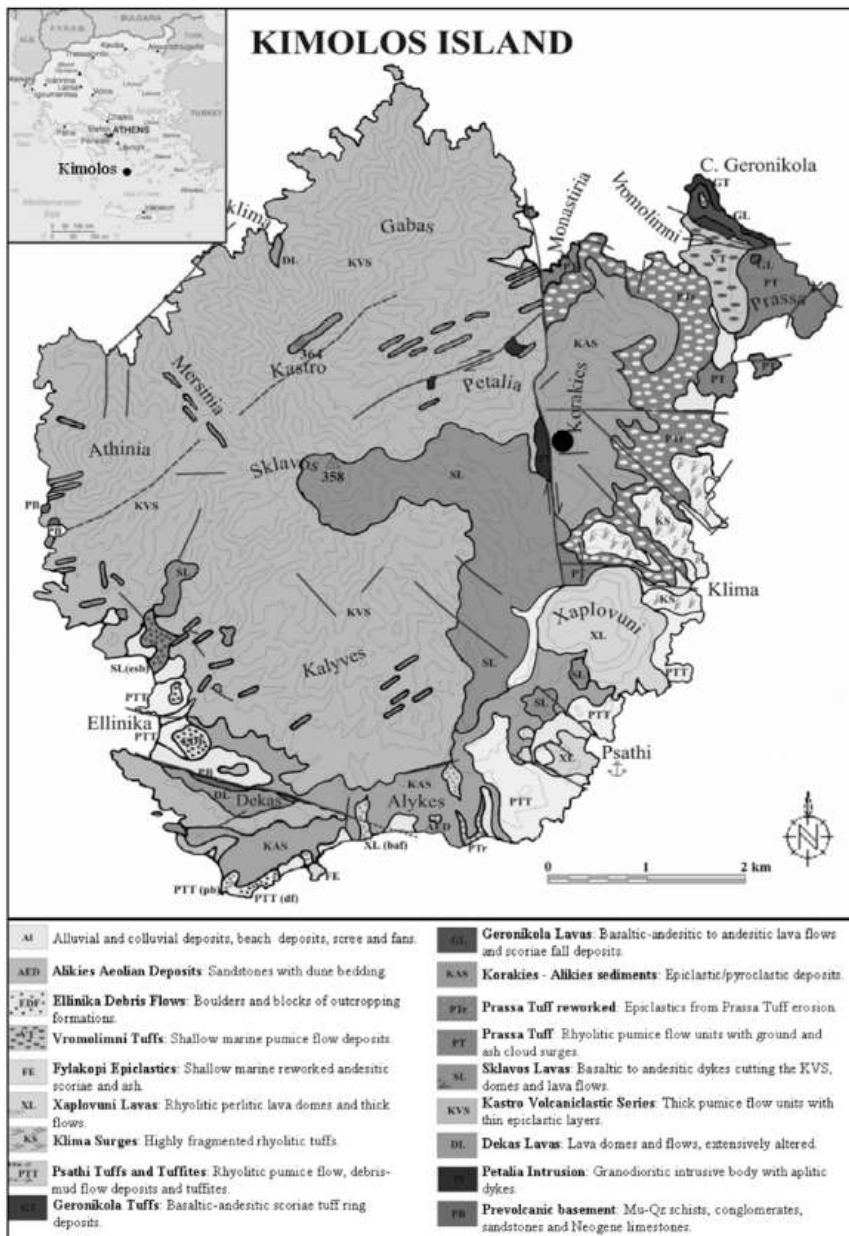


Figure 9: Geological map of Kimolos Island showing the main structural features and the location of the Mn ore deposit in the Korakies area (black dot) (modified from Francalanci et al., 2007).

Source: Lykakis, N. and Kiliyas, S. P. (2010). Epithermal Manganese Mineralization, Kimolos Island, South Aegean Volcanic arc, Greece. *Bulletin of the Geological Society of Greece*, 43, 2646-2656.

At the northwest shores and specifically at the Agioklima bay, there are occurrences of **lavas, hydrothermally altered**, with 25 meters thickness. The minerals occurring are Feldspars from the parent rock, quartz, argillic minerals and zeolite. (Fyticas and Vougioukalakis, 1992).

Kastro ignimbrite, is the main formation that covers the biggest part of Kimolos. It's thickness overcomes the 400 meters. It is composed of pumice flows and glass, hydrothermally altered. These units have 3-15 meters thickness and slopes between 5° and 30° from N to NW (Fyticas and Vougioukalakis, 1992).

The **pre-volcanic background** of Kimolos appears in the West of the island (Athinias) with 2 occurrences. The northern occurrence is consisted of changes between conglomerate and sandstone, intensely tectonized and uplifted from lava intrusion. The southern occurrence is composed from mica quartz schists, which are intensely tectonized and uplifted from lava intrusion (Fyticas and Vougioukalakis, 1992)

Granitic intrusion appears in the center of the island, around from the mound Petali in 3 occurrences. It is a small granitic intrusion, which was crystallized near surface from magmatic intrusions at the beginning of volcanic activity (Pliocene). This granite is consisted from orthoclase, plagioclase, biotite, quartz, hornblende, Fe and Ti oxide, epidote, apatite, titanite and zircon (Fyticas and Vougioukalakis, 1992).

Andesitic – Dacitic lavas occur all over Kimolos, except from the northeast section of the island with NE-SW direction and the biggest occurrence is observed in the bay. Monastries (SW) with thicknesses between 1-30m and slopes 70°-90°. The lavas are holocrystalline and have subhedral to allotriophic texture. Due to hydrothermal alteration, these lavas present secondary minerals like quartz, zeolite, chlorite, amorphous silicon, montmorillonite and calcite (Saint Andrea island, Ellinika) (*Fyticas and Vougioukalakis, 1992*).

Kimolos village breccia occurs in Kimolos village and spreading to southwest. It is composed from angular pieces from andesitic- dacitic lava, intensely welded from hydrothermal solution deposits. These beds have thickness 15 meters, direction NE-SW and slopes 20-30° to SE (*Fyticas and Vougioukalakis, 1992*).

Ignimbrite of the Prassa area covers the east part of the island and it is consisted of changes between terrestrial and submarine modules of pyroclastic flows and large wave deposits of total thickness exceeding 200 m. The lower section of the formation occurs in Prassa area and it is successive pyroclastic flows of pumice and glass shards, intensely altered from hydrothermal activity (occurrences of bentonite and zeolite). The upper part of the formation is composed of very fine grade tuff with typical structures of dunes and antidunes and cross-layer structure. It is supposed to be a acidic magma, intensely crushed, which is deposited by largewave mechanisms and hydromagnetic volcanic erosion (*Fyticas and Vougioukalakis, 1992*). **The samples that we are using are extracted from this mine, which is developing in this formation.**

Pumice flows occur at the SW section of the island in Ellinika and Saint George cape. It is huge pieces of pumice, with diameter of 3 meters. The floor and basement of the formation are consisted of offshore tuff, with typical yellow color and 2-3 meters thickness with very good bedding and between the floor and basement there is pumice deposit (*Fyticas and Vougioukalakis, 1992*).

Submarine pyroclastic are mentioned at Saint George cape and is andesitic ash and stone ash with typical pillow structure. These occurrences have been deposited in marine environments without displacement from the exit point, as the fragile pillow structure (pillow lavas) is maintained (*Fyticas and Vougioukalakis, 1992*).

Geronikola tuffs are occurring at the NE section of the island and specifically at Geronikola cape and Vromolimni bay. Geronikola tuffs are made of tuffs that were created from intensely crushed andesitic magma and contain parts of andesitic bombs with 20-40 cm diameter. Typical traces of bombs and cross-layer structure, are shown on the ash. There is also an inverse gradient of the deposits, a slope to the south and a thickness of 45-50 meters (*Fyticas and Vougioukalakis, 1992*).

Korakies Pyroclastic breccia, contain breccia with maximum thickness of 30 meters and angular to lightly rounded lava pieces with cement and matrix of same composition (*Fyticas and Vougioukalakis, 1992*).

Psathi pyroclastic are tuffs and submarine tuffs, which are contain pumice and lithics. They are occurring at west and east of Psathi's bay and at Xaplovouni, under lava at north and south of the formation. At the lower part of the formation, a chaotic structure of pyroclastic flow is prevailing, without bedding, but it contains pumice, intensively bubbled with microcrystals of plagioclase and sanidine. At the upper part, pumice with plagioclase, biotite, sanidine, Fe and Ti oxides and pieces of perlite και smaller percentages of lithics, is observed (Fyticas and Vougioukalakis, 1992).

Lava flows are observed at the SE section of Kimolos, at Xaplovouni and Psathi. These lavas are perlitic rhyoliths with crystals of sanidine, orthopyroxene, plagioclase, hornblende, biotite and Fe and Ti oxides (Fyticas and Vougioukalakis, 1992).

At the southern section of Kimolos, specifically at Pyrgos and Kalamitsi, **alluvial scree and eluvial deposits and marine sediments** are observed. The lower part of the formation contains deltaic conglomerates, sandstones and at the upper part, conglomerates, sandstones and argillic (marine deposition). In the deltaic deposits, pieces of altered Kastro Ignimbrite, pre-volcanic background, silicified lavas and fine grade volcanic rocks (Fyticas and Vougioukalakis, 1992).

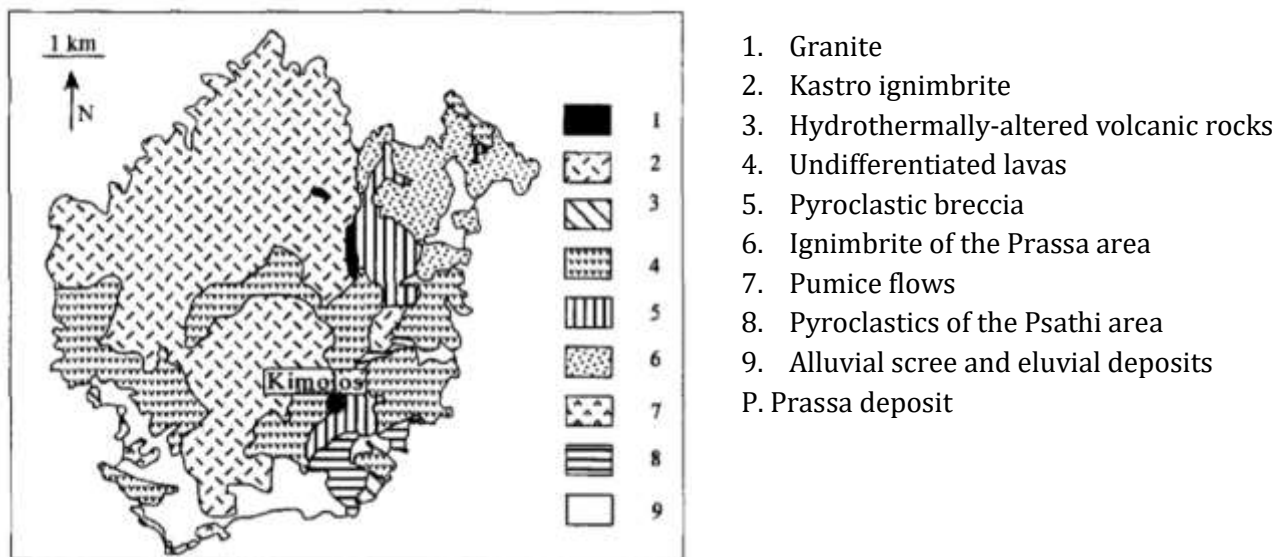


Figure 10: Simplified geological map of the Kimolos Island modified after Fyticas and Vougioukalakis (1993). Source: Christidis G.E., P.W. Scott (1997) The origin and control of color of white bentonites from the Aegean islands of Milos and Kimolos, Greece.

The Kimolian bentonite is from the deposit at Prassa and is formed from the unwelded Prassa ignimbrite, the alteration being structurally controlled. Prassa ignimbrite appears in eastern Kimolos with the following formations: Korakies Pyroclastic breccia, Psathi pyroclastic, Mersinis pyroclastic and Geronikola tuffs. Bentonite lavas are occur between volcanic tuffs with high quality pozzolana and volcanic zeolite tuffs with mediocre quality pozzolana.

Prassa deposit, contain bodies of high quality white bentonite restricted to areas adjacent to faults. The maximum body is 30 - 35 m across and continues at depth beyond a visible 10 m. The main body is dominated by the development of six different alteration zones (*Christidis and Dunham 1994*). The fresh volcanic glass is replaced by a thin transition zone, and then successively into yellowish, grey, and white bentonite, the latter two having no noticeable grit content. The white bentonite constitutes a 5m thick zone situated between a plastic grey bentonite, and a light gray - white opal-bearing bentonite (*Christidis and Dunham 1994*).

Geology of Wyoming

Wyoming is a state in the mountain region of the Western - Northern United States. The state of Wyoming has 23 counties.



Wyoming's geology includes some of the oldest Archean rocks in North America. These rocks are overlaid by **thick marine and terrestrial sediments**, which have been formed during the Paleozoic, Mesozoic and Cenozoic and they include **oil, gas and coal** deposits. Throughout its geologic history, Wyoming has been uplifted several times

during the formation of the Rocky Mountains, which **produced complicated faulting that traps hydrocarbons**. (*Lageson and Spearing, 1988*)

Geologic history, stratigraphy and tectonics

Precambrian (4.6 billion years ago to 541 million years ago) term applies to all geologic time from the planet's origin to the beginning of the Cambrian.

At 3.6 billion years ago in the Archean age, **schist and gneiss** were formed in the Wyoming Craton, which constitute the Precambrian crystalline basement rocks of Wyoming. Radioactive dating of rocks exposed at the surface of the Medicine Bow Mountains. indicates two igneous-intrusive events (2.7 billion years ago and 1.7 billion years ago). Furthermore, a thick metasedimentary cover containing fossilized cyanobacteria (stromatolites) is observed, which are as old as 1.7 billion years. These cyanobacteria constitute evidence of some of the first known life forms on earth. Also, the Sherman **Granite** represents a younger Precambrian magmatic igneous-intrusive body. Precambrian rocks seem to be exposed at the core of many uplifts.

The Wyoming Craton was sutured together with the Superior Craton and Hearne Craton during the Trans-Hudson Orogeny. The Wyoming Craton was a separate continent until it joined the proto-North American continent Laurentia 1.86 billion years ago. Along its southern margin, the Wyoming Craton is faulted against younger Proterozoic rocks from 1.7 billion years ago, which form the Front Range, extending into Colorado. The Mullen Creek-Nash Fork fault zone extends northeast to the Black Hills. (*Lageson and Spearing, 1988*)

Paleozoic (541-251 million years ago)

Shallow tropical seas dominated Wyoming during the Paleozoic. Cambrian and Ordovician deposits, subsidence of the land is recorded, that resulted in westward transgression of the sea and deposition of marine sediments (**gravel, sand, mud, limestone, and dolomite**). Therefore, the Cambrian Gros Ventre Formation is made up of shale and limestone, overlain by the **Ordovician Bighorn Dolomite** and the **Mississippian Madison Limestone**. In the Silurian, **unconformities** appeared in the stratigraphic record due to periodic widespread erosion or lack of deposition on the Wyoming shelf.

Mountain-building events like the ancestral Rocky Mountains that commenced in the Pennsylvanian period uplifted the crust and eroded sediments, depositing them into adjacent, low-lying basins where an inland sea still covered the land., like **Tensleep Sandstone**.

In the Permian, organic-rich marine sediments were deposited in the western seaways while nearshore tidal flat sediments accumulated in the central and eastern parts of the state, resulting in the thick sequences of red **siltstone, shale, gypsum, and sandstones** we see today. (*Wyoming State Geological Survey- Geologic history*)

Mesozoic (252-60 million years ago)

Deposition of **red sediments, bed formations and mudstone** in rivers, which bear well-preserved dinosaur fossils continued throughout the Triassic period, with more terrestrial conditions prevailed.

The Jurassic period is marked by minor crustal uplift and transgressive/regressive sequences of the sea. Marine clay, mud, and sand were deposited, and marine fossils were widely preserved. During the periods when Wyoming was dominated by a continental environment, **fluvial** systems deposited **clay, silt, and sand**. Dinosaurs inhabited the land during the Jurassic and many world-renowned fossil remains have been discovered at sites across the state. (*Wyoming State Geological Survey*)

During the Cretaceous, a renewed marine transgression produced the Western Interior Seaway covered most of the state, forming sandstone and the thick, organic-rich Thermopolis Shale, Mowry Shale and Cody Shale, which are a major source of oil. (*Lageson and Spearing, 1988*) By the end of the Cretaceous, the Sevier orogeny was underway and the Overthrust Belt was developing. The end of the Mesozoic also marks the extinction of dinosaurs in the geologic record. (*Wyoming State Geological Survey- Geologic history*)

Cenozoic (66 million years ago-present)

Conditions of dryness have continued since the end of the Cretaceous, through the Cenozoic and the Laramide orogeny that began in Wyoming in the Late Cretaceous, uplifted the Rocky Mountains. Deformation started during the Paleocene, and the orogenic event was completed by mid-Eocene. This deformation caused **thrust faults**, which formed the Wind River Range, Bighorn Range and Laramie Range, with more ductile sedimentary rocks folded over Precambrian igneous rocks at the core of each range and it can be particularly visible in Clarks Fork Canyon, the Beartooth Range and the Gros Ventre Range. Sediments from highlands were removed and deposited into surrounding basins, creating **mountain rose**, due to erosion.

Large quantities of **oil and gas** are trapped beneath the anticline formations that have been formed by the west dipping, low angle faults of the overthrust belt. Throughout the Paleocene, extensively **coal beds** have been formed as highlands eroded, burying organic material. For example, in the Fort Union Formation, coal beds present thickness 100 meters.

Playa lakes, accumulated the oil shale Green River Formation, which include numerous fossils, like Lake Gosiute and Lake Uinta, in the Eocene.

In the Shirley Basin, south of Casper, Wyoming, the Wind River Formation has a brilliant white color imparted by rhyolite ash fall in the form of volcanic eruptions further west in the Basin and Range Province. Cenozoic had a period of volcanic activity occurred, depositing **volcaniclastic rocks, flows, intrusive-volcanic bodies, and ash. Rhyolitic ash** falling in the Oligocene, Miocene and Pliocene, created white color formation like Wind River Formation.

The entire Rocky Mountain region was significantly uplifted, and the Pleistocene Ice Age began. During Pleistocene, the uplift and then the erosion formed the Teton Range and the Yellowstone Caldera in its present location. Nowadays, there are still earthquakes in the state that suggest continued crustal movement.

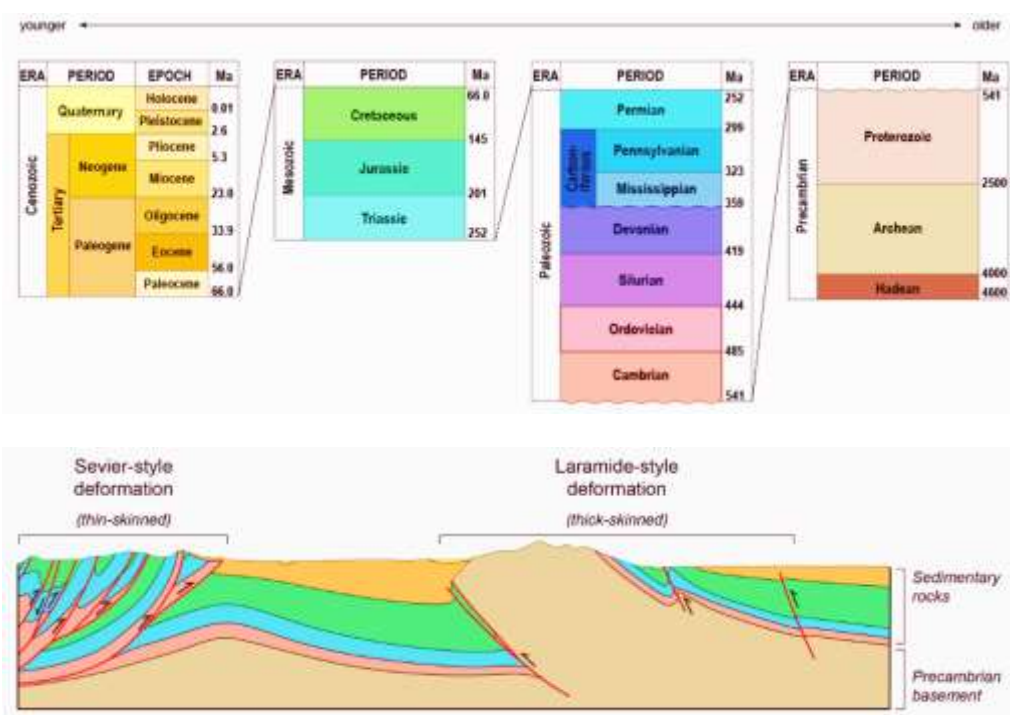


Figure 11:
Deformational Styles:
 The cross section below highlights the difference between Sevier-style and Laramide deformation. Sevier-style thrust faulting is confined to sedimentary rocks above the Precambrian basement (i.e. thin-skinned). Laramide structures offset Precambrian basement rocks (i.e. thick-skinned).
 Source: Wyoming State Geological Survey

Wyoming bentonites are the product of in situ alteration of volcanic ash deposits in a shallow marine environment in Cretaceous times (Late Albian to early Cenomanian). Even though the origin is represented as incidental explosive volcanism, the stratigraphy of the bentonites seem to share a close relationship to the sedimentological and tectonic history of the Cretaceous. Major bentonite beds occur in the same cyclic sedimentary sequence which, from bottom to top, comprises shale, coal, bentonite, and finally shale grading to sandstone and conglomerate (*Slaughter and Earley, 1965*). These sediments were derived from erosion of an actively rising mountain belt in central Idaho, Utah and Nevada with subsequent river transportation to the Mowry Sea basin. Outcrops of major bentonite deposits are present in many parts of Wyoming where Cretaceous sediments are exposed at the surface. (*Smellie John, Conterra AB, 2001*).

The most important outcrops are centered in the Northern Black Hills (Clay Spur District), Southern Black Hills (Colony District), Kaycee District and Eastern Bighorn Basin District, as seen in Figure 14.

GENERALIZED GEOLOGIC MAP OF WYOMING

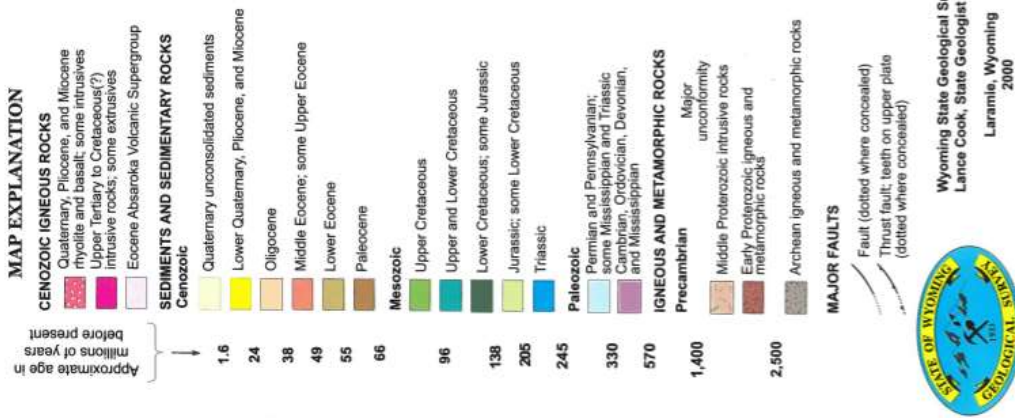
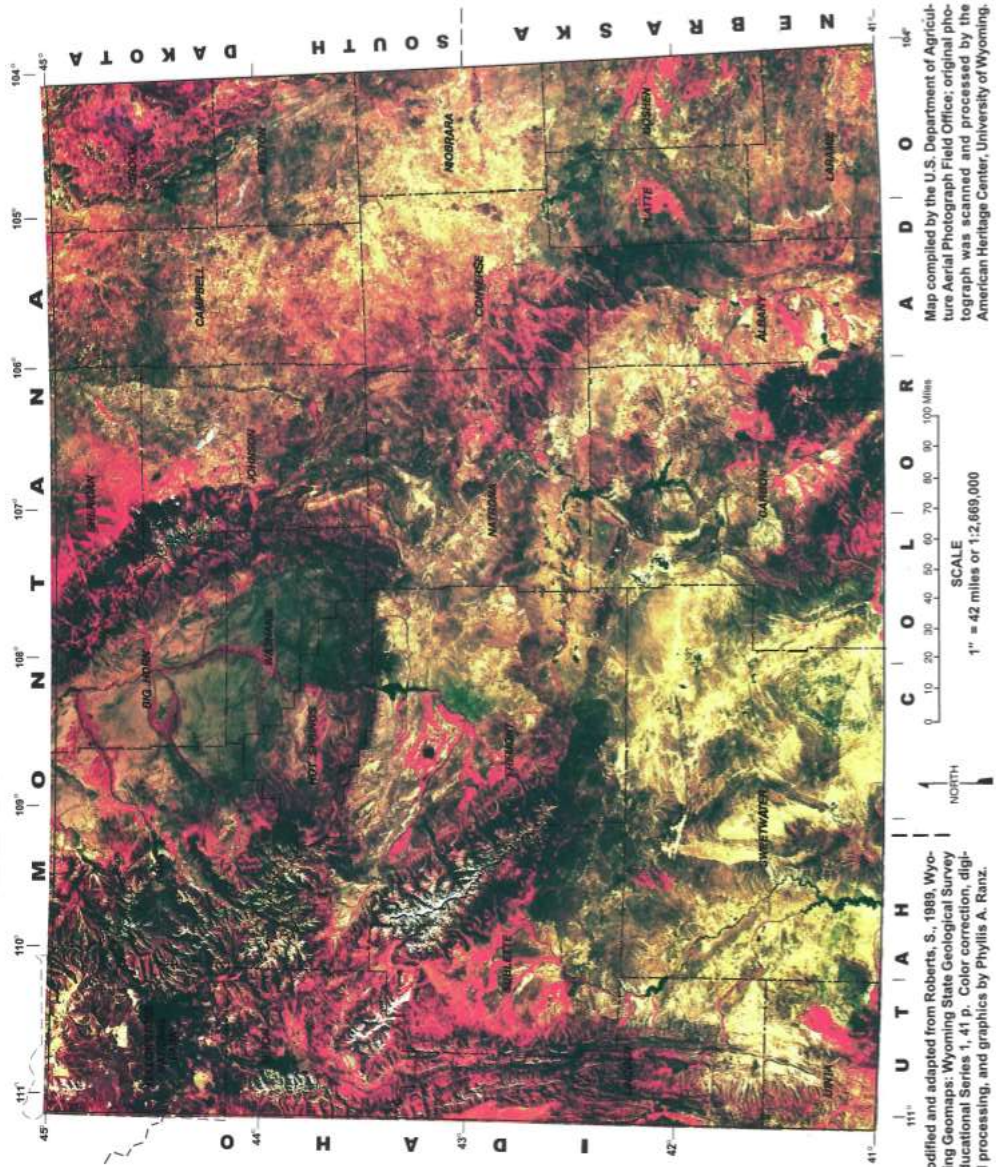


Figure 12: Generalized Geologic Map of Wyoming
Source: Wyoming State Geological Survey

LANDSAT IMAGE OF WYOMING

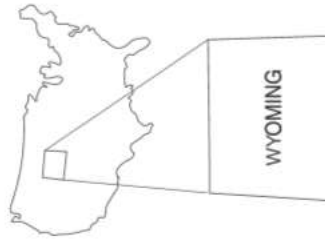


Map compiled by the U.S. Department of Agriculture Aerial Photograph Field Office; original photograph was scanned and processed by the American Heritage Center, University of Wyoming.

Modified and adapted from Roberts, S., 1989, Wyoming Geomaps: Wyoming State Geological Survey Educational Series 1, 41 p. Color correction, digital processing, and graphics by Phyllis A. Ranz.

EXPLANATION

This is a LANDSAT image of Wyoming as viewed from an unmanned, Earth-orbiting, NASA satellite. The image is a composite of many smaller images taken from 570 miles above the Earth's surface. The colors are not true visible colors: vegetation shows up as bright red patches, especially noticeable in and around the mountains (forested) and along and near rivers (stream vegetation and irrigated lands); water bodies like Yellowstone Lake (in the northwest corner of the image) and numerous other lakes and reservoirs are black; basins and low-lying areas are mostly shades of yellow, gray, green, and light brown; mountains and upland areas tend to be darker browns and some have white snow. A few of the white spots are clouds; for example, there are white clouds and their shadows on the east side of the Bighorn Mountains. County names and boundaries have been overlaid to assist in locating features.



Wyoming State Geological Survey
Lance Cook, State Geologist
Laramie, Wyoming
2000

Figure 13: Landsat Image of Wyoming
Source: Wyoming State Geological Survey

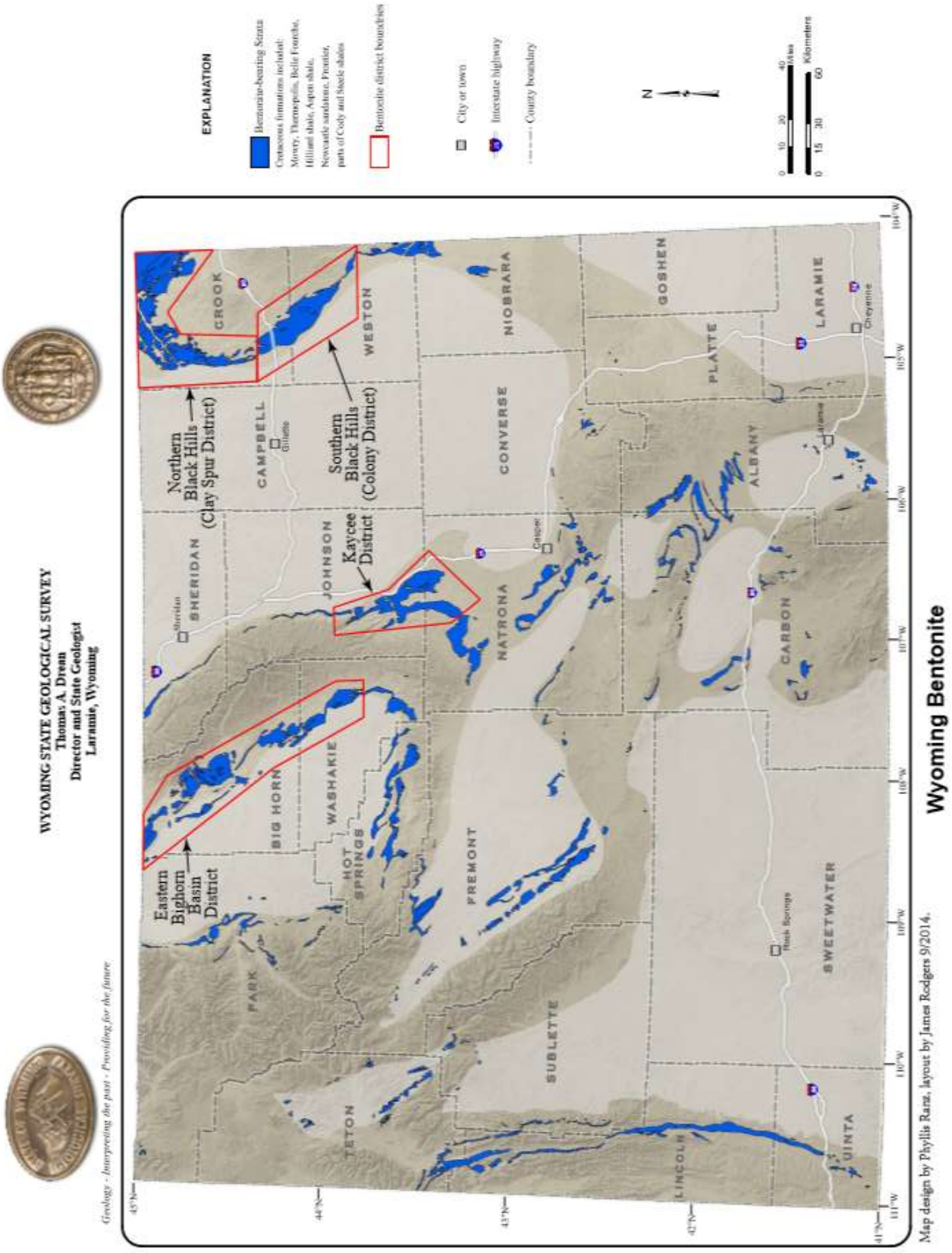


Figure 14: Wyoming Bentonite
 Source: Sutherland Wayne M., Dreaan Thomas A. (2014) Wyoming Bentonite, Wyoming State Geological Survey

Samples

The samples that were used for the analysis below were from:

- **Kimolos, Greece**

1A: Gray Bentonite, which appears in the extraction pond and is in immediate contact with sample 1B

1B: Masticha, high quality bentonite, which thickness is 2-3 meters and it is sandwiched between gray and doff-white bentonite in the same quarry. It appears on the NW-W section of the mine and in the extraction pond (*Roussos Mine- Bentomine Kimolian Enterprises*)

- **Wyoming, USA**

These analysis will result the differences or similarities between Greek and American Bentonite.

Analysis

FT-IR

After grinding the samples with mortar and place approximately 40-50 grams of each into glass containers, the containers were placed in the oven overnight at 70 °C in order to dry.

A very small amount of the predried samples and the dried ones was placed in the GladiATR, in order to analyze them and detect the differences.

Sample	Initial Mass (g)	Empty (g)	Predried Mass (g)	Dried Mass (g)
Kimolos 1A	50,08	150,43	200,51	195,17
Kimolos 1B	44,48	150,40	194,98	189,14
Wyoming	50,29	150,51	200,80	195,05

Table 6: masses before and after drying



Figure 15: GladiATR Vision – Diamond ATR with Sample View. Spectral range is 4000–400 cm⁻¹ with standard FTIR optics.

The results from FT-IR spectrum are given below. Spectral range is 4000–400 cm⁻¹ with standard FTIR optics. Each figure shows FT-IR spectra of each bentonite and it combines Transmittance (%) with Wavenumber (cm⁻¹) for predried and dried samples, but also Absorbance with Wavenumber (cm⁻¹) for only dried ones.

Tables 7-12 present the relation between the FT-IR bands and the OH-groups for dioctahedral smectites. Position and shape of the OH stretching band in the IR spectra of smectites is influenced mainly by the nature of the octahedral atoms to which the hydroxyl groups are coordinated (*Madejova, 2003*).

Results

Greece Kimolos Bentonite 1A

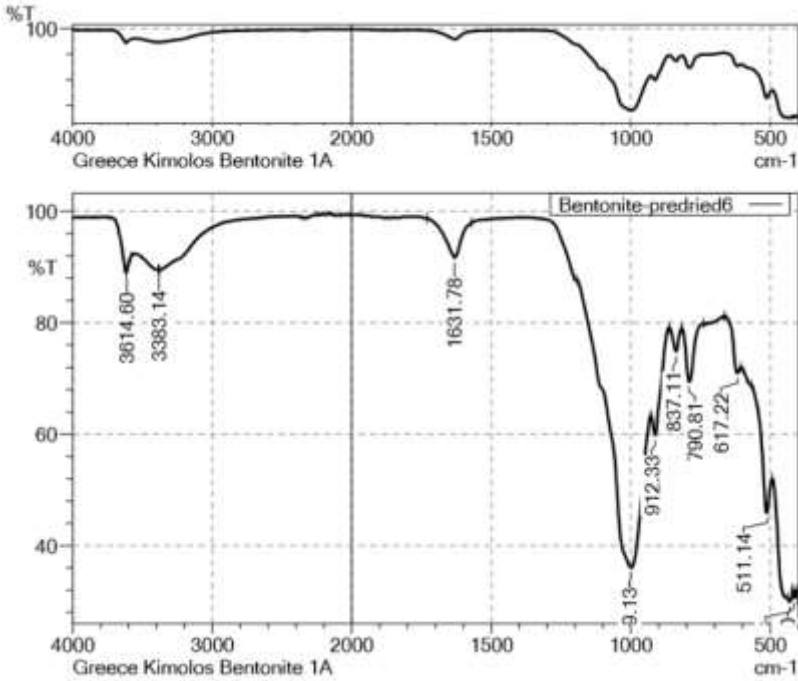


Figure 16: FTIR spectrum of Kimolos 1A Bentonite before drying

Predried	
430,13	δ (Si-O-Si)
511,14	δ (Si-O-AlVI)
617,22	Al-O, Si-O out of plane vibrations
790,81	ν (Si-O) of SiO ₂ impurity
837,11	δ (Al-Mg-OH)
912,33	δ (Al-Al-OH)
999,13	Si-O of other silicates like kaolinite or and illite
1631,78	δ H-O-H
3383,14	ν H-O-H
3614,6	ν (X-O-H), X=Al, Mg

Table 7

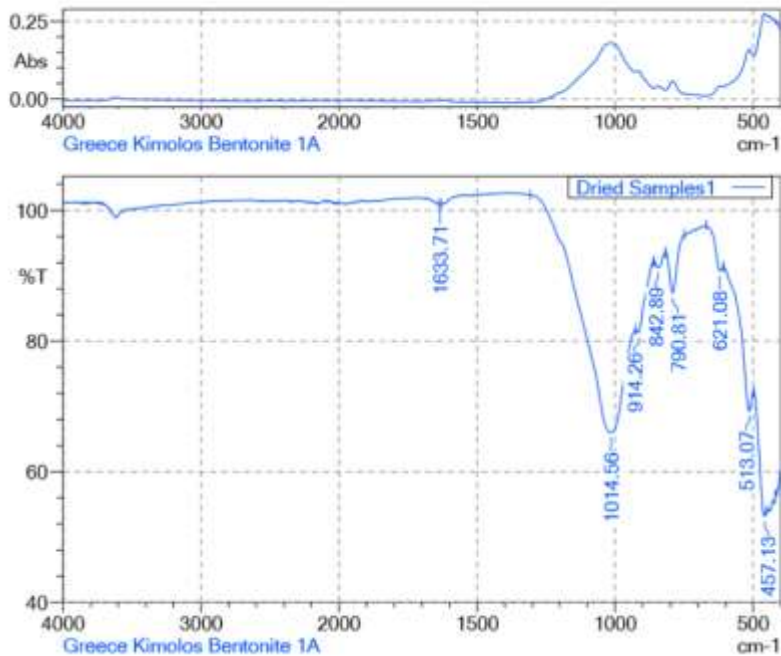


Figure 17: FTIR spectrum of Kimolos 1A Bentonite after drying

Dried	
457,13	δ (Si-O-Si)
513,07	δ (Si-O-AlVI)
621,08	Al-O, Si-O out of plane vibrations
790,81	ν (Si-O) of SiO ₂ impurity
842,89	δ (Al-Mg-OH)
914,26	δ (Al-Al-OH)
1014,56	ν (Si-O) in plane vibrations
1633,71	δ H-O-H

Table 8

Note:

δ bending

ν stretching

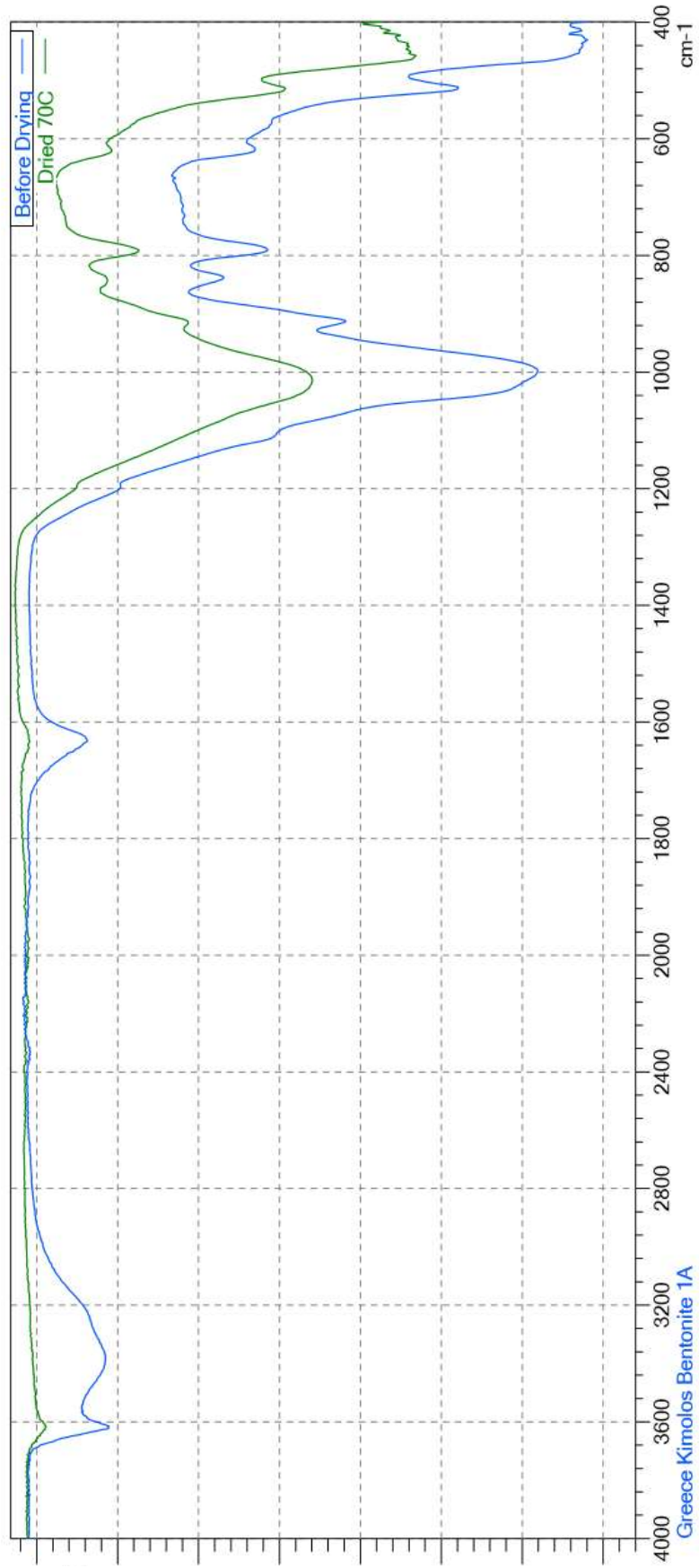
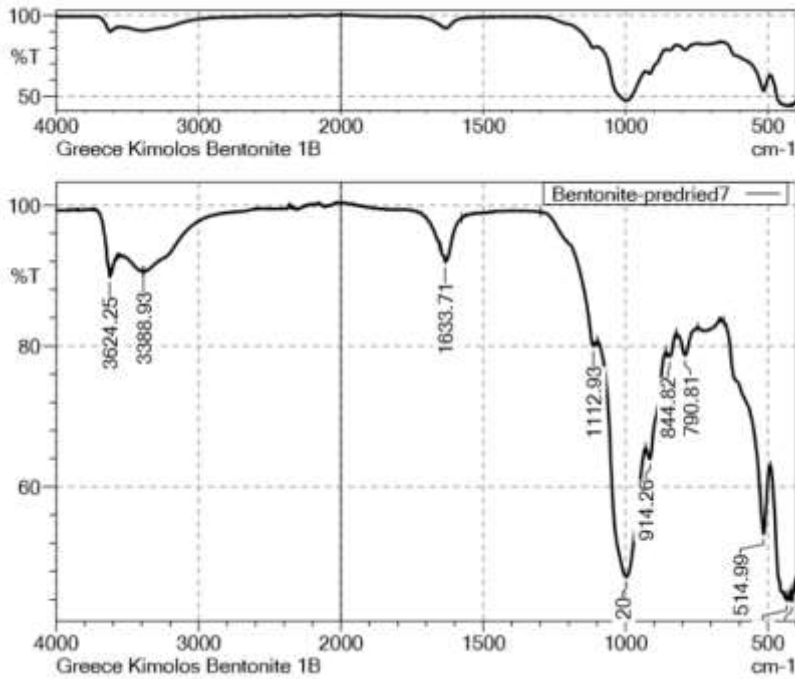


Figure 18: Comparison of FTIR spectrum of Kimolos 1A Bentonite before and after drying

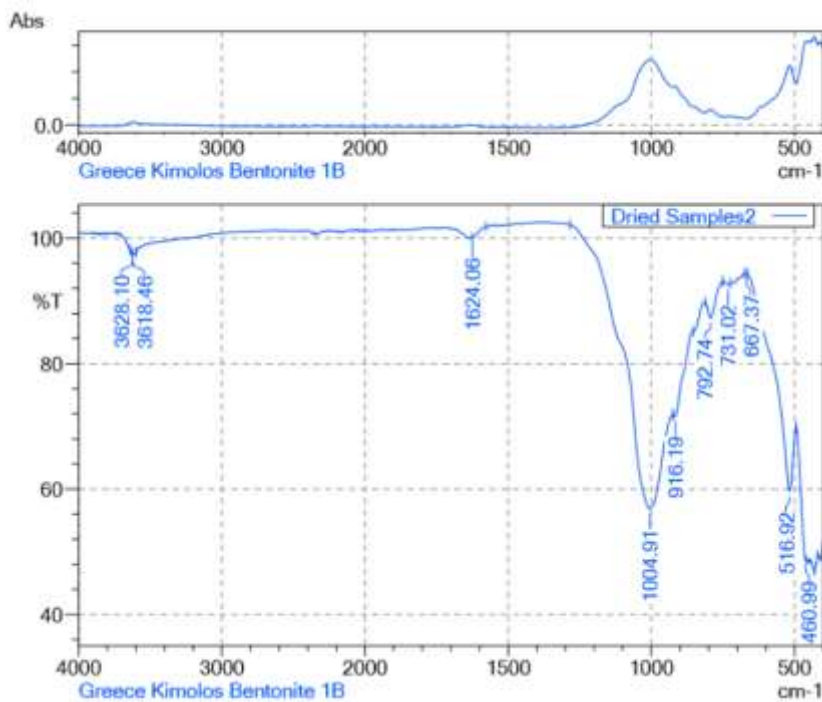
Greece Kimolos Bentonite 1B



Predried	
433,98	δ (Si-O-Si)
514,99	δ (Si-O-AlVI)
790,81	u (Si-O) of SiO ₂ impurity
844,82	δ (Al-Mg-OH)
914,26	δ (Al-Al-OH)
997,2	Si-O of other silicates like kaolinite or and illite
1112,93	Si-O stretching
1633,71	δ H-O-H
3388,93	u H-O-H
3624,25	u (X-O-H), X=Al, Mg

Table 9

Figure 19: FTIR spectrum of Kimolos 1B Bentonite before drying



Dried	
460,99	δ (Si-O-Si)
516,92	δ (Si-O-AlVI)
667,37	Al-O, Si-O out of plane vibrations
731,02	
792,74	u (Si-O) of SiO ₂ impurity
916,19	δ (Al-Al-OH)
1004,91	Si-O of other silicates like kaolinite or and illite
1624,06	δ H-O-H
3618,46	u V(OH) stretching
3628,1	u (X-O-H), X=Al, Mg / (OH stretching)

Table 10

Figure 20: FTIR spectrum of Kimolos 1B Bentonite after drying

Note:

δ bending

u stretching

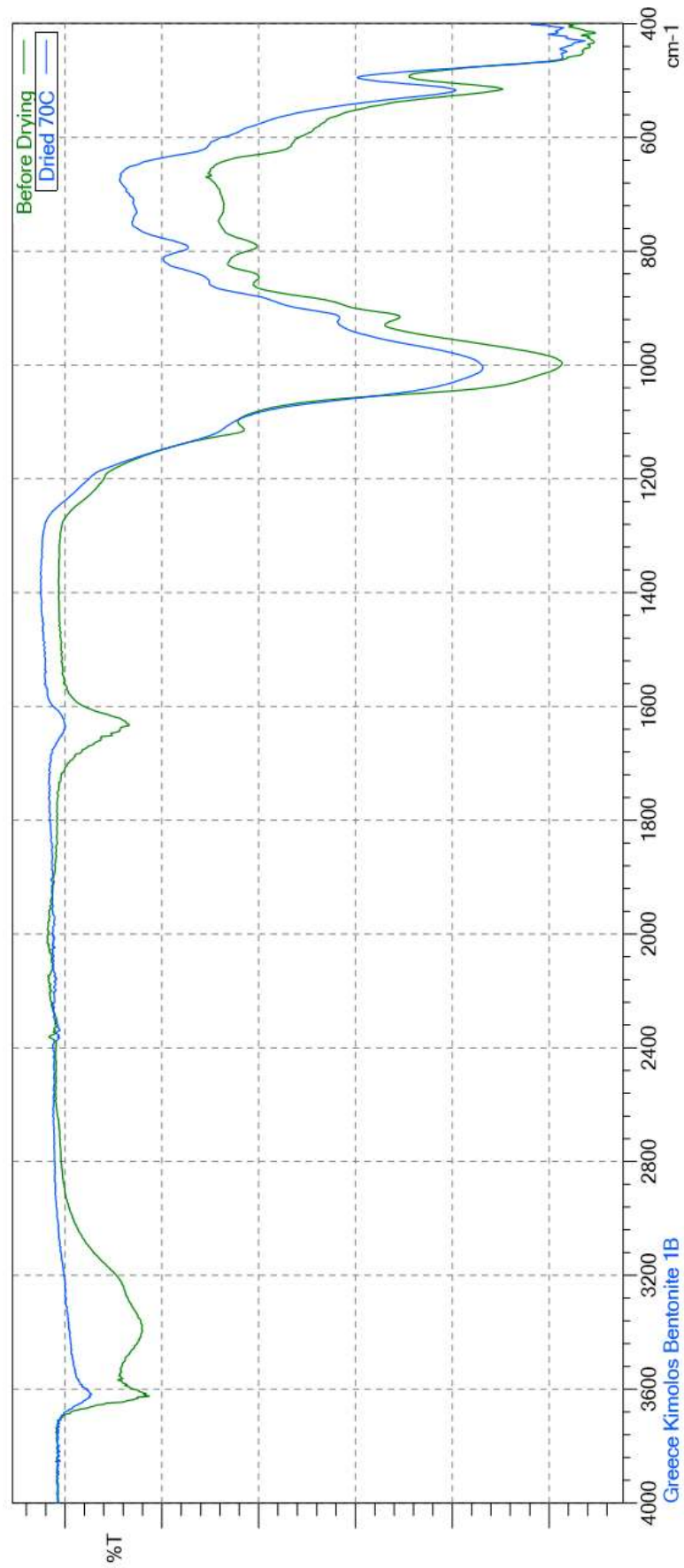


Figure 21: Comparison of FTIR spectrum of Kimolos 1B Bentonite before and after drying

Wyoming Bentonite

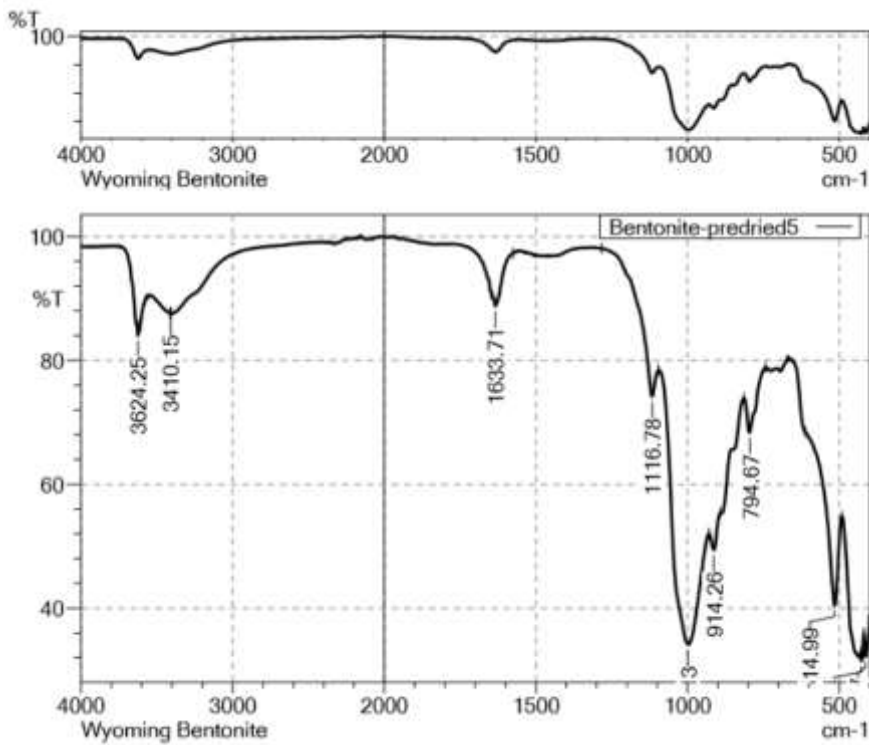


Figure 22: FTIR spectrum of Wyoming Bentonite before drying

Predried	
426,27	δ (Si-O-Si)
514,99	δ (Si-O-AlVI)
794,67	u (Si-O) of SiO ₂ impurity
914,26	δ (Al-Al-OH)
999,13	Si-O of other silicates like kaolinite or and illite
1116,78	u Si-O stretching
1633,71	δ H-O-H
3410,15	u H-O-H
3624,25	u (X-O-H), X=Al, Mg

Table 11

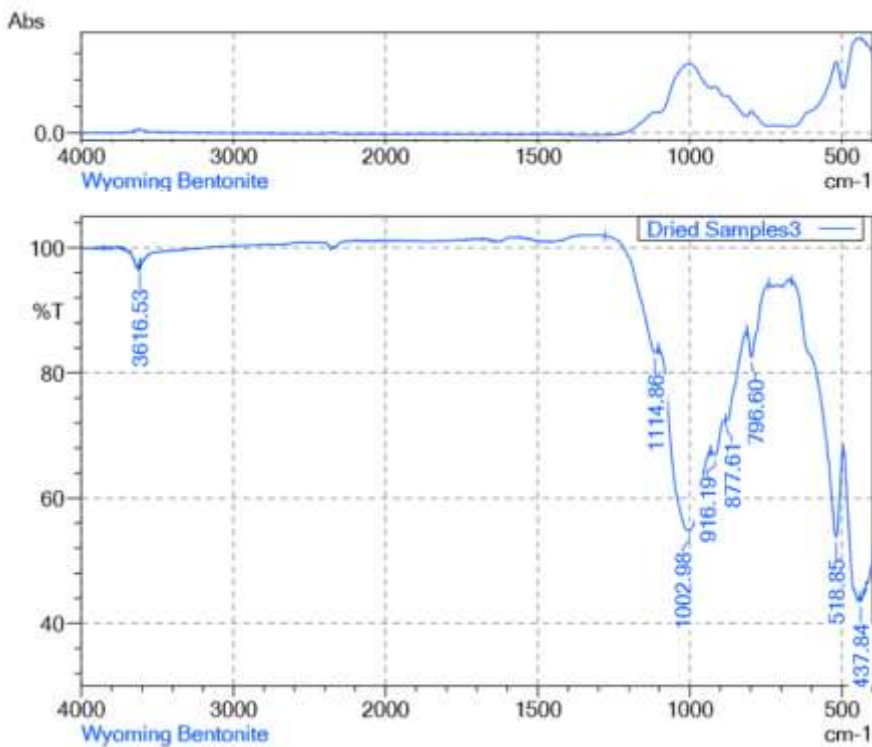


Figure 23: FTIR spectrum of Wyoming Bentonite after drying

Dried	
437,84	δ (Si-O-Si)
518,85	δ (Si-O-AlVI)
796,6	u (Si-O) of SiO ₂ impurity
877,61	δ Al-Fe-OH
916,19	δ (Al-Al-OH)
1002,98	Si-O of other silicates like kaolinite or and illite
1114,86	u (Si-O) out of plane vibrations
3616,53	u (X-O-H), X=Al, Mg

Table 12

Note:
 δ bending
 u stretching

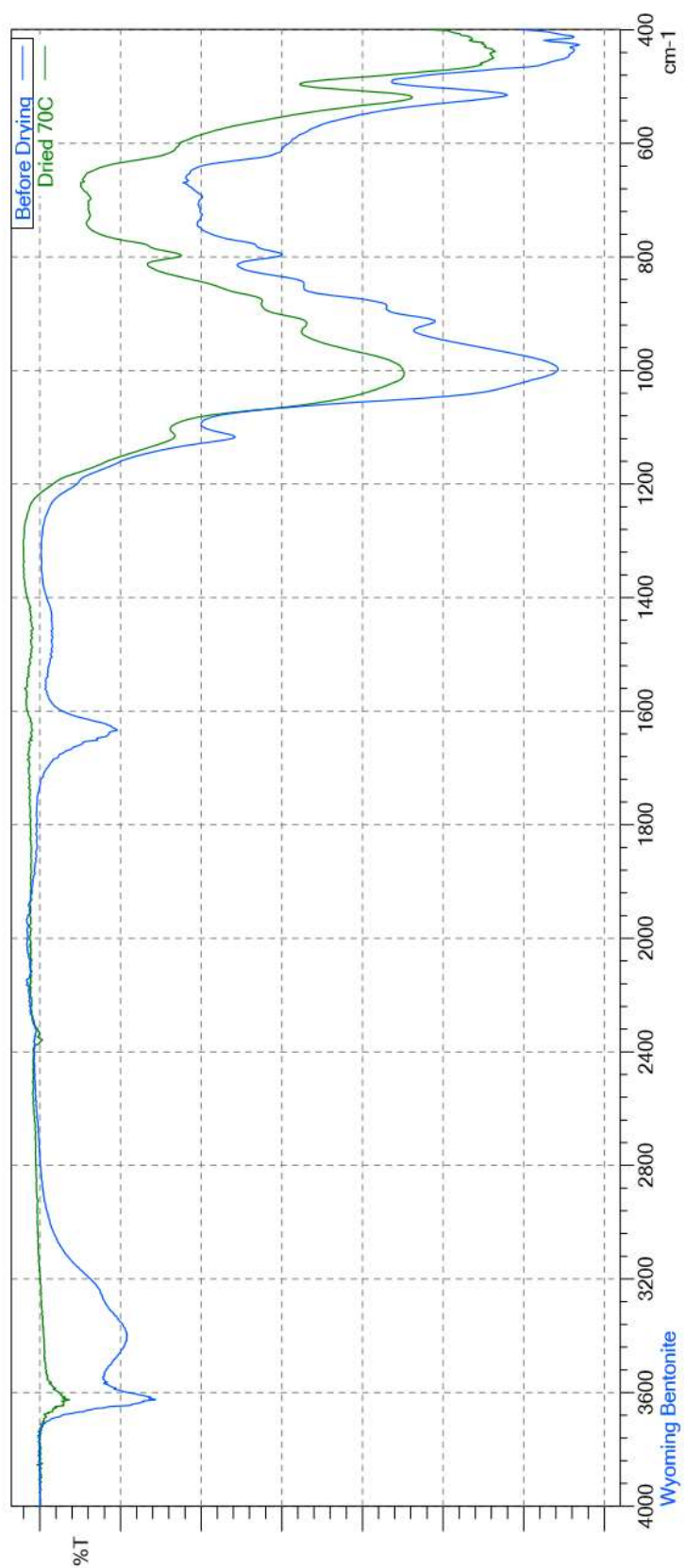


Figure 24: Comparison of FTIR spectrum of Wyoming Bentonite before and after drying

Comparison Predried

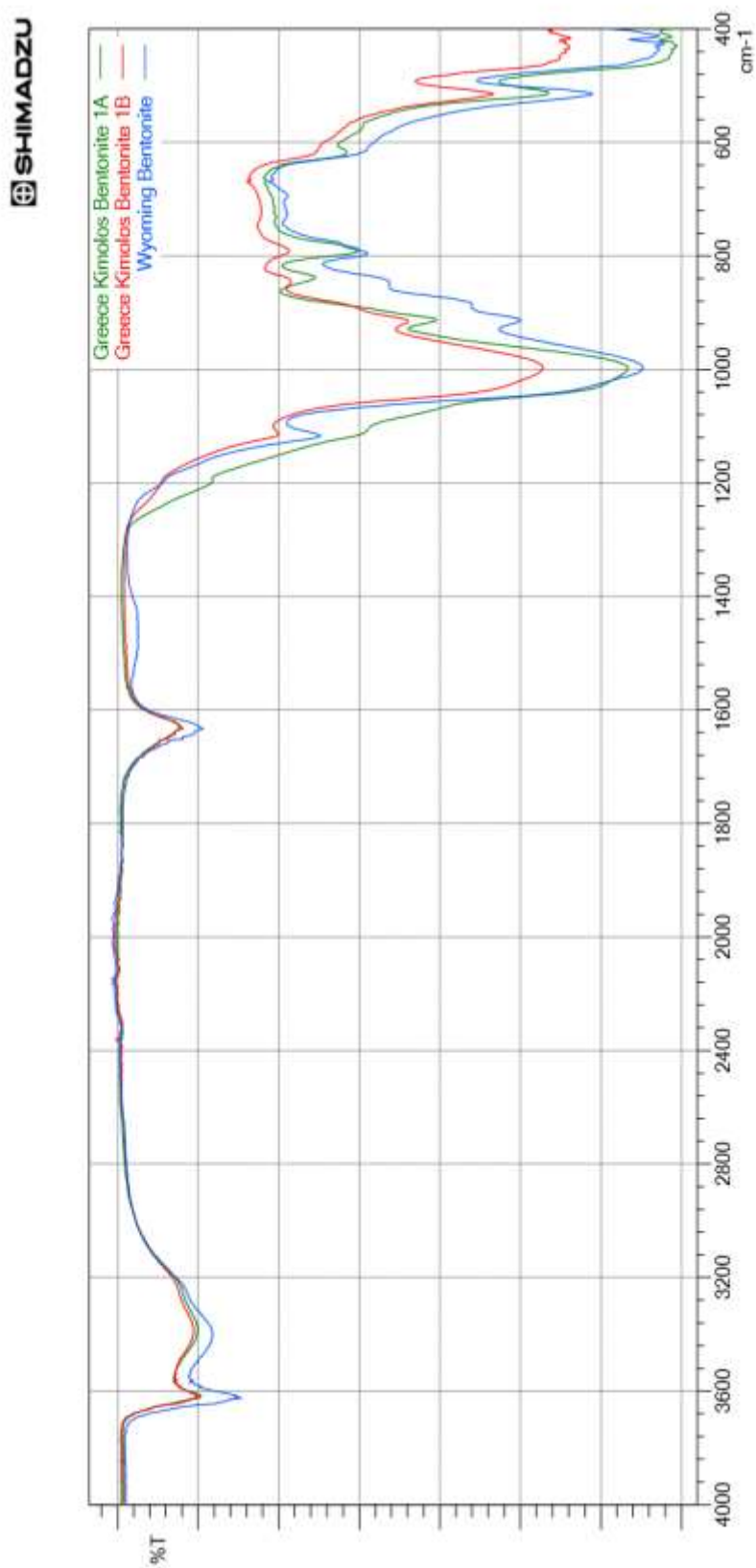


Figure 25: Comparison of FTIR spectrum of all Bentonites before drying

Comparison Dried

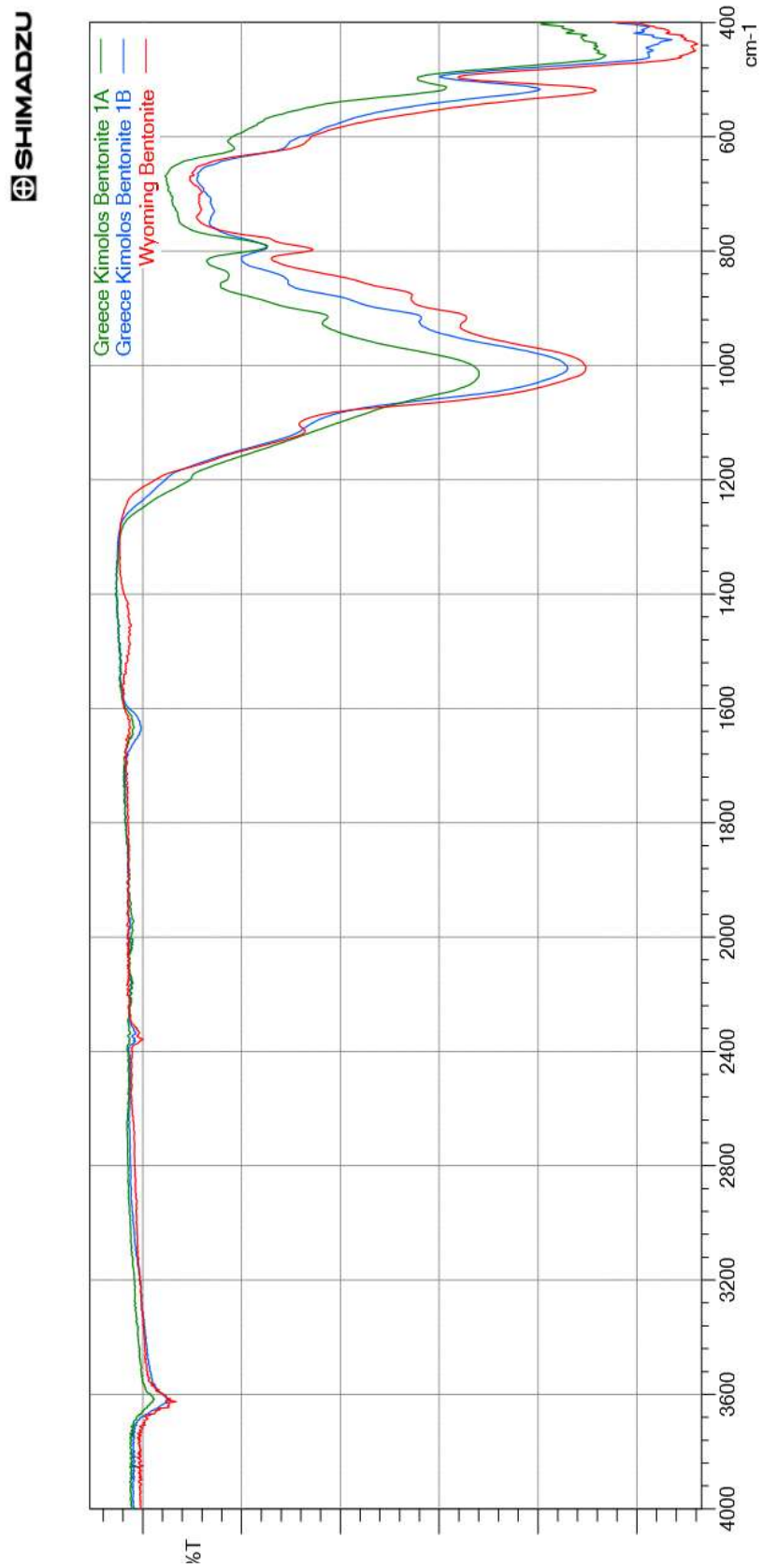


Figure 26: Comparison of FTIR spectrum of all Bentonites after drying

- The absorption band at 3614.6 (1A^P), 3618.46 (1B^D), 3616.53 (W^D), 3624.25 (1B^P, W^P) cm⁻¹, are typical for dioctahedral smectites and is due to **stretching vibrations of structural OH** groups of bentonites
- The broad band at 3383.14 (1A^P), 3388.93 (1B^P) and 3410.15(W^P) cm⁻¹, is due to O-H **stretching vibrations of adsorbed water**, while the **bending vibration of water** observed at 1631.78 (1A^P), 1633.71 (1A^D,1B^P), 1642.04 (1B^D), 1633.71 (1B^D, W^P) cm⁻¹.
- The IR spectra of dioctahedral smectites show only one broad band in the 1040-1020cm⁻¹ region due to **Si-O stretching** vibrations.
- The bands at 912.33 (1A^P), 914.26 (1A^D, 1B^P, W^P) and 916.19 (1B^D, W^D) cm⁻¹ are attributed to **Al-Al-OH** bending vibration, while the band at 837.11 (1A^P), 842.89 (1A^D) and 844.82 (1B^P) cm⁻¹ corresponds to **Al-Mg-OH** bending vibration.
- The peak at 877,61 cm⁻¹ observed only in dried Wyoming bentonite, could be ascribed to **Al-Fe-OH bending** vibration.
- In Wyoming predried sample, the appearance of two peaks at about 915cm⁻¹ (**δ Al-Al-OH**) and about 843cm⁻¹ (**δ Al-Mg-OH**) reflect partial substitution of octahedral Al by Mg.
- **Si-O stretching of quartz** (SiO₂) impurity appears at 790.81 (1A^P, 1A^D, 1B^P), 792.74 (1B^D), 794.67 (W^P), 796.6 (W^D)cm⁻¹.
- The bands at 511.14 (1A^P), 513.07 (1A^D), 514.99 (1B^P, W^P), 516.92 (1B^D)and 518.85 (W^D) cm⁻¹ are due to the **Si-O-AlVI bending** band (AlVI is Al in octahedral positions), while the 457.13 (1A^D) and 460.99 (1B^D) or less, bands to the **Si-O-Si bending** vibration which is characteristic for smectites.

Bentonite samples: 1A^P: Kimolos 1A predried, 1A^D: Kimolos 1A dried, 1B^P: Kimolos 1B predried, 1B^D: Kimolos 1A dried, W^P: Wyoming predried, W^D: Wyoming dried

When compared to FTIR data of Kimolos bentonites and bentonites which have formed in different geological environments like Wyoming bentonites, almost identical data were obtained in the present study. In all the samples the bands at about 3380-3410 cm⁻¹, are due to O-H stretching vibrations of adsorbed water, are not detected after drying. The absorption band at 844.82 cm⁻¹ from Kimolos 1B before drying, which corresponds to Al-Mg-OH bending vibration, isn't detected after drying. Also, sample Kimolos 1B presents absorption band at 667.37 cm⁻¹, which is due to Al-O, Si-O out of plane vibrations but its only detected after drying. Furthermore, Wyoming sample loses its bending vibration of water after drying and it's the only sample that presents Al-Fe-OH bending vibration, after its dried.

Atomic Absorption



This analysis requires the preparation of standard solutions, in order to define the absorbance in Calcium and Sodium in the samples by using the Atomic Absorption Flame Emission Spectrophotometer AA-6200 (SHIMADZU). The preparation begins by using 50 ml testing tubes. The volumes (V_1) of Multi Cation Standard 2 for IC (Sigma Aldrich) were calculated as follows:

Figure 27: Atomic Absorption Flame Emission Spectrophotometer AA-6200 (SHIMADZU)

C_1 (M)	C_2 (M)	V_2 (mL)	V_1 (mL)
1000	15	50	0,750
	10		0,500
	5		0,250
	1		0,100
	0,5		0,050

$$C_1 V_1 = C_2 V_2$$

$$V_1 = \frac{C_2 V_2}{C_1}$$

Table 13

Standard sample preparation

The volumes above were transferred in the testing tubes by using a pipette. The solution was diluted till 50 mL with deionized water. Calcium results were acceptable but for Sodium, the red-highlighted volumes of Multi Cation Standard, are not acceptable because they exceed the upper limit of the instrument. In that case more standards were produced with the following volumes: 0,025 mL, 0,075 mL, 0,175 mL. This step was made in order the program to build the calibration curve for each element.

Sample preparation

Approximately 0,5 gr of each bentonite sample were weighted and placed in iPrep vessels.

The unique dual seal of the new iPrep™ allows for the highest working conditions of any microwave digestion vessel. This means it can digest extremely difficult materials such as PET and bunker oil with ease. It also will digest twice as much sample as a typical high performance vessel. This allows for better homogeneity and lower detection limits. The 110 mL volume provides a 10 percent enhancement over similar vessel types.

(Source <http://cem.com/en/mars-6>)

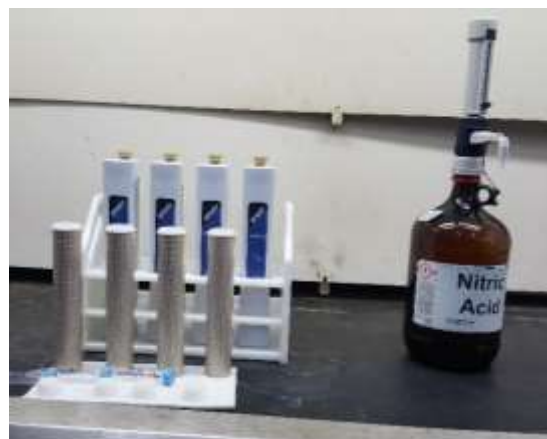


Figure 28: iPrep vessels and nitric acid

Then 10mL of HNO₃ were poured into the iPrep vessels. After sealed them carefully they were placed into CEM Mars 6™ Microwave Digestion System for 30 minutes in order to be digested. The program choosed was clay. The higher temperature that it reached was 201°C. When cooling is achieved the digested samples were transferred into 50 ml test tubes and ready to be analyzed at Atomic Absorption Flame Emission Spectrophotometer.



Figure 29: CEM Mars 6™ Microwave Digestion System

Samples	Ca		Na	
	<u>Concentration</u>	<u>Absorbance</u>	<u>Concentration</u>	<u>Absorbance</u>
Kimolos 1A	3,4746	0,2372	6,0332	3,0480
Kimolos 1B	2,9744	0,2091	5,2864	2,7025
Wyoming	6,4117	0,4022	4,5443	2,3592

Table 13.1

Table 13.1 shows similar amounts of Ca in all of the samples, with Wyoming presenting little higher amounts. Same applies from the Na, but with Kimolos 1A showing higher amounts.

Ca(422.7nm)

Analyst:

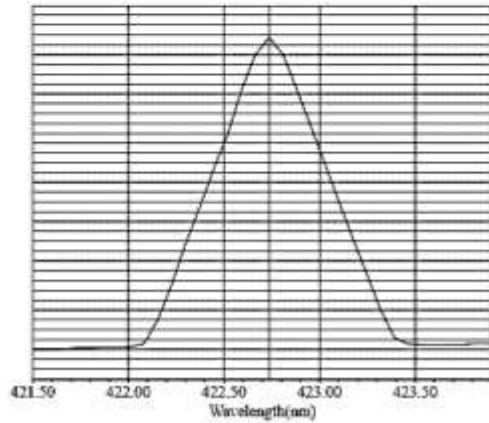
File Comment:

Comment:

Flame

Optics Parameters

Element:	Ca
Socket #:	1
Lamp Current Low(mA):	10
Wavelength(nm):	422.7
Slit Width(nm):	0.7
Lamp Mode:	NON-BGC



Peak(nm) : 422.74

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	2.0
Flame Type:	Air-C2H2

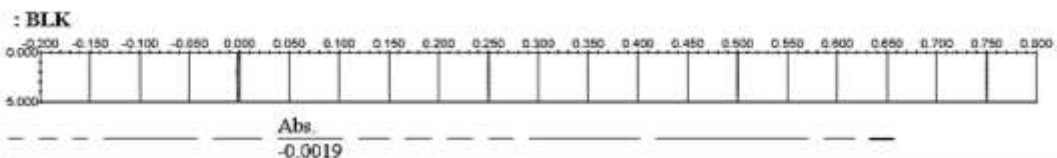
Measurement Parameters

Order:	1st
Zero Intercept:	No
Conc. Unit:	NONE
Repetition Sequence:	SM-SM...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num Repts.	Max Repts.	RSD Limit	SD Limit
Blank	1	1	99.90	0.00000
Standard	1	1	99.90	0.00000
Sample	1	1	99.90	0.00000
Reslope	1	1	99.90	0.00000

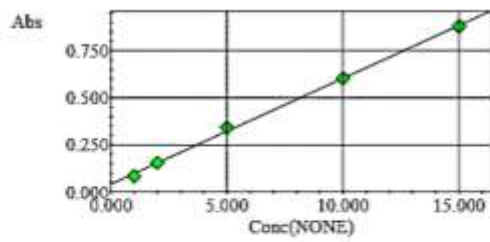
QA/QC Parameters

QC Type	Judge Calc.	Standard Value	Out of Control Remark
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Date	Time
3/28/2019	4:42 PM

Calibration Curve (C# : 01)

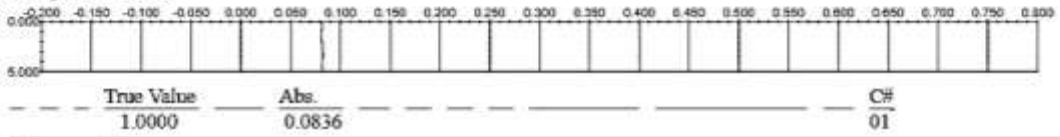


Conc	Abs
(NONE)	
1.0000	0.0836
2.0000	0.1554
5.0000	0.3422
10.0000	0.6033
15.0000	0.8794

Abs=0.0561783Conc+0.0420033

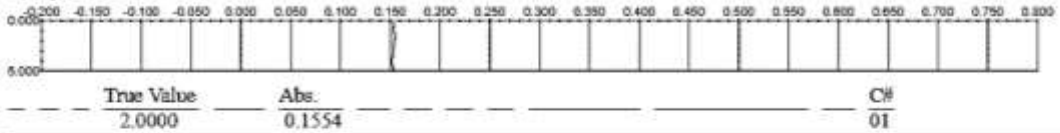
r=0.9993

Ca 0,05 mL : STD



Date 3/28/2019 Time 4:43 PM

Ca 0,1 mL : STD



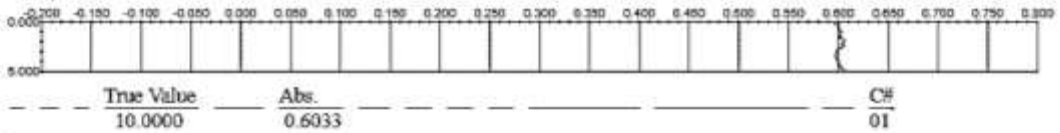
Date 3/28/2019 Time 4:44 PM

Ca 0,250 mL : STD



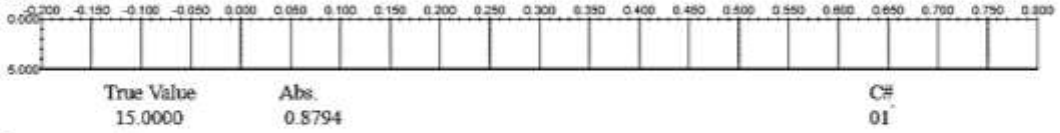
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Ca 0,500 mL : STD



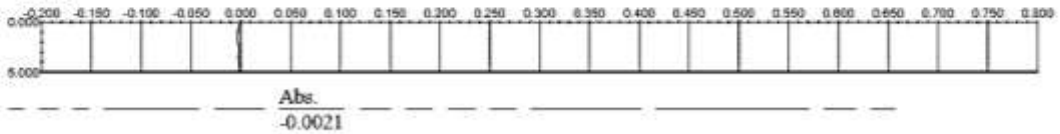
Date 3/28/2019 Time 4:45 PM

Ca 0,750 mL : STD



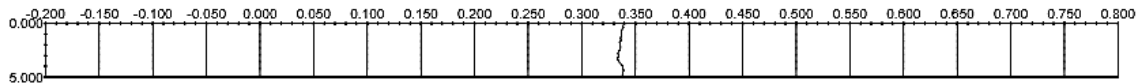
Date 3/28/2019 Time 4:46 PM

: BLK



Date 3/28/2019 Time 4:46 PM

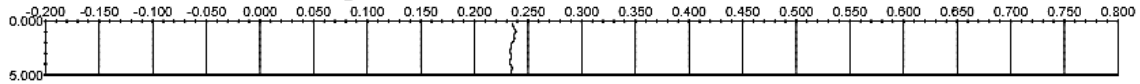
CHECK : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
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C# Date Time
 01 3/28/2019 4:48 PM

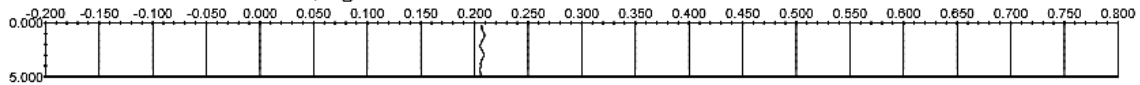
Greece Kimolos Bentonite 1A 0,46gr : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
3.4746	0.2372	1.000000	1.00	1.00	1.000000	3.4746	NONE

C# Date Time
 01 3/28/2019 4:54 PM

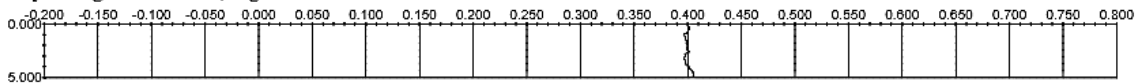
Greece Kimolos Bentonite 1B 0,48gr : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
2.9744	0.2091	1.000000	1.00	1.00	1.000000	2.9744	NONE

C# Date Time
 01 3/28/2019 4:55 PM

Wyoming Bentonite 0,53gr : UNK

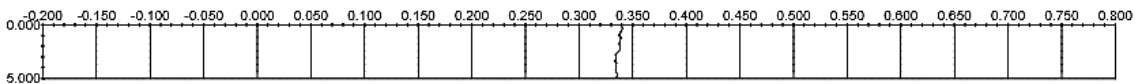


Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
6.4117	0.4022	1.000000	1.00	1.00	1.000000	6.4117	NONE

C# Date Time
 01 3/28/2019 4:56 PM

: CAL Check Out of Control Remark : OK

: UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
5.2796	0.3386	1.000000	1.00	1.00	1.000000	5.2796	NONE

C# Date Time
 01 3/28/2019 4:58 PM

Na(589.0nm)

Analyst:

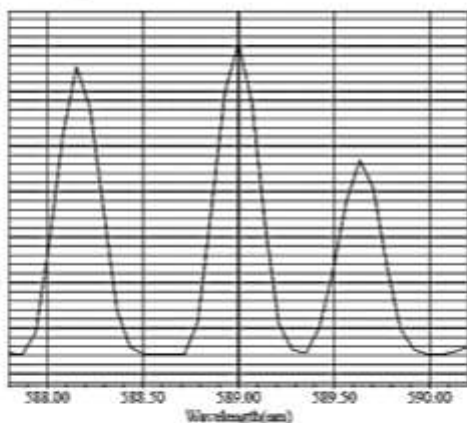
File Comment:

Comment:

Flame

Optics Parameters

Element:	Na
Socket #:	2
Lamp Current Low(mA):	12
Wavelength(nm):	589.0
Slit Width(nm):	0.2
Lamp Mode:	NON-BGC



Peak(nm) : 589.00

Atomizer/Gas Flow Rate Setup

Fuel Gas Flow Rate(L/min):	1.8
Flame Type:	Air-C ₂ H ₂

Measurement Parameters

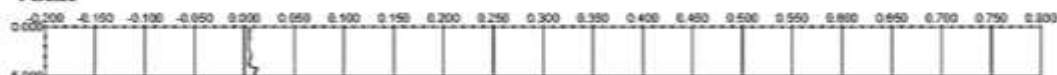
Order:	1st
Zero Intercept:	No
Conc. Unit:	NONE
Repetition Sequence:	SM-SM...
Pre-Spray Time (sec):	3
Integration Time (sec):	5
Response Time:	1

	Num Repts.	Max Repts.	RSD Limit	SD Limit
Blank	1	1	99.90	0.00000
Standard	1	1	99.90	0.00000
Sample	1	1	99.90	0.00000
Reslope	1	1	99.90	0.00000

QA/QC Parameters

QC Type	Judge Calc	Standard Value	Out of Control Remark
---------	------------	----------------	-----------------------

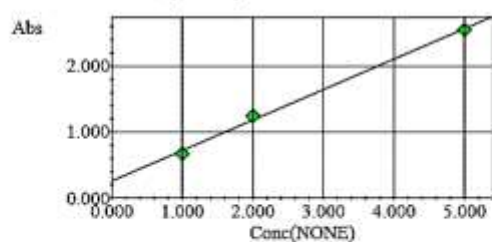
: BLK



Abs.
0.0064

Date	Time
3/28/2019	5:36 PM

Calibration Curve (C# : 01)

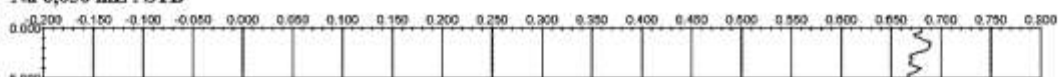


Conc	Abs
(NONE)	
1.0000	0.6703
2.0000	1.2478
5.0000	2.5536

Abs=0.462619Conc+0.256915

r=0.9981

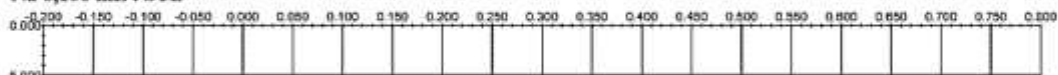
Na 0,050 mL : STD



True Value	Abs.	C#
1.0000	0.6703	01

Date 3/28/2019 Time 5:45 PM

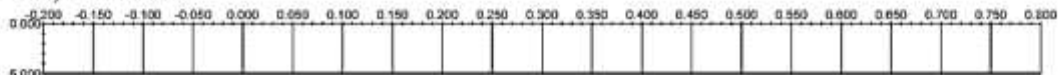
Na 0,100 mL : STD



True Value	Abs.	C#
2.0000	1.2478	01

Date 3/28/2019 Time 5:46 PM

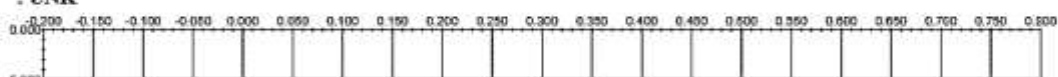
Na 0,250 mL : STD



True Value	Abs.	C#
5.0000	2.5536	01

Date 3/28/2019 Time 5:47 PM

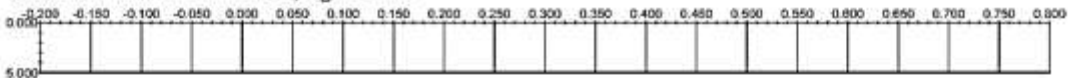
: UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
2.1698	1.2607	1.000000	1.00	1.00	1.000000	2.1698	NONE

C# 01 Date 3/28/2019 Time 5:52 PM

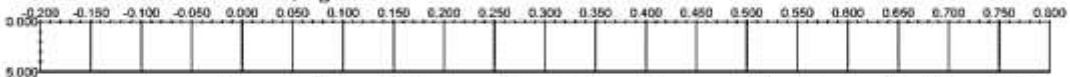
Greece Kimolos Bentonite 1A 0,46gr : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
6.0332	3.0480	1.000000	1.00	1.00	1.000000	6.0332	NONE

C# Date Time
01 3/28/2019 5:55 PM

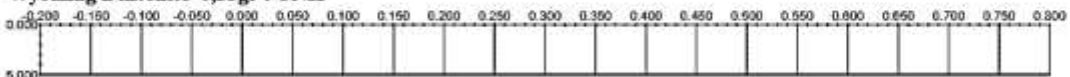
Greece Kimolos Bentonite 1B 0,48gr : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
5.2864	2.7025	1.000000	1.00	1.00	1.000000	5.2864	NONE

C# Date Time
01 3/28/2019 5:55 PM

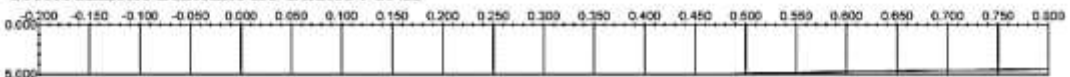
Wyoming Bentonite 0,53gr : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
4.5443	2.3592	1.000000	1.00	1.00	1.000000	4.5443	NONE

C# Date Time
01 3/28/2019 5:56 PM

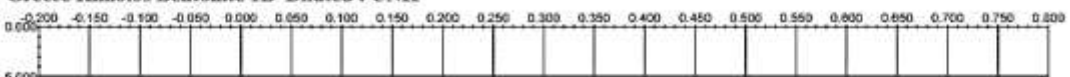
Greece Kimolos Bentonite 1A Diluted : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
4.3558	2.2720	1.000000	1.00	1.00	1.000000	4.3558	NONE

C# Date Time
01 3/28/2019 6:12 PM

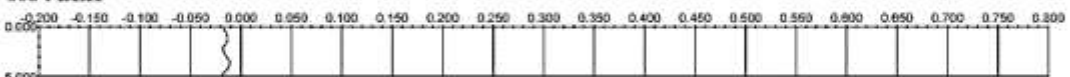
Greece Kimolos Bentonite 1B Diluted : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
5.0523	2.5942	1.000000	1.00	1.00	1.000000	5.0523	NONE

C# Date Time
01 3/28/2019 6:13 PM

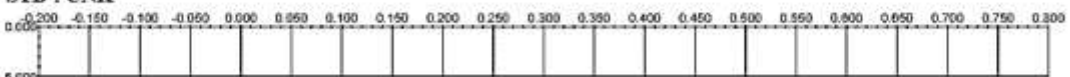
008 : BLK



Abs.
-0.0148

Date Time
3/28/2019 6:14 PM

STD : UNK



Conc.	Abs.	WF	VF	DF	CF	Actual Conc.	Actual Conc. Unit
2.2489	1.2973	1.000000	1.00	1.00	1.000000	2.2489	NONE

C# Date Time
01 3/28/2019 6:15 PM

Ion Chromatography

Ion chromatography (or ion-exchange chromatography) is a chromatography process that separates ions and polar molecules based on their affinity to the ion exchanger. So it is able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulfate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range.

Ion chromatography, a form of liquid chromatography, measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Sample solutions pass through a pressurized chromatographic column where ions are absorbed by column constituents. As an ion extraction liquid, known as eluent, runs through the column, the absorbed ions begin separating from the column. The retention time of different species determines the ionic concentrations in the sample.

Sample preparation:

2 gr of each sample, was placed into test tubes, respectively. Then, 1000mL of deionized water were placed into a glass bottle and the glass bottle was put into Ultrasonic cell disruptor (Microson™) all night. After that, 2,33423 gr of Pyridinedicarboxylic acid and 2,171 mL of 70% HNO₃, were added into the glass bottle, that was removed from the Ultrasonic cell disruptor. The glass bottle was putted in incubator shaker (Innova 4000) at 37°C, until the mixture was diluted. Afterwards, 496,8 mL of deionized water and 3,2 mL of the mixture above., were placed into a new glass bottle and 10 mL of the its content were placed into each test tube that contains 2gr of sample. The test tubes were shaken, centrifuged and the supernatant of each tube was extracted, filtered and placed into new test tubes.



***Figure 30:** Metrohm Ion chromatography system*



***Figure 31:** Ultrasonic cell*



***Figure 32:** Incubator shaker - Innova 4000*

Then, iron chromatography test tubes with 1 ml capacity were filled with the filtered solution and deionized water as follows in Table 14. The last step was placing the tubes into the Metrohm Ion chromatography system, to be analyzed.

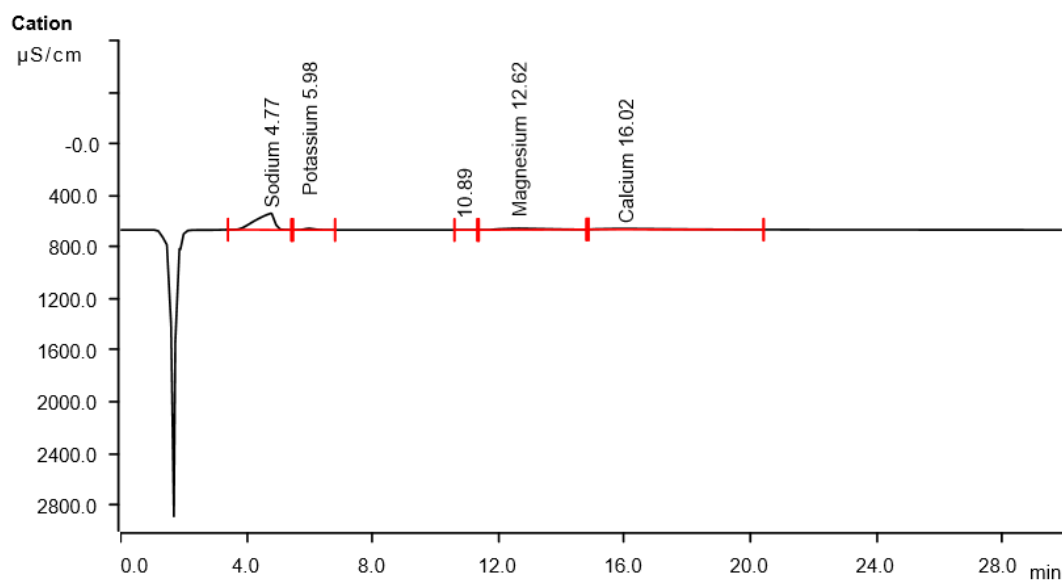


Figure 33: Ion chromatography test tubes

Filtered solution (mL)	Deionized H ₂ O (mL)
1	0
0,5	0,5
0,2	0,8
0,1	0,9
0,05	0,95
0,01	0,99

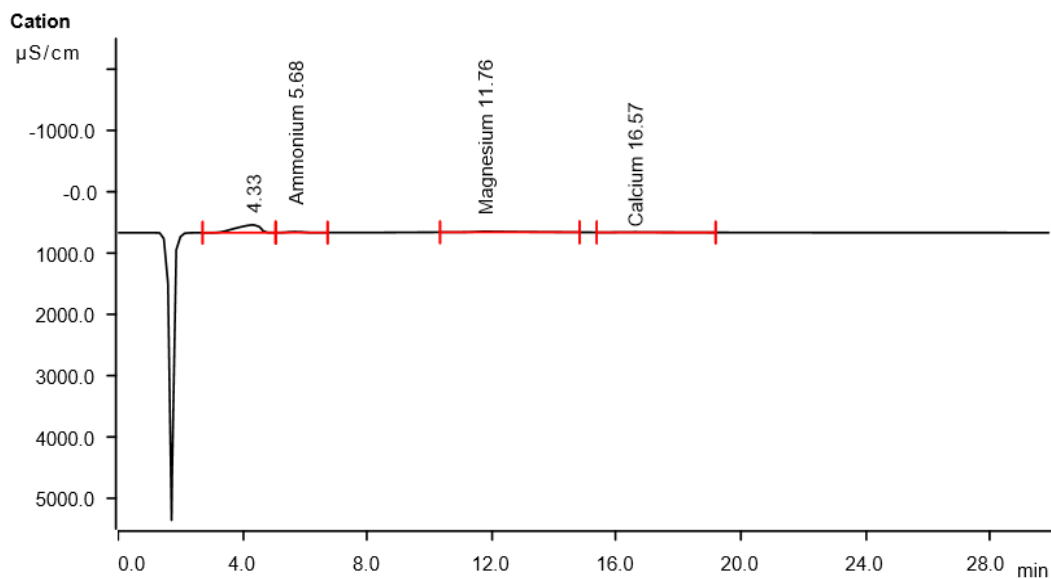
Table 14

Kimolos 1A: Nitric



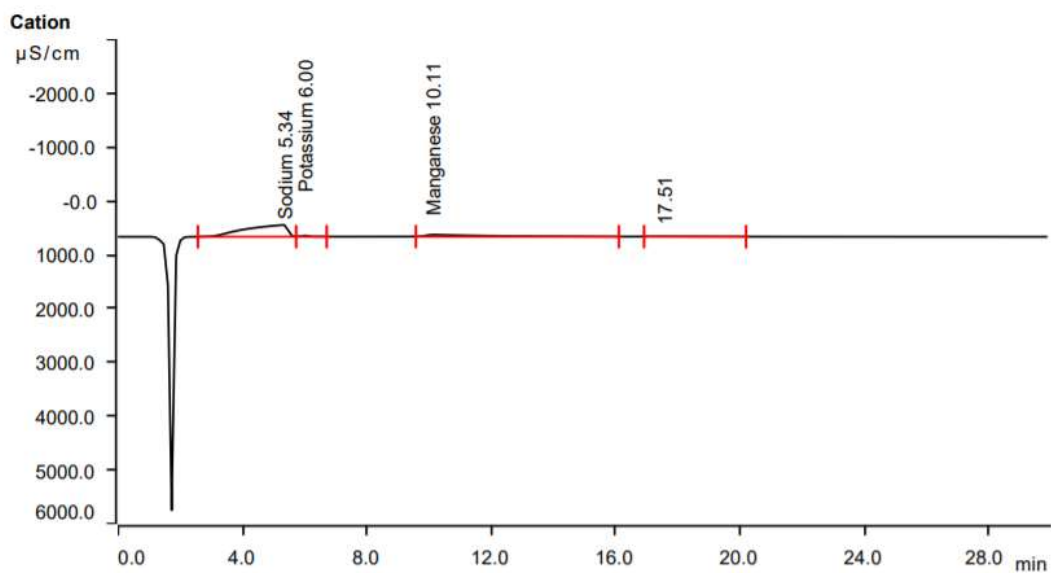
Peak number	Retention time (min)	Area (µS/cm) x min	Height (µS/cm)	Concentration (ppm)	Component name
1	4.772	87.2608	128.413	528.101	Sodium
2	5.977	4.0901	11.639	53.662	Potassium
3	10.892	0.0854	0.223	invalid	
4	12.617	16.6266	10.531	125.571	Magnesium
5	16.018	16.1636	6.769	63.737	Calcium

Kimolos 1B: Nitric



Peak number	Retention time min	Area ($\mu\text{S/cm}$) x min	Height $\mu\text{S/cm}$	Concentration ppm	Component name
1	4.332	111.1788	126.791	invalid	
2	5.682	7.6662	13.006	48.713	Ammonium
3	11.763	22.8491	13.888	172.481	Magnesium
4	16.570	6.5802	4.106	30.283	Calcium

Wyoming: Nitric



Peak number	Retention time min	Area ($\mu\text{S/cm}$) x min	Height $\mu\text{S/cm}$	Concentration ppm	Component name
1	5.343	341.8855	219.785	2057.636	Sodium
2	6.000	5.5038	19.169	71.327	Potassium
3	10.110	75.5648	35.227	876.280	Manganese
4	17.510	1.8349	1.453	invalid	

	Kimolos 1A (ppm)	Kimolos 1B (ppm)	Wyoming (ppm)
Sodium	528,11		2057,636
Potassium	53,662		71,327
Magnesium	125,571	172,481	
Calcium	63,737	30,283	
Ammonium		48,713	
Manganese			876,280

Table 14.1

As seen in Table 14.1, Kimolian bentonite contain Magnesium and Calcium, but 1A contains Sodium and Potassium too and 1B Ammonium. On the other hand, Wyoming bentonite includes Sodium, Potassium at higher amounts than Kimolian 1A, but also Manganese. Wyoming bentonite is a natural sodium bentonite and that explains the very high amount of Sodium.

Thermal Analysis

The thermal decomposition of bentonite sample was followed by means of simultaneous DSC using Mettler Toledo DSC823e setup (showing in Figure 34 and 35). The measurements were performed employing open alumina crucible (150ul) filled with approximately 0,04 gr of dried bentonite sample (at 70°C) and a corresponding empty referent crucible. All experiments were done in the temperature range from 50 °C to 600 °C with a heating rate of 20 K/min.

Method: dt 1.00s

[1] 50.0 – 600.0 °C, 20.00 K/min

[2] 600.0 °C, 5.00min

[3] 600.0 – 50.0 °C, -20.00 K/min

The diagrams/curves below, resulting from the analysis, illustrates the heat flow in conjunction with the temperature and the time.

As already mentioned, Montmorillonite is the dominant smectite mineral in bentonite. Montmorillonite shows a large low-temperature endothermic peak system, which size, shape and temperature depends on the suturing cation. Normal montmorillonite, shows at about 600°C a medium-small endothermic peak and at about 600°C – 550°C a small S-shaped endothermic-exothermic peak. Those two peaks are caused by loss of sorbed moisture, largely interlayer, dihydroxylation and structural change (Kimolos 1B). Abnormal montmorillonite, present curves with either two relatively small endothermic peaks at about 500-600°C (Kimolos 1A, Wyoming curves). These differences are due to energy relations between the hydroxyl groups bonding, like difference in composition.



Figure 34:

Source: <https://www.prweb.com/releases/2007/04/prweb513426.htm>



Figure 35: Source: www.mt.com - Mettler Toledo – Module DSC823e - Differential scanning calorimetry for all requirements

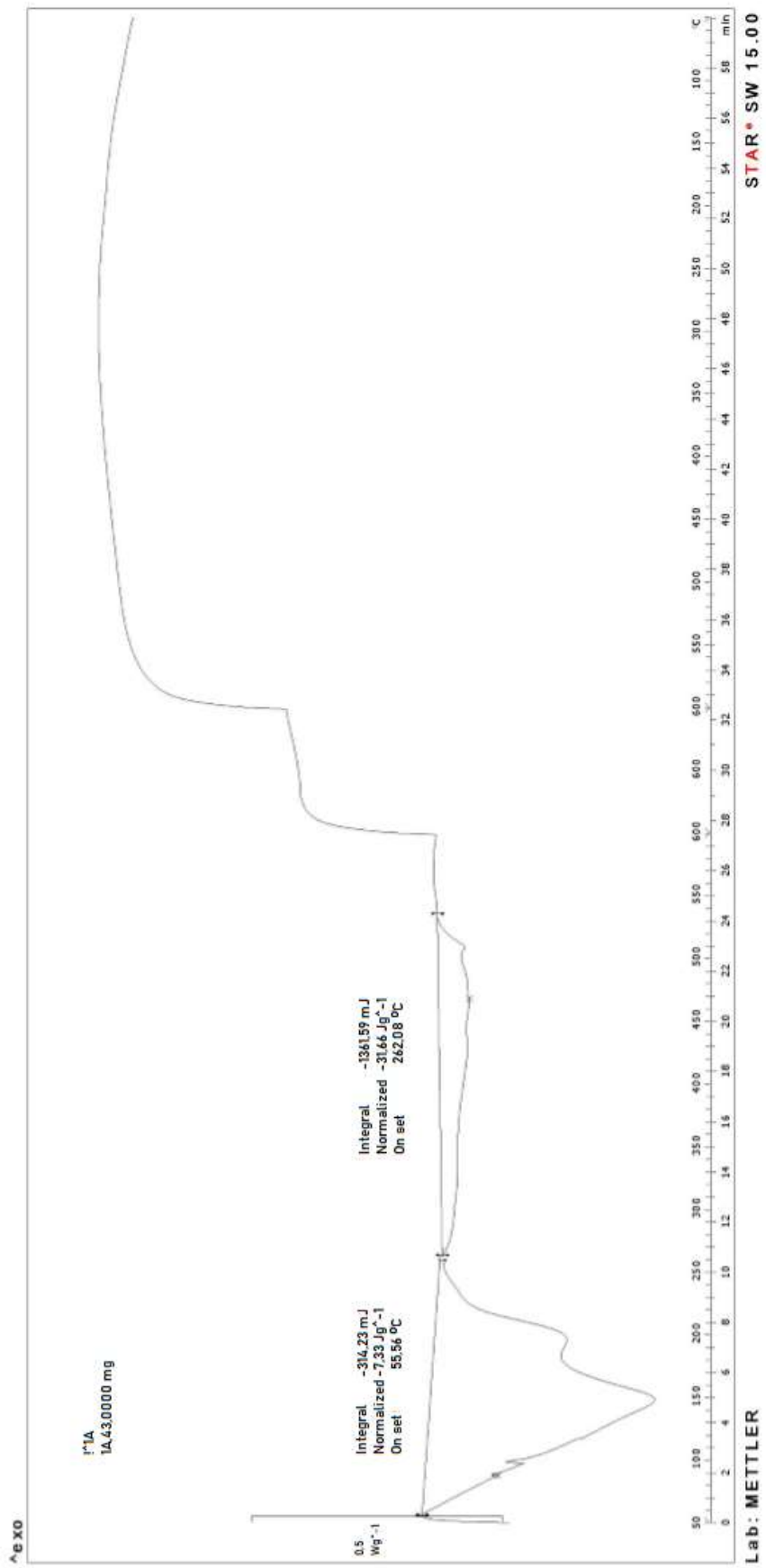


Figure 36: Thermal Curves of Kimolos 1A bentonite

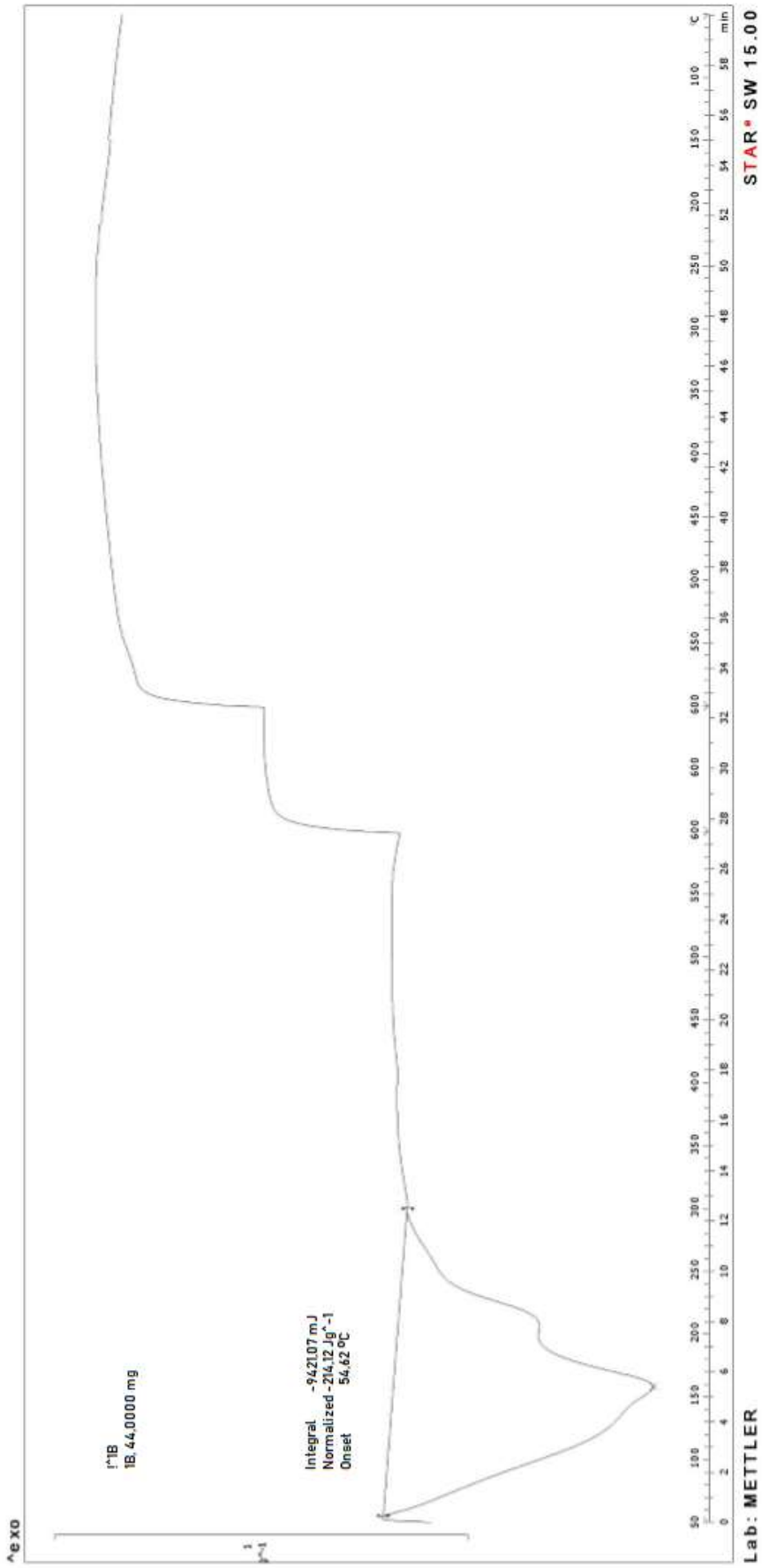


Figure 37: Thermal Curves of Kimolos 1B bentonite

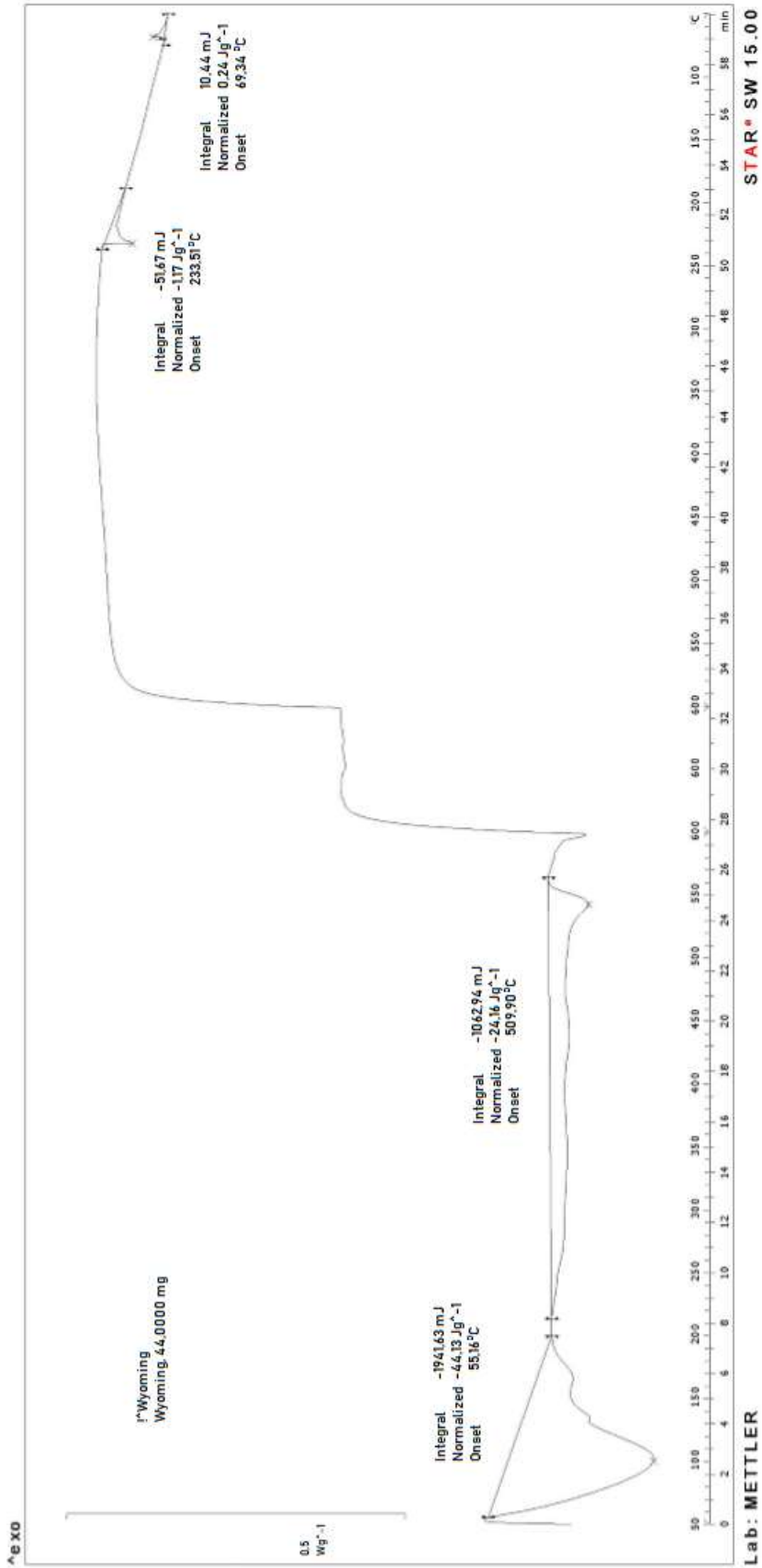


Figure 38: Thermal Curves of Wyoming bentonite

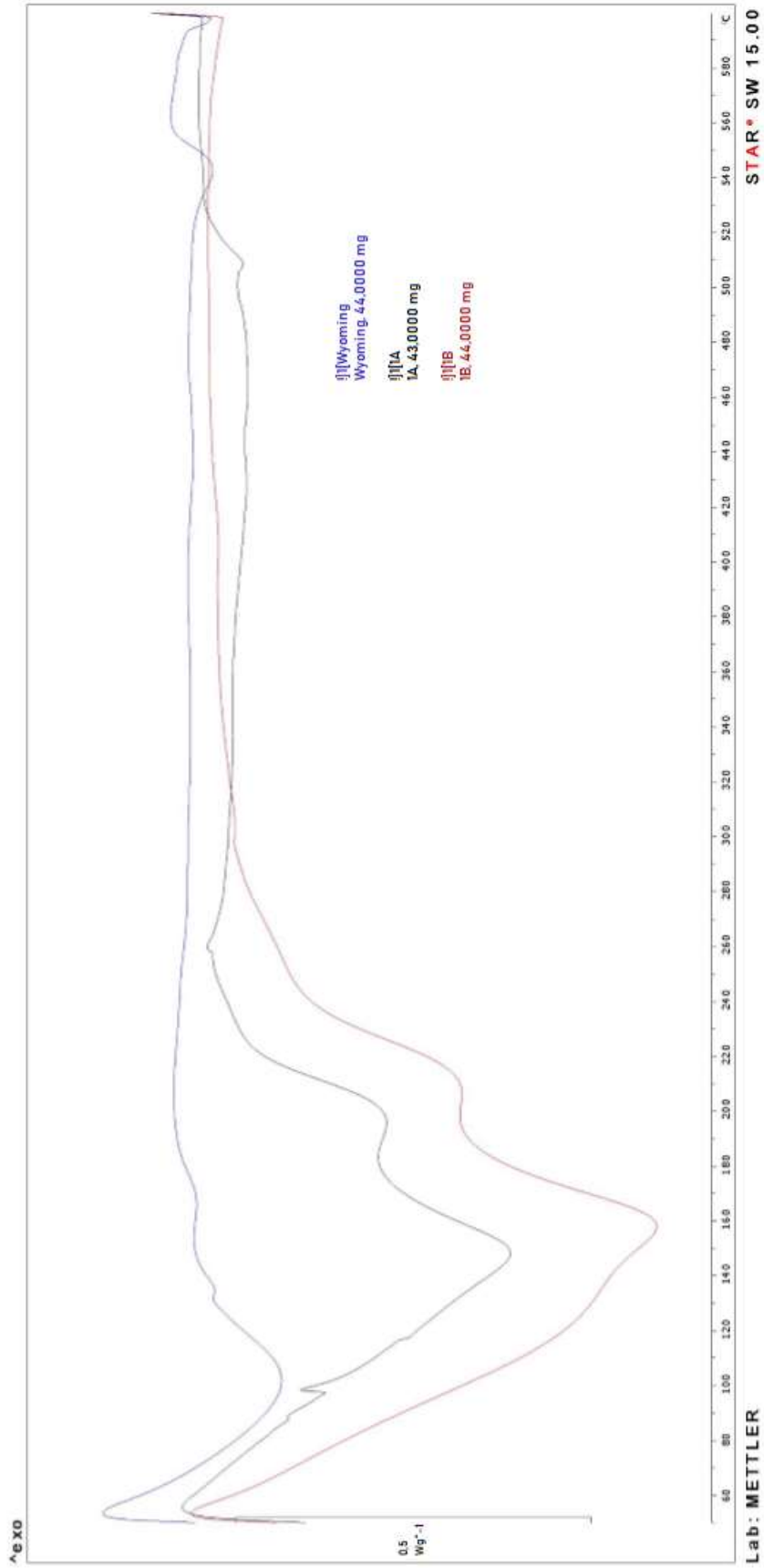


Figure 39: Thermal Curves of all bentonite samples

Loss of Ignition

Loss on ignition (LOI) is a test used in inorganic analytical chemistry and soil science, particularly in the analysis of minerals and the chemical makeup of soil. It contains strongly heating ("igniting") a sample of the material at a specified temperature, allowing volatile substances to escape, until its mass ceases to change. This may be done either in air, or in some other reactive or inert atmosphere. The simple test typically consists of placing a few grams of the material in a pre-ignited crucible and determining its mass, placing it in a temperature-controlled furnace for a set time, cooling it in a controlled (e.g. H₂O-free, CO₂-free) atmosphere, and redetermining the mass. The process may be repeated to show that mass-change is complete.



Figure 40: moisture-free glass container

Samples Preparation:

1. Weight the empty crucibles (*Empty*)
2. ~1 g of each sample was weighted (*Initial Mass*) and placed into a crucible
3. Weighted again the crucibles (*Before Drying*) and placed them into the oven at 105 °C overnight
4. Then the containers were taken off the oven and placed into a moisture-free glass container to cool off and in order not to get any humidity.
5. After they have cooled off we weight them again (*After Drying*) and place them into the furnace at 1050 °C for two hours
6. Step 4 was repeated
7. After they have cooled off we weight them again (*After firing*)



Figure 41: Furnace 1050 °C

These data with mathematical equations are given in Table 11 resulting the Loss of Ignition (LOI) which is necessary in order to make pearls for XRF.

	Initial Mass (g)	EMPTY (g)	Humidity						LOI				
			Before Drying (g)	After Drying (g)	Weight Loss (g)	dry mass (g)	Humidity (%)	Aver. Humidity	dry mass (g)	Before Firing (g)	After Firing (g)	Weight Loss (g)	LOI (%)
Kimolos 1A	1,0247	18,7476	19,7723	19,6729	0,0994	0,9253	9,70	1,5504	0,9030	19,6729	19,6150	0,0579	6,26
Kimolos 1B	1,0037	18,2949	19,2986	19,1771	0,1215	0,8822	12,11	1,5928	0,8789	19,1771	19,1021	0,0750	8,50
Wyoming	1,0014	17,8662	18,8676	18,7621	0,1055	0,8959	10,54	1,5649	0,8946	18,7621	18,7031	0,0590	6,59

Table 15

XRF

XRF analysis includes the chemical analysis of aluminosilicate minerals in glass-pearl form with x-ray fluorescence technique. The elements analyzed are silicon, aluminum, titanium, iron, carbon, magnesium, sodium and potassium oxides.

Samples Preparation:

- Samples grinding
- Sieving through +200 mesh
- Glass-pearl creation:
 1. 7 g of Lithium Tetraborate reagent were weighted into a melting pot
 2. the balance was tared off into order to place 1,4 g of sample
 3. mix thoroughly the components
 4. these steps were repeated for all the samples
 5. the CLAISSE FLUXY device was putted into operation
 6. the melting pots were putted in the right positions
 7. the upper part of the device was putted also in the right position
 8. chose melting program: P-3-Start
 9. after a few seconds, a noise is heard like pop which means that the gas flow has started, and we spark the exit point of gas.
 10. When approximately 15 minutes are passed the samples are pouring into molds in order to form the glass-pearl
 11. After glass-pearls are cooled off, labels are placed on them the glass pearls are placed into the XRF for analyzing.



Figure 42: CLAISSE FLUXY device



Figure 43: XRF

Sample name	Sum of concentration	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	LOI
		Si	Al	Ti ³	Fe	Mg	Ca	Na ³	K	
Kimolos 1A	98,88	72,93	13,12	0,12	0,90	3,08	0,89	0,53	1,05	6,26
Kimolos 1B	97,48	61,42	18,72	0,17	1,75	3,73	1,11	0,73	1,36	8,50
Wyoming	98,40	62,09	19,00	0,16	4,13	2,36	1,61	1,90	0,57	6,59

Table 16: Concentration of oxides

Result type: Concentration

The higher amount of each oxide, between the 3 samples, is presented with bold letters.

	LOWER LIMIT%	UPER LIMIT%
SiO₂	42,37	78,39
Al₂O₃	11,31	39,22
TiO₂	0,01	2,39
Fe₂O₃	0,08	12,94
MgO	0,18	8,40
CaO	0,03	12,17
Na₂O	0,07	4,84
K₂O	0,06	11,80

Table 17: Lower and Upper limits of oxides concertation for bentonites

All of the concentrations are within the limits of oxides concertation.

Kimolos 1A sample is presenting the highest concentration of SiO₂.

Kimolos 1B sample is presenting the highest concentration of TiO₂, MgO and K₂O.

Wyoming sample is presenting the highest concentration of Al₂O₃, Fe₂O₃, CaO and Na₂O.

XRD

XRD analysis provides definitive mineralogical analysis of different minerals and the characterization of their phase of a bentonite, both in terms of clay and non-clay constituents.

Sample Preparation Steps (the samples should have fine grinding)



The metallic device that is used to fill the slide and the spatula that helps in transferring the sample



The under part of the metallic slide is placed on the metallic device



The sample is placed on the inside circle of the slide and its pressed with the metallic cylinder until we have excess of sample



Then, with a sharp object (razor blade) the excess sample is removed and tossed away. This will result a smooth surface.



The slide is carefully removed from the metallic device



In the end, the slide is placed on the sampleholder and inserted in the XRD machine

Using standard search procedure, the bulk mineralogy can be determined. After comparing the X-ray diffraction patterns of sample bentonites with peak heights of particular minerals, data can be provided. At this point, impurities that may have adverse effect can be detected. Some of them are, Calcite which works like acid user during acid-activation, Gypsum, which can affect the rheological properties and Cristobalite, which is usually considered as health hazard and may also act as a cementing agent, the presence of which can lead to poor physico-chemical performance.

Relations Between Theta and Minerals for Bentonites

Main peak of Smectite

5,7° - 6° (14-15 Å) : Calcium

7° (12 Å) : Sodium

If smectite's peak isn't symmetrical, there is a possibility that we have a mixture.

If the last peak is at :

- 62°: Montmorillonite or Beidelite
- 60°: Nontronite, Saponite, Hectorite

8,9° Mica / Illite (Silica Groups)

- Biotite
- Muscovite
- Phlogopite

9,9° Clinoptilolite (Zeolite)

11,6° Gypsum

12° Kaolinite

21,65° Tridymite

22° silica

pointy peak : cristobalite (thin and fine crystallized)

smoother circled peak : opal CT (open peak)

In the same theta, it exists an overlay peak of feldspar. If the peak at 22° is till 80% of the main peak of Feldspar we have Feldspar. But if it more than 80% we have cristobalite.

21,2° Goethite

~25° Anatase (Ti oxide)

26,65° Quartz, but also 2nd peak for muscovite (In order to choose, we should search if other peaks are covered from Qz)

26,8° – 27,5° K-Feldspar (Sanidine)

27,7° – 28° Feldspar (Anorthite, Albite)

Carbonates

29,4° Calcite

30,7° Ankerite (Fe, Mg,)

30,9° Dolomite

31,9° Siderite (it occurs when there is excess of Fe)

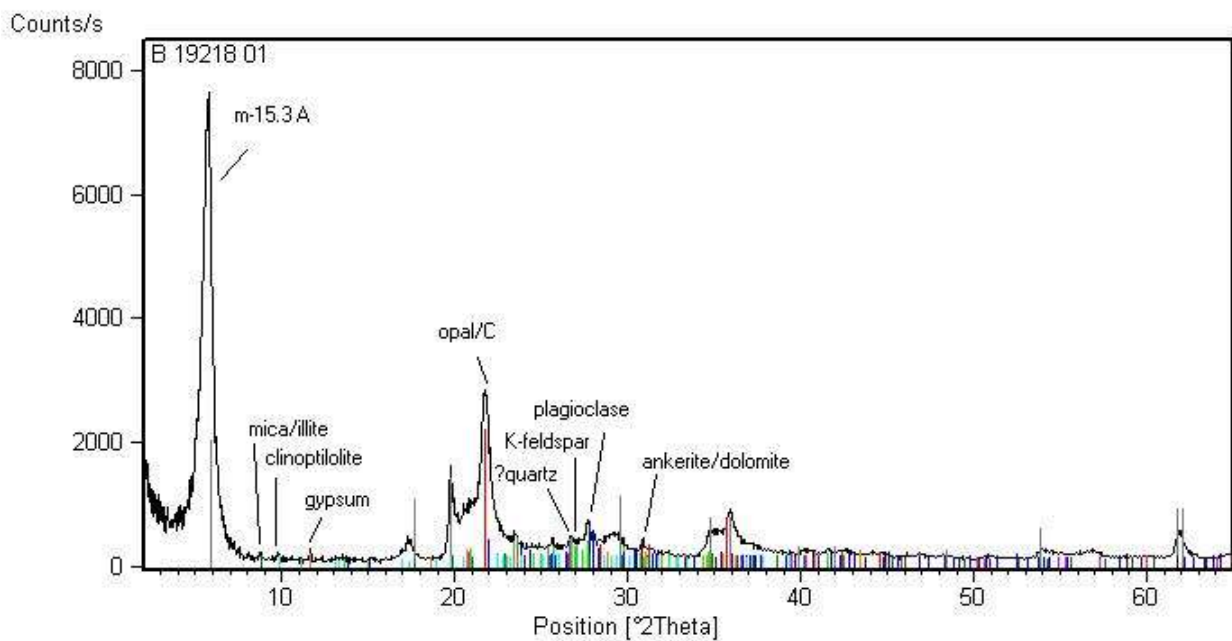


Figure 44: X-ray diffraction patterns of Kimolos 1A bentonite

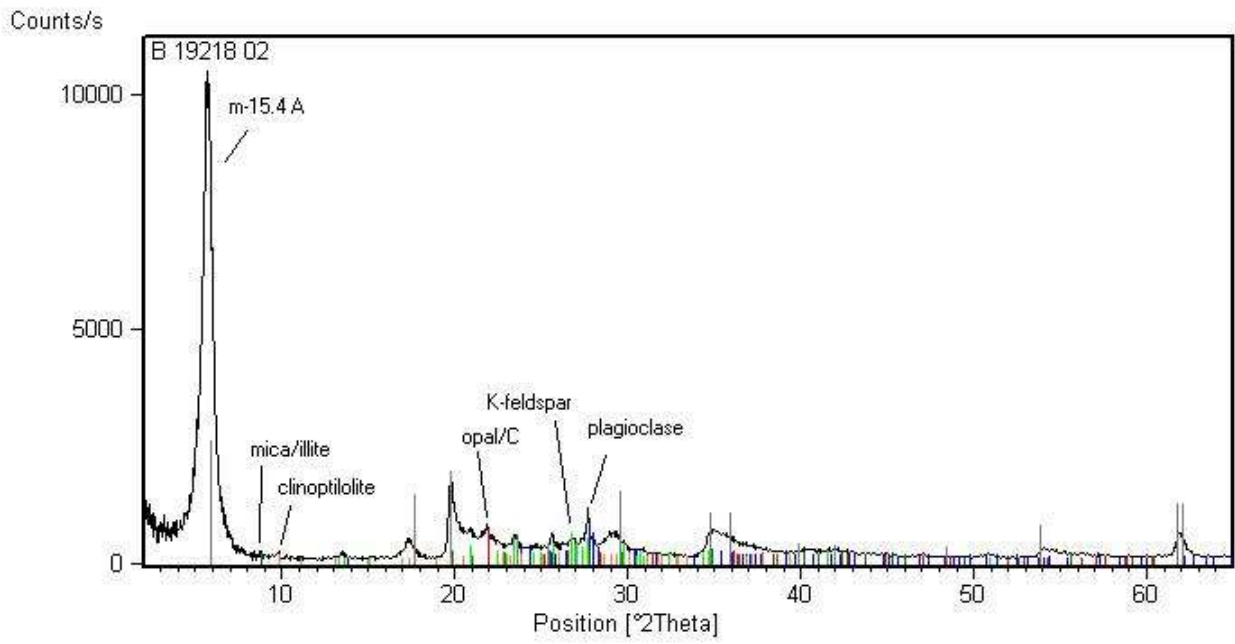


Figure 45: X-ray diffraction patterns of Kimolos 1B bentonite

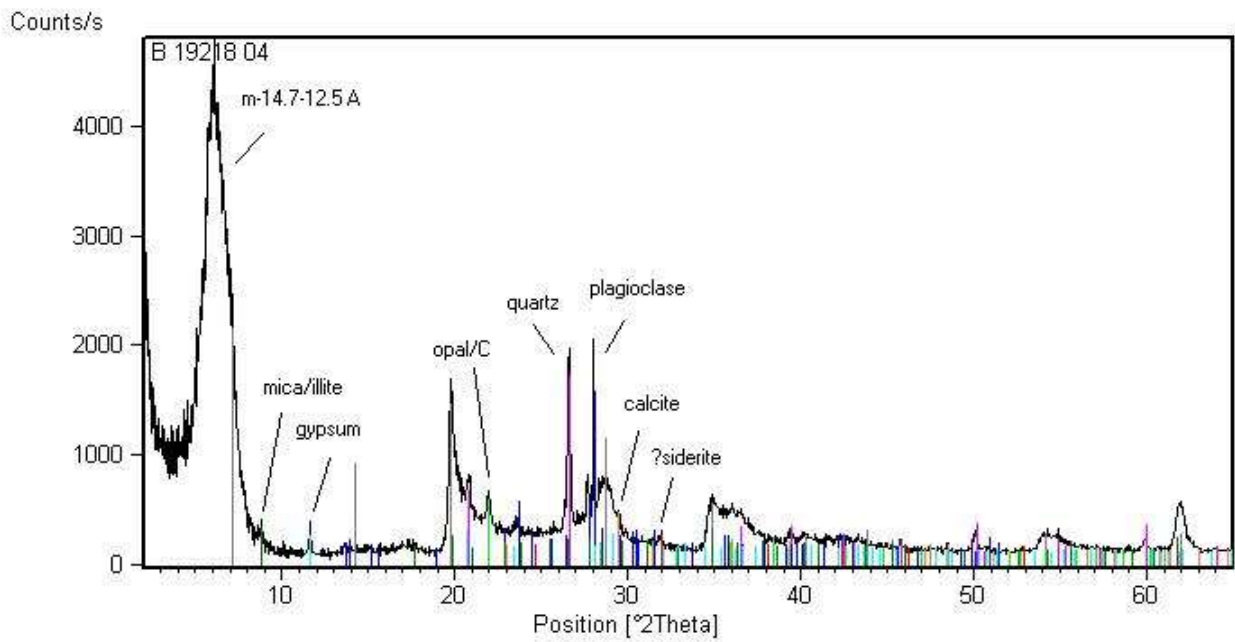


Figure 46: X-ray diffraction patterns of Wyoming bentonite

XRD - Rietveld

Rietveld refinement is used for characterization of crystalline materials. The neutron and x-ray diffraction of powder samples results in a pattern characterized by reflections (peaks in intensity) at certain positions. The height, width and position of these reflections can be used to determine many aspects of the material's structure. The Rietveld method uses a least squares approach to refine a theoretical line profile until it matches the measured profile (fitting). (Glover Grant T., Bin Mu, 2018) The introduction of this technique was a significant step forward in the diffraction analysis of powder samples as, unlike other techniques at that time, it was able to deal reliably with strongly overlapping reflections. (Glusker J.P, Trueblood K.N., 2010)

So, with this method a quantitative analysis is performed by using the XRD diagrams. The measurements were made with “Bent quantification” program (start angle:4.0, end angle: 7.0, step size: 0.03, time per step (s): 10.0). Analysis duration is 6 hours.

The quality of the diagram (fitting) is depending on the factors above:

Rpw: total adjustment error (<10%)

Rexp: minimum theoretical error - ideal fitting (higher fitting parameters, higher value)

Rphase: fitting error in each phase – high value means bad fitting quality (it should be <10%)

Sample preparation:

1. 4 ml of dry sample and 8 ml ethanol is placed in the McCrone tubes
2. The tubes are placed in the McCrone device for 45 seconds total
3. Every 15 seconds the mixture is poured in the crucible and 8 ml ethanol are placed in the tube and in the McCrone device again.
4. Then the crucible is placed in the
5. After the sample is putted in the fume cupboard in order to dry
6. The dried sample is sieved (<10 μ m)
7. The sieved sample is placed in the slide with the side loading device
8. At the end, the slide is placed in the XRD device.



Figure 47: McCrone tubes



Figure 48: McCrone device



Figure 49: Side loading device



Figure 50: Slide

Kimolos 1A

Mineral	Quantity%
Calcite	0.8±0.3
Clinoptilolite	3.3±0.6
Opal/C	19.5±2.2
Gypsum	0.9±0.2
Mica/illite	1.7±0.6
Plagioclase	2.9±0.6
K-feldspar	7.9±0.5
Smectite	62.9±4.0

Table 18

Fitting Error	Value %
Rpw%	6.8
Rexp%	2.5
Rphase% max	7.3

Table 19

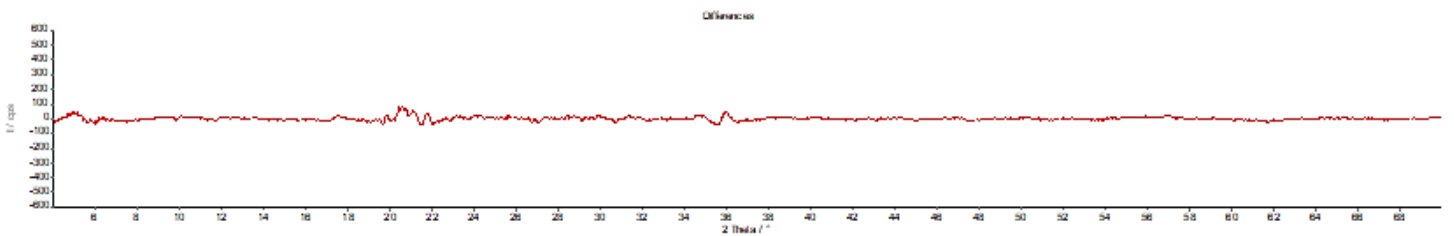
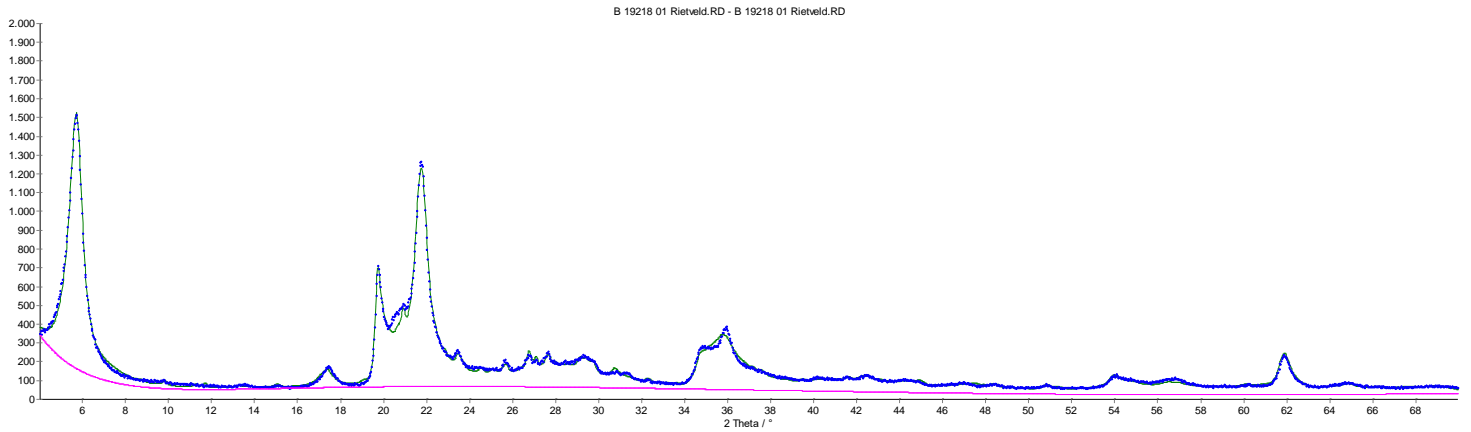


Figure 51: Kimolos 1A Rietveld

Kimolos 1B

Mineral	Quantity%
Clinoptilolite	3.0±0.6
Opal/C	2.6±0.4
Mica/illite	3.2±0.7
Plagioclase	4.9±0.6
K-feldspar	9.9±0.8
Smectite	76.4±3.6

Table 20

Fitting Error	Value %
Rpw%	6.7
Rexp%	2.5
Rphase% max	7.9

Table 21

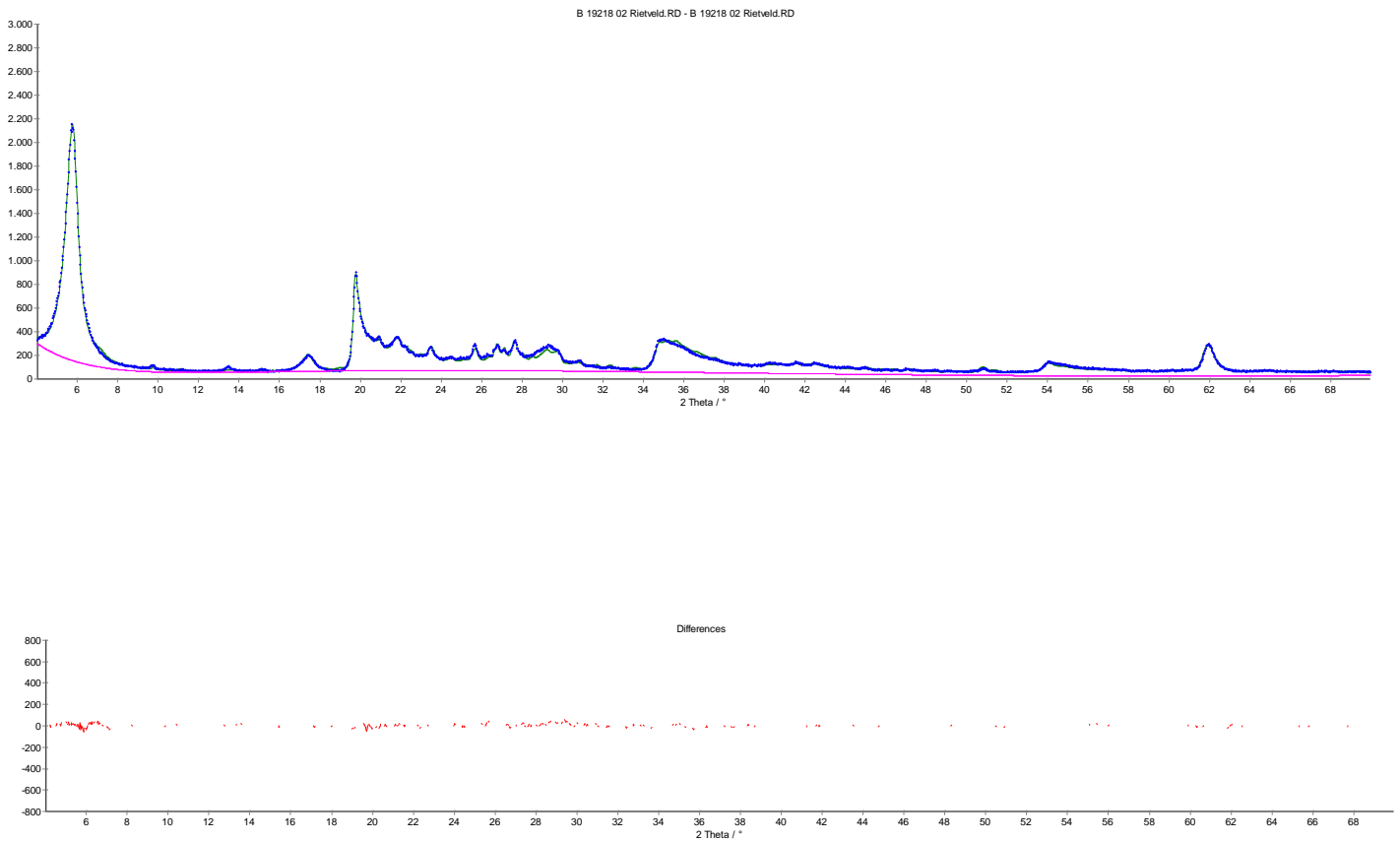


Figure 52: Kimolos 1B Rietveld

Wyoming

Mineral	Quantity%
Calcite	1.5±0.3
Opal/C	1.3±0.3
Gypsum	1.0±0.3
Siderite	0.4±0.2 ?traces
Plagioclase	5.2±0.6
Quartz	7.7±0.4
K-feldspar	3.6±0.4
Smectite	79.3±5.3

Table 22

Fitting Error	Value %
Rpw%	7.0
Rexp%	2.6
Rphase% max	8.7

Table 23

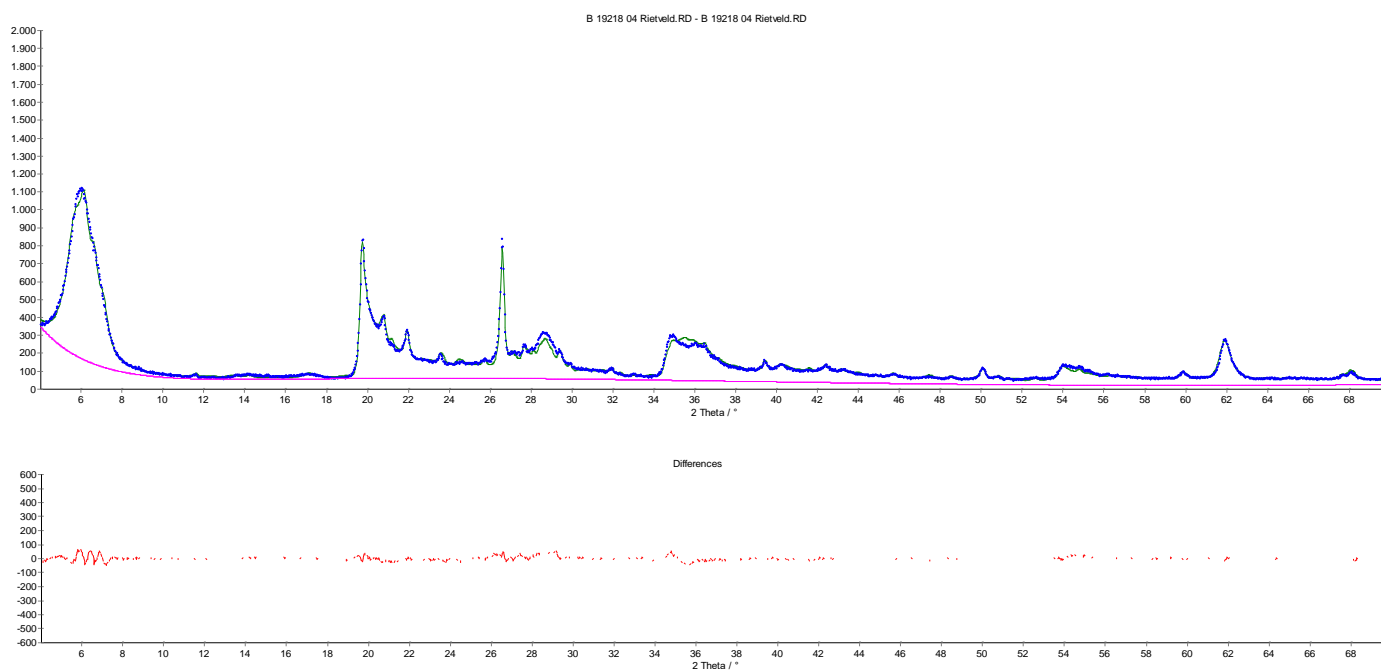


Figure 53: Wyoming Rietveld

Note: Error estimation was performed by the GOAL conception of the BGMN software. The estimated standard deviation 3σ is given for a confidence interval of phase abundances. As such error propagation method does not include any systematic sources of errors, the given confidence intervals are commonly an optimistic estimation

In all of the samples K-Feldspar was detected, with Kimolos 1B having the largest amount and Wyoming the lowest one. Also, they present Plagioclase with Wyoming appears to have the highest amount and Kimolos 1A the lowest one.

Furthermore, opal/c is detected to all of the samples with Kimolos having the largest amount and Quartz only in Wyoming sample and indicates that due to older age, initial Opal/C have transformed to Quartz with diagenesis.

On the other hand, Clinoptilolite and mica/illite appears only in Kimolos bentonites and it is verifying the fact that Wyoming sample in FT-IR analysis didn't appear Al-Mg-OH vibrations. Gypsum, and calcite appears only in Kimolos 1A and in Wyoming.

Siderite (FeCO_3) appears only in Wyoming and which explains why is the only sample that presents Al-Fe-OH bending vibration at FT-IR analysis. Smectite at it was thought appears to all samples with the highest amounts of the rest minerals.

Methylene Blue Test - CEC

Methylene blue adsorption test is a simple and reliable method to determine the presence and properties of clay minerals in soils and rocks, especially in the first stages of research. The quantity of Methylene Blue that is being absorbed from the bentonite, it is an indirect but meaningful assessment of exchangeable ions and crystallization of the montmorillonite, so in the quality of the bentonite. If a significant amount of methylene blue is adsorbed by the soil or ground rock material, this may indicate the presence of swelling clay minerals, although there exist other substances that also may adsorb methylene blue (*Verhoef, 1992*). Low values of adsorption generally indicate low swelling activity (*Stapel and Verhoef, 1989*). Therefore, low values reveal the presence of either very low amount of swelling clay or certain amount of non-swelling clays.

The method is based on the titration of a suspension of dispersed bentonite with a solution of methylene chloride until saturated.

Execution steps:

- With this method we can test either, dried bentonites at 105°C overnight or, natural bentonites with moisture presence.
- 0,50 gr of bentonite sample were weighted and transferred into conical flask 250ml
- 5 cm³ of Pyrophosphoric natrium $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ and 50 cm³ of deionized water, were placed into the conical flask
- The flask was placed on the magnetic stirrer for 3 minutes and at the same time it was heated up for 5 minutes without being boiled
- The flask was removed and left to cool
- 2ml of H_2SO_4 5N were placed in the conical flask and was stirred for half a minute.
- The titration of methylene blue is starting by adding a high amount at first (80-90% of the necessary volume of the solution is added at once)

- One drop of the suspension was removed with a stirring glass rod and placed on the filter paper. If not a light blue halo appear round the blue spot ,the titration is continued until light blue halo appear round the blue spot
- Then the addition is stopped the addition of MB solution and the flask is stirred with a magnetic stirrer
- One drop of the suspension was removed with a stirring glass rod and placed on the filter paper. If a light blue halo appear round the blue spot ,the maybe there is excess of MB solution. The procedure should be repeated with less titrate and if the light blue halo appear round the blue spot, this is the end point.
- If don't, 0,5-1 cm³ of MB solution is added
- One drop of the suspension was removed with a stirring glass rod and placed on the filter paper. If a light blue halo doesnt appear round the blue spot , the previous step is repeated. If yes, the flask is stirred for two minutes .
- One drop of the suspension was removed with a stirring glass rod and placed on the filter paper. If a light blue halo doesn't appear round the blue spot, 0,5-1 cm³ of MB solution is added. If a light blue halo appear round the blue spot, that doesn't disappear after a while, this the end point. The ml of titration used are written down.

	M.B.A. (ml/0.5 g)	G (% standard)	Montmorillonite (%)	MB Titre	mg/g (Dutch)	mg/g (VDG)
Kimolos 1A	23,5	84,75206964	63,56405223	5,861958	500	305
Kimolos 1B	30,3	112,2724926	84,20436942	5,861958	659	404
Wyoming	25,8	93,92063336	70,44047502	5,861958	553	338

Table 24

Samples	CEC (meq/100g)
Kimolos 1A	131,6
Kimolos 1B	169,68
Wyoming	144,48

Table 24.1

$$CEC = 100 / f \times V \times NMB$$

f: is the sample weight

V: is the required methylene blue volume at the time of titration

NMB: 0.028 N

CEC is conventionally expressed in meq/100 g (Rengasamy and Churchman 1999) which is numerically equal to centimoles of charge per kilogram of exchanger (cmol(+)/kg)

A unique characteristic of clay minerals is the cation-exchange capacity (CEC). In soil science, the CEC is defined as the degree to which a soil can adsorb and exchange cations. CEC refers to the quantity of negative charges in soil existing on the surfaces of clay and organic matter. The negative charges attract positively charged ions (cations), hence the name cation exchange capacity.

The primary factor determining CEC is the clay and organic matter content. Therefore, higher quantities of clay and organic matter yield higher CEC. CEC values for clays, i.e. the number of exchangeable charges, are typically between 1 and 150 milliequivalents (meq) per 100 g of dry clay. By rate of comparison, typical CEC values for smectite are 80 to 170 meq / 100 g. One meq of negative charge on a clay particle is neutralized by one meq of a cation. Although the exchange reactions do not usually affect the structure of the clay minerals, important changes in the physical and physicochemical properties of the soil may occur. It is also noteworthy that clays with high specific surface areas and high negative charge usually have high CEC values (Camberato 2001 - Source: Brandon Thomas Pitre, 2012)

Percentage of Carbon and Sulfur presence

This method is calculated the percentage of carbon and sulfur presence.

Sample preparation:

1. The device that is used is LECO
2. 1 spoon of IRON CHIP ACCELERATOR and 1 spoon of LECOCEL II are placed in the cup
3. The cup is weighted and the balance is tared and 0,04 gr of standard sample is placed in order to check the device
4. Step 2 is repeated
5. The cup is weighted and the balance is tared and approximately 0,1 gr of bentonite sample is put in the cup in order to analyze.
6. In the middle of the samples we use again the standard one in order to check the device's quality.



Figure 54: LECO machine

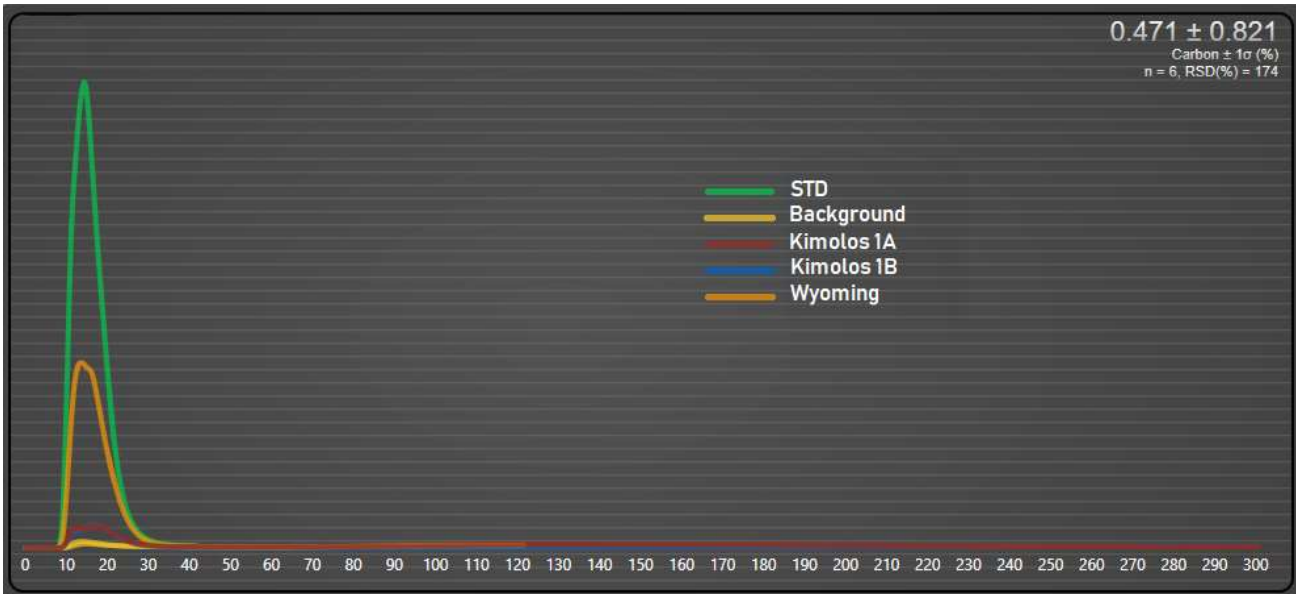


Figure 55: spoon

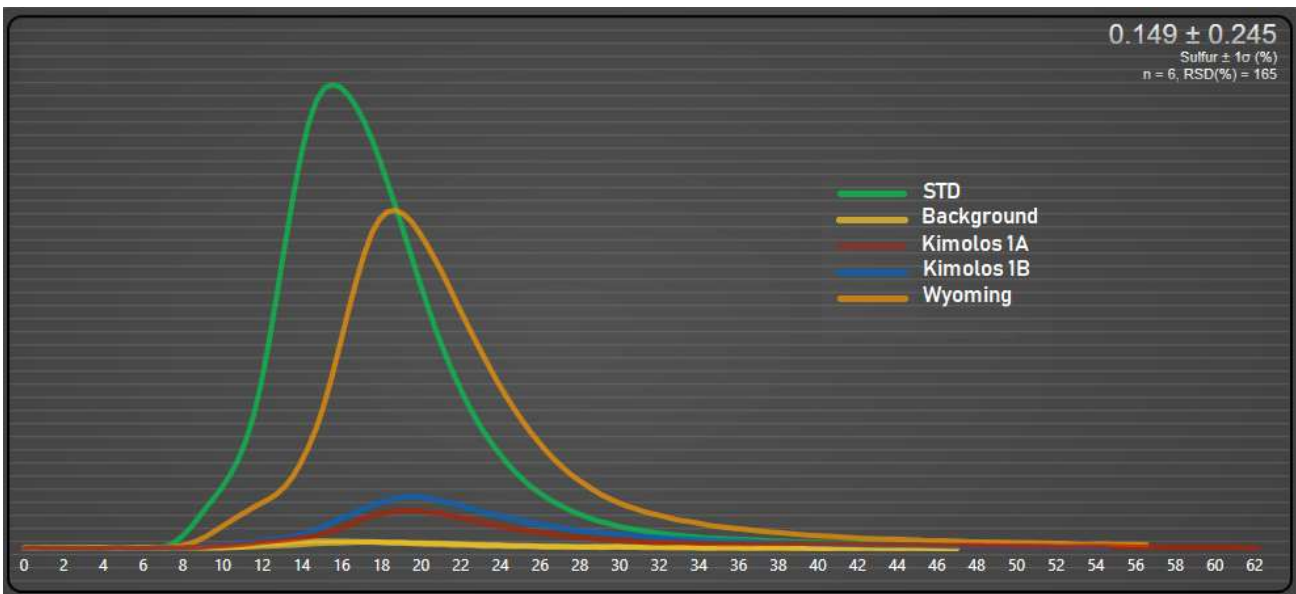


Figure 56: cup

Carbon Analysis



Sulfur Analysis



	<i>Carbon %</i>	<i>Sulfur %</i>
STD	2,12	0,624
Background	0,00478	0,000315
Kimolos 1A	0,174	0,0278
Kimolos 1B	0,125	0,0372
Wyoming	0,397	0,202

Table 25

As it is presented in Table 25, Sulfur % is significantly higher in Wyoming sample than Kimolos samples. Kimolos 1A Carbon percentage is matching 1B's, but Wyoming's is a little higher. Wyoming's higher percentages in Carbon, Sulfur are due to oil and gas occurrences and coal beds, but also due to gypsum. This is resulting from Wyoming's geological history.

Conclusion

Even though Kimolos and Wyoming are thousands of miles away and they belong to different continents, which have different geological history, bentonites of both places seem to have many similarities. Kimolos is mainly consist of igneous and volcanic rocks. Wyoming, on the other hand, is mainly consist of sedimentary rocks like limestones, dolomites, sandstones, mudstones, evaporates and shale. Nonetheless, it also contains igneous, volcanic and metamorphic rocks. Also, it is worth mentioning, that there are occurrences of oil, gas and coal beds.

First of all, both bentonites show similar chemical bonds with FT-IR analysis, expect from Al-Fe-OH bending vibration which only occurs in Wyoming Bentonite and indicates the presence of siderite.

Secondary, with atomic absorption analysis, similar amounts of Ca and Na have occurred within the bentonites. Furthermore, after Iron chromatography analysis it seems that Kimolos 1A and Wyoming contain potassium that is probably due to pumice for Kimolos 1A and K-feldspar, mica and illite for both of them. Both Kimolos samples show magnesium, probably due to Mg-montmorillonite and dolomite or ankerite and calcium due to calcite and gypsum, which is calcium sulfate. Ammonium occurs at Kimolos 1B sample that probably indicate the presence of K-feldspar and plagioclase. Sodium can be found in Kimolos 1A due to clinoptilolite or due to seawater that contains NaCl and in Wyoming because the bentonite there, is a natural sodium bentonite. Also manganese is detected in Wyoming, perhaps due to the manganese deposit that lies in the Laramie Mountains and it is interbedded in limestone and sandstone of the Casper formation, of Carboniferous age, which here overlies the granite. Moving on to thermal analysis all of the samples react the same way at the heat flow.

Furthermore, XRF analysis, Wyoming present higher amounts of Fe (Fe_2O_3) probably due to siderite and Na (Na_2O) in comparison with Kimolos. Then, XRD and Rietveld analysis verify the speculations above, by revealing the minerals of each samples. In addition, XRD analysis show that the peaks of montmorillonite are in different position because of Kimolos having Calcium Smectite and Wyoming being a Sodium variety of Smectite. Also, Rietveld analysis presents Opal/C at Kimolos samples and Quartz at Wyoming sample and indicates that due to older age, initial Opal/C have transformed to Quartz with diagenesis.

Moreover, Methylene Blue Test is contributed in CEC determination of the samples. CEC is found similar in all of the samples, with Kimolos 1A having the lowest value and Kimolos 1B having the highest. Finally, Carbon and Sulfur percentage analysis, showed much higher values of Ca% and S% in Wyoming bentonite than Kimolos ones. That is due to Wyoming's geology that contain oil and gas and coal beds. All of the above indicate that Kimolos and Wyoming bentonites have many similarities and negligent differences.

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