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Method Development for the Analysis of Aluminum, Calcium, Magnesium and Iron in Sedimentary Rocks

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METHOD DEVELOPMENT FOR THE ANALYSIS OF ALUMINUM, CALCIUM, MAGNESIUM AND IRON IN SEDIMENTARY ROCKS

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METHOD DEVELOPMENT FOR THE ANALYSIS OF ALUMINUM, CALCIUM, MAGNESIUM AND IRON IN SEDIMENTARY ROCKS

An Abstract of the thesis by
Zainab Ali Alhawdar

The focus of this study involved the analysis of sedimentary rocks by using atomic absorption spectroscopy. There are three classifications of sedimentary rocks: organic, formed as a result of vital activity of organisms such as coal; non-organic (chemical), formed in the process of evaporation of concentrated mineral solution such as limestone, dolomite, gypsum, salt and chert; and clastic (fragmental), formed from pre-existing rocks as a result of their fragmentation followed by further hardening and cementing such as conglomerate, breccia, sandstone, siltstone and shale.

There are various analytical methods for analyzing sedimentary rocks, all of which require dissolving and digestion of the rock samples. The next step after digestion involves the burning off of organic content, and followed by separation of the silicates from all the other elements. Once the separation is achieved, then the analysis for the elements in the samples is performed using atomic absorption spectroscopy (AAS).

The study focused on the analysis of four elements: aluminum, calcium, iron and magnesium. Standard solutions of aluminum, calcium, iron and magnesium were made with their concentrations ranging from 500-1000 ppm. Four unknown samples of sedimentary rocks labeled: XGP1, XGP2, XGP3 and XGP4, were analyzed by atomic absorption spectroscopy at instrument settings that are specific to each element. The percentage of each element in the samples used was determined and is reported in the body of the thesis.

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CHAPTER I

INTRODUCTION

The crust of the Earth is formed of minerals and rocks, which constitutes more than one-third of raw materials utilized in the various spheres of people's activities. No adequate engineering construction could be performed without thorough geochemical studies such as this one. Without an understanding of in-depth processes of chemical composition of rocks, an effective use of mineral resources is impossible; thus, an accurate investigation of rocks is vitally important for promoting successful economic activity.

1.1. MAIN ROCK FORMING FACTORS

Rock is a geological body that can be characterized by a special composition (e.g. plagioclase, orthoclase, clay, quartz etc.), structure and texture (e.g. grained, chalky, bedded, homogeneous etc.). In other words, rock is an aggregate of particles of the same or different nature[1].

The formation of rock is a permanent process: after having been formed, rocks are worn down and then are reformed. This process, known as the rock cycle or geochemical

cycle[2], lasts for thousands of years. The six following most crucial processes underlying rock formation[1] are defined below:

    a. Tectonic movements of lithosphere, resulting in stretching, which leads to heating and thinning of the lithosphere and excessive pressure of tectonic plates when knocking against each other[3].

    b. Volcanic eruptions, which are a powerful driving force behind the transportation of particles. Volcanic dust, ejected to a significant height during an explosion, remains suspended during long periods of time and then covers large geochemical areas as it settles[4].

    c. Weathering implies physical (mechanical), chemical or biological decomposition of the rocks thus changing their chemical composition and forming secondary minerals[5]. The process of weathering is primarily based upon oxidation and dissolving; its rate is determined by climatological conditions such as frost, droughts, heat etc. [6].

    d. Chemical reactions and bioprocesses in the aqueous media (primarily marine).

    e. Increased pressure and temperature in the interior of the Earth.

    f. Melting, degassing, recrystallization, precipitation and other physicochemical processes.

Rock formation represents a system of interconnected phenomena as discussed above[7]. If we trace the history of shale, for example, we can draw a chain of successive transformations influenced by various factors, as can be seen in Figure 1[1,2]:
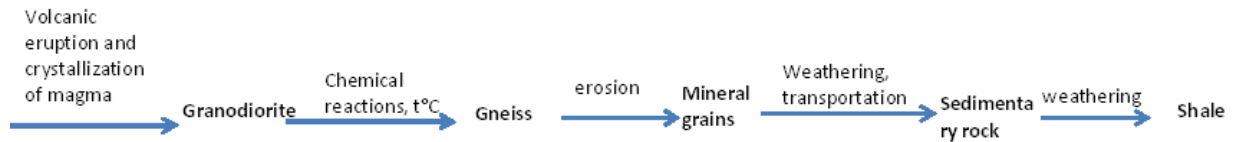
Figure 1. Geological history of shale

From this we could conclude that during over the geochemical cycle the rock is affected by a complex set of factors.

1.2. TYPES OF ROCKS

Rocks can be classified according to several characteristics[2]:

–   Structure (petrographic approach), indicating the manner of construction of the rock and the way its components are connected with each other. This characteristic affects crystal morphology, relative grain size etc.

–   Texture (grain packing, roughness, orientation, etc.).

–   Mineralogical composition.

–   Chemical composition.

–   Geological origin.

The classification of rocks given here is based on their origin and composition. Generally, the rocks can be classified as shown in the Figure 1. However, Frost, R.B., and Frost, C.D.[7] offer an extra category for igneous rocks being hypabyssal or subvolcanic. Also, an alternative approach to the classification of sedimentary rocks is provided[4].

The types of rocks shown in Figure 2 can be characterized as follows.
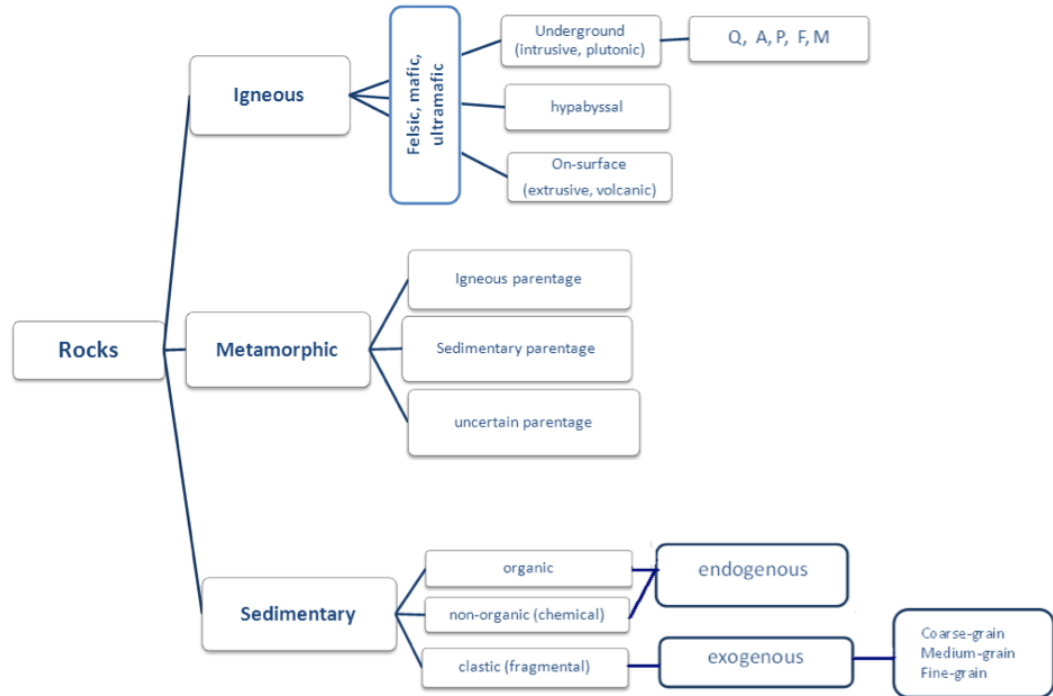
Figure 2. Classification of rocks (adapted from refences 1, 2 and 7)

1.2.1. IGNEOUS (MAGMATIC) ROCKS:

Igneous (magmatic) rocks were formed in or on Earth in two ways:

a. Underground, when crystallization and solidification of magma occurred inside the crust (plutonic or intrusive type), represented by granite, diorite, and gabbro.

b. On the surface, through crystallization and solidification of magma on the Earth's surface. Such types of rocks are referred to as extrusive or volcanic (e.g. pumice, obsidian and basalt).

The hypabyssal type of igneous rocks is the intermediate between volcanic and plutonic rocks. They were formed underground, but at a shallow depth. Examples of this type are dolerite and picrite.

Basically, igneous rocks can be described as felsic (feldspar + silica), mafic (Mg + Fe), or ultramafic (felsic minerals absent). The felsic rocks are light-colored, and the ultramafic are of dark color.

Igneous rocks have a chemical composition that may include the following oxides: Na_2O, K_2O, CaO, FeO, MgO, Fe_2O_3, Al_2O_3, SiO_2, and TiO_2. However, all of these oxides are rarely present in the rock altogether. They formed the minerals from which the International Union of Geological Sciences (IUGS) classification of plutonic rocks stems, where Q, A, P, F, and M stand for quartz, alkali feldspar, plagioclase, feldspathoids, and mafic minerals respectively. The rock considered as Q, A, P, or F-type means that the content of mafic minerals in it is less than 90%[7].

1.2.2. METAMORPHIC ROCKS:

Metamorphic rocks are any type of rock that has undergone metamorphic changes under the impact of increased temperature and pressure ($150 - 200℃$, 1500 bars)[1]. The core of the changes transforms the mineral into a different form, such as marble and gneiss.

While investigating metamorphic rocks, one is usually interested in the conditions of metamorphism and the type of its deformation, but the most crucial question is its origin, i.e. the parent rock (the protolith). Thus, they can be classified into three types according to their parentage (sedimentary, igneous, and uncertain). The first group can be represented

by quartzite, quartzose, pelite, and psammite, which are metamorphic equivalents of chert, sandstone, shale, and impure sandstone respectively. Rocks of clearly igneous parentage have very few protoliths (mainly ultramafic and alkaline). The rocks of uncertain origin can be categorized into two groups: mafic and quartzo-feldspathic.

1.2.3. SEDIMENTARY ROCKS:

Sedimentary rocks, in contrast to igneous and metamorphic rocks, were formed on the Earth's surface at low temperatures and pressures. The vast majority of rocks that are found on the Earth's surface are sedimentary. The major factors affecting formation of sedimentary rocks are sedimentation of clasts, biochemical processes in aqueous media and deposition of particles driven by the force of water, wind, ice or gravity. This type of rock could originate either from fragments of rocks having undergone mechanical or chemical weathering, or from biochemical processing of fossil remains.

Sedimentary rocks can be classified into three broad categories:

– Organic, formed as a result of vital activity of organisms such as coal.

– Non-organic (chemical), formed in the process of evaporation of concentrated mineral solution such as limestone, dolomite, gypsum, salt and chert.

– Clastic (fragmental), formed from pre-existing rocks as a result of their fragmentation followed by further hardening and cementing such as conglomerate, breccia, sandstone, siltstone and shale.

Sometimes, however, a different approach to classification of sedimentary rocks is used, as can be seen Figure 2. They are divided into exogenous (analogue to clastic) and

endogenous (organic and non-organic) groups. Exogenous rocks, according to their clasts' size, can be defined as coarse-grain, medium-grain and fine-grain rocks. Endogenous rocks include carbonate, evaporite and siliceous rocks.

For the formation of sedimentary rocks, the following stages are crucial:

–   Weathering of older rocks as a result of the joint impact of solar energy, freezing-thawing cycles, abrasion, erosion, hydration, oxidation and biodigestion of rocks.

–   Evaporation and crystallization of minerals from solutions.

–   Transportation of materials in the solid or dissolved state and their deposition or sedimentation.

–   Lithification (consolidation), which is a general term for the processes of porosity destruction (compaction, cementation, etc.).

As a result of these processes, four fundamental groups of particles arise which serve as the building materials of sedimentary rocks when taken in different proportions[5]:

a.   Terrigenous siliciclastic particles. The majority of igneous, metamorphic and old sedimentary rocks consist mostly of silicate minerals. Under the impact of water, ice or wind, these rocks, fragmented during the process of weathering, were transported together with clay and other land-derived minerals into depositional basins. Their further lithification led to formation of sandstones, conglomerates and shales.

b.   Chemical (biochemical) constituents. This is the process by which the precipitated minerals of either chemical or biochemical origin are usually referred. These materials form intrabasinal sedimentary rocks (cherts, evaporites, phosphorites, and limestones).

c.   Carbonaceous constituents (humic materials, sapropelic residues and bitumen) were formed from plant tissue, zooplankton, chemical transformation of petroleum, etc. Coals were primarily formed of these kinds of constituents.

d.   Authigenic constituents. These are minor constituents, which were usually added to the sedimentary rocks during their burial as a result of precipitation of pore water inside the pile. They include quartz, clay, calcite, gypsum, and hematite.

1.3. FACTORS AFFECTING THE CHEMICAL COMPOSITION OF ROCKS

Because weathering is the most important rock-forming process, the composition of rocks is entirely dependent on its rate and processes involved. Among the three types of weathering, the one that fully addresses the chemical and mineralogical composition of rocks is chemical weathering. The factor that contributes the most to chemical weathering is the presence of water and dissolved gases.

There are a number of chemical processes involved in weathering, Those processes are listed below[3,4,8]:

1.   Congruent solution:

SiO_2 (quartz) + $2H_2O \rightarrow H_4SiO_4$ (silicic acid)   (Direct solution)

$CaCO_3 + H_2O + CO_2 \rightarrow Ca^{2+} + 2HCO_3^-$ (Carbonation)
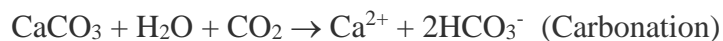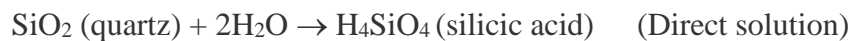
For the examples shown in the preceding reactions, complete dissolution of the soluble minerals in water (H_2O) is called direct solution. Dissolution of the soluble minerals in water (H_2O) and carbon dioxide (CO_2) is called carbonation. Calcite, gypsum, dolomite and halite are highly soluble minerals while quartz is less soluble.

2.   Hydrolysis:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2K^+$$
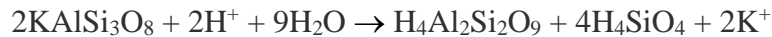
For the example shown in the preceding reactions, the dissolution can be illustrated by forming kaolinite rock ($H_4Al_2Si_2O_9$) from orthoclase feldspar rock ($2KAlSi_3O_8$).

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow H_4Al_2Si_2O_9 + 4H_4SiO_4 + 2Na^+$$
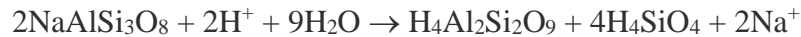
For the example shown in the preceding reactions, the dissolution can be illustrated of forming kaolinite rock from albite ($NaAlSi_3O_8$).

Hydrolysis is of great importance for the release of metals from the minerals broken down by acids. The reaction is between the H^+ and OH^- ions of water and ions of silicate minerals. Due to the fact that this type of dissolution is incomplete, it is called an incongruent dissolution.

3.   Oxidation and reduction:

This is the process when an element has lost an electron in minerals to dissolved oxygen. Iron and manganese are the common elements in silicate minerals such as biotite and pyroxenes. The following reactions illustrate the transformation of pyrite and rhodonite into hematite and pyrolusite respectively:

$$2FeS_2(pyrite) + 15/2O_2 + 4H_2O \rightarrow Fe_2O_3\ (hematite) + 4SO_4^{2-} + 8H^+$$

$$MnSiO_3\ (rhodonite) + 1/2O_2 + 2H_2O \rightarrow MnO_2\ (pyrolusite) + H_4SiO_4$$
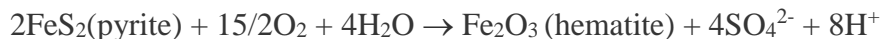
4.   Hydration and dehydration:

This is the process involves water hydration or dehydration of minerals. Hematite rock (Fe_2O_3) hydrates to form goethite rock ($FeOOH$) by the following reaction:

$$Fe_2O_3 + H2O \rightarrow 2FeOOH$$

Gypsum rock ($CaSO_4 \cdot 2H_2O$) loses water to form anhydrite ($CaSO_4$) according to the following reactions:

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O$$
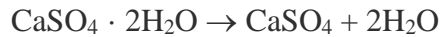
5.   Ion exchange, particularly, cation exchange:

This is the process where ions in a mineral are exchanged with ions in a solution. Cation exchange is of significant importance for the alteration in the forms of clays and zeolites, which can be seen from the following reactions:

$$K\text{-clay} + Mg^{2+} \rightarrow Mg\text{-clay} + K^+$$

$$Ca\text{-zeolite} + Na^+ \rightarrow Na\text{-zeolite} + Ca^{2+}$$
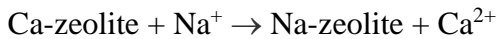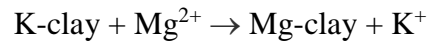
6.   Chelation:

This is the formation of a complex compound of metals with organic substances having a ring structure. The metals are bound in such a way that they are prevented from precipitation under a wide range of pH values.

Another important factor affecting the chemical composition of rocks, particularly sedimentary rocks, is subaerial weathering, during which two important chemical rock-forming processes take place:

–   Development of the secondary minerals, mostly clay, iron oxides or hydroxides and aluminum oxides or hydroxides that occur during the processes of hydrolysis and simple dissolution.

–   Production of soluble materials from which limestones and cherts are formed in seawater environment due to hydrolysis, oxidation and simple dissolution.

The work presented in this thesis is aimed at the analysis of the geochemical composition of sedimentary rocks. Understanding of the chemical composition of these rocks is highly relevant to the agricultural as well as to the petroleum-producing industries.

1.4. ANALYSIS TECHNIQUES

A primary technique that is traditionally used in the analysis of sedimentary rocks is Petrographic microscopy. This technique was first introduced in 1849 and has been the primary laboratory tool used in the analysis of sedimentary rock[5] until recently where it is being replaced by a number of other techniques which include and list:

- The sieve and pipette analysis – for defining the size of the grains.
- Backscattered electron microscopy, Fourier analysis, X-radiography – for determining structure.
- X-ray fluorescence, inductively coupled argon plasma emission spectrometry (ICP), secondary ion mass-spectrometry (SIMS), atomic absorption spectroscopy (AAS) – for investigating the sample's chemical composition.

1.4.1. STRENGTHS AND WEAKNESSES OF EACH ANALYSIS TECHNIQUE

X-ray fluorescence is one of the classical analytical methods, being successfully put into practiced since 1928. Generally it's based on the ionization of atoms in the sample exposed to short-length x-rays or gamma rays. While falling onto the lower orbital from the unstable excited position, the atom emits radiation with the unique spectrum, which can

be successfully used for identification of this atom. The advantages of the method include high accuracy of the analysis and, for the elements of interest include of aluminum, calcium, iron and magnesium, analysis lines are precisely defined.

However, the method has a drawback, sometimes the sample preparation for the x-ray fluorescence becomes a problem, which is connected with the necessity to maintain the strict geometry of the sample.

Inductively coupled plasma emission spectrometry (ICP) is a powerful up-to-date analytical tool for the analysis of sedimentary rocks. The basics of the method include converting the sample solution into an aerosol and directing it into plasma, where at the temperature of 10000 K analyzed elements exist as free atoms in the gaseous phase. While relaxing to the ground state, they emit protons, whose energy spectra allow identification of elements[9]. Among the advantages of the method there are usage of the inert carrier (argon), and ability to analyze up to 70 elements at the same time, including the elements of interest.

The weaknesses of the method are the necessity of thorough sample preparation (digestion, extraction), and the complexity of method and high cost of the equipment involved.

Secondary ion mass-spectrometry (SIMS) is the method for analyzing the composition of solids which implies sputtering the surface of the sample with the beam of primary ions and obtaining analytical signals from the secondary ions and its measurement with the help of the mass-spectrometer. The undisputable advantages of the method are the possibility of analyzing of all the elements and detection limits in ppb rate (10^{-6} gram per 1 gram of sample).

The weak points of the method are quite significant. First of all, the requirements to the physical properties of the sample; and, secondly, one can face serious difficulties converting data collected from the mass-spectrometer into mass or concentration.

Atomic Absorption Spectrophotometer (AAS) is an analytical technique for determining the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram in a sample. Atomic absorption spectrometry has multiple uses in various areas of chemistry: clinical analysis, environmental analysis, pharmaceuticals, industry and mining.

Atomic absorption spectroscopy is based on the absorption of light with a specific energy by a ground state atom causing it to undergo an excitation to a higher energy state. The intensity of light absorbed by an element is proportional to its concentration. The intensity of light absorbed at a specific wavelength will increase as the number of atoms of the selected element in the light path increases. Atomic absorption spectroscopy requires a primary light source, an atom source, a monochromator, a detector, electronics and data display or reporting system.

The light source uses a different lamp for each element to be determined. The atom source produced free atoms from the sample. The most common atom source is an air/acetylene or nitrous-oxide/acetylene flame. The monochromator is used to isolate the specific wavelength of light to be measured. The detector is used to measure the light accurately. The electronics are used to process the date signal. The data display or reporting system is used to show the results[10,11]. The various components of a typical atomic absorption spectrometer are shown in the schematic diagram found in figure 3.

Figure 3. Perkin Elmer Instrument Atomic Absorption Spectrophotometer

1.5. THE ATOMIC ABSORPTION SPECTROMETER WORKS

The sample--through which radiation of a chosen wavelength that is using a hollow cathode lamp (HCl), and is of a very narrow bandwidth (0.001nm) is sent—is atomized in the flame. Since the cathode is constructed of the analyzing element, the radiation will be specific to that element only. The most current gas mixtures used is air/acetylene or nitrous-oxide/acetylene which flows into the nebulizer creating a partial vacuum which causes the solution containing the analyzing element to be aspirated into the nebulizer, via a plastic capillary tube, which is then converted into an aerosol. The oxidant/aerosol is then swept into the spray chamber where it is mixed with the fuel gas. The mixture is then forced into the flame, which is of a sufficiently high temperature to cause the atomization of the analyst element. The free atoms thus formed absorb radiation from the HCL which is focused onto

the center of the flame about 5-10mm above the burner slot. This radiation has now been

attenuated by an amount related to the concentration of free atoms in the flame and hence

in the solution now enters the monochromator. This allows only a narrow region of the

spectrum, typically 0.5nm centered on the pre-selected wavelength of the resonance line of

the analyzing element, to pass into photomultiplier. This amplifies the resulting display.

The schematic diagram[11] is shown in Figure 4.
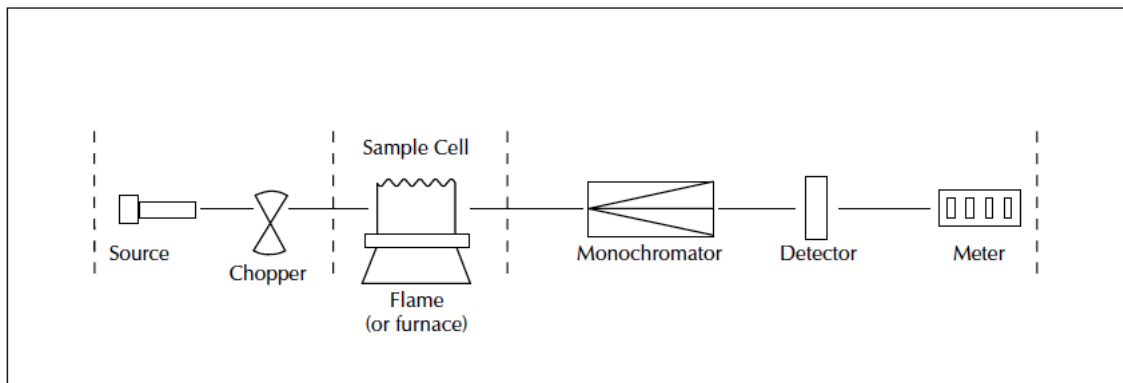
Figure 4. The schematic digram

1.6. METHODOLOGIES USED IN ROCK DIGESTIONS

There are various analytical methods for analyzing rocks, all of which require

complete dissolution and digestion of the rock samples. The next step after the digestion

involves the burning off of organic content, which is followed by the separation of the

silicates from other elements. Once the separation is achieved, analysis of the elements is

carried out using Atomic Absorption Spectroscopy.

1.6.1. DIGESTION USING HYDROCHLORIC ACID:

The use of hydrochloric acid (HCl)[12] to digest rocks is an old method. In this open-vessel digestion method, the rock sample is first ignited in a platinum crucible to burn off the organic contents. The platinum crucible is used to avoid decrepitating of the rock samples. Following this initial step, the ignited residue is placed in a porcelain casserole and digested by adding a solution of 5% HCl (v/v). This digestion is normally done at temperatures below the boiling point of the acid (110°C). As a result, complete dissolution and digestion of the rock samples is not achieved, leading to inaccurate analysis of the rock material. Another drawback of this method is the fact that HCl under the temperature conditioned mentioned above does not efficiently break down the strong Si-O bond of silicates leaving the silicates as insoluble material that is difficult to separate from the digested solution.

1.6.2. DIGESTION USING AMMONIUM BIFLURIDE AND NITRIC ACID:

Another open-vessel method that is widely used in the digestion of rock material involves the use of a mixture of ammonium bifluoride (NH_4HF_2) and nitric acid (HNO3)[13]. This method replaced a hydrofluoric acid (HF) digestion method that, although very efficient in breaking-down the silicate Si-O bonds, utilizes the highly toxic and corrosive HF. Ammonium bifluoride which is less corrosive than HF was found to react with silicate efficiently at high temperatures (230°C). In the ammonium bifluoride method, solid NH_4HF_2 is initially added to the rock sample in screw-top Teflon vials and is heated in an oven at temperatures as high as 230°C. Once sufficient time was allotted to insure complete

decomposition of the silicates, nitric acid was used to complete the digestion process. It was proven to be effective and safe, the ammonium bifluoride/HNO3 method is not economical due to the high price of the screw-top Teflon vials used as vessels.

1.7. DISSOLUTION/DIGESTION METHOD USED IN THIS WORK

Due to the relatively high price of the screw-top Teflon vials used in the method discussed in section 1.6.2, we developed a procedure where the NH_4HF_2/HNO_3 digestion of the rock samples is carried out in non-screw-top Teflon vessels that if suitable will render the method more economical than the procedure traditionally carried out in the literature. The research discussed in this thesis describes the use of this method in the analysis of the geochemical compositions of sedimentary rocks of unknown compositions from Oklahoma City collected from various sites and at different depths. The efficacy of this method will be tested by analyzing a sample of limestone with a known chemical composition.

CHAPTER II

EXPERIMENTAL

2.1. MATERIALS

The material listed below is used as obtained from the listed companies without further processing.

Aluminum metal (Al) was purchased from Sigma.

Ammonium Bifluoride (NH_4HF_2) was purchased from Fisher Scientific Company.

Calcium carbonate ($CaCO_3$) was purchased from Sigma.

Deionized distilled water (H_2O).

Hydrochloric acid (HCl) was purchased from Sigma.

Iron metal (Fe) was purchased from Sigma.

Lanthanum Oxide (La_2O_3) was purchased from Sigma.

Limestone rocks.

Magnesium metal (Mg) was purchased from Sigma.

Nitric acid (HNO_3) was purchased from Sigma.

Phosphoric acid (H_3PO_4) was purchased from Sigma.

Potassium chloride (KCl) was purchased from Fisher Scientific Company.

Teflon vessels were purchased from Fisher Scientific Company.

Unknown samples analysis (XGP1, XGP2, XGP3 and XGP4).

2.2. PREPARATION STANDARD SOLUTIONS

2.2.1. PREPARATION OF ALUMINUM STANDARD SOLUTION

An amount of 1.0113 g of aluminum metal was weighed using an analytical balance and was placed in a beaker. 15 mL of concentrated hydrochloric acid (HCl) was added, followed by 5 mL of concentrated nitric acid (HNO_3) that was added into the beaker that contained the aluminum metal. Then, the beaker was covered by a watch glass. The beaker was warmed gently for 4 minutes or until all of the aluminum reacted completely. The solution was transferred to a 1-liter volumetric flask. The volumetric flask was then filled to the 1L mark with deionized water to give 1011.3-ppm aluminum stock solution.

An amount of 95.0000 g of potassium chloride (KCl) was weighed using an analytical balance and was transferred to a 1-liter volumetric flask. The volumetric flask was then filled to the 1L mark with deionized water.

Standards were made from stock aluminum to use as calibration standards at the time of analysis. The stock solution of aluminum was mixed with potassium chloride. To each 100 mL of standard solution alike 2 mL of potassium chloride solution was added.

Aluminum was partially ionized in the nitrous oxide-acetylene flame. To suppress ionization, potassium chloride was added to the stock solution. The addition of a readily ionizable element such as potassium was used to overcome enhancement interference from other alkali metals.

2.2.2. PREPARATION OF CALCIUM STANDARD SOLUTION

An amount of 3.0000 g of calcium carbonate ($CaCO_3$) was weighed using an analytical balance, was placed in a beaker and was dried in the oven at 180°C for 1 hour. After the calcium carbonate was dried, 1.2501 g of $CaCO_3$ was weighed and was placed in a beaker. 25.00 mL of concentrated hydrochloric acid (HCl) was added, followed by 25.00 mL of deionized water that was added into the beaker that contained calcium carbonate and was stirred using a stir rod to make a solution. The solution was then transferred to a 1-liter volumetric flask. The volumetric flask was then filled to the 1L mark with deionized water to give 500.6-ppm calcium stock solution.

An amount of 29.0003 g of Lanthanum Oxide (La_2O_3) was weighed carefully and was placed in a beaker. 250 mL of concentrated hydrochloric acid (HCl) was added to the beaker. Because this reaction was violent, the mixture was slowly and carefully stirred under the hood with a stir rod to make lanthanum chloride solution. The lanthanum chloride solution was then transferred to a 500 mL volumetric flask. The volumetric flask was then filled to mark with deionized water.

Standards were made from stock calcium to use as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample 1 mL of $LaCl_3$ was added[14].

Calcium was partially ionized in the nitrous oxide-acetylene flame. To suppress ionization, lanthanum chloride was added to the stock solution. The addition of a readily ionizable element such as potassium was used to overcome enhancement interference from other alkali metals.

2.2.3. PREPARATION OF IRON STANDARD SOLUTION

An amount of 1.0032 g of iron metal was weighed using an analytical balance, was cleaned and was placed into a beaker. 15 mL of concentrated hydrochloric acid (HCl) was added, followed by 5 mL of concentrated nitric acid (HNO_3) that was added to the beaker that contained the iron metal. Then, the beaker was covered by a watch glass. The beaker was warmed gently for 3 minutes to dissolve the iron and generate a solution. The solution was then transferred to a 1-liter volumetric flask. The volumetric flask was then filled to the 1-liter mark with deionized distilled water to give 1003.2-ppm iron stock solution.

Standards were made from stock iron to use as calibration standards at the time of analysis. To each 10 mL volume of calibration standard and sample 1 mL of phosphoric acid was added.

Iron was partially ionized in the air-acetylene flame. To suppress ionization, phosphoric acid was added to the stock solution.

2.2.4. PREPARATION OF MAGNESIUM STANDARD SOLUTION

An amount of 1.0159 g of magnesium metal was weighed using an analytical balance, was cleaned and was placed in a beaker. 15 mL of concentrated hydrochloric acid (HCl) was added, followed by 5 mL of concentrated nitric acid (HNO_3) that was added into the beaker that contained the magnesium metal. Then, the beaker was covered by a watch glass. The beaker was warmed gently for 4 minutes to dissolve the magnesium and make a solution. The solution was then transferred to a 1-liter volumetric flask. The volumetric

flask was then filled to the 1L mark with deionized water to give 1015.9-ppm magnesium stock solution.

2.3. LIMESTONE ROCKS

The Standard Specific Interest Group method for analysis of limestone[12] was used to test known limestone rock for percentages of calcium and magnesium. The results obtained for the known calcium rocks reflected the known values for the calcium and magnesium in the known limestone sample. Having determined the validating of the method, the method was used for the analysis of the unknown samples.

2.3.1. PROCEDURE FOR LIMESTONE

Limestone rocks were crushed by mortar and pestle. A sample of 0.5014 g of limestone was weighed using an analytical balance and was placed in a clean platinum crucible. The platinum crucible was covered by a platinum lid and was ignited for 1 hour at 1000°C slowly at first to avoid loss by decrepitation. The ignited residue was then cooled in a desiccator and was weighed again. The ignited residue was transferred into a 300 mL porcelain casserole. 10 mL of water was added to the ignited residue and was mixed by a stir rod. 5 mL of concentrated hydrochloric acid (HCl) was added into the porcelain casserole and was gently heated to facilitate the breakdown of Si-O bond in silicate. The mixture was then dried for 1 hour in an electric oven at 150°C. The mixture was then cooled at 40°C for 30 minutes in the electric oven. 5 mL of concentrated hydrochloric acid was

added to the mixture of solid, followed by adding an amount of water equal to the hydrochloric acid. Then, the porcelain casserole was covered by a porcelain lid. The sand bath was heated. Then the porcelain casserole was placed in the sand bath and heated for 10 minutes. The mixture was then filtered through filter paper into a 400 mL beaker and the residue was washed with concentrated hydrochloric acid (1:10). Next, the porcelain casserole and the filter paper were washed twice by hot water (about 60-90°C). The mixture of limestone filtrate was returned into the same porcelain casserole, 10 mL of concentrated hydrochloric acid was added, followed by 10 mL of water that was added into the porcelain casserole. The mixture of limestone was placed into the electric oven and was heated for 1 hour at 150°C. The mixture was then filtered again through filter paper into a 400 mL beaker, and the residue was washed with concentrated hydrochloric acid (1:10). Then, the porcelain casserole and filter paper were washed twice by hot water (about 60-90°C). The solution of limestone filtrate was then transferred into a clean glass Erlenmeyer flask and the glass Erlenmeyer flask was covered. Limestone filtrate was analyzed by atomic absorption spectroscopy at a specific setting to determine the percentage of calcium and magnesium it contained.

2.4. DIGESTION UNKNOWN SAMPLES (XGP1, XGP2, XGP3 AND XGP4)

2.4.1. UNKNOWN SAMPLE (XGP1)

The physical appearance of unknown sample XGP1 was bulky dark grayish and dark white with white. It had few fine rounded fragments, fine displayed concretion and was bulky sized, as can be seen in Figure 5.

The unknown sample XGP1 was digested using the same procedure as was used for limestone. A sample XGP1 of 0.5189 g was weighed using an analytical balance and was transferred into a clean platinum crucible, thus obtaining the XGP1 filtrate.

2.4.1.1. ANALYSIS OF XGP1 FILTRATE

XGP1 filtrate was analyzed in three ways to obtain suitable results. In the first test 1.00 mL of XGP1 filtrate by a volumetric pipet was transferred to a 250-mL volumetric flask. The volumetric flask was then filled to the 250-mL mark with deionized water and was labeled sample XGP1a. The sample was analyzed using atomic absorption spectroscopy at specific setting to percentages of aluminum, calcium, iron and magnesium. In the second test, an amount of 2.00 mL of XGP1 filtrate was transferred to a 250-mL volumetric flask. The volumetric flask was then filled to the 250-mL mark with deionized water and was labeled sample XGP1b. The sample was then analyzed using atomic absorption spectroscopy at a specific setting to percentages of elements. In the third test the whole XGP1 filtrate was analyzed using atomic absorption spectroscopy at a specific setting to find its percentages of elements.

Figure 5. XGP1 sample

2.4.2. UNKNOWN SAMPLE (XGP2)

The physical appearance of unknown sample XGP2 was very bulky dark grayish, white and brownish. It had few fine rounded fragments, fine displayed concretion and was small sized, as can be seen in Figure 6.

The sample XGP2 was digested using a new method: Total Rock Dissolution Using Ammonium Bifluoride (NH_4HF_2) in Screw Top Teflon Vials: A New Development in Open-Vessel Digestion[13].

2.4.2.1. PROCEDURE FOR XGP2

The sample XGP2 was ground by mortar and pestle. A sample of 0.5025 g was weighed using an analytical balance and was placed in a Teflon vial. A sample of 2.0014 g of ammonium bifluoride (NH_4HF_2) was weighed using the analytical balance, was transferred into the Teflon vial and the vial was covered by a cap. The vial was heated at

230°C for 3 hours in an electric oven. 2 mL of nitric acid was added into the vial. Then, the vial was capped and was heated on a hot plate at 160°C for 1 hour. The vial was then cooled about 2 hours in a desiccator. The vial was then opened and was evaporated to dry at 160°C. 1.00 mL of nitric acid and 1.00 mL of deionized distilled water was added to the final residue. The vial was recapped and was heated at 120°C for 6 hours in the electric oven. The final residue was transferred to a 100 mL polyethylene bottle. 2% (2:98) of nitric acid was added to the total mark. The final solution was then analyzed using atomic absorption spectroscopy to find the percentages of elements such as aluminum, calcium, iron and magnesium.

Figure 6. XGP2 sample

2.4.3. UNKNOWN SAMPLE (XGP3)

The physical appearance of Unknown sample XGP3 was bulky gray and white. It had more fine rounded fragments, fine displayed concretion and was medium sized, as can be seen in Figure 7.

The sample XGP3 was digested using the same procedure as was used for XGP2, thus obtaining the XGP3 filtrate. However, an amount of 0.5000 g of XGP3 was weighed using an analytical balance and was placed in a Teflon vial. An amount of 2.0016 g of ammonium bifluoride (NH_4HF_2) was weighed using the analytical balance and was transferred to the vial. The vial was covered, thus obtaining the final solution. The final solution was then analyzed using atomic absorption spectroscopy to find the percentages of elements such as aluminum, calcium, iron and magnesium.

Figure 7. XGP3 sample

2.4.4. UNKNOWN SAMPLE (XGP4)

The physical appearance of Unknown sample XGP4 physical appearance was dark grayish and white. It had more fine rounded fragments, fine displayed concretion and was small sized, as can be seen in Figure 8.

The sample XGP4 was digested using the same procedure as was used for XGP2 and XGP3, thus obtaining the XGP4 filtrate. However, an amount of 0.5009 g of XGP4 was weighed using an analytical balance and was placed in a Teflon vial. An amount of

2.0057 g of ammonium bifluoride (NH_4HF_2) was weighed using the analytical balance and was transferred to the vial. The vial was covered, thus obtaining the final solution. The final solution was then analyzed by atomic absorption spectroscopy to find the percentages of elements such as aluminum, calcium, iron and magnesium.

Figure 8. XGP4 sample

CHAPTER III

RESULTS AND DISCUSSION

3.1. ALUMINUM STANDARDS CURVE

After the aluminum standard solution was made with 1011.3 ppm, 125.00 mL of aluminum standard was transferred to a 500-mL volumetric flask. The volumetric flask was then filled to the 500-mL mark with potassium chloride and was labeled (C1) 252.83 ppm of secondary stock solution aluminum. Five standards were made from the secondary stock solution at concentrations (C2) of: 25.28, 50.57, 75.85, 101.13 and 126.41 ppm. The standards were diluted with potassium chloride to yield 100 mL volumes. The standards were then analyzed by atomic absorption spectroscopy using the following settings[15]: 10 mA of lamp current, acetylene fuel, nitrous oxide oxidant, 309.3 nm of wavelength and 0.2 nm of slit width. The results are shown in Table 1.

# mL of stock	Concentration C1 ppm	Concentration C2 ppm	Absorbance
10.00	252.83	25.28	0.065
20.00	252.83	50.57	0.143
30.00	252.83	75.85	0.208
40.00	252.83	101.13	0.271
50.00	252.83	126.41	0.318

Table 1. Absorbance readings for aluminum standards

The fourth column for the standards that were prepared gave absorbance readings, which were plotted, and the standard curve, shown in Figure 9, generated the linear relationship and the molar extinction coefficient to be applied using the Beer-Lambert Law. The data had a correlation coefficient of 0.99253, as shown in Figure 9.

Figure 9. Aluminum standards curve

3.2. CALCIUM STANDARDS CURVE

After the calcium standard solution was made with 500.6 ppm, 5.00 mL of calcium standard was transferred to a 1000-mL volumetric flask. The volumetric flask was then filled to the 1000-mL mark with lanthanum chloride and was labeled (C1) 2.50 ppm of secondary stock solution calcium. Four standards were made from the secondary stock solution at concentrations (C2) of: 0.10, 0.50, 1.00 and 1.50 ppm. The standards were diluted with lanthanum chloride to yield 25 mL volumes. The standards were then analyzed by atomic absorption spectroscopy using the following settings[15]: 10 mA of lamp current, acetylene fuel, nitrous oxide oxidant, 422.7 nm of wavelength and 0.2 nm of slit width. The results are shown in Table 2.

# mL of stock	Concentration C1 ppm	Concentration C2 ppm	Absorbance
1.00	2.50	0.10	0.124
5.00	2.50	0.50	0.148
10.00	2.50	1.00	0.193
15.00	2.50	1.50	0.253

Table 2. Absorbance readings for calcium standards

The fourth column for the standards that were prepared gave absorbance readings, which were plotted, and the standard curve, shown in Figure 10, generated the linear

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relationship and the molar extinction coefficient to be applied using the Beer-Lambert Law. The data had a correlation coefficient of 0.98138, as shown in Figure 10.
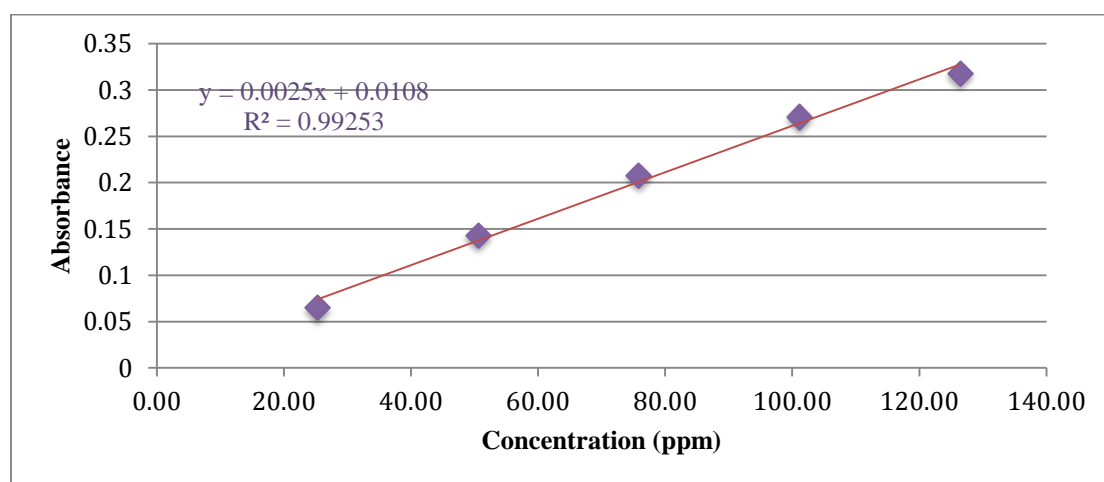

Figure 10. Calcium standards curve

3.3. IRON STANDARDS CURVE

After the iron standard solution was made with 1003.2 ppm, 1.5 mL of iron standard was transferred to a 100-mL volumetric flask. The volumetric flask was then filled to the 100-mL mark with deionized water and was labeled (C1) 15.05 ppm of secondary stock solution iron. Five standards were made from the secondary stock solution at concentrations (C2) of: 0.60, 3.01, 6.02, 9.03 and 12.04 ppm. Amounts of 0.1, 0.5, 1, 1.5 and 2 mL of phosphoric acid were added to the five standards respectively and were diluted with distilled water to yield 25 mL volumes. The standards were then analyzed by atomic absorption spectroscopy using the following settings[15]: 5 mA of lamp current, acetylene fuel, air oxidant, 248.3 nm of wavelength and 0.2 nm of slit width. There results are shown in Table 3.

# mL of stock	Concentration C1 ppm	Concentration C2 ppm	Absorbance
1.00	15.05	0.60	0.124
5.00	15.05	3.01	0.221
10.00	15.05	6.02	0.351
15.00	15.05	9.03	0.522
20.00	15.05	12.04	0.615

Table 3. Absorbance readings for iron standards

The fourth column for the standards that were prepared gave absorbance readings, which were plotted, and the standard curve, shown in Figure 11, generated the linear relationship and the molar extinction coefficient to be applied using the Beer-Lambert law. The data had a correlation coefficient of 0.99351, as shown in Figure 11.
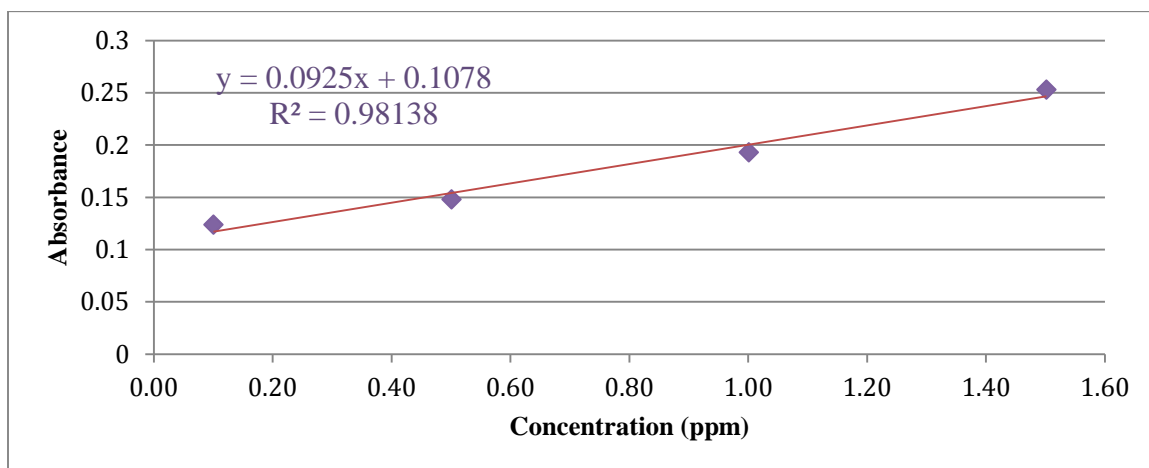

Figure 11. Iron standards curve

3.4. MAGNESIUM STANDARDS CURVE

After the magnesium standard solution was made with 1015.9 ppm, 0.50 mL of magnesium standard was transferred to a 500-mL volumetric flask. The volumetric flask was then filled to the 500-mL mark with distilled water and was labeled (C1) 1.02 ppm of secondary stock solution magnesium. Six standards were made from the secondary stock solution at concentrations (C2) of: 0.040, 0.10, 0.20, 0.30, 0.41 and 0.51ppm. The standards were diluted with distilled water to yield 50 mL volumes. The standards were then analyzed by atomic absorption spectroscopy using the following settings[15]: 4 mA of lamp current, acetylene fuel, air oxidant, 285.2 nm of wavelength and 0.2 nm of slit width. The results are shown in Table 4.

# mL of stock	Concentration C1 ppm	Concentration C2 ppm	Absorbance
2.00	1.02	0.04	0.168
5.00	1.02	0.10	0.229
10.00	1.02	0.20	0.378
15.00	1.02	0.30	0.470
20.00	1.02	0.41	0.572
25.00	1.02	0.51	0.930

Table 4. Absorbance readings for magnesium

The fourth column for the standards that were prepared gave absorbance readings, which were plotted, and the standard curve, shown in Figure 12, generated the linear relationship and the molar extinction coefficient to be applied using the Beer-Lambert law. The data had a correlation coefficient of 0.93205, as shown in Figure 12.
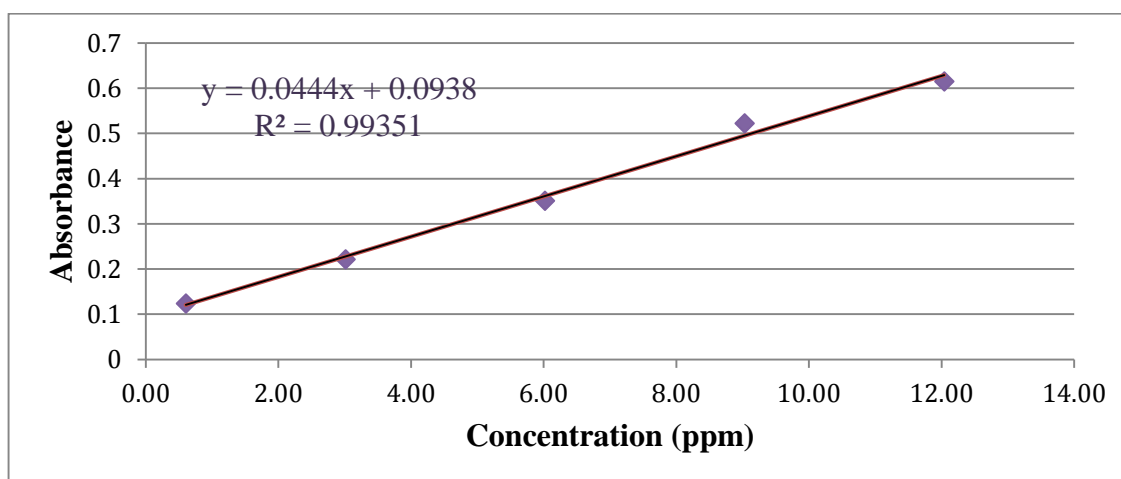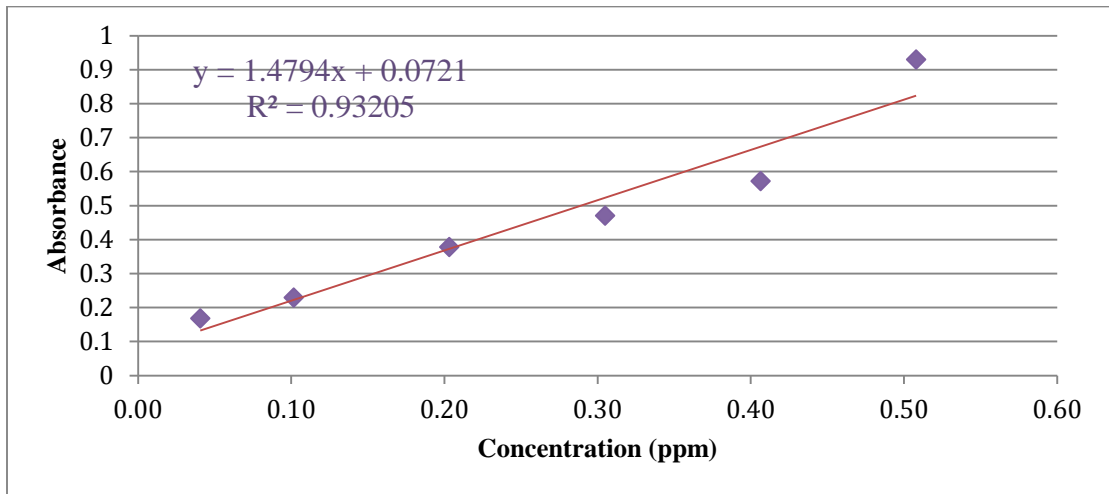

Figure 12. Magnesium standards curve

3.5. ESTIMATED UNCERTAINTY VALUES[16]

Slopes (m) and intercepts (c) of all elements in the standards' curves were used to calculate the uncertainty in the ppm concentrations of XGP parent samples. The calibration line is given by the equation below. As can be seen in Figure 13, the equation was used to calculate the uncertainty values for X_o (ppm). The results are tabulated in Table 5.

$$u_{x_o} = \frac{SE_{yx}}{m} \times \sqrt{\frac{1}{k} + \frac{1}{n} + \frac{(y_o - \overline{y})^2}{m^2 \times (n-1) \times s_x^2}}$$

Figure 13. The calibration line equation

	Al	Fe	Ca	Mg
Slope, m	0.0025	0.0925	0.0444	1.503
Intercept, c	-0.0108	-0.1080	-0.094	-0.0721
Measured y-values, yo (Absorbance values)				
XGP1	0.006	0.428	0.438	0.167
XGP2	0.012	0.655	0.476	0.778
XGP3	0.014	0.492	0.429	0.311
XGP4	0.010	0.387	0.487	0.369
Mean Y-values, yo (Absorbance values)	0.011	0.491	0.458	0.406
Calculated x-values, xo (ppm)	8.520	6.470	12.419	0.318
Standard Error of Regerssion, Seyx	0.010	0.009	0.019	0.080
No of y-readings, k (unknown)	4	4	4	4
No of calibration readings, n	5	4	5	6
Mean of y-values, y-bar	0.201	0.180	0.367	0.458
Sample variance of x-values, s^2	1598.012	0.370	20.916	0.031
Estimated uncertainty, u(xo) (ppm)	4.681	0.335	0.302	0.035
Estimated uncertainty, 95% CI	2.694	0.072	0.286	0.034

Table 5. Calculated uncertainty values in X

3.6. PERCENTAGES OF ELEMENTS IN LIMESTONE

The percentages of calcium and magnesium in the limestone sample used in this study were determined using the dissolution/digestion method developed in this work. The results are shown Table 6.

Sample	Percentage of Ca	Percentage of Mg
Limestone	25.75	0.0134

Table 6. Percentages of calcium and magnesium in limestone

The experimental values of the percentages of Ca and Mg obtained in this study are in agreement with the values obtained from the limestone samples purchased from Thorn Smith (sample number 115, 1967 Series), where it was determined that the percentages of calcium and magnesium are 29.36 and 0.0, respectively. This supports the efficacy of the method developed in this work as a valid procedure for the analysis of the chemical composition of sedimentary rocks.

3.7. PERCENTAGES OF ELEMENTS IN UNKNOWN SAMPLES (XGP1, XGP2, XGP3 AND XGP4)

An amount of 1mL of solution unknown samples XGP1, XGP2, XGP3 and XGP4 were transferred to 5-mL volumetric flasks. The volumetric flasks were then filled to the 5-mL with distilled water and were labeled XGP1, XGP2, XGP3 and XGP4. The diluted unknown samples were analyzed by atomic absorption spectroscopy at specific settings that were related to each element, as shown in Table 7. Aluminum was not detected in any of the diluted samples and iron was not detected in XGP1, XGP2 and XGP3 but was detected in XGP4.

Unknown sample	Absorbance of dilute sample of Al	Absorbance of dilute sample of Ca	Absorbance of dilute sample of Fe	Absorbance of dilute sample of Mg
XGP1	Not detectable	0.428	0.438	0.167
XGP2	Not detectable	0.655	0.476	0.778
XGP3	Not detectable	0.492	0.429	0.311
XGP4	Not detectable	0.387	0.487	0.369

Table 7. Absorbance readings of dilutes samples

Table 8 shows the absorbance readings of unknown filtrate samples XGP1, XGP2, XGP3 and XGP4. The unknown filtrate samples were detected for elements such as Al, Ca, Fe and Mg in XGP1, XGP2, XGP3 and XGP4 except for the iron, which was not detected in XGP1.

Unknown sample	Absorbance of Al	Absorbance of Ca	Absorbance of Fe	Absorbance of Mg
XGP1	0.006	2.983	6.654	0.997
XGP2	0.012	3.119	7.220	1.959
XGP3	0.014	3.099	6.454	1.909
XGP4	0.010	3.108	7.284	1.825

Table 8. Calculated absorbance of filtrate unknown samples

From the absorbance readings of unknown samples and the equations of each element of standards curves the percentages of each element were calculated, as shown in Table 9. These results will be later compared with other studies.

Unknown sample	Percentage of Al	Percentage of Ca	Percentage of Fe	Percentage of Mg
XGP1	0.0000925	0.267	2.271	0.00494
XGP2	0.000180	0.443	2.251	0.0357
XGP3	0.000210	0.312	2.211	0.0121
XGP4	0.000150	0.226	2.594	0.0150

Table 9. The percentages of elements in unknown samples

Table 10 shows the converted percentages of elements to milliequivalents per 100g that were in the unknown samples. These results will be compared with soil samples analysis from Oklahoma.

Unknown sample	Percentage of Al (meq per 100 g)	Percentage of Ca (meq per 100 g)	Percentage of Fe (meq per 100 g)	Percentage of Mg (meq per 100 g)
XGP1	0.01	13.4	50.73	0.412
XGP2	0.02	22.2	56.33	2.975
XGP3	0.023	15.6	49.40	1.008
XGP4	0.017	11.3	57.95	1.250

Table 10. The percentages of elements (meq per 100 g)

The soils samples analysis from Oklahoma by Dennis[17], Parsons[17], Zaneis[18] and Kingfisher[18] were developed in sedimentary rocks and were taken from different counties in Oklahoma. The depths in their studies were drilled between 40-90 inches. Samples in this study are obtained from sedimentary rocks and are taken at comparable depths. The second and third columns for the percentages of calcium and magnesium show that the values of their studies[19] are consistent with the values of this study undertaken by Alhawdar, as shown in Table 11. Although their samples were dissolved with hydrogen peroxide (H_2O_2) to remove organic content, these samples in this study were dissolved with ammonium bifluoride (NH_4HF_2) and nitric acid (HNO_3). To further contrast methods, their samples were analyzed using Beckman DU flame spectrophotometers with photomultiplier attachment but samples in this study were analyzed using atomic absorption spectroscopy.

Study	Percentage of Ca (meq per 100 g)	Percentage of Mg (meq per 100 g)
Dennis	14.5	5.9
Parsons	9.7	4.8
Zaneis	5.4	5.1
Kingfisher	4.3	6.5
Alhawdar		
XGP1	13.4	0.412
XGP2	22.2	2.975
XGP3	15.6	1.008
XGP4	11.3	1.250

Table 11. Comparison of results of this study with literature values

The percentages of different samples in igneous rocks by Bernas[20] are shown in Table 12. To compare the methods in Bernas and Alhawdar's studies, both their samples were analyzed using the same instrument that atomic absorption spectroscopy. Bernas' samples were dissolved with hydrofluoric acid (HF) and vessels made of Teflon were used. The samples in this study, in contrast, were dissolved with ammonium bifluoride (NH_4HF_2) and nitric acid (HNO_3) and Teflon vials were used. Although Bernas' samples were developed in igneous rocks and the samples in this study were developed in sedimentary

rocks, the second, third, fourth and fifth columns for the percentages of elements in different samples show the values of Bernas' study are consistent with the values of the study undertaken by Alhawdar in Table 9.

Samples	Percentage of Al	Percentage of Ca	Percentage of Fe	Percentage of Mg
Granite	7.67	0.98	1.32	0.24
Diabase	7.84	7.60	7.52	3.84
Australite	6.08	1.84	3.83	0.92
Philippinite	7.08	2.10	3.65	1.42

Table 12. Percentages of elements in silicates

The percentages of different samples in clay minerals[21] are shown in Table 11. In their studies, the samples of clay minerals in rocks were recovered from the Trans-Atlantic Geotraverse hydrothermal mound. The samples were gathered between 15 and 121 meters below the seafloor from various areas of the Trans-Atlantic Geotraverse mound.

Comparing the percentages of unknown samples in Table 9 in this study with the percentages of clay minerals in Table 13 in their studies shows different percentages because of different locations and compositions.

Sample	Percentage of Al	Percentage of Ca	Percentage of Fe	Percentage of Mg
9R-1, 67-71	16.11	2.62	13.25	8.59
10R-1, 79-74	15.41	8.90	12.75	9.88
10R-2, 11-14	17.78	4.62	19.24	10.63

Table 13. Percentages of elements in clay minerals

The purpose of the studies of Dennis, Parsons, Zaneis and Kingfisher was to determine amounts and kinds of clays present in Oklahoma soils. Their analysis suggested which plants could grow according to location. Their analysis also suggested amounts of fertilizer − as well as chemical composition − that could be used to maximize crop production, given the geochemical structure of soil found at various locations.

The purpose of Bernas' study was to develop a comprehensive and simple analytical scheme for determining all the major and minor constituents in silicates by atomic absorption spectrometry. It was important to investigate and develop an environment that would prevent contamination and at the same time prove advantageous when applied to atomic absorption measurements.

The objective of their studies[21] was to determine clay minerals and chemical composition from different areas in the Trans-Atlantic Geotraverse mound. Also, it was to investigate rocks and determine if there was a correlation between secondary silicate mineralogy and selected heavy metal concentrations and more.

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