



بسم الله الرحمن الرحيم

Sudan University of Science and Technology

College of Graduate Studies



**Investigation of Some Acid Radicals Content in Trona Ore
Samples (Sudan)**

إستقصاء محتوى بعض الشقوق الحمضية في عينات من خام العطرون (السودان)

A Thesis submitted in partial fulfillment for the requirements of the degree
of master in chemistry

By

Ahlam Hassan Mohammed Altahir

(B.Sc.Honors, Chemistry)

Supervisor:

Dr. Omer Adam Mohamed Gibla

January 2022

إستهلال

قَالَ تَعَالَى:

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ هُوَ اللَّهُ الْخَلِيقُ الْبَارِئُ الْمُصَوِّرُ لَهُ الْأَسْمَاءُ الْحُسْنَى يُسَبِّحُ لَهُ مَا

فِي السَّمَوَاتِ وَالْأَرْضِ وَهُوَ الْعَزِيزُ الْحَكِيمُ ﴿٢٤﴾

صدق الله العظيم

سورة الحشر الآية (٢٤)

Dedication

I dedicate this work to my parents,

Husband,

Brothers,

Sisters and my lovely son (Alwsela).

Acknowledgment

First of all my endless thanks to Allah, Almighty, for giving me health and strength to complete this work.

My greater and deep thanks to my supervisor Dr. Omer Adam Mohamed Gibla for his guidance, and encouragement throughout the time of this research.

greater thanks to the members of chemistry department of "SUST", to my colleagues and friends for their help.

Abstract

The aim of this study was to investigate the occurrence of the main acid radicals in Sudanese Trona ore samples. Eight (8) Trona ore samples were obtained from Khartoum state local markets and Elfasher city markets at Northern darfor state. The measured parameters included pH values, moisture content, concentration of carbonate (CO_3^-), hydrogen carbonate (HCO_3^-), sulfate (SO_4^-) chloride (CL^-), silicon dioxide (SiO_2), and phosphorous (P). pH meter was used for pH values determination. Moisture content was determined by electrical furnace. Carbonate, hydrogen carbonate and chloride concentrations were measured titrimetrically. Sulfate concentration was obtained by analysis as (BaSO_4). Phosphorous content was determined by gravimetric analysis UV-Vis spectrophotometer. The analysis of samples showed different pH values and moisture content. The chemical parameters also showed different concentrations. pH-values range from (8.87 to 9.70). Moisture content ranges from (5.00% to 20.72%). The range of carbonate as (Na_2CO_3) was found to be (10.95 % to 47.47%), the hydrogen carbonate as (NaHCO_3) ranges from (3.35% to 50.66%). Chloride as (NaCL) ranges from (1.11% to 49.62%). Sulfate as (Na_2SO_4) ranges from (zero to 2.72%). Silica as (SiO_2) ranges from (1.29% to 68.31%). Phosphorous as (P) was found to range from (0.0002% to 0.0024%). The pH values indicate relatively alkalinity in all samples. Moisture content was found to be low in three samples (5.00%, 5.16% and 5.23%) and relatively high in four samples (17.65% to 20.72%). The highest carbonate content was shown by two samples as (37.03% and 47.47%). The highest bicarbonate content was shown by three samples as (43.01%, 43.35% and 50.66%). The highest chloride content was shown by one sample as (49.62%). The highest sulfate was (2.72%). Silica as (SiO_2) showed high values in three samples as (30.44%, 35.82% and 68.31%). Phosphorous content was very low in the eight samples.

المستخلص

هدفت هذه الدراسة لاستقصاء وجود الشقوق الحمضية الرئيسية في عينات من خام العطرون السوداني. تم الحصول على ثمانية (8) عينات لخام العطرون من الأسواق المحلية بولاية الخرطوم وسوق مدينة الفاشر بولاية شمال دارفور. المتغيرات المقاسة شملت قيمة الأس الهيدروجيني ومحتوى الرطوبة وتركيز الكربونات (CO_3^{2-}) والكربونات الهيدروجينية (HCO_3^-) والكبريتات (SO_4^{2-}) والكلوريد (Cl^-) وثاني أكسيد السليكون (SiO_2) والفسفور (P). استخدم جهاز قياس الأس الهيدروجيني لتحديد قيم الأس الهيدروجيني. تم تحديد محتوى الرطوبة باستخدام الفرن الكهربائي. تم قياس تراكيز الكربونات والكربونات الهيدروجينية والكلوريد بالمعايير. تركيز الكبريتات تم الحصول عليه بالتحليل الوزني على هيئة (BaSO_4). محتوى الفسفور تم تحديده باستخدام جهاز المطيافية الضوئية للطيغ البنفسجي والمرئي (UV-Vis). أظهر تحليل العينات قيم مختلفة للأس الهيدروجيني ومحتوى الرطوبة. المتغيرات الكيميائية أيضا أظهرت تراكيز مختلفة. تراوحت قيم الأس الهيدروجيني بين (9.70 - 8.8). محتوى الرطوبة تراوح بين (5.00% - 20.72%). محتوى الكربونات على هيئة (Na_2CO_3) تراوح بين (47.47% - 10.95%)، الكربونات الهيدروجينية على هيئة (NaHCO_3) تراوحت بين (50.66% - 3.35%). والكلوريد في صورته (NaCl) تراوح من (49.62% - 1.11%). الكبريتات على هيئة (Na_2SO_4) تراوحت من (2.72% - zero). السليكون في صورته (SiO_2) تراوح بين (68.31% - 1.29%). والفسفور في صورته (P) تراوح بين (0.0024% - 0.0002%). قيم الأس الهيدروجيني أظهرت قلوية عالية نسبيا في كل العينات. محتوى الرطوبة كان منخفضا في ثلاثة عينات (5.00%, 5.23% 5.16%). وعالية نسبيا في أربعة عينات (20.72% - 17.65%). اعلي محتوى للكربونات ظهر في عينتين (47.47%, 37.03%). اعلي محتوى للكربونات الهيدروجينية ظهر في ثلاث عينات (50.66%, 43.35%, 43.01%). أظهرت عينة واحدة اعلي محتوى للكلوريد (49.62%). اعلي محتوى للكبريتات كان (2.72%). السليكون (SiO_2) أظهر قيم عالية في ثلاثة عينات (68.31%, 35.82%, 30.44%). محتوى الفسفور كان منخفضا جدا في العينات الثمانية.

Table of Contents

Title	Page
إستهلال	I
Dedication	II
Acknowledgment	III
Abstract	IV
المستخلص	V
Table of Contents	VI
List of Tables	IX
List of Figures	X
Chapter One	
1.Introduction and literature review	1
1.1 Trona	1
1.2 Some trona deposits world wide	4
1.3 Formation of Trona Ores	6
1.4 Occurrence of Trona Ores	7
1.4.1Trona in USA	8
1.4.2 Trona in Nigeria	11
1.4.3 Trona in Turkey	13
1.4.4Trona in Sudan	14
1.4.5 Locations and types of Trona in Sudan	15
1.4.5.1 Elatrune area	15
1.4.5.2 Eljabel Trona	15
1.4.5.3 Abuzaema Trona	15
1.4.5.4 Kambodia Trona	15
1.4.5.5 Elakhder and Elahmer Trona	16
1.4.5.6 Elsalam Trona	16

1.4.5.7 Elsilail Trona	16
1.4.5.8 Ummbahatay Trona	16
1.4.5.9 Eldaleiba Trona	16
1.4.5.10 Elnukheila area	17
1.4.5.11 Elgaa Elmasriya trona	17
1.4.5.12 Elgaa Elgadima trona	17
1.5 Chemical composition of Trona ores	19
1.6 Uses of Trona	22
1.6.1 Industrial use of Trona	23
1.6.1.1 Production of sodium carbonate (Na ₂ CO ₃)	24
1.6.1.1.1 Leblanc process for sodium carbonate	24
1.6.1.1.2 Solvay process	25
1.6.1.1.3 Hou's process	26
1.6.1.2 production of calcium hydroxide	28
1.6.1.3 Production of sodium hydroxide from sodium carbonate and calcium hydroxide	28
1.6.1.4 Sodium hydrogen carbonate	28
1.6.1.5 Sodium silicate Production	29
1.7 Some specification naturally occurring trona (Sudan)	30
1.8 Objectives of the study	32
Chapter Two	
2. Materials and methods	33
2.1 Collection of samples	33
2.2 Chemicals	33
2.3 Instrumentation	34
2.4 Determination of sodium carbonate and sodium hydrogen carbonate	34
2.5 Determination of chloride Cl ⁻	35

2.6 Determination of sulphate as sodium sulphate	35
2.7 Determination of phosphorus	35
2.8 Determination of silica (SiO ₂)	36
2.9 Determination of moisture	36
2.10 Determination of pH	36
Chapter Three	
3. Results and discussion	37
3.1 pH values of trona ore samples	37
3.2 Sodium carbonate and sodium hydrogen carbonate content of trona ore samples	38
3.3 Moisture and silica content of Trona ore samples	39
3.4 Sodium chloride, sodium sulphate and phosphorous content in Trona samples	40
Conclusion	42
Recommendations	43
References	44

List of Tables

Table	Page
Table1.1: Local names and physical description of Trona ores samples from North East of Nigeria	12
Table1.2: Chemical constituents of different trona sampls	19
Table1.3: Color,pH value, $\text{CO}_3^{=}$, HCO_3^- and SiO_2 content of Trona	20
Table1.4: Trona composition according to intermountain chemical crop	20
Table1.5: Natural Trona composition	21
Table1.6: sodium carbonate and sodium hydrogen carbonate of Beypazari trona samples	21
Table1.7: Chemical composition representative Beypazari trona samples	22
Table1.8: Amounts of sodium carbonate imported by sudan from different countries	23
Table1.9: Amounts of sodium hydroxide imported by sudan from different countries	23
Table1.10: physical properties of Trona in Sudan	31
Table 3.1: pH values of trona ore samples	37
Table3.2: Sodium carbonate and sodium hydrogen carbonate content (%w/w)	39
Table3.3: Moisture and silica content (%w/w)	40
Table3.4: Sodium chloride, sodium sulphate and phosphorous content in trona samples (%w/w)	41

List of Figures

Figure	Page
Figure1.1: Wyoming's natural soda ash production since the late 1940	9
Figure1.2 Map of Wyoming state design and layout by Phyllis Ran,	10
Figure1.3: Locality and geological setting of the Beypazari basin and adjacent area	13
Figure1.4: Locations of the Trona area	18
Figure1.5: Geological map of Atron area	18

Chapter one

Introduction and literature review

Chapter one

1.Introduction and literature review

1.1 Trona

Trona is a relatively rare sodium rich mineral which is mined and processed into soda ash (International mineral Association, 1995). Soda ash is a significant economic commodity because of its several applications in the manufacturing industries (Raw materials Research and Development Council; 1988, Zanna,*et al.*, 2018).

Trona is a naturally occurring mineral, which is chemically known as sodium sesqui carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), or tri sodium hydrogen carbonate ($\text{Na}_3\text{H}(\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$). It is an evaporative mineral occasionally encountered as saline lake deposit. Crude Trona or Trona ore, consists primarily of 80-90 % sodium sesqui carbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and some less amounts of sodium chloride (NaCl), sodium sulfate (Na_2SO_4), in addition to organic matter, and some insoluble materials such as sand, clay or shales. Trona contains about 70% sodium carbonate which is refined to produce sodium compounds, particularly pure soda ash (Na_2CO_3) and baking soda (Fathia, 2017).

The naturally occurring form of sodium carbonate minerals is sometimes known as sesqui carbonate, urao or Trona. It gets its name from a discarded Arabic word for native salt, "Atrone", which is derived from the word "atron" .It is a double salt of sodium carbonate and sodium bicarbonate, which is soluble in water. The crystals of this mineral are transparent white, but due to the presence of impurities it appears gray, brown, pink and even black in nature. Its density is $2.1\text{g}/\text{cm}^3$. The main sources of salt manufacturing in the world are sea water, salt lakes, and rock salt (Deer, *et al.*, 1990, Susan; 2012, Zanna, *et al.*, 2018, Esra, 2021).

Trona is erroneously called potash in Nigeria, despite of the fact that, it contains low levels of potassium compared to sodium, sometimes below detection levels. Two varieties of Trona are known in Nigeria, the whitish and the red-white. Trona is also known as “Kaun” in Yoruba and “Kanwa” in Hausa as a dried lake salt that, contains mainly sodium carbonate (Omajali BJ, *et al.*, 2010). Trona is also described as a crude mixture of various salts and other constituents, essentially the hydrated basic sesqui carbonate with some impurities such as clay, sand, potassium, magnesium, silicon, calcium, iron, aluminium and titanium (M. Iwunze1, 1988, J.M.Nielsen, 1999).

Trona “ $\text{Na}_3(\text{HCO}_3).2\text{H}_2\text{O}$ ”, which is also known as potash or kanwa, is a secondary mineral in gozzans of metallic ore deposits as weathering product of primary iron containing mineral (Palach, *et al.*., 1951, Sherman, 1952, Rose and Sutir, 1971, Zuma, 2004).

According to Ameh AO *et al.*, “2009”, Naata, *et al.*, “2018” Esra, *et al.*., “2021”, it is the most abundant sodium alkali mineral. It is an important table salt and the second most commonly used salt in Nigeria. It is also used as salt of tobacco to produce tobacco snuffs, as tenderizing agent, laundering agent, in scouring of wood, in bath salts, in pharmaceuticals and to facilitate fermentation (Makanjuola AA, *et al.*, 1975).

Trona as non-marine evaporate, ($\text{Na}_2\text{CO}_3.\text{NaHCO}_3$) in the Eocene Green River formation in Wyoming (US) accounts for-90% of the global commercial soda ash reserves (Bolen, 2018),but is not associated with evidence for nearby, coeval volcanism (smith, *et al.*.,2008, chetel, *et al.*.,2011).Trona($\text{NaHCO}_3.\text{Na}_2\text{CO}_3.2\text{H}_2\text{O}$) is the most abundant soda mineral and nahcolite(NaHCO_3), precipitate from alkaline brines in hydrologically-closed lakes (Eugster and Jones,1968). Trona deposits are normally,

mechanically mined, using either continuous or longwall mining technique and sometime combination of them. Then, the raw trona can be processed by different methods such as sesqui carbonate, monohydrate, alkali extraction and carbonation processes. Presently, the well-known sodium carbonate minerals used in production of soda ash are trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$), thermonatrite ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and natrone ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). Only trona with 70.3% Na_2CO_3 content is of commercial interest (Sibel Gezer, 2016).

Trona may be expected to occur in association with other secondary minerals, such as iron magnesium phosphates, kainite " $\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$ ", carnallite " $\text{KCl} \cdot \text{MgCl}_2 \cdot 5\text{H}_2\text{O}$ " and poly halite " $\text{K}_2\text{CaMg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ " (Montimer, 1994, Garrels and Christ, 1965). Generally in these environments phosphates may be derived from FePS or other phosphorus containing sulpho salts because wide range of secondary phosphates and carbonates display a wide range of stoichiometries even when the only other anion present in the lattice is hydroxide and only one metallic action is involved (Palache, *et al*., 1993, Rose and Sutir, 1971, Nriagu and Moore, 1984, Fleicher, 1987, Esra, 2021).

The word trona entered English by way of either Swedish (Trona), or Spanish (Trona), with both possible sources having the same meaning as English, which are both derived from the Arabic name "Trona" which in turn is derived from the Arabic natron and Hebrew (natruna), that comes from ancient Greek (nitron), derived ultimately from ancient Egyptian (ntry or nitry) (Isam, 2017, Wikipedia).

Trona is the common name for sodium carbonate (Na_2CO_3), a white odorless powder. The mineral is semi-translucent and yellowish brown to amber in color, which tends to weather to white or gray. The amount and type of organic impurities and other minerals, such as halite (NaCl), affect

the color and texture. Trona has a vitreous or glassy luster and of large, prismatic crystals or thick layers of massive fine-grained crystals which have a cloudy appearance.

Many minerals contain sodium carbonate, but Trona is by far the most important. The widely-used products of soda ash and sodium bicarbonate are produced from Trona, primarily by heating the material to drive off the water content, followed by refining and purification (Robert W.G.T.A.Drean ,2014).

1.2 Some Trona deposits world wide

Trona is found at Owens Lake and Searles Lake, California; the Green River formation of Wyoming and Utah; the Makgadikgadi Pans in Botswana and in the Nile Valley (C.Michael, 2008). Trona near Green River, Wyoming forms the largest known deposit in the world and lies in layered evaporate deposit below ground, where Trona was deposited in a lake during the Paleogene period (Wyoming Mining Association 2017). Trona has also been mined at Lake Magadi in the Kenyan Rift Valley for nearly 100 years. The northern part of Lake Natron is covered by a 1.5 m thick trona bed (Manega, P. C Bieda, S, 1987). It occurs in 'salt' pans in Etosha Nation Park in Namibia (Eckardt, *et al.*,2001). Beypazari region in Ankara Province of Turkey has about 33 Trona beds in two fault-bound lensoid bodies in and above oil shales of the lower Hirka formation, 16 in the lower and 17 in the upper body(Helaci,C,1998). The Wucheng basin Trona mine, in Henan Province of China has 36 Trona beds (693-974 m deep), the lower 15 beds are 0.5-1.5 m thick, thickest 2.38 m, and the upper 21 beds are 1-3 m thick, with a maximum of 4.56 m hosted and underlain by dolomitic oil shales of the wulidui formation(Zhang, Youxun, 1985).

The mineral ore has also been found in magmatic environments. Research has shown that Trona can be formed by autometasomatic reaction of late-

magmatic fluids or melts (or supercritical fluid-melt mixtures), with earlier crystallized rocks within the same plutonic complex, or by large-scale vapor unmixing in the very final stages of magmatism (Marki, 2002).

There are dominantly two, sesqui carbonate and monohydrate processes, used to convert mined Trona into pure soda ash (Na_2CO_3). In the sesqui carbonate process, trona ore is dissolved in water and the solution can be separated from the insolubles and sodium sesqui carbonate is crystallized by cooling. The crystals are then separated from the mother liquor and finally, calcined to recover the soda ash (Na_2CO_3).

In the monohydrate process Trona ore is calcined first to convert it to bicarbonate, then to sodium carbonate, and is then dissolved in water. The resulting solution is then separated from the insolubles and sodium carbonate monohydrate is precipitated by evaporative crystallization. The monohydrate crystals are then separated from the mother liquor and dried to recover soda ash (Sibel Gezer; 2016). Sodium salts occur in large deposits in which, Carbonate rocks represent about 20% of all sedimentary matter. Sands and clays of certain places in the desert often show substantial concentrations of sodium carbonates and in a few rarer cases, quite substantial deposits of reasonable pure sodium sesqui carbonate are found in a form which geologists term to as evaporates. According to Maiduguri Soda-ash production Company of Nigeria (2018), Trona ores commonly contain 2.4 % NaCl , 20% Na_2CO_3 , 26.5% Na_2SO_4 , 30.8% CaCO_3 , 2.0% CaSO_4 , 1.4% insoluble solids and 3.2% water (Esra, 2021).

Trona deposit has limited distribution in the Earth's crust, but extraordinary concentrations can be found in some places, commonly in combination with borate and other salt deposits. Four main continental Trona provinces are recognized at a global scale. They are located in Anatolia (Turkey),

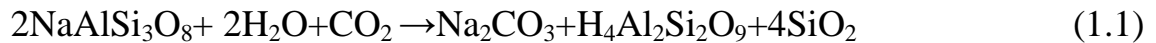
Wyoming (USA), Whuceng(China) and Botswana (Southern Africa). The origin of Trona deposit is related to alkaline volcanism, thermal spring activity, closed basins and arid climate. Quaternary sodium carbonate minerals (Trona minerals) are present in salars(Andes), playa lakes (Lake Van, Turkey and Botswana) and salt pans (USA and Tibet).

Many minerals contain “ Na_2CO_3 ”, but the three that, are most important from a worldwide commercial standpoint are Trona, nahcolite, and pirssonite, which are produced in limited countries, along with subordinate bradleyite, shortite and thenardite. Pirssonite occurs in organic-rich muds (oil shales). Trona and nahcolite are precipitated subaqueously (in lake waters) and as an interstitial phase in playa muds. Evaporate minerals are closely related to pyrite in oil shales and are also associated with diagenetic silicates (Mg-rich smectites, zeolites, K-feldspar, searlesite and idiomorphic quartz) and dolomite formed by reaction of alkaline brines pyroclastic deposits.

Natural sodium carbonate minerals or soda minerals are exploited commercially either from buried fossil Trona deposits formed in Tertiary playa-lake sediments or, by extraction from the brine of recent alkaline lakes and piayas. Most of the world’s commercial trona deposits are mined by underground and solution mining methods. Many modern industries use industrial Trona minerals (Cahit helvaci 2019, altinli IE, 1976).

1.3 Formation of Trona Ores

Because of its high chemical reactivity sodium is never found uncombined in the nature. Igneous rocks contain sodium combined with oxygen, silicon and other metals, in the form of double silicate, such as feldspar ($\text{NaAlSi}_3\text{O}_8$). Under the effect of water and carbon dioxide, feldspar and similar rocks become weathered to yield sodium carbonate, clay and silica.



The soluble carbonate is washed from the weathered rocks by rain, and it may accumulate in land or seas where, after intense evaporation, the solid salt may be deposited as sodium sesqui carbonate ($\text{NaCO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$).

Natron is naturally occurring mixture of sodium carbonate decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) as a kind of soda ash and about 22.7% sodium bicarbonate (NaHCO_3) which is also called nahcolite or baking soda, along with small quantities of house hold salt or halite (NaCl) and some other impurities, Natron has a white a color when pure, varying to gray or yellow with impurities. Natron deposits are sometimes found in saline lake beds in arid environments. Throughout the history Natron had many practical applications which are still resonate in the wide range of modern uses (Maha, M.H, 2006)

Such deposits have been observed in actual formation during the last 100 years in several of the salt lakes of California and in the large African lakes on the Tangana-kenya border. Probably of the earliest example is the Egyptian glass were made alkali leached out of surface clays at Wadi Elnatron, and Sahara and even the Nile Valley (Eldoma. M.A 2003, Susan, 2012).

1.4 Occurrence of Trona Ores

According to Eldoma (2003), Trona was discovered in Western Sudan about 10,000 years ago. Most deposits are geologically young. The most common types of Trona occurrence include:

- Natron crystals in cool wet environment on the bottom of ponds or at shallow depth in slat marches as in wadi Northern of Egypt.

- Powdery efflorescence of thermonatrite on the surface. Examples of this type are the alkaline soils of lower Danube River, lake Nyasa Tanzania and some deposits of Sudan.
- Relatively hard deposits, either around the shore or at the bottom of shallow alkaline lakes or ponds, examples of such deposit are those of lake Magadiat Kenya, Elatarun, Eldaleiba and Elnukheila basins in Sudan.
- Old deposit of Trona, as nahcolite or other sodium carbonate bearing minerals like those of Green River formation of Wyoming.
- In solution as a constituent of brine, either surface or sub surface as Searles lakes in California.

A deposit of this last type has also been found at Eldaleiba basin east of Elatarune area as sub surface crust on the top of the hard deposit of trona. Light soda ash can be extracted from this concentrated brine by evaporation in open containers.

In all these forms “Na₂CO₃” has been found to be more or less mixed with other salts, such as sulphate “SO₄⁼”, chloride “CL⁻” and other trace impurities including sand, clay, and metals such as potassium “K”, silicon “Si”, magnesium “Mg”, calcium “Ca”, iron “Fe”, aluminum “AL” and titanium “Ti”. It may coexist; with other minerals such as gypsum (CaSO₄.2H₂O).

1.4.1 Trona in USA

According to Robert .W, *et al.*, 2014, the largest known Trona deposits in the world are in southwestern Wyoming in the Wilkins Peak Member of the Green River Formation. The layered trona deposits range in depth from (800 to 2,200) feet below the surface. This is known as “bedded Trona”. This resource was deposited (40 to 50) million years ago in a freshwater

lake called Lake Gosiute, which covered most of what is now the Green River Basin. The Green River Basin of southwestern Wyoming contains the largest Trona resource in the world at over 127 billion tons, of which more than 40 billion tons are reserves(economically) minable with current technology). At the current rate of production assuming a moderate growth in the rate of 1 to 2%.Wyoming’s Trona reserves should last well over 2,000 years. Sweetwater County, Wyoming is a major contributor of Trona to the world. The state is the state’s top international exporter. Wyoming also supplies about 90 percent of the nation’s soda ash. The lake is believed to have covered over 15,000 square miles figure (1.2).

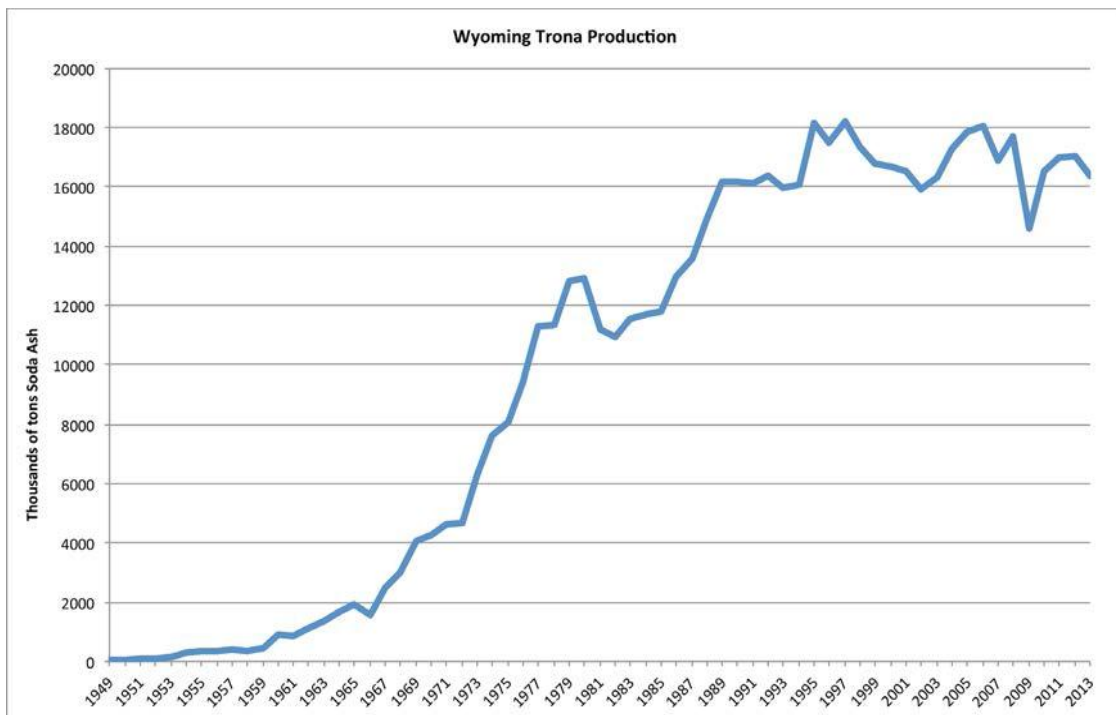


Figure 1.1 Wyoming’s natural soda ash production since the late 1940.

Source :- (Robert .W, *et al.*, 2014).

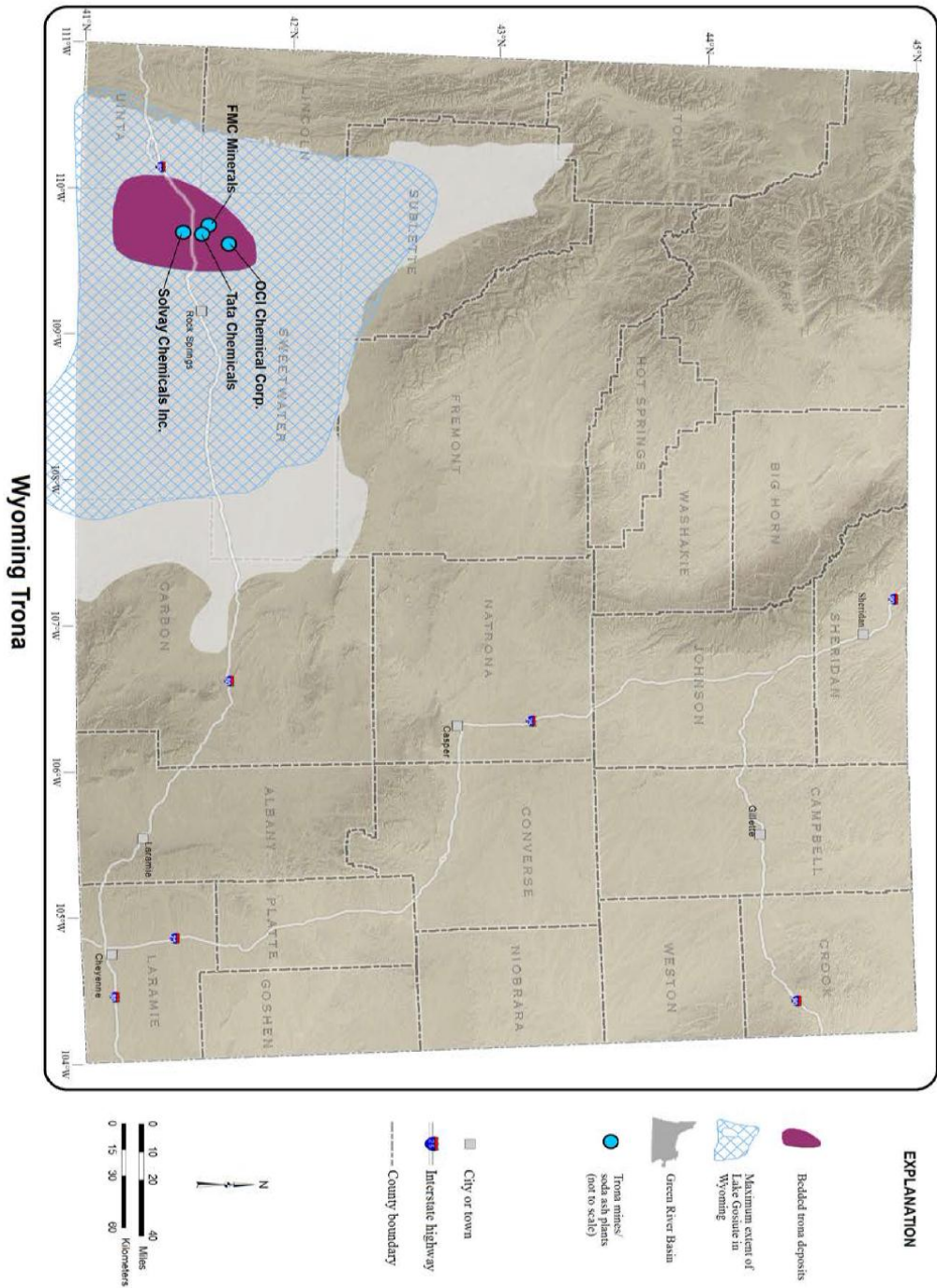


Figure 1.2 Map of Wyoming state design and layout by Phyllis Ran, 9/2014.

According to Robert W, *et al* .,(2014), Lake Gosiute fluctuated dramatically in size over a period of several million years, in response to alternating wet and dry climate variations. When it shrunk in size, the waters became supersaturated with elements such as Na, Ca, Mg and oth-

ers. These elements represent the building block molecules that, when combined, form mineral deposits such as trona. The massive beds of Trona and other minerals were then deposited by precipitation, and through evaporation, the shrinking volume of water could no longer keep those compounds in suspension. Inter bedded with the Trona beds there are successions of marly calcareous shales, oil shales, siltstones, and sand stones. In (2013), Wyoming mines produced more than 16 million tons of Trona and employed 2,328 people. .World production amounted to 14 million tons and came from Botswana, Kenya, Mexico, Turkey, Uganda, and a few other countries. More than 39 million tons of synthetic soda ash were also produced in (2013), primarily in China and India.

1.4.2 Trona in Nigeria

In Nigeria, Trona is widely found along chad basin areas of Borno, Yobe and Adamawa states. Trona exists as encrustation in dried-up lakes and it is called “Kangwa” among the Hausa speaking tribes.

It is used locally as an ingredient for animal appetizer, cooking soup and medicinal purposes. Trona mining which is mainly in Borno and Yobe states are still in small scale and the operation involves mainly the surface mining using shovels by local people (Ministry of Soil and Mineral Development, 2000).According to Zanna, *et al* .,(2018) Trona ores of commonly contains 2.4 % NaCl, 20 % Na₂CO₃, 26.5 % Na₂SO₄, and 30.8 % CaCO₃, 2.0 % CaSO₄, 1.4 % insoluble solids and 3.2 % water.

Trona occurs in saltpans and dry lakebeds, ascending ground water may have deposited it. This mineral is dark colored and occurs as aggregates in desert soils and it may be found with other secondary minerals. Trona deposits have also been reported in many of the interdunal oasis in the Northern part of Yobe State. Detailed description of the deposits is shown

in Table 1.1 especially those of Yobe State have been given by Nkeweurem 1994 (Zuma, 2004).

Table1.1 Local names and physical description of Trona ores samples from North East of Nigeria

S/No	S/Code	Name	Description
1	DTRBO1	Trona, Hausa-Kafikafi	Greasygrey, massive aggregates
2	DTRBO2	Trona,Hausa-Gurro Kanuri-Zarau	Grey massive aggregates
3	DTRBO3	Trona, Hausa-WadudumFarinKanwa; Kanuri-Sutair	Whitish grey aggregates, massive.
4	DTRBO4	Trona Hausa-Nuku	Wassive aggregates, brownish-Yellow, dull.
5	DTRBO5	Trona, Hausa-Gasaba, Kanuri-Arou	Mirror, grayish-yejlow crystal, luminescence non transparent, occurs in about 21m length at the location
6	DTRBO6	Trona, Hausa-Jam Kanwa, kanuri-klekieme	Grey uneven massive
7	DTRBO7	Trona, Hausa-Morso	Irregular masses, grayish white aggregates
8	DTRBO1	Trona,Hausa –Mangul	Brownish-grey with characteristic brownish – red dark
9	DTRBO2	Trona, Kanuri-Mandacheu	Massive grey to yellow aggregates
10	DTRBO3	Trona, Kanwa	Grayish-white aggregates
11	DTRBO4	Trona,kanwa	Dark-grey greasy massive
12	DTRBO5	Trona, potash	Light-grey, uneven aggregate
13	DTRBO1	Trona Hausa-kanwanlibiya	Massive grey aggregate

Source:-Zuma, *et al* .,2004).

1.4.3 Trona in Turkey

The Neogene Beypazari basin is one of the most economically important basins in Turkey. It contains lignite (figure 1.3), bituminous shale, and Trona deposits. This basin is mainly filled by fluvial, lacustrine, and volcano-sedimentary rocks. The Neogene sedimentary sequence in this basin is divided into eight formations (Helvacı and İnci, 1989). In the region between Beypazari and Nallihan, geological maps at a scale of 1:25,000 have been prepared (figure 1.3). Stratigraphic sections were measured at different locations to determine the distribution of rock units and the locations of facies changes and tectonic features of the basin, as well as for determining the geological setting of the Trona deposits.

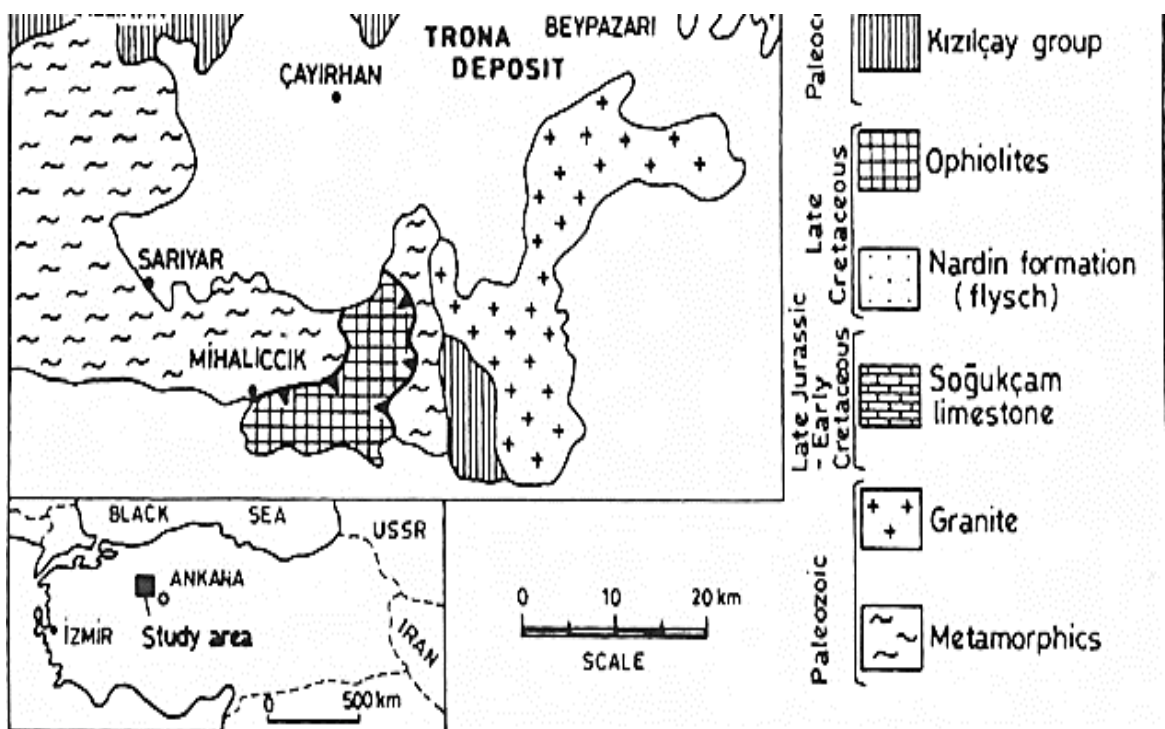


Figure 1.3 Locality and geological setting of the Beypazari basin and adjacent area

The Neogene Beypazari basin is limited on the North by the West Pontid mountain belts. This part of the Pontids consists of metamorphic, volcanic, and sedimentary rocks, which are Paleozoic to Tertiary in age (Ketin, 1966,

Saner, 1979). The Middle Sakarya massif consists mainly of metamorphic, acid-plutonic, and ultrabasic rocks, and occurs on the south edge of the Beypazari basin (Saner, 1979). Tertiary volcanic rocks are distributed in both the North Eastern part of the basin and between the Beypazari and Kizilcahamam areas (Figure 1.3). Pre-Neogene sedimentary rocks ranging from Paleocene to Eocene in age limit the Neogenebasinto the west (Helvaci, *et al .*, 1989, Esra,2021).

The Turkish natural soda (trona volcano-sedimentary rocks in the interior of central Anatolia). Turkey is approximately 100 km North West of Ankara. The Trona deposit is present at 130-140 m deep, in layers which are thicker and richer in the quality compared to the ores in Wyoming (USA). This is the second largest deposit in the world (total reserves about 300 million tons) with 84 % trona content (Ann Rev US, 2002).

1.4.4 Trona in Sudan

In Sudan, Trona which is known as, Atrune is found at the North and NorthWest of the country in many locations eg: at Abu hamad, 200 kilometers North West of Ariab area, River Nile state, Northern Darfour state at many old oasis, and old dry lakes such as El Nakhiela, Elslaim, Alga,a and Al Dalieb (Ahmed Adli A, 1998).

Trona in the differnet basins was found in many forms as hard beds at the middle and bottoms of the old lakes or disseminated through the sand in the upper part. It is also found as efflorescence crust on the surface of the soil, and can be found in brine water at some basins as in Daleba and Atrun basin. After drilling, sampling and chemical analysis, the evaluation of the deposit at different basins was made by Geological Research Authority of Sudan. According to its estimates the total reserve is about 38,460,000 tons. The average quantity of sodium carbonate in the crude stocks is about 60%; the net expected sodium carbonate is 23,076,000 tons. The deposit is

recoverable depending on the availability of rainfall and underground water, fig (4,5). (Idris, *et al* ., 1996, Isam I M Ahmed, 2017).

1.4.5 Locations and types of Trona in Sudan

Susan, *et al.*, 2012, Esra, *et al.*, 2021, describe the locations of Elatrune and Elnukheila as the only two locations known in the North – Western Sudan desert. Trona deposit in Sudan has been given different local names according to the quality and colors such as:-

1.4.5.1 Elatrune area

This area lies at the intersection of latitude ($18^{\circ}9'57''$) and longitude ($26^{\circ}37'03''$) at a distance of 45 Km from Elfashir and 92Km from Rahib wells.

1.4.5.2 Eljabel Trona

This area is located at $18^{\circ}09'23''$ N and $26^{\circ}37'14''$ E. This type was found at the foot of small hills made up of sandstone. It seems to be deposited by outlet spring from the hill side, because all other deposits of this type were found along the side of the small ridges. This type which is hard salt rock, is not preferred by the local consumers because of the difficulty of its dissolving, due to co-precipitated sand and silica.

1.4.5.3 Abuzaema Trona

This is located at $18^{\circ}9'56''$ N and $26^{\circ}3''$ E. Here the Trona fragments vary in size from one to five cm in diameter, and overlain 17 cm of wet loose sand containing big fragment of crystalline Trona with radiated needle shapes of sodium carbonate. The commercial Trona has been taken from this bed which is of high percentage of soda ash.

1.4.5.4 Kambodia Trona

Kambodia Trona is located at $18^{\circ}10'12''$ N and $26^{\circ}36'34''$ E. This deposit was found to be buried under more than 2.5m layer of loose sand due to the activity of mobile dunes.

1.4.5.5 Elakhder and Elahmer Trona

These two types are green and red in color. Elakhder type is located at $18^{\circ} 9' 51''$ N and $26^{\circ} 38' 39''$ E, and Elahmer type located at $18^{\circ} 11' 00''$ N and $18^{\circ} 10' 12''$ E. They are found at the west side of the main camp of Elatrune, they have a well crystalline whitish needle-shape salt (Susan, *et al.*, 2012, Esra, *et al.*, 2021).

1.4.5.6 Elsalam Trona

This type is mostly preferred by the consumers in Sudan. It is found on the surface of the whole basin with thickness of 25 cm. It is whitish in color, and formed of pure trona. It is located at $18^{\circ} 11' 32''$ N and $26^{\circ} 36' 44''$ E (Susan, *et al.*, 2012, Esra, *et al.*, 2021).

1.4.5.7 Elsilail Trona

This type of Trona is located in the main basin of Elatrune at $18^{\circ} 10' 15''$ N and $26^{\circ} 37' 31''$ E. It's found as nodules throughout the thin beds, with size ranging from 2 to 3 cm in the first 30 cm depth which is composed of loose sand medium to coarse grains followed by hard crystalline. Trona salt of whitish gray color is at the lower 10 cm below.

1.4.5.8 Ummahatay Trona

This type is located at $18^{\circ} 10' 05''$ N and $26^{\circ} 37' 38''$ E. The Trona deposit is found on the surface of the soil, at a depth of 30cm as whitish concentrated sandy Trona, overlain by a hard Trona salt which is 20 cm thick, lies on brownish aeolian sand.

1.4.5.9 Eldaleiba Trona

This deposit is located at about 6 km west of main producer of the light Trona. It is high demanded in local markets and suitable for export. Two bed Trona type is formed by drawing the brine water to the surface by

pumps and then the crystalline Zabad Trona can be collected after a period of several days.

1.4.5.10 Elnukheila area

These Trona deposits are 161 km North-West of Elatrun at $19^{\circ} - 15' - 46''$ N and $26^{\circ} - 10' - 27''$ E. Trona deposits in this area are discovered during the last 10 years in the North West of Elnukheila oasis near the old known deposit of Elгаа Elmasriya. For a long time it was exploited by the Egyptians who used Trona for the salt by camel. This deposit was found in depression hollowed to by Aeolian weathering of wind in sand and lake deposits. Trona deposit found within these sediments had been formed by the same mechanism of ground water evaporation as in Elatrun area.

1.4.5.11 Elгаа Elmasriya Trona

This deposit is characterized by the presence of sulphate, which is found only in Elatrune area.

1.4.5.12 Elгаа Elgadima Trona

This deposit is found in hallow depression between sand stone rock of Silurian age. Trona in this area is of high quality than that of Elгаа Elmasriya (Susan, *et al* ., 2012, Esra, *et al* ., 2021).

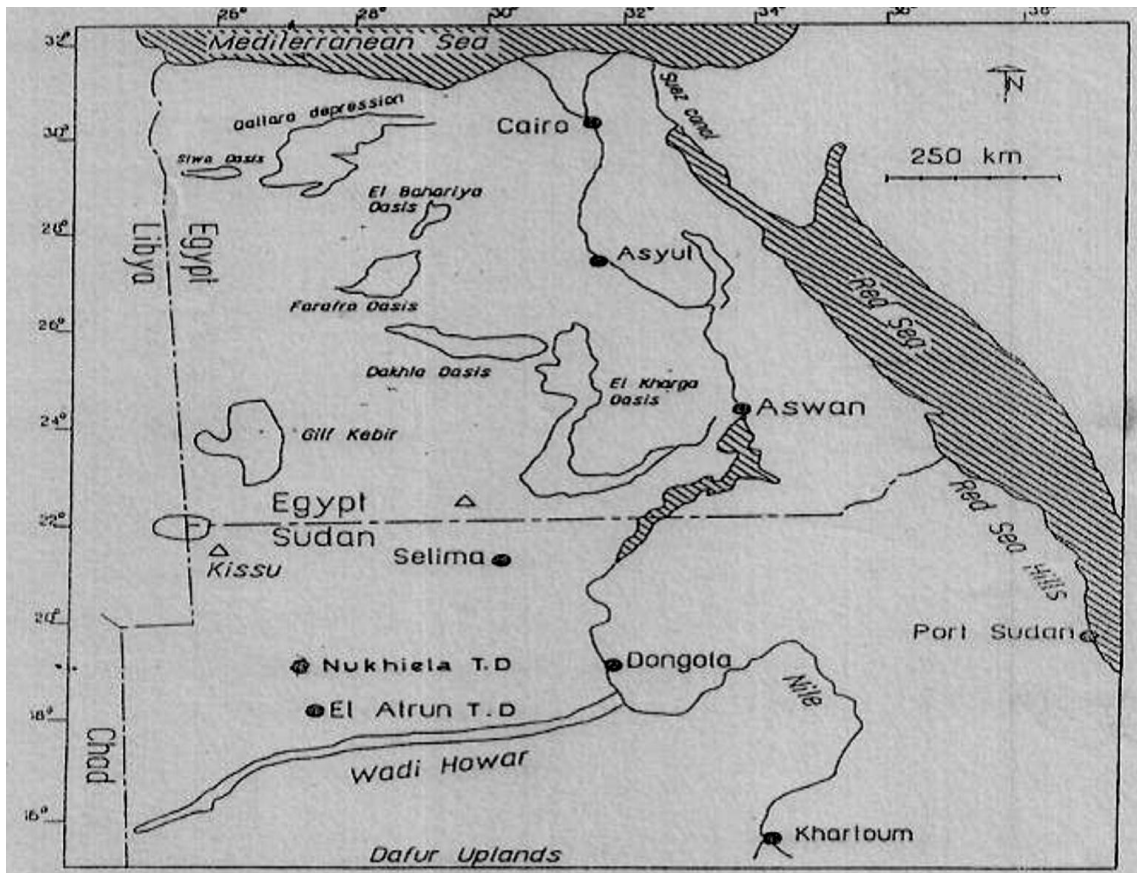


Figure 1.4 Locations of the Trona area

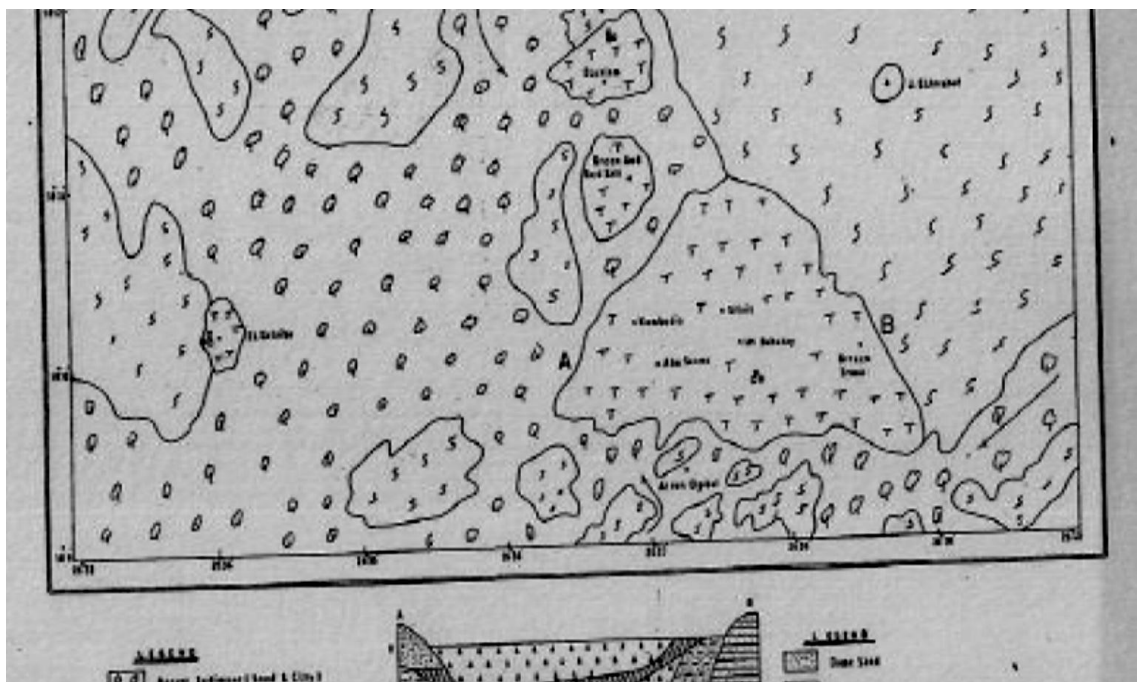


Figure 1.5 Geological map of Atrun area

1.5 Chemical composition of Trona ores

The main purpose in Trona analysis is the quantitative determination of its water soluble content. In most cases, Trona contains clays and some minerals. The kind, quantity and separation of clays and other carbonate compounds from aqueous phase require different analytical methods.

Eldoma, 2003 reported that Trona constituents were carbonate (35.74%), bicarbonate (16.27%), chloride (06.80%), sulphate (00.42%) silica (10.75%) and others (00.80%).

Ahmed, *et al* .,2005 analyzed Trona samples from different Trona mining areas showing significant variations of Na^+ , K^+ , Ca^{2+} , Mg^{2+} , CO_3^{2-} , Cl^- , SO_4^{2-} , HCO_3^- as well as acid insoluble materials in (Table1.2).

Table1.2: Chemical constituents of different Trona samples (Ahmed, 2005).

Sample area	Acid Insoluble %	Na %	K %	Ca %	Mg %	CO_3^{2-} %	HCO_3^- %	Cl^- %	SO_4^{2-} %	Total %
Eldeleibe	16.57	33.09	0.60	0.007	0.06	29.50	9.33	8.30	1.48	98.94
Elnukheila	16.50	30.91	1.17	0.450	1.05	2.20	0.98	29.0	29.0	99.63
Western Dongola	38,74	25.63	0.14	0.005	0.03	25.20	7.70	0.89	0.89	98.05
Elsalam	9.43	37.79	0.57	0.005	0.04	34.20	9.47	1.53	1.53	98.05
Local market	45.78	23.26	0.53	0.005	0.03	18.00	6.04	0.71	0.71	99.44

Susan, *et al* ., 2012, analyzed Trona samples collected from Dongola, Atbara and Portsudan market. The study reported almost similar pH values and HCO_3^- content, but different CO_3^{2-} and significantly high SiO_2 (Table1.3).

Table1.3: Color, pH value, CO_3^{2-} , HCO_3^- and SiO_2 content of Trona (Susan 2012)

Location	Color	pH	CO_3^{2-} %	HCO_3^- %	SiO_2 %
Dongola	White	9.73	19.05	6.25	34.480
Atbra	White	9.53	14.4	6.4	48.828
Portsudan	Grey	9.51	14.52	6.25	48.282

H.K.Zaana, 2018, Reported Nigeria trona ores composition as CaCO_3 (30.8%), Na_2SO_4 (26.5%), Na_2CO_3 (20%), NaCl (2.4%), CaSO_4 (2.0%), insoluble solids(1.4 %) and water (3.2%).

The following approximate analysis of the trona ore was furnished by the Intermountain Chemical Corp (Smith, 1942;H. B. Lindeman, 1954).

Table 1.4: Trona composition according to intermountain chemical crop

Constituent	%w/w
Na_2CO_3	45.30
NaHCO_3	35.90
CL^-	0.09
$\text{SO}_4^{=}$	0.03
Fe	0.05
SiO_2	1.10
water	15.40
Insoluble	3.50-15.00

Table1.5: shows the major constituents of Trona in USA, where the availability of Na_2CO_3 , NaHCO_3 and moisture are dominating.

Table 1.5 Natural Trona composition (D.Bonaventura, 2017).

Constituent	Na_2CO_3	NaHCO_3	Na_2SO_4	Insolubles	H_2O	Others
Percentage	46.53%	34.82%	0.568%	2.980%	14.92%	0.182%

According to Sibel Gezer; (2016), Beypazari Trona deposits collected from different layers showed high Na_2CO_3 and NaHCO_3 content in there composite samples (table 1.6). But one sample showed relatively low total Trona content.

Table1.6: Sodium carbonate and sodium hydrogen carbonate of Beypazari Trona samples

Constituent	U3	U4	U5	U6
Na_2CO_3	34.48	43.06	43.09	43.44
NaHCO_3	27.84	37.76	35.45	35.25
Total alkalinity% Na_2CO_3	52.04	66.88	65.46	65.69
Trona %	73.53	91.82	91.88	92.63

Table (1.7) shows the chemical composition of Beypazari Trona samples where Na_2CO_3 and NaHCO_3 contents were almost similar and the amount of the insoluble and ignition loss were relatively high.

Table1.7: Chemical composition representative Beypazari Trona samples (Sibel, 2016)

Constituent	%w/w
NaHCO ₃	33.00
Na ₂ CO ₃	38.59
Total alkalinity ,%Na ₂ CO ₃	59.40
Insoluble	15.30
NaCL	0.025
Na ₂ SO ₄	0.026
Ignition loss	25.27
Trona	84.70

1.6 Uses of Trona

According to Isam I M Ahmed, *et al* .,2017 ,Trona is a common source of soda ash which is a significant economic commodity because of its applications in manufacturing glass, chemicals, paper, detergents, and textiles. It is used as food additive and for purification of water. It is used to remove sulfur from both flue gases and lignite coals. Trona had been used for decades in many industries. Trona is used for air pollution control throughout the country. Trona is used throughout North America in animal feed.

In Westen Sudan Trona is given to animals especially sheeps and camels either in crushed form for licking or dissolved in water for drinking. According to Omer A.Gibla, 2001, animals consume Trona either to enhance digestibility or to suplemity some essential minerals which are lacking in their natural feed. According to supplant the general administration of customs research and information department, report

(2007), Sudan important Na_2CO_3 from different countries (China, India, Romania, Egypt and others in the period 2000-2006) as shown by Table 1.8.

Sudan was also reported to import different amounts of caustic soda NaOH for some local industries such as textiles, detergents, soap and edible oil refining table 1.9 (Isam, 2017).

Table 1.8: Amounts of sodium carbonate imported by Sudan from different countries:-

Year	2000	2001	2002	2003	2004	2005	2006
Na_2CO_3 (tons)	32	800	414	686	567	786	236

Source:- Isam(2017)

Table 1.9: Amounts of sodium hydroxide imported by Sudan from different countries

Year	2008	2009	2010	2011	2012
NaOH (tons)	170	60	180	112	88

Source:-Isam(2017)

1.6.1 Industrial use of Trona

In industry two commercial processes are used to remove the insoluble materials from Trona ores and produce soda ash. These sesqui carbonate process and the monohydrate process. The monohydrate process is the most widely employed in industry. In this process Trona is converted to soda ash in a multistep purification techniques known as calcination, dissolution, clarification, filtration, and crystallization(O. Ozdemir, *et al* .,2010).

Soda ash is an essential ingredient in industry, from chemicals to home products such as baking soda. The main use of soda ash is for making glass

because soda ash lowers the melting point of silica. Soda ash is also used in making soaps, detergents, water purifiers, flue gas desulfurization equipment, paper, and many other products (A. Drean, 2014).

1.6.1.1 Production of sodium carbonate (Na₂CO₃)

Sodium carbonate may be obtained as trihydrate “Na₂CO₃.3H₂O” and anhydrous salt “Na₂CO₃” or decahydrate Na₂CO₃.10H₂O, which is readily effloresces to form the monohydrate (Na₂CO₃.H₂O) which is also known as thermonatrite or crystal carbonate. Heptahydrate “Na₂CO₃.7H₂O” is not known in mineral form.

The anhydrous Na₂CO₃ or calcined soda, is formed by heating the hydrates or when sodium hydrogen carbonate such as in the final step of Solvay process.

The decahydrate may be crystallized from aqueous solutions in a temperature ranging from -2.1 to +32.0 °C. The heptahydrate can be formed in the narrow range 32.0 to 35.4 °C and above this temperature the monohydrate forms (T.W.Richards, *et al.*, 1914).

1.6.1.1.1 Leblanc process for sodium carbonate production

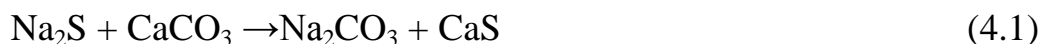
In the year 1792, the French chemist Nicolas Leblanc suggested a process for producing Na₂CO₃ from normal salt, sulfuric acid, limestone, and coal. In the first step, NaCl is treated with H₂SO₄ to produce sodium sulfate (salt cake) and hydrogen chloride:



The salt cake and crushed limestone were reduced by heating with coal in two steps (Christian Thieme, 2000). The first step is the carbothermic reaction where coal reduces sulfate to sulfide:



The second step is the reaction that produce Na_2CO_3 and CaS :



This mixture is called black ash. The soda ash is then extracted from the black ash with water. Evaporation of this extract yields solid sodium carbonate. This extraction process was termed to as lixivating.

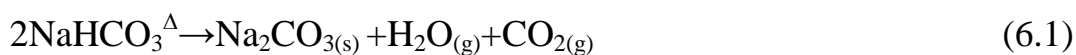
The hydrogen chloride acid produced by leblanc process is a major source of air pollution, and calcium sulfide as byproduct also represent a waste disposal issue. However, it remains the major method for sodium carbonate production until the late 1880s (Clow, *et al.* ,1952; Kiefer, 2002).

1.6.1.1.2 Solvay process

By the year 1861, the Belgian industrial chemist Ernest Solvay developed a new method by reacting NaCl , NH_3 , H_2O and CO_2 to produce NaHCO_3 and NH_4Cl (Christian, 2000).



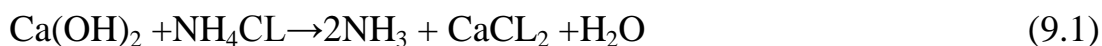
NaHCO_3 will be converted to Na_2CO_3 by heating.



Carbon dioxide (CO_2) in this process is obtained from thermal decomposition of calcium carbonate (CaCO_3).



Ammonia will be regenerated by treating NH_4Cl it with $\text{Ca}(\text{OH})_2$ which is obtained by dissolving CaO in water .



Solvay process recycles its ammonia and consumes only NaCl and CaCO₃. Calcium chloride is the only waste product. The process is substantially more economical than Leblanc process, which generates two waste products, CaSandHCL. Solvay process was quickly came to dominate sodium carbonate production worldwide. By the year 1900 about 90% of Na₂CO₃ was produced by Solvay process, and the last Leblanc process plants were closed in the early 1920s (Christian Thieme, 2000).

The second step of Solvay process, heating NaHCO₃, is used on a small scale by home cooks and in restaurants to make sodium carbonate for culinary purposes including pretzels and alkali noodles. The method is appealing to such users because NaHCO₃ is widely sold as baking soda, and the temperatures required are ranging from 121 °C to 149°C for converting baking soda to sodium carbonate (McGee, Harold, 2010).

1.6.1.1.3 Hou's process

This process was developed by the Chinese chemist Hou Debang (1930s). The earlier steam reforming byproduct CO₂ was pumped through a saturated solution of sodium chloride and ammonia to produce sodium bicarbonate.



The produced NaHCO₃ will be collected as a precipitate due to its low solubility and then heated to approximately 80 °C - 95 °C to yield pure Na₂CO₃ similar to the last step of Solvay process. More NaCl is added to

the remaining solutions of ammonium and sodium chloride, also more ammonia is pumped at 30-40 °C in this solution. The solution temperature is then lowered (below 10 °C). Solubility of ammonium chloride is higher than that of sodium chloride at 30 °C and lower at 10 °C. Due to this temperature –dependant solubility difference and the common –ion effect, ammonium chloride is precipitated from sodium chloride solution.

The Chinese name of Hou's process is coupled to the upper process and offers better economy by eliminating the production of calcium chloride, since ammonia no longer needs to be regenerated. The byproduct ammonium chloride can be sold as a fertilizer.

M. Aldoma, *et al* .,2013, described Na₂CO₃ production procedure as follows the solid raw material of Trona ore is crushed into fine particles, leached with warm water (at 30 -40 °C), and then filtered to remove silica and other water insoluble material in order to obtain a clear solution. To separate the undesirable soluble matter from the clear solution and obtain pure sodium carbonate, the solution was sent to a pilot plant which consists of a storage reservoir, an evaporation reservoir, a crystallization reservoir and a dry reservoir unit. In this pilot plant, sodium carbonate solution is concentrated in the evaporation reservoir by solar energy until the concentration reaches 30%, then the solution was sent to the crystallization reservoir. At the crystallization stage, the yield of sodium carbonate crystals increases. With a proper drainage of sodium carbonate crystals followed by washing with distilled water, pure crystals of sodium carbonate can be obtained. Thereafter, the crystals will be dried to 150-160 °C for 48 hours to remove water of crystallization and to convert the traces of sodium bicarbonate into sodium carbonate.

1.6.1.2 Production of calcium hydroxide (Ca(OH)₂)

Esra, *et al.*, 2021, For Ca(OH)₂ production pure limestone (CaCO₃) is to be crushed to reduce its particle size in order to be fed to kiln step. In the kiln, the crushed CaCO₃ is heated to about 900⁰C where it decomposes into CaO and CO₂. $\text{CaCO}_{3(s)} \xrightarrow{\Delta} \text{CaO}_{(s)} + \text{CO}_{2(g)}$ (14.1)

CaO is then added to water at 30-50 ⁰C, to obtain calcium hydroxide (slaked lime) in an exothermic reaction.



The main disadvantage of calcium hydroxide, is its partial solubility in water, to give (Ca⁺²) and (OH⁻).



1.6.1.3 Production of sodium hydroxide from sodium carbonate and calcium hydroxide

Sodium carbonate that produced from the purification process is then reacted with calcium hydroxide. The result of the reaction is a solid precipitate of calcium carbonate and an aqueous solution of sodium hydroxide which is more alkaline than sodium carbonate. The solution is separated from solid the precipitate and then concentrated using solar energy evaporation (Esra; 2021).



1.6.1.4 Sodium hydrogen carbonate (NaHCO₃)

Esra, *et al.*, 2021, Sodium hydrogen carbonate is widely used in purification processes of gaseous products from combustion of solid fuels. In the seventies of the last century, many studies on sodium sorbents were conducted. They included the use of natural nahcolite (NaHCO₃) in the dry

flue gas desulphurization process. Nahcolite changes its microstructure as a result of decomposition at elevated temperatures, forming an inhomogeneous structure, which is very reactive in contact with acid gases. Similar properties are possessed by synthetic sodium bicarbonate. As a result of thermal activation, the decomposition of sodium bicarbonate to Na_2CO_3 occurs. It influence on decreasing of molar volume of decomposed (NaHCO_3) during releasing of gaseous products of decomposition. Carbon dioxide and water vapor, result in breaking apart of compact structure and formation of pores with high surface area. The temperature of decomposition varies in a range of 60 to 400°C (Chemik, 2012).

The produced in such process is characterized by a more developed surface area in comparison with crystalline NaHCO_3 and this leads to an increase in its reactivity.

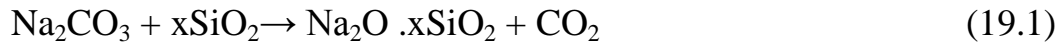


The reactivity of NaHCO_3 depends mainly on its grain size and structure. Fine grains react more efficiently, than larger ones. The examined material should be subjected to grinding before thermal activation in order to develop its surface area. The surface area and pore size distribution in the modified NaHCO_3 can be determined by using modern methods to obtain the surface topography and structure (Heda ,*et al* ., 1999; keener, *et al* .,2000).

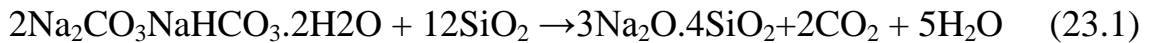
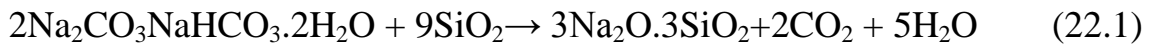
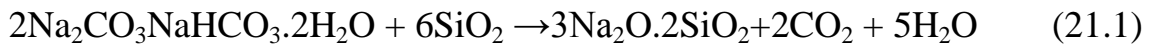
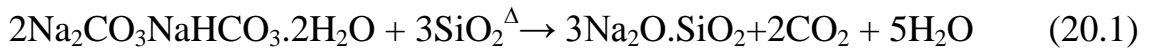
1.6.1.5 Sodium silicate Production

Sodium silicate is a colorless material. It is a mixture of sodium oxides and silicon or silica, with a varying ratios of Na_2O and SiO_2 , ranging from $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ to $2\text{Na}_2\text{O} \cdot \text{SiO}_2$ by properly proportion at the reactants. Sodium silicates varying in ratio from $\text{Na}_2\text{O} \cdot 1:6\text{SiO}_2$ to $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ are known as colloidal silicates. These are sold as 20% to 50% aqueous solutions called

water glass. Sodium silicate cullets are produced by the direct fusion of precisely measured portions of pure silica sand (SiO_2) and soda ash (Na_2CO_3) in oil and gas or electrically fired furnaces at temperatures above $1100\text{ }^\circ\text{C}$.



Trona and quartz powders were used to produce sodium silicate cullets. The batches with different $\text{SiO}_2:\text{Na}_2\text{O}$ molar ratios can be prepared and mixed according to the equations below:



Powder mixtures will be placed in a porcelain crucible and separately fired at $1150\text{ }^\circ\text{C}$ and $1200\text{ }^\circ\text{C}$ for 2 hours. These fused melts should be drawn from the kiln and poured into water to solidify. The resulting products (cullets) were characterized by using scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis (Özkan, *et al.*, 2016, Esra, 2021).

1.7 Some specification naturally occurring Trona (Sudan)

Isam, 2017, reported some general information about Trona ores of Sudan. His reported information can be a base for further specification for “Atrune” deposits that distributed in so many areas of West mountains parts of the country.

Table1.10: physical properties of Trona in Sudan

Property	Observation
Product name	Trona
Alternate product name	Sodium sesqui carbonate (impure naturally occurring form)
Chemical formula	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
General use	pH adjustment in water or waste water, flue gas desulfurization, coal treatment
Odor	Odorless
Appearance and color	Light Brown solid, crystal or powder
Flash Point	Inflammable
Melting Point	$> 70^\circ \text{C}$
1% Solution Ph	About 9.8
Solubility in Water	16.0 -50 F
Specific Gravity	2.112 g/cm

1.8 Objectives of the study:

The objectives of this study are:-

1. To determine the availability of the main acid radicals CO_3^{-2} , HCO_3^- , Cl^- , SO_4^{-2} and P in Sudan Trona samples.
2. To measure the pH values for different Trona samples.
3. To determine the range of moisture content in the different Trona samples.
4. To compare the findings of the present study with some results that reported by researchers in the countries where Trona ores were studied for economic and scientific purposes.

Chapter Two

Materials and methods

Chapter Two

2. Materials and methods

2.1 Collection of samples

Eight samples of Trona ore were obtained from different markets. Three samples from Khartoum state and five samples from Northern Darfor state (Elfasher).

2.2 Chemicals

- Hydrochloric acid (HCl) (assay 36.5%-38%, density 1.3, M.wt 36.46 Merck CAS number 7647-01-0).
- Barium chloride (BaCl₂) (assay 99.999%, density 3.856g/ml, M.wt 208.23, Merck CAS number 10361-37-2).
- Silver nitrate (AgNO₃) (Assay ≥99.0%, density 5.8, M.wt 169.87, Merck CAS number 7761-88-8).
- Potassium chromate (KCr(SO₄)₂.12H₂O) (assay ≥98%, density 1.83 g/ml, M. wt 499.40, Merck CAS number 7788-99-0).
- Sodium hydrogen carbonate (NaHCO₃) (density 2.160 g/ml, M.wt 84.01, Merck CAS number 144-55-8).
- Ammonium molybdate ((NH₄)₆Mo₇O₂₄.4H₂O)(assay 81-83%, density 2.498g/ml, M.wt 1235.86, Merck CAS number 12054-85-2).
- Antimony potassium artrate (K₂(SbO)₂C₈H₄O₁₀.3H₂O) (assay 99-103%, density 2.600g/ml, M.wt 667.9, Merck CAS number 28300-74-5).
- Ascorbic acid (C₆H₈O₆) (assay 99-100.5%, density 1.65 g/ml, M.wt 176.12, Merck CAS number 50-81-7).
- Sulphuric acid (H₂SO₄)(assay ≥98%, density 1.8g/ml, M.wt 90.08, Merck CAS number 7664-93-9).

2.3 Instrumentation

- pH meter (jenway,prime,3510 pH meter).
- Oven 105 °C (Carbolite, parsons lane, hope valley, S 33 6RB,England ,Serial NO 21-100122, CWF 12/13, max temp 1200°C).
- Sensitive analytical balancen (AS60-220.X2, 60/0.01mg,220mg/0.1mg-internal calibration).
- Furnace(SAF Therm sant furnace 30-3000 °C ,1400 °C lab and small industrial pouplar Box furnace, working Temp:1300 °C, heater: Quality SIC Rod).
- Spectrophotometer UV-Vis-Optical spectrometer (part number HF7888 UV-Vis NIR, form factors:dimensions;700x150x250mm,weight 28kg, total range350-1080/0nm, fixed3nm-8nm resolution*0.3pm-0.8pm, resolution0.02/cm).

2.4 Determination of sodium carbonate and sodium hydrogen carbonate

Five grams of each Trona sample was finely grinded and dissolved in hot distilled water to extract “ Na_2CO_3 ” and “ NaHCO_3 ” from SiO_2 . The solution was filtered and the remaining SiO_2 on the filter paper was thoroughly washed with hot distilled water until free from carbonates. The filtrate was quantitatively transferred in a 250 mL volumetric flask and completed to the mark with distilled water. 25 mL each sample solution was titrated against 0.01M HCl to ph.ph end point, and methyl orange indicator drops were then added and flask content was titrated against the same 0.01M HCl till the end point.

2.5 Determination of chloride Cl^-

One gram of each Trona sample was dissolved in 100 mL distilled water and heated to boiling point. The filtrate was then titrated against saturated solution silver nitrate by potassium chromate to end point.

2.6 Determination of sulphate as sodium sulphate

One gram of each Trona sample was accurately weighed. 5 mL of concentrated HCL was added and followed by 50 mL distilled water. The mixture was heated and filtered in 250 mL volumetric flask and completed to the mark by distilled water. 50mls of the prepared solution was transfer to 500 mL beaker, 200 mLs of barium chloride for one hour and the precipitated was filtered paper and ignited at (800-900°C) in crucible. The crucible was then cooled and weighed. Ignition, cooling weighing steps were repeated until constant weight was obtained

2.7 Determination of phosphorus

A stock solution of phosphorous was prepared by dissolving (0.4393 grams) of KH_2PO_4 in distilled water and completed to one liter to obtain (1000 ppm) concentration. Then a series of standards was prepared ranging from (0.01 to 0.3

ppm) from the stock solution. 2.5 grams of each Trona sample was weighed into a 150 mL Erlenmeyer flask and dissolved in distilled water.

50 mLs of each sample solution were digested at 121 °C for (40 minute), after addition of 1 mL (11N H_2SO_4) and 5 mL of (NaHSO_3) solution. Each digested sample was filtered and diluted to 50 mL. To 50 mL of each sample and/or standard 1 mL (11 N H_2SO_4) and 4 mL of ammonium

molybdate-antimony potassium tartrate were added. After well mixing 2 mL of ascorbic acid solution were added and well mixed also.

After 5 minutes the absorbance of each solution was measured by UV-Vis spectrophotometer at wave length (650nm). Phosphorous concentrations were determined for the different samples from the standard curve of the series.

2.8 Determination of silica (SiO₂)

One gram of each trona sample was weighed in a Petri dish and dissolved in 5ml of saturated HCl and 50 mL of distilled water on a water bath at 100 °C for 15 minutes with continuous stirring. The was then filtered in 250 mL volumetric flask through 41 ashless filter paper. The insoluble residue was washed by distilled water dried and transferred to then put in a weighed platinum crucible and burn in a flame. The crucible was then inter to furnace at 1000°C to four thirty and finally weighed. The percentage of “SiO₂” was then calculated.

2.9 Determination of moisture

Two gram of each Trona sample was weighed and dried in oven at 105 °C to two hour.

2.10 Determination of pH

Five grams of each Trona sample was accurately weighed and will dissolved in 25 mL distilled water. The pH value was for each solution was measured by pH- meter.

Chapter Three

Results and Discussion

Chapter Three

3. Results and discussion

3.1 pH values of Trona ore samples

As show by table the aqueous solutions of all samples showed alkaline pH values ranging from 8.87 to 9.70 with average value as (9.42). Susan (2012) reported pH values ranging from 9.51 to 9.73.

Table 3.1: pH values of Trona ore samples

Sample No	pH
1	9.70
2	9.61
3	9.64
4	9.35
5	9.38
6	9.47
7	8.87
8	9.34

3.2 Sodium carbonate and sodium hydrogen carbonate content of Trona ore samples

Table(3.2) shows Na_2CO_3 and NaHCO_3 content of trona ore samples

Samples (NO 1 and 2) showed the highest Na_2CO_3 content where the lowest content was shown by samples (NO 3 and 7). Samples (NO 5 and 8) showed similar Na_2CO_3 content (25.75 and 25.35). Smith (1942), Eldoma (2003), Sibel (2016) and D. Bonaventura (2017) reported high Na_2CO_3 content in trona ores as (45.30%, 35.74%, 38.59% and 46.53%) respectively. Ahmed (2005) reported low Na_2CO_3 content in his study as (2.20%).

Samples (NO 4, 5, 6 and 8) showed high values of NaHCO_3 content as (50.66%, 43.35%, 29.21% and 43.01%) respectively. The lowest NaHCO_3 values were shown by samples (NO 2, 3 and 7). Reported highest by Smith (1942), Sibel (2016), D. Bonaventura (2017) reported high NaHCO_3 content in Trona ores as (35.90%, 33.00% and 34.82%) respectively. low NaHCO_3 content was reported by Ahmed (2005) as (0.98%) and Susan (2012) as (6.40%).

Table 3.2: Sodium carbonate and sodium hydrogen carbonate content (%w/w)

Sample No	Na ₂ CO ₃ %	NaHCO ₃ %
1	47.47%	22.57%
2	37.03%	10.06%
3	14.29%	3.35%
4	20.99%	50.66%
5	25.75%	43.35%
6	18.95%	29.21%
7	10.95%	6.31%
8	25.35%	43.01%

3.3 Moisture and silica content of Trona ore samples

As show by table(3.3),Samples (NO 4, 5 and 8) showed relatively high moisture content as (20.72%, 20.58% and 19.99%) respectively. Lowest moisture content was shown by samples (NO 1, 3 and 7) as (5.23%, 5.00% and 5.16%). The remaining two samples showed different values as 14.06% and 17.65%.

It may clearly observe that SiO₂ content was higher in the samples that show low moisture content.

H.K.Zanna (2018) reported moistures content as 3.2% and Smith (1942%),H. B. Lindeman (1954) as 15.40%.Smith (1942), H. B. Lindeman (1954) reported SiO₂ content as 1.10%, Edoma (2003) 10.75% and Susan

2012 34.480%, 48.282 and 48.828%. Sample (No 3) showed very high SiO₂ content. This sample may be highly content contaminated with sand. It showed very low amounts of Na₂CO₃ (14.29%) and NaHCO₃ (3.35%) as shown in (table 3.2). Samples (No 2, 6 and 7) may be classified as low quality Trona samples depending on their high SiO₂ content. Sample (NO 4) showed significantly low SiO₂ content (1.29%).

Table3.3: Moisture and silica content (%w/w)

Sample No	Moisture	SiO ₂ %
1	5.23%	8.97%
2	17.65%	30.44%
3	5.00%	68.31%
4	20.72%	1.29%
5	20.58%	6.76%
6	14.06%	35.82%
7	5.16%	15.55%
8	19.99%	6.62%

3.4 Sodium chloride, sodium sulphate and phosphorous content in Trona samples

As shown by table (3.4), the highest (NaCL) content was shown by sample (No 7) as (49.62%), followed by (8.02%) in sample (No 1). The lowest (NaCL) content was show by sample (No 6).

Ahmed (2005) reported high NaCL content (29.0%). The NaCL content of Trona ores was reported by Smith (1942) and H.B Lindeman (1952) as (0.09%).

Na₂SO₄ showed very low availability in all samples. This strongly agree with the findings that reported by Eldoma (2003) 00.42%, Ahmed (2005) 1.48%, 0.89%, 1.53% and 0.71%,Sible (2016) 0.026%, D.Bonaventrura (2017) 0.568%, H.B.Zaana (2018) 2.0%.

All the samples showed significantly low phosphorous availability.

Table 3.4 Sodium chloride, sodium sulphate and phosphorous content in Trona samples (%w/w)

Sample No	NaCL%	Na ₂ SO ₄ %	P%
1	8.02%	1.25%	0.0020%
2	4.71%	N.D	0.0013%
3	4.67%	2.72%	0.0012%
4	5.02%	0.99%	0.0002%
5	2.20%	0.60%	0.0024%
6	1.11%	0.59%	0.0009%
7	49.62%	1.72%	0.0024%
8	2.31%	0.53%	0.0011%

Conclusion

- The objectives of the present study are to investigate the availability of the main acid radicals CO_3^{-2} , HCO_3^- , Cl^- , SO_4^{-2} and P in Sudan Trona samples. To measure the pH values for different Trona samples. To determine the range of moisture content in the different Trona samples. To compare the findings of the present study with some results that reported by researchers in the countries where Trona ores were studied for economic and scientific purposes
- Three samples showed moisture content within a range of 5%. Other three samples showed relatively high moisture content within a range of 20%. Two samples showed moisture content as 14.06% and 17.65%.
- The pH values were found to be typically basic, ranging from 8.87% to 9.70%, which agree with Susan (2012) 9.73%, 9.53% and 9.51%. These findings may enhance suggest that.
- Trona deposits are mainly consist of Na_2CO_3 and NaHCO_3 .
- Na_2CO_3 content was ranging from (10.95% to 47.47%) and NaHCO_3 content ranges from (50.66% to 3.35%).
- Significantly high NaCL content was shown by only one sample as (49.62%).
- SiO_2 content was ranged from 1.29% to 68.31%.
- All the analyzed samples showed low sulfate (Na_2SO_4) concentrations (N.D to 2.72%).
- Phosphorous (P) content was significantly low in all samples, ranging from (0.0002% to 0.0024%).

Recommendations

- More scientific research and economic assessment may be needed to evaluate the promising future of using Sudanese Trona deposits as source of soda ash production.
- Further physiochemical characterization may be required to distinguish the areas that are rich with Na_2CO_3 and NaHCO_3 from the areas where the ores are dominated by Na_2SO_4 or NaCl , as shown by many studies.
- Further wide survey may be required to determine the total amounts of Trona ore that can be mined to satisfy the local needs of the industrial sector
- More specifications and quality content characterization may be required to evaluate the possibility of exporting Trona ores as raw material or in form of its manufactured products such as (Na_2CO_3 , NaOH or $\text{Ca}(\text{OH})_2$).

References

Ahmed, Adli A., (1998), Sudan Industrial Minerals and Rocks, Center for Strategic Studies, Khartoum, Sudan.

Ameh, A., Isa, M., Ahmed, A. S. and Adamu, S. B.,(2009). Studies on the use of Trona in improving the test extract from Hibiscus sabderiffa Calyx. *Nigerian Journal of Pharmaceutical Sciences*,**8**. 7-12.

Alexander P. Hammond, Alan R. Carroll, Ethan C. Parrish, M. Elliot Smith and Tim K. Lowenstein The Aspen paleoriver: Linking Eocene magmatism to the world's largest Na-carbonate evaporite (Wyoming, USA) 2019 Geological Society of America. For permission to copy, contact editing@geosociety.org.

A. Drean, Director and State Geologist 2014.

Bolen, W.P., 2018, Soda ash, in Mineral Commodity Summaries 2018: Reston, Virginia, U.S. Geological Survey, p. 152–153.

Cahit Helvacı Dokuz Eylül University Bornova-Yzmir, Turkey The Beypazari trona deposit, Ankara Province 1998, Turkey. *Wyoming State Geological Survey Public Information Circular 40*.

Christain Thieme(2000) "Sodium Carbonate ". Ullmann's encyclopedia of industrial chemistry. Weinheim:Wiley-VCH. doi:10.1002/14356007.a24-299. ISBN 978-3527306732.

Clow, Archibald and Clow, Nan L.(1952).Chemical Revolution, (Ayer Co Pub, June 1952), PP.65-90.

C.Michael Hogen(2008) Makgadikagdi, The Magalithic portal,ed. A. Burnham.

Deer, W. A., Howk, R. A., and Sussman, J. (1992). An Introduction to the rock forming minerals. *2nd edition*, Harlow: longman ISBN 0582300940.

Eldoma, M.(2003). Production of Soda Ash from Sudanese Trona.MSC University of Gezira.

Eckardt, F.D.Drake.,N.,Goudie,A.S., White, K.,Villes, H(2001). The role of playas in pedogenic crust formation in the Central Namib Desert: a theoretical model. *Earth surface process and Landforms*,**26**(11),1177-1193.

Essa 2017 Synthesis and Characterization of Amorphous Silica from White Sand and Natural 16-17.

Esra 2021 Investigating Minerals Content of Trona Ore (Sudan). M.SC.honers chemistry Sudan University of Science and Technology.

Fathia (2017) Synthesis and Characterization of Amorphous Silica from White Sand and Natural Trona,M.SC.honers chemistry SUST Sudan University of Science and Technology.

Fleicher, M.(1987). Glossary of mineral species. *Mineralogical Record Inc*,**5**, 80-96.

Frint, W.(1971). Processing of Wyoming Trona. Issue contributions to Geology, 10-43.

Helvaci, C.,1998. The beypazari trona deposit, Ankara, province, Turkey.in:Dyni, J.R.,Jones, R.w.(Eds.), proceeding of the first international soda-ash conference., volume 11,v.40:Laramie,WY,public information Circular-Geoligical survey of Wyoming,PP.67-103.

H. K. Zanna, H. J. Gunda, F. W. Tikau and S. M. Gero (2018) Assessment of Heavy Metals in Trona from Yobe State, Nigeria **6**(1),10-15.

Isam I.M. Ahmed 2017, Production of Saustic Soda From Natural Trona M.Sc. in Chemistry. AL-Neelain University.

J.M. Nielsen, J. Afric. Earth Sci. **29** (2), 423 (1999). doi:[10.1016/S0899-5362\(99\)00107-4](https://doi.org/10.1016/S0899-5362(99)00107-4).

Kiefer, David M.(January 2002). ‘‘It was all about alkaline’’ Today’s Chemist at work. **11**(1):45-6.

Markl, G., and Baumgartner, L.(2002) pH changes in peralkaline late-magmatic fluids. Contributions to Mineralogy and Petrology, **144**,331-346.

Manega, P. C Bieda, S 1987.Modern sediment of Lake Natron, Tanzania. *Sciences Geologiques. Bulletin* **40**,83-95.

Makanjuola, A. A. and Beetlestone, J. G.(1975). Some chemical and mineralogical notes on 'kaun'. Journal of Mineral Geology ,**10**. 1-2.

Maha, M.H, 2006, Utilized of Trona for Neutralization in chrome M.SC. Thesis, University of Gezira.

McGee, Harold(2010).’’For old-Fashioned Flavor, Bake the Baking soda’’ The New York Times. Retrieved 25 April 2019.

M. Iwunze, Nig. J. Sci. Tech. **4**, 64 (1988).

Omajali, B. and Momoh, S., 2010. Effects of kanwa on rat gastrointestinal phosphatases. *International Journal of pharmaceutical Sciences and nanotechnology* **3**, 1147-1152.

Omer, A. Gibla.(2001). Elemental analysis of salt licks. M.SC.honers chemistry Sudan University of Science and Technology.

Özkan(2015)Production of Sodium Silicate Cullets by Using Trona 5th International Science Congress and Exhibition APMAS2015, Lykia, Oludeniz.

Palache.S.L.Rose and Sutir 1971, Nriagu and Moore1984, Fleicher1987.

Robert, S. G. and Geert-Jan, W (2007). Mixed Solvent Reactive

Recrystallation of Trona (Sodium sesqui-carbonate) into Soda (Sodium carbonate anhydrate). *Hydrometallurgy* ,**88** . 75- 91.

Smith, M.E., Carroll, A.R., and Mueller, E.R., 2008a, Elevated weathering rates in the Rocky Mountains during the Early Eocene Climatic Optimum: *Nature Geoscience*, v. 1, p. 370–374, <https://doi.org/10.1038/ngeo205>.

Smith, H. I., 1942, Trona in Wyoming:Am. Inst Min. Met. Eng. Tech. Pub. 1489.

Susan N.H.Mustafa (2012), Determination of the Major Chemical Constituents of three types of Trona.M.SC.honers chemistry .Sudan University of Science and Technology.

Sibel Gezer 2016.Assessment of soda ash calcination treatment of Turkish trona ore E3S Web of Conferences **8**, 0101

Thomas A. Drean(2014), Robert W. Gregory, Minerals Geologist Wyoming State Geological Survey.

The Maiduguri Soda-ash production Company Limited, unpublished document, Nigeria 2018.

Wyoming Mining Association 2017, at <http://www.wyomingmining.org/>.

U.S. Geological Survey, At [http:// minerals.usgs.gov/minerals/pubs/commodity /soda_ ash/index. Html # mcs.](http://minerals.usgs.gov/minerals/pubs/commodity/soda_ash/index.html)

Zhang, Youxun, 1985. Geology of the Wucheng trona deposit in Henan, China in: Schreiber, B.C., Warner, H.L. (Eds.) Sixth international symposium on salt, 1, PP. 67-73.

Zuma Journ 2004, Trace element in trona deposits of North East of Nigeria, *of pure and applied sciences* **6**(1).