



Sudan University of Science and Technology



College of Graduate Studies

Investigating Minerals Content of Trona Ore (Sudan)

استقصاء المحتوى المعدني لخام العطرون (السودان)

A Thesis submitted in Partial Fulfillment of the Requirements of the Degree of Master in Chemistry

By

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استهلال

قال تعالى:



صدق الله العظيم

[الأنبياء:٨٣]

Dedication

TO my lovely parents.

To my Brothers and Sisters.

To all members of my extended family.

Acknowledgement

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

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

My thanks and acknowledgement will be extended to my brother (**Eihab**)for his financial support ,continuous help and encouragement.

My thanks to the members of chemistry department of "SUST".Greater thanks to my colleagues and friends for their continuous support and help.

Abstract

Trona is a natural salt which is traditionally used in Sudanese homes as food additive and for many other purposes. The aim of this study was to investigate the minerals content of Tronaores of Sudan. Trona ore samples were obtained from different markets .Two sample were purchased from Khartoum markets and three samples were obtained from Northern DarfourState (Elfasher).

Macro, trace and toxic mineral contents were determined by inductively coupled plasma spectroscopy. The five samples showed higher sulfur content ranging from (390 to13000 μ g/L),potassium showed lower concentrations in all samples (9.5 -170 μ g/L) as macro mineral,followed by Na (530 -1200 μ g/L), Fe(69 - 1300 μ g/L), Al (34 - 29000 μ g/L), Mg (<0.59 - 1100 μ g/L), P(48 - 170 μ g/L), Ca (120 -520 μ g/L) and Si (24 -560 μ g/L). Boron was the most available trace mineral in samples (1,2,3and 4) ranging from (4.4 - 110 μ g/L) and not detected in sample (No 5).The second available trace mineral was Mn (5.1 - 70 μ g/L), followed by Cu (8.8 -17 μ g/L), Cr (2.5 -16 μ g/L), Zn(3.1 -13 μ g/L) and Ti(1.2 - 10 μ g/L). Pt ,V ,Ni and Co were detected in some samples .Sample (No5) showed mineral contents was clearly different from the other four samples. The main available macro minerals in this sample were S (390 μ g/L), Na (530 μ g/L),P (65 μ g/L) and K(12 μ g/L).

All toxic minerals showed low concentrations in the five samples or not detected. Sample (No.3) showed Sr (20 μ g/L), Ba(7 μ g/L) and Cd (5.3 μ g/L).Sample (No.4) showed trace levels of As (20 μ g/L),Sr (7.3 μ g/L), Cd(4.3 μ g/L),Ba(2.2 μ g/L),Hg (1.2 μ g/L) and Be (<0.12 μ g/L).Sample (No5) was free from trace and toxic minerals . Pb and Sb are not detected in the five samples .The low toxicity content may indicate that, Trona as a natural product is highly safe for human consumption.

المستخلص

العطرون ملح طبيعي يستخدم تقليديا في المنزل السوداني كمضاف غذائي ولعدة أغراض أخرى. الغرض من هذه الدراسة هو استقصاء المحتوى المعدني لخامات العطرون السوداني. تم الحصول على عينات العطرون من أسواق مختلفة تم شراء عينتين من أسواق الخرطوم وثلاثة عينات من ولاية شمال دارفور (الفاشر).

تم تحديد محتوى المعادن المكبرة،الاثرية والسامة باستخدام جهاز بلازما الحث المزدوج .أظهرت العينات الخمسة محتوى عاليا من الكبريت بتدرج منμg/L)،البوتاسيوم أظهر تراكيز منخفضة في كل العينات μg/L)كمعدن مكبر. يليه الصوديوم

(530 μg/L)، الحديد (530 μg/L)، الالمونيوم (μg/L) (69 _1300 μg/L)، المغنيسيوم (<0.59 _1100 μg/L)، الفسفور (<0.59 _1100 μg/L)، الكالسيوم

(4) للعنات (2,2 و 20) والسيليكون (2,4 μ 560 و 2,50) البورون كان المعدن الأثري الأكثر وفرة في العينات (2,3 و 4) يتدرج من (2,10 μ 2,10 μ 2,10

*محتوى السمية المنخفض في العينات يمكن أن يكون مؤشرا الى أن العطرون كمنتج طبيعي يعتبر صالحا للاستخدام البشري بدرجة عالية من السلامة.

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Chapter one

Introduction

Introduction

1.Trona

Trona is a naturally occurring form of sodium carbonate minerals. It may be named as « sesqui carbonate», «urao» or «trona ».The general formula for the compound is [NaCO₃.NaHCO₃.2H₂O](Susan ;2012).Trona gets its name from a discarded Arabic word for native salt, "Atrone", which is derived from the word "atron" a double salt of sodium carbonate and sodium bicarbonate. Trona is soluble in water. Crystals of this mineral are transparent white. But due to impurities the mineral appears gray, brown, pink and even black in nature, It's density is 2.1g/cm³.The main sources of salt manufacture in the world are sea water salt lakes, and rock salt (Deer et al ;1990, Susan ;2012 ,Zannaetal 2018)

Sodium sesqui carbonate is a solid material that is found in nature in a form of dihydrate salts of sodium carbonate and bicarbonate having chemical formulaNa₂CO₃.NaHCO₃.2H₂O. It can be found in many parts of the world like Kenya, Sudan, Turkish, Nigeria, Mexico and United States.(Garrett, 1992;Eldoma etal ; 2013).

It is tri sodium hydrogen carbonate dihydrate, Na₃ (CO₃)(HCO₃).2H₂ (Deer et al ;1990).

Trona is a complex salt of sodium carbonate (Na₂CO₃) and sodium bicarbonate (NaHCO₃). Despite many studies regarding the flotation of soluble salts, there are few studies about the flotation of carbonate salts. Micro flotation experiments with pure Na₂CO₃ and NaHCO₃ salts showed that excellent flotation of NaHCO₃ could be achieved with both anionic and cationic collectors. On the other hand flotation of Na₂CO₃ is generally difficult (Ozcan and Miller,2002,O. Ozdemir ;2009).

According to Naata et al;(2018).Trona also known as _Kaun' in Yoruba and _Kanwa' in Hausa is a dried lake salt that contains mainly of hydrated sodium carbonate (Na₂CO₃. NaHCO₃. 2H2O)(Omajali BJ et al ;2010). It is the most abundant sodium alkali mineral (Ameh AO et al; 2009). It is an important table salt and the second most commonly used salt in Nigeria (Makanjuola AA et al;1975). It is called potash despite having low amount of potassium, sometimes below detection level (Omajali BJ et al ;2010). Two varieties of Trona are known in Nigeria, the whitish and the red-white (red) (Omajali BJ et al ;2010)]. It is used as salt of tobacco to produces tobacco snuffs, as tenderizing agent, as laundering agent, in scouring of wood, in bath salts, in pharmaceuticals and to facilitate fermentation (Makanjuola AA et al;1975).

The trona may be expected to occur in association with other secondary minerals, such as iron magnesium phosphates, kainite, MgS0₄ KCI.3H₂0, carnallite,KCl.MgCl₂.5H₂0 and poly halite $K_2CaMg(S0_4)$ 4• 2H₂0 (Montimer; (194),Garrels and Christ; (1965). Generally in these environments phosphates may be derived from FePS or other phosphorus containing sulphosalts because wide range of secondary phosphate 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 a!, !9S L Rose and Sutir, 1971, 1971; Nriagu and Moore, 1984; Fleicher, 1987).

The pure material contains 70.3% sodium carbonate and by calcination the excess CO₂ and water can be driven off, yielding natural soda ash. The terms soda ash and sodium carbonate are used interchangeably. Trona calcining is a key process step in production of soda ash from the relatively cheap Trona ore. The calcination reaction may proceeds in a sequence of steps. Depending on the conditions, it may result in formation of either sodium carbonate monohydrate (Na₂CO₃.H₂O), sodium sesqi carbonate (Na₂CO₃.NaHCO₃). (Sibel Gezer1;2016)

2

1.2 Trona deposits

An ore deposit may be define as body of rock, which contains metallic compounds or native metals in sufficient quantity which can be of economic importance ,so that one or more metals can be profitably extracted is it referred to as mineral ore.

In its strictest sense, ore refers only to metal or metals bearing minerals, but in common usage, a few of the nonmetallic minerals such as sulfur and fluorine are included. Building stones and industrial materials such as abrasives, clays, light weight aggregates, and salts are not considered ore, they are classified as industrial rocks and minerals or economic minerals.(Susan; 2012)

Sodium salts occurs in large deposits in a desert region Carbonate rocks represent about 20 percent 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 evaporates. The trona ores 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 (The Maiduguri Soda-ash production Company Limited, unpublished document, Nigeria(2018).

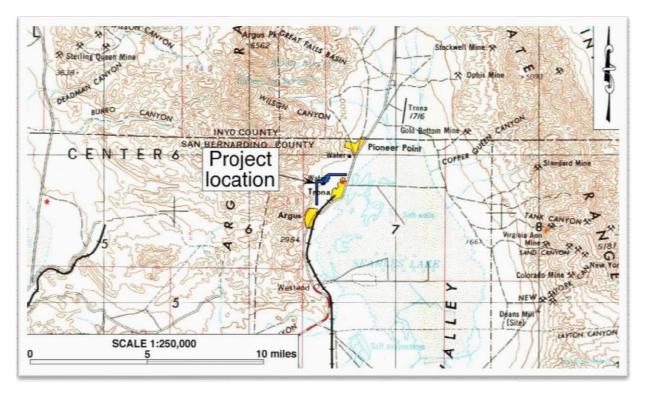
The characteristic constituent of the so-called " Natron lakes " is sodium carbonate; but this compound is always accompanied by sodium chloride and sodium sulfate. The deposits of such lakes are of peculiar character and often include Natron (Na₂CO₃.HO) Trona (Na₂CO₃.NaHCO₃.2H₂O) and few amount of Gaylussite (CaCO₃.Na₂CO₃.5H₂O) (Susan ; 2012)

1.3Trona ore occurrence world wide:

1.3.1. Trona in USA

Wyoming is a major contributor to the total world production of Trona ,which is mined and then processed into soda ash ,as a significant economic commodity because of it's application in manufacturing glass, chemicals paper.

According to(Tom Dodson ;2019)Trona is an unincorporated community in San Bernardino County, California. In 2015 it had a population of approximately1,900Trona is at the western edge of Searles Lake, a dry lake bed in Searles Valley, southwest of Death Valley. The town takes its name from the mineral trona, abundant in the lakebed.Between January and April 2019, CRM TECH performed a cultural resources study on the area designated for the proposed Industrial Lime Production Plant Project near the unincorporated community of Trona, San Bernardino County, California Fig(1.1)



Fig(1.1). Project vicinity. (Based on USGS Trona, Calif., 30' x60' quadrangle [USGS 1969])

1.3.2. Trona in Nigeria

According to (K.E. Imafidon et al;2016)Nigeria's government revitalized concern in the exploration of solid minerals in the past, could perhaps explain the reason for the use of naturally occurring inorganic substances (salts) by the people for various purposes (Aribido et al., 2001,Oyeleke OA;1981). One of such geological mineral is —kaunl erroneously called potash although it contains low amount of potassium compared to sodium. Kaun(trona) is the second most commonly used salt in Nigeria. In Hausa,it is called —kanwa.

In Nigeria Trona is a natural food additive, its main uses are in cooking tough food material such as skins, bones, beans, maize., and it is also used in the preparation of a delicacy called owo in Edo and Delta States of Nigeria. Studies involving rats have indicated that high levels of trona in cooked foods and drinking water may be detrimental to health (Oyeleke, 1988) and hemolytic to human (Sodipo et al;1993) .The toxic nature of trona was observed in nursing mothers around Zaria and Malumfashi areas of Northern Nigeria as far back as 1974(Davidson et al; 1974) ,reported peripartum cardiac failure in foetus, forty days after birth. (Bamaiyi and Momoh; 2010)

1.3.3 Trona in Turkey

The NeogeneBeypazari basin is limited on the north by the West Pontid mountain belts. This part of volcanics 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 northeastern part of the basin and between the Beypazari and Kizilcahamam areas (Fig1.2).

Pre-Neogene sedimentary rocks ranging from Paleocene to Eocene in age limit the Neogene basin to the west.

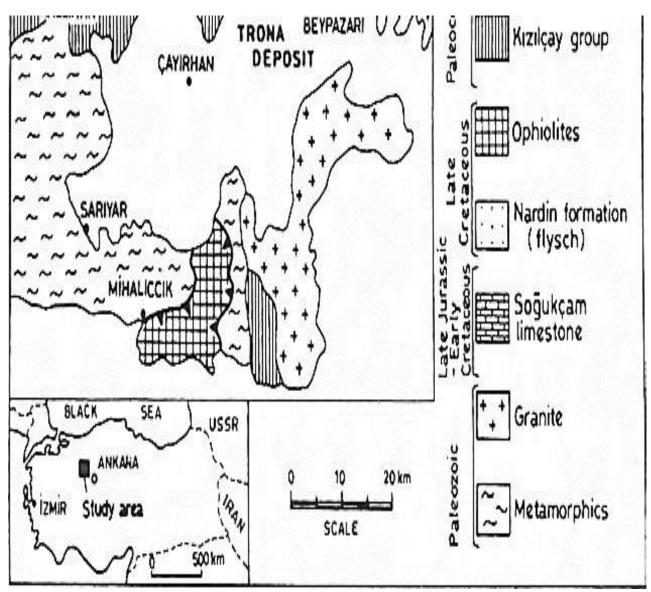


Fig. (1.2):Locality and geological setting of the BeypazariTurkish

The NeogeneBeypazari basin is one of the most economically important basins in Turkey, containing lignite, bituminous shale, and trona deposits. Fluvial, lacustrine, and volcano-sedimentary rocks mainly fill this basin. The

Neogene sedimentary sequence in this basin is divided into eight formations (Inci and others, 1988; Helvaci and Inci, 1989).In the region between Beypazari and Nallihan, geological maps at a scale of 1:25,000 have been prepared .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 thegeological setting of the trona deposit.(Cahit Helvaci;1998)

In TurkishTronawas discovered incidentally by the General Directorate of the Mineral Research and Exploration while carrying out a drilling project of the lignite deposits in the summer of (1982). An extensive exploratory drilling program was undertaken during the period 1983-1985 on behalf of the Etibank Company. Some 64 drill holes have been completed in the area to date.

1.4 Sudan

Trona deposits in western Sudan was discovered about 10,000 years ago. Most Trona deposits are geologically young. Some of the most common types according to Susan et al (2012) are:

- I. Atron crystals in cool wet environment on the bottom of ponds or at shallow depth in slat marches .
- II. Powdery efflorescence of thermonatrite on the surface.
- III. Relative hard deposits, either around the shore or at the bottom of shallow alkaline lakes or ponds.

Examples of such deposit are those of Elaterun, Eldaleiba and Elnukheila basins in Sudan.

Because of chemical activity of sodium, it is never found in nature uncombined. Igneous rocks contain sodium combined with oxygen, silicon and other metals, in the form of double silicate. Of these ores of the commonest is feldspar NaAlSi₃O₈. By the action of water and carbon dioxide, feldspar and similar rocks become weathered to yield sodium carbonate, clay and silica.(Susan et al; 2012)

$$2NaAlSi_{3}O_{8}+2H_{2}O+CO_{2} \rightarrow Na_{2}CO_{3}+H_{4}Al_{2}Si_{2}O_{9}+4SiO_{2}$$

aAl though end wide field of these deposits the Sudan imports almost all the soda ash needed for industries. The characterization of the rich Natron deposit in north western. Sudan in preparation for their development is an argent take for several reasons.

- The preliminary analysis shows that many of the deposits are economically feasible for development.

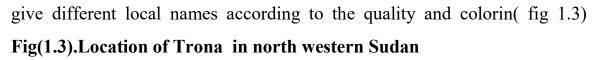
-There are large quantities of the natural deposits available in several locations.

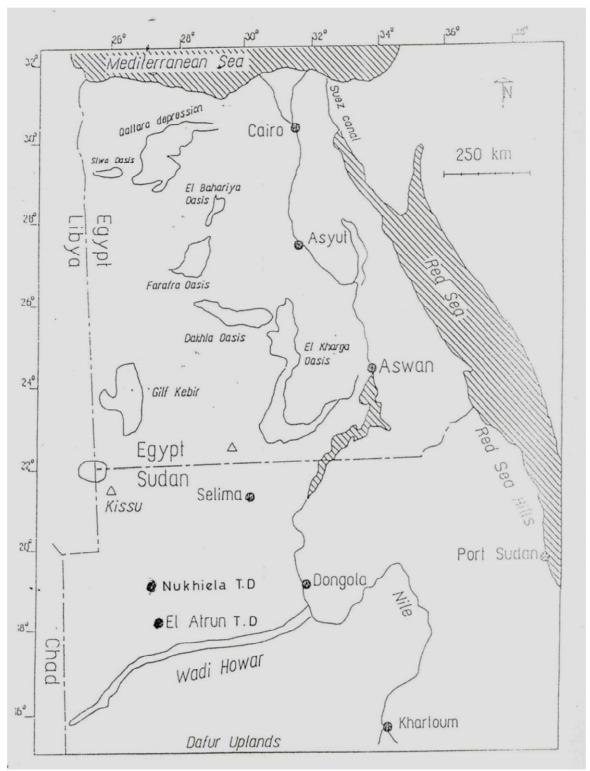
- Progressively increasing quantities of Soda ash are needed for old and new industries in the country(Husameldine ;2004)

1.4.1. Locations and types of Trona in Sudan

Trona deposit in north western Sudan was discovered since the beginning of the previous century by the local nomads who used Natron for their sheep's and camels consumption. Al though wide field of these deposits is available, Sudan imports almost all the soda ash needed for industries from other countries .(Susan et al ; 2012).

Eldoma etal (2013) repeated thatElatrun and Elnukheila are two known location in the North – Western Sudan desert.Trona deposits in Sudan have





Fig(1.3).Location of Trona in North western Sudan

1.4.1.1Elatrun area

Lie at the intersection of latitude (180-9—57=) and longitude (260-37—03=) at a distance of 45 Km from Elfashir, 92Km from Rahib mountain

1.4.1.2 Abuzaema Trona

Is located at 180 9- 56= N and 260 3= E. Trona fragments vary in size from 15 cm in diameter, and overlain 17 cm of wet loose sand containing big fragment of crystalline trona with shapes of sodium carbonate. The commercial Trona is normally taken from this bed which is of high percentage of soda ash.

1.4.1.3 Kambodia Trona

This located at 180 10- 12= N and 260 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.(Susan et al; 2012)

1.4.1.4 Elakhder and Elahmer Trona

Are green and red in color respectively .Elakhder type is located at 180 9-51 N and 260 38- 39 E. whereas Elahmer type is located at 180 11- 00 N and 180 10- 12 E. They are found at the west side of the main camp of Elatrun, they have a well crystalline whitish needle-shape salt.

1.4.1.5 Elsalam Trona

Is located at 180 11- 32 N and 260 36- 44 E. Thisisthe most preferable type for consumers in Sudan. It is found on the surface of the whole basin with thickness of 25 cm, whitish in color, and formed of pure trona samples.

1.4.1.6 Ummbahatay Trona

Is located at 180 10- 05= N and 260 37- 38= E. The Trona deposit here is found on the surface of the soil, 30cm whitish concentrated sandy Trona, overlained by a hard Trona of 20 cm thick.

1.4.1.7 Eldaleiba Trona

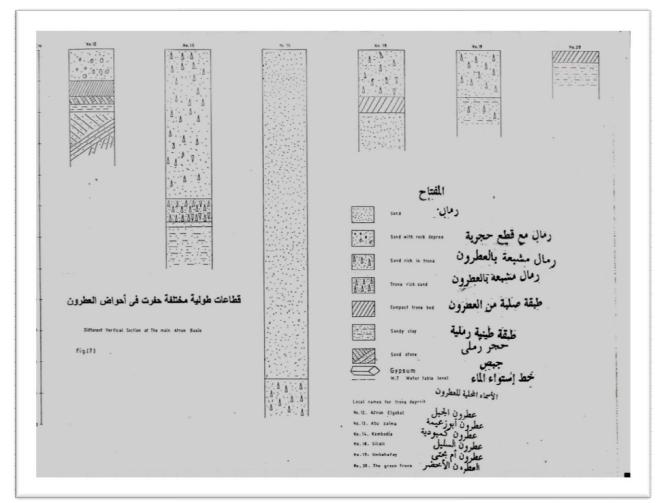
This deposit is located at about 6 km west of main producer of the light Trona, which is in much demanded in local market and suitable for export. Zabad type is formed by drawing the brine water using pump trona or abad on the surface to be collected after period of several days.

1.4.1.8 Elnukheila area

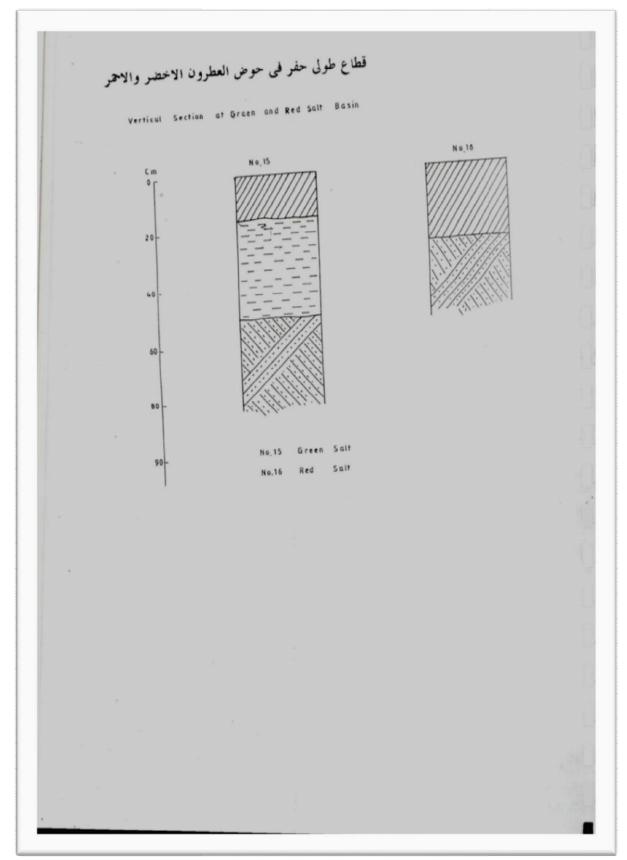
This is Trona deposit field is 161 km to North western of Elatrun at about 190 - 15- 46 N and 260- 10- 27 E.It is deposit in this area was discovered during the last 10 years in the North West of Elnukheila oasis near the old known deposit of Elgaa Elmasriya, is along exploited by the Egyptians who take the salt of Trona from Sudan to Egypt on camel backs .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.

1.4.1.9 Elgaa Elgadima Trona

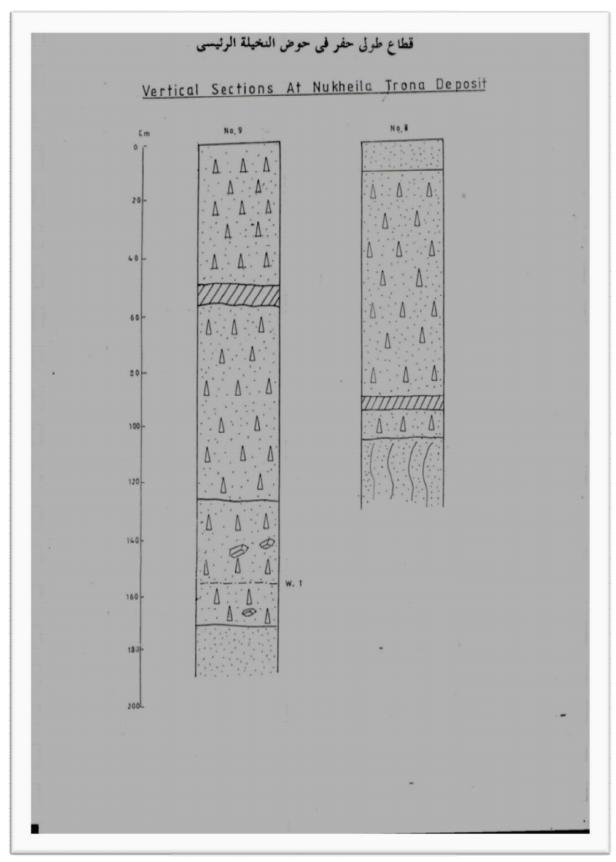
The deposit is found in hallow depression between sand stone rock of Silurian age. Trona in this area is of high quality than ElgaaElmasriya.



Fig(1.4) .Different vertical Sections at the main Atron Basin Fig



(1.5).Vertical Section at Green and Red salt Basin Fig (1.6) .Vertical



section at NukheilaTrona deposit

1.5Uses of Trona ore

1.5.1 general uses:

Susan (2012) reported that Trona is fed to cattle's to improve digestion and milk production .

H.K. Zanna et al (2018) stated that Trona is likely used in Nigeria as ingredient for animal appetizer, cooking soup and medical purposes

1.5.2 Medical uses :

Nata'ala et al ;(2018) reported antifungal activity of white Trona against the dermatophytic fungi or ring worm infection . They reported that the high pH of Trona may be behind the antifungal activity of white Trona samples .Nata'ala et al ; concluded that Trona has a promising potential in the treatment of fungi associated with dermatophytosis

1.5.3 Industrial uses :

Glass, Detergents, Leather Tanning, Water softening.

I.Ozkan (2015), reported that , Trona can be used instead of soda ash to produce sodium silicate collets

1.5.3.1 Sodium carbonate production

From Historical back ground sight of view two chemical process were used for Na ₂CO₃ production these are:

a)Leblanc process

In this process sodium sulfate that was normally obtained from the reaction between NaCl and H_2SO_4 for the industrial production of HCl according to the equation below.

 $2NaCl + H_2SO_4 \rightarrow Na_2SO_4(aq) + 2HCl(g)$ (1)

Sodium sulfate will be reduce by heating it with a mixture of carbon and CaCO₃

$$Na_2SO_4 + CaCO_3 \xrightarrow{\triangle} Na_2CO_3 + 2CO_2 + CaS$$
 (2)

b) Solvay process

In this method saturated sodium chloride solution will be treated by ammonia gas and carbon dioxide .carbon dioxide is normally obtained from the thermal decomposition of limestone ($CaCO_3$).

$$\begin{array}{c} & \bigtriangleup \\ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_3(g) \end{array} \tag{3}$$

The reaction mixture will produce NaHCO₃which decomposes by temperature to give Na₂CO₃

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$$
(4)

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \tag{5}$$

Sodium carbonate is converted from trona in a multistage purification process; calcination, dissolution, clarification, filtration, and crystallization .The processes for the recovery of sodium carbonate from trona deposits and other sodium bicarbonate containing sources of sodium carbonate was reported by

Robert et al (2007). This was carried out by using a mixed solvent containing ethylene glycol and water, the stability of trona ore is decreased due to increasing of the boiling point of the solution, spontaneously recrystallized to anhydrous sodium carbonate and $(Na_2CO_3.3NaHCO(s))$. The sodium bicarbonate content was decomposed thermally in the mixed solvent into sodium carbonate and crystallized as pure anhydrous sodium carbonate. Calcining any of sodium carbonate source yields sodium carbonate with various physical properties, crystal size, shape and bulk density (Sommers, 1960) .Production of sodium carbonate from trona solution can be achieved by a spray dryer reactor (Doganet al;1997). The production of sodium carbonate from trona deposits by processes of leaching and crystallization can also be applied (Martins and Martins; 1997,Nasuet al;1996).

The solid raw material of trona ore is(Aldoma et al;2013) crushed into fine particles, leached with warm water (at 30 -40° C), and then filtered to remove silica and other water insoluble materialsin order to obtain a clear solution. To separate the undesirable soluble matter from the clear solution and obtain pure sodium carbonate, the solution sent to a pilot plant which consists of a storage reservoir, an evaporation reservoir, a crystallization reservoir and a dry reservoir unit .These units are ordered as illustrated in(Fig. 1.7) In this pilot plant, sodium carbonate solution is concentrated in the evaporation reservoir by solar energy until the concentration reaches 30%, then the solution 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. (Aldoma et al;2013)

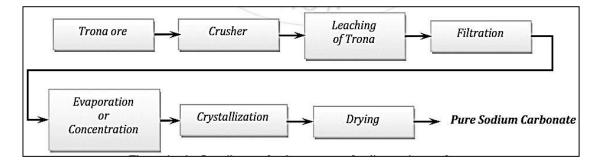


Fig. (1.7):Recovery of (Na₂CO₃) from trona ore(Aldoma et al;2013)

1.5.3.2Calcium hydroxide production

Calcium hydroxide or hydrate lime Ca(OH) traditionally called slaked ,is limestone and a strong base with pH values above 12 in saturated solution ,it is Stable under ordinary conditions but absorbs carbon dioxide from air to form calcium carbonate. It easily handled, and is cheap, it is refined from limestone (CaCO₃). Calcium hydroxide products are used in water treatment, pH control, paper manufacture, cement manufacture and leather tanning industries .It is also used as an additive in petroleum industry. Calcium carbonate isused as kiln feed to produce calcium oxide. The goal of the kiln operation is to produce lime from "perfectly calcinated limestone (Thomas ; 1997).

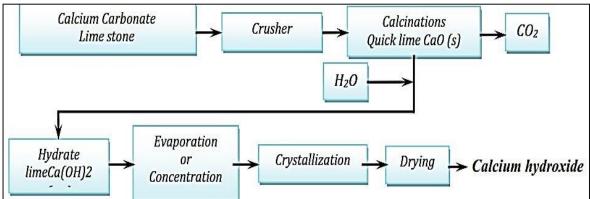


Fig.(1.8).Production of calcium hydroxide from calcium carbonate.

Pure limestone is to be crushed to reduce the particle size in order to be fed to kiln step. In the kiln the crushed limestone is heated to about 900° C using wood fire. This is called the calcinations process Fig. (1.8) .Calcium carbonate decomposes into calcium oxide a quicklime and carbon dioxide as shown in(equation 1).

This decomposition reaction is reversible in the presence of carbon dioxide gas.

$$\begin{array}{c} \bigtriangleup \\ \text{CaCO}_3(s) \xrightarrow{} \text{CaO}(s) + \text{CO}_2(g) \end{array}$$
(6)

When calcium oxide is added to water at 30-50 0 C, it is converted to calcium hydroxide (slaked lime) in an exothermic reaction (Equation 2)

$$CaO(s) + H_2O(1) \rightarrow Ca(OH)_2(s) + Heat$$
 (7)

The main disadvantage of calcium hydroxide, however, is that it is partially soluble in water. But the ionization of the calcium hydroxide in an a9ueous solution gives calcium cations (Ca^{+2}) and hydroxyl group (OH) as shown in (Equation 3).

$$Ca(OH)_2(s) \leftrightarrow Ca^{2+}(aq) + 2OH(aq)$$
 (8)

1.5.3.3 Recovery of NaOH from produced Na₂CO₃and CaCO₃:

The sodium carbonate produced from the purification process is reacted with the calcium hydroxide produced in the calcinations process according to the precipitation reaction shown in Equation (4). 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 precipitate and then concentrated using solar energy evaporation as shown in Fig. (1.9).

$$Ca(OH)_2 (aq) + Na_2CO_3 (aq) \rightarrow 2NaOH (aq) + Ca_2CO_3(s)$$
(9)

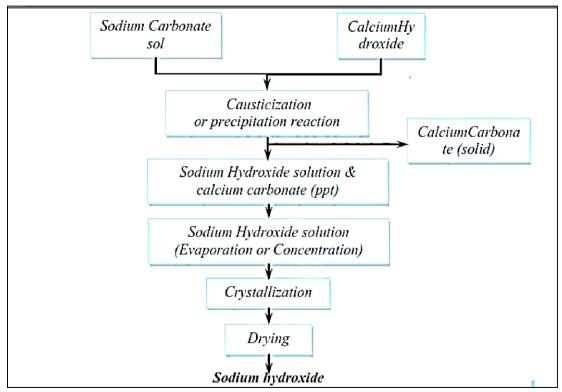


Fig. (1.9).Recovery of NaOH from produced Na₂CO₂ and CaCO₂

1.5.3.4 Sodium bicarbonate (Na HCO₃):

Sodium bicarbonate is widely used in purification processes of gaseous products from combustion of solid fuels. In the seventies of the 20 century, studies on sodium sorbents were conducted. They included the use of natural (nahcolite) natural sodium bicarbonate in the dry flue gas desulphurization process. Nahcolite changes it's 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 sodium carbonate occurs. It influence on decreasing of molar volume of decomposed sodium bicarbonate (NaHCO₃) during releasing of gaseous products of decomposition: carbon dioxide and water vapor, resulting in breaking apart of compact structure and forming of pores with high surface area. The temperature of decomposes varies in a range of 60 to 400°C (Chemik ;2012).

Sodium carbonate produced in such process is characterized by a more developed surface area in comparison with crystalline sodium bicarbonate.

This lead to an increase in it's reactivity.

Equation (5) show the reaction process.

$$2\text{NaHCO}_3 \xrightarrow{\Delta} \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{HO}$$
 (10)

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

1.5.3.5 Production of sodium silicate cullet's from Trona:

According to I.Ozkan (2015,2016) sodium silicate is a color less compound of sodium and silica oxides .It range of chemical formula varying in (Na₂O) and (SiO₂) content or ratios. Sodium silicates are produced in the form of a variety of compounds ranging from Na₂O.4SiO₄ to $2Na_2O.SiO_2$ by properly proportioning the reactants.

Sodium silicates varying in ratio from $Na_2O.1.6SiO_2$ to $NaO.4SiO_4$ are known as colloidal silicates .These are sold as 20% to 50% aqueous

solutions called water glass. Sodium silicate cullet's are it's produced by the direct fusion of precisely measured portions of pure silica sand and (SiO_2) and soda ash (Na_2CO_3) in oil ,gas an electrically fired furnaces at temperature above 1100 C⁰ as shown by reaction

 $Na_2CO_3 + xSiO_2 \rightarrow NaO.xSiO_2 + CO_2$ (11)

To produce sodium silicate cullets, trona and quartz powders , batches with different SiO_2 : Na_2O from molar ratios should be mixed according to the

equations below:

$$2Na_2CO_3NaHCO_3 \cdot 2H_2O + 3SiO_2 \rightarrow 3Na_2OSiO_2 + 2CO_2 + 5H_2O,$$
(12)

$$2Na_2CO_3NaHCO_3 \cdot 2H_2O + 6SiO_2 \rightarrow 3Na_2O2SiO_2 + 2CO_2 + 5H_2O,$$
(13)

$$2Na_2CO_3NaHCO_3 \cdot 2H_2O + 9SiO_2 \rightarrow 3Na_2O3SiO_2 + 2CO_2 + 5H_2O,$$
(14)

$$2Na_2CO_3NaHCO_3 \cdot 2H_2O + 12SiO_2 \rightarrow 3Na_2O4SiO_2 + 2CO_2 + 5H_2O.$$

(15)

1.6 Minerals content of Trona ores:

Omer A.Gibla (2001) studied three trona samples and two " arab salt "

samples .The Trona showed pH value as (9.959, 10.022 and

10.036), calculate content as (9.45, 13.33 and 23.3%), bi carbonate content as

(10.79, 19.8 and 19.30%), chloride content as(7.10, 2.22 and 1.78). The two Arab salt samples showed PH values as (9.920 and 7.57), carbonate content as (0.5 and zero %), bicarbonate content as (4.97 and 0.89%) and chloride content as (33.73 and 51.48%). This may enhance clearly the difference between sample (No5) and the other four samples in the present study. The very low availability of toxic minerals in the analyzed trona samples strongly agree with findings reported by Omer A.Gibla(2001).

Table (1.1):pH values of CO₃⁼, HCO₃ andCl content of Trona samples (Omer A,Gibla;2001)

Sample				
	pH value	CO ₃ %	3 %	%
Trona(1)	9.959	9.45	10.79	7.10
Trona(2)	10.022	13.33	10.8	2.22

Trona(3)	10.035	23.3	19.30	1.78
Arab salt(1)	9.420	0.56	4.97	33.73
		0.00	0.89	51.48
Arab salt(2)	7.57			

 Table (1.2): Elemental Composition of Trona (Nata'ala et al ;2018)

Element	Type of T	Type of Trona	
	White	Red	
Ca (mg/kg)	1.20	1.00	
Na (mg/kg)			
	8300	9500	
K (mg/kg)			
	4400	1800	
Cl (mg/kg)			
	1.44	0.36	
Mg (mg/kg)			
	0.10	0.15	
P (mg/kg)	2.25	4.07	
	3.35	4.07	

In a study carried by Na'ata et al ;(2018) for red and white Trona samples the highest sodium content was 9500 mg/kg and 8300 mg/kg and the lowest content was 0.15 mg/kg and 0.10 mg/kg .potassium content of red and white Trona samples was reported to be 4400 mg/kg and 1800 mg/kg respectively

Inegbenebor and Inegbenebor (2004) analyzed thirteen(13) Trona samples collected from the troughs of lake chat areas of Borno and Yobe states of

Nigeria ,together with sample from Libya in North Africa .The reported Na₂O ranges as (35.4 $_$ 42.3%) ,K₂O (0.95 $_$ 3.01%) , ZnO (0.4 $_$ 1.95%), PbO(0.65 $_$ 5.2%), Al₂O₃(0.6 $_$ 2.1%), MgO(1.28 $_$ 3.5%) ,CaO(0.5 $_$ 4.6%) and FeO(0.2 $_$ 2.8%).

Inegbenebor reported carbonate content in the range of $(32.2 \ 36.1\%), PO_4^{=}$

(1.42 _3.8%), SO₄⁼ (0.75 _ 1.8%) and PH value range as (8.3 _ 8.7)

1.6.1 Heavy metals content of Trona

Heavy metals are natural component of earth crust and they cannot be degraded or destroyed. In asmall content they enter our bodies through food, drinking water and air. As trace elements some heavy metals like copper, selenium and zinc are essential to maintain the metabolism of human body. However, at higher concentrations they can lead to poisoning (John and Duff, 2002). Heavy metal dangerous because they tend to bioaccumulation. Bioaccumulation means an increase in the concentration of a chemical in biological concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down, metabolized or excreted. The danger of bioaccumulation of trace metals in bio organism has in recent times reported by many workers. These workers attributed the incidents to indiscriminate disposal of domestic waste ,industrial waste and natural source (Ndiokwere, 1983 and Usman et al., 2003)The fate of trace metals such as lead (Pb), zinc (Zn), iron (Fe), copper (Cu), and manganese (Mn) in the food web is of great concern owning to their impacts on the entire ecosystem. (Zanna et al;2018).

Heavy metals (µg/g)								
Locations	Pb	Zn	Fe	Cu	Mn			
Margadu	4.22	25.30	0.52	4.90	0.21			
0,000	(1.07)	(0.08)	(0.05)	(0.22)	(0.01)			
Dogon Kuka 1	4.80	36.25	0.22	5.60	0.22			
-00	(0.05)	(0.02)	(0.10)	(0.06)	(0.03)			
Dogon Kuka 2	6.19	28.90	0.61	7.80	0.24			
	(0.06)	(0.05)	(0.03)	(0.12)	(0.02)			
Garbi	5.65	34.10	0.86	5.22	0.23			
	(0.03)	(0.01)	(0.12)	(0.03)	(0.02)			

Table(1.3): Heavy metals Content of Nigeria Trona samples(Zanna at el;2018)

Values in parenthesis refer to the standard deviation of five analyses.

The heavy minerals Pb, Zn, Fe, Cu and Mn in trona were determined in The mean concentration of Fe in the trona were; $0.52 \ \mu g/g$ in Margadu, $0.22 \ \mu g/g$ in DogonKuka 1,0.61 $\ \mu g/g$ in DogonKuka 2 and 0.86 $\ \mu g/g$ in Garbi. The relative comparison in descending order atconcentrations of Fe is; Garbi .DogonKuka2 .Margadu>DogonKuka 1. The high level of Fe couldbe associated with the metal iron been precipitated from host rock during mineralization.

The main purpose in trona analysis is the quantitive determination of water soluble- forms . In most cases, Tronais present in clays and other minerals, Despite of fact .Clays and other carbonate compounds that can be separated from aqueous phase require different kind of analytical methods.

Ahmed et al. (2005) analyzed five different samples from Eldeleiba, Elnukheila, Elsalam, Western Dongolaand the last one sample from the local market. He determined moister, silica, sodium, potassium, calcium, carbonate, bicarbonate, chloride and sulphate .(Table 1.4)

No sample	sample	Acid	Na	K	Ca	Mg	CO32-	HCO3 ⁻	CL-%	SO4	Total
		insoluble %	%	%	%	%	%	%		%	%
1	Eldeleibe	16.57	33.09	0.60	0.007	0.06	29.50	9.33	8.30	1.48	98.94
2	Elnukheila	16.50	30.91	1.17	0.450	1.05	2.20	0.98	29.0	29.0	99.63
3	Western Dongola	38.74	25.63	0.14	0.005	0.03	25.20	7.70	0.89	0.89	98.05
4	Elsalam	9.43	37.79	0.57	0.005	0.04	34.20	9.47	1.53	1.53	98.05
5	Local market	45.78	23.26	0.53	0.005	0.03	18.00	6.04	0.71	0.71	99.44

Table (1.4): Chemical constituent of Trona samples (Ahmed et al 2005)

Table (1.5) lists the chemical analysis results of the trona powder. Its high NaO and loss of ignition content indicates the purity of the ore. XRD analysis of the Trona powder according to the XRD database, the powder sample contains trona, nitrite, natron and nahcolite phases. The index number given in the parenthesis in shows the XRD pdf card number according to the JCPDS-ICDD formats.(Oludeniz et al; 2015)

Table(1.5): Minerals content of Trona powder .(Oludeniz et al ;2015)

Oxides [wt%]	SiO_2	Al_2O_3	$\rm Fe_2O_3$	MgO	CaO	Na_2O	K_2O	MnO	LOI
Trona	0.16	0.03	< 0.04	0.18	0.17	49.75	< 0.01	< 0.01	42.70

Table (1.4) lists the recipes of di erent sodium silicatecullets prepared

According to Eqs. (6,9). The composition of the recipes and melting temperature played agreat role on the viscosities of the sodium silicate melts The viscosity of the melt became higher with increasing quartz amounts. SSR4 could not be poured due to its high viscosity at 115^oC. Therefore, it was not possible to get samples from this recipe at 1150^oC.

Raw materials	SSR1	SSR2	SSR2	SSR4
Trona [wt%]	71.52	55.67	45.56	38.57
Quartz [wt%]	28.48	44.33	54.44	61.43 $^{\circ}$

Table (1.7): Chemical analysis of different samples from Atrun area(Edress M.A;2017)

Area	CO ₃	нсо	SO ₄	Cl	Ca	Na	Insoluble Reside
Elsalam	41.9	5.3	0.16	1.3	N.D	25.6	17_9
Elnukheila area	0.6	0.2	29.2	21.4	0.6	24.4	19.6
Algabal Trona 12	N.D	0.9	1.8	13.9	N.D	10.7	72.2
Algabal Trona 12	N.D	0.6	0.3	1.2	N.D	0.2	33.6
Abuzaema13/1	5.2	2.1	0.7	2.9	0.2	1.2	75.6
Abuzaema13/1A	30.4	4.5	0.2	1.1	0.6	13.1	33.5
Abuzaema13/1B	4.7	6.8	0.12	1.2	1.2	0.8	49.9
Elsalam 17	8.13	8.9	16.0	38.1	N.D	12.1	45.6
Elsalam 18	25.6	3.5	0.17	0.5	N.D	12.1	45.6
Ummbahatay	19.4	1.3	0.7	3.1	0.1	8.5	55.2
Elakhder Trona20	23.9	2.7	0.8	2.9	0.1	10.1	38.9
Altrona	5.9	1.8	1.0	34.8	0.9	21.2	27.3
Elakhder 20/15	23.5	1.5	2.0	3.4	0.1	10	41.6
ALzabd	47.8	N.D	1.2	19.1	0.1	25.6	3.8

Area								
	CO ₃	HCO ₃	Cl	SO ₄	Na	K	Cu	Insoluble
								Reside
ELgaaElmasria11	6.0	6.1	0.44	4.16	2.9	0.23	0.03	76.7
ELgaaElmasria1A	30.0	3.05	0.53	2.0	16.4	0.16	0.2	26.4
Elnukheil 9/3	6.0	4.6	9.3	7.37	16.6	1.8	-	39.51
Elnukheil 8/3	21.0	3.1	0.44	6.2	13.0	0.5	0.36	42.26
Elnukheil 8/1	12.0	3.1	0.44	20.9	14.5	0.4	0.4	42.01
Elnukheil 10/1	27.0	3.1	2.8	12.0	9.2	0.3	0.16	30.05
Elnukheil10/10	21.0	3.1	3.7	7.8	16.8	0.4	0.12	40.4
Eldaleiba hagrmoia 12A	33.0	4.6	0.59	1.80	19.4	0.12	0.13	30.1

Table (1.8): Chemical analysis of different samples from Atrun andElukeila areas(Edress M.A;2017).

H.k. Zanna et al;(2018)studied Trona samples from Yobe state of Nigeria .the reported the ranges of minerals occurrence as Pb (4.22- 6.9 μ g/g), Zn (22.65 - 36.25 μ g/g), Fe(0.22- 0.86 μ g/g), Cu(5,6 - 7.8 μ g/g),and Mn (0.21 - 0.24 μ g/g).The study showed the percentage of common compounds that are normally available in Trona ores as NaCl (2.4%), Ca₂SO₃ (20%), Na₂SO₄ (26.5%) ,CaCO₃(30.8%),CaSO₄(2%) insoluble solids (1.4%) and water (3.2%).

Mubark A.Eldoma et al ;(2013) produced Na_2CO_3 , $Ca(OH)_2$ and NaOH of from Trona ore. The purity of the three products of high purity were reported to be as 95.8% Na_2CO_3 , 92.97% $Ca(OH)_2$ and 87.6 % NaOH. Eldoma et al; study (2013) reported chemical composition of Trona ore samples as

Na(28.55%), $CO_3^{=}$ (35.47%), HCO₃(16.27%), K (0.55%), Mg (00.02%),Ca(00.05%),Fe(00.05%),Cl(6.80%) ,SO₄(00.42%),insoluble residue (10.75%) and others (00.80)

1.7 Objectives of the study:

The objective of the present study are

- To investigate the availability of macro minerals father than Ca, Mg, K, P and Fe in Trona ores.
- To measure the concentrations of the bio essential trace minerals in Trona deposit sample.eg Mn, Zn, Cu and Se.
- To measure the occurrence of some hazard as and toxic minerals ,to investigate how safe is the Trona ore for animals consumption and as food additives in some Sudanese nutrients , eg Pb,Hg ,Cd, As, Sb, Ba , Sn and Sr.
- > To show how far is the Arab salt deposits differ four Trona deposit

Chapter Two

Materials and Methods

2-Materials and Methods

2.1 Collection of samples.

Two samples were purchased from Al-Khartoum shabi market and two samples were collected from Almaha market (North Darfour). The fifth sample was purchased from ELfashir city market .

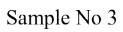




SampleNo1

Sample No2







Sample No4



Sample No5

Fig (2.1): Images of samples

2.2. Chemicals

• HNO₃ (with Purity range(69_72%), product code: 16560)

2.3. Instrument

• ICP (Shimadzu's ICPE-9000 multiple ICP emission spectrometer)

2.4. Methods of analysis

2.4.1. ICP analysis of Trona samples

1 g of each Trona sample was weighed 0.1 ml of concentrated HNO_3 and 5 ml de-ionized water were added .Each mixture was then filtered through filter paper(Watman).In a25ml volumetric flask and completed to the mark with de-ionized water. There will of each samples was injected to the ICP instrument .

Chapter Three

Results and Discussion

3. Results and Discussion

			Sample N0		
Mineral					
	1	2	3	4	5
S	11000	1600	4700	13000	390
Na	1200	900	1200	950	530
Fe	69	120	1300	1300	N.D
AI	34	120	1100	29000	N.D
Mg	81	110	1100	510	<0.59
Р	160	48	180	170	65
Са	120	120	520	350	N.D
Si	24	58	140	560	N.D
К	53	9.5	78	170	12

Table (3.1): Minerals of macro availability in Trona samples (µg/L).

The five Trona samples showed significantly high availability of sulfur, ranging from (390 μ g /L) in sample (No5) to (4700 μ g /L) in sample (No3). This may be an indication for the presence of sulfate (So₄) as one of the main compounds of Trona samples .Such suggestion may be enhanced by the considerably high concentrations of Na, Mg , Al and Fe in same samples .

Sulfur occurrence(S) may also indicate presence of sulfide ions.

A.Eldoma reported sulfate concentration in Trona ore sample as (0.42%).Susan (2012) reported sulfate concentration as (29%) in ore Trona sample.

Edress M.A(2017)reported sulfate occurrence in Trona ores up to 20.9% in some samples.

Inegbenebors (2004) reported (SO₄) content up to (1.8%).

In the five sample sodium (Na) was the most available cation, followed by Mg, Al, Fe, Ca and K. High sodium content is an expected result ,because Trona ore was reported to be dominated by sodium containing compounds especially carbonate and bicarbonate (CHEMIK ;2012). According to M. K. Nata'ala (2018) the results also indicate that the sodium level is higher than all the elements present and potassium level having quite a low concentration compared to that of sodium, this agreeOmajali and Sanni(2018),Susan (2012), I.Ozkan (2016) and A.Eldoma(2013).

Iron concentration was relatively high in the four samples (No 1,2,3 and 4)and not detected in sample No(5).Zanna et al; (2018) showed moderate availability of Fe in some Trona samples.

Phosphorous (P) showed relatively high availability in the five samples. Since the majority of Phosphorous containing compounds are insoluble in water, the analyzed samples may contain reasonable amounts of sodium or potassium phosphate as water-soluble salts.

According to Inegbenebors(2004) phosphors content was reported to range between (1.42 and 3.8%) as PO₄.

Silicon (Si) availability is expected because Trona deposits in Sudan are normally mined from sandy areas.

The presence of Al and Si was shown to be relatively low in samples (No 1 and 2)and high in samples (No 3 and 4) I.Ozkan (2015) reported SiO₂ as (0.16 %) and Al₂O₃ as (0.03%) in Trona ores.

<u>- 1 ubic (0.2)</u>	Sample No								
Mineral									
	1	2	3	4	5				
В	49	4.4	32	110	N.D				
Mn	14	5.1	70	48	N.D				
Cu	9.8	8.8	13	17	N.D				
Cr	3.3	2.5	15	16	N.D				
Zn	3.1	3.7	13	13	N.D				
Ti	1.2	1.7	10	4.7	N.D				
Pt	N.D	26	N.D	35	N.D				
V	N.D	N.D	<0.47	1.9	N.D				
Ni	N.D	N.D	N.D	7.2	N.D				
Со	N.D	N.D	N.D	4.1	N.D				

Table (3.2) : Trace minerals availability in Trona samples (μ g/L) .

All micro minerals availability in sample(No5) were found to be below the detection limit of the instrument .

Boron was the most available mineral in the analyzed samples (1,2,3and 4),but not detected micro mineral in sample (No 5) this may indicate a presence of borax as a main constituent in Trona ores.

Titanium (Ti)showed very low availability .Such occurrence of (Ti) is unexpected, since the element is one of the most available minerals in the earth crust .Sample (No 4)differ from the other samples by showing fair occurrence for the ten trace minerals Cr ,Co ,Mn, B ,Ti, Ni,V and Pt. Zanna et al (2018) reported relatively high Zn content ,but almost similar of Cu ,and Mn .

In sample (No 5)the availability of all trace mineral was found to be under the detection limit of the instrument (ICP).Sample (5)was the fare differ from the other four samples of Trona deposits.

The micronutrients Mn, Cr, Cu, and Zn showed fair availability in sample No. (1,2,3 and 4).

Cobalt (Co)and Nickel (Ni)were found only in sample (No 4)in low level

.Vanadium (V)was shown is very low concentrations in samples (No 3 and

4).Platinum showed relatively high availability as $(26 \text{ and } 35\mu g/L)$ in samples (No 2and 4).Sample (No 5)showed different results when compared with the other four samples.

In general view sample (No 5) showed clear differences from the other four samples (Table 3.1 ,3.2 and 3.3). This may indicate strong difference in the chemical compositions of the deposits of Trona ores.

The physical appearance of sample (No 5) looks different from the others. Some previous studies referred to certain deposits as Arab salt .It was reported to be used as stable salt in western and northern Sudan in the former times(Omer A.Gibla;2001) This type of ore may require a further separate research investigations.

Mineral	Sample No							
	1	2	3	4	5			
Ba	< 0.33	<0.45	7.0	2.2	N.D			
Sr	<0.27	< 0.36	20	7.3	N.D			
Cd	N.D	N.D	5.3	4.3	N.D			
As	N.D	N.D	N.D	20	N.D			
Hg	N.D	N.D	N.D	1.2	N.D			
Be	N.D	N.D	N.D	< 0.12	N.D			
Sb	N.D	N.D	N.D	N.D	N.D			
Pb	N.D	N.D	N.D	N.D	N.D			

Table (3.3): Toxic minerals in Trona samples(μ g/L).

Sample (No 5) was shown to be free from any detectable amount of the toxic minerals.

Lead (Pb) and Antimony (Sb) were not detected, in the five samples .This may not agree with Zanna et al;(2018) who reported lead content up to (6.19 μ g/g) in Trona ores. Omer A. Gibla (2001) reported that Trona ores did not show lead content. Beryllium (Be),Arsenic (As)and Mercury (Hg) were detected only in sample (No 4).Cadmium(Cd) was detected in very low levels in two samples (No 3 and 4).Barium and Strontium(Sr) were found to be available in four samples ,with relatively high content in sample(No 3). In a general view (Table 3.3)we may conclude that the toxic minerals availability in Trona deposits were significantly low. Compare to other sample elsewhere, as a result, we can state that, the consumption of Trona deposits by animals in a crushed form or in water solution could be safe and may cause no any hazardous effects through the food cycle.

Inegbenebor and Inegbenebor (2004) reported relatively high lead content in 13 Trona sample where it range from 0.65% to 5.2 % as "PbO".

Conclusion

Based on results obtained, it could be concluded that :

- The analyzed Trona samples showed significantly high availability of sulfur, ranging from (390 to 4700µg /L).
- Sodium was found to be the most available cation , followed by Mg, Al, Fe and K .
- Phosphorous showed relatively high in all samples.
- Cobalt and Nickel were detected in only one sample .

 Lead and Antimony were not detected in all samples.
- The micronutrients Mn, Cr, Cu, and Zn showed fair availability in four samples.
- Platinum showed relatively high availability as (26 and 35µg/L)in two samples
- The consumption of Trona deposits by animals in a crushed form or in water solution could be safe depending on the low availability of the hazardous minerals.
- One sample showed clearly different minerals concentrations form the others .

Recommendations

- More investigations and sampling efforts may be needed for the availability of toxic minerals.
- Further evaluation may be required to determine the possibility economic production of pure Na₂CO₃ ,NaOH and Ca(OH)₂ from Trona ores.
- X-ray diffraction analysis may be important to show the crystal structure of the ores and to show the major negatively charged
- ions such as SO_4 , Cl or NO_3 .

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