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# THE GEOCHEMICAL AND PHYSICOCHEMICAL PROPERTIES OF NATRON OCCURRENCES IN TURKEY

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## ABSTRACT

Natron, $Na_2CO_3$. $10H_2O$, is a rare forming mineral which precipitates in evaporative conditions. It is observed in Turkey within Neogene volcanosedimentary sequences. It is important in terms of pointing out the presence of industrial raw materials like Trona and Thenardite. Natron was formed under the control of physicochemical parameters and they can be found only by means of detailed researches. The physical, chemical and petrographical properties of this white, soft and platy-fibrous mineral were determined. The trace elements contents were measured ; SEM, XRD and DTA techniques were used. The studies show that it has been formed, at the end of the first evaporation period due to the increasing $H_2O$ activity and the change in $HCO_3/CO_3$ ratio.

**KEY WORDS :** Natron, evaporites, volcanism, Neogene, Turkey.

## 1. INTRODUCTION

Natron is formulated as $Na_2CO_3$. $10H_2O$ , and it was observed generally together with Thermonatrite in some localities (Bradley & Eugster, 1969), (Eugster & Smith, 1965), (Suner, 1989, 1991a,b, 1993, 1994a,b), (Hardie & Eugster, 1970), (Keys, 1979). It shows the transition to Thermonatrite as a result of an increase in temperature and a decrease in water activity. This mineral can be formed in atmospheric conditions and evaporative environments like playa-lakes together with Trona, Nahcolite, Gaylussite, Halite, Thenardite in accordance with the chemistry of solutions that are responsible for the formation of this kind of accumulations (Eugster,1970,1979), Helvaci et al.,1989),(Suner,1994b). Determination of this mineral is significant because it may point out the possibility of the presence of some industrial raw materials, such as Trona, which can not be easily determined by field researches.

## 2. REGIONAL GEOLOGY

Beypazari - Çayirhan Basin has an economic importance with the respect to the presence of industrial raw materials. The minerals determined within the Neogene volcanosedimentary sequence, may be classified in two groups one of which is the second largest natural sodium carbonate deposits in the World, Trona deposits, while the other group is consisted of rare forming minerals which are accumulated within the same sequences in the form of very small occurrences(Suner, 1989, 1991a, 1992, 1993, 1994).

Natron and other rare-forming evaporative minerals , such as Thermonatrite, Nahcolite, Pirrsonite, Shortite , had been formed in the same sequences which were consisted mainly of tuffs, tuffites, marlstones, claystones, bituminous shale. The rocks observed in the basin are classified and defined as follow : a) a metamorphic basement, b) a granodioritic interruption c) Jurassic - Cretaceous carbonate

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rocks d) Cretaceous flysch and limestones e) Mesozoic ophiolitic rocks f ) Eocene - Paleocene clastic sedimentary rocks g) Neogene volcanics h) Miocene lacustrine rocks i) Clastic sedimentary rocks (Helvaci et al.,1989),(Suner,1993). Natron were found in the lacustrine Miocene rocks that were consisted of six units ranging in thickness from 60 m to 350 m. All these units had been deposited conformably. Natron was determined on the upper sector of the lower parts of the lower trona horizon within the

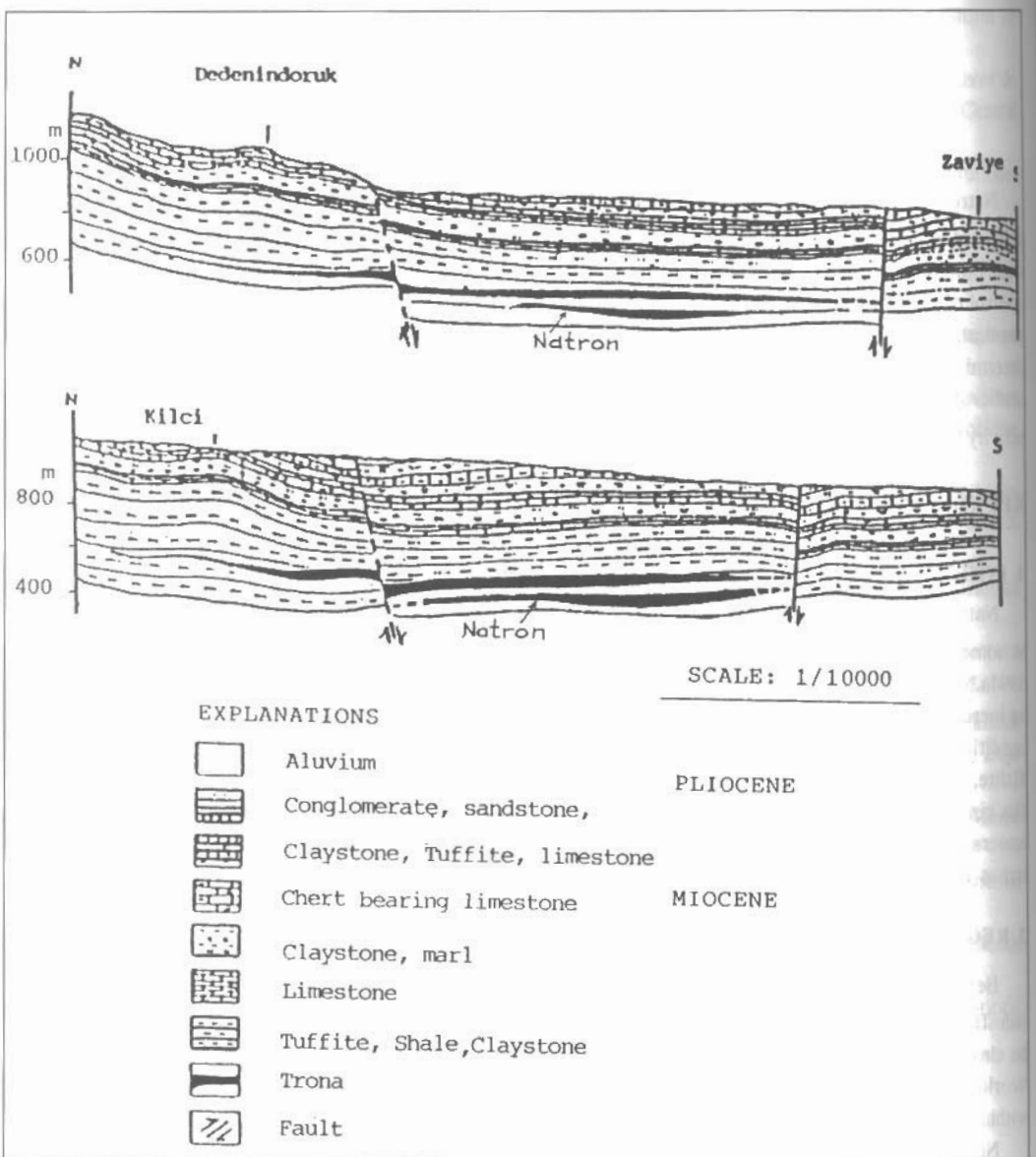


**Fig. 1:** Geological cross section of Beypazari basin

sequences because of the progressive tectonism during that time, all the Miocene units had been subjected to extension and compression regimes ; therefore, these accumulations were composed in the form of many thin levels or lenses. Obviously, the tectonism had affected the formerly deposited accumulations and [illegible] That process resulted in

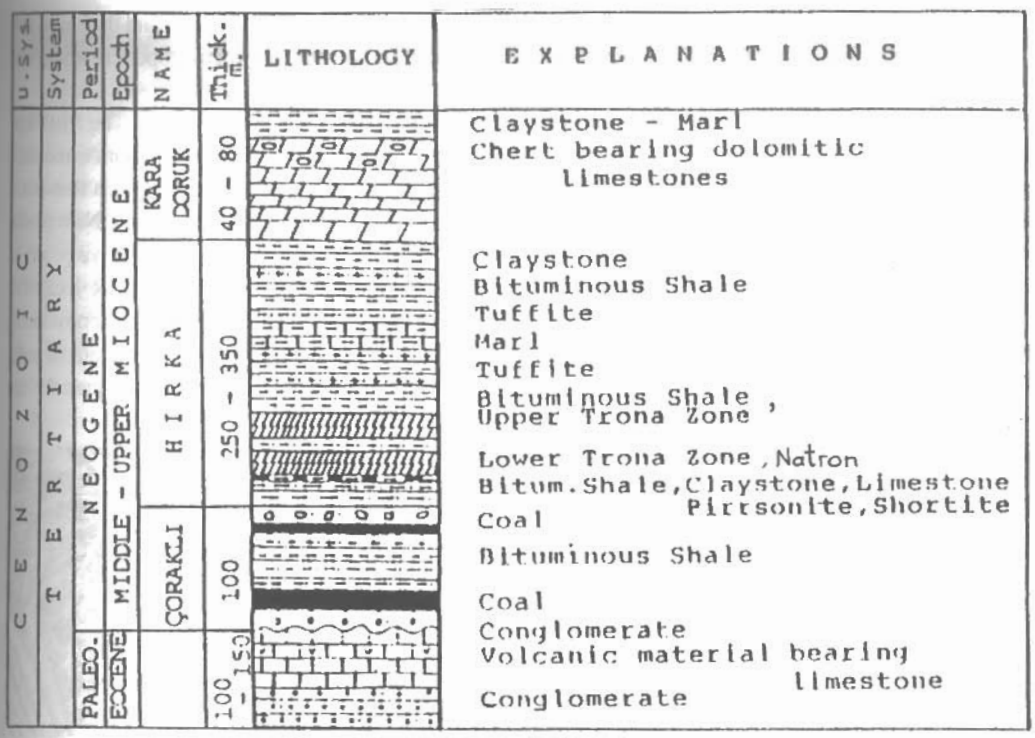


Fig. 2: Geological stratigraphic section of Neogene Beypazari Basin

modification of the volcanosedimentary sequences and the trona levels had been formed. Natron and other rare forming minerals had been occurred within different parts of the sequences depending on their chemical compositions.

## 3. MATERIAL AND METHODS

The first determination of Natron was carried out by means of macroscopic observations on the drilling samples containing tronas and claystones- marlstone complexes. The samples were studied under binocular microscope and tested by XRD, DTA and SEM techniques. XRD investigations were performed under the conditions of $2\theta = 1°$, Ni filter, Cu (Ka). DTA studies are made under the conditions of Pt-Pt/Rh thermoelement, normal atmosphere,10/Min. heating speed and 2.5 mm./min. recorder speed. SEM investigations were also performed; Jeol type JSM-35 Electron Microprobe was used. The chemical analyses were performed by gravimetric, colorimetric and spectrometric methods (Bürküt, 1985). Major and trace element analyses were carried out by means of classic wet chemical methods ; $Na_2CO_3$ analyses were achieved by using E-536 and EA-21 combined electrode , 0.1 N HCL and $Na_2CO_3$ as a reference solution

## *4. MINERALOGICAL AND PETROGRAPHICAL STUDIES*

Natron was observed associated with together with trona , the main mineral in the basin. They were generally determined in the upper parts of trona .On the other hand Thermonatrite, another rare mineral, $Na_2CO_3.H_2O$, was also identified in the same sequence and under the same mode of occurrence bearing very similar physical characteristics. Therefore, it is quite difficult to distinguish these two minerals from each others particularly by macroscopic studies; hence detailed studies like XRD and others such as DTA

and SEM are required for precise determination. Both two minerals are white in color and they have soft and fibrous structures. The studies performed under binocular and polarizing microscopes revealed that they had been formed a thin platy cover on the surface of tronas.

XRD and DTA studies were performed and their patterns are presented in Fig. 5 and 6. The XRD data are very useful in the determinations of evaporative minerals, especially for hydrated sodium carbonates such as Thermonatrite, Natron, Trona etc. Furthermore , the DTA analyses are more precise than XRD data, due to their exact data about dehydrations which is evidently important in Natron and Thermonatrite definitions. Two peaks observed at 29.35 and 30.46 2Θ are the most distinctive points in XRD determinations ; DTA remarks of Natron are characterized by a single dehydration peak located at 17° C and also by a large endothermic decomposition peak as it is seen in the Fig.4. The decomposition of Natron is exceptionally completed around 150° C, that is the earliest point among the other hydrated soda-related minerals such as Trona, Nahcolite, Thermonatrite. Therefore, DTA data are significant for the studies.

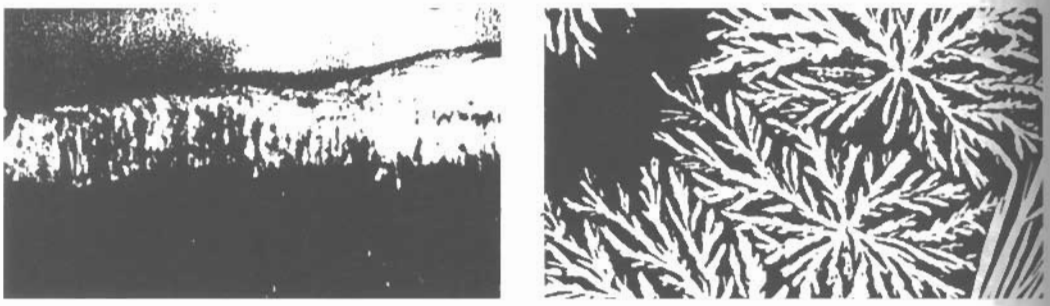

**Fig. 3:** Natron crust on the pure Trona hand-specimen (a) and Natron features of thin section (b). Fringe of acicular Natron crystals on radially fibrous Trona crystals. Cross section X 10

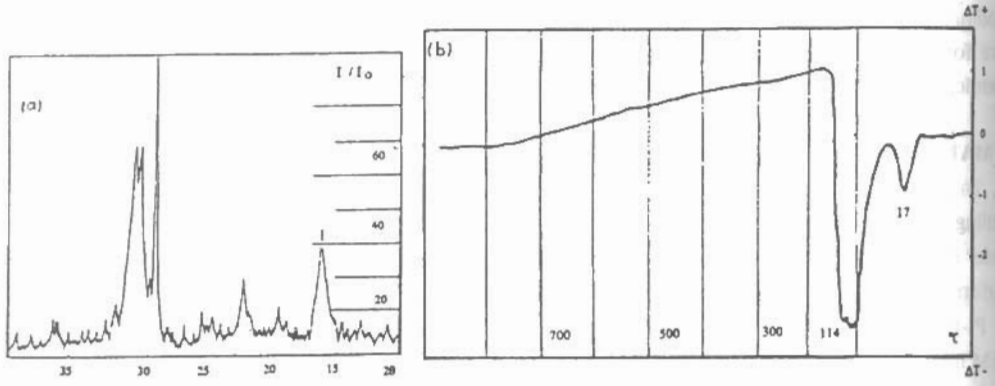


**Fig. 4:** XRD (a) and DTA curves (b) of Natron mineral

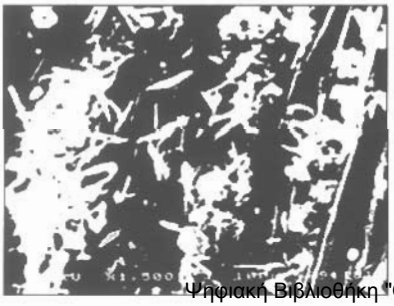

**Fig. 5:** SEM image of Natron. Fibrous and acicular crystals on trona planes

As a result of the investigations, characteristic fibrous and acicular Natron crystals were determined. As equal crystal dimensions are common it is thought that rapid formation processes were determinative in the paragenetic evolution in the basins. The mineral was observed generally along the cracks within tronas in the form of small seams.

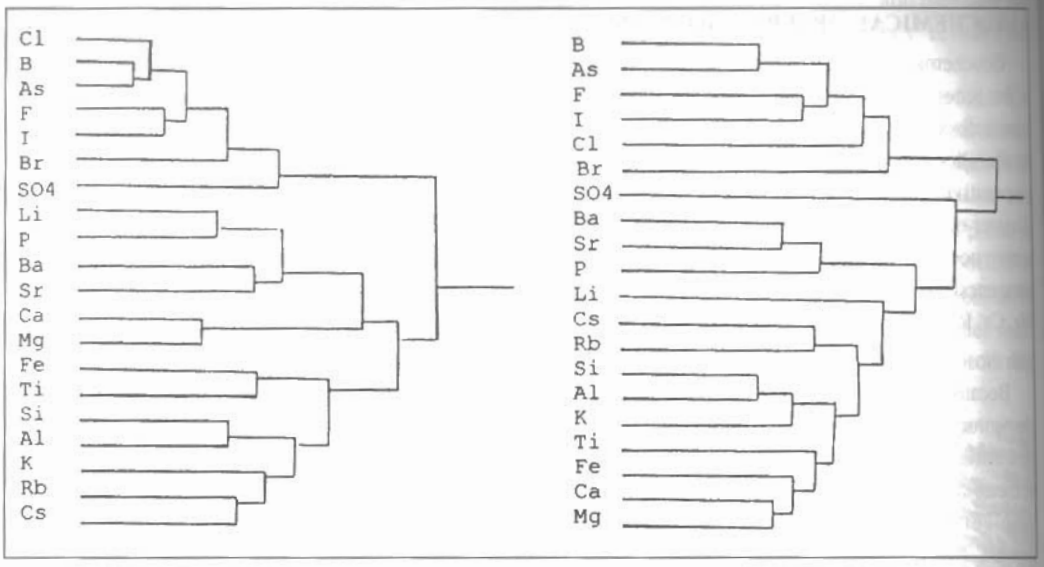


**Fig. 7:** The cluster results performed on the samples of natron(a) and trona(b)

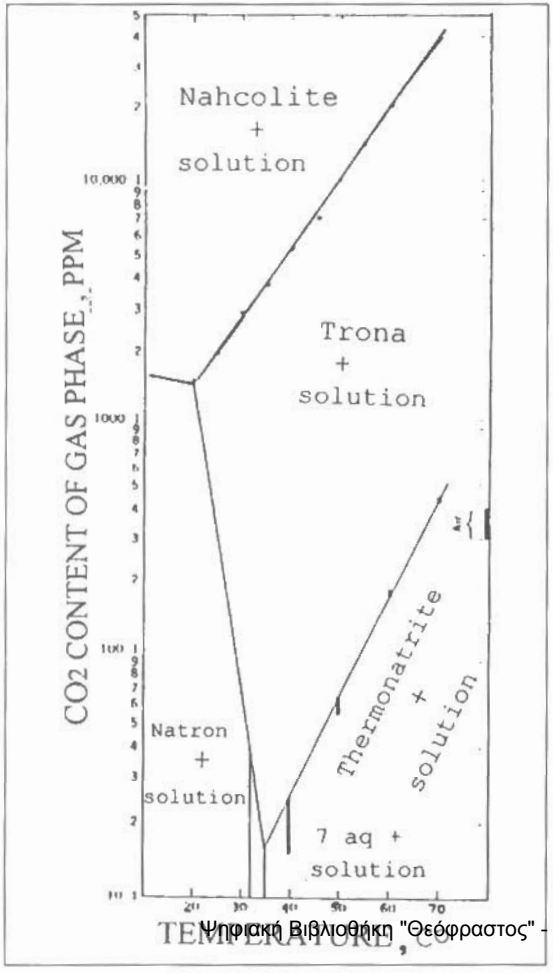


**Fig. 8:** Na-$CO_3$-$HCO_3$ stability diagram ( Na % / T, °C) (Bradley & Eugster,1969)

Trona is the main mineral in all the diagrams because of having the highest stability among the other evaporative carbonate minerals observed in the studied basin. Therefore, trona is the widely known mineral in the world. On the other hand, trona can easily form under the effect of atmospheric conditions and the partial pressure of $CO_2$. That property provides it the advantage of forming in actual lacustrine lake as it is precipitated today in the lake Chad and Magadi. On the contrary , Natron formation is restricted in term of Na % , although it can also form under atmospheric conditions

## 7. RESULTS AND DISCUSSIONS

Natron may form primarily or secondarily from solutions or from evaporative minerals such as early formed carbonates and bicarbonates which have been precipitated

according to composition of the solutions during the starting periods of the formation of the Beypazari Basin.

$$2\,(Na_2CO_3.NaHCO_3.2H_2O) + 25\,H_2O \longrightarrow 3\,(Na_2CO_3.10H_2O) + CO_2$$

Trona → Natron

Not only Na-bearing carbonates but also Ca / Na double carbonates and bicarbonates may be responsible for Natron formation as it is explained below.

$$2Na_2CO_3.2MgCO_3.Na_2SO_4 + 2(Na_2CO_3.CaCO_3.5H_2O) + 40\,H_2O \longrightarrow$$

Gaylussite

$$\longrightarrow 4(Na_2CO_3.10H_2O) + 2CaMg(CO_3)_2 + (Na_2SO_4.10H_2O)$$

Natron

In general, all Na-bearing evaporative minerals, mainly trona, natron, thermonatrite are very soluble occurrences. Therefore, they may easily decompose under the effect of meteoric parameters and then they turn into liquid phases. Consequently, it is difficult to identify them in the field. Because of this case, they had been protected by sedimentary sequences such as claystones, marlstones, tuffs and tuffites as it is seen in Beypazari volcanosedimentary basin where many rare forming minerals had been formed very scatteredly within the units. Natron is one of these minerals and it is postulated that it had been formed from the trona in the upper sector of the lower trona horizon.

## 8. CONCLUSIONS

Natron is a rare forming mineral and its properties are explained in detail, to our knowledge, in this study for the first time .The mineral was determined within the volcano sedimentary sequences in Turkey. The mineralogical and geochemical characteristics were investigated. The physicochemical parameters under which Natron has been formed and deposited were discussed. The possible relations to other observed evaporate species in terms of formation conditions were investigated.

All determined Natron occurrences are observed in the form of thin crust either on the upper parts of the main trona levels or within claystone-marlstone units. They were observed very rarely in the whole trona deposits and they are also determined on the drilling samples. The trona deposits had been formed in the form of two disconnected seams and Natron were only found in the upper parts of the lower trona seams. The mineral is soft and white in color and carries fibrous and acicular structures. Because of large amount of water molecule, i.e. $10H_2O$, it can form under the effect of high activity of $H_2O$. Due to the presence of many trona levels and also actual tectonism, necessary Na and $CO_3$ ions are present in the concentrated solutions. On the other hand $CO_3/HCO_3$ ratio is equal to 1 in the structure of trona, which is another critical point responsible for the formation conditions. Atmospheric conditions are also not a limiting factor during the crystallization of Natron.

Macroscopic studies revealed that Natron was found associated with trona generally within claystone-marlstone units. These assemblages were also determined during the SEM studies. Geochemical analyses focused on the content of major and trace elements also exhibits a similarity between these two minerals. The cluster analyses were performed and the same trend was obtained except $SO_4$ which has clustered over all elements in Natron possibly indicating to the effect of more oxidizing conditions during the formation steps of Natron.

In the studied basin, Natron, as explained before, was determined on the upper part of the lower horizon; on the contrary, Nahcolite was found on the upper part of the upper trona horizon

(Suner,1994,b). This different deposition is a result of different formation conditions which were responsible for two main evaporation periods in the basin.

At the end of the first period, because of the increasing $CO_3/HCO_3$ ratio and the activity of $H_2O$ and temperature, Natron has found the suitable conditions for formation in a very limited time period. During this stage, condensed solutions have also contributed Natron crystallization in the form of small pockets under the effect of diagenesis. On the other hand, at the closing time of the basin, Natron has not been formed because of the increasing $HCO_3$ content due to entrance of fresh waters into the basin. Therefore, the upper part of the basin were covered by Nahcolite, ($NaHCO_3$) crust, which was formed under the effect of low temperature and of high $CO_2$ activity.

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