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NAHCOLITISATION: AN EXAMPLE FROM THE BEYPAZARI BASIN (TURKEY)

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ABSTRACT

Nahcolite ($NaHCO_3$) is a rare mineral and it has been formed, in general, in closed lacustrine basins depending largely on physicochemical conditions. This mineral has been found in the uppermost part of the Beypazari Neogene basin (Turkey) together with trona mineral ($Na_3H(CO_3)_2.2H_2O$). In this basin, Nahcolites have been deposited secondarily from the solutions generated from tronas, as a result of the increase of HCO_3 and H_2O activities. This way of formation was termed as Nahcolitisation and this process takes place because of the incongruent melting property of the trona. The petrographical and geochemical data have also supported the presence of this process which was the main reason of nahcolite formation in the basin.

INTRODUCTION

Nahcolite ($NaHCO_3$) is a rare mineral.It has been found in primary inclusions in apatite crystals (Aspden, 1980), in organic rich sediments (Reitsema 1980), in volcanic environments (Key 1979) and in the Beypazarú Neogene Basin, Turkey (Suner 1991 a & b). In the Beypazari deposits it had been formed together with other sodium and calcium carbonate-bicarbonates. Its colour is ranging from white to grey on pure samples and it is formulated as $NaHCO_3$. This mineral had been deposited generally in nodular forms in clayey and dolomitic matrixes(Suner 1989, Reitsima 1980). The most distinctive property of Nahcolites which show very similar macro - microscopic features to those of trona and other sodium carbonate minerals is the twinning structure which is easily observed in thin sections(Suner, 1989). Nahcolitisation is the term used for the transformation of trona. The formation and precipitation of Nahcolite depend largely on temperature and as well as on sodium, carbonate and bicarbonate contents of brines. It can be deposited directly from brines or as a secondary mineral as a result of transformation from trona, another sodium carbonate. In this paper, on the basis of recent investigations of the Beypazari deposits (Suner 1989 a & b, 1991 a & b,1992) the procedure and physico - chemical principles of Nahcolitisation will be discussed.

FORMATION OF NAHCOLITE

The formation conditions of Nahcolites can be studied by taking into account two main parameters the geologic and the physico - chemical ones.

Geologic conditions : Nahcolites had been formed, in general, fault-

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related and in closed lacustrine basins. Volcanic activity is an important parameter which contributes not only the necessary ions but the tectonic elements being responsible for the evolution of basin. Usually these conditions are also suitable for the formation of other carbonate minerals such as trona $Na_3H(CO_3)_2.2H_2O$, pirssonite $Na_2Ca(CO_3)_2.2HO$, gaylussite $Na_2Ca(CO_3)_2$ $5H_2O$, halite, analcime, magnesite and smectite group minerals (Bradley-Eugster, 1969; Eugster, 1979; Suner, 1989).In general, these sodium minerals have been deposited, alternating with shales, claystones, volcanics and limestones, forming small and nodular accumulations (Suner, 1991,1992).In the Beypazari deposit, nahcolites which constitute the known largest reserves of in Utah (USA), has been observed in the uppermost part of trona levels, which were deposited two disconnected seams.

Physicochemical conditions : Nahcolite has been deposited depending largely on physicochemical parameters and their change were very effective for the formation and transformation of this mineral. The main parameters are $^aCO_2$, ^aNa, ^aH_2O, $^aHCO_3$ and temperature. Those can be discussed on three and four-component phase diagrams, which are very useful particularly in understanding the formation paths of salt deposits (Eugster, 1979, Suner, 1992).

NAHCOLITISATION IN THE BEYPAZARI DEPOSITS

Nahcolite has been formed primarily from the solutions containing Na and HCO_3 in appropriate proportions or secondarily from solutions generated from tronas (precipitated in earlier stage), as a result of increasing HCO_3 activity. This second way of formation was termed as Nahcolitisation. Nahcolites, found in the Beypazarú deposits, were observed mainly together

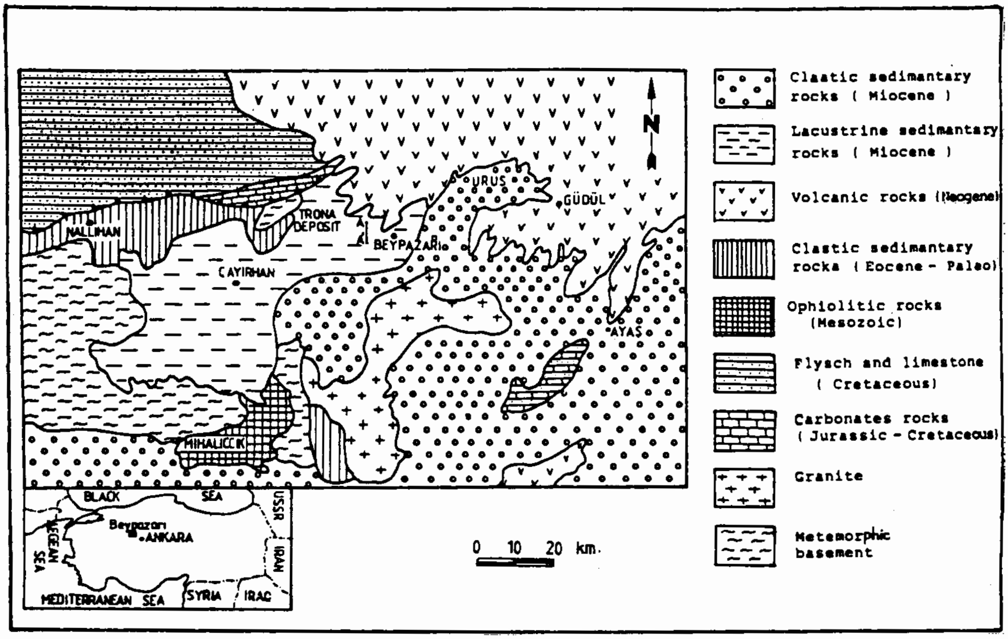

Fig. 1: Geological map of the area with the Nahcolite and trona bearing formations of the Neogene deposits (Suner, 1992).

with tronas and more rarely in the form of single and nodular accumulations which have been formed through nahcolitisation.

This phenomena can be formulated and explained by the reaction mechanisms stated below :

$CO_2 + H_2O + Na_2CO_3.NaHCO_3.2H_2O \longrightarrow 3NaHCO_3 + 2H_2O$

In this procedure, CO_2 has been used for the production of HCO_3 as follows :

$CO_2 + H_2O + CO_3 \longrightarrow 2HCO_3$

$CO_2 + H_2O \longrightarrow H + HCO_3$

As a result of the above reactions, the amount of HCO_3 in the solutions increased and reached to form nahcolite. In all these procedures, the most remarkable point is the incongruent melting property of trona, which is the main reason of trona - nahcolite assemblages in evaporative basins.

The assemblage Trona - Nahcolite - Natron, has been studied and some crystallisation paths are plotted in Figure 2. Depending on the formation ways, the mineralogy and paragenesis of sodium carbonate deposition could be discussed. Three possible paths has been investigated and examplified on the basis of the mineralogy and geology of Nahcolites in the Beypazarύ deposits.

As it is shown in figure 2, nahcolite has the largest crystallisation area and it forms mainly from the solution which contain HCO_3 and CO_3 in equal proportions, under the effect of high H_2O activity. Nahcolite forms mainly in the beginning and closing time of the sedimentation in the basin because of the high water and bicarbonate content and due to the low temperature conditions which are generally more effective at these periods. During these various formation steps, nahcolitisation is largely depend on the first crystallisation point. In other words, the composition of the solutions from which the first formation of nahcolite is observed is very important (Fig.2).

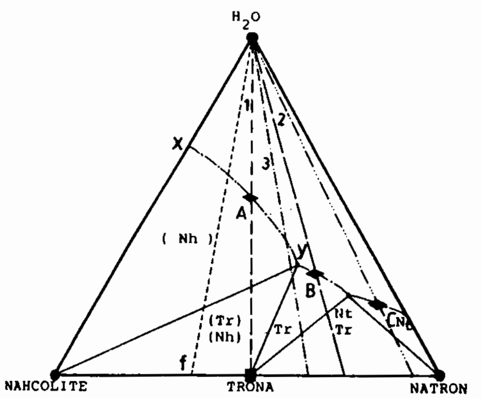

Fig. 2: Nahcolite - Natron - H_2O ternary diagram (Bradley & Eugster,1969).Nh: Nahcolite, Tr: Trona, Nt: Natron

In this system, Y is a physicochemically unchangeable point where trona and Nahcolite crystallisation exists. At this point, trona and nahcolite crystals are in equilibrium with the solution and the composition of the system is 21.84 % nahcolite, 44.82 % natron and 33.34 % H_2O. The system is now blocked, unless all crystallised nahcolites are converted to tronas. Then, system can continue to work giving trona crystals and H_2O content decreases.

In other words, in this first case, during evaporation, trona and nahcolites cannot crystallize from the same solution at the same time. Either trona or nahcolite may crystallise as long as evaporation continue. In some cases, as a result of the high concentration of $NaHCO_3$, the composition of the solution cannot reach to the Y point ; therefore trona cannot form. On the other hand, the filling of sedimentary materials into basins was the other reason for the interrupting of crystallisations in this kind of systems.

In the second case, the increase of H_2O in the system, by the entrance of solutions and fresh waters to the basin from various sources, caused a higher activity of H_2O, changing the composition of the system from Y toward X or even to a higher point. This procedure provides results to the conversion of trona to nahcolite mainly to nahcolitisation.

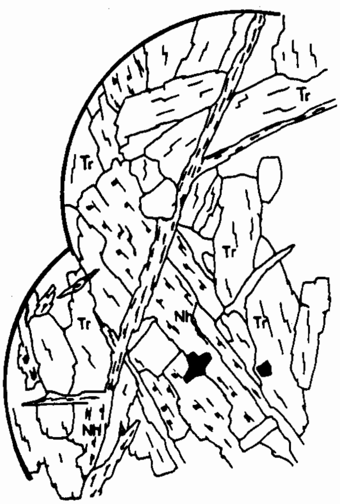

Fig. 3: Microscopic view of Nahcolites (Nh) and Tronas (Tr), X 26, (Suner,1989).

Nahcolites,discovered in Beypazari, have formed generally by the second process. Not only petrographical data but also chemical analyses and geochemical observations supports this conclusion. They have been found out in the upper parts of trona levels and mostly together with tronas instead of single nodular forms and seams. Only the uppermost levels of the deposits nahcolites have been partly accumulated in nodular forms. In Figure 3 and Table 1, the observed petrographical and geochemical similarities between tronas and nahcolites are presented. The chemical analyses were performed by gravimetrical and spectrometric methods (Bórkót, 1985).

It is important to note that nahcolites cannot form under atmospheric conditions, as it is shown in Figure 4 ; only trona,natron and thermonatrite, depending on the temperature, can formed under the effect of atmospheric CO_2,that is 300-400 ppm. In other words, under atmospheric conditions, nahcolites have to convert to natron or trona depending on the formation temperature. The necessary CO_2 content, in the solutions, for the formation of nahcolites is more than 1700 ppm and this requires the entrance at very high amounts of HCO_3 entrance to the basin from different sources, which most probably were provided by rivers at the closing period of the Beypazari Basin.

As it is noticed in Figure 4; the increase of CO_2 into the solutions results to an increase of bicarbonate ratio, (HCO_3/HCO_3 + CO_3). This new composition of the solution may favour the formation of Nahcolite formations. In that case, physicochemically, this requires an increase in temperature and trona as a more stable phase will crystallise instead of nahcolites (Fig.4). On the other hand, most probably rivers and other continental sources will create a decrease in temperature. Therefore, in the formation of nahcolites, the increase of temperature and CO_2 in solutions are two contrary-working factors.

For this reason, nahcolitisation is the most favorable way in Nahcolite formation. In other words, nahcolite occurrences are mainly the result of nahcolitisation process, which starts as a result of a sudden increase in the HCO_3 content of the solutions under the effects of burial sedimentary processes.

At the end of evaporation period, filling the basin by volcanosedimentary material and covering trona levels favourable conditions are created for the conversion of trona to nahcolite. Under the effect of these geologic conditions, the solutions circulating in the buried sediments, caused the conversion and trona started to dissolve. Therefore, the conversion mechanism was started after fresh waters and sedimentary materials had filled up and covered trona levels. Pore solutions were also responsible for the procedure.

	Al	Mg	Ca	K	Sr	Cs	B
Trona	266	7859	1172	19	214	631	18
Nahcolite	118	7410	1110	23	198	576	9
	Rb	**Fe**	**F**	**Ti**	**Ba**	**As**	**Li**
Trona	11	65	4875	3	575	284	3
Nahcolite	16	61	3075	-	538	180	5

Table 1: The average major and trace element contents in nahcolites and tronas (Suner,1989,1991,1992).

Buried sedimentary environments and their circulating solutions create a suitable environments for nahcolitisation, particularly concerning the CO_2 content because atmospheric conditions were out of question. Furthermore, these conditions favors the presence of organic matters, which with the bacterial fermentation produce 13C-rich carbon dioxide and controls the formation of nahcolite rather than trona (Reitsema 1980). Nahcolitisation, as it is explained, is observed in closed environments and buried sequences after trona crystallisation depending on the composition of the solutions. The increase of the HCO_3 content results to the trona dissolution and to the nahcolite formation. The last trona levels at the Beypazarú deposits were mostly converted to nahcolite. In some cases, the HCO_3 content of the solutions, was not high enough to give the total conversion which is shown by the way f in Figure 2.

CONCLUSIONS

The most important conclusions can be summarized under following seven points :

1- Nahcolite is a rare forming mineral in the world and its deposition is largely depend on the physicochemical conditions.

2- Nahcolitisation is a process which takes place because of the incongruent melting property of the trona .

3- The decrease of temperature and the increase of the HCO_3 and H_2O contents in the solutions favors the nahcolitisation process.

4- The solutions within the buried sediments are largely responsible for the nahcolitisation process (non-atmospheric conditions).

5- As a result of high sedimentation rate the nahcolitisation takes place very rapidly resulting to accumulation of nahcolite.

6- Under the atmospheric conditions, as trona being the most stable sodium-carbonate phase, nahcolite crystallisation is very limited.

7- Nahcolites discovered in the Beypazarú basin were mostly formed because of the nahcolitisation process.

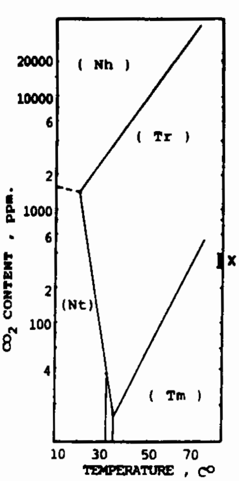

Fig. 4: Trona (Tr) - Nahcolite (Nh) - Natron(Nt) - Thermonatrite (Tm) stability as a function of temperature and CO_2 content. (Bradley-Eugster,1969)

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