Geology of the Wucheng Trona Deposit in Henan, China

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INTRODUCTION

Modern alkali lakes with trona sediments are distributed in Nei Menggu, Xinjiang and other provinces in China and are also found in other parts of the world, such as the well-known Sears Lake in the U.S. and Magadi Alkali Lake in Kenya. However, ancient trona deposits are rare and only two have so far been discovered: the Green River trona deposit (Eocene in age) in Wyoming in the U.S. and the Wucheng trona deposit (late Eocene in age) in Henan province of China. Trona deposits are of an evaporite type but somewhat different in origin from other salt deposits, such as those having halite and sylvite, and have their special metallogenic conditions and depositional mechanisim.

GEOLOGICAL CHARACTERISTICS OF THE WUCHENG TRONA DEPOSIT

Regional and Ore-District Geology

The Wucheng Basin, which contains the trona deposit, is a Tertiary fault basin that began to form and develop in the late Eocene epoch. It covers an area of 260 km^2 and is controlled by two sets of faults striking northwest and northeast, respectively, and resulting in a roughly elliptical form for the basin (Figure 1). The Archean mixed gneiss occurs in its south part, Paleozoic schist and metamorphic intermediate-basic volcanic rock, etc. in the north, east and west, and the Yanshanian granites in the south and northwest.

The whole interior of the basin is occupied by the Cenozoic rock formations, with the terrigenous clasts-evaporite more than 2,400 m thick. The stratigraphic units are described in ascending order as follows:

Lower Tertiary—the late Eocene Maojiapo Formation (purplish red conglomerate and sandstone, 530 m thick), the Lishegou Formation (greyish yellow and green sandstone and mudstone, with argillaceous dolomite and low-quality oil shale in the upper part, 580 m thick), the Wulidui Formation (grey argillaceous dolomite and oil shale, with salt and soda in the lower part 850 m thick), and the Dazhangzhuang Formation (greyish-green thick-bedded silt mudstone with low-quality oil shale, 300 m thick)

Upper Tertiary—variagated or brown sand conglomerate and sandy mudstone, overlying the Lower Tertiary in an angular unconformity, (0 to 200 m thick).

The basin is well closed, steep in the south and gentle in the north, with the center of subsidence near the south side and the maximum depth of about 2,000 m.

Geology of the Deposit

The alkali deposit occurs in the lower member of the Wulidui Formation of the Lower Tertiary, 650 to 970 m below the surface. It is multi-bedded, strikes ENE and generally dips 8° to 10° towards SSE and covers an area of 4.6 km^2.

The deposit has altogether 36 ore beds, each of which has a foot wall consisting of brown oil shale and an upper wall of silt-bearing argillaceous dolomite. The lower 15 beds are generally 0.5 to 1.5 m thick, with the maximum of 2.38 m, and consist of trona, the upper 21 beds are generally 1 to 3 m thick, with maximum of 4.56 m, and consist of mixed rock salt and trona. Therefore, the whole ore-bearing stratum is divided into two: the lower trona section and the upper salt-trona section. Besides, it can be divided into seven ore associations from bottom to top according to rhythic features, which are arranged in an imbricate form sequentially from the northwest to the southeast.

The chemical composition of the ore beds is mainly Na_2CO_3, $NaHCO_3$ and NaCl, with traces of other elements such as K and Br. Analyses show that the average percentage of the chemical components of the trona beds

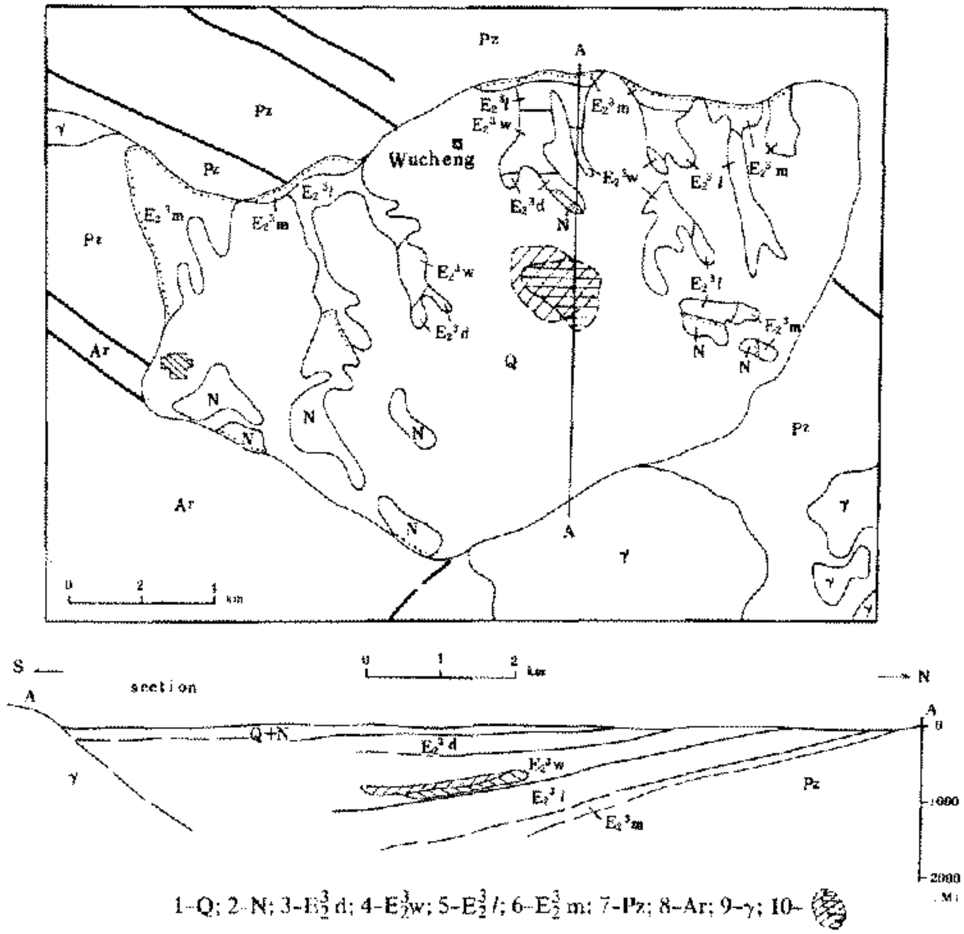

Figure 1. Sketch of the regional geology of the Wucheng trona deposit. (Modified from the 12th Geological team of henan). 1. Quaternary System; 2. Upper Tertiary; 3-6. Lower Teritary (3. Dazhangzhuang F; 4. Walidui F; 5. Lishigou F; and 6. Maojiapo F.); 7. Paleozaic; 8. Archean; 9. Granite; and 10. Soda ore (vertical line: trona of lower part; horizontal line: salt and soda of the upper part).

are as follows: $NaHCO_3$ = 40.28, Na_2CO_3 = 28.23, NaCl = 0.54, SO_4^{2-} = 0.02, H_2O = 9.42 and water-insoluble substances = 21.21.

The content of water-insoluble substance in these ore beds is remarkably high because of the presence of thin argillaceous dolomite and other muddy matter, while in the upper salt-trona beds the muddy intercalations are decreased, thus reducing the content of water-insoluble substance.

Trona is the predominant salt mineral of the deposit, and halite and nahcolite come second. Shortite and northupite are found associated with trona in ore beds but are mostly limited to foot and upper walls (mainly in footwall oil shale) as granular aggregates, laminations or a dentritic form (cross-cutting but not disturbing the bedding). (In China, shortite was first discovered in the Wucheng area). In country rocks, there are also pyrite, pyrrhotite, dolomite, clay minerals, calcite, opal, analcite and dry asphalt, etc.

Sedimentary Characteristics for the Ore-bearing Sections

1. The deposit is characterized by well-developed rhythmic sedimentation in the ore-bearing strata. The lowest beds are rhythmites composed of silt-bearing argillaceous dolomite-oir shale-ore bed (Figure 2). The lower ore-bearing section consists of trona, containing rhythmites generally 4 to 6 m thick, whereas the upper ore-bearing section consists of salt-trona, containing rhythmites 8 to 12 m thick and oil shale and ore beds thicker than those of the lower ore-bearing section.

Obviously, every rhythmite reflects a process of concentration, i.e., a change from the fresh lake water to the saline. At first the Ca- and Mg-carbonate precipitated abundantly, and then the brine became concentrated and trona precipitated. In the late portion of a depositional cycle, a chloride stage occurs during which the halite is deposited. All the trona precipitated on the oil shale, which is widely distributed. The area, where the shale is highly concentrated, strongly layered, comparatively

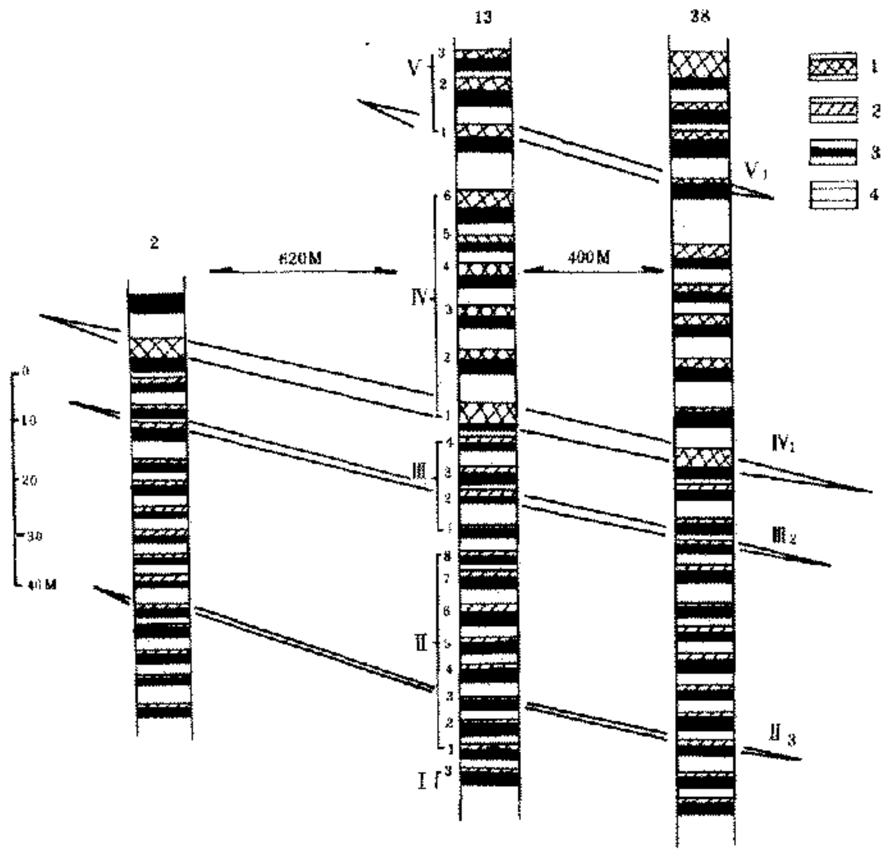

Figure 2. Sketch of the texture of and comparison between rhythmites in the ore-bearing sections. 1. Salt-trona ore; 2. Trona ore; 3. Oil shale; and 4. Silt-bearing argillaceous dolomite or dolomitic mudstone.

thick and rich in oil, is just the area where trona is precipitated. Moreover, lumps or thin beds of trona are often found in the oil shale near the ore beds. This demonstrates an alkaline water medium is the environment for the oil shale deposition, which is basically consistent with that for the trona precipitation.

2. The chemical composition of the ore bed shows a regular change both vertically and laterally. As exemplified by the No. 1 bed of Ore Association IV (Figure 3), we find the lowest part is dominated by Na_2CO_3 and $NaHCO_3$, with rare NaCl; the marginal part is dominated by $NaHCO_3$; the middle part is dominated by NaCl, with less $NaHCO_3$ and Na_2CO_3; and the uppermost part has a smaller extent, with decreased NaCl but increased $NaHCO_3$ and Na_2CO_3 laterally, has no NaCl sediments in its southwest and southeast marginal zones. This indicates that during the concentration of the brine, the area of the water body gradually reduced, resulting in a smaller extent of NaCl deposition.

The above mentioned features can only be found in well-developed horizons. Due to the influence of various factors, the trona bed is absent from the uppermost part of many horizons, but in the Ore Associations VI and VII some horizons are dominated by NaCl, indicating a trend of strong concentration for the chloride brine. This is in accordance with the general law of development for carbonate lakes.

3. It is important that in the ore-bearing section, even in the sediments of the whole basin, no sulphate minerals have been found. Generally, these minerals commonly occur in carbonate lakes. For instance, mirabilite and other minerals of the same type occur in modern soda lakes in China but are absent from the study area.

ORIGIN OF THE TRONA DEPOSIT

A trona deposit is of the same metallogenic series as salt deposits. It is not the product of a simple brine evaporation but has its own particular metallogenic conditions and sedimentation mechanism.

Metallogenic Conditions

Sedimentary environment. The Wucheng Basin is an inland basin of terrestrial salt-lake sediments. No evidence of marine sediments has been found through stratigraphic and palaeontological studies. The possibil-

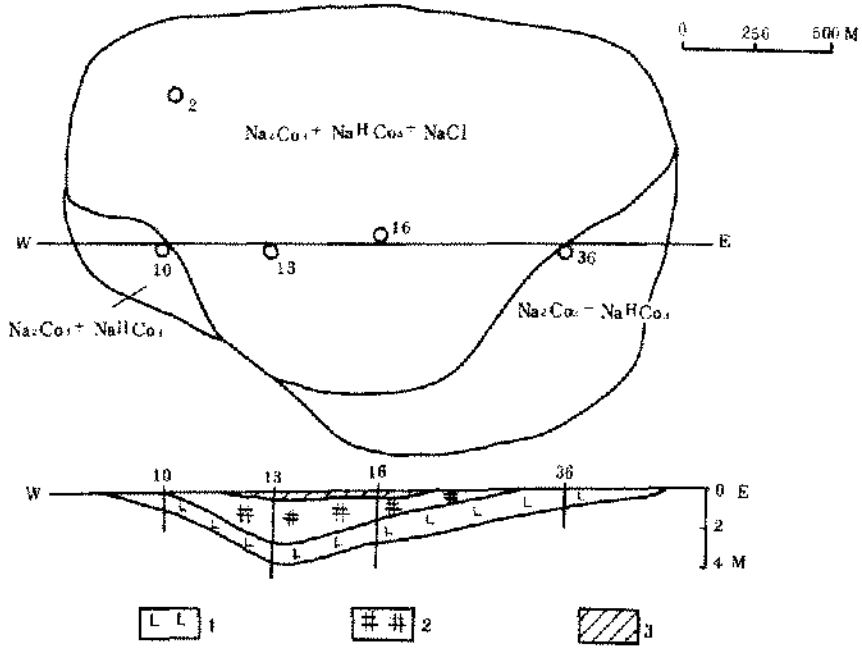

Figure 3. Distribution of chemical composition for the No. 1 bed of the Ore Association IV. 1. $Na_2CO_3 + NaHCO_3 > 70\%$, $NaCl < 3\%$; 2. $NaCO_3 + NaHCO_3 < 20\%$, $NaCl = 60\text{-}70\%$; and 3. $Na_2CO_3 + NaHCO_3 > 40\%$, NaCl is about 50%.

ity of a marine environment may also be excluded because trona must precipitate in a carbonate lake. In other words, the precipitation of trona can only be caused by the carbonate-type of water in which the carbonate ions are highly concentrated and the pH greater than 9 (still greater as the soda-forming proceeds), i.e. the chemical type of the water must meet the formula $(CO_3^{2-} + HCO_3^-)/(Ca^{2+} + Mg^{2+}) > 1$. Seawater is quite different. It is of the water of magnesium sulphate type. All the data of seawater evaporation experiments show that trona cannot be precipitated from seawater. It follows that the trona ore can only be produced in terrestrial carbonate-water lakes. Moreover, only when large amounts of Na^+ exists can the sodium carbonates be precipitated after the deposition of Ca- and Mg-carbonate. Therefore, the recharge of carbonate-type water rich in sodium is one of the basic conditions for the formation of a trona deposit.

The Wucheng Basin is surrounded by metamorphic and igneous rock according to the analysis by the Regional Survey Team of the Henan Geological Bureau, these rocks contain 4.80% to 5.90% of Na_2O, 0.32% to 1.36% of CaO and 0.1% to 0.73% of MgO. Obviously, the surface water and phreatic water flowing through the rocks would bring abundant Na^+ to the lake basin. These waters are all of a bicarbonate type.

The analysis of the representative spring water from the northern margin of the basin indicates that the water contains 381.54 mg/L of HCO_3^-, 2 mg/L of SO_4^{2-} and 2.73 mg/L of Cl^-. The recharge of this type of water is the necessary condition for the deposition of the trona of the Wucheng deposit.

Relation between trona and organic matter. The formation of a trona deposit requires, besides the recharge of the carbonate-type of water, the continuous supply of abundant CO_2. Figure 4 provides the theoretical basis for this problem. The contents of CO_3^- and HCO_3^{2-} in the solution are related to the partial pressure of CO_2, as shown by the equilibrium formula $CO_3^{2-} + CO_2 + H_2O \rightleftharpoons 2HCO_3^-$. If there is a continuous supply of CO_2, nahcolite and trona would be formed; if not, soda or thermonatrite would be formed. Obviously the formation of a trona deposit requires the supply of abundant CO_2. But what is the source of the CO_2? As mentioned above, before the deposition of trona, extensive oil shale had already been deposited. During that time, a lot of planktonic organisms died. Undoubtedly the decomposition of the remains of the organisms to release CO_2 would become the main source of the CO_2 in the lake water. Therefore, the deposition of trona has a close genetic relation with organic matter, which is also maybe the reason why the trona is deposited immediately above the oil shale.

It can be seen that the recharge of the Na-rich water of carbonate type from metamorphic and igneous rocks and the presence of abundant organic matter are the most important conditions for the formation of a trona deposit. This is quite different from other salt deposits, namely, the trona deposits have a special source of ore material. Without these two conditions, no trona deposits would be

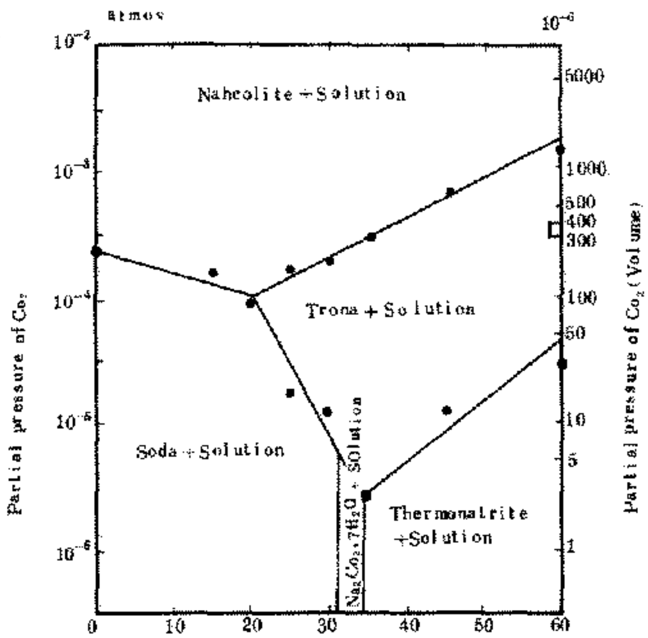

Figure 4. PCO_2–T diagram of the system of $NaCO_3$-$NaHCO_3$-H_2O. (After Qui Yihua et al., Manual of Salt Mineral Determination).

formed, as has also been demonstrated by some other trona deposits in China and other countries.

For example, modern alkali lakes are also found in Ih Ju League and Xilin Gol League of Nei Menggu and in Hami of Xinjiang. The water recharged to these lakes is all dominated by the HCO_3– Cl-Na or HCO_3-Na type, and the soda beds are just in the black ooze. In the Biyang Depression of Henan Province, highly concentrated alkaline brine occurs in the interbedded dolomite and oil shale in the lower part of the upper Eocene. The Green River trona deposit in the U.S. is also of terrestrial sediments of a carbonate lake, and strongly similar to the Wucheng deposit. The most interesting similarity is that the Green River deposit also has the sedimentary rhythmite of oil shale-trona-marl and its trona bed also occurs immediately above the oil shale (Deardorff, 1971). Eugster (1971) held that trona is deposited in a non-marine sedimentary environment. Through observation in the Magadi alkali Lake, he found that the blue-green and red algae and the organisms in the lake can produce abundant gas, and he considered that this gas may be the main source of CO_2 for the precipitation of trona from high-pH (bicarbonate-poor, lake brines).

Tectonics, paleogeography and paleo-climatology. The Wucheng Basin is an asymmetric elliptical fault basin, down-faulted on the south and overthrusting onto other tectonic units on the north, and is bounded by marginal faults on the southwest and southeast (Figure 1). A major boundary fault on the north margin of the Huaiyang Rise bounds the basin on the southwest. This fault strikes northwest and is a large, deep, extensive fault. It controls a series of Mesozic and Cenozoic basins in Henan Province through its hereditary activities and becomes their southern boundary fault, as exemplified by the Biyang Depression to the northwest of Wucheng Basin and the Loshan Sag and Huangchuan Sag to the southeast. The fault bounding the basin on the southeast strikes northeast. Faults with similar trends are developed in the surrounding area and also bound the above mentioned sags.

It is this tectonic framework that has led to the well-closed intermont basin. On the south of the basin is the high Tongbai Range, and on the north are hills. The basin receives recharge of water from surrounding areas but has no discharge channels. Therefore, it is a good place for the collection and concentration of brine to form a deposit. The lithological, petrographical and paleohydrodynamic direction studies show that there were two rivers on the northwest and the northeast, respectively, which flowed into the basin, and that the area of the lake basin was much smaller in the late Eocene than in the earlier period and changed with the climate, and salt-alkali precipitated bed by bed with the alternation between dilution and concentration of the lake water. (Figure 5).

During the trona-forming period, the Wucheng Basin was in a subtropical climate zone with a repeated arid-semi-arid climate alternation, which is consistent with the paleoclimatic zone of central-south China in the same period (Wu Ping et al. 1980). We will not discuss it in detail here.

These paleogeographic and paleoclimatological conditions are necessary and important for the formation of evaporite. In this respect, a trona deposit is consistent with other salt deposits. In general, a structurally controlled closed basin is favourable for the accumulation and concentration of brine, and the alternation between arid and semi-arid climates may cause the evaporation of alkaline brine to precipitate alkali minerals. Although the modern alkali lakes in Nei Menggu and other places in China are distributed in temperate or temperate-frigid zones, they are all characterized by an arid or semi-arid climate. Their alkali sediments are mostly soda, often crystalized under low temperature in winter, with relatively less trona. This shows that they are quite different from the subtropical alkali lakes in which trona is the predominant sediment and that the CO_2 supply is probably deficient. All this remains to be studied.

Petrographic conditions. Petrographic conditions may exert a strict control on the trona deposit. During the alkali-forming period (late Eocene epoch), the facies-zone assemblage of the Wucheng Basin occurred as an obvious "bull's eye" pattern, thin in the center and thick on the margin, with the alkali minerals being present in the oil shale-dolomite facies zone of the center. The U.S. Green River trona deposit has the petrographic charac-

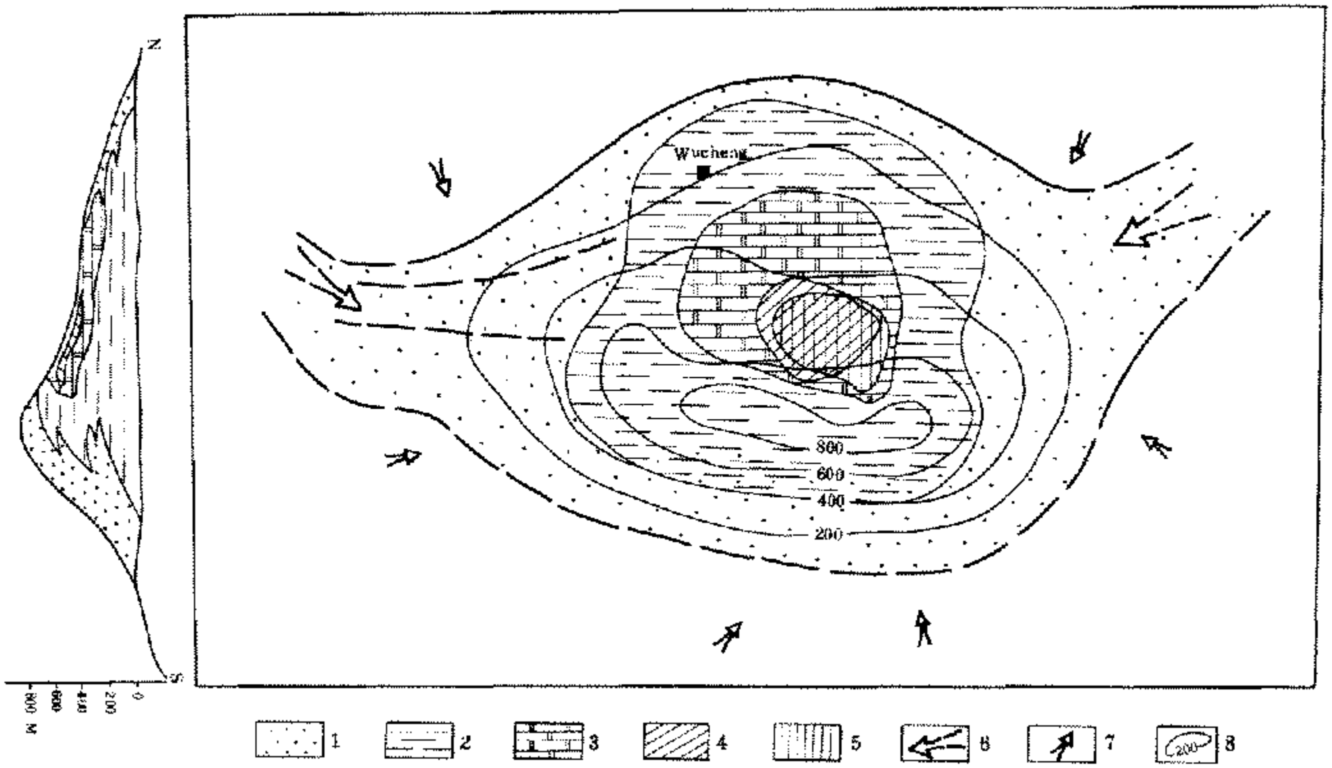

Figure 5. Facies-paleogeographic sketch of the late Eocene (Wulidui epoch) Wucheng Basin (slightly modified from 12th Geological Team of Henan province). 1. Lake shore sandstone facies; 2. Silt-mudstone-oil shale facies; 3. Oilshale-dolomite facies; 4. Trona; 5. Trona-rock salt; 6. Flowing direction of river; 7. Derivation of alkali material; 8. Thickness contours of sediments.

teristics similar to those of the Wucheng deposit and shows the same petrographic zonation: sand-mudstone on the basin's margin and marl and oil shale, rich in Mg matter, occurring in the center, and within this range trona and halite are deposited. The petrography of the two trona deposits indicates that the sound combination of dolomite, oil shale and trona is not only significant in the explanation of their origin but also valuable to the exploration of other ancient trona deposits.

Deposition of Trona

Through the above-mentioned analysis of metallogenic conditions, we may summarize the processes of brine accumulation in alkali lakes as follows; the water of a carbonate type is recharged to the lake basin through surface run-off, underground infiltration and spring etc.; during the arid period, abundant inflow of surface water is stopped, the evaporation exceeds the recharge, and the movement of ground water changed from the predominantly horizontal to the predominantly vertical. Due to strong evaporation, crystallized alkali material can occur on the mud flat on the margin of the lake basin; then, the material may be dissolved and taken into the lake by spring water or blown into it by wind, and it may also migrate into the lake due to the underground circulation of water, resulting in higher alkali concentration for the lake water. These phenomena can be observed in all modern alkali lakes.

With the evaporation of water, the brine becomes more concentrated and the alkali mineral may precipitate. This precipitation requires not only the evaporation of water but also an adequate supply of CO_2. Besides, the pH of the solution should be greater than 9 and would continue to rise; there should be abundant organic matter and a comparatively strong reducing environment for the bottom water (what mineral will be formed is dependent on this bottom water environment). The observation of salt crystallization process of Owens Lake in the U.S. shows that three minerals (natron, trona and nahcolite) crystallized at the surface of the lake and then dropped onto the bottom but were all converted into trona within one and a half years. It follows that proper temperature, CO_2 content and state of the lake's surface water may cause the precipitation of three minerals, but its bottom water is favourable for the stability of trona and may finally cause the formation of it.

The interaction of organic matter, sulfate ions and bacteria activities may produce CO_2 and H_2S; the CO_2 is immediately reabsorbed and $NaHCO_3$ is continuously produced, thus forming the trona:

$$SO_4^{2-} + 2C + 2H_2O \xrightarrow{bacteria} H_2S + 2CO_2 + 2OH \rightarrow H_2S + 2HCO_3^-.$$

From this formula, it can be seen that the CO_2 produced by the decomposition of organisms is very important to the formation of trona.

After the brine is highly concentrated, the minerals will be precipitated separately due to the difference in their solubilities. For instance, soda is generally formed in winter but trona under relatively high temperature. Under the same temperature, e.g. at 40°C, the solubility of $NaHCO_3 \cdot H_2O$ is 33.2% but that of $NaHCO_3$ is only 11.3%. Obviously, nahcolite will be precipitated first. The bottom, especially the mariginal part, of alkali beds of the Wucheng deposit is often dominated by nahcolite and the upper part by trona. This deposition order is clearly related to solubility.

There is no soda mineral, usually formed under relatively low temperature, in the alkali beds, indicating that during the alkali-forming period the temperature was relatively high, and before the brine became dry, the supply of CO_2 was quite sufficient.

The deposition rate of the trona bed is relatively high. In the Magadi lake, trona was deposited at a rate of 2 to 5 cm/year. In the Wucheng deposit, trona beds often contain thin mud laminations, probably representing the alternative deposits in the rainy and the dry season in each year. From this it can be deduced that the trona of the deposit was deposited at the rate of at least 2 cm/year. However, due to the change in climate and the recharge of fresh water, the continuous deposition of alkali material was interrupted and the superficial alkali bed was dissolved. For the upper ore section, NaCl saturated the relevant brine and crystalized, which is probably related to more stable deposition and extended period of the variation of climate. Therefore, this section's rhythmites are enlarged and trona beds thickened.

Future Studies

Few trona deposits have so far been discovered in China. In particular, only one ancient trona deposit, the Wucheng deposit, is found. The level of the study of these deposits is still low, and there are some problems worthy of further study. For instance, sulphate minerals are absent in the deposit. Why? There may be two reasons: 1) the brine originally received little supply of SO_4^{2-} and could not become saturated with the ion in its subsequent concentration; 2) the desulphurization by bacteria under reduction conditions might reduce the originally deficient sulphate to H_2S, which later escaped into the air or formed pyrite and other minerals (the pyrite bed often found on the contact between argillaceous dolomite and trona bed in the deposit may be produced by this process).

The Green River alkali deposit of the U.S. also lacks sulphate minerals. The above explanation, however, is not perfect because in modern alkali lakes the sulphate mineral (mirabilite) is commonly found, as distinguished from ancient alkali deposits. It is worthy of future study why there is such a great difference between the modern alkali lakes and the ancient alkali deposits. Indeed, there are also modern alkali lakes, such as Magadi Lake, in which no sulphate mineral is present, but the source of salt material is quite another question. The material of a salt deposit may be derived from many sources. The salt material may come from, besides the release of arrested salt and the resolution of salt, the activities of magmas and movement of deep brines which may bring salt. It is considered that Magadi Lake has obtained the deep alkali material rising along the East Africa Rift. Whether these hypotheses are applicable to the Wucheng alkali deposit remains to be carefully studied. For example, no evidence of the activity of basaltic magma, which may bring abundant CO_2, has been found in the Wucheng area, and the recharge of redissolved salt is impossible because there is no older salt deposits in the surroundings of the Wucheng deposit.

Moreover, there are some other problems. What law is there regarding the control of the conditions such as material source and climate on alkali deposits of different types (i.e., one dominated by trona sediment and the other by soda sediment)? Under what conditions is the highly concentrated alkaline brine formed, which is so rarely seen in the Biyang Depression of Henan? All these are the subjects remaining to be further explored in the study of alkali deposits in China.

ACKNOWLEDGMENTS

The abundant practical data used in this paper were obtained commonly by the author and his colleagues, including Zhao Shengcong and Guo Hongzhi, from the 12th Geological Team of Henan Province, Guo Zhimin and He Chuanyong from the laboratory of the Henan Geological Bureau, and Wu Ping and Shen Deqi from the Yichang Institute of Geology and Mineral under the Ministry of Geology and Minerals have also studied the Wucheng deposit and written their own papers on it, which were also used for reference in this study. The author is grateful to all of them.

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