On Biochemical Formation of Salt Deposits

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Abstract A water/salt system in an evaporative environment is both a physicochemical region and a biological one. All the parameters of the system, such as the salinity, temperature and CO_2 partial pressure, are affected by halophilic bacteria. The system controls salt deposition but is modified by an accompanying ecological system; therefore it should be called a water/salt/biological system. Salt minerals result from accumulation of the remains of bacteria/algae, namely, bacteria/algae formation; whereas biological, biophysical and biochemical processes provide full evidence for organic involvement. Consequently, salt deposits should not be called purely chemical but biological/chemical ones. This new argument supplements and develops the traditional idea and helps perfect the mineralization theory of salts and even general deposits, thus giving guidance to prospecting for salt deposits.

Key words: salt deposits, biochemistry, genesis

1 The Origin of the Project

Salt deposits are called evaporite deposits due to their transformation from solute to crystalline form in evaporative environments. They are considered exogenetic by most geologists but endogenetic by a few. Furthermore, some Chinese and foreign deposits textbooks still categorize them as chemically sedimentary mineral deposits, even involving a purely chemical or solution process. Unfortunately, the relationship between salt deposits and organisms or organic processes has not drawn any attention until recently. This situation probably results from the viewpoint of biologists that high-salt, high-alkali water bodies represent forbidden zones or "extreme environments" for organisms to live. They used to view salt-hosting strata as barren strata which originated from saline waters and do not have organic fossils. Smith and Zobel (1937) reported for the first time in the 1930's that certain bacteria communities actually do live in the Great Salt Lake in the United States. Upon the 1970's, the existence of organisms in salt lakes was generally acknowledged, thanks to swift progress in biological and ecological research. At the same time, many achievements were made in the application of advanced technology, equipment and testing methods. Advances were made in the study of fossils from salt strata, modern or ancient, resulting in the discovery of large numbers of organic fossils. The role of organisms in deposition of salt minerals received a great deal of attention. New findings and data contradict the purely chemical process explanation, forcing us to revise and supplement our idea of how salt deposits form. Challenging the purely chemical model, the authors established a biochemical sedimentary model for salt deposits.

2 Some Evidence Refuting the Concept of Formation of Salt Deposits via Purely Chemical Sedimentation

2.1 Modern salt lakes, including artificial salt ponds, commonly have large numbers of organisms living in them. These organisms are a significant biological force stimulating the deposition of salt minerals and are a biological resource with a substantial volume

In the past, biologists believed that saline waters are a lifeless world, having no organisms, not even microorganisms. Despite that, in the last 30 years notable progress has been made in the study of the biology, ecology and geochemistry of salt lakes. This is due to expanding salt production and increased exploitation of medical and edible halophilic algae. Most scholars hold that, while higher salinity and lower O-solubility of saline waters are a very unfavourable environment for organisms to live in, organic communities do appear in large quantities leading to extremely high organic productivity. The unfavourable environment geatly decreases the number of organic varieties. A considerable number of salt organisms, such as bacteria, algae, protozoa, saline shrimps and saline flies, have been recognized in the Great Salt Lake (Post and Felix, 1982). In some typical NaCl, Na_2SO_4, Na_2CO_3 and K/Mg salt-type lakes in Tibet, Qinghai, Inner Mongolia, Xinjiang, etc., Chinese scholars have found multiple varieties of saline shrimps, as well as various types of halophilic and alkaliphilic bacteria. These organisms were studied for their morphology, physiology and physiochemistry, and molecular biology (Wang Dazheng, 1994). Other Chinese scholars have conducted much work in this field. Zheng Mianping et al. (1985) surveyed halophilic algae in the Zhabuye Caka (Lake) of Tibet. Wei Dongyan et al. (1986, 1992), after studying the organisms in the Barkol Salt Lake of Xingjiang, concluded that the lake represents an ecological system in which different organisms constitute a simple, interdependent food chain. Yuan Jianqi et al. (1990) pointed out that the degree of mineralization, chemical composition and physical geography of a salt lake have an impact on the living and breeding of its organic communities, and vice versa.

Reports from salt lakes found that salt lake organisms form an agent powerful enough to govern the mineralization of salt lakes and contain organic resources rich enough to rank just after the mineral resources in value.

2.2 There are plenty of organic fossils in old salt sediments, proving that they were deposited in the same, or similar, sedimentary environment as ecological systems of modern salt lakes

Have organic fossils which are analogous to the living organisms seen in modern salt lakes been preserved in salt strata? This question was satisfactorily answered through advanced testing technologies. In the early 60's, Soviet scholars found halophilic bacteria and algae remains in the Permian sylvite sequences in the Upper Kama district. According to Cai Keqing et al. (1984), remains of bacteria dotted on the faces of hydroloeweite crystals from boron-bearing beds in the Da Qaidam Lake. Liu Qun et al. (1987) found organisms similar to bacteria in the sylvite mine of Zhengyuan. Wei Dongyan et al. (1991, 1992, 1994) conducted systematic research into faecal fossil of saline shrimps and fossils of halophilic bacteria after finding them in Quaternary halite, mirabilite and thenardite beds of many salt lakes in Xinjiang and Late-Middle Quaternary mirabilite/trona and natron beds of some salt lakes in Inner Mongolia. Moreover, Wei probed organic fossils collected from some pre-Quaternary salt sequences. He identified probable fossilized faeces of saline shrimps and fossils of bacteria and algae in Tertiary halite beds in eastern China, Palaeocene potash beds in Mengyejing and Jurassic halite/glauberite beds in Anning, both of Yunnan province. Especially Wei Dongyan found in Ordovician halite beds of northern Shaanxi province organic fossils similar to saline shrimps and bacteria. The findings of all these people prove the widespread existence of organic fossils in salt sediments, old or young, and hence similarity of the sedimentary regimes of old salt sediments with the ecological systems of young salt lakes.

2.3 Based on studies of biomarking compounds or molecular fossils, the salt deposition environment is essentially a biochemical world

Biomarking compounds, or molecular fossils, are organic compounds biosynthesized by organisms that may be modified by geological processes,yet retain evidence of their biological source, currently better used for rehabilitating primary organic sources, determining salinities and temperatures of original water bodies, and accordingly rebuilding the primary environment.

Biomarking compounnds have been successfully applied in determining oil-forming sources. Signs of biomarking compounds have been detected in salt/ultrasalt sediments since the 1980's. Shang Huiyuan and Jiang Naihuang (1983) reported that the salt-bearing strata contain high amounts of gammacerane in the Qaidam and Jianghan basins. Jiang Jigang and Fu Jiamo (1986) revealed that evaporite strata carry n-alkanes of even/odd predominance and gammacerane in higher quantities. Later, other scientists pointed out that some salt-bearing strata have a lower Pr/Ph ratio (Fu et al., 1986) and higher amounts of such organic compounds as β-carotane (Jiang and Fowler, 1986), pregnane (Ten et al., 1986), squalane (Ten et al., 1986), 2, 6, 10-trimethyl-7-(3-methyl-butyl)-dodecane (Kening, et al., 1990), ducylthiophene (Shen et al., 1986), decyl-dibenzothiophene (Hughes, 1984; Jiang Naihuang et al., 1994), 2-methyl-docosane (Connan et al., 1986), and 4-methyl-sterane (Wang Ruiliang, 1994).

Research indicates that certain biomarking compounds are genentically connected only with certain organic genera, for example, isoprenoid alkanes related only to organic sources of halophilic bacteria, gammacerane to the dehydroxylation of the tetraphymenol of protozoa under reducing conditions, and so on.

After thoroughly investigating the biomarking compounds in thick Ordovician halite beds in northern Shaanxi, China, we found that the Pr/Ph ratio is lower, the hopane/sterane ratio is higher and β-carotane, gammacerane, pregnane, homopregnane and the like are widespread. All this demonstrates that these halite beds were formed in a high-salinity, strongly reducing, aquatic algae/bacteria-rich sedimentary environment. The organic fossils so far recognized are consistent with the foregoing biomarking compounds.

3 Role of Organisms in Deposition of Salt Minerals

3.1 Immediate deposition of microorganic remains

Scanning electron images have shown that salt minerals, like gypsum, halite, mirabilite, thenardite, glauberite, sylvite and carnallite are all laden with numerous, shape-varying halophilic bacterium-alga fossils, forming characteristic ultramicro-organic textures. These microorganic fossils make up as much as 30–95% (commonly over 50%) of the contents of the salt minerals. This cannot be explained convincingly by purely chemical deposition but can by the bulk accumulation of the remains of countless microorganisms. Based on the statistics from scanning electron micrographys during precipitation of salt mainerals, one m^3 of brine contained the following numbers of halophilic bacteria: 7×10^{17} for gypsum, 2×10^{18} for thenardite and 5×10^{19} for sylvite. Obviously, the numbers of bacteria increase with salinity of the brine. Such tremendous numbers were capable of fostering a strong natural agent for the salt lake to be mineralized. Various salt minerals were precipitated soon after the death of salt microorganisms. The accumulation took place with the precipitation or crystallization. Judging from the above accounts, salt sediments are essentially bacterium (alga) formations.

3.2 Biological-physical deposition

Earlier it was mentioned that the faecal fossil or similar products of saline shrimps gives salt ores a distinctive granular texture containing faecal pellets. This texture differing completely from that of ores associated with purely chemical deposition. The texture embodies the combination of biological and physical depositions. Firstly, faecal pellets or similar materials have a genetic tie with metabolism of organism, or biological process, which produced them, and then they are deposited together with salt minerals by sinking, representing a physical process. For these, the texture may be attributed to a double process, biological plus physical. They are mostly autochthonous and seldom allochthonous in terms of deposition.

Saline shrimps, typical of filter feeders, excrete faecal pellets which are mingled with organic and inorganic detrital materials, thus showing a fragmental texture similar to, but essentially different from, an intraclast texture.

3.3 Biochemical deposition

In saline water bodies with ongoing salt deposition, biochemical deposition freguently takes place in the following several ways:

3.3.1 Collection of ore-forming elements

In the course of biological progression, the hydrobios in lakes and vegetation on the lake banks collect large amounts of alkali metals, alkali-earth metals, chlorine, sulphur, etc. Na constitutes the external cations and K forms their internal cations of their cells. Chemical elements and simple compounds can be accumulated chiefly by the decomposition of the remains of hydrobios, like saline shrimps, protozoa, algae, and so on. Microorganisms, such as inorganic-fed sulphur bacteria, are able to eventually oxidize reduced sulphur into sulphate through the following reaction:

$$CO_2+H_2S+O_2+H_2O \xrightarrow{\text{bacteria}} CH_2O+SO_4^{2-}+2H^+$$

3.3.2 Change in the medium parameters of brine with biological activities

The medium parameters of brine include pH, Eh, temperature and even isotope compositions of sulphur and the like. All of these are subject to change due to biological activities.

(1) Acids and alkalis released during biological metabolism of halophilic organisms influence pH and Eh of brine, and the change in pH and Eh would in turn have a great impact on the evaporative conditions of the brine, ultimately affecting salt mineralization.

(2) With as many as hundreds of millions of organisms per m^3, saline shrimps, red halophilic bacteria and algae can absorb a great deal of solar energy, greatly increasing the water temperature and as a result the water evaporation loss. This is not only favourable for salt precipitation but for deposition of thermophilous minerals also. A long-unresolved question of why salt minerals can precipitate from saline waters over 80℃ is expected to be answered by this.

(3) Organisms in saline waters, particlarly bacteria, can exercise a significant impact on isotope compositions of elements, e.g. promoting the fractionation of sulphur isotopes. In a closed system, the isotope fractionation of sulphur may reach more than 30‰ due to the reduction of sulphate by bacteria. An example supporting this comes from the Sichuan basin where $\delta^{34}S$ value of the evaporite sequences in the No. 2 Member of the Jialinjiang Formation reaches as much as 34.2–37.6‰.

(4) Organisms may serve as a purifier for saline waters because they, as filter feeders, purify them by adsorbing their detrital materials and depositing them as faecal pellets. They often consume algae in brine as food, thereby playing a purifying role.

3.3.3 Shifting between depositional types

Activities of organisms, especially bacteria, can bring about a shift between depositional types. For example, sulphur bacteria shifts the depositional type from sulphate to carbonate according to the following reaction:

$$CaSO_4+CH_4 \xrightarrow{\text{Sulphur bacteria}} CaS+2H_2O+CO_2$$
$$CaS+2H_2O \longrightarrow Ca(OH)_2+H_2S$$
$$Ca(OH)_2+CO_2 \longrightarrow CaCO_3+H_2O$$

4 Conclusions

The traditional idea of chemical deposition of salt minerals is that they precipitate in a water/salt system under evaporative conditions. This idea regards salt deposition as being controlled by only the salinity, temperature, CO_2 partial pressure, etc. of the system. Based on our data, we believe this is an incomplete explanation, seriously ignoring the tremendous role played by organisms during salt deposition. In fact, a water/salt system in an evaporative environment is both a physicochemical regime and a biological one. All of the above physical parameters of the system are affected by halophilic bacteria. The system controls salt deposition but it is modified by an accompanying ecological system; therefore it should be called a water/salt/biological system. Salt minerals, as described earlier, result from the accumulation of the remains of bacteria/algae, namely, bacteria/algae formations, while biological, biophysical and biochemical processes, also as previously mentioned, provide full evidence for organic involvement. Consequently, salt deposition is caused not by purely chemical processes but by biological/chemical processes. Salt deposits should not be termed as purely chemical but biological/chemical. This new argument should be acknowledged to supplement and enhance the traditional idea, helping perfect the mineralization theory of salt and even general deposits and hence giving guidance to prospecting for salt deposits.

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