



Article Estimation of the Ambient Temperatures during the Crystallization of Halite in the Oligocene Salt Deposit in the Shulu Sag, Bohaiwan Basin, China

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Abstract: The centimeter-scale halite rhythmites in the first member of the Shahejie Formation in the Shulu Sag of the Bohai Bay Basin are investigated, and the Eocene to early Oligocene paleoenvironmental characteristics of a typical saline lake basin are restored by reconstructing the temperature and compositional information of ancient brines. The obtained homogenization temperatures (Th) of fluid inclusions range from 6.5 to 49.2 °C, with a relative lower Th from transparent halite samples than from gray halite samples. This suggests different temperature conditions and a probable association with seasonal changes. The ion contents of halite fluid inclusions reveal the lake brine is a Na-Mg-K-Ca-Cl type and reached the initial stage of halite deposition. The transparent halite samples plotted within different phase regions than the gray halite samples on plots of ion contents and showed significant change within phase regions. Combined with the observed cm-scale rhythm in the evaporite sequences of the Shulu Sag, these results suggest a shallow water environment and frequent dilution by inflows of fresher water caused by seasonal climate change. The gray halite formed under higher temperatures and increased inflow conditions, and the transparent halite formed under lower temperatures and decreased inflow conditions. Compared with the Jiangling Sag in Hubei Province in southern China, the Shulu Sag may have been less affected by igneous rocks in the Es1 Formation due to the material source, and the concentration of trace elements such as lithium, strontium and boron in the ancient salt lake brine was lower.

Keywords: rhythm; fluid inclusions; halite; Shulu Sag; Bohaiwan Basin

1. Introduction

The evolution of saline basins is one of the research focuses of sedimentology and thus has attracted extensive attention. In these basins, salt minerals such as halite provide key information on the quantitative reconstruction of paleoenvironments [1–8]. Moreover, large amounts of effective and high-quality source rocks have been found in saline basins. This is typified by the Meso-Cenozoic continental basin of China, where most high-quality source rocks are associated with the development of saline basins [9–11].

Genetic formation issues of the dominant salt sediments are unavoidable when researching the environmental development of saline basins. However, arguments still exist over whether these salt sediments formed in deep or shallow waters [12]. Proponents of the former highlight stratified brine in deep water environments as playing a fundamental role in the formation of salt layers [13–15], but proponents of the latter suggest that salt sediments are products of continuous concentrations in shallow water despite the presence of a deep basin [16–18]. The widely developed Paleogene to Neogene rock salt in the Bohai Bay Basin acts as a substantial research object to solve these disputes.

The Bohaiwan Basin is one of the most important petroliferous basins in China. Large thick salt rocks of the Paleogene Shahejie Formation (Fm) developed in the Shulu Sag



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). within the basin and thus provide unique opportunities for studying the environmental reconstruction of saline lacustrine basins and their related genetic formation. The sedimentary characteristics of the first member of the Shahejie Formation show that halite-bearing rocks with a "thin interlayer" of salt display characteristics of shallow water genesis and extremely high paleotemperatures of the salt formation period [19,20]. In this article, we focus on halite between interbedded clastic layers, and conduct a detailed analysis of the homogeneity temperature and composition of halite fluid inclusions. This study provides abundant and reliable evidence for evaluating halite genesis and the paleoenvironment.

2. Geological Setting

The Shulu Sag is located in the southern Jizhong Depression of the Bohaiwan Basin (Figure 1). It is a fault basin formed during the Eocene and has a pre-Paleozoic to Paleozoic basement [21]. The Eocene-Oligocene sediments of the Kongdian Fm and Shahejie Fm in the Shulu Sag mainly consist of mud, marl, mud-bearing gypsum, and halite (Table 1). The Kongdian Fm and the fourth member of the Shahejie Fm are the sedimentation product of the onset of the Shulu Sag, and are characterized by clastic sediments along the sag borders and mudstone and mud-bearing gypsum in the sag interior. The second and third members of the Shahejie Fm are gray-green and gray-white siltstones in the north part of the sag, gypsum in the south-central part and gypsum, and halite in the south. During the deposition of the first member of the Shahejie Fm, tectonic activity was relatively peaceful, and a large evaporite deposit characterized by gypsum and halite occurred at the bottom of this formation in mostly arid climate [22,23]. The evaporite sequence in the first member of the Shahejie Fm was dated to the Oligocene age [24]. The lacustrine deposition of the Shulu Sag disappeared at the end of the Paleogene due to tectonic uplift and transitioned into deposition on a plain.

Geological Time	Formation	Thickness (m)	Lithology		
Oligocene	SF 1	0–800	The lower part: red and black mudstone, carbonate, gypsum, argillaceous gypsum and salt rock. From north to south in the southern part of the depression, the lithology was marked by limestone-dolomite-gypsum-halite		
			The upper part: light grey fine sandstone, siltstone and amaranth mudstone		
Eocene	SF 2	0–400	interbedded brown, purple mudstone and light grey fine sandstone		
	SF 3 0–2200		brown and grey breccia, breccia composed mainly of limestone or dolomite, brownish gray, grey mudstone, local shale and grayish fine sandstone ir the upper		
	SF 4 500–100		Clastic sediments mainly developed around the periphery of the basin, and mudstone sedimentary rocks and mud paste emerged in the center of the depression		

Table 1. Characteristics of the Shahejie Formation in Shulu depression, Bohai Bay Basin, North China.



Figure 1. (a) Simplified tectonic map and location of the Shulu Sag, Bohaiwan Basin. (b) Outline map showing the structural units of the Shulu subbasin. (c) Cross section of geological interpretation of the Shulu subbasin. Nm—Minghuazhen Formation; Ng—Guantao Formation; E3d—Dongying Formation; E3s1—first member of the Shahejie Formation; E3s2—second member of the Shahejie Formation; E2k-E3s4—Kongdian Formation and fourth member of the Shahejie Formation; C-P—Carboniferous-Permian; O– Ordovician.

3. Materials and Method

3.1. Core Materials and Halite Sample

The studied core S1 is located south of the Shulu Sag (Figure 1). The recovered sediments belonged to the first member of the Shahejie Fm, and had multiple sedimentary cycles and rhythms characterized by the alternation of halite beds and thin interbedded clastics (Figure 2). In total, 1725 halite beds separated by interbedded clastics were observed from 299.38 m of core sediments. Halite beds are usually 5–30 cm thick, with a maximum thickness of 1.27 m and a minimum thickness of less than 1 cm. The halite is usually transparent and gray, and a few thin red halite beds appear in the core. Halite crystals are often euhedral or subhedral and have diameters varying from 2 mm to 3 cm. The transparent halite beds are commonly thicker than the gray halite, which contains more muds, plates, or columnar anhydrite within intercrystalline halite (Figure 3). Thin interbedded clastics are mainly composed of mud, halite, and anhydrite. In addition, thinner interbedded clastics



are observed at the contact between the transparent and gray halite beds, and halite crystals in these interbedded beds are often as small as 1–2 mm.

Figure 2. Petrology and sampling location of the studied core S1.



Figure 3. Halite and anhydrite co-existed in well S1 of the Shulu depression. The image on the left is single-polarized light and the image on the right is orthogonal-polarized light. A = anhydrite, H = halite.

Two sections of core sediments were collected from S1 core. These core sediments show well-preserved sedimentary rhythms characterized by gray halite beds, transparent halite beds and interbedded clastic beds. In total, two primary halite samples were collected for analysis of homogenous temperatures and chemical components of halite fluid inclusions.

3.2. Method

The method for homogenization temperature analyses in our study follows that of Benison and Goldstein [3]. Careful attention was given to avoid dissolution and overheating during sample preparation. Unpolished halite samples were separated into fragments ca. 0.5–1 mm thick with a knife along the cleavage planes. Before the cooling stage, detailed petrographic studies were conducted for each halite fragment sample. Large amounts of well-preserved fluid inclusions occurred in the halite of the first member of the Shahejie Fm. These halite fluid inclusions were often square- or rectangular-shaped and were 2–30 μ m in diameter, with a few reaching 50 μ m in diameter (Figure 4). Primary halite inclusions are cumulate- and chevron-shaped and often occur near the cores of halite crystals. These inclusions are dominated by single-phase liquid or two-phase liquid-vapor inclusions. Few three-phase inclusions from the cumulate- and chevron-shaped inclusions were collected for analysis in this paper.



Figure 4. Primary fluid inclusions in halite.

Analysis of the homogenization temperature of halite fluid inclusions was conducted in the NLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences. All samples were first placed in a freezer at -18 °C for 7–10 days to artificially nucleate vapor bubbles. After removal from the freezer, the samples were quickly placed in a Linkam ThMSG600 device to cool to -18 °C at a rate of 0.5 °C/min, and individual primary liquid fluid inclusions were documented, including mapping and photographically recording the size, shape, and distribution of fluid inclusions. Then, the heating stage was achieved by warming the samples to 15 °C at a rate of 1 °C/min. Thereafter, the rate was lowered to 0.1 °C/min until all artificially nucleated vapor bubbles disappeared.

The LA-ICP-MS technique has been successfully applied to the determination of fluid inclusions in halite of various ages [25–30]. The ion contents of halite fluid inclusions were analyzed at the National Research Center for Geoanalysis (NRCGA, PRC) using the method of Sun et al. [31]. We utilized an Element 2 plasma mass spectrometer (Finian, Frankfurt am Main, Germany) interfaced with a UP213 laser (New Wave) to determine the ion components of halite fluid inclusions, mainly Li, B, K, Ca, Mg, Sr, and Rb. The wavelength was 213 nm, and the pulse width was 4 ns. Halite fragments were obtained from primary halite crystals using a knife to cut along the cleavage planes and then glued on glass slides. Before the analyses, the LA-ICP-MS parameters were optimized for sensitivity and stability. The spot size and ablation time varied for different samples. The preablation laser warm-up took approximately 15 s. The signal acquisition time was 60 s, and laser ablation was conducted at a rate of 60 laser firings per minute. External and internal standards were used for calibration [31]. Solutions with different ion concentrations of elements were sealed into quartz microcapillary tubes to serve as the standard samples. Both tested and standard samples were placed in the laser ablation sample chamber. The Na content was 68 g/L, measured at room temperature, and used as the internal standard in halite inclusions.

In total, 191 homogenization temperature (Th) data points were obtained (Table 2 and Figure 5). Samples 1 (Figure 5a) and 2 (Figure 5b) yielded Th ranges of 6.5–48.5 °C and 10.5–49.2 °C, and average Th values of 30.9 °C and 32.6 °C, respectively.

Sample	Colour	Depth	Number	$Th_{min}/^{\circ}C$	Th _{max} /°C	Th _{avg} /°C	Th _{med} /°C
1–1	gray	3028.68	19	15.6	46.7	31.5	31.7
1–2	transparent	3028.71	17	7.5	44.8	27.6	28.5
1–3	gray	3028.76	29	17.7	48.5	34.3	33.4
1–4	transparent	3028.00	19	6.5	45.2	28.1	29.8
2-1	transparent	3166.74	17	15.6	49	34.6	35.4
2–2	gray	3166.76	18	11.4	49.2	33.2	34.6
2–3	transparent	3166.78	20	14.9	46.5	31.5	33.7
2–4	transparent	3166.80	15	10.5	45.7	31.5	32.3
2–5	gray	3166.82	21	10.9	48.7	34.2	37.7
2-6	transparent	3166 84	16	10.6	45	30.6	30.4

Table 2. Th data of halite inclusions of the studied core S1.





The calculated ion contents of halite inclusions from sample 1 yielded Mg^{2+} , K^+ , and Ca^{2+} contents ranging from 1214.72 to 8720.72 mg/L, from 210.32 to 15,692.79 mg/L, and from 20.44 to 194.95 mg/L, with average contents of 4327.69 mg/L, 2297.61 mg/L, and 75.50 mg/L, respectively (Table 3). The content variation range of the trace elements lithium, boron, rubidium, and strontium in sample 1 were 0.78–33.87 mg/L, 13.80–71.79 mg/L, 5.71–86.84 mg/L, and 0.03–1.76 mg/L, with average contents of 16.28 mg/L, 36.43 mg/L, 27.32 mg/L, and 0.72 mg/L, respectively. Sample 2 showed Mg^{2+} , K^+ , and Ca^{2+} content ranges of 1036.36–6996.68 mg/L, 567.44–4163.23 mg/L, and 51.52–584.68 mg/L, with average contents of 3907.93 mg/L, 1626.64 mg/L, and 150.65 mg/L, respectively (Table 4). The content variation range of the trace elements lithium, boron, rubidium, and strontium in sample 2 was 0.30–97.13 mg/L, 5.61–380.30 mg/L, 3.34–22.41 mg/L, and 1.01–6.74 mg/L, with average contents of 32.03 mg/L, 38.26 mg/L, 9.66 mg/L, and 2.60 mg/L, respectively.

	Number -	Calculated Ion Concentrations (mg/L)							
Sample		Li	В	Mg	К	Ca	Rb	Sr	
1–1	1-1-1	17.45	58.85	6011.28	2381.85	79.58	29.26	0.94	
	1-1-2	26.83	23.17	3623.64	210.32	20.44	6.58	0.19	
	1-1-3	21.23	40.28	5712.64	469.37	26.53	26.27	0.41	
1–2	1-2-1	31.44	55.87	6838.97	945.69	194.95	51.12	1.36	
	1-2-2	32.67	71.79	8720.72	1163.01	152.44	37.70	1.38	
	1-2-3	12.47	24.58	5083.92	776.69	77.29	44.40	0.78	
	1-2-4	13.89	57.63	6842.48	15,692.79	89.18	86.84	1.76	
1–3	1-3-1	0.78	13.80	1604.96	913.73	42.00	11.15	0.23	
	1-3-2	12.15	16.91	1214.72	891.62	22.69	11.66	0.03	
	1-3-3	9.35	16.54	1540.33	1084.72	46.52	5.71	0.08	
	1-3-4	33.87	15.12	5429.28	457.36	123.31	18.11	1.06	
1–4	1-4-1	2.57	29.33	3642.54	2900.85	61.93	19.90	0.78	
	1-4-2	11.05	35.55	3604.63	2324.01	37.41	18.65	0.76	
	1-4-3	17.06	50.79	5119.33	3256.74	120.57	37.64	0.76	
	1-4-4	5.39	29.34	3775.27	1476.22	43.93	10.67	0.43	
	1-4-5	12.30	43.31	4030.13	1816.78	69.25	21.49	0.64	

Table 3. Ion contents of halite fluid inclusions from sample 1.

 Table 4. Ion contents of halite fluid inclusions from sample 2.

Sample	Number	Calculated Ion Concentrations (mg/L)							
		Li	В	Mg	К	Ca	Rb	Sr	
2–1	2-1-1	26.31	7.32	3333.70	1680.41	187.14	9.23	3.82	
	2-1-2	0.70	27.47	3770.25	2034.66	74.63	9.01	2.34	
	2-1-3	3.81	24.77	4374.57	1716.70	313.30	15.55	3.96	
2–2	2-2-1	21.00	33.42	3853.14	956.91	51.60	4.86	1.26	
	2-2-2	47.45	36.46	3701.09	1113.07	147.02	3.34	1.01	
	2-2-3	0.40	5.61	2450.28	1868.62	208.14	12.90	4.90	
	2-2-4	28.48	17.80	2826.30	1031.29	92.74	3.51	1.19	
2–3	2-3-1	26.56	23.84	3337.34	1196.46	158.47	5.41	2.89	
	2-3-2	39.91	18.37	5713.76	970.13	51.52	5.41	1.65	
	2-3-3	0.30	20.69	5617.26	2337.89	584.68	9.05	2.34	
	2-3-4	26.88	19.64	6996.68	2942.81	192.79	19.71	4.66	
2–4	2-4-1	2.06	10.18	4334.51	1339.71	127.12	10.25	1.97	
	2-4-2	58.56	33.79	6791.65	4163.23	192.29	18.46	3.87	
	2-4-3	42.65	18.26	4499.81	1495.59	62.86	4.41	1.25	
	2-4-4	15.42	13.20	4971.70	2851.68	185.88	14.96	1.99	
2–5	2-5-1	61.49	-	1481.70	2358.38	127.04	22.41	6.74	
	2-5-2	-	-	1036.36	934.26	135.50	13.67	4.60	
	2-5-3	63.04	24.10	2286.72	868.50	75.70	3.34	1.07	
	2-5-4	52.85	21.82	2420.97	567.44	76.18	13.70	1.88	
	2-5-5	31.78	18.43	2712.10	1070.32	74.56	3.73	1.23	
2–6	2-6-1	32.82	380.30	6598.26	1628.37	57.54	5.50	1.15	
	2-6-2	97.13	39.89	5075.22	1297.82	156.43	7.50	2.18	
	2-6-3	25.14	8.07	1698.95	988.36	131.91	6.24	1.82	

5. Discussion

5.1. Representativity and Validity of the Data

Changes in physico-chemical conditions will destroy the primary information preserved in fluid inclusions, including dissolution, recrystallization, breakage, recementation, and deformation [32]. Therefore, identification of primary halite fluid inclusions is crucial for analyses of the Th and the ion content of fluid inclusions. Calibration for distinguishing the primary and secondary halite fluid inclusions has been established by previous works [33–35]. It is thought that primary halite fluid inclusions often occur in the form of negative cubic crystals, similar to those of the hosted halite, and are characterized by banded or chevron crystals, with most having a similar size. However, the secondary fluid inclusions often have irregular crystals and develop along cleavage cracks or fractures. Moreover, they occur separately as single inclusions, or are inserted across two or more halite crystals in the form of an inclusion group. All selected samples in this study were primary fluid inclusions characterized by banded or chevron crystals. Gas inside fluid inclusions often leads to anomalously high Th [2,35]. We compared photos of fluid inclusions taken before and after cooling to ensure that no two-phase gas-liquid inclusions were used for Th analysis. In addition, the consistency of the Th of fluid inclusion assemblages (FIAs) can indicate the possibility of fluid inclusion alterations associated with thermal re-equilibration [3,36]. Our data show that all Ths within an FIA had Th ranges of <15 °C, meeting the guidelines that Th is likely not altered by thermal re-equilibration if 90% of Th data within a single FIA vary within a 10–15 °C interval [3,36]. Fluid inclusions in halite would be stretched to relieve the high internal pressure due to over-pressured conditions during sample burial and thus yield a higher Th [37–40]. Our results do not show a relationship between inclusion size and Th (Figure 6). The above lines of evidence suggest that our fluid inclusions were unaltered by thermal re-equilibration. Therefore, the Th data of our study were reliable and valid.



Figure 6. Relationship between homogeneous temperature and inclusion size of fluid inclusion in halite of well S1.

For ion content analyses of halite fluid inclusions, our results show that the determined signal for the first 10 s of laser ablation represents the background value; a stable signal of

Na, K, Mg, and Ca; and a slight fluctuating signal of Rb, Sr, and B (Figure 7). The Na signal rapidly increased at 12 s because the halite surface was ablated, and the simultaneous signals of other elements did not change significantly. Then, accompanied by the gradual fading of the Na signal, the other signals quickly decreased to the level of background values. When halite fluid inclusions were ablated by a laser at 19 s, all elements, especially K, Mg, Ca, and Sr, displayed instantaneous increases in signal intensity. Evaporation experiments for seawater from the Yellow Sea in China showed that when halite was initially deposited, Li, B, Rb, Sr, and K were nearly preserved in the residual brine because they do not easily enter crystal lattices [41]. This is consistent with our results, as no minerals with Li, B, Rb, Sr, and K were identified. In addition, changes in the content of these elements showed synchrony, thus suggesting a reliable result.



Figure 7. MS signal intensity vs. time for single fluid inclusion in halite.

5.2. Paleo-Temperature Reconstruction

Primary fluid inclusions in halite are usually contained in cumulate and chevron crystals that precipitate at the air-water interface or at the bottom of shallow water [1,2,42]. Therefore, the Th of halite fluid inclusions records brine surface temperatures during halite deposition in shallow environments. Moreover, analyses and observations of laboratory-grown and modern halite have demonstrated that the maximum Th from fluid inclusions can be equivalent to the highest brine temperatures during halite crystallization [2,43,44].

Therefore, we conclude that the obtained Th of 6.5–49.2 °C with an average of 31.8 °C can represent the surface temperature of the lake in the Shulu Sag when halite formed. This temperature condition is consistent with the relatively hot subtropical-tropical climate revealed by pollen data [45,46], as well as the brine temperature of 17.7–50.7 °C derived from the Th of halite inclusions from other cores in the sag [7]. In addition, it should be noted that Ths from samples of transparent halite are commonly lower than those of gray halite, with average, median, and maximum Ths lower than 1.7–5.7 °C, 0.9–5.4 °C, and 0.2–3.7 °C, respectively (Figure 8, Table 2). This suggests a rise in the temperature of approximately 4 °C from the deposition of transparent halite to gray halite.



Figure 8. (a) Homogenization temperature curves of fluid inclusions in halite. (b) A positive correlation between homogenization temperature (Th) and Mg^{2+} content.

5.3. Reconstruction of Ancient Brine Composition

Generally, salt mineral assemblages are determined by the composition of inflow materials, especially when brine is concentrated during the deposition of bittern. For instance, Ca is depleted when carbonate and gypsum are deposited at the initial evaporation stage. Na and Cl are increasingly consumed by the deposition of halite. During this time, Mg dominates the residual brine. When the brine concentration reaches 60–70 times the original seawater concentration, Mg-bearing minerals start to deposit, and thus K enriches the residual brine. At the last stage of evaporation, kainite and carnallite are deposited [47]. These lines of evidence suggest that the composition of brine, especially the content of Ca and SO₄, often determines the salt mineral assemblages after gypsum is formed [48]. Studies of the Yellow Sea in China and Searles Lake in California have also shown that salt mineral assemblages are strongly affected by the ion content of brine and the composition of inflows [41,49].

Our results show that the brine of the Shulu Sag is of the Na-Mg-K-Ca-Cl type [48,50–53]. K and Mg were almost completely preserved in the residual brine, and only small percentages were depleted by the crystallization of halite. In contrast, the Ca content showed obvious oscillation due to the deposition of gypsum that occurred within intercrystalline halite, suggesting periodic inflows of fresher water. By comparing the change of Mg²⁺ content with the change of the homogeneous temperature of fluid inclusions, we found that the temperature of the ancient salt lake brine was negatively correlated with the content of Mg²⁺ (Figure 8).

The NaCl-KCl-MgCl-H₂O phase diagram shows that all data plotted in the phase region of initial halite deposition and remained far away from those of sylvite and carnallite deposition [50], implying that lake water was evaporated in the initial halite depositional stage. In addition, plots of transparent halite samples showed more frequent changes in phase regions and were closer to the phase region of sylvite and carnallite than gray halite samples, suggesting periodic dilution and concentration (Figure 9).



Figure 9. Plot of inclusion composition in phase diagram. H = halite; Car = carnallite; Syl = sylvinite; Bi = bischofite. a and b are the NaCl-KCl-MgCl-H₂O quaternion phase diagrams of sample 1, (a) indicates the local amplification of (b); (c,d) are the NaCl-KCl-MgCl-H₂O quaternion phase diagrams of sample 2, (c) indicates the local amplification of (d).

5.4. Genetic Formation of Interbedded Clastic Sediments

Evaporite sequences of the core S1 in the Shulu Sag displayed multiple sedimentary cycles and rhythms typified by the frequent alternation of halite with clastics. That suggests that halite formed under shallow water conditions and thus was fragile to environmental changes [50]. During the rainy season, clastic materials flew into the lake and quickly formed thin clastic beds overlying halite, or partly dissolved the underlying halite that

occurred within intercrystalline halite due to the fast crystallization of halite under shallow water conditions. Therefore, we conclude that periodic inflows during the wet or rainy season facilitate the frequent interbedded clastic sediments in the core S1. Similar clastic interbeds have also been observed in other salt basins and are thought to be linked with wet conditions [4,54].

On the basis of the H-O isotopes of halite fluid inclusions, Zhao et al. (2015) [20] suggested that meteoric water provided the main supply for the Shulu Sag during the deposition of halite in the first member of the Shahejie Fm. The values of the H-O isotopes showed frequent oscillations associated with the formation of interbedded mudstone but showed a similar trend as the K⁺ content of halite. This evidence implies that the lake brine was diluted by the inflow of fresher water after it was evaporated into a very high concentration of ions. The frequent dilution of the lake brine was also evidenced by the plotted phase regions that vary from halite samples with different colors.

Similar halite rhythms with different colors and interbedded clastic or gypsum layers have also been also reported from the salt sequences of the Dead Sea and are thought to be a response to seasonal changes [55–58]. In S1 core, transparent halite is commonly thicker than gray halite within a single rhythm, despite diagenetic compaction. Moreover, the gray halite was deposited at 4 °C higher Th than the transparent halite. Therefore, we infer that the formation of rhythms in core S1 and the related changes in brine temperature were likely caused by changes in the seasonal temperature. In fact, the controlling effect of temperature on the sedimentation rate of halite has been detected in the modern Dead Sea, and reveals a sedimentation rate of more than 0.5 mm/day in winter and less than 0.2 mm/day in summer [59].

In short, the continuous accumulation of the thick salt sequence of the first member of the Shahejie Fm resulted from the coupled hot climate and constant subsidence of the Shulu Sag [50]. During the evolution of the saline lake, inflows of fresh water partly dissolved the already-deposited halite and deposited mud layers. During ongoing evaporation, gypsum and gray halite layers were deposited. During the drier winter season, the flux of terrigenous material decreased, and transparent halite with low Ths and high concentrations of ions were deposited. The frequent dilution and concentration cycle revealed in this study is of significance for interpreting the evolution of saline basins.

5.5. The Source and Prospects of Li

In the Jiangling Sag and Qianjiang Sag of the Jianghan Basin in the South China Block and the Jitai Basin in Jiangxi, a large number of evaporites and brine developed during the Cretaceous-Paleogene period which were rich in potassium, lithium, rubidium, of cesium, bromine, iodine, and boron [59]. This brings inspiration and confidence to the exploration of new energy minerals in the Bohai Bay Basin, which is also located in the Rift Valley system in eastern China. The concentrations of lithium, strontium, rubidium, and boron in the brine of GangK1 in Jiangling Sag are, respectively, 80 mg/L, 230 mg/L, 60 mg/L, and 900 mg/L, which, in fluid inclusions, is much higher than that in Shulu Sag. Liu and coworkers [60] suggested that the enrichment of lithium, boron, rubidium, and cesium in the brine of Mesozoic and Cenozoic basins in South China is related to the basalt eruption and granite intrusion in this area. The distribution of igneous rocks in Jizhong Depression of Bohai Bay Basin is more in the north and less in the south, and the Paleogene-Neogene igneous rocks are concentrated in the north of the Jizhong Depression, such as the Langgu and Baxian Depression, and Section 1 of Shahejie Fm. Although the igneous rocks are mainly developed in the south of the Jizhong Depression, there are no igneous rocks in the Shulu Depression [61]. The possibility of deep source replenishment is smaller than that of the Jiangling Depression, with large-scale igneous rock distribution inside the depression. This is the main reason for the low trace element concentrations, such as lithium, boron, rubidium, and strontium, in the ancient salt lake brine during the sedimentary period of Shahejie Formation in the Shulu Depression.

6. Conclusions

- (1) Homogenization temperatures of fluid inclusions in halite from the first member of the Shahejie Fm of the Shulu Sag were used to quantitatively reconstruct the local lake surface temperatures from the late Eocene to early Oligocene. The resulting Th ranged from 6.5 to 49.2 °C and averaged 31.8 °C, representing the prevailing lake surface temperature and agreeing with the reported warm climate derived from pollen analyses. The revealed Th of transparent halite samples was lower than that from gray samples, suggesting different temperature conditions and a probable association with halite deposition and seasonal changes.
- (2) The ion contents of halite fluid inclusions were obtained to reconstruct the chemical composition of the salt lake during halite formation. The lake brine was a Na-Mg-K-Ca-Cl type and reached the initial stage of halite deposition. The transparent halite samples plotted within different phase regions than the gray halite samples on plots of ion contents, and their phase regions showed significant change, suggesting a shallow water environment and frequent dilution by inflows of fresher water.
- (3) The cm-scale rhythm in the evaporite sequences of the Shulu Sag is likely associated with seasonal climate change and periodic inflow of fresh water. The gray halite formed under higher temperatures and increased inflow conditions, and the transparent halite formed under lower temperatures and decreased inflow conditions. This evolutionary process provides crucial information for studying the genetic formation of high-quality source rocks and K-/Li-enriched brine. Compared with the Jiangling Sag in Hubei Province in southern China, the Shulu Sag may have been less affected by igneous rocks in the Es 1 Formation due to the material source, and the concentration of trace elements such as lithium, strontium, and boron in the ancient salt lake brine was lower.

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