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Research Article

Reconstruction of Polyhalite Ore-Formed Temperature from Late Middle Pleistocene Brine Temperature Research in Kunteyi Playa, Western China

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Kunteyi Salt Lake (KSL), located in the northwest of the Qaidam Basin (QB), is rich in polyhalite resources. However, there is no relevant research on the ore-formed temperature of polyhalite in nature, such as KSL. The homogenization temperature (T_h) of salt mineral inclusions can directly reveal the form temperature of minerals. In view of the poor diagenesis of polyhalite in KSL, almost no polyhalite crystals are formed. Therefore, the ore-formed temperature of polyhalite in KSL is revealed by using the T_h of fluid inclusions in halite associated with polyhalite as a substitute index. A total of 472 T_h data from 34 halite samples and 34 maximum homogenization temperature (T_{hMAX}) data ranged from 17.1°C to 35.5°C, among which 24 data were concentrated at 17-23°C and the average value is 22.1°C. Brine temperature of other salt lakes in QB and paleoclimate characteristics of the study area were combined. It suggests that the temperature conditions of polyhalite mineralization in the study area are generally low. However, under the overall low-temperature background, polyhalite seems to be easily enriched at relatively high temperature; for example, the content of polyhalite is generally high in the first relatively dry and hot salt-forming period, and the brine temperature at the peak stage of polyhalite at 45 m is relatively high, which indicates that the high temperature conditions promote the formation of polyhalite in KSL. As far as the overall relationship between temperature and polyhalite is concerned, polyhalite is deposited at both low temperature and relatively high temperature, which verifies the previous understanding that polyhalite is a mineral with wide temperature phase, and also shows that temperature has a limited effect on polyhalite formation under natural conditions. In addition, combined with the chemical composition of halite fluid inclusions, it is found that the concentration of Mg^{2+} in nature has an influence on the temperature measurement process. According to the previous experimental research, speculate that the actual temperature of ancient brine and ore-formed temperature of polyhalite in KSL are lower than the measured T_h. The confirmation of the influence of Mg^{2+} on temperature measurement is convenient for more accurate reconstruction of the metallogenic temperature of evaporite such as polyhalite. The research on the ore-formed temperature of KSL polyhalite enriches and perfects the polyhalite mineralization theory and provides theoretical basis for the basic and applied research of polyhalite.

1. Introduction

As a hydrated K, Ca, and Mg sulfate mineral $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$, polyhalite is widely distributed in evaporite deposits, although the phase diagram study shows that the metallogenic conditions are harsh. It is a new trend in the development of international potash fertilizer industry to make potassium sulfate (SOP) from polyhalite [1, 2]. Therefore, the research on polyhalite has never been interrupted. With the bottleneck of searching for potassium salt deposits in China and the depletion of potassium salt resources, polyhalite as a potassium-bearing mineral will become an important continuous potassium resource. Some typical foreign polyhalite deposits, such as Permian in England, Drawell Basin in America, and Great Kavir Basin in Iran and Spain, are mainly marine sediments and mostly metasomatic secondary minerals [3–5]. The Triassic polyhalite in the Sichuan Basin is the most typical in China. Studies have shown that it was formed by metasomatism of anhydrite from foreign K^+- and Mg^{2+}-rich solutions, and some scholars believe that it was formed by metasomatism of gypsum by seawater concentration [6–8]. Polyhalite also have been discovered in the Tertiary salt-bearing series in Lop Nur, Jianghan Basin, and Bohai Bay [9–11]. The polyhalite in the Qaidam Basin (QB) is mainly distributed in KSL in the northwest of the basin, and other salt lakes are also distributed but not large-scale. Kunteyi polyhalite was located in the prospecting stage in the early stage and has been further studied in recent years. The study shows that the polyhalite produced in the halite layer is widely distributed and low in content, while the clastic layer is narrow in distribution and high in content, and it is considered that the polyhalite in the halite layer is a primary mineral [12, 13]. Metallogenic simulation study proves that its formation is related to Tertiary oilfield brine upwelling along the fault, and the higher the temperature, the more favorable it is for mineralization [14]. In recent years, the laboratory experimental study of polyhalite has increased, the effect of high-temperature calcination on the mineral structure of polyhalite was observed [15, 16], and thermodynamics and metallogenic facies area of natural polyhalite were studied [17–19]. It can be seen that the research on polyhalite has been comprehensive, but there are few reports on the ore-formed temperature of polyhalite in nature.

The polyhalite produced in the halite layer of KSL is a primary mineral, which provides the possibility to study its ore-formed temperature by using the T_h of the fluid inclusions in the primary halite associated with polyhalite. Fluid inclusions in halite can provide direct, quantitative paleo-temperature data. The "cooling nucleation" method of pure liquid-phase primary halite fluid inclusion [20] can accurately test the brine temperature during the crystallization of halite. The T_h of the primary single liquid-phase halite fluid inclusions distributed in cumulate and chevron halite crystal growth bands can reflect the temperature and variation characteristics of ancient brine during salt formation [21–26]. The T_h recorded by halite fluid inclusions in shallow water is similar to atmospheric temperature, which is widely used in paleoclimate research [27–32]. The reliability of the T_h index of halite fluid inclusions and the maturity of its testing technology are further explained. In this work, the temperature of KSL brine is reconstructed by studying the T_h of the primary halite fluid inclusions in the core halite salt layer; finally, the ore-formed temperature of polyhalite is revealed directly.

The ore-formed temperature of salt minerals is mostly studied directly by using fluid inclusions in the minerals. Because all the salt lakes in QB are inland Quaternary modern salt lakes, the polyhalite minerals deposited in them have poor diagenesis, are mostly soil-like cements, and have no inclusions developed, so it is impossible to directly use their inclusions to study the ore-formed temperature. Therefore, the study of ancient brine temperature indirectly indicates the characteristics of polyhalite ore-formed temperature, which is rarely reported in the study of evaporite mineralization temperature. It is feasible in theory, an exploratory study, and a certain initiative. The initiation and implementation of this research method will greatly facilitate the revelation of the significance of temperature to potassium salt minerals such as carnallite and sylvinite and other evaporated salt minerals with unsatisfactory inclusions. Although this research is groundbreaking and distinctive, at the same time, there are some shortcomings. A total of 34 samples were collected in the evaporation salt layer of about 51 m, and 472 temperature data were measured. This data is small, and the data closer to the actual situation cannot be obtained from the statistical significance to the maximum extent.

2. Geological Setting

KSL is a secondary faulted basin in the northwest of QB, which consists of Kunteyi Dry Salt Lake, Kunteyi Lake, and Potassium Lake (Figure 1). It is a chloride-type comprehensive deposit with dry salt lake and brine lake coexisting, mainly composed of halite and potassium salt [33]. At the end of the early Pleistocene, with the separation of Qaidam ancient lakes, the Kunteyi Basin became a secondary lake basin in QB and gradually evolved into a dry salt lake [34]. This area is located in the tectonic units—Kunlun fold system and Qilian fold system, which was formed under the strong influence of Altun Mountain strike-slip fault, showing well-developed fault blocks and strong folds, with many faults developed and having an important impact on the mineralization of salt lakes [35, 36]. There is no surface recharge water body in the study area. The ice and snow melt water in the northern Altun Mountain replenishes the groundwater in front of the mountain through bedrock fissures and surface flood infiltration. The deep water discharge as seeps along the fault and the confined water at the front of the alluvial fan also account for a certain proportion of recharge [37]. In addition, the large (small) Haerten River supplies the salt lake by underground undercurrent after entering Sugan Lake, which is an important river supply source in the lake area [1]. Borehole ZK3608 is located near the mineral deposition center of Kunteyi Playa. The average sedimentation rate of Kunteyi Salt Lake since 730 ka is $4\,m/10^4a$ [38]. According to this deposition rate, the age of 75.25 m of the ZK3608 final hole is about 188 ka. ZK3208 is adjacent to ZK3608 and has the same stratigraphic sequence. Based on the chronological data of ZK3208 [39], it is calculated that the final pore age of ZK3608 is about 180 ka, which is basically consistent with the age obtained by the sedimentation rate, so it is determined to be the late Middle Pleistocene.

The study of the salt-forming period in western QB shows that the cold and dry climate since the middle and late Pleistocene has led to the concentration of lake water until it dried up, which is an important salt-forming period [41]. Through the study of minerals and elements in the core

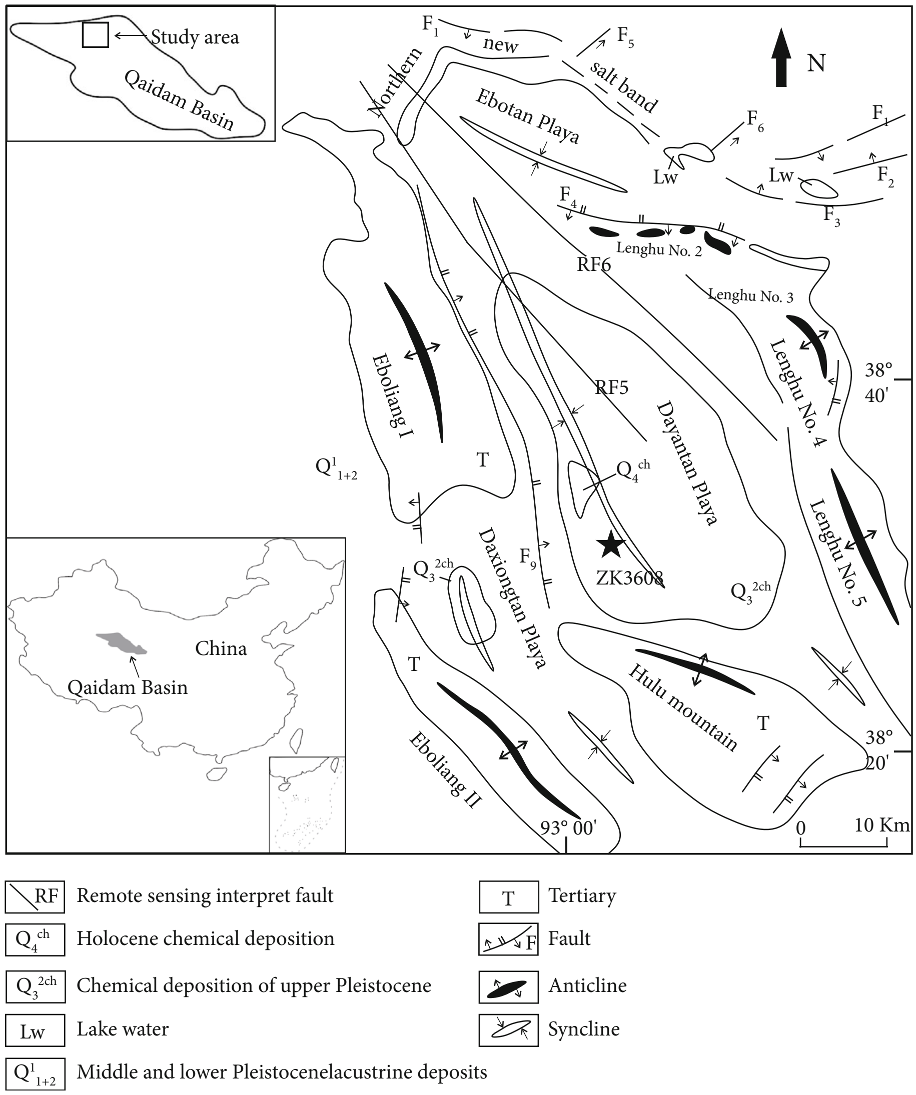

Figure 1: Schematic geological map of Kunteyi Playa in QB, China, and the location of core ZK3608 (modified after [40]).

section ZK3208 of Dayantan, it is found that the salt layer was formed in dry and cold acidic oxidation environment, and the salt-forming environment in the middle and late stage was mainly dry and cold [28]. The study of δ^{37}Cl of rock salt shows that the climate in the study area has developed from 240 ka to a drier and colder direction [42]. The CONISS clustering program divides the sediments from borehole 1045 in the Kunteyi Basin since the late Pleistocene into three mineral assemblage zones, all of which reflect the dry and cold climate [43]. It shows that the climate environment is mainly dry and cold in the middle and late salt-forming stage of Kunteyi Salt Lake.

3. Materials and Method

The petrographic observation instrument of halite and fluid inclusions is a Zeiss polarizing microscope (Axioskop 40 Pol); a Linkam THMS 600 (manufactured in England) cooling and heating stage frozen using liquid nitrogen was employed for the measurement of T_h. The temperature range measured by this instrument is -196 to +600°C, and the error is ±1°C.

3.1. Materials. Halite samples for T_h analysis were collected from the borehole ZK3608 in the Dayantan depression in the Kunteyi Playa of northwest QB (Figure 1). ZK3608 lithology has a depth of 75.25 m and contains 9 evaporite-clastic sedimentary cycles [13]. According to the systematic sorting and cataloging of core profiles, the halite layer is 51.1 m in total and primary polyhalite is widely distributed in the halite layer (Figure 2). A total of 45 halite samples were obtained by high-resolution sampling of the halite layer. Preliminary screening of lithosol particles with obvious primary characteristics, such as self-crystallization, was performed for systematic observation of petrography. Primary halite refers to the halite evaporated from lake water, and the crystals are mostly cumulate crystals and chevron crystals [44–46]. Cumulate crystals and chevron crystals

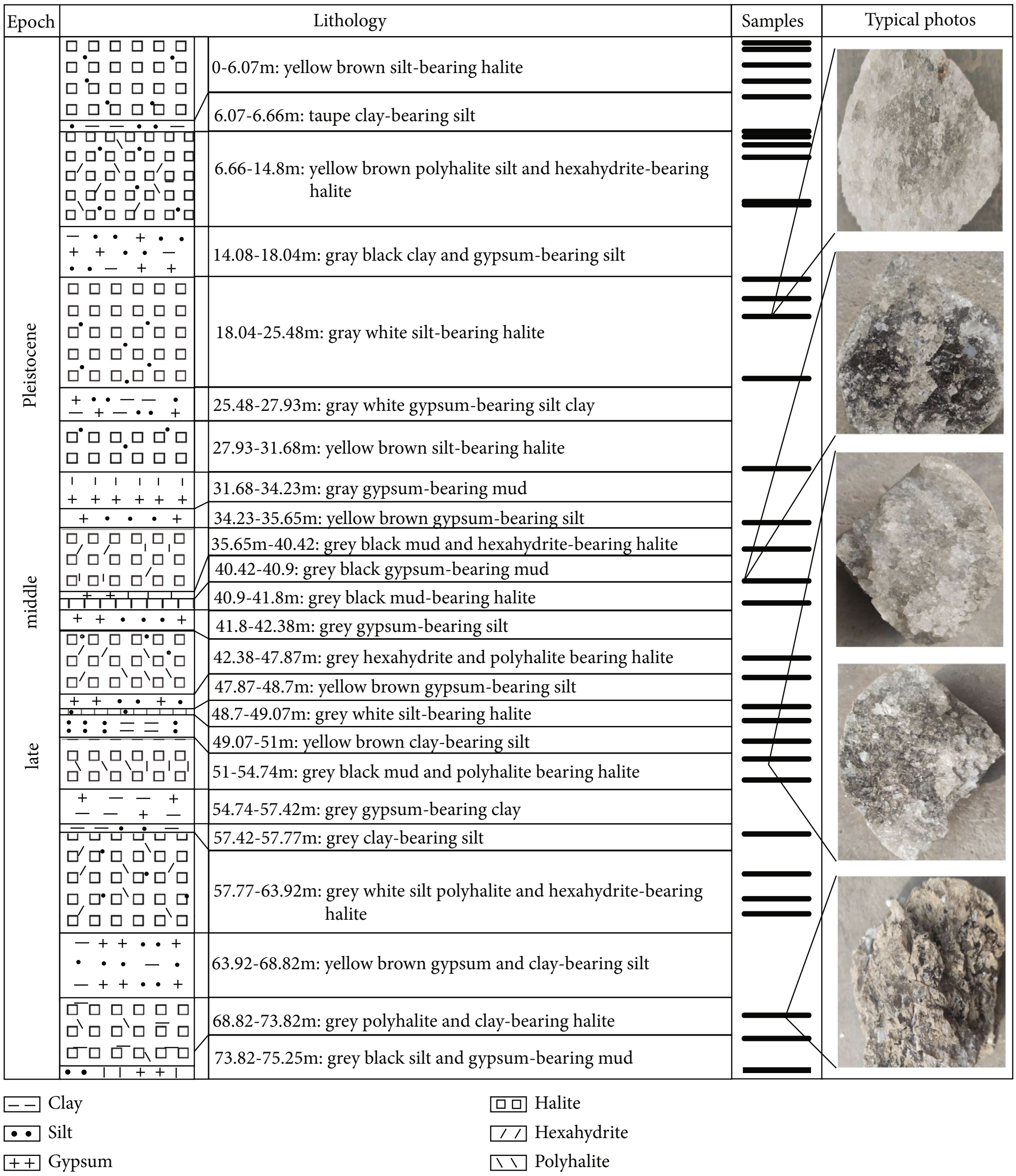

Figure 2: ZK3608 lithology description, sampling point location, and typical hand specimen.

dominate these samples (Figure 3). The primary fluid inclusions are mostly distributed along the growth zone of primary halite and also show cumulate and chevron distribution characteristics. The sample analytical methods followed those work [23]. Halite chips were prepared by cleaving 2–3 mm thick fragments with a razor blade. The prepared halite slices containing primary fluid inclusions are stored in a plastic box with a desiccant for temperature measurement. Some inclusions are gas-liquid two-phase because they cannot provide accurate temperature. Only the primary single-phase aqueous liquid inclusions within cloudy fluid inclusion bands in chevron and cumulate crystals were selected in our study for homogenization temperature analysis. Through observation of the whole rock sample of the halite salt layer, typical primary polyhalite is found, which is associated with halite. The boundary between the two minerals is clear, and there is no sign of metasomatism, which is the primary mineral precipitated from brine (Figure 4). It can be seen from hand specimen observation that gray-white polyhalite minerals are associated with halite (Figure 4). This provides direct mineralogical evidence for retrieving the ore-formed temperature of polyhalite from the temperature of ancient brine.

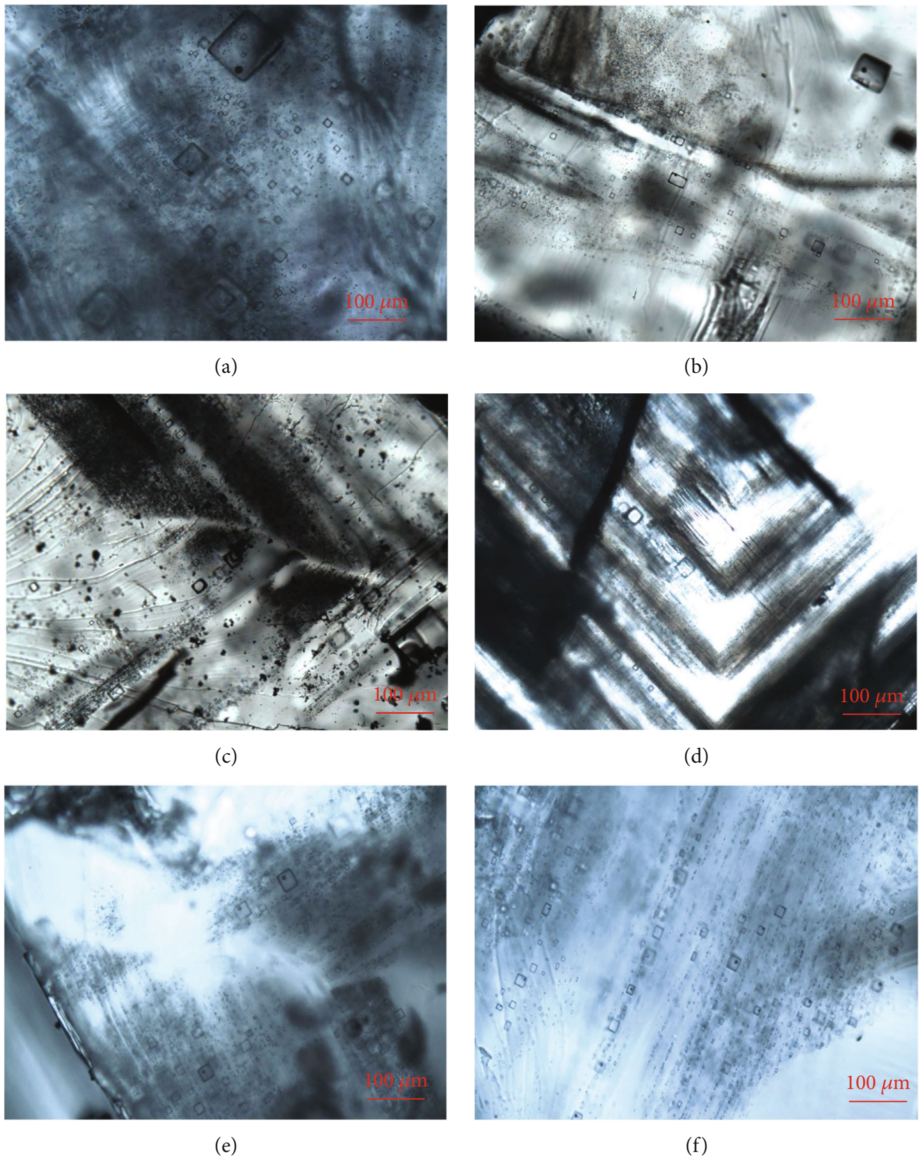

FIGURE 3: Petrologic characteristics of halite fluid inclusions: (a, b) fluid inclusion banding containing gas-liquid two-phase inclusion; (c, d) chevron fluid inclusion banding distribution structure; (e, f) a large number of gas-liquid two-phase inclusions appear after freezing with liquid nitrogen.

3.2. Method. There are two ways to freeze and nucleate halite fluid inclusions: one is to freeze slowly in the refrigerator for about two weeks and the other is to freeze quickly with liquid nitrogen on the cold and hot stage. Through the experimental study on the T_h of synthetic halite fluid inclusions, it is proven that the rapid freezing of liquid nitrogen can also provide reliable temperature data [47, 48]. We used liquid nitrogen rapid freezing and refrigerator slow freezing methods to test the T_h of artificially synthesized halite fluid inclusions and found that the maximum T_h data obtained by the two methods are very close to the set constant temperature evaporation temperature [49]. This method is also widely used in the study of T_h of fluid inclusions in salt-bearing strata such as the Jialingjiang Formation in the Sichuan Basin, Shashi Formation in the Jiangling Sag, Mengyejing in Yunnan, and Qarhan Bieletan section and Cordillera de los Andes in South America [50–54]. It shows that it is feasible to use liquid nitrogen to freeze and nucleate directly on the cold and hot stage, and this temperature measurement work is also carried out by using a liquid nitrogen rapid freezing method.

Firstly, the sheet to be measured is placed on a cold and hot stage, connected with liquid nitrogen and cooled to -18°C. On the premise of ensuring that the inclusions do not freeze and not damage the size and shape, some single liquid-phase halite inclusions appear to have bubbles due to condensation and contraction, forming gas-liquid two-phase inclusions. Then, after enough gas-liquid two-phase inclusions appear, the temperature rise test is carried out. In order to ensure the data to be as accurate as possible, the temperature rise rate is 0.5°C/min within 15°C, and the rate drops to 0.1°C/min when the temperature is above 15°C [23, 24]. The temperature at which the vapor bubbles disappeared was recorded. All the sample

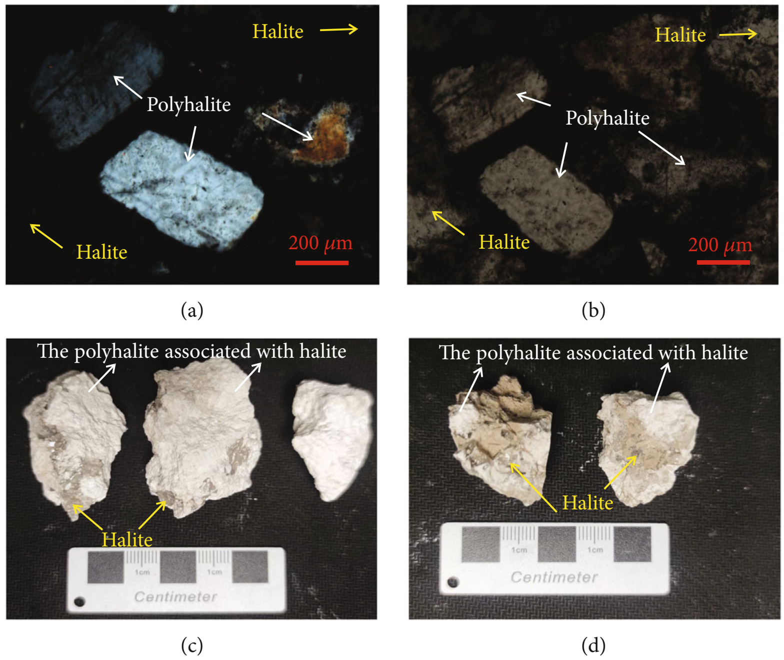

Figure 4: The microscopic morphology of polyhalite in KSL: (a, b) the relationship between polyhalite and halite in the halite layer; (c, d) relationship between polyhalite and halite in the hand specimen (from [55]).

preparation and microthermometric works were made in Minerals Lab, Qinghai Institute of Salt Lakes, Chinese Academy of Sciences.

4. Results and Discussion

Although a total of 45 halite samples were obtained, among them, 5 halite samples (nos. 4, 27, 28, 33, and 37) did not develop fluid inclusions and 6 samples (nos. 16, 17, 23, 24, 26, and 31) did not freeze out bubbles needed for temperature measurement after long-term freezing. So an amount to 472 fluid T_h data was observed and measured from 34 halite samples (Table 1). In 472 temperature data, the minimum is 4.5°C, the maximum is 35.5°C, and the average value is 17.0°C (Table 1). Characteristics of temperature data of 34 halite samples are shown in Table 1. Since the T_{hMAX} is often used to study brine temperature, this paper mainly discusses the characteristics of the T_{hMAX} of 34 halite samples. The T_{hMAX} of 34 halite samples ranges from 17.1 to 35.5°C, with an average value of 22.1°C, among which the temperature of 24 samples is between 17 and 23°C (Figure 5). In a word, the overall temperature is low.

4.1. Fluid Inclusion T_h and K^+, Mg^{2+}, and Ca^{2+} in KSL Halite. Thirty-four samples with enough T_h data were frozen by liquid nitrogen, so that the bubble appearance time was basically within 1.7 h. However, the freezing time of no. 16, 17, 23, 24, 26, and 31 samples was close to or exceeded 5 h, respectively (Table 2); still, no bubbles appear, so give up the T_h test. The scholar pointed out that freezing nucleation is difficult for some halite samples buried deep and deposited with potassium and magnesium salts [56]. Besides the experimental study on the effects of K^+, Mg^{2+}, and Ca^{2+} content on the T_h of fluid inclusions in halite, it was found that the higher the Mg^{2+} content, the more difficult it is to freeze and nucleate, and the content of K^+ has certain influence but is not the main factor [48]. The 40 halite samples obtained from ZK3608 not only tested the homogenization temperature of fluid inclusions but also tested the chemical composition of fluid inclusions [57]. The mean contents of K^+ and Mg^{2+} in 40 halite fluid inclusions are 17.1 g/l and 41.2 g/l, respectively, and the median contents of K^+ and Mg^{2+} are 12.5 g/l and 39.4 g/l, respectively [57]. The sample information of 6 unfrozen nucleation and adjacent horizons is shown in Table 2, and the composition data of sample 26 without inclusion is also shown. Samples 23, 24, and 26 have high K^+ and Mg^{2+} content; in particular, Mg^{2+} content far exceeds the average and median of Mg^{2+} in 40 halite fluid inclusions. In addition, it was found that samples 16, 17, and 31 had high K^+ and Mg^{2+} contents, especially Mg^{2+} contents, and samples in adjacent 5horizons (15, 18, 30, and 32) had the same high K^+ and Mg^{2+} contents. Even though a few inclusion data were obtained, the freezing time was longer (Table 2). It shows that not only the contents of K^+ and Mg^{2+}, especially Mg^{2+}, have an influence on freezing nucleation during temperature measurement of fluid inclusions in halite under laboratory conditions, but also the same scientific problems exist under actual natural conditions.

In addition, the experimental study shows that compared with the simple sodium chloride system, the existence of K^+, Mg^{2+}, and Ca^{2+} will cause the T_{hMAX} of halite fluid inclusions to be higher than the actual brine temperature during crystallization; in particular, K^+ has a significant impact [48]. The existence of K^+ and Mg^{2+}, especially Mg^{2+}, has an impact on the temperature measurement process. It is reasonable to believe that the existence of K^+, Mg^{2+}, and Ca^{2+} under natural

Table 1: Summary of homogenization temperatures of halite fluid inclusions.

Serial no.	T_{hMIN} (°C)	T_{hMAX} (°C)	T_{hAVG} (°C)	Depth (m)	N	Serial no.	T_{hMIN} (°C)	T_{hMAX} (°C)	T_{hAVG} (°C)	Depth (m)	N
01	12.7	23.0	17.2	1.0	13	18	10.7	19.0	14.8	37.6	16
02	14.0	22.0	17.4	1.5	15	19	9.5	25.0	17.2	39.9	24
03	15.2	25.6	20.2	2.6	15	20	9.0	22.5	16.2	41.5	8
04	15.6	25.4	19.1	3.8	20	21	15.5	31.0	22.4	45.5	8
05	19.8	35.5	25.8	4.9	12	22	10.5	19.3	15.3	46.9	19
06	15.5	22.0	18.2	7.4	13	23	4.5	22.0	9.9	49.0	18
07	12.0	22.0	16.3	7.8	9	24	12.0	22.0	16.1	50.0	14
08	11.6	30.0	21.8	8.4	17	25	13.0	19.5	15.9	51.5	16
09	9.3	18.6	15.8	9.3	6	26	10.2	19.3	14.3	52.8	12
10	13.0	21.0	15.8	12.5	7	27	13.0	25.8	21.2	54.3	6
11	15.1	26.1	20.6	12.7	12	28	16.1	28.0	23.1	58.2	14
12	9.9	17.5	14.3	18.1	7	29	12.1	18.4	14.7	61.1	13
13	18.0	18.0	18.0	19.5	1	30	9.0	18.1	13.4	62.9	18
14	11.0	17.9	14.8	20.8	22	31	9.7	17.1	12.8	64.0	10
15	10.0	20.5	15.9	25.3	19	32	13.0	21.0	16.2	71.2	13
16	11.5	19.6	15.8	31.8	24	33	13.0	19.2	15.6	73.0	19
17	10.5	19.0	15.4	35.7	20	34	11.9	20.1	15.5	75.3	12

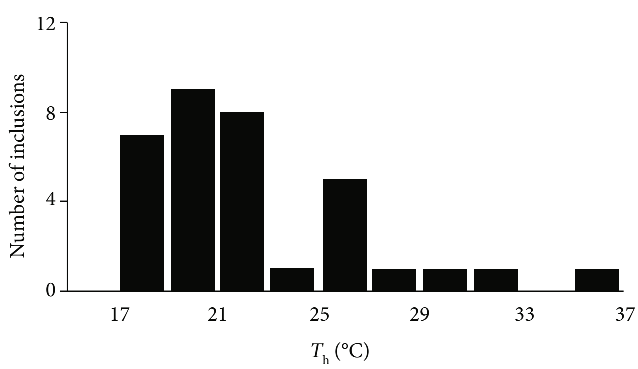

Figure 5: The T_{hMAX} distribution in the Kunteyi halite of borehole ZK3608.

Table 2: The samples without temperature data and K and Mg contents in halite about the same deposition stage.

Original no.	Freezing time (h)	Amount	Depth (m)	AVGρ(K) (g/l)	AVGρ(Mg) (g/l)
15	5.0	8	45.5	25.4	78.0
16	>5.0	0	44.5	17.8	82.4
17	>5.0	0	43.3	18.2	63.3
18	3.0	8	41.5	7.1	32.3
23	>5.0	0	30.5	8.0	46.6
24	>5.0	0	29.0	16.7	77.1
26	>5.0	0	24.9		
30	3.5	1	19.5	11.7	47.9
31	>4.3	0	19.2	12.5	48.4
32	4.0	7	18.1	15.7	47.9

conditions, especially K^+, will lead to the higher T_{hMAX} of halite fluid inclusions. As for whether the existence of K^+ and Mg^{2+} plasma affects the temperature measurement process and leads to high temperature, it needs further study, but it can be proven that the existence of K^+ and Mg^{2+} plasma does affect the T_h results under natural conditions. Combined with the chemical composition of ZK3608 halite fluid inclusions [57], the T_{hMAX} of 34 halites ranging from 17.1 to 35.5°C may be higher than the temperature in different historical periods in the study area. Although the specific height cannot be quantified at present, it can be determined that the actual brine temperature and polyhalite ore-formed temperature are a little lower than the tested T_{hMAX} in the study area since the late Middle Pleistocene.

4.2. Paleotemperature since the Late Middle Pleistocene of KSL

4.2.1. Brine Temperature in KSL and QB. In laboratory- and nature-grown halite crystals, the T_{hMAX} all matched the brine temperature [22, 29, 58]. The results showed that the T_{hMAX} ranges from 17.1 to 35.5°C with an average of 22.1 (major concentration 17-23°C) (Figure 5). Since the salt lakes in QB are the common characteristics of Quaternary modern salt lakes in nonmarine environment, our results can be compared with the previous brine temperature data in different geological ages in the basin. Reported temperatures for QB modern brine evaporites range from 17.9 to 38.2°C [26]. Salt lake brine temperatures in the Qarhan Salt Lake (southeast QB) range from 23 to 40°C [59]. Brine temperatures of the Chaka Salt Lake (southeast QB) generally range from 19 to 25°C but can reach 30°C in August [27]. The T_h of halite fluid inclusions in Yiliping Salt Lake reflects the temperature variation range of ancient brine from 21.4°C to 30.1°C [60]. The temperature of ancient brine in the northern area of Bieletan in Qarhan Salt Lake is mainly concentrated at 15-20°C, and some horizons can reach 28°C and

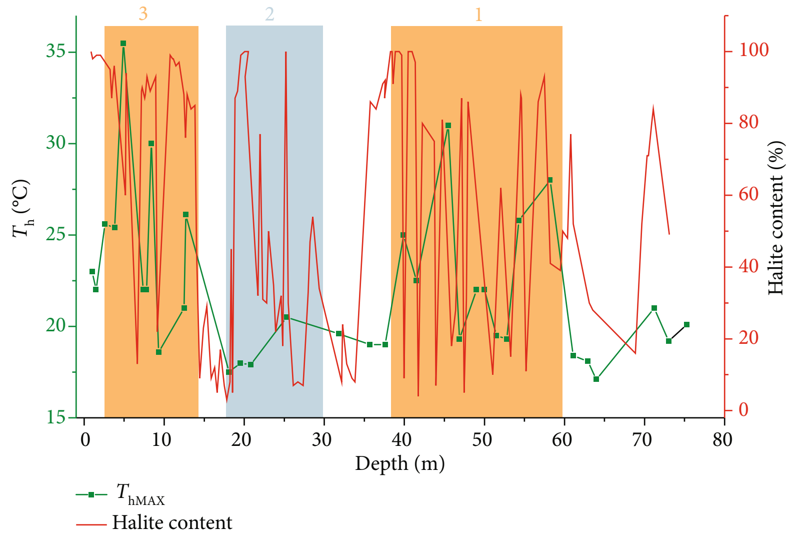

FIGURE 6: Relationship between halite content and ancient brine temperature in the ZK3608 core.

the high-temperature horizons promote the deposition of potassium salt [54]. Core SG-1 was located in Chahansilatu of northwest QB. Based on the study of Mg^{2+} isotopes of polyhalite and bloedite in core samples, it was suggested that there is existence of a warm dry climate in the QB, with brine temperature as high as ~70°C at 0.39 Ma, 0.36 Ma, and 0.12 Ma [61]. According to unpublished age data of ZK3608 ($y = 0.249x - 16.611$), 0.36 Ma and 0.12 Ma correspond to 73.0 m and 13.0 m of ZK3608, respectively, and the latest T_h of halite fluid inclusion results is 19.2°C (72.9 m) and 26.1°C(12.7 m), respectively. It reflects these two periods, and the temperature is relatively high. However, according to isotope results, it is questionable that there is a high temperature of 70°C.

The temperature are generally consistent with the brine temperature that halite precipitates, which can well reflect the brine temperature. Compared with the brine temperature of other salt lakes in the QB, the range of 17.1-35.5°C is reasonable, but the temperature is mainly concentrated at 17-23°C (Figure 5), which is generally lower than that of other salt lakes.

4.2.2. Halite Fluid Inclusion T_h with Mineral. Halite deposit is the most direct mineral reflecting the sedimentary evolution degree of salt lake, and halite is the mineral that has been running through since the salt formation of KSL. Therefore, through the remarkable sedimentary characteristics of halite, it shows that there are three main salt-forming periods since the Middle Pleistocene in Kunteyi Salt Lake (Figure 6). Combining the relationship between ancient brine temperature and main salt-forming periods, it can be clearly seen that the brine temperature is generally higher in the 1st (59.79-38.26 m) and 3rd (14.05-0 m) salt-forming periods, while the salt content in the 2nd salt-forming period (29.35-18.37 m) gradually increases, but the brine temperature is always at a lower level (Figure 6). The evaporation rocks in KSL were formed in dry, cold, and slightly acidic oxidation environment [39]. Temperature results show that KSL not only has salt formation in the cold period but also has salt formation in a relatively warm period, which is dominant. According to the systematic study of salt deposits in the arid salt-forming center areas in China since Quaternary (the salt lake areas in the west of the Qaidam Basin and the east of Tarim Basin), there are several cold-dry salt-forming periods and warm-dry salt-forming periods, while there is a strong cold-wet salt-forming period in 180-140 ka [62]. The salt-forming period of salt lakes in the Qaidam Basin responded to the Quaternary glacial period of Qinghai-Tibet Plateau to a certain extent, especially in the salt lakes in the western Qaidam Basin, where halite salt layers of the penultimate glacial period (MIS6) were widely developed [63, 64], while the second low-temperature salt-forming period (29.35-18.37 m) divided in this work can be seen from the ZK3608 age frame ($y = 0.249x - 16.611$) whose age span is 185-140.5 ka. Obviously, this low-temperature salt-forming period recorded this strong cold and wet event, and it was also a response to the salt-forming period of the penultimate glacial period. To some extent, it shows that the temperature trend of halite fluid inclusions is correct. The ancient brine temperature reflected by halite fluid inclusions shows that the brine and environment temperature in the main salt-forming periods (the first and third salt-forming periods) of KSL is higher, which belongs to a relatively warm and dry salt-forming mode, while the short salt-forming period in the second salt-forming stage belongs to cold and wet salt forming. These three salt-forming stages are the main sedimentary periods of polyhalite, among which the first and third relatively warm and dry salt-forming periods account for a large proportion. It shows that the ore-formed temperature of polyhalite in KSL is extensive. On the other hand, it shows that in KSL, a relatively dry and hot salt-forming model is dominant, which promotes the extensive production and deposition of polyhalite.

The phase diagrams of epsomite, hexahydrite, and kieserite under certain temperature and humidity conditions [65] are shown in Figure 7. In a certain range of humidity,

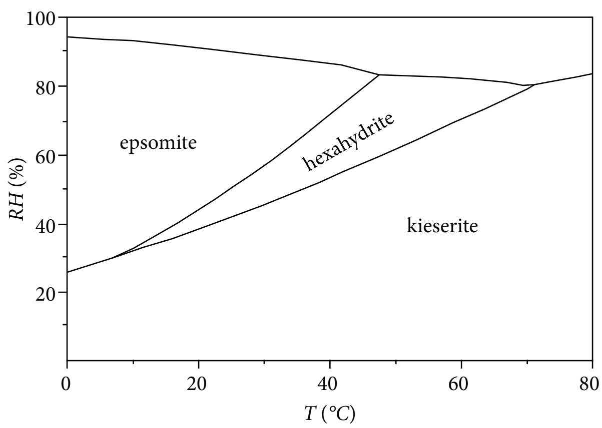

Figure 7: Diagram of existence conditions of epsomite, hexahydrite, and kieserite (modified from [65]).

with the increase in temperature, the phase area of salt discharge in hexahydrite increases slowly. According to [57], ZK3608 mineral was analyzed by X-ray powder diffractometry (XRD), and hexahydrite was scattered in the lithology. Comparing the hexahydrite content of ZK3608 with the T_{hMAX} of halite fluid inclusions (Figure 8), we can see that there is a high similarity between the hexahydrite content and the T_{hMAX}, and the hexahydrite is relatively high in the three main high-temperature stages, but almost no hexahydrite is released in the low-temperature stage. Although the distribution range of hexahydrite release is narrow in the high-temperature stage near the surface, it is a fact that more or less hexahydrite release is precipitated in the high-temperature stage of the core profile, and there is no or only a few hexahydrite release in the low-temperature stage. As far as magnesium sulfate salt is concerned, epsomite tends to be produced at low temperature and high humidity, kieserite tends to be produced at high temperature and moderate humidity, and hexahydrites sandwiched between them are easy to form at moderate temperature and humidity (Figure 8). Combined with the mineral phase diagram of magnesium sulfate double salt, in view of the actual geological background of drought and low temperature in the Kunteyi area, it is unrealistic for epsomite and kieserite to appear in the drill core profile, but it is reasonable for hexahydrite to appear. XRD results of ZK3608 mineral show that only hexahydrite does appear [13]. What is important is that the variation trend of hexahydrite content in the core profile is similar to the T_{hMAX}, which is in accord with the relationship between temperature and hexahydrite revealed by the phase diagram. It shows that the T_h of halite fluid inclusions reflects the actual temperature in the study area to a certain extent.

According to the sediment assemblage and its variation characteristics of KSL, it can be divided into 9 evaporite-clastic sedimentary cycles, and the closer to the surface, the thicker the halite layer [39, 57]. It shows that the climate change in the study area is generally characterized by oscillation and drying. The T_{hMAX} of ZK3608 halite fluid inclusions increases gradually from bottom to top and fluctuates on the way, which reflects the variation characteristics of paleoclimate in the study area.

Chlorite generally exists only in glacial areas and in the surface environment with weak chemical weathering, while illite shows that the climate is dry and cold and the leaching effect is weak. The clay mineral combination of chlorite and illite is considered to exist only in glacial areas [66, 67]. Muscovite is the main illite mineral, and there is a certain amount of chlorite and muscovite deposits in the ZK3608 clastic layer. Although the clay minerals in salt lakes reflect the climate characteristics of the source region more, the content of clay minerals is often low during the dominant period of chemical deposition [68]. Chlorite and muscovite, which should have been deposited in the clastic layer of salt lake, developed in great quantities in the second salt-forming period and deposited with evaporite at the same time, which corresponds to the low T_{hMAX} stage of halite fluid inclusions (Figure 8). Obviously, the lower temperature of ancient brine and the deposition of a large number of chlorite and muscovite in this period (Figure 8) are the environmental response to the strong cold and humidity during 180-140 ka [62]. The cold glacial climate environment resulted in a large number of chlorite and muscovite in the surrounding alpine provenance, which were transported to salt lake and deposited with evaporite at the same time due to the humid climate conditions. However, in the first relative dry-hot salt-forming period, chlorite and muscovite deposited in the clastic layer between evaporated rock layers and with the T_{hMAX} of halite fluid inclusions showed a flipped relationship (Figure 8), which confirmed the characteristics of this mineral deposited in the clastic layer. According to the analysis of sedimentary characteristics of minerals, including halite, hexahydrate, muscovite, and chlorite, it is confirmed that the T_{hMAX} of ZK3608 halite fluid inclusions truly reflects the temperature changes of ancient brine in KSL since the middle Pleistocene.

4.2.3. Temperature of Ancient Brine Response to Paleoclimate Variation in the Study Area. The T_h of primary halite fluid inclusions in shallow water can be used to indicate air temperature, indicating that paleotemperature is closely related to brine temperature. As mentioned earlier, the climate of KSL has been mainly dry and cold since the late Pleistocene. Deep borehole (SG-1) was located in Chahansilatu in western QB close to Kunteyi Playa, and research of stable isotopes of carbonates from the SG-1 core suggests that since 0.6 Ma, the climate in northwest China has been in a long-term dry and cold state, which is mainly affected by global cooling, especially cooling in the high latitudes of the Northern Hemisphere [69]. A 600 m deep core (SG-3) of lacustrine-playa deposits was obtained from the western Qaidam Basin, and sporopollen results show that from 0.6 Ma and 0.15 Ma to late Pliocene, Ephedraceae-dominated desert prevailed response to long-term global cooling [70]. As far as climate is concerned, both regional short-time scale climate characteristics and global long-time scale climate conditions have proven that the paleoclimate in the study area has been mainly dry and cold since the end of the late Pleistocene.

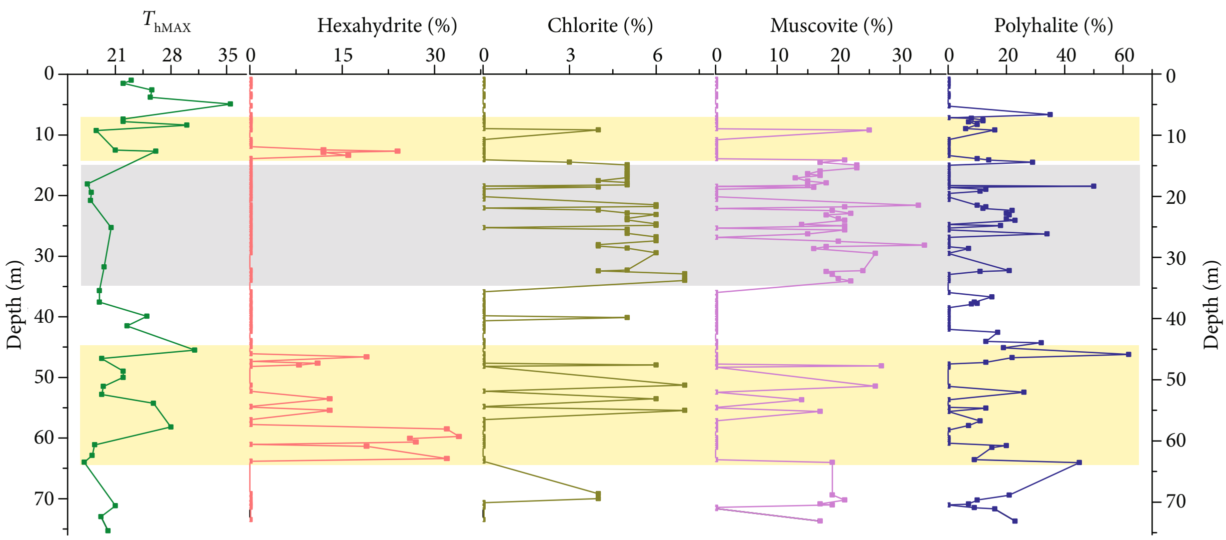

Figure 8: Plots showing concentrations of different minerals along the depth of the borehole and its relationship with T_{hMAX}.

Through the evidence of brine temperature of other salt lakes in QB, mineral sedimentary, and paleoclimate characteristics in the study area, it shows that the temperature range of 17.1-35.5°C, mainly concentrated at 17-23°C, faithfully reflects the ancient brine temperature characteristics of KSL since the late Middle Pleistocene.

4.3. Ore-Formed Temperature of Polyhalite in KSL. Salt minerals were divided into three types: cold phase, warm phase, and wide temperature phase, and polyhalite was identified as wide temperature-phase mineral [62]. The widespread existence of polyhalite in ancient and modern evaporite deposits [71], to a certain extent, explains the wide temperature range of polyhalite mineralization in nature. It can be seen from the phase diagram of the five-element system superimposed by calcium ions that the polyhalite phase area is very small when the temperature is less than 32.5°C, and the polyhalite phase area expands rapidly when the temperature is 55°C [72]. Polyhalite crystallisation slows down, when at lower temperatures [73]. Polyhalite can be synthesised under laboratory conditions by a reaction of gypsum with appropriate solutions in the ternary system K_2SO_4-$MgSO_4$-H_2O at temperatures above 70°C [74]. Through EQL/EVP hydrogeochemistry software, the Kunteyi polyhalite ore-forming fluid was simulated under different temperature conditions, and it was found that low temperature was not conducive to polyhalite mineral deposition, while polyhalite was easy to deposit under high-temperature conditions [75]. In Lop Nur western China, polyhalite has been deposited many times in a short time, which is considered to be mainly affected by climate fluctuations with high temperature [10]. The polyhalite microfabrics in an Alpine evaporite melange of Eastern Alps have a formation temperature of 61.4°C in the presence of halite [76]. As mentioned earlier, the salt lake brine temperature was at a high level during the formation of polyhalite in SG-1 drilling at Chahansilatu [61]. Whether it is the indoor experimental study of polyhalite or the exploration of the formation temperature of polyhalite in nature, it shows that polyhalite is more inclined to form at higher temperature.

Although paleoclimate research shows that the climate of KSL is relatively dry and cold in this period, through combining the relationship between evaporite and ancient brine temperature, it is found that brine and environment temperature was relatively high when the main evaporite was formed in KSL, while polyhalite was mainly formed in this relatively high-temperature salt formation process. In addition, polyhalite peaks at 46 m, and the temperature of ancient brine is relatively high. It is proven that the enrichment characteristics of polyhalite in KSL at relatively high temperature in this low-temperature environment are consistent with the conclusion that polyhalite is easier to develop at high temperature. At the same time, the polyhalite developed in the first and third relatively dry and hot salt-forming environments, while the polyhalite also developed in the second strongly cold and humid salt-forming environment (Figure 8), which indicated that the polyhalite in KSL has strong adaptability to temperature and is a mineral with a wide temperature phase. It also proves to some extent that temperature has a limited effect on the formation of polyhalite. Numerous evidences show that polyhalite tends to be deposited at high temperature, and the low temperature of brine in KSL during this period may be one of the reasons why polyhalite did not develop on a larger scale.

5. Summary and Conclusion

(1) Polyhalite is mostly formed in the relatively high-temperature stage in the low-temperature environment, and the relatively high-temperature conditions promote the formation of polyhalite in KSL

(2) Polyhalite has a strong adaptability to temperature and is a mineral with a wide temperature phase; while temperature has limited influence on

polyhalite formation, it is deposited at different temperatures

(3) In the evaporite geological environment, in sedimentary areas with high K^+ and Mg^{2+} content, especially in areas with high Mg^{2+} content, Mg^{2+} has an important influence on the freezing process of the cooling nucleation method of halite fluid inclusions. We according to the previous experimental research speculate that the actual ore-formed temperature of polyhalite in KSL is lower than the measured T_h

Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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