Ore-Forming Fluid Evolution of Shallow Polyhalite Deposits in the Kunteyi Playa in the North Qaidam Basin

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Polyhalite occurrence in the Kunteyi Playa in the Qaidam Basin has been known for many years. However, the genetic mechanism of this deposit remains unclear. In this study, a typical section in the playa depocenter is selected to study the polyhalite mineralogy combined with the homogenization temperature and composition of halite fluid inclusions in shallow evaporitic strata. The results show that 1) the main evaporite minerals in the strata are halite and polyhalite; no common gypsum is found; 2) analyses of homogenization temperatures of halite fluid inclusions indicate that a higher temperature is needed for polyhalite generation compared with other saline minerals; and 3) the fluid inclusion chemical analysis shows that they are sulfate-type minerals with a shortage of Ca. Thus, it can be concluded that the formation of polyhalite is not related to gypsum replacement, and deep oilfield brines may provide a Ca source and a higher temperature for polyhalite formation, where the mixing and interaction occurred between K- and Mg-enriched sulfate brines and deep Ca-enriched brines under the control of climate and tectonics in the study area. While most polyhalite was generated natively, some formed during secondary generation, which was potentially related to replacement with carnallites or sylvites.

Keywords: Kunteyi Playa, Qaidam Basin, polyhalite, sedimentology, mineralogy, halite fluid inclusion, water-salt interaction

INTRODUCTION

Many complex chemical and physical processes occur during brine evolution in an actual salt lake system, and it remains difficult to explain certain specific mineral generation. These processes range from the dissolution to precipitation of various minerals, which depend on a variety of climate and other geological environmental conditions. Precipitation of polyhalite (Ca2MgK2(SO4)4·2H2O) is an important process that occurs during brine evaporation. Understanding polyhalite generation is critical for explaining the evolution of specific salt lakes in salt lake systems. As an important potassium-
bearing mineral, polyhalite has been found in many evaporite basins worldwide (Warren, 2006). Most researchers believe that it is produced by the conversion of Ca-rich minerals that interact with a specific fluid at a later stage of brine evolution (Stewart, 1965; Pierre, 1985; Harville and Fritz, 1986; Li and Han, 1987; Wei, 1987; Liu et al., 2008; Liu et al., 2010; Ma et al., 2010; García-Veigas et al., 2013; Holt et al., 2014; Niu et al., 2015). Some have also considered that it can also be generated by multiphase fluid interaction between Ca-rich brines and K-Mg-rich ones (Stewart, 1965; Perthisot, 1971; Wang and Zheng, 2014). The transformation of gypsum to polyhalite requires brine with high K, Mg, and SO4, which has been used to decipher the origin of polyhalite in the Delaware Basin in the United States and the Zdrada Platform in Poland (Harville and Fritz, 1986; Peryt et al., 1998). In the Miocene marine Great kavir evaporite basin in central Iran, the inflow of CaCl2-rich brine accounts for the absence of primary polyhalite (Rahimpour-Bonab et al., 2007). Ultra-micro-analyses of halite fluid inclusions, developed by Petrichenko (1973), have been widely applied to study the evolution of ancient seawater and brine from halite fluid inclusions (Petrichenko et al., 2002; Kovalevych et al., 2006, 2009; Meng et al., 2014). The concentrations of K, Mg, Ca, and SO4 in a fluid inclusion (>20 μm) can be determined using this method (Kovalevych et al., 2009). By analyzing the components of halite inclusions and saturation indices of the main evaporite minerals, Garcia-Veigas et al. (2013) revealed that the Miocene polyhalite in the Granada Basin in Spain was mainly formed during the early stage of halogeneses. Polyhalite has also been extensively deposited in modern environments. In the Californian shore lagoon in the United States, after detailed investigation, the Holocene polyhalite is thought to have formed during the early stage of evaporite genesis, with CaSO4 being replaced (Hardie, 1968). Most polyhalite studies are based on marine environments, while polyhalite deposition in continental settings is rarely considered. The Kunteyi Playa, located in the northern Qaidam Basin in China, is known for its large-scale modern inland lacustrine polyhalite deposits. The geological reserves of polyhalite in the playa are approximately 200 million tons (Li et al., 1990). To the best of our knowledge, no work has systematically studied the formation mechanism of polyhalite deposits in this playa, except for some simple descriptions in earlier exploration works. Therefore, we selected a shallow section near the surface to conduct systematic studies to discuss the polyhalite genesis and better understand the evolution of this special playa. In this study, we demonstrate how the combined information from sedimentary characteristics, polyhalite mineralogy, and halite fluid inclusions support the evolution of brine and the polyhalite deposition processes in the Kunteyi Playa.

**GEOLOGICAL SETTING**

The Qaidam Basin, located in the northern Qinghai–Tibet Plateau, has an area of 120,000 km² and an average elevation of 3,000 m. It is confined to the tectonic belts of Qilian Mountain, Kunlun Mountain, and Altyn Mountain, which controlled the basin evolution. The Qaidam Basin was generated as a result of multistage strike-slip activities accompanied by strong uplift on the Altyn Fault belt since the Cenozoic (Yin et al., 2002; Li et al., 2006). There were at least three strong uplifts (~30 Ma, ~8 Ma, and ~2.6 Ma) during the Cenozoic that affected and changed the tectonic development in the basin (Pan et al., 2015). Outcrops of Cenozoic strata occur along the northern and western basin edges. From bottom to top, these strata comprise seven formations: the Lulehe (E1-2), Lower Ganchaigou (E3), Upper Ganchaigou (N1), Lower Youshashan (N2), Upper Youshashan (N2), Shizigou (N3), and Qigequan formations (Q1-2) (Shen et al., 1993; Wang et al., 1997).

The Kunteyi Playa covers an area of 1,680 km² in the northern Qaidam Basin (Figure 1). The playa is characterized by an extremely dry climate with an average precipitation of only 15.7 mm per year, while the average evaporation rate is as high as 3,095.9 mm per year (Zhang and Xuan, 1996). Although one seasonal river, the Qingshui River, recharges the border of this playa, there is no other surface water recharging it, which makes it a closed basin surrounded by the tectonic belts of the Eboiliang to the west, Hulushan to the south, and Lenghu to the east (Wang et al., 1997). Zhang (1987) concluded that the playa was separated from an ancient pan-lake in the Qaidam Basin during tectonic movement in the Late Pliocene and then formed as an isolated subbasin. During the Early and Middle Pleistocene, the basin sedimentary environment primarily alternated between a salt lake and saline-semisaline water. The salt lake environment was characterized by halite deposition, while gypsum deposition was a feature of the saline-semisaline water environment. It was affected by neotectonic movement during the Late Pleistocene when the western part of the Qaidam Basin continued to uplift, and the Kunteyi Playa was already isolated. At this time, the depth of Kunteyi Lake was shallower than during the Early and Middle Pleistocene and the sedimentary environment changed from a saline-semisaline water environment to a salt lake environment. Since the Late Pliocene and Quaternary, the uplift of the Kunlun Mountains and the Altyn Tagh Mountains caused the development of several secondary or subsidiary basins, and these basins ultimately evolved into playas with climatic desiccation (Chen and Bowler, 1986). The evaporite sediments occurred mainly from 0.97 Ma to 0.03 Ma, with halite and gypsum as the major evaporites, with some mirabilite and polyhalite minerals (Han et al., 1995; Wang et al., 1997; Huang and Han, 2007).

Polyhalite deposits are commonly found in brine aquifers and silt-rich aquitards in shallow strata, which are the most important solid K-containing minerals. However, polyhalite in the basin cannot be exploited directly because of its low dissolution rate and low permeability (Yuan et al., 2018). This type of mineral is mainly distributed in the Pleistocene stratum on the west side of the basin, and its deposition probably occurred during the middle to late stage of the Middle Pleistocene (Wei et al., 1993). The buried depth of polyhalite is about 6–65 m, characterized as lenses. The maximum thickness of a single layer of the ore bed is up to 12 m, and the minimum is 0.3 m. The maximum thickness of the bed is up to 18.1 m; results from chemical analysis suggested that the average content of K2SO4 is 3.95% (Liu et al., 2010).
MATERIALS AND METHODS

An approximately 6-m thick section with polyhalite deposits near borehole ZK3208 in the Kunteyi Playa was investigated in this study (Figure 1). Seventeen samples (BD-01–17) were collected based on the lithologic characteristics of the sections. The sample BD-01 being collected in the depth of 0.20 m is dark brown silty clay with halite and trace gypsum. BD-02 (0.50 m in depth) is white fine-grained halite crust and brown silt. BD-03–BD-05 (0.70 m, 1.20 m, 1.70 m) are brown clayey silt with fine-grained and semieuhedral halite. BD-06 and BD-07 (2.20 m, 2.70 m) are brown clayey silt with halite and fine sand. BD-08–BD-10 (2.90 m, 3.50 m, 3.70 m) are pale yellow, loose fine sand with scattered halite and minor clay. BD-11 and BD-12 (3.90 m, 4.10 m) are grey medium-coarse grain halite with minor mud. Samples BD-13 and BD-14 (4.30 m, 4.50 m) are brown polyhalite with minor scattered halite and mud. BD-15–BD-17 (4.80 m, 5.20 m, 5.70 m) are characterized as grey medium-coarse grain halite with minor polyhalite and mud (Figures 2, 3). To ensure sample representativeness, the exposed loose sediments on the surface of the section were removed before sampling.

The mineralogical investigations consisted of three main parts. First, every 100 g representative sample was crushed to 60 mesh, and 3–5 g was weighed and ground continually to 200 mesh. The samples were then scanned by X-ray diffraction (XRD) (X’Pert Pro) continually with a working condition of 30 mA and 40 kV. Three samples (BD-10, BD-13, and BD-14) with a high proportion of polyhalite were selected to analyze the micromorphology and chemical components using scanning electron microscope—energy dispersive spectrometer (SEM-EDS) (JSM-5610LV/INCA series, Max Resolution HV3.5 nm, Min Resolution LV5.0 nm, Magnification: 35–30 million times). All experiments were performed at the Salt Lake Analysis Center at the Qinghai Institute of Salt Lakes, Chinese Academy of Sciences.

The cooling nucleation approach was used to measure the homogenization temperature of halite fluid inclusions (Lowenstein et al., 1998; Benison and Goldstein, 1999; Meng et al., 2011; Meng et al., 2013; Zhang et al., 2016). First, a 0.5 mm thin slice was removed from the selected halite crystal using a razor blade along a cleavage plane. Then, detailed petrographic observations on every segment were performed, and the pure liquid fluid inclusions with primary chevron shape characteristics were marked and documented clearly under the microscope. All the samples were rapidly cooled to 18°C and held. When nucleation vapor bubbles emerged, the homogenization temperature was measured on a cooling–heating stage (LINKAM THMSG600, LINKAM THMSG600, LINKAM THMSG600).
measurement range: 196–600°C, error: ±1°C) coupled with a microscope (Axioskop 40 Pol, eyepiece lens ×10, objective lens ×20, 50×). After the set-up, the heating stage was warmed at a rate of 0.5°C/min up to 15°C. Finally, the temperature was lowered at a rate of 0.1°C/min until all artificially nucleated vapor bubbles disappeared (homogenized).

Ultra-micro-analysis of halite fluid inclusions was performed in this study as follows.

1) Fluid inclusion extraction. A series of well-preserved salt crystals was selected and cleaned before drying in an oven at warm temperatures. Then, like the criterion of homogenization temperature analysis, the characteristics of geometry and distribution of a series of 0.3–0.5 mm thin slices were removed from the selected halite crystals using a razor blade along a cleavage plane and were observed to determine the fluid inclusion origin. Furthermore, under the microscope, fluid from the inclusions was extracted using a conical microdrill with a capillary glass tube.

2) Measurement of major elements. Special reagents were added to interact with the extracted fluid from the inclusion, depending on the specific ions to be measured. (NH₄)₂C₂O₄ (5%) was added to determine the Ca, BaCl₂ (30%) to determine SO₄, Na₂CO₃(NO₂)₂·0.5H₂O (3%) to determine K, C₆H₁₂N₄ (30%) and K₄[Fe(CN)₆]·3H₂O (15%) to determine lower concentrations of Mg (<6 g/L), and C₆H₁₂N₄ (30%) and (NH₄)₂C₂O₄ (15%) to determine higher Mg concentrations (>6 g/L). Reaction stoichiometries are presented below.

\[
\begin{align*}
SO_4^{2-} + BaCl_2 & \rightarrow BaSO_4 \downarrow \\
Ca^{2+} + (NH_4)_2C_2O_4 \cdot 0.5H_2O & \rightarrow CaC_2O_4 \cdot 3H_2O \downarrow \\
K^+ + Na_2[Co(NO_2)_3]Na[Co(NO_2)] & \cdot 0.5H_2O \rightarrow K_2Na[Co(NO_2)]_6 \downarrow \\
Mg^{2+} + C_6H_12N_4 + K_4[Fe(CN)_6] & \\
3H_2O & \rightarrow 2MgCrO_4 \cdot 3C_6H_12N_4 \cdot 15H_2O \downarrow
\end{align*}
\]

The depleted reagent added depends on the reactions studied, which are visually controlled under a microscope. This always exceeds the amount of element to be precipitated. The capillary glass tube was sealed and centrifuged until the ultimate precipitation reactions were completed. The volumes of the precipitate and solution formed during this process were measured separately and then compared to those formed from a standard solution (Petrichenko, 1973). To minimize the measurement error, we obtained a series of analysis data for each component in the inclusions; the error rate decreased to 16–17% by two to three parallel analyses (Petrichenko, 1973). The minimum quantity of the studied ions needed for such an error rate is (in g/L) 0.8 for K, 1.0 for Mg, 0.9 for Ca, and 0.5 for SO₄, and the smaller values are not very precise. These experimental analyses were performed at the State Key Laboratory of Paleobiology and Stratigraphy, Nanjing Institute of Geology and Paleontology, Chinese Academy of Sciences.
RESULTS

Petrography
The whole section for the study included the upper and lower sections (Figure 1B). The sediments in the upper section (from 2.70 m to the surface) were mainly composed of brown to dark brown fine sand and halite, with a thinly mirabilite deposited on the section surface. The lower section (from 5.70 to 2.70 m upwards) is characterized as (C) a grey clay-bearing halite layer with large halite crystals (~0.3–1.5 cm diameter); (D) a white to grey salt-containing sand layer, local white polyhalite lenses existed; (E,F) a horizontal polyhalite-enriched sublayer was the main polyhalite formation layer.

Mineralogy
Observation under a microscope and XRD results showed that the saline minerals mainly consisted of fine- to coarse-grained halite, grey massive polyhalite, and gypsum. Moreover, a few sylvites and syngenites were found locally in the upper part (Table 1). Clastic sediments coexisted with saline minerals. Halite was the most common saline mineral sublayer that could be easily identified and was the main polyhalite formation layer (Figure 3E). The polyhalite distributions were much more heterogeneous, as they contained a higher level in white matrix than in grey-yellow ones. The fourth part was a grey or grey-white, middle to coarse granular halite (Figure 3F), where recrystallization phenomena were significant. Polyhalite was mixed within the grey silt in this layer. According to the description above, compared to salt layers, polyhalite minerals were mainly deposited in the silt/clay between two significant salt layers.
and was present in each layer. In some layers, the halite was nearly pure, which is consistent with our field observations. Polyhalite was another main saline mineral found in most layers, characterized as fine-grained structure, 0.01 to 0.05 mm in length; the types of single crystal are leaf-like, needle-like, and fibrous (Figure 4). The percentage of polyhalite in most layers was no more than 20%, and only a few samples contained more than 40%. It is interesting that gypsum minerals were only found in the upper layer (from 2.7 m to the top) and were not detected in the lower part (from 5.7 to 2.7 m). In fact, we repeatedly tested all samples to avoid measurement errors. However, the second result was almost the same as that of the first. Therefore, the lower part did not contain gypsum. In addition, quartz was the main mineral in clastic sediments, and other clastic minerals detected by XRD included albite, chamosite, and muscovite.

### TABLE 1 Components of minerals of seventeen samples in study area (%).

| No.  | Depth/m | Halite | Polyhalite | Gypsum | Dolomite | Calcite | Quartz | Albite | Chamosite | Muscovite |
|------|---------|--------|------------|--------|----------|---------|--------|--------|-----------|-----------|
| BD-01| 0.2     | 43     | 11         | 2      | 1        | 6       |        | 38     |           |           |
| BD-02| 0.5     | 26     | 8          | 2      | 1        | 9       | 11     | 12     | 30        |           |
| BD-03| 0.7     | 63     | 12         | 12     | 5        |         |        | 2      |           |           |
| BD-04| 1.2     | 58     | 13         | 10     | 1        | 2       | 15     | 18     | 13        | 4         |
| BD-05| 1.7     | 19     | 9          | 2      | 2        | 18      | 13     | 4      | 23        |           |
| BD-06| 2.2     | 10     | 14         | 10     | 1        | 2       | 23     | 15     | 4         | 20        |
| BD-07| 2.7     | 9      | 12         | 3      | 4        | 6       | 23     | 13     | 30        |           |
| BD-08| 2.9     | 19     | 19         | 2      | 12       | 36      | 17     | 1      | 7         |           |
| BD-09| 3.5     | 32     | 31         | 2      | 1        | 22      | 8      | 6      |           |           |
| BD-10| 3.7     | 29     | 31         | 5      | 5        | 27      | 9      |        |           |           |
| BD-11| 3.9     | 85     | 11         | 4      |          |         |        |        |           |           |
| BD-12| 4.1     | 65     | 16         | 7      | 7        | 7       | 3      | 2      |           |           |
| BD-13| 4.3     | 35     | 43         | 15     | 2        | 3       | 5      |        |           |           |
| BD-14| 4.5     | 18     | 54         | 20     | 3        | 3       | 5      |        |           |           |
| BD-15| 4.8     | 52     | 22         | 12     | 15       |         |        |        |           |           |
| BD-16| 5.2     | 98     | 2          | 2      |          |         |        |        |           |           |
| BD-17| 5.7     | 98     | 1          | 1      |          |         |        |        |           |           |

**FIGURE 4** Photos of microscope of morphology of polyhalite. (A) and (B) indicate the polyhalite in transition layer between layers of halite and clastic; (C) and (D) refer to the morphology of polyhalite in halite layer.
FIGURE 5 | Images of minerals from SEM (left) and relatively the results of mineral spectrums from EDS (right). In image (A) (from sample BD-10), the scanning area purple rectangle is an aggregation of some minerals. In image (B) (from sample BD-13), the scanning point is a polyhalite piece. In image (C) (from sample BD-14), on a larger scale (10 μm), it shows a more complicated component.
Cauliflower-like polyhalite surrounded by medium-coarse-grained halite crystals and clay mineral particles was observed under SEM (Figure 5A). The EDS results showed that the polyhalite aggregates were mainly composed of polyhalite with siliceous clasts and halite facies. The EDS results suggest that the aggregation or mixture is mainly composed of polyhalite, but some siliceous clastic material and halite coexist with it. In Figure 5B, the contents of K and Mg were obviously higher than those of S(SO₄) and Ca; however, the Cl content was also very high. This implies that, except for polyhalite, some potash minerals, such as sylvite (KCl) and carnallite (KMgCl₃ · H₂O), probably were present in the sample. The evidence indicates that when polyhalite was deposited, the brine evolved into a K- and Mg-enriched stage. In fact, the coexistence of polyhalite with K-bearing chlorides was also found in the Qarhan salt lake (Yang et al., 1993; Yuan et al., 1995). In Figure 5C, the chemical component of the sample is more complicated than that of the former sample, which suggests a complex of minerals. Therefore, although some chloride minerals were not detected by XRD, they probably existed, indicating that the brine was highly concentrated and enriched in K and Mg.

**Homogenization Temperatures of Halite Fluid Inclusions**

The cooling nucleation approach was used to measure the homogenization temperature of halite fluid inclusions. The results show that the fluid inclusion temperature gradually decreased from the bottom to the top of the section (Table 2). A possible explanation might be related to the effect of the solar pool event due to brine delamination or extreme surface heat from the inland desert (Zambito and Benison, 2013; Wang and Lowenstein, 2017).

**TABLE 2:** Homogenization temperatures of halite fluid inclusions.

| Test series | Tested numbers | Size/μm | Phase at 25°C | Temperature range/°C | Average temperature/°C |
|-------------|----------------|---------|---------------|----------------------|------------------------|
| BD-12       | 5              | 12–20   | liquid        | 22.9–30.8            | 27.4                   |
| BD-13       | 5              | 12–30   | liquid        | 43.1–58.8            | 54.9                   |
| BD-14       | 3              | 11–14   | liquid        | 44.1–57.6            | 52.3                   |
| BD-16       | 2              | 20      | liquid        | 47.1–53.1            | 50.1                   |
| BD-17       | 11             | 10–24   | liquid        | 54.9–80.2            | 71.8                   |

**FIGURE 6:** Photos of halite fluid inclusions. (A,B) indicate the primary chevron halite, sampled from BD-12. (C) is the photo of inclusion before freezing. (D) shows that vapor bubbles emerged after freezing, sampled from BD-17.
Many fluid inclusions were found in chevron-type halite crystals (Figure 6), which can form at the bottom of salt lakes that are less than 60 cm in depth as a result of competitive growth (Handford, 1990; Meng et al., 2013). The maximum homogenization temperature can reach 80.2°C, which records the bottom water temperatures of that time.

### Chemical Components of Halite Fluid Inclusions

The results for the chemical components and types of halite fluid inclusions are shown in Table 3. The concentrations of K, Mg, and SO₄ were much higher than those of modern brines in this area, and Ca was not observed in the fluid inclusions. Compared with K in secondary fluid inclusions (2 g/L) in the bottom salt layers (BD-16, BD-17), the value in primary fluid inclusions was up to 30 g/L. In the upper salt layers, the concentration values of K in both the primary and secondary fluid inclusions were similar (~30 g/L). However, the values of Mg and SO₄ changed significantly and were disorderly. We can conclude that there might be a syngenetic or parasyngenetic origin of these fluid inclusions.

### Discussion

#### Mineral Assemblages and Their Sedimentological Significance

Traditionally, polyhalite is a type of secondary mineral, as it is considered to be a substitute for gypsum and usually coexists with Ca-SO₄ minerals (Hardie, 1968; García-Vegas et al., 2013; Holt et al., 2014). It is important to identify the types of sedimentological environment and genesis of polyhalite minerals. However, in this study, gypsum was not detected in the lower part of the clay sediments. The replacement of gypsum by polyhalite does not occur in these clastic sediments, and these polyhalites are probably primary minerals, similar to the coexistence of these minerals with salts. Many polyhalite crystals coexist with clastic sediments, which can even be over 50%. The simulation results using the EVP/EQL program show that when concentrated K- and Mg-enriched brines mix with Ca-enriched deep brine (also called oilfield brine), a nearly pure polyhalite was formed (Ai et al., 2018). In fact, some ions are more enriched in fine-grained clastic sediments (e.g., peat, clay, etc.) than in salt lake brines. A comparison of lake brine and mud brine from Xiao Chaidan Lake in the Qaidam Basin shows that the main chemical components are obviously more enriched in mud brine than those in lake brine (Du et al., 2016). Therefore, it is postulated that the polyhalite in clastic sediments is precipitated after highly concentrated underground mud brines enriched with K and Mg mixed with the later intruded Ca-enriched deep brine.

The section is divided into two parts from bottom to top: the lower part (polyhalite in salts without gypsum) and the upper part (polyhalite in clastics with gypsum) (Figure 7). In the lower part (II), there were more salts and less clastic sediments. The obvious characteristic is the absence of gypsum, whether in salt or clastic sediments. For polyhalite in halite and without gypsum, these minerals are usually considered to be primary (Wei et al., 1993). Recently, studies on Triassic polyhalite deposits in the Sichuan Basin have shown that polyhalite coexisting with halite is considered to be primary and precipitated after seawater in Ca mixed with seawater enriched in K and Mg (Zhong et al., 2020). Ca ions were not detected in the primary or secondary fluid inclusions in halite (Table 3), which indicates that these polyhalites precipitated after halite formation. Considering that the brine evolved into the stage of potash deposition (Figure 8), the brine should be highly enriched in K and Mg. It is quite possible that these polyhalites formed after the mixing of K- and Mg-enriched brines with deep Ca-enriched fluids (Han et al., 1982).

The precipitation in the upper part (I) of the sediments may have experienced a drier environment and the concentration of brine was higher because of the occurrence of some potassium-bearing salt minerals. The type of polyhalite coexisting with gypsum or other CaSO₄ minerals (syngenite) in this part is less than 15%, which indicates that the polyhalite in the upper part was derived from gypsum replacement. The same conclusion was drawn by Wei et al. (1993).

Furthermore, a five-member system mesostable phase diagram of the ore-forming fluid (K–Na–Mg–SO₄–Cl) is shown in Figure 8. All observed fluids reached the point of K–Mg-containing mineral precipitation. Primary fluid inclusions in the bottom salt layers (BD-16, BD-17) were spotted in the sylvite phase zone, which suggested that the sylvite precipitation stage occurred when salt began to precipitate. However, the projection points of secondary inclusions from the same samples were found in the carnallite phase zone. This can be explained by the formation of secondary halite after the brine evolved to sylvite precipitation coupled with further evaporation processes. This also suggests that the brine entered the stage of sylvite precipitation when halite formed, and the concentration of this brine increased during the later halite formation. The projection points of both primary and secondary inclusions in sample BD-11 from the upper layer were located approximately in the phase zone of sylvite or picromerite, which also suggested that the halite and sylvite precipitation stages were coincident. During the

| Sample no. | Type of inclusion | K(n)  | Mg(n)  | SO₄(n) |
|------------|------------------|-------|--------|--------|
| BD-11-1    | Primary          | 39.0 (4) | 71.8 (2) | 80.6 (2) |
| BD-11-2    | Primary          | 29.7 (2) | 65.4 (3) | 47.4 (2) |
| BD-16-1    | Primary          | 31.8 (2) | 57.0 (4) | 47.6 (2) |
| BD-17-1    | Primary          | 35.0 (3) | 56.1 (2) | 53.8 (3) |
| BD-11-1    | Secondary        | 32.3 (2) | 46.8 (1) | 39.8 (2) |
| BD-11-2    | Secondary        | 33.1 (2) | 77.8 (2) | 86.6 (4) |
| BD-16-1    | Secondary        | 2.0 (2) | 119.2 (1) | 38.3 (2) |
| BD-17-1    | Secondary        | 14.3 (1) | 97.3 (1) | 30.2 (3) |
late period of enhancement of the secondary mineralization and recrystallization process for halite, these inclusion features changed a little in the closed environment.

Formation Condition and Ore-Formed Fluid Evolution of Polyhalite Deposits

The lithology of the observed strata of the Kunteyi Playa shows alternating precipitation of evaporites and clastic sediments. Evaporites started to precipitate 730 ka, and the salt lake encountered eight significant fluctuation exchanges between dry hot and wet cold climate conditions (Han et al., 1995; Liu et al., 1998). After 240 ka, the paleoclimate tended to be drier, which intensified the role of evaporation in the area. Furthermore, water recharge was also reduced. Therefore, it was characterized as a gradually drier condition for the deposition of environmental sediments (Liu et al., 1998). The brine was concentrated via evaporation gradually, with enrichment in K and Mg; thus, it provided the necessary materials for polyhalite formation.

Apparently, the fluid inclusions in these salt crystals are characterized by different high temperatures. The majority of nonferrous metals derive ultimately from igneous processes associated with magmatism (Blundy et al., 2021). This conclusion suggested that geothermal fluids provided both a circumstance of high temperature and Ca-rich brine for polyhalite formation. Zhao et al. (2010) reported that halite fluid inclusions from Qarhan salt lakes have a homogeneous temperature as high as 200°C, which is thought to be related to the effect of solar pool events. Regardless of the reason for the former scenario, the homogenization temperature data from fluid inclusions suggests that there was a high temperature environment for the formation of evaporites such as halite and polyhalite. In fact, in geological history, a high temperature (about 73°C) recorded in the Permian Nippewalla Group (North America) ephemeral lake halite showed that an extremely high temperature event could occur in salt lakes (Zambito and Benison, 2013).

During the evolution of polyhalite precipitation from brine, the Ca ion was always low in the brine, which could be impossible for the precipitation of large amounts of polyhalite only with this type of brine itself. Near the Kunteyi Playa, it has been reported that deep oilfield water is rich in Ca (Li et al., 2016; Shi et al., 2016). Combined with the homogenization temperature results shown in Homogenization Temperatures of Halite Fluid Inclusions, we suggest that the deep oilfield Ca-rich water is the major source of Ca for polyhalite formation. Homogenization temperatures results showed that the minimum of the brine temperature was 22.9°C, and the range of phase zone for polyhalite precipitation increased as the temperature increased. This condition was
favorable for polyhalite formation, even on a large scale. According to the inclusion temperature results, the halite formation temperature is more than 20°C, and it increases up to 40°C–60°C, where polyhalite is enriched (Table 2). On a large scale, we conclude that brine with a higher temperature is an important factor for polyhalite formation. Tectonic conditions, as another important factor, provided a necessary conduit for deep Ca-rich water to the playa for polyhalite formation. To summarize, the complex conditions for polyhalite formation are the result of multi-impacts of rigorous climate, tectonic movements, and original materials.

The results of this study showed that brine evaporation evolution and polyhalite formation underwent complex physical and chemical processes, three important stages of which were included. Initially, the sulfate type of brine evolved to the step of K-containing mineral precipitation (such as sylvite and picromerite), which is a significant characteristic of K- and Mg-rich brine. Subsequently, polyhalite was formed as a result of high temperature deep Ca-rich brine injected into the evaporative basin. Because the polyhalite-rich formation occurred at the sylvite or carnallite precipitation stage, parts of these polyhalites may have formed as a result of metasomatism of these earlier formed K-bearing chlorides. Finally, an extremely dry climate and very limited supply of surface water caused restricted sedimentation in the basin; thus, the polyhalite was preserved. To date, no further corresponding petrographic evidence has been found to prove whether the interaction of these two types of brines underwent a process that produced a CaSO₄ mineral, which was then quickly metasomatized by polyhalite.

CONCLUSION

In this study, in order to obtain the evidence of the formation of polyhalite in Kunteyi Playa, a multiapproach of sedimentology, mineralogy, and halite fluid inclusion analyses is utilized. The following conclusions were drawn from the analysis of the results.

1) Halite, gypsum, and polyhalite are commonly the major saline minerals but gypsum is not found in the lower part of the profile, which suggests that polyhalite formation in the lower part is not necessarily connected with the replacement by CaSO₄-containing minerals. The polyhalite coexisting with CaSO₄-containing minerals (gypsum or synngenite) in upper part of the section should be a secondary mineral occurrence. The polyhalite coexisting without CaSO₄-containing minerals, whether in salts or in clastic, is probably primary.

2) During salination, the temperature of original brine had exceeded 20°C or even much higher, and the formation of polyhalite ranged from 40°C to 60°C; it provided a vital condition for large-scale polyhalite formation. Because polyhalite is a kind of Ca–Mg–K-rich mineral, the primary brines for its formation should contain K–Mg-rich mother brine and Ca-rich water. From this analysis, it is reasonable to infer that the formation of polyhalite occurred in the late stage of salt lake evolution.

3) During the mixing action between K–Mg-rich sulfate brine and deep Ca-rich oilfield brine, it underwent multicoupled physical and geochemical processes to form polyhalite, most of which was deposited as primary mineralization.
DATA AVAILABILITY STATEMENT
The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS
XY contributed to conception and design of the study. XZ, FM, JS, and AG organized the database. HC, YL, WM, WL, QT, JI, and YD contributed to the collection of samples and performed the statistical analysis. All authors contributed to manuscript revision and read and approved the submitted version.

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