

## Research Article

# A Rapid Cu Enrichment Mechanism from Cu-Bearing Brine in Kuqa Basin, Xinjiang, China: Controlled by Crystallized Sequence of Saline Minerals

Yangtong Cao  and Haiming Xu

*MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China*

Correspondence should be addressed to Yangtong Cao; [cyt1941@126.com](mailto:cyt1941@126.com)

Received 28 January 2021; Revised 14 March 2021; Accepted 16 March 2021; Published 26 March 2021

Academic Editor: Rongxi Li

Copyright © 2021 Yangtong Cao and Haiming Xu. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Sediment-hosted copper deposit is usually related to arid climate, ancient saline lake basin, and brine. The Kuqa Basin filled with giant-thickness evaporite units is located in the northern Tarim Basin, Xinjiang, China. It is famous for sandstone-hosted Cu deposits formed by syndimentary processes. However, our recent studies reveal that Cu enrichment is closely related to brine on the surface of clastic rocks in the basin. It is shown that green Cu mineral coexisting with halite and gypsum occurred in the fractured fault belts of sandstones or was precipitated with halite on the surface of maroon clay in the scallops of sandstone. By SEM, EDS, and geochemical analysis methods on Cu-mineralized solid samples and brines, respectively, combined with previous geological evidence, our studies demonstrate that green Cu mineral is paratacamite, and it occurred with gypsum, halite, secondary glauberite, natural copper, and probably lead chloride on the fractured fault belts of sandstones or surface of clay. Meanwhile, the precipitation of paratacamite is controlled by a crystallized sequence of saline minerals accompanying with evaporated-concentrated course of brine in which gypsum, secondary glauberite, paratacamite, and halite are crystallized in turn. The Cu-bearing brine derived from meteoric waters and ancient seawater has a powerful capacity to leach metallic ions from its surrounding rocks and can be formed in a very short time (10 days is OK) in normal pressure and temperature conditions; also, the cycle of surface-Cu enrichment (mineralization) is only a few months (no more than 5). These indicate that a rapid Cu enrichment mechanism from Cu-bearing brine occurs on the earth's surface of the evaporite basin. The mechanism might be supposed to make an enormous amount of metal mineralization in a short time if considered from a large-scale spatial viewpoint. By contrast with the lengthy geological period, the short evolutionary cycle of Cu enrichment (mineralization) is obviously different from the previous cognition.

## 1. Introduction

Sandstone-hosted Copper deposit is only the second largest to porphyry copper in the ultralarge copper ores of the world. It is mainly located in the 20°-30° latitudinal range on both sides of the equator. There are close relationships among Cu enrichment, arid climate, ancient saline lake basin, and brine [1–3]. The brine usually with low temperature derives from evaporated-concentrated seawater or leached rock salt by meteoric water in the ancient saline lake basin and becomes the main carrier for more kinds of metal ions such

as copper [4–7]. It is reported that ions such as Cu, Fe, Zn, Ag, and Au migrate by clathrate forms in the brine, which has no substituted function on activation, migration, and enrichment of metal ions in the process of metal mineralization [8–14]. The Cu-bearing brine generally migrates along fractured fault belts, cross-bedding planes, and other paths and finally reaches favorable sites for Cu enrichment or mineralization.

The Kuqa Basin filled with giant-thickness evaporite deposits is located in the northern margin of Tarim Basin, Xinjiang Uygur Autonomous Region of northwestern China.

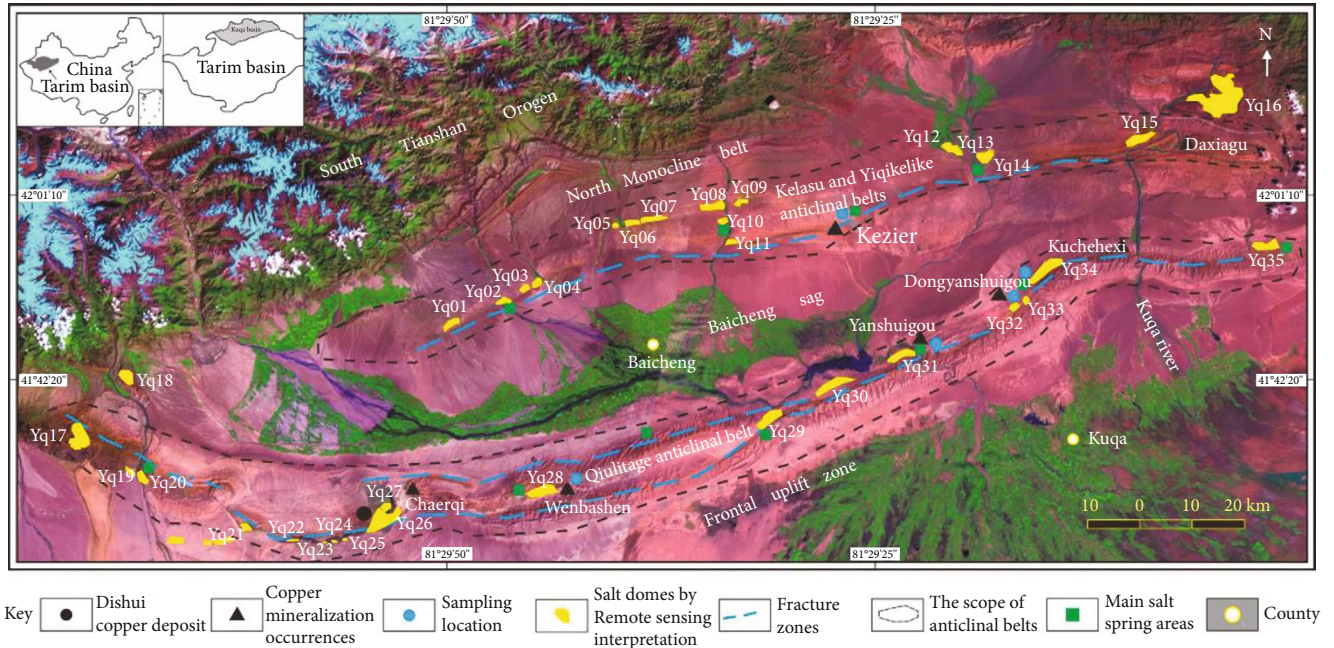


FIGURE 1: Schematic map of structure and sampling locations in Kuqa Basin.

These deposits contain a set of salt-bearing layers comprised of rock salt, gypsum rock, and clastic rocks [15, 16]. Influenced by tectonic activities and meteoric water, the evaporite was leached and dissolved, so it resulted in a series of salt springs and crystalline halite on the surface of the Neogene layers [17]. In recent studies on the evaporite and ore prospecting of potash, occasionally, we found a close relationship between Cu enrichment and brine, so some field investigations were carried out. The results show that there is a coexisting relationship among the green Cu mineral, halite, and gypsum. These minerals usually occur in fractured fault belts in the Neogene Jidike and Kangcun Formations comprised of clastic rocks. Previous studies have shown that the surface-Cu enrichment formed in the arid climate environment in the basin, and it originated from the Cu-bearing brine of the underlying evaporite units which migrated upward along fault belts to the surface [15, 16], but the cycle and era of Cu enrichment are unknown. Compared with the period of geological evolution, the mineralization cycle of Cu enrichment from beginning to ore formation is frequently studied over several tens to millions of years. However, recent research reveals that the surface-Cu enrichment has been formed in a very short time. Maybe a long period of Cu ore formation is needed, but these indicate a type of rapid Cu enrichment mechanism correlated with evaporation on the surface in the evaporite basin.

## 2. Geological Setting

The Kuqa Basin in Xinjiang is located in the tectonic belts between the South Tianshan Orogen and the Tarim Basin and is interpreted as a rejuvenated foreland basin [18–22]. The basin was initially opened in the Late Permian [21] and

continued its formation until the Late Triassic [23]. It was finally established in the Jurassic [24]. In the Late Eocene, because of the tectonic effects due to the collision of the Indian and Eurasian plates [25], the Tarim Plate collided with the South Tianshan Orogen. In the Late Oligocene, sedimentation in the Kuqa Foreland Basin was resumed, thereby rejuvenating the Kuqa Foreland Basin. From north to south, the basin is characterized by a north monocline belt, the Kelasu and Yiqikelike anticlinal belts, the Baicheng sag, the Qilutage anticlinal belt, and the frontal uplift zone (Figure 1). The two anticlinal belts are the main tectonic zones of the basin.

In ascending order, the stratigraphic units can be divided into the Kumugeliemu Group, Suweiyi Formation (Paleogene), Jidike Formation, Kangcun Formation, and Kuqa Formation (Neogene). The sediments are mainly interpreted as river-lake facies in the Paleogene [26]. The Kumugeliemu Group is comprised of giant-thickness evaporite series [15, 27, 28], and the Suweiyi Formation is composed of small amounts of rock salt, gypsum rock, fine sandstone, and siltstone. The Jidike Formation is composed of river-lake sediments, whereas the Kangcun and Kuqa Formations contain mainly piedmont facies composed of conglomerates, pebbly sandstone, siltstone, and mudstone.

The east-west orientation fault zones were developed in the basin where it was filled with evaporite, oil, and gas, so along the line of fault zones, a series of outcrops of salt domes were intruded onto surface rock units of the anticlinal axis in a tectonic compression setting (Figure 1). Salt springs can be observed everywhere on the earth's surface in the basin, and the Cu enrichment (mineralization) is mainly located in the two anticlinal belts, generally adjacent to salt domes (Figure 1). It is reported that the green Cu mineral is



(a)



(b)



(c)



(d)



(e)



(f)

FIGURE 2: Continued.

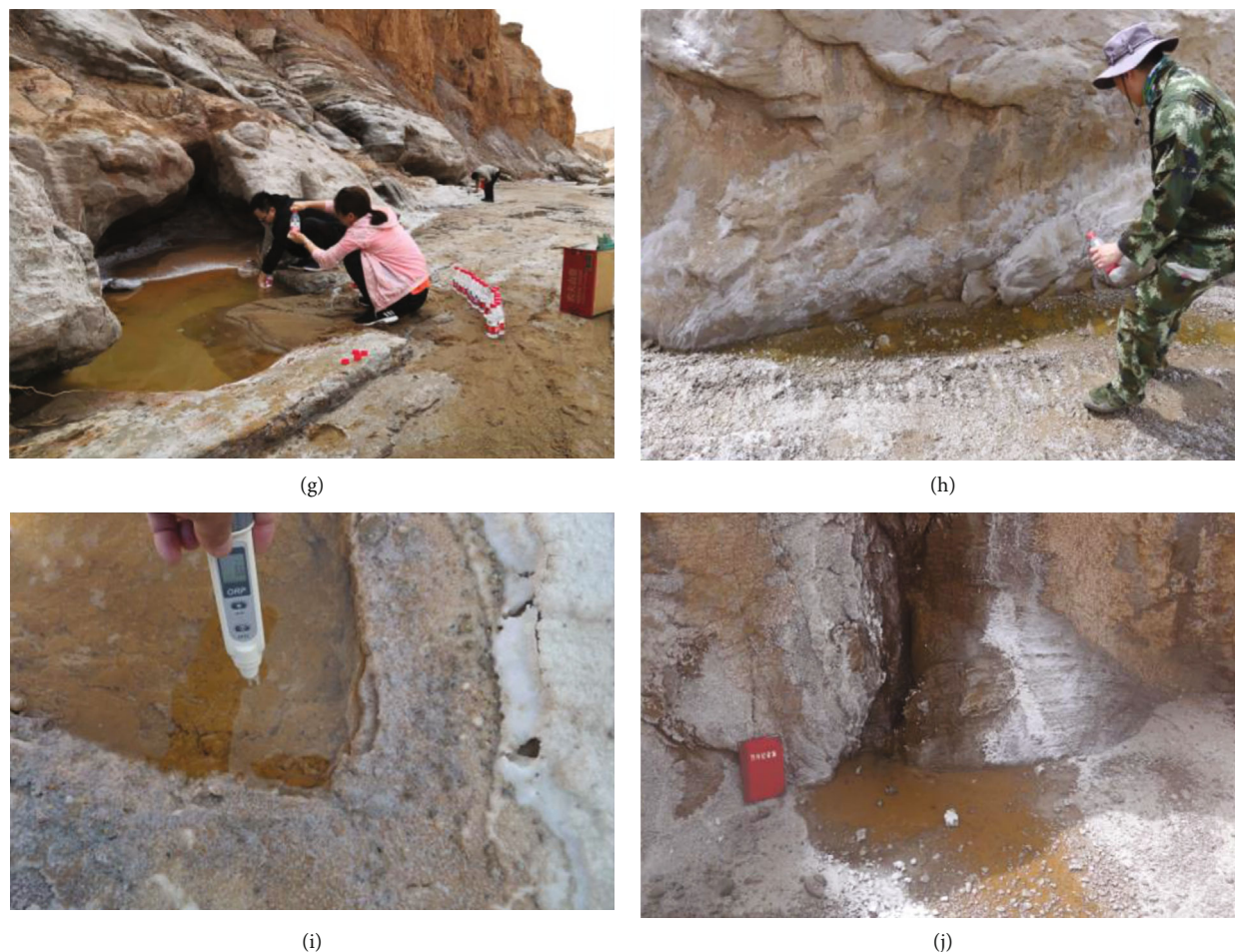


FIGURE 2: Sampling locations of brine and Cu-mineralized halite (gypsum). (a) Fractured fault belts of sandstone named “a” (the Kezier Cu mineralization occurrence); (b) Cu-mineralized halite (gypsum) of a site (sample no. KC-G<sub>1</sub>); (c) fractured fault belts of sandstone named “b” (the Kezier Cu mineralization occurrence); (d) Cu-mineralized halite (gypsum) of b site (sample no. KC-G<sub>2</sub>); (e) green Cu mineral and white halite on the surface of mud located in the scallops of sandstone (sample no. KC-G<sub>3</sub>); (f) image magnification of photo (e); (g) the surface brine in the Kezier Cu mineralization occurrence; (h) the surface brine in the Dongyanshuigou Cu mineralization occurrence; (i) the surface brine in the Wenbasha Cu mineralization occurrence; (j) the surface brine in the east about 1.5 km away of Dongyanshuigou Cu mineralization occurrence.

paratacamite, commonly coexisting with halite and gypsum, which occurred in the gypsum veins of sandstones in the Jidike and Kangcun Formations [17].

### 3. Methods

Three representative samples (KC-G<sub>1</sub>, KC-G<sub>2</sub>, and KC-G<sub>3</sub>) are selected from Cu-mineralized halite (gypsum) in the Cu mineralization occurrence named Kezier, northeastern Kuqa Basin (see Figure 1 for sampling locations, Figures 2(a)–2(f)). The samples (KC-G<sub>1</sub> and KC-G<sub>2</sub>) are collected from fractured fault belts of the grey-white medium- to coarse-grained sandstone of the Kangcun Formation (Figures 2(a) and 2(c)). Sample KC-G<sub>3</sub> is a green crystalline mineral collected from the surface of maroon moist-mud located in concave of the grey-white medium- to coarse-grained sandstone. Field investigations show that the green Cu mineral coexists with halite as tasted with briny taste. The surface brines were, respectively, collected from Cu mineralization occurrences

named Kezier, Wenbasha, Yanshuigou, and Dongyanshuigou, also the gully about 1.5 km away from Dongyanshuigou, where salt crystals can be seen all over the place. The part sites of samples are given in Figures 2(g)–2(j).

The analytical methods employed in this study include scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and hydrochemical analysis, for studying the possible geneses and enrichment mechanisms of copper. The solid samples were performed at the Key Laboratory of Deep-Earth Dynamics, Institute of Geology, Chinese Academy of Geological Sciences, Beijing, using the FEI Nova Nano SEM450 equipped with Gatan MonoCL4 and OXFORD X-Max (50 mm<sup>2</sup>), and the backscattered electron (BSE) images were taken under operating voltage of 15–20 kV and the working distance of 13.5 mm. With regard to 13 surface brines, the component analysis on salt and metal ions (such as K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and Cu<sup>2+</sup>) was carried out at the MNR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources,

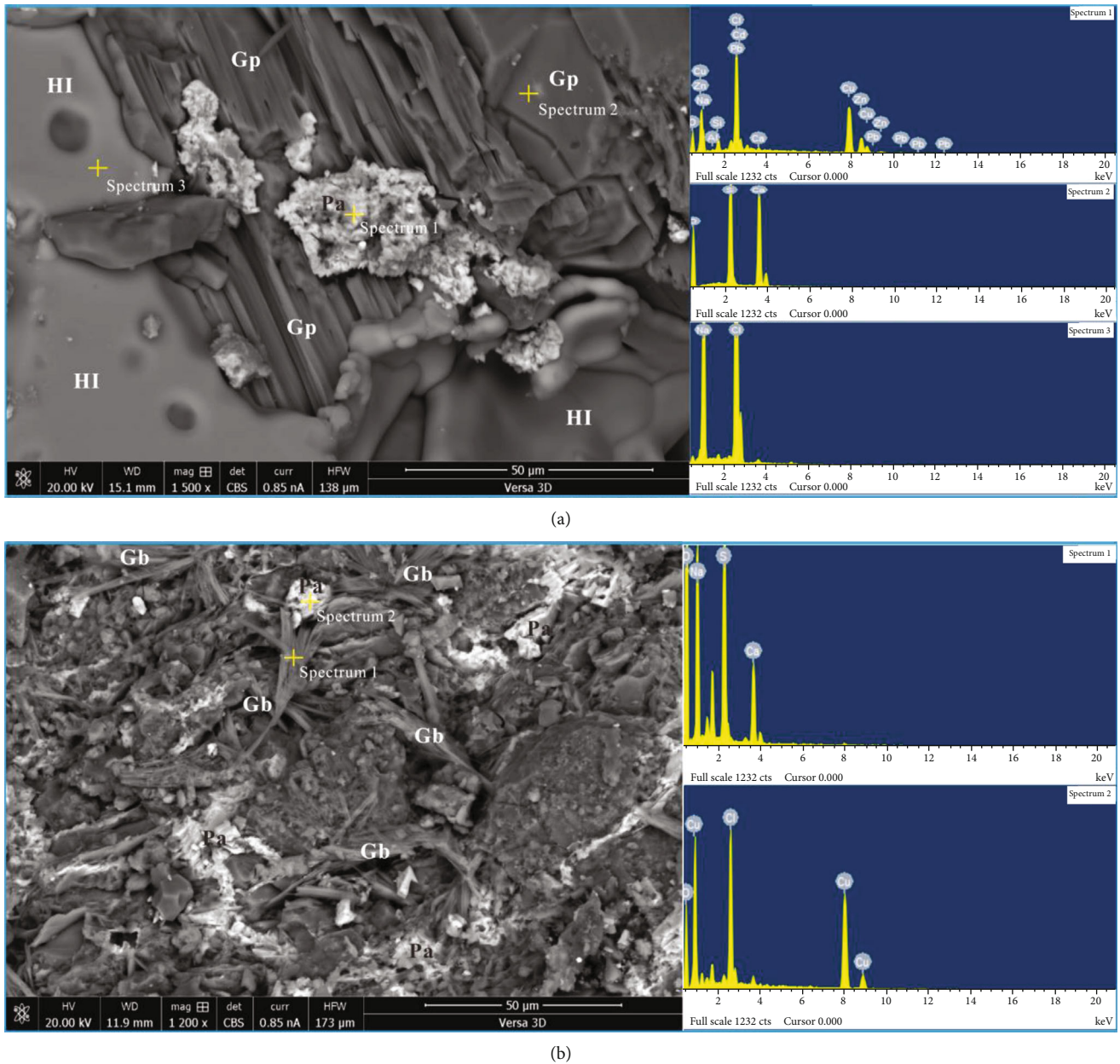


FIGURE 3: SEM and EDS analysis of sample KC-G<sub>1</sub>. (a) and (b) are BSE images, whereas the rest of the graphs are EDS spectrums. Pa: paratacamite; Gp: gypsum; Gb: glauberite; HI: halite. (a) Left: SEM image; right: EDS graph. The white mineral, containing mainly Cu, Cl, O, and a few Si, Al, Ca, Pb, and Zn, is paratacamite (Cu<sub>2</sub> (OH)<sub>3</sub> Cl) and may contain clay minerals, Zn and Pb. The ash black mineral containing Ca, S, and O is gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). The grey mineral containing Na and Cl is halite (NaCl). (b) Left: SEM image; right: EDS graph. The radial material is glauberite (Na<sub>2</sub>SO<sub>4</sub>·CaSO<sub>4</sub>). The white mineral containing Cu, Cl, and O is paratacamite (Cu<sub>2</sub> (OH)<sub>3</sub> Cl).

Chinese Academy of Geological Sciences, Beijing, using the Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-AES) (model: SPECTRO ARCOS SOP).

**4. Results**

The results on SEM and EDS analysis of 3 samples can be summarized and seen in Figure 3, Tables 1 and 2, Figure 4, Table 3, Figure 5, and Table 4. The results reveal that halite (abbreviated HI, the same below, Figure 3(a) and spectrum 3), gypsum or anhydrite (abbreviated Gp, the same below, Figure 3(a) and spectrum 2), glauberite (abbreviated Gb,

the same below, Figure 3(b) and spectrum 1), and atacamite or paratacamite (abbreviated Pa, the same below, Figure 3(b) and spectrum 2) coexist in the sample KC-G<sub>1</sub>. Combined with previous geological evidence on mineral analysis of Cu-bearing gypsum veins in sandstone of the basin [17], we conclude that the discoverable minerals of sample KC-G<sub>1</sub> are halite, gypsum, glauberite, and paratacamite. In addition, the white grain in Figure 3(a), containing mainly Cu, Cl, O, and a few elements such as Si, Al, Ca, Pb, and Zn (Table 1), is paratacamite (Cu<sub>2</sub> (OH)<sub>3</sub> Cl) and may contain clay minerals, Zn and Pb. In the same way, sample KC-G<sub>2</sub> contains halite, paratacamite, and natural copper

TABLE 1: The concentration of elements on grains in SEM of Figure 3(a).

Elements	Weight (%)	Mole (%)
Spectrum 1		
OK	11.86	30.26
NaK	3.89	6.91
AlK	0.46	0.69
SiK	2.18	3.16
ClK	17.82	20.52
CaK	0.58	0.59
CuK	41.06	26.38
ZnK	15.77	9.85
CdL	2.32	0.84
PbM	4.07	0.80
Total	100.00	
Spectrum 2		
OK	56.86	74.73
SK	20.14	13.21
CaK	23.00	12.07
Total	100.00	
Spectrum 3		
NaK	41.63	52.38
ClK	58.37	47.62
Total	100.00	

TABLE 2: The concentration of elements on grains in SEM of Figure 3(b).

Elements	Weight (%)	Mole (%)
Spectrum 1		
OK	60.71	72.91
NaK	18.08	15.11
SK	15.17	9.09
CaK	6.03	2.89
Total	100.00	
Spectrum 2		
OK	23.96	51.50
ClK	17.13	16.62
CuK	58.91	31.88
Total	100.00	

(Figure 4, Table 3). Sample KC-G<sub>3</sub> contains halite, gypsum, probably lead chloride (PbCl<sub>2</sub>), and paratacamite involved in a few elements Si, Al, Ca, K, Pb, and Zn (Figure 5, Table 4).

The main chemical components of thirteen surface brines are summarized in Table 5.

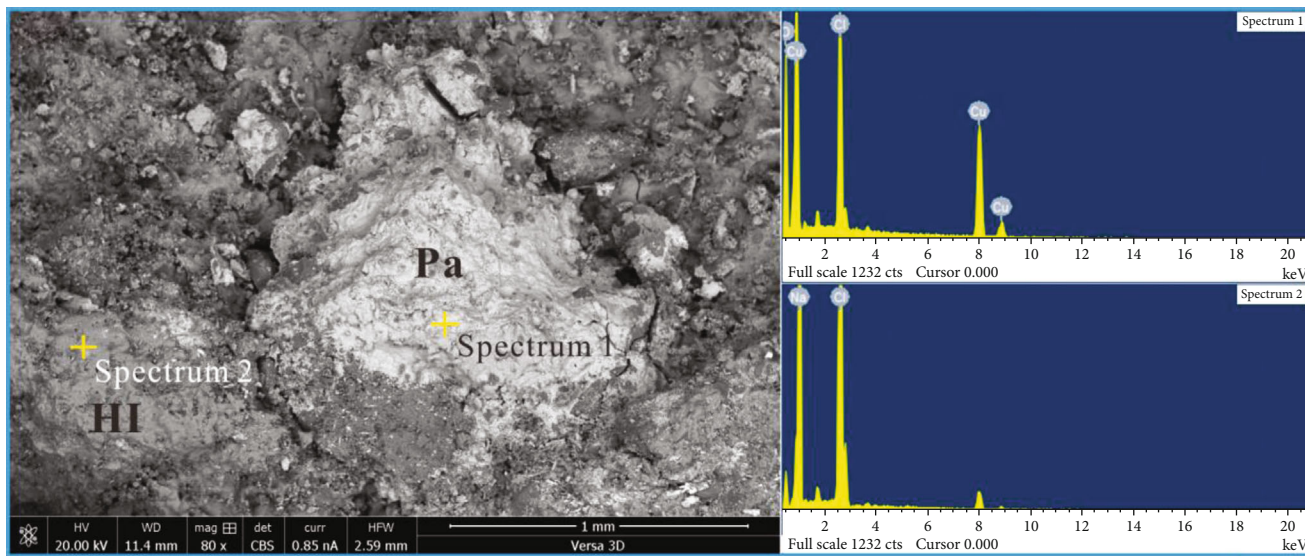
## 5. Discussion

*5.1. Sources and Developmental Cycle of Cu-Bearing Brine.* The evaporite in the Kuqa Basin formed from the evaporation of seawater in the Neo-Tethys Ocean. Salt springs and

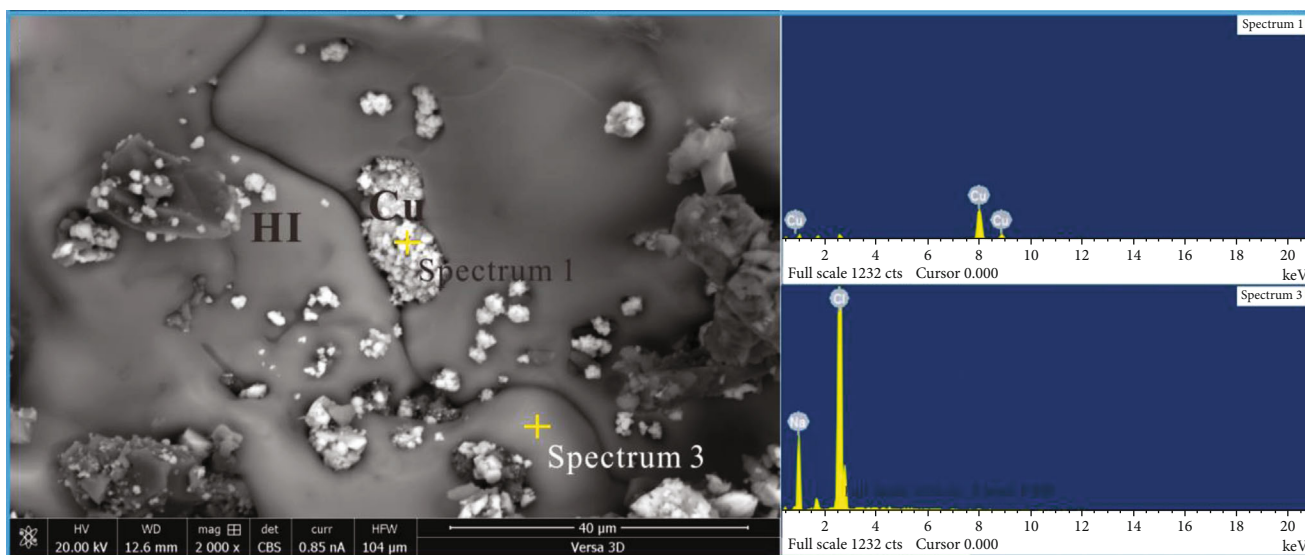
crystalline blooms occur throughout the earth's surface of the whole basin (Figures 1 and 2(g)). As a Mesozoic-Cenozoic evaporite basin, the Kuqa Basin is a favorable site for brine formed because of evaporite units composed of rock salt and gypsum rock. Cai et al. [29] analyzed the water of the Paleogene rock units in the Tarim Basin and showed characteristics of seawater including high average content of bromine and Br \* 10<sup>3</sup>/Cl, for example, respectively, 92 mg/l and 0.78 (Paleogene rocks) in comparison to 33.4 mg/l and 0.28 (Neogene rocks) and 15.3 mg/l and 0.09 (Quaternary units). The values are markedly different from those in the Neogene and Quaternary units. The salinity of water from the Neogene and Quaternary rock units is 202.94 g/l and 353.46 g/l, respectively [29], and is inferred to have originated from the near-surface where the salt concentrations are low. Therefore, salt in the brine must have originated from the dissolution of evaporite or from salt domes interacting with freshwater via surface fractures.

The brine is a type of compounded water from which derives meteoric waters and the Neo-Tethys Ocean seawater by research on its hydrogen and oxygen isotopes [23]. It has a powerful capacity to leach the metallic ions from its surrounding rocks, so an experiment was designed to verify it. 22 samples (such as rock salt, gypsum rock, sandstone, and mudstone) collected from different kinds of rocks were leached by saline in diverse days (Table 6). Because of 10% average value (Wt) on composition of sodium chloride in the Kuqa Basin by previous geochemical analysis on 135 surface-water samples [23], the saline with 10% sodium chloride (Wt) was made up to leach the metallic ions of samples. These results indicate that the concentration of Cu ion in the saline is changed accompanied with different samples or days in the conditions of 25°C (Table 6). The average value of Cu ion in the filtrate is 0.2532 (mg/l, the same below) in a 10-day period, accordingly 0.2571 in 20 days, 0.1815 in 30 days, and 0.2621 in 90 days, and the highest value is 0.6280. Compared with analysis results on 13 brine samples, the values of Cu ion among 3 samples collected from the Kezier area are much higher than those in the other areas, 0.315, 0.225, and 0.330 (Table 5). The value of composition is similar to that of filtrate obtained indoors; meanwhile, the Cu-bearing brine occurring on the surface of the Kezier area is revealed. In addition, our experiment demonstrates that the saline can extract Cu ion quickly from surrounding rocks and come into Cu-bearing saline in a very short time (only 10 days) compared with a long geological period, so too the brine. The copper is derived from not only clastic rocks but also evaporite (Table 6).

*5.2. Genetic Mechanism of Cu-Mineralized Evaporite in Fractured Fault Belts of Sandstone.* By the results of SEM and EDS, green Cu-mineralized samples are concluded with the main composition of paratacamite, natural copper, halite, gypsum, and glauberite. Because of powerful capacity for extracting mineral ions, sometimes the brine contains ions such as zinc, lead, silicon, and aluminum, so the crystalline paratacamite might contain a few clay minerals, zinc and lead. Paratacamite is generally associated with brine and arid climate. It is a secondary mineral that roots in the interaction



(a)



(b)

FIGURE 4: SEM and EDS analysis of sample KC-G<sub>2</sub>. (a) and (b) are BSE images whereas the rest of the graphs are EDS spectrums. Pa: paratacamite; HI: halite; Cu: natural copper. (a) Left: SEM image; right: EDS graph. The white mineral containing Cu, Cl, and O is paratacamite (Cu<sub>2</sub> (OH)<sub>3</sub> Cl). The grey mineral containing Na and Cl is halite (NaCl). (b) Left: SEM image; right: EDS graph. The white mineral containing Cu is natural copper (Cu). The grey mineral containing Na and Cl is halite (NaCl).

of primary copper minerals and brine [30–33]. In the course of Cu-bearing brine migrated along the fractured fault belts of sandstone, paratacamite was separated out accompanying with crystallized salt minerals. Because the depositional sequence of salt minerals is controlled by their different solubility, such as gypsum, halite, and potassium-magnesium salt crystallized in turn, the occurrence of paratacamite must also be controlled for its chemical composition of element chlorine.

Based on the paragenetic sequence of the samples studied, gypsum crystallized first, followed by halite. The paratacamite occurs on the surface of the gypsum, as well as in pores that show evidence of enlargement from dissolution

of gypsum (Figure 3(a)). The radial and acicular glauberite (Figure 3(b)) correspond to the secondary glauberite, formed through the interaction of brine enriched in Cl<sup>-</sup> and Na<sup>+</sup> with an external fluid enriched in SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> during later periods of evolution of the brine and after the crystallization of gypsum [34, 35]. These indicate that the paratacamite was precipitated after gypsum and that gypsum experienced dissolution after crystallization. Therefore, during the Cu-bearing brine migration along the fractured fault belts, the gypsum crystallized and subsequently dissolved by the residual brine, in which SO<sub>4</sub><sup>2-</sup> and Ca<sup>2+</sup> reacted with Cl<sup>-</sup> and Na<sup>+</sup> in the residual brine to crystallize the secondary glauberite, so that the Cl<sup>-</sup> became redundant after SO<sub>4</sub><sup>2-</sup>,

TABLE 3: The concentration of elements on grains in SEM of Figure 4.

Elements	Figure 4(a) Weight (%)	Mole (%)	Elements	Figure 4(b) Weight (%)	Mole (%)
	Spectrum 1			Spectrum 1	
OK	34.62	63.33	CuK	100.00	100.00
ClK	17.94	14.81	Total	100.00	
CuK	47.45	21.86		Spectrum 3	
Total	100.00		NaK	15.33	21.83
	Spectrum 2		ClK	84.67	78.17
NaK	35.50	45.91	Total	100.00	
ClK	64.50	54.09			
Total	100.00				

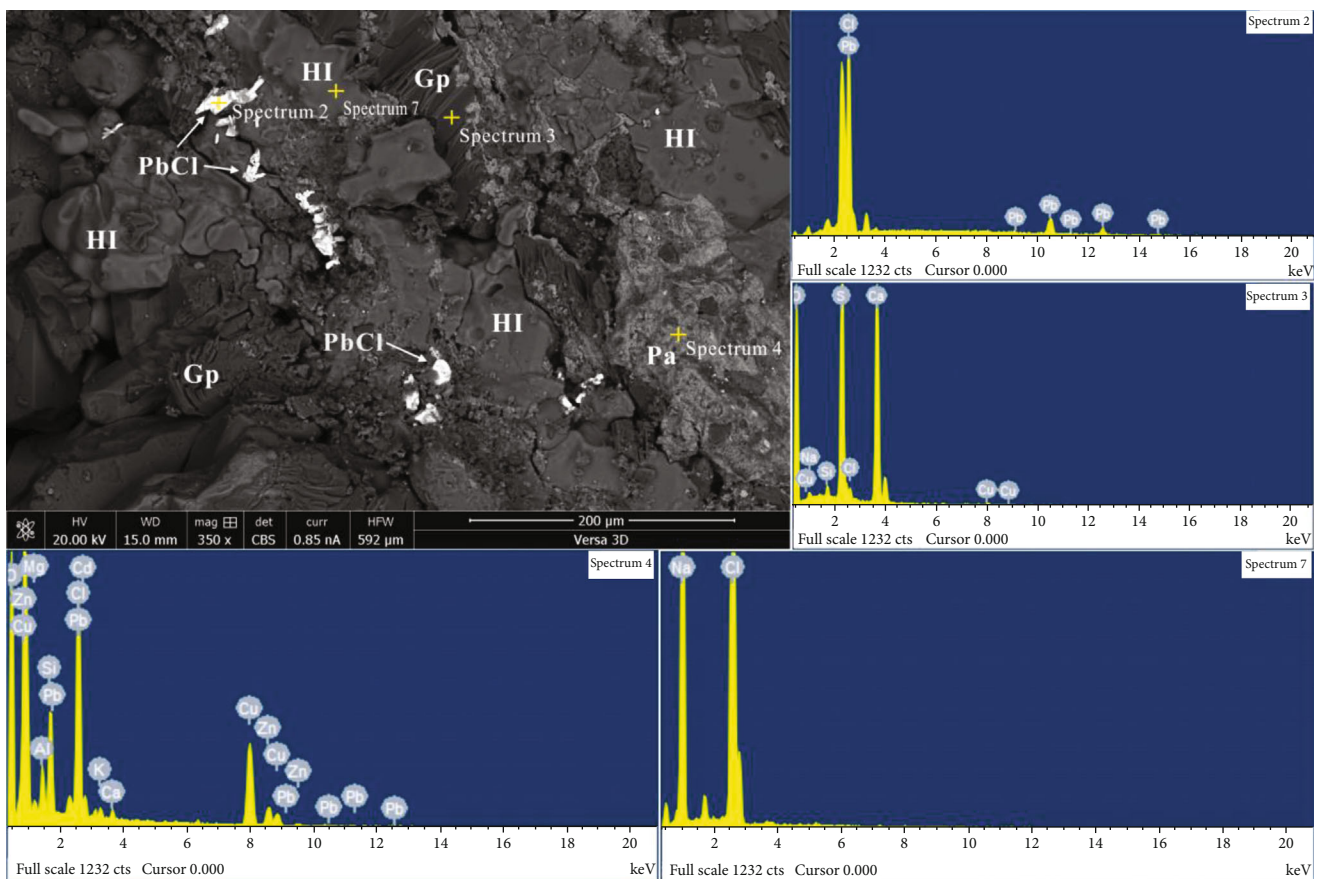


FIGURE 5: SEM and EDS analysis of sample KC-G<sub>3</sub>. The upper left is a BSE image whereas the rest of the graphs are EDS spectrums. Gp: gypsum; Pa: paratacamite; HI: halite. The bright white mineral containing Pb and Cl might be PbCl<sub>2</sub>. The white mineral, containing Cu, Cl, O, and a few Si, Al, Ca, K, Pb, and Zn, is paratacamite (Cu<sub>2</sub>(OH)<sub>3</sub>Cl) and may contain clay minerals, Zn and Pb. The grey mineral containing Na and Cl is halite (NaCl). The ash black mineral containing Ca, S, and O is gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O).

Ca<sup>2+</sup>, and Na<sup>+</sup> expended. The redundant Cl<sup>-</sup> in the brine reacted with Cu and OH<sup>-</sup> to form paratacamite. Finally, halite crystallized from the residual brine. Meanwhile, other metal ions such as lead and zinc might be precipitated by lead chloride (PbCl<sub>2</sub>) (bright-white grains and its spectrum 2 in Figure 5), also the elements of clay minerals such as silicon and aluminum (white grains and their spectrum 1 in Figure 3(a)).

Halite, paratacamite, and natural copper are discovered in a paragenetic relationship in the sample KC-G<sub>2</sub> (Figures 4(a) and 4(b)), especially the natural copper that occurs on the surface of halite (Figure 4(b)). Some Cu grains lie in the pores of halite, and others do not. But compared with spectrums of halite in Figures 4(a) and 4(b), the spectral lines of sodium and chlorine are different from each other, and the sodium declined in spectrum 3 of Figure 4(b). All



TABLE 4: The concentration of elements on grains in SEM of Figure 5.

Elements	Weight (%)	Mole (%)
	Spectrum 2	
ClK	33.94	69.92
PbM	66.06	30.08
Total	100.00	
	Spectrum 3	
OK	63.65	79.57
SK	17.07	10.59
CaK	19.29	9.83
Total	100.00	
	Spectrum 7	
NaK	30.61	38.88
ClK	69.39	61.12
Total	100.00	
	Spectrum 4	
OK	43.41	69.62
MgK	0.92	0.97
AlK	2.16	2.05
SiK	4.84	4.42
ClK	12.82	9.28
KK	0.32	0.21
CaK	0.52	0.33
CuK	24.52	9.90
ZnK	6.75	2.65
CdL	1.00	0.23
PbM	2.74	0.34
Total	100.00	

the appearances are reflected in the EDS chart (Table 3). Based on the datum of Table 3, the atomic ratio of chloride to sodium is nearly 1:1 (54.09:45.91) (spectrum 2 in Figure 4(a)) and 3:1 (78.17:21.83) (spectrum 3 in Figure 4(b)), which showed an unbalanced feature of atomic amount between chloride and sodium. Enriched chloride that occurred in the halite indicates that some chloride ion in the brine reacted with Cu and OH<sup>-</sup> to form paratacamite, and sodium ion reacted with Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> to form the secondary glauberite. But the genetic mechanism of natural copper is still unknown at present.

**5.3. Crystallized Cycle of Cu Mineralized on the Surface of Clay.** The Cu deposit on the surface of maroon clay is observed in the scallops of grey-white medium- to coarse-grained sandstone in the Kezier area (Figures 1, 2(e), and 2(f), sample no. KC-G<sub>3</sub>) on August 16, 2019. Field investigations show that green Cu mineral and white halite have already been precipitated on the surface of clay, but the clay is moist and the halite was precipitating along with the clay getting dryer and dryer. We infer that more and more halite must be crystallized on the argillaceous surface afterwards. In this way, it is offered as evidence that the halite must be crys-

tallized later than the paratacamite. As we did not see the geological phenomenon at the same site when we did a field investigation during the whole of April of that year in the Kuqa Basin, therefore, the crystallized cycle of paratacamite is no more than 5 months (from April to August). These indicate that there is a rapid Cu enrichment mechanism from Cu-bearing brine at normal pressure and temperature (NPT) conditions in the earth's surface of the Kuqa Basin.

The rapid Cu enrichment on the surface of clay occurs in a stratified form but only occurs on the surface, not in the interior of the clay (Figure 2(f)). These hint that when the Cu-bearing brine which carried a little clay flowed along the sandstone's surface, the clay was deposited persistently in the scallop; correspondingly, the minerals were precipitated accompanying with the brine evaporation.

The mineral composed of elements Pb and Zn, maybe lead chloride, is paragenetic with paratacamite, halite, and gypsum in the sample KC-G<sub>3</sub> (Figure 5, Table 4). It indicates that the brine contains not only copper but also lead ions. Our research demonstrates again that the depositional metal minerals from brine are controlled by crystallized sequence of saline minerals.

Previous research on paratacamite from gypsum veins in sandstones of the Kuqa Basin is considered that the Cu-bearing brine comes from deeper rock units. It migrates upward along the fractured fault belts of sandstone to the surface and is concentrated in arid climate condition [17], but the developmental time and cycle of the brine are unknown. These make the developmental time and cycle of Cu enrichment uncertain. The cycle may be several to tens of millions years or persist in a more distant geologic period. Now, we realize that the growth cycle of Cu-bearing brine is about 3 months (sometimes only 10 days), and the cycle of Cu enrichment only needs no more than 5 months, also in normal pressure and temperature conditions. Pei et al. [36] put forward a type of mineralization mechanism (event geology stimulating anomalous ore-forming processes with economic super-accumulation of metals), and we also think the rapid Cu enrichment mechanism might make an enormous amount of metal mineralization come into being if considered from a large-scale viewpoint. Compared with the mineralization of hypothermal deposits, the surface-Cu enrichment with normal pressure and temperature is controlled by a crystallized sequence of saline minerals, and the cycle of Cu mineralization is only a few months. Even if the mineralization is in multiple stages, it is still a very short time compared to several to tens of millions years in the geologic period. These are different from the previous cognition of Cu enrichment or mineralization.

## 6. Conclusions

So we can draw some conclusions as follows:

- (1) The surface-Cu enrichment showed by paragenetic sequence with paratacamite, gypsum, halite, secondary glauberite, natural copper, and probably lead chloride occurs on the fractured fault belts of sandstones or the surface of clay. It is a close relationship

TABLE 5: Main chemical components of the surface brine.

Sample numbers	K <sup>+</sup> (mg/l)	Na <sup>+</sup> (g/l)	Ca <sup>2+</sup> (g/l)	Mg <sup>2+</sup> (g/l)	SO <sub>4</sub> <sup>2-</sup> (g/l)	Cl <sup>-</sup> (g/l)	Cu <sup>2+</sup> (mg/l)
YSG-W1	112.76	31.51	2.60	0.80	4.89	53.12	<0.004
DYSG-W1	133.96	70.00	9.39	2.56	1.59	124.06	<0.004
DYSG-W2	134.30	66.62	9.23	2.54	1.68	124.70	<0.004
DYSG-W3	242.50	108.52	11.98	3.52	0.78	205.31	<0.004
DQ8-W1	115.82	31.65	2.62	0.78	4.95	51.90	<0.004
DQ8-W2	104.70	29.81	2.58	0.77	4.89	48.03	<0.004
WBS-W1	190.52	109.64	1.43	0.73	5.76	176.05	<0.004
WBS-W2	44.90	13.47	0.94	0.64	5.22	16.90	<0.004
KZE-W1	288.48	110.05	9.56	1.70	0.90	186.56	0.160
KZE-W2	293.04	109.40	9.60	1.69	0.90	189.66	0.315
KZE-W3	281.80	96.31	7.89	1.96	0.63	164.29	0.225
KZE-W4	295.22	96.71	9.93	2.16	0.72	167.35	0.330
KZE-W5	8.76	1.75	0.80	0.12	2.67	2.33	<0.004

TABLE 6: Concentration of Cu ion in the saline from different rocks leached and days.

Sample numbers	Lithology	Cu (mg/l)			
		10 days	20 days	30 days	90 days
0811KC-BCH-G7	Amaranthine rock salt	0.4368	0.3935	0.4132	0.1107
0811KC-BCH-G2	Celadon rock salt	0.4462	0.4622	0.2534	0.1621
0811KC-YSK-G5	Cyan-grey rock salt	0.3585	0.432	0.2928	0.1936
0811KC-YSKD-G5	Yellow-white silty gypsum rock	0.2593	0.2881	0.2043	0.1526
0811KC-YSKD-G6	Yellow-white silty gypsum rock	0.2683	0.298	0.1831	0.1132
0812KC-AGX-S10	Celadon silty gypsum rock	—	0.1555	0.0785	0.1953
0811KC-YSKD-G4	Celadon silty gypsum rock	0.1952	0.1122	0.0712	0.5266
0812KC-KCHX-G4		0.2682	0.2674	0.2017	0.2429
0812KC-KL2-G4-2	Grey-white medium- to coarse-grained sandstone with Cu mineralization	0.2525	0.2253	0.1554	0.2808
0812KC-KL2-G9		0.2915	0.2932	0.2107	0.2588
0812KC-AGX-TKD		0.2376	0.2071	0.1031	0.2031
0811KC-S1-G4		0.2489	0.289	0.2373	0.6280
0812KC-KL2-G14A	Celadon siltstone with Cu mineralization	0.2383	0.2944	0.1728	0.2871
0812KC-KCHX-G5		0.2712	0.2587	0.1691	0.3565
0812KC-AGX-TK3		0.2103	0.1891	0.1179	0.3446
0812KC-AGX-TK1		0.1970	0.1612	0.0793	0.2465
0812KC-KCHX-G2	Grey-white medium- to coarse-grained sandstone with Cu mineralization	0.1956	0.1322	0.0361	0.2838
0812KC-KCHX-G3		0.1826	0.0844	0.1294	0.2691
0812KC-AGX-S18	Celadon siltstone	0.2523	0.2601	0.2043	0.2938
0812KC-AGX-S16	Celadon gypseous siltstone	0.259	0.2921	0.2917	0.2256
0812KC-KCHX-G9	Celadon mudstone	0.2424	0.2671	0.1988	0.1197
0812KC-KL2-G5	Grey-white medium- to coarse-grained sandstone	0.2576	0.2934	0.1886	0.2712
Average values		0.2532	0.2571	0.1815	0.2621

between the Cu enrichment and Cu-bearing brine derived from leached rocks and evaporite units by meteoric waters and ancient seawater

- (2) The occurrence of paratacamite is controlled by a crystallized sequence of saline minerals accompanying with evaporated and concentrated brine in which

gypsum, secondary glauberite, paratacamite, and halite are crystallized in turn

- (3) With normal pressure and temperature conditions, the Cu-bearing brine can be formed in a very short time (10 days is OK). The cycle of surface-Cu enrichment or mineralization is also only a few months (no

more than 5). These indicate a rapid surface-Cu enrichment from Cu-bearing brine in the evaporite basin. So the enrichment mechanism might be supposed to make an enormous amount of metal mineralization in a very short time if considered from a large-scale viewpoint. By contrast on the lengthy geologic period, the rapid enrichment mechanism is different from the previous cognition of Cu enrichment or mineralization

## Data Availability

The experimental datum used to support the findings of this study is included in the manuscript and supplementary material.

## Conflicts of Interest

The authors declare no conflict of interest.

## Acknowledgments

This study was supported by the Basic Research Project for the Central Public Welfare Scientific Institutions (YYWF201716) granted by the Institute of Mineral Resources, CAGS, and the National Natural Science Foundation of China (41972082).

## References

- [1] J. K. Warren and R. H. Kempton, "Evaporite sedimentology and the origin of evaporite-associated Mississippi Valley-type sulfides in the Cadjebut mine area, Lennard shelf, Canning Basin, Western Australia," in *Basin Wide Diagenetic Patterns: Integrated Petrologic, Geochemical, and Hydrologic Considerations*, I. P. Montanez, J. M. Gregg, and K. L. Shelton, Eds., pp. 183–205, SEPM Special Publication, Tulsa OK, 1997.
- [2] J. K. Warren, *Evaporites: Sediments, Resources, and Hydrocarbons*, Springer, Verlag Berlin Heidelberg, 2006.
- [3] J. M. Zientek, M. L. Parks, H. L. Dicken, C. L. Dicken, and the US Geological survey global copper mineral resource assessment team, *Assessment of Undiscovered Copper Resources of the World*, vol. 619, U.S. Geological Survey Scientific Investigations Report, 2019, 2015 (ver.1.1, May 24, 2019).
- [4] W. S. Xu, Z. J. Yao, and W. T. Han, "A study of the content characteristics of copper, lead, zinc, strontium and barium in sedimentary anhydrite and their activation and migration," *Geoscience*, vol. 5, pp. 79–90, 1991.
- [5] K. X. Tan, *Geochemistry and Dynamics of Metallization on Copper Mineral of Sandstone*, Earthquake Public House, Beijing, 1998.
- [6] F. Grandia, A. Canals, E. Cardellach, D. A. Banks, and J. Perona, "Origin of ore-forming brines in sediment-hosted Zn-Pb deposits of the Basque-Cantabrian Basin, northern Spain," *Economic Geology*, vol. 98, no. 7, pp. 1397–1411, 2003.
- [7] P. N. Southgate, T. K. Kyser, D. L. Scott, R. R. Large, S. D. Golding, and P. A. Polito, "A basin system and fluid-flow analysis of the Zn-Pb-Ag mount Isa-type deposits of northern Australia: identifying metal source, basinal brine reservoirs, times of fluid expulsion, and organic matter reactions," *Economic Geology*, vol. 101, no. 6, pp. 1103–1115, 2006.
- [8] H. L. Cao, R. M. Hua, B. Rao, and L. W. Qiu, "Preliminary experimental study on dissolution of metal elements in oil field brine of Jiyang depression, Shandong Province," *Geological Review*, vol. 48, pp. 444–448, 2002.
- [9] W. Li, "Some problems on movement and enrichment of aurum," *Journal of Yunnan University (Natural Sciences)*, vol. 11, p. 30, 1989.
- [10] J. W. Johnson, E. H. Oelkers, and H. C. Helgeson, "SUPCRT92: a software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C," *Computers and Geoscience*, vol. 18, no. 7, pp. 899–947, 1992.
- [11] A. A. Migdisov, A. E. Williams-Jones, and O. M. Suleimenov, "Solubility of chlorargyrite (AgCl) in water vapor at elevated temperatures and pressures," *Geochimica et Cosmochimica Acta*, vol. 63, no. 22, pp. 3817–3827, 1999.
- [12] S. M. Archibald, A. A. Migdisov, and A. E. Williams-Jones, "An experimental study of the stability of copper chloride complexes in water vapor at elevated temperatures and pressures," *Geochimica et Cosmochimica Acta*, vol. 66, no. 9, pp. 1611–1619, 2002.
- [13] H. R. Mark and P. James, "Sulfide mineral precipitation from hydrothermal fluids," *Reviews in Mineralogy & Geochemistry*, vol. 61, pp. 609–631, 2006.
- [14] D. Asael, A. Matthews, S. Oszczepalski, M. Bar-Matthews, and L. Halicz, "Fluid speciation controls of low temperature copper isotope fractionation applied to the Kupferschiefer and Timna ore deposits," *Chemical Geology*, vol. 262, no. 3–4, pp. 147–158, 2009.
- [15] Y. T. Cao, C. L. Liu, H. J. Yang, Q. Y. Gu, P. C. Jiao, and Y. H. Lu, "Identification and correlation of evaporites sedimentary cycle in Kuqa Basin of Paleogene and Neogene," *Journal of Palaeogeography*, vol. 12, pp. 31–41, 2010.
- [16] Y. T. Cao, C. L. Liu, P. C. Jiao et al., "Evaporite deposition and potassium enrichment prospect from Upper Cretaceous to Paleogene in Yarkand Basin, Xinjiang," *Mineral Deposits*, vol. 35, pp. 300–314, 2016.
- [17] Y. Cao, C. Liu, P. Jiao, and C. Wang, "Paratacamite from gypsum veins in sandstones of the Kuqa Basin, Xinjiang, China: implications for a new epigenetic Cu enrichment mechanism," *Resource Geology*, vol. 66, no. 2, pp. 114–126, 2016.
- [18] C. Z. Jia, "Evolution of slab structure in Tarim Basin," in *Corpus of Research on Modern Geology (First)*, Q. Dai, Q. R. Liu, and J. L. Li, Eds., pp. 22–31, Nanjing University Press, Nanjing, 1992.
- [19] S. A. Graham, M. S. Hendrix, L. B. Wang, and A. R. Carroll, "Collisional successor basins of western China: impact of tectonic inheritance on sand composition," *Geological Society of America Bulletin*, vol. 105, no. 3, pp. 323–344, 1993.
- [20] S. L. Cao, F. J. Chen, and C. R. Luo, "Numerical modeling of subsidence mechanism of a Meso-Cenozoic foreland basin in North Tarim," *Oil and Gas Geology*, vol. 15, pp. 113–120, 1994.
- [21] H. F. Lu, D. Jia, D. S. Cai, S. M. Wu, and C. M. Chen, "Evolution of slab structure in Paleozoic in Tarim Basin and in the west in Tianshan mountain," in *The New Evolution of Petroleum Geology in Tarim Basin*, X. G. Tong, D. G. Liang, and C. Z. Jia, Eds., pp. 235–245, Science Press, Beijing, 1996.
- [22] L. Huaifu, D. G. Howell, J. Dong et al., "Rejuvenation of the Kuqa foreland basin, northern flank of the Tarim Basin,

- Northwest China,” *International Geology Review*, vol. 36, no. 12, pp. 1151–1158, 2010.
- [23] C. L. Liu, P. C. Jiao, Y. T. Cao, and Y. Z. Chen, *Interior Report on Large-Scale Minerogenetic Conditions and Prediction Technique of Potash in Tarim Basin*, 2010.
- [24] G. Q. He, M. S. Li, D. Q. Liu, Y. L. Tang, and R. H. Zhou, *Evolvement and Metallogenesis of Lithosphere in Paleozoic in Xinjiang China*, Xinjiang Peoples Publishing House and Hongkong Culture and Educate House, Urumqi and Hongkong, 1994.
- [25] L. Z. Guo, Y. S. Shi, H. F. Lu, Q. B. Li, J. X. Dai, and R. Q. Liu, “The two distances domino effect on India Slab and Tibetan Plateau,” in *Corpus of Research on Modern Geology (First)*, Q. Dai, R. Q. Liu, and J. L. Li, Eds., pp. 1–7, Nanjing University Press, Nanjing, 1992.
- [26] L. J. Zhang, D. L. Li, Y. S. Sun, and M. Chen, “Analysis of characteristics of sedimentary reservoir between Cretaceous and Palaeogene in the western part of the Kuqa depression,” *Natural Gas Geoscience*, vol. 17, pp. 355–360, 2006.
- [27] X. X. Zhou, “The features of tertiary halite-gypsum caprocks and their control on forming of oil and gas pools in Kuqa depression,” *Journal of Palaeogeography*, vol. 2, pp. 51–57, 2004.
- [28] L. J. Tang, Z. J. Jin, C. Z. Jia, X. J. Pi, and S. P. Chen, “Multi-cyclic salt tectonics and oil-gas accumulation in Tarim Basin,” *Science China Series D*, vol. 34, pp. 89–97, 2004.
- [29] C. F. Cai, B. W. Mei, T. Ma, and F. G. Zeng, “Origin and evolution of oilfield waters in the Tarim basin,” *Geological Review*, vol. 43, pp. 650–656, 1997.
- [30] L. Ye and T. G. Liu, “The discovery of atacamite in Xinjiang and its significance,” *Acta Mineralogica Sinica*, vol. 17, pp. 78–81, 1997.
- [31] X. Y. Li, Y. Jiang, and Y. G. Zhang, *Research Index Minerals of Copper Deposit: Atacamite in Arid Climates*, Xinjiang Nonferrous Metals, 2003.
- [32] S. Y. Wang, Y. S. Wang, X. L. Zhong, and R. Zhao, “The function of the mineral characteristics of atacamite in the process of mine finding,” *Xinjiang Geology*, vol. 21, pp. 251–252, 2003.
- [33] K. Y. Bai and Z. X. Han, “Paratacamite of Kanggu'ertage gold deposit in the Xinjiang Uygur Autonomous Region of China,” *North Western Geology*, vol. 40, pp. 114–117, 2007.
- [34] J. Q. Zhu and W. X. Hu, “Types and geneses of glauberite in the Anning basin, Yunnan Province,” *Journal of Hebei College of Geology*, vol. 12, pp. 34–42, 1989.
- [35] Q. T. Yang, “The origin and analysis sedimentary environment analysis of glauberite,” *Acta Sedimentologica Sinica*, vol. 7, pp. 137–141, 1989.
- [36] R. F. Pei, Y. X. Mei, J. W. Li et al., “Event geology stimulating anomalous ore-forming processes with economic super-accumulation of metals,” *Acta Geologica Sinica*, vol. 80, pp. 1509–1517, 2006.