ROLE OF NaCl IN ORE-FORMING OF

SAND-SHALE TYPE COPPER DEPOSITS [①]

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ABSTRACT Ore-forming fluids of sand-shale copper deposits in Meso-Cenozoic Diwa basins in South China are hot brine solutions composed mainly of NaCl, an important mineralizer. Studies on chemical kinetics and thermodynamics showed that NaCl plays an important part in the ore-forming process of sand-shale copper deposits: (1) NaCl can obviously increase the dissolution rate of copper minerals in source bed, and catalyse the dissolution and migration of copper; (2) Cu and Cl^- can form stable cuprous chloride complexes to migrate, which are mainly $CuCl^0$, $CuCl_2^-$ and $CuCl_3^{2-}$; (3) the increase of NaCl concentration in solutions can enlarge the solubility of copper by orders of magnitude.

Key words dissolution kinetics   thermodynamics   cuprous chloride complex   NaCl sand-shale type copper deposits

1 INTRODUCTION

Sand-shale type copper deposit is an important resource of copper in the world. A number of sand-shale copper deposits occur in Meso-Cenozoic Diwa basins such as Central Yunnan, HuiLi, HengYang *et al* in South China. Cu-bearing rock series are all red and light grey clastic sedimentary rocks. Copper deposits relate closely to salt deposits. The upper of Cu-bearing formation is salt-bearing formation, and ore-forming fluids are hot brine with high salinity composed mainly of NaCl. This paper discusses the role of NaCl in the ore-forming of sand-shale copper deposits through experiments of chemical kinetics and analysis of thermodynamics.

2 ORE-FORMING FLUIDS

Analyses of H, O, C, S, Pb isotope, trace element and REE indicated that ore-forming fluids of sand-shale copper deposits in Diwa basins in South China are Cu-bearing hot brine solutions evolved from meteoric water during cycle of water-rock interaction in Cu-bearing rocks, and

Cu is derived from Cu-bearing rocks and Cu-rich basement rocks and old copper deposits, sulfur is derived mainly from bacterial reduction of sulfate in beds[1, 2].

Results of mineral inclusions of sand-shale copper deposits in Dayao, Haojiahe, Datongchang and Chejiang in South China are shown in Table 1. It can be seen that ore-forming solutions are composed mainly of Na^+, K^+, Ca^{2+}, Cl^- and SO_4^{2-}, and belong to brine solutions, and are in accordance with the chemical composition of ore-forming fluids of main sand-shale copper deposits, i. e. Cu-transporting closed basin brines[3].

Activity coefficient of ions and complexes with electronic charge in NaCl solutions can be estimated from the Debye-Hückel equation[4]:

$$\lg \gamma_j = \frac{Z_j^2 A_\gamma I^{1/2}}{1 + a B_\gamma I^{1/2}} + b_\gamma I \qquad (1)$$

where γ_j is the activity coefficient of j species, A_γ and B_γ are Debye-Hückel parameters, I is the ionic strength, Z_j is electronic charge, a is the ion size parameter.

By means of Eqn. (1) and average concent-

Table 1   Main compositions of ore-forming fluids of sand-shale copper deposits in China and comparison with that in world[3] (mol/L)

		K^+	Na^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	SO_4^{2-}
China	Range	0.01~0.413	0.089~0.726	0.054~0.256	0.003~0.042	0.013~0.246	0.198~1.189	0.007~0.268
	Average	0.153	0.469	0.119	0.018	0.093	0.517	0.114
	Activity	0.09	0.276	0.01	0.001	0.055	0.304	0.01
World	Range	0.02~0.3	0.3~4.5	0.01~0.4	0.01~1.7		0.05~6.0	0.01~2.0
	Average	0.1	3	0.1	0.5		3	0.4

ration in Table 1, activity coefficient calculated is 0.5885 for monovalent species and 0.0834 for divalent species in ore-forming solutions. Activities of different species are calculated from activity coefficients and shown in Table 1.

Results of inclusion measuring indicated that the temperature of ore-forming fluids is lower. The temperature ranges over 116~145 ℃ and averages 133 ℃ for diagenetic ores, and ranges over 158~205 ℃ and averages 182 ℃ for reworked ores in Dayao copper deposit. In Haojiahe copper deposit, the mineralizing temperature ranges over 161~167 ℃ and averages 164 ℃. The salinity of ore-forming fluids of sand-shale copper deposits is high. In Dayao, the salinity ranges over 8.0%~12.2% and averages 9.7% for diagenetic ores, and averages 15.0% for reworked ores. In Haojiahe the salinity is in the range of 7.3%~9.0% and averages 7.8% for diagenetic ores, and in the range of 10.4%~16.8% and averages 12.0% for reworked ores.

The pH values of inclusions in Dayao range from 6.30 to 6.74, and average 6.57, which are near neutral environment and in accordance with the conclusion by Birnbaum et al[5] and Haynes[3], i.e. the growth of sulfate reductive bacteria causes the neutralization of ore-forming solutions.

3   CHEMICAL KINETICS OF FORMING OF ORE-BEARING FLUIDS

The discussions above show that ore-forming fluids of sand-shale copper deposits are hot brine solutions composed mainly of NaCl. In order to discuss the role of NaCl in the ore-forming processes, dissolution kinetics of chalcocite, chalcopyrite and bornite in NaCl solutions are experimented. Experimental samples were collected from Dayao copper deposit, Yunnan, Datongchang copper deposit, Sichuan and Chejiang copper deposit, Hunan. Minerals of chalcocite, chalcopyrite and bornite were separated from the smashed samples in 60~100 mesh through heavy-media separation and hand-picking under binocular microscope.

Kinetic experiments were carried out in water bath. The temperature of experiment was 70 ℃, and pH value of reaction solutions was 7.0, and the concentration of NaCl was 0~3 mol/L. In experiments, 1~5 mL solutions were taken in every 8 h for determination of concentration of Cu using an atomic absorption spectrography with an accuracy of 10^{-7}. After experiments, except the measured Cu concentration in solutions, the reaction solution was filtered and the weight of Cu of secondary precipitation was measured by using cuprous ammonia complex ion spectrophotometric method. Then reaction rates of every experiment were calculated from the rate law of mineral dissolution[6].

The results are listed in Table 2 which shows that dissolution rates of chalcocite, chalcopyrite and bornite increase obviously with the increasing of NaCl concentration in solutions. Mapping with logarithm of rate vs the square root of NaCl ionic intensity in solutions shows a good linear correlations, i.e. the logarithm of dissolution rate is directly proportional to the square root of NaCl ionic intensity in solutions.

The analyses of geology and geochemistry indicated that Cu-bearing basement rocks and old copper deposits in basement are far source rocks, and Cu-bearing rocks, i.e. red clastic sedimentary rocks are near source beds. In old copper deposits in basement rocks such as Dongchuan-Yimen type deposits on the frontier of central

Table 2   Dissolution rates of copper minerals in NaCl solutions with different concentrations at 70 ℃ and pH= 7

Mineral	Experiment No.	$c(NaCl)$ $/(mol·L^{-1})$	Dissolution rate $/(pmol·cm^{-2}·s^{-1})$
Chalcocite	cc70- 13	3. 00	20. 131
	cc70- 7	2. 00	11. 327
	cc70- 14	1. 50	8. 945
	cc70- 19	1. 00	5. 629
	cc70- 20	1. 00	5. 644
	cc70- 15	0. 50	3. 912
	cc70- 16	0. 10	2. 109
	cc70- 17	0. 01	1. 674
	cc70- 18	0. 00	1. 560
Chalcopyrite	cp70- 11	3. 00	6. 274
	cp70- 10	2. 00	4. 451
	cp70- 2	1. 00	3. 086
	cp70- 1	1. 00	3. 128
	cp70- 3	0. 50	2. 420
	cp70- 4	0. 10	1. 306
	cp70- 5	0. 01	0. 829
Bornite	bn70- 1	2. 00	0. 850
	bn70- 2	0. 50	0. 752
	bn70- 3	0. 10	0. 594
	bn70- 4	0. 01	0. 465

Yunnan basin, copper minerals are mainly chal-cocite, chalcopyrite and bornite. Chalcocite and chalcopyrite occur also in wall rock of ore-red beds. Therefore, results of kinetic experiment in the paper showed that NaCl in solutions can in-crease obviously the dissolution rates of copper minerals in source bed, and catalyses the dissolu-tion of copper and the formation of ore-forming fluids.

4   STABILITY OF CUPROUS CHLORIDE COMPLEXES IN ORE-FORMING SOLU-TIONS

Complexes take an important role in the dissolution and migration of ore metal ele-ments[7]. Ore-forming fluids of sand-shale cop-per deposits are hot brine solutions composed mainly of NaCl. So Cu and Cl^- can form cuprous chloride complexes to migrate.

The stability constants of cuprous complex-es including $CuCl^0$, $CuCl_2^-$, $CuCl_3^{2-}$, $CuCl^+$, $CuCl_2^0$, $CuCl_3^-$ and $CuCl_4^{2-}$ in the range of tem-perature 25~ 300 ℃ are calculated by using iso-coulombic approach[8]. The results described in Fig. 2 show that chloride complexes of monova-lent copper have big stability at low temperature (< 200 ℃) whose stability constants are greater than those of chloride complexes of divalent cop-per by several orders of magnitude. Therefore, monovalent cuprous chloride complexes are favourable to the transporting of copper.

The temperature affects the stability of cuprous chloride complexes. The stability con-stants of divalent cuprous chloride complexes in-crease obviously with a rise of temperature, and those of monovalent cuprous chloride complexes decrease first with the rise of temperature, and
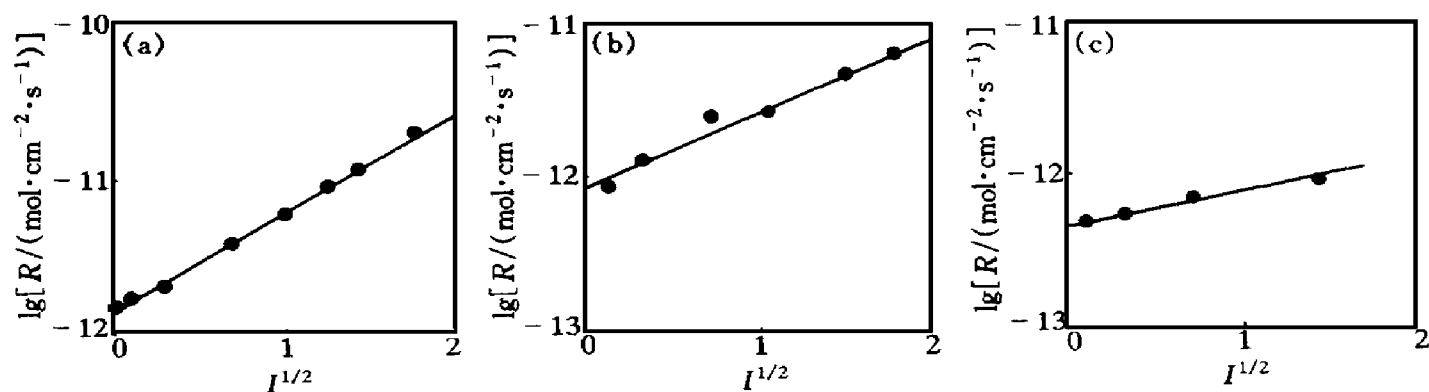
Fig. 1   Dissolution rates of chalcocite(a), chalcopyrite(b) and bornite(c) as a function of NaCl ionic intensity at 70 ℃ and pH= 7
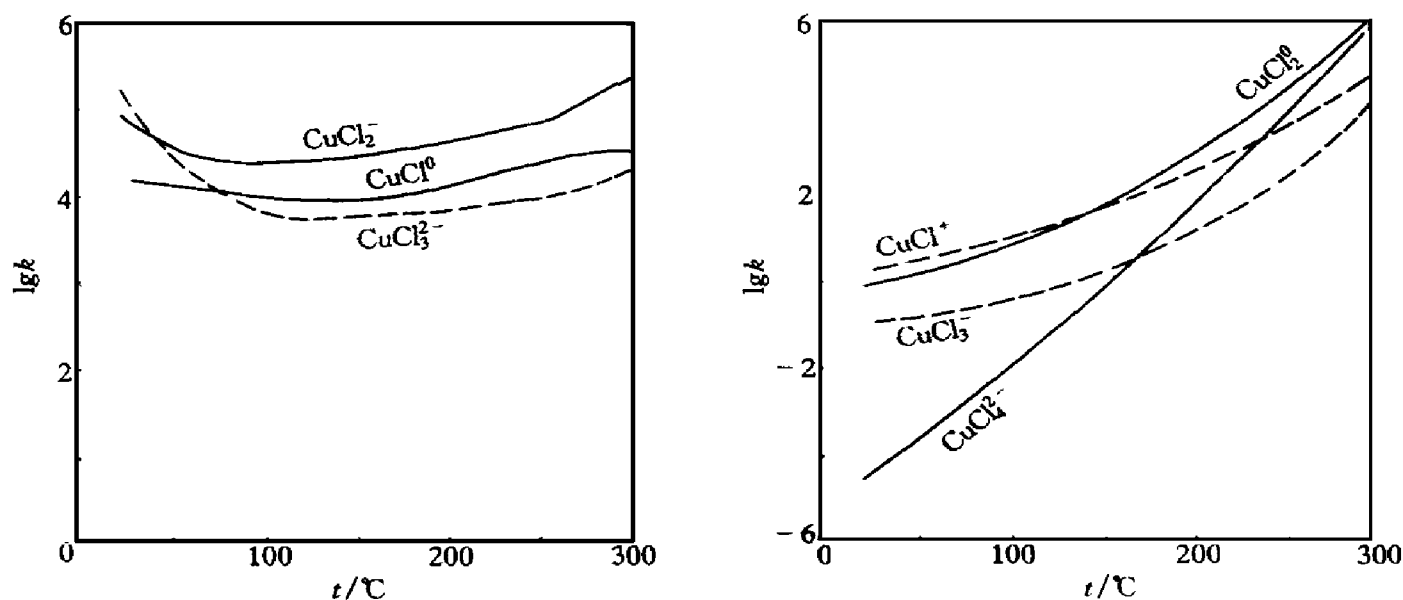
Fig. 2　Stability constants of cuprous chloride complexes as a function of temperature

reach the minimum at $100 \sim 150\ ℃$, then increase slightly with the rise of temperature. This is in accordance with main ore-forming temperature of sand-shale copper deposits.

5　THERMODYNAMICS OF DISSOLUTION AND MIGRATION OF COPPER

Because there are anions of Cl^-, SO_4^{2-}, CO_3^{2-} and OH^- in ore-forming solutions, the dissolution and migrating form of copper in ore-forming solutions are controlled by reactions listed in Table 3. The maximum solubility of copper and activities of various cuprous complexes in ore-forming solutions are calculated by means of mass action law and 20 reactions in Table 3, and the results are listed in Table 4.

Table 4 shows that the activities of monovalent cuprous chloride complex $CuCl^0$, $CuCl_2^-$ and $CuCl_3^{2-}$ in ore-forming solutions of sand-shale copper deposits are maximum, and larger than that of other complexes by $3 \sim 20$ orders of magnitude. Three cuprous chloride complexes above are more than 99% of dissolved total copper in solutions, and $CuCl^0$ and $CuCl_2^-$ are more than 95%. Therefore, Cu exists and transports mainly with $CuCl^0$ and $CuCl_2^-$, secondly $CuCl_3^{2-}$.

In calculating activity of cuprous complexes using mass action law and Table 3, the activities

Table 3　Main reactions controlling dissolution and migration of Cu in ore-forming solutions and their equilibrium constants

| Reaction	$\lg k$	
	100 ℃	150 ℃
$CuO + H_2O = Cu^{2+} + 2OH^-$	-19.58	-20.13
$CuSO_4 \cdot 3Cu(OH)_2 =$ $4Cu^{2+} + 6OH^- + SO_4^{2-}$	-63.21	-60.69
$Cu_3(OH)_2(CO_3)_2 =$ $3Cu^{2+} + 2OH^- + 2CO_3^{2-}$	-43.47	-42.94
$Cu_3(OH)_4SO_4 =$ $3Cu^{2+} + 4OH^- + SO_4^{2-}$	-43.86	-42.29
$CuCl_2 \cdot 3Cu(OH)_2 =$ $4Cu^{2+} + 2Cl^- + 6OH^-$	-62.72	-59.68
$2Cu^+ = Cu^+ Cu^{2+}$	3.00	1.58
$Cu^+ + Cl^- = CuCl^0$	3.94	3.92
$Cu^+ + 2Cl^- = CuCl_2^-$	4.35	4.45
$Cu^+ + 3Cl^- = CuCl_3^{2-}$	3.89	3.80
$Cu^{2+} + Cl^- = CuCl^+$	0.94	1.66
$Cu^{2+} + 2Cl^- = CuCl_2^0$	0.01	1.70
$Cu^{2+} + 3Cl^- = CuCl_3^-$	-0.47	0.23
$Cu^{2+} + 4Cl^- = CuCl_4^{2-}$	-1.80	-0.06
$Cu^{2+} + OH^- = Cu(OH)^+$	6.05	6.03
$Cu^{2+} + 2OH^- = Cu(OH)_2^0$	13.77	13.90
$Cu^{2+} + 3OH^- = Cu(OH)_3^-$	14.85	15.09
$Cu^{2+} + 4OH^- = Cu(OH)_4^{2-}$	16.67	17.17
$Cu^{2+} + SO_4^{2-} = CuSO_4^0$	2.91	3.43
$Cu^{2+} + CO_3^{2-} = CuCO_3^0$	6.78	7.05
$Cu^{2+} + 2CO_3^{2-} = Cu(CO_3)_2^{2-}$	10.06	10.34

of SO_4^{2-} and CO_3^{2-} are considered as a fixed value, and the activity of Cl^- as a variable, the relationship between the activity of total copper and the activity of Cl^- in solutions is obtained, which is described in Fig. 3. The solubility of copper (i. e. activity of total copper) increases

Table 4　Activity of cuprous complexes and total copper in ore-forming solutions(mol/ L)

Temperature	100 ℃		150 ℃	
pH	6	7	6	7
Cu^+	1.91×10^{-4}	1.91×10^{-5}	1.4×10^{-3}	1.4×10^{-4}
Cu^{2+}	3.66×10^{-5}	3.66×10^{-7}	7.41×10^{-5}	7.41×10^{-7}
$CuCl^0$	0.4991	0.0499	3.5095	0.3509
$CuCl_2^-$	0.3857	0.0386	3.5430	0.3543
$CuCl_3^{2-}$	0.0401	0.0040	0.2369	0.0237
$CuCl^+$	9.5×10^{-5}	9.5×10^{-7}	1.01×10^{-3}	1.01×10^{-5}
$CuCl_2^0$	3.4×10^{-6}	3.4×10^{-8}	3.37×10^{-4}	3.37×10^{-6}
$CuCl_3^-$	3.4×10^{-7}	3.4×10^{-9}	3.4×10^{-6}	3.4×10^{-8}
$CuCl_4^{2-}$	4.7×10^{-9}	4.7×10^{-11}	5.3×10^{-7}	5.3×10^{-9}
$Cu(OH)^+$	4.1×10^{-7}	4.1×10^{-8}	7.9×10^{-7}	7.9×10^{-8}
$Cu(OH)_2^0$	2.2×10^{-7}	2.2×10^{-7}	5.9×10^{-7}	5.9×10^{-7}
$Cu(OH)_3^-$	2.6×10^{-14}	2.6×10^{-3}	9.1×10^{-14}	9.1×10^{-3}
$Cu(OH)_4^{2-}$	1.7×10^{-20}	1.7×10^{-18}	1.1×10^{-19}	1.1×10^{-17}
$CuSO_4^0$	3×10^{-4}	3×10^{-6}	2×10^{-3}	2×10^{-5}
$CuCO_3^0$	6.3×10^{-5}	6.3×10^{-5}	4×10^{-5}	4×10^{-5}
$Cu(CO_3)_2^{2-}$	5×10^{-9}	5×10^{-7}	6.3×10^{-10}	6.3×10^{-8}
ΣCu	0.9256	0.0926	7.2944	0.7291

Composition of solutions: $a(Cl^-) = 0.3$, $a(SO_4^{2-}) = 0.01$, $f(CO_2) = 0.24$
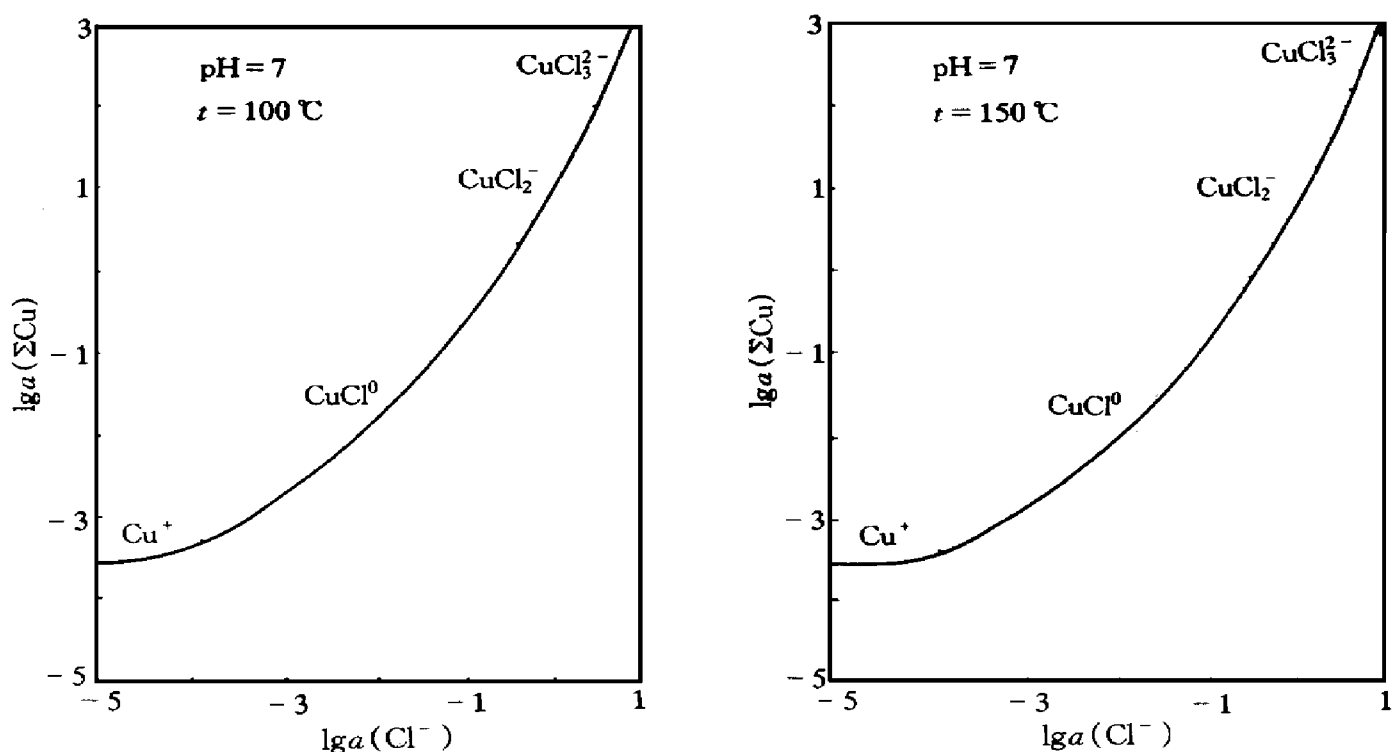
Fig. 3　Relation of activity of total copper to Cl^- activity in ore-forming solutions

with a rise of Cl^- concentration in solution by orders of magnitude. Therefore, NaCl in solutions is avaliable to the dissolution and migration of copper; contrarily, the decreasing concentration of NaCl will bring about the precipitation of copper minerals, and the accompanying of copper deposits with salt deposits in space.

6　CONCLUSIONS

To sum up the analyses above, NaCl plays an important role in the ore-forming of sand-shale copper deposits:

(1) Ore-forming fluids are hot brine solutions composed mainly of NaCl.

(2) NaCl can increase obviously the dissolution rates of copper minerals in source bed, and catalysis the dissolution and migration of copper.

(3) Cl^- and Cu can form stable cuprous chloride complexes to migrate which are mainly monovalent cuprous chloride complexes including $CuCl^0$, $CuCl_2^-$ and $CuCl_3^{2-}$, and more than 99%

of activity of dissolved total copper.

(4) The increasing of Cl^- concentration in solutions can enlarge obviously the solubility of copper by orders of magnitude.

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