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Thermodynamic parameters of reactions of basic copper carbonates formation with participation of organic complexing agents

In the article some of thermodynamic parameters for the processes which are possible in nature during the formation of the malachite and azurite are described. The authors have shown that the formation of basic carbonates from copper sulfide ores is thermodynamically more favorable than that from its oxide minerals. The presence of complexing agents promote the dissolution of oxide forms of copper and involve its ions into secondary mineralogenesis. It is found that the hydroxy acids largely promote the formation of a malachite and azurite than the similar amino acids.

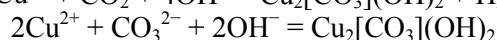
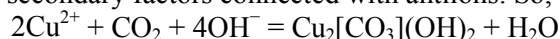
Key words: malachite, azurite, complexing agents, thermodynamic of mineralogenesis.

Natural processes of the minerals formation are characterized by variety and frequently high complexity. In the most general case they can be divided on endogenous and exogenous processes. Among other, process of formation of malachite and azurite from a sulphidic copper ores by oxidation and a carbonatization in the water environment belongs to the exogenous one [1–4]. Natural malachite $\text{Cu}_2[\text{CO}_3](\text{OH})_2$ is a valuable decorative and ornamental stone, and also important ore of copper, as well as related mineral azurite $\text{Cu}_3[\text{CO}_3]_2(\text{OH})_2$, especially in a zone of the copper field oxidation. The studying of thermodynamic aspects of the malachite and azurite formation was published in a number of works [5–9] and it is still very interesting in respect to formation from various primary copper minerals.

The various organic complexing agents which contains in soils can participate in the formation processes of basic copper carbonates [10–13]. The occurring in these cases reactions, as a rule, are studied insufficiently from the thermodynamic point of view. A number of different factors influence on these processes; the chemical character of complexing agents and initial carbonates is significant among them. The thermodynamic evaluating the possibility of passing for these reactions give essential contribution in the knowledge of mineral formation processes.

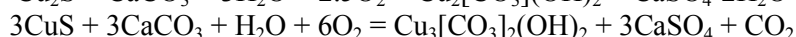
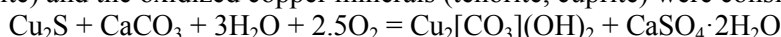
For studying thermodynamics of malachite and azurite formation reactions a number of thermodynamic calculations of changes of enthalpy, entropy and Gibbs energy of reaction at 273–373 K with participation of various initial substances has been carried out. Besides various copper minerals, they included carbonate agents in the form of the carbonate ion, the dissolved and gaseous carbon dioxide; an oxidizer — oxygen in the dissolved and gaseous form; and also water and hydroxide ions. As a source of copper ions the sulphidic and oxidized minerals, such as covellite CuS and tenorite CuO , were investigated.

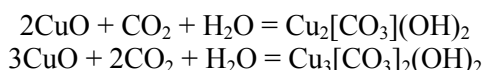
At the first stage of calculations the model reactions equations have been presented in the ionic form for elimination of influence of the secondary factors connected with antiions. So, for reactions:



absolute value of enthalpy change of reaction decreased at transition from a gaseous form of carbon dioxide to dissolved and further to a carbonate ion while value of entropy change increased. Value of change of Gibbs energy for the reaction remained in the range from –250 to –185 kJ/mol (at 298.15 K). When the oxygen in the system is added, there is a further decrease in magnitudes of thermodynamic characteristics: enthalpy change of reaction makes from –505 to –475 kJ/mol, change of Gibbs energy from –395 to –420 kJ/mol. Thus, oxidation allows to increase efficiency of the proceeding reactions. Besides, in the right part of the equations there are free electrons that points to possibility of electrochemical stimulation of the considered processes.

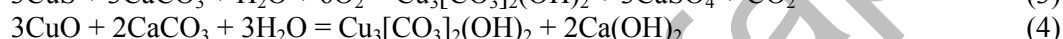
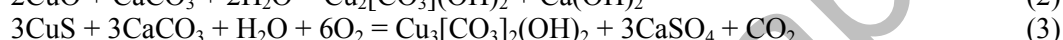
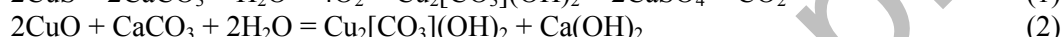
At the second stage, the reactions of formation of malachite and azurite from sulphidic (such as covellite and chalcocite) and the oxidized copper minerals (tenorite, cuprite) were considered:



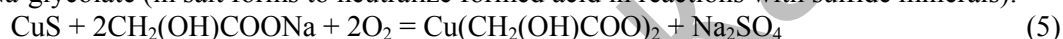


Formation of malachite from sulphidic minerals is characterised by very high thermodynamic parameters: enthalpy change from -930 to -1620 kJ/mol, entropy change from -550 to -730 J/mol·K, and change of Gibbs energy from -770 to -1400 kJ/mol. The formation of azurite from sulphidic minerals at oxidation is also has high thermodynamic parameters (change of Gibbs energy up to -2000 kJ/mol). Formation of copper carbonates from the oxidized minerals has less thermodynamic efficiency due to bigger stability of the oxygen substances; value of Gibbs energy is close to zero and even in certain cases has positive magnitude at higher temperatures. Thus, it is possible to increase efficiency of mineralogenesis by using of coordination substances.

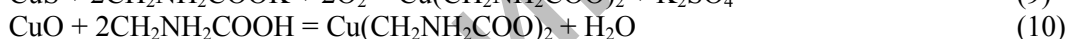
Under natural conditions the most widespread geochemical complexing substances are humic and fulvic acids. At this stage we made thermodynamic estimation of basic copper carbonates formation probability with participation of primary structural fragments of humus acids such as the simplest α -hydroxy and α -amino acids. The following reactions were considered — without complexants:



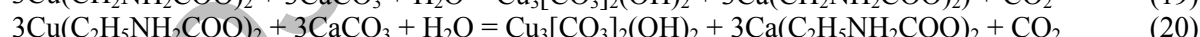
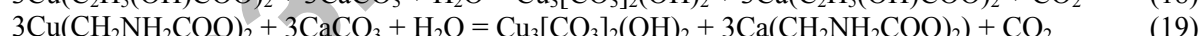
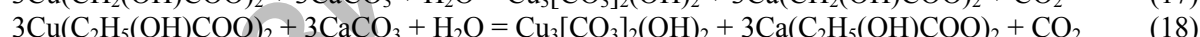
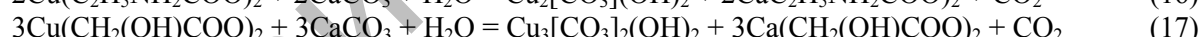
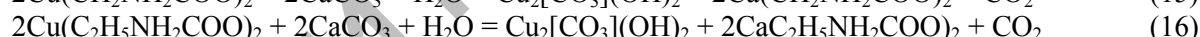
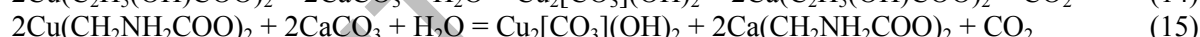
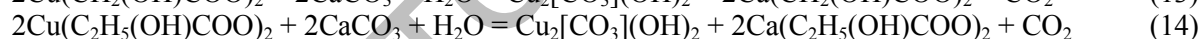
with complexant Na-glycolate (in salt forms to neutralize formed acid in reactions with sulfide minerals):



and analogical reactions with participation of Na-lactate (7, 8), K-glycinate (9, 10) and Ca-alanate (11, 12):



and final reactions of malachite (13–16) and azurite (17–20) formation from copper complexes with participation of glycolates (13, 17), lactates (14, 18), glycinate (15, 19) and alanates (16, 20):



The results of the calculations at standard temperature are shown in Table 1.

Table 1

Thermodynamic functions of the reactions (1–20) at 298.15 K

Reaction	$\Delta_r H^\circ(298)$, kJ/mol	$\Delta_r S^\circ(298)$, J/(mol·K)	$\Delta_r G^\circ(298)$, kJ/mol
1	2	3	4
1	-1475.85	-700.378	-1267.031
2	50.010	-47.502	64.173
3	-2264.92	-963.737	-1977.583
4	134.111	-74.488	156.32
5	-815.109	-558.696	-648.534
6	-91.872	-219.646	-26.384
7	-810.004	-551.583	-645.550
8	-88.943	-220.901	-23.081

	1	2	3	4
9		-841.594	-432.506	-712.642
10		-29.940	-37.998	-18.611
11		-858.41	-493.467	-711.286
12		-17.480	-14.630	-13.118
13		73.193	291.353	-13.674
14		71.352	289.680	-15.016
15		195.785	245.329	122.640
16		185.910	220.225	120.250
17		112.373	366.041	3.238
18		109.612	363.531	1.225
19		296.26	297.005	207.708
20		281.449	259.349	204.124

The reactions with participation of copper sulphide are characterized with high values of parameters at direct mineral formation and reactions with intermediate formation of copper complexes. It is seen that complexants promote the transition of oxidized copper into solution (Fig. 1). The malachite and azurite precipitation from copper complexes with hydroxy acids is thermodynamically probable, especially at case of lactates. The reactions with participation of amino acids have positive magnitudes of Gibbs energy change; nevertheless, it can be marked some tendency to decrease the value at increasing of carbon chain.

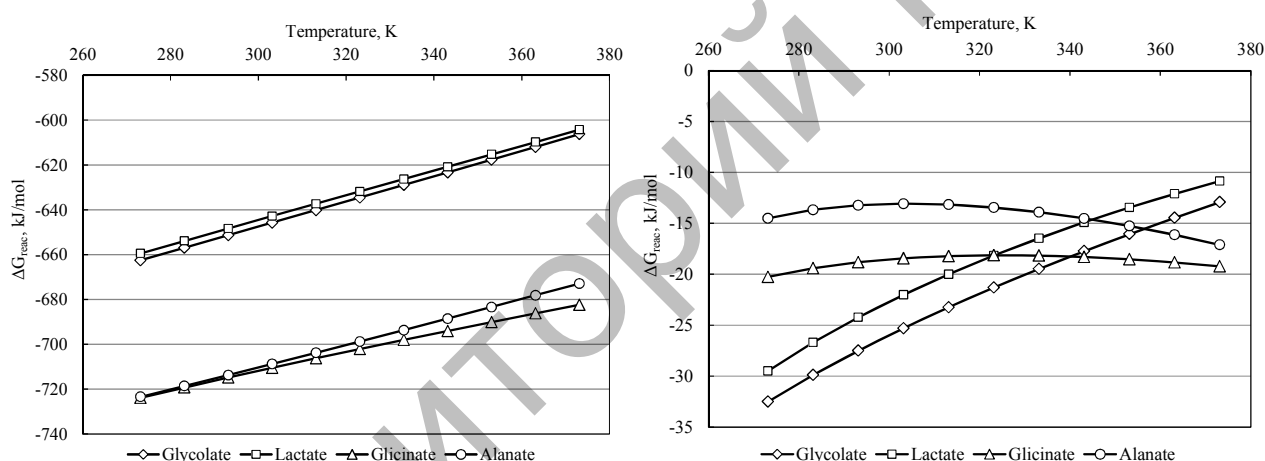
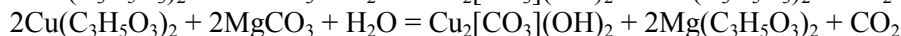
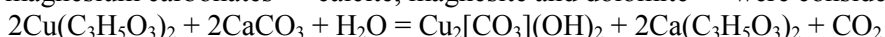


Figure 1. Temperature dependence of Gibbs energy change in reactions of dissolution of sulphide (left) and oxide (right) copper minerals with participation of complexing agents

Lactic (L-2-hydroxypropanoic) acid is one from complexing agents occurring in the nature. Lactic acid is available in industrial quantities and can be viewed as potential reagent for intensification of the mineralogenesis processes. In this case the important advantage is its ecological safety. The formation of copper complexes with lactate-ions prevent its fast precipitation in poorly soluble compounds; this fact enlarge a migration route of copper ions in environment.

The main sources of carbonate-ions at natural conditions are carbonates of calcium and magnesium. Thus, the thermodynamical parameters for reactions of copper (II) lactate with mostly widespread in the nature calcium and magnesium carbonates — calcite, magnesite and dolomite — were considered:



The thermodynamic calculations in temperature range 273–373 K show that the malachite formation is possible in the reactions with participation all of considered carbonate rocks (Table 2). The upper negative value of Gibbs energy change is observed for reaction with calcium carbonate; the reaction with participation of magnesium carbonate is considerably more profitable in energy aspect. It is may to expect some mean values for the reaction with participation of dolomite, but its thermodynamic parameters are closer to the reaction with participation of calcite.

Thermodynamic functions of malachite formation reactions at 298.15 K

Mineral	$\Delta_r H^\circ(298)$, kJ/mol	$\Delta_r S^\circ(298)$, J/(mol·K)	$\Delta_r G^\circ(298)$, kJ/mol	log K_{eq}
Calcite	71.35	289.7	-15.02	2.631
Magnesite	5.128	178.1	-47.96	8.404
Dolomite	61.94	272.7	-19.36	3.392

The reactions of azurite formation at these circumstances are characterized by higher values of enthalpy change and entropy change, as well as positive value of Gibbs energy change at environmental temperatures (Fig. 2). Thus, the reactions of azurite formation with participation of complexing agents are less probable thermodynamically than the reactions of malachite formation.

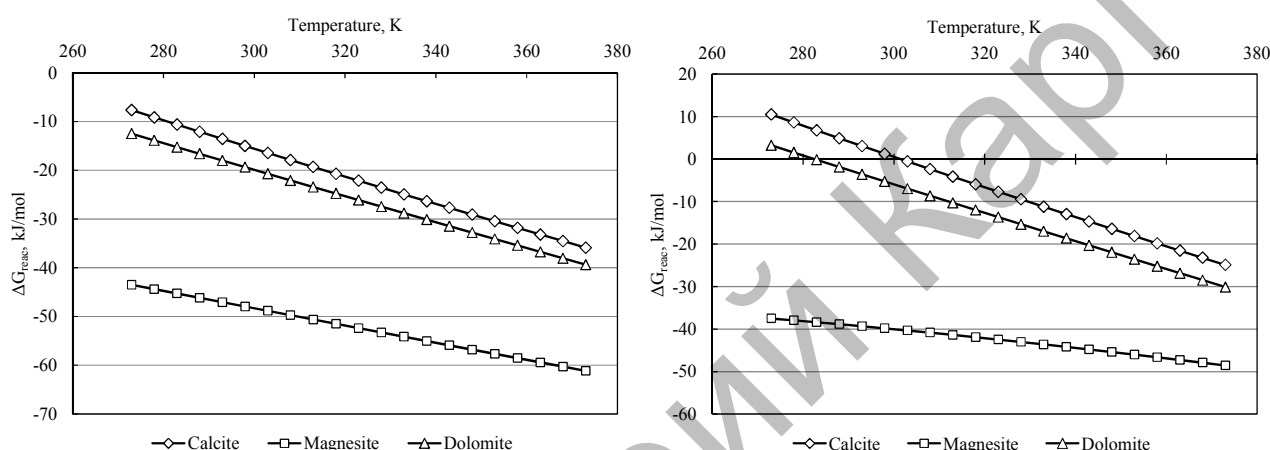


Figure 2. Temperature dependence of Gibbs energy change in reactions of precipitation of malachite (left) and azurite (right) from copper complexes with lactate-ions on various carbonate collectors

It should be noted that the using in the calculations thermodynamic data for hydrated forms of initial and final substances has an effect on thermodynamics of the processes. At the same time, in most causes, the value of Gibbs energy change stay negative.

Small values of Gibbs energy change and equilibrium constant show that the reaction with participation of lactates are carried out closely to equilibrium conditions. This fact indicate at possibility of formation of well-shaped malachite aggregates.

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Органикалық комплекстүзушілердің қатысуымен жүретін негізгі мыс карбонаттарының түзілу реакцияларының термодинамикалық өлшемдері

Мақалада табиғатта пайда болатын малахит мен азуриттың кейбір термодинамикалық процестері сипатталған. Авторлардың зерттеуі бойынша, оксидті минералдарға қарағанда сульфидті кендерден алынатын негізгі карбонаттар термодинамикалық жағынан тиімдірек. Комплекс түзушілердің жүйеде болуы мыстың оксидті формаларын ерітуге әсер етеді және мыс иондарының екіншілік минерал түзуіне мәжбүр етеді. Аналогты аминқышқылдармен салыстырғанда гидроксикышқылдар малахит пен азуриттың пайда болуына көбірек мүмкіндік туғызады.

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Термодинамические параметры реакций образования основных карбонатов меди в присутствии органических комплексообразователей

В статье описаны некоторые термодинамические процессы, которые могут протекать при образовании малахита и азурита в природе. Авторами показано, что образование основных карбонатов из сульфидных руд меди термодинамически более выгодно, чем из ее оксидных минералов. Присутствие комплексообразователей способствует растворению оксидных форм меди и вовлечению ее ионов во вторичное минералообразование. Установлено, что гидроксикислоты в большей степени способствуют образованию малахита и азурита, чем аналогичные аминокислоты.