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THERMODYNAMIC MODELLING OF THE CINNABAR AND METACINNABAR COEXISTENCE

N. Slovotenko

Ivan Franko National University of Lviv,
4, Hrushevskyi St., 79005 Lviv, Ukraine
E-mail: nslovotenko@gmail.com

Polymorphic transitions between cinnabar and metacinnabar have been studied using numerical physicochemical modelling of mineralization in the GEM-Selektor software package (GEMS3). System components were selected with the simulation of medium- and low-temperature hydrothermal conditions; in the reaction, solutions were taken with salinity of 8, 16, 20 and 40 wt. % NaCl eq. The buffer equilibrium of oxidizing–reducing conditions was maintained with H_2S–H_2SO_4. The pressure was changed from 100 to 1 000 bar. The temperature interval of estimation of mineral equilibrium states was 225–525 °C. Increasing pressure promotes the metacinnabar formation. The stability field of existence of metacinnabar expands at higher values of pressure, and the change in salinity of solutions does not affect the conditions of polymorphic transformation.

Key words: cinnabar, metacinnabar, thermodynamic modelling.

The laws of the geochemical reactions course remain vague in many cases, even in the presence of a large number of empirical data. From the standpoint of understanding the details of any geological phenomenon, the physicochemical modelling of natural processes of mineral formation remains acute. The phenomena of polymorphism and polymorphic transitions between the various phases of a single chemical composition are of a particular interest. In our work, we use the method of numerical physicochemical modelling of mineralization in the GEM-Selektor (GEMS3) modelling package [3, 4].

The object of our study was a hydrothermal system in which sulphides are formed, with polymorphic transformation of cinnabar into metacinnabar.

Cinnabar, a lower-temperature α-HgS polymorph, has a chain structure. High-temperature β-HgS polymorph – metacinnabar – has a structure of sphalerite type. The thermodynamic characteristics of the transition of cinnabar–metacinnabar have been investigated in [1]. The laboratory investigations concerning the cinnabar and metacinnabar solubility have been performed in [2]. The thermodynamic data in the system Hg–Zn–(Fe)–S of zincous metacinnabar in the mercury deposit at Levigliani (Apuane Alps, northern Tuscany) are brought in [5]. In our investigation, we are keen to find out particular features of the polymorphic process in the concrete conditions of the hydrothermal system.

Thermodynamic calculations of the equilibrium involving minerals, gas mixtures and aqueous solutions are essential to understanding processes relevant to hydrothermal ore-forming systems. We are employing GEMS3 software package based on the Gibbs energy minimization (GEM) technique, which makes it possible to model thermodynamically non-ideal multi-component-multiphase systems that include dilute to concentrated aqueous solu-

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tions, mineral solid solutions, supercritical fluids, gases, silicate and metal melts, and sorption phases [3, 4]. The program package is equipped with powerful and highly accurate GEM-algorithms, allowing for simultaneous calculation of multiple stable phases. The kind and amount of solids as well as the speciation of the dissolved species precipitated are calculated.

The initial composition of the simulated system is shown in the Table; the composition of the simulated system is calculated in relation to 1 kg of water. The components of the system were selected with the simulation of medium- and low-temperature hydrothermal conditions. The solutions with salinity of 8, 16, 20 and 40 wt. % NaCl eq. took part in the reaction. The buffer equilibrium of the oxidation–reduction conditions was maintained using H_2S–H_2SO_4 pair of components. The pressure was changed from 100 up to 1 000 bars. The temperature interval of estimation of mineral equilibrium states varied between 225 and 525 °C.

Briefly characterizing the results of the simulation, it should be noted that metacinnabar is formed only at elevated pressure values which agrees well with [2]. At a pressure of 100 bars in the temperature range of 225–300 °C only cinnabar is deposited (Fig. 1). So as far other component species – FeS and CuS (see Table) – exist in the initial system, it is worthy to expect that other sulphide phases will coexist with Hg phases. So in this case only pyrite accompanied to cinnabar (see Fig. 1).

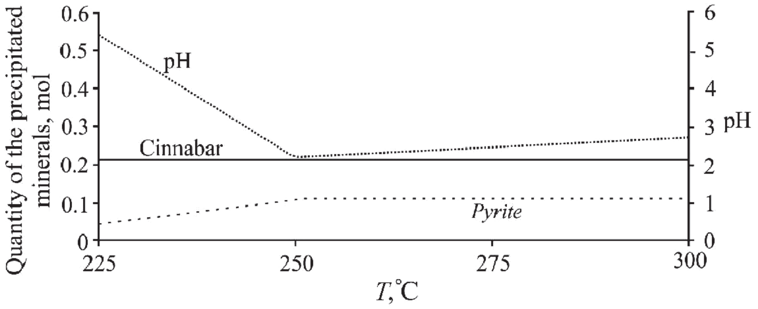


Fig. 1. The results of numerical physicochemical modelling.
Polymorphic transformation of cinnabar to metacinnabar does not take place in this temperature interval and at the pressure of 100 bars.

Component composition of the modelling system

Reactants	Quantity, g
FeS	50
CuS	50
HgS	50
H_2S	1
H_2SO_4	1
H_2O	1 000
Fe_2O_3	1
FeOOH	1
NaCl	80 (160, 320, 400)

Metacinnabar formation took place at the 200 bar pressure, and it began at 363 °C point temperature up to 401 °C (Fig. 2). So the transition of the cinnabar to the metacinnabar occurs at 363 °C. The temperature range of stability of metacinnabar at this pressure was 363–401 °C. Acid-base alteration during the process is shown on the second vertical axis (see Fig. 2, *a*). It demonstrates that cinnabar existed strictly in the more acid conditions than metacinnabar. At temperatures above 400 °C precipitated mercury instead of Hg sulphides. An oxidation–reduction potential line is reflection symmetrical to the pH-line (see Fig. 2, *b*). In all modelling variants there is a symmetrical placement of pe-lines to pH-lines. So we decided to limit its figures and show it changes only in Fig. 2, *b*. As oppose to previous modelling results in this case not only pyrite but bornite and chalcopyrite were precipitated, and these sulphides continue to coexist in the next experiments at higher pressure with the mercury phases (Fig. 3). Changes in pH are correlated with the transition of bornite–chalcopyrite: bornite is formed in acidic conditions, and chalcopyrite – in alkaline. The acidity–alkalinity changes do not reflect in polymorphic transformations of the cinnabar and metacinnabar.

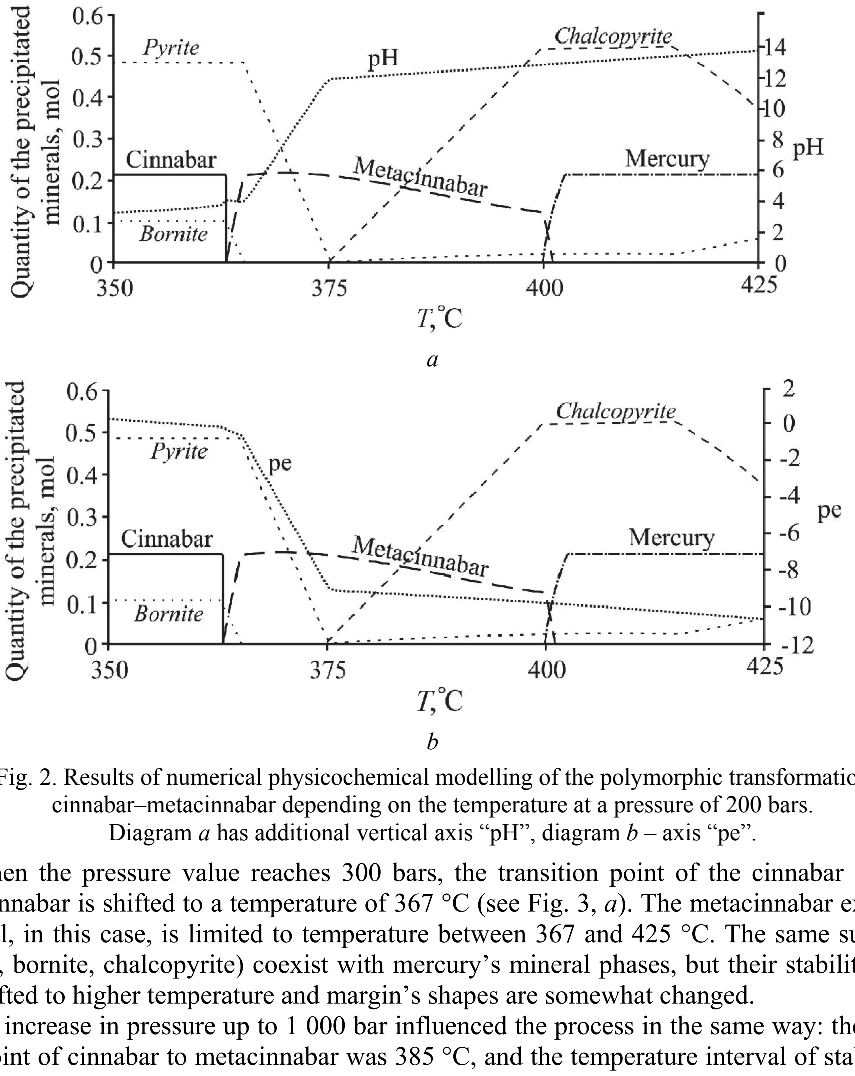
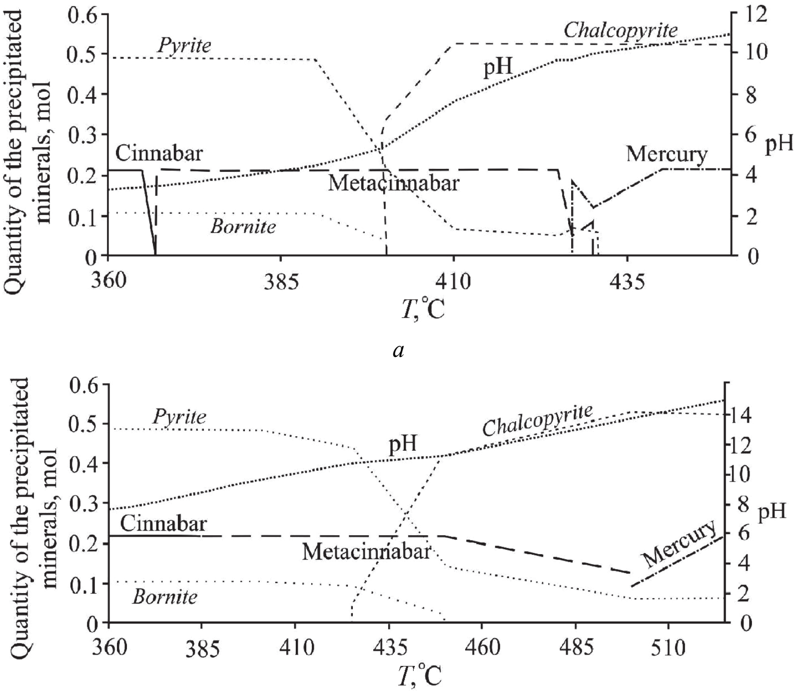


Fig. 2. Results of numerical physicochemical modelling of the polymorphic transformation cinnabar–metacinnabar depending on the temperature at a pressure of 200 bars. Diagram *a* has additional vertical axis “pH”, diagram *b* – axis “pe”.

When the pressure value reaches 300 bars, the transition point of the cinnabar into the metacinnabar is shifted to a temperature of 367 °C (see Fig. 3, *a*). The metacinnabar existence interval, in this case, is limited to temperature between 367 and 425 °C. The same sulphides (pyrite, bornite, chalcopyrite) coexist with mercury’s mineral phases, but their stability fields are shifted to higher temperature and margin’s shapes are somewhat changed.

An increase in pressure up to 1 000 bar influenced the process in the same way: the transition point of cinnabar to metacinnabar was 385 °C, and the temperature interval of stability of the metacinnabar expanded even more, namely 385–500 °C (see Fig. 3, *b*). Above these temperatures, the metacinnabar decomposes with the release of native mercury.



a

b

Fig. 3. Results of numerical physicochemical modelling of the polymorphic transformation cinnabar–metacinnabar depending on the temperature at a pressure of 300 (*a*) and 1 000 (*b*) bars.

The gradual change in salinity (see Table) in no way affected the change in the temperature intervals of mineral phase coexistence. The pH-value changes in the same way during these processes: at higher temperature it grew constantly (see Fig. 2–4). An exception is the first case, when only one stable phase of cinnabar was precipitated (see Fig. 1). Minerals forming succession changes constantly with growing temperature and pressure: from cinnabar to metacinnabar and mercury.

Consequently, an increased pressure contributes the formation of metacinnabar. This logically follows from the need to reorient the links of cinnabar chain crystalline structure to a more dense crystalline structure of metacinnabar. The stability field of metacinnabar existence expands at higher pressure values, and the solutions salinity changes do not affect the conditions of polymorphic transformation.

REFERENCES

1. Мельчакова Л. В. Переход киноварь–метациннабарит (энтальпия и температура перехода, теплоемкость) / Л. В. Мельчакова, И. А. Киселева // Геохимия. – 1989. – № 11. – С. 1663–1668.
2. Dickson F. W. The stability relations of cinnabar and metacinnabar / F. W. Dickson, G. Tunell // Amer. Mineral. – 1959. – Vol. 44, N 5–6. – P. 471–487.

3. GEM-Selektor geochemical modelling package: revised algorithm and GEMS3K numerical kernel for coupled simulation codes / D. A. Kulik, T. Wagner, S. V. Dmytrieva [et al.] // Computational Geosciences. – 2013. – Vol. 17. – P. 1–24.
4. GEM-Selektor geochemical modelling package: TSolMod library and data interface for multicomponent phase models / T. Wagner, D. A. Kulik, F. F. Hingerl, S. V. Dmytrieva // Canadian Mineralogist. – 2012. – Vol. 50. – P. 1173–1195.
5. Mineral assemblages in the Hg–Zn–(Fe)–S system at Levigliani, Tuscany, Italy / A. Dini, M. Bevenuti, P. Lattanzi, G. Tanelli // European Journal of Mineralogy. – 1995. – Vol. 7, N 2. – P. 417–428.

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ТЕРМОДИНАМІЧНЕ МОДЕЛЮВАННЯ СПІВІСНУВАННЯ КІНОВАРІ ТА МЕТАЦИНАБАРИТУ

Н. Словотенко

Львівський національний університет імені Івана Франка,
вул. Грушевського, 4, 79005 м. Львів, Україна
E-mail: nslovotenko@gmail.com

За допомогою числового фізико-хімічного моделювання мінералоутворення в програмному пакеті GEM-Selektor (GEMS3) досліджено поліморфні переходи між кіновар'ю та метацинабаритом. Компоненти системи підібрано для імітації середньо- й низькотемпературних гідротермальних умов. У реакції брали участь розчини з солоністю 8, 16, 20 та 40 мас. % NaCl-екв. Буферну рівновагу окиснювально-відновлювальних умов підтримували за допомогою H_2S–H_2SO_4. Тиск змінювали від 100 до 1 000 бар. Температурний інтервал оцінки мінерального рівноважного стану – 225–525 °C. Оскільки в системі є не лише Hg, Fe та S, а й Cu, то перетворення кіновар–метацинабарит супроводжувалися осадженням піриту, халькопіриту й борніту. Зміна показника pH корельована переходом борніт–халькопірит: борніт утворюється за кислих умов, халькопірит – за лужних. На поліморфних перетвореннях сульфідів ртуті варіації кислотності–лужності не позначилися. Зміни окисно-відновного потенціалу фіксовані тим, що халькопірит стабільний за відновлювальних умов, а борніт – за більш окиснювальних.

Якщо за P = 100 бар у температурному інтервалі 225–300 °C відкладається тільки кіновар, то вже за 200 бар у точці 363 °C відбувається перехід кіноварі у метацинабарит. За такого тиску температурний проміжок стабільності метацинабариту становить 363–401 °C. Якщо значення тиску сягає 300 бар, то перехід кіновар–метацинабарит зміщується до точки 367 °C, а інтервал існування метацинабариту обмежений значеннями 367–425 °C; відповідно, за P = 1 000 бар перехід відбувається за 385 °C, а температурний інтервал стабільності метацинабариту стає ще ширший – 385–500 °C. За вищих значень температури метацинабарит розкладається з виділенням самородної ртуті.

Отже, утворенню метацинабариту сприяє підвищення тиску. Це логічно випливає з необхідності переорієнтації зв'язків ланцюжкової структури кіноварі у щільнішу структуру метацинабариту. Поле стабільності існування метацинабариту розширюється за вищих значень тиску, а зміна солоності розчинів не впливає на умови поліморфних перетворень.

Ключові слова: кіновар, метацинабарит, термодинамічне моделювання.