# Thermodynamic Models of Redeposition of the Substance of Pb–Zn Ore Veins at a Carbonate Barrier upon Reactivation of Hydrothermal Processes

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Abstract—The methods of equilibrium—dynamic modeling have been applied to evaluate the probability of redeposition of previously formed Pb–Zn vein ore substances at a carbonate barrier upon reactivation of a hydrothermal system. The natural prototype is the Ursdon ore occurrence (Dzhimidon ore field, North Ossetia, Russia) in Oxfordian limestone  $(J_3)$ ; the formation of polymetallic vein deposits of the region occurred in the pre-Callovian time of the Middle Jurassic. Calculations have been performed using the HCh software package, which includes the Unitherm thermodynamic database (the H–O–K–Na–Ca–Mg–Al–Si–Fe–C–Cl–S–Zn–Pb–Cu system described by 54 minerals and 78 particles of an aqueous solution). It has been established that late low-temperature hydrothermal solutions may provide pyritization, silicification, and the formation of Pb–Zn mineralization in carbonate rocks. The deposition of quartz and sulfides occurs along fractures and at the dissolution front of carbonate rocks.

Keywords: equilibrium-dynamic modeling, sources of ore material, polymetallic vein deposits, carbonate barrier

**DOI:** 10.3103/S0145875224700789

### INTRODUCTION

Polymetallic mineralization zones were identified on the northern extensions of the ore zones of the Dzhimidon Deposit among the Upper Jurassic carbonate formations of the Rocky Ridge during the exploration work conducted in 2009–2010 by the Sevosgeologorazvedka JSC on the surface of the Dzhimidon ore field (Sadon mining district, North Ossetia, Russia). This type of mineralization is completely new for Mountainous Ossetia. Moreover, the formation of all vein Pb-Zn deposits in the district (E Zgid, Sadon, Arkhon, Kholst, Dzhimi, etc.) occurred in pre-Callovian time  $(J_2)$  (Nekrasov, 1980). It can be assumed that the hydrothermal system was reactivated in the Late Jurassic or Cretaceous time. The activation could have been initiated by intense tectonic movements that affected both ore veins  $(J_2)$ and carbonate rocks  $(J_3)$ . Low-temperature mineralized waters  $(100-150^{\circ}C)$  could have interacted with the substance of previously formed ore veins at a depth of 3-4 km, which resulted in the formation of orebearing hydrothermal solutions. These solutions reached carbonate rocks via fracture channels and, upon reaction with them, formed a new type of ore occurrence. Among them are the Ursdon, Efremovskoe, and Kariukhokh ore occurrences in carbonate rocks  $(J_3 ox)$  that spatially lie on the continuation of the ore-controlling faults of the Bozang and Tsagarsar ore zones (Dzhimidon Deposit), but at a distance of several kilometers.

Our study was aimed at the creation of quantitative equilibrium–dynamic models of redeposition of the substance of polymetallic veins at the carbonate barrier for the reconstruction of the mechanisms and conditions of the formation of ore mineralization.

### MATERIALS AND METHODS

The Ursdon ore occurrence on the right side of the Ursdon River, 500 m to the north and 100 m upstream of the village of the same name at the foot of the southern escarpment of Mount Kariukhokh, was the direct prototype for our studies. The ore occurrence is confined to a pack of organogenic—detrital limestone overlying the horizon of Callovian conglomerate  $(J_2cl)$ . It is a linear zone of fractured limestone ferru-



**Fig. 1.** Primary outcrops of silicified and pyritized limestone  $(J_3)$  at the Ursdon ore occurrence with strong limonitization due to oxidation of pyrite.

ginized from the surface (Fig. 1); numerous slip planes occur in intensely crushed limestone. Primary sulfides are largely leached. According to the data of Sevosgeologorazvedka JSC, the Zn content in the ore occurrence reaches 1.0% and lead reaches 0.2–0.5%.

We collected three samples from the ore occurrence: one at the outcrop itself (URS-1) and two at a distance of 5 and 15 m (URS-2 and URS-3). The contents of Ca, Si, Fe, S, Zn, Pb, and Cu were analyzed in ground samples by X-ray fluorescence (Niton XL3t900S-He GOLDD; Chair of Geochemistry, Moscow State University). The accuracy was controlled by a series of domestic and foreign standard samples (GSO 793-76, 1230-77, and 2029-79; NIST RCRA, GBM 307-14, 308-3, 309-1, 906-10, 911-16, and 915-7). The discrepancy between the measured and certified values of the content of ore elements does not exceed 5–10%.

Equilibrium-dynamic modeling of the redeposition of ore body material at a carbonate barrier was performed using the HCh software package (Shvarov, 2008), which includes the Unitherm thermodynamic database (the H-O-K-Na-Ca-Mg-Al-Si-Fe-C-Cl-S-Zn-Pb-Cu system, described by 54 minerals and 78 particles of aqueous solution).



Fig. 2. The two-reactor calculation scheme in the type 1 model.

#### **RESULTS AND DISCUSSION**

Calculations were performed for many variants of two types of models. The type 1 model is the interaction of ore-bearing solution with carbonate rock only; the type 2 model is a combination of deposition of substance from ore-bearing solution in the feeder channel and upon its reaction with calcite. The variants change the number of successive flow reactors, the composition of the ore and the initial hydrothermal solution, the ore/solution and rock/solution ratios, the temperature, and the pressure.

Figure 2 shows a simple calculation scheme for the **type 1 model**: zero reactor, where the initial ore-free solution reacts with the substance of the ore vein at  $T_0$  and  $P_0$ ; the first reactor, where the ore-bearing solution from the zero reactor reacts with calcite at  $T_1$  and  $P_1$ . In each reactor, an equilibrium state is achieved.

The ore composition in the zero reactor is as follows: quartz (Qtz), pyrite (Py), sphalerite (ZnS), galena (PbS), and chalcopyrite (ChPy) in various proportions. The temperature and pressure in the reactors may be the same or decrease in the first reactor. The initial solution with the composition of 1 m NaCl,

occurrence, wt %							
Sample	Ca	Fe	Si	S	Zn	Pb	Cu
URS-1	16.1	5.89	16.6	9.52	0.0345	0.027	0.0019
URS-2	38.8	0.27	1.2	0.21	0.0063	0.0016	0.0013
URS-3	39.3	0.18	0.9	0.18	0.0018	0.0009	0.0023

Table 1. The contents of some elements at the Ursdon ore occurrence, wt %

 $0.5 m H_2CO_3$ , and 1 kg H<sub>2</sub>O is adopted in most calculations. It is similar to the composition of the barren solution from the ore formation models that describe the formation of polymetallic deposits in the region (the justifications were given earlier by Borisov et al. (2006, 2019, 2022), etc.). Up to N = 20 waves of solutions pass through the reactors. Each subsequent portion of the solution reacts with all the substance formed at the previous step.

The variant with identical T and P in reactors is as follows:  $T = 100^{\circ}$ C and P = 100 MPa. The ore composition in this calculation is as follows (wt %): 74.95, Qtz; 20, Py; 4, ZnS; 1, PbS; and 0.05 ChPy. The initial solution after the reaction with ore (100 g) in the zero reactor becomes ore-bearing. Its characteristics are as follows: pH 3.1, Eh -0.1 V; total concentrations of Fe =  $8.7 \times 10^{-7} m$ , Zn =  $5.7 \times 10^{-5} m$ , Pb =  $4 \times 10^{-6} m$ ,  $Si = 1.1 \times 10^{-3} m$ ,  $Cu = 1.3 \times 10^{-7} m$ , and  $S(II) = 6.2 \times 10^{-7} m$  $10^{-5}$  m (hereinafter, m corresponds to the molal concentration, i.e., mol/1000 g H<sub>2</sub>O). When such a solution interacts with calcite (100 g) the pH increases to 5, Eh decreases to -0.24 V, and the concentrations of the components decrease to Fe =  $8.4 \times 10^{-7}$  m, Zn =  $7.1 \times 10^{-7} m$ , Pb =  $4.8 \times 10^{-8} m$ , Cu =  $2.2 \times 10^{-8} m$ , and S(II) =  $1.5 \times 10^{-6} m$  (the concentration of Si decreases slightly). It is evident that the reaction with calcite results in the deposition (in total from 21 portions of the solution) of sphalerite, up to  $1 \times 10^{-3}$  mol; galena, up to  $8 \times 10^{-5}$  mol, copper sulfides (chalcopyrite, bornite Brn, chalcocite Chl), up to  $1 \times 10^{-6}$  mol; and quartz, up to  $1.5 \times 10^{-5}$  mol. Pyrite is not formed.

The formation of sphalerite-galena mineralization is a positive result of this variant. However, quartz is precipitated to a much lesser extent than sulfides and there is no pyrite at all. The Ursdon ore occurrence has a high degree of limestone silicification and pyritization, which is clearly manifested in the outcrop by the development of a limonization zone (Fig. 1, Table 1). Thus, the considered version of the model only partially corresponds to the data for the real object. It should be noted that the data in Table 1 cannot provide a complete characterization of the ore occurrence. Within the clearly expressed zone of ferruginization of limestone only one sample (URS-1) was collected. However, it is clearly evident that the contents of Fe, Si, Zn, and Pb in Sample URS-1 are higher by more than an order of magnitude in comparison with those in Samples URS-2 and URS-3.

When we lower the temperature to 90°C in the reactor with carbonate (the other parameters remain unchanged) the composition and characteristics of the ore-bearing solution correspond to the variant considered above. Almost identical contents of sphalerite, galena, and copper sulfides are precipitated, but the content of quartz increased by two orders of magnitude (up to  $4 \times 10^{-3}$  mol). Silicification increased, but pyritization did not occur. The results obtained in the model with two reactors upon the passage of 21 portions of the solution may be considered as preliminary or qualitative only. They show that nonferrous metal sulfides are the first to be precipitated upon the reaction of the ore-bearing solution with calcite. We may assume that precipitation of pyrite requires change in the composition and weight of the ore in the zero reactor, as well as increase in the interaction time (N).

In the modified model, the carbonate rock is represented by three successive flow reactors (Fig. 3) with increasing weights of calcite (20, 50, and 100 g). Calculations with increasing weight of rock in flow reactors were previously used by us to model the metasomatic zoning of rocks hosting mineralization (Borisov, 2000).

The ore composition in this model is as follows (wt %): 77.499, Qtz; 20, Py; 2, ZnS; 0.5, PbS; and 0.001, ChPy. In the zero reactor, 5 g of ore interacts with the initial chloride–carbon dioxide solution. Calculations were performed for two variants: (1) the temperature in all reactors is constant (100°C); (2) the temperature in the zero reactor is 100°C, and in three reactors with carbonate it decreases to 90°C. Fifty-one portions of the solution pass through all reactors (N = 50 and the count starts from 0). The N values may be considered as a relative time scale.

At a constant temperature in all reactors (left part of Fig. 4), it is clearly evident that the pyrite content rapidly increases as zinc and lead sulfides dissolve in the first reactor and are redeposited in the next reactor. This process begins with complete leaching of sphalerite and galena from the original ore. After passage of 25-30 portions of the solution the following assemblages are stable: Py + Qtz ( $1 \times 10^{-5}$  and  $3 \times 10^{-6}$  mol) in the first reactor, ZnS + PbS + Qtz + Py in the second reactor, and Cal + ZnS + PbS + Qtz in the third reactor. With further development of the process (at N > 35), the pyritization area extends to the second reactor and partially to the third one. It should be noted that pyrite will also be deposited in the reactors upon the reaction with calcite, but in the variant of complete absence or very small content of Zn, Pb, and Cu sulfides in the original ore (in a separate series of calculations).

When the temperature in limestone was reduced (right part of Fig. 4, N = 30-35) in the first reactor, the mineral association, compared to the isothermal variant, remained similar, but with a significant predominance of quartz over pyrite: Qtz + Py (7 × 10<sup>-3</sup>)

and  $3 \times 10^{-5}$  mol). There are no significant differences between the second and third reactors.

The main result of calculations by the considered model is the establishment of the probability of precipitation of quartz, pyrite, and Zn, Pb, and Cu sulfides via the reaction with carbonate rocks under the isothermal conditions. A slight decrease in temperature in the carbonate rock enhances its silicification and pyritization.

The area of mineral precipitation may be expanded in the model, which additionally takes the mineral formation in fractures of carbonate rocks that supply orebearing solutions into account. Figure 5 shows a multi-reactor calculation scheme for the type 2 model: zero reactor, initial ore  $(T_0, P_0)$ ; reactors 1–5, the "empty" fracture space in carbonate rocks, where a model vein is formed from the ore-bearing solution upon the temperature decrease (from  $T_1 - P_1$  to  $T_5 - P_5$ ); and in reactors 1k-3k, calcite in the near-fracture space (weighing 20, 50, and 100 g) with T-P' corresponding to those in reactors 1-5. The latter three reactors represent microfractured and porous space in the carbonate rock next to the main vein in the model. Our calculations were performed for each temperature level. As an example, Fig. 5 shows only two temperature levels  $(T'_2 \text{ and } T'_4)$  at which the solution from the fracture channel interacts with limestone in three flow reactors.

Let us consider the results of calculations via the second type model, when the temperature upon the reaction with the ore is 150°C. A gradual decrease in T from 140 to 100°C (a step of 10°C) occurs in reactors 1–5. Calcite reacts with the solution from the fracture channel at a constant temperature (reactors 1k–3k).

An increase in the temperature upon the reaction of the initial solution with the ore (in contrast to the options considered above) results in an increase in the total concentrations of the components:  $Fe = 2 \times 10^{-6} m$ , Zn = $1.7 \times 10^{-4} m$ , Pb =  $1.8 \times 10^{-5} m$ , Si =  $2.5 \times 10^{-3} m$ ,  $Cu = 1.4 \times 10^{-6} m$ , and  $S(II) = 1.9 \times 10^{-4} m$  (pH 3.3, Eh -0.13 V). We described the precipitation of material in fractures via the layer mechanism (Borisov, 2000, etc.), when a separate layer of minerals is precipitated from each portion of the ore-bearing solution from the zero reactor, and the solution in equilibrium with them flows into the next reactor with a decrease in temperature. The same solution from the fracture channel under isothermal conditions reacts with calcite in a system of three flow reactors. In this interaction, each subsequent portion of the solution completely processes the substance formed at the previous step. Such an interaction mechanism is named reactionary (Borisov, 2000). Thus, the layer and reaction mechanisms of the ore formation are combined in the type 2 model. Some of the calculation results (with N = 10) for one of the variants of the type 2 model are shown in Fig. 6.

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Fig. 3. The multi-reactor calculation scheme in the type 1 model.

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**Fig. 4.** The results of calculations for the type 1 model (three successive reactors with calcite). The variant with a constant temperature in all reactors ( $100^{\circ}$ C) is shown on the left. The variant with a decrease in temperature to  $90^{\circ}$ C in the carbonate rock is on the right. The interval along the waves of the ore-bearing solution (*N*) with a change in mineral associations by reactors is marked with a dotted line.

The data in Fig. 6 require some explanation. The minerals that are precipitated in the model vein with decreasing temperature are shown to the left of the dotted lines, but this is the only layer formed at N = 10. Quartz and sulfides are precipitated on all preceding solution waves (from 0 to 9) as well, i.e., the total amount of new formations is higher by an order of magnitude than shown in Fig. 6. For example, at 140°C,  $3.7 \times 10^{-3}$  mol of quartz are precipitated in total, and only  $3.4 \times 10^{-4}$  mol in one layer. The same is true for pyrite: in total,  $4 \times 10^{-6}$  mol, and in one layer,  $3.7 \times 10^{-7}$  mol. At this temperature, sphalerite (up to  $3.3 \times 10^{-4}$  mol) and galena (up to  $4.3 \times 10^{-5}$  mol) are precipitated. With decreasing temperature (from 140 to 100°C in Figs. 6a and 6b; from 140 to 130°C in Figs. 6c and 6d), the content of precipitated substance decreases, since the concentrations of the components in the ore-bearing solution decrease. A typical quartz-polymetallic vein is formed.

The minerals formed upon the reaction with calcite (reactors 1k-3k in Fig. 5) are shown to the right of the dotted lines. Calcite is not shown in Fig. 6. In the 11th (N = 10) wave of solutions from the fissure channel it was completely dissolved in reactor 1k (closest to the dotted line), partially dissolved in reactor 2k, and very poorly dissolved in reactor 3k. The precipitation of quartz and sulfides in these reactors is uneven. The content of quartz compared to the vein decreases by 2 orders of magnitude (up to  $5 \times 10^{-6}$  mol in reactors 1k and 2k, Fig. 6a). It is evident from Figs. 6a and 6b that the maximum precipitation of sphalerite (3.4  $\times$  $10^{-4}$  mol), galena (2.4 ×  $10^{-5}$  mol), and chalcopyrite  $(1.9 \times 10^{-7} \text{ mol})$  occurs in reactor 2k, where calcite is partially dissolved. It should be noted that these contents are commensurate with the total precipitation of sulfides in the vein at this temperature level. Figures 6c and 6d show the situation at a higher temperature of interaction of the solution with calcite (130°C). In this



Fig. 5. The multi-reactor calculation scheme in the type 2 model. The numbers of the reactors are shown next to them.

case, the maximum precipitation of sphalerite ( $7.8 \times 10^{-4}$  mol) and galena ( $7.6 \times 10^{-5}$  mol) occurs in reactor 1k, while that for chalcocite occurs in reactor 2k. Quartz and sulfides are not precipitated in the latter reactor. Pyrite is formed only when calcite is completely dissolved, which is clearly visible in Figs. 6b and 6d ( $2.2 \times 10^{-8}$  mol at  $100^{\circ}$ C and  $1.4 \times 10^{-7}$  mol at  $130^{\circ}$ C).

The efficiency of pyrite deposition may be increased by decreasing the ore/water ratio in the zero reactor. One of the results of such calculation is shown in Fig. 7.

In this calculation option the ore weight in the zero reactor is reduced to 5 g (it was 100 g in previous calculations). The ore composition is as follows (wt %):

74.95, Qtz; 20, Py; 4, ZnS; 1, PbS; and 0.05, ChPy. Since the contents of sphalerite, galena, and chalcopyrite in the original ore are lower, their leaching occurs faster. Thus, sphalerite is completely leached from the ore at N = 11; galena, at N = 10; chalcopyrite, at N =7. Compared to the option considered above, this leads to differences in the precipitation of these minerals in the vein and in the near-vein space upon the reaction with calcite. In the model vein, sphalerite and galena are precipitated in the first 12 layers, while copper sulfides are precipitated in 8 layers. Quartz and pyrite are deposited in all layers up to N = 20. Therefore, in one layer at N = 20, only these two minerals are shown in Fig. 7 to the left of the dotted line. From  $4.5 \times 10^{-6}$  to  $1.1 \times 10^{-6}$  mol pyrite are precipitated in this layer. The total pyrite content in the vein in all layers is signifi-



**Fig. 6.** The results of calculation via the type 2 model. Mineral precipitation in veins and upon the reaction with calcite. (a-b) 5 reactors from 140 to 100°C, fracture channel; 3 reactors at 100°C, reaction with calcite: (a) major minerals, (b) minor minerals; (c-d) 2 reactors from 140 to 130°C, fracture channel; 3 reactors at 130°C, reaction with calcite: (c) major minerals, (d) minor minerals. The dotted line separates the vein formation region (left) and the reaction region with carbonate rock (right).



Fig. 7. The results of calculations via the type 2 model with a decreasing ore/water ratio. Precipitation of minerals in fracture channels and upon the reaction with calcite (passage of 21 solution waves). (a) Major minerals; (b) minor minerals.

cantly higher:  $4.4 \times 10^{-5}$  mol at 140°C and  $1 \times 10^{-5}$  mol at 100°C. This is higher by an order of magnitude than that obtained in the variant shown in Fig. 6.

What happens in the near-vein space (three reactors to the right of the dotted line)? A clear maximum of pyrite precipitation (up to  $9.2 \times 10^{-6}$  mol) is formed in the first two reactors, against the background of complete calcite dissolution. However, this maximum is almost equal to the total pyrite content in the vein. The maximum precipitation of sphalerite (4.2 ×  $10^{-4}$  mol), galena ( $2.9 \times 10^{-5}$  mol), and chalcopyrite ( $3.7 \times 10^{-7}$  mol) occurs in the middle reactor. In the latter reactor, calcite dissolves partially and pyrite precipitation does not occur in it, but quartz and ore minerals are accumulated.

Thus, we may suggest that the type 2 models may provide mineralization comparable to that observed at the Ursdon ore occurrence. The plane of contact between the ore vein and carbonate rocks may be seen at the outcrop (Fig. 1).

The models could be made more complex. For example, the mobilization zone of ore components could be represented by several reactors with different ore compositions rather than by one reactor. However, in reality, this depends on knowledge of the path along which the solution passed. This cannot be established. It would be possible to change the temperature and the step of its decrease in the fissure channel, but this requires additional research, which is unlikely to have a fundamental effect on the results. Variants with a decrease in pressure and changes in the composition of the ore-free solution do not provide additional information.

### CONCLUSIONS

The studied equilibrium-dynamic models demonstrate that a carbonate barrier promotes the precipitation of quartz, pyrite, and Zn, Pb, and Cu sulfides, even under isothermal conditions. Previously formed polymetallic deposits could be the source for the components of such ores upon reactivation of the hydrothermal system. Sphalerite, galena, and copper sulfides are precipitated at the early stages of the formation of ore occurrences in carbonate rocks. The preferential and maximum precipitation of pyrite in this system occurs later along the solution-supplying fractures and in the space of the host carbonate rocks with complete mobilization of Zn, Pb, and Cu sulfides from the source of these components. A slight decrease in the temperature of the ore-bearing solution in carbonate rocks leads to a significant increase in quartz precipitation. The studied processes of reprecipitation of ore components at the carbonate barrier may occur on polymetallic deposits, as well as on other ore objects.

#### **FUNDING**

The study was a part of the state task Development of integrated methods of physical, prospecting, and environmental geochemistry (no. 121061600048-7).

#### CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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#### Translated by A. Bobrov

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