

Thermodynamic Simulation of the Genesis of Filling Veins

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Abstract—Thermodynamic models are analyzed that were proposed for the origin of base-metal filling veins during the cooling of mineralizing fluids (succession of multiwave stepped flow reactors with a step of 10°C from 350 to 100°C, 1 kbar) in the root part of a hydrothermal system at the reaction of barren solutions with the host granite containing clark concentrations of ore-forming elements (370°C, 1 kbar). The thermodynamic simulation was conducted for the H–O–K–Na–Ca–Mg–Al–Si–Fe–C–Cl–S–Zn–Pb–Cu system with 50 minerals of constant composition, four complex (multisite) ideal solid solutions (chlorite, epidote, actinolite, and carbonate), and 78 species of the aqueous solution. The following possible mechanisms of the filling of free space in fractures and the origin of veins are considered: layer-by-layer deposition, reaction replacement, and reaction–layer deposition (recycling of a given number of earlier layers). The first results for reaction–layer models are reported. The reaction–layer models more smoothly describe the increase in the Pb/Zn ratio updip orebodies, which is typical of several deposits, and may explain the simultaneous crystallization of significant amounts of sphalerite and galena. The regularities in the distribution of Zn, Pb, and Cu in cross sections of mineralized base-metal veins at the Sadon deposit are compared with the thermodynamic simulation results.

INTRODUCTION

This paper is aimed at clarifying the genetic mechanisms responsible for the development of filling veins and analyzing in detail the possible structures of the orebodies and their spatiotemporal variations during the mineralizing process. The field studies were conducted at Pb–Zn vein deposits of the Sadon base-metal district in North Ossetia (Kholst, Arkhon, Verkhniy Zgid, and Dzhimi). Our fieldwork at these deposits was conducted with the purpose of determining the conditions and mechanisms of the origin of mineralized veins at these hydrothermal deposits. The methodical approach used thereby combined the geochemical study of the detailed distribution structures of elements in primary halos and veins (with continuous sampling conducted with a step of 2–5 cm) and computer-based thermodynamic simulation of the processes that occurred in the hydrothermal system [1–6]. Our investigation pioneered in developing qualitative physicochemical models for deposits of this type.

The inspection of regularities in the distribution of Zn, Pb, and Cu in the halos around steeply dipping Pb–Zn orebodies and in the veins themselves led us to a series of genetic conclusions [2, 6]. According to one of them, the mobilization area of the ore-forming components and sulfide sulfur was spatially restricted to the junction zone between the regional Sadon–Unal normal fault of the general pan-Caucasian trend and splay shear fractures and ruptures in its northern lying wall, in which mineralized veins developed. The zone was characterized by rock loosening (their more extensive fracturing, shearing, grinding, etc.), which could increase the intensity of the interaction between the

host granites and aqueous solutions of various geneses and lead to the development of mineralized hydrotherms.

Based on this genetic geological concept, we consider dynamical equilibrium models for interaction between discrete elements of the ore-forming hydrothermal system: the mobilization area, the area of transport of components and the development of veins, and the area in which alteration halos were formed.

The possibility of the origin of ore-forming solutions by the mobilization of ore components during interaction between a barren hydrothermal fluid and granite was demonstrated elsewhere [3, 6]. It was established that multistage interaction between chloride–carbonate barren hydrothermal fluids of constant composition and granites (at 310–420°C and 0.4–1 kbar) results in a significant increase in the concentrations of elements in the leaching solutions (from $n \times 10^{-5}$ – $n \times 10^{-6}$ to $n \times 10^{-3}$ – $n \times 10^{-4}$ *m*) without any changes in the external conditions. The concentrations of metals in the leaching solutions significantly varies in the course of the mobilization processes. In most of the models, the succession of leaching of metals is the same: the early solutions are dominated by Zn, which give way to Pb- and Cu-dominant solutions and, finally, to fully barren solutions during the closing stages of the process. The sulfide sulfur concentrations in the leaching solutions are $n \times 10^{-2}$ – $n \times 10^{-3}$ *m*, which is sufficient for the crystallization of sulfides of ore-forming elements when the conditions change.

These results provided the basis for the simulation of processes in an ascending flow of solutions coming from the zone of metal mobilization in the Sadon-type

granites. Our earlier publications [4–6] treated two “marginal” mechanisms that could produce filling veins: a model of layer-by-layer deposition (each solution batch coming to a conduit fracture produces minerals, which do not react with later solution batches, i.e., discrete layers are deposited, and, correspondingly, the vein composition may vary from the very first to later layers) and the model of reaction deposition (when earlier minerals react with any new solution batch, i.e., each solution batch coming from the mobilization zone fully recycles the material of the vein, and, thus, at any given moment of time, a new uniform composition of the vein is formed at its discrete updip cross sections). The specifics of the simulation techniques will be discussed below. Earlier [5, 6], we analyzed the effects of temperature, pressure, and the composition of the incoming solutions and unaltered rocks on the mineralizing processes in the veins and compared our simulation results with geochemical data on natural mineralized veins. It was demonstrated that our models, on the whole, correctly describe the spatiotemporal evolution of the hydrothermal system and regularities in the distribution of elements in the vein bodies, as well as highly accurately reproduce qualitative and quantitative characteristics of natural mineral assemblages. The stages in the mineralizing process are determined by the evolution of a single source of ore-forming components, which are mobilized from granite. Compared to the model of reactional deposition, the model of layer-by-layer deposition was determined to be able to more adequately account for the tendency of the Pb/Zn ratio to increase updip the orebodies and to better explain the regularities in the distributions of elements and the temperatures at which ore minerals started to crystallize. This model found further support in other parameters [5, 6].

However, it appeared to be virtually impossible to reproduce several distinctive features of Pb–Zn vein mineralization within the framework of the layer-by-layer deposition model. These were the simultaneous crystallization of sphalerite and galena, high concentrations of ore components in the near-selvage rocks, and others. Conceivably, these problems can be attacked within the guidelines of some “intermediate” reaction-layer models, but it was impossible to conduct calculations of this type in 1998–1999, until a new version of the HCh program package [7] was developed (our results published in [5, 6] were obtained with the GBFLOW computer program). A new version of the HCh program package enabled us to carry out calculations with multisite ideal solid solutions. Another significant limitation imposed on the possibility to verify the simulation results was the lack of geochemical data on cross sections in natural vein orebodies at different levels updip the bodies. Our specialized fieldwork in 2000 provided the first data of this kind for two veins. All the aforesaid stimulated new investigations into the mechanisms producing the veins.

The principal tasks of this study were formulated as follows:

(1) To develop and analyze models for the reaction-layer mechanisms producing veins with the introduction of solid solutions into the list of possible solid phases.

(2) To compare the simulation results for distinct mechanisms with newly retrieved geochemical data on the regularities in the distributions of ore-forming elements in discrete cross sections of the veins.

SIMULATION CONDITIONS AND METHODS

Our methodological approach was based on the analysis of models for the origin and evolution of a hydrothermal system from the mobilization area of the ore-forming material to the areas of ore deposition and the development of halos considered as a succession of interrelated self-organizing events and phenomena.

The models were developed under the following assumptions:

The temperature at the deposits in question varied over the interval 415–65°C (the quartz–galena–sphalerite ore stage occurred at 345–120°C), and the temperature gradients were in places as high as 20–40°C per 100 m updip the veins [8, 9]. It is therefore logical to assume that a temperature decrease was one of the principal factors controlling ore deposition. In this paper, we consider mobilization processes only at 370°C (this is 25°C higher than the maximum temperature of the productive stage) and vein development at 350–100°C.

The pressure varied over a general range of 2.3–0.1 kbar [9]. A pressure close to the lithostatic pressure at the inferred paleodepth of 2.5–3.0 km seems to have corresponded to 0.8–1 kbar. Earlier, we demonstrated [5, 6] that a pressure decrease from reactor to reactor approximating a vein does not notably affect the mineralizing process. Because of this, it is possible not to further complicate the system and carry out the calculations for a fixed pressure value. The model discussed herein deal with processes at a constant pressure of 1 kbar, which can be regarded as a certain reference value.

Solutions. The gas–liquid inclusions [8, 9] had a predominantly chloride–carbonate composition (with more than 50% chlorides). Different variants of solution compositions were discussed in [3, 5, 6], but here were present only calculations based on the chemistry of the primary barren solution of model IS-2 [3, 6], the reference model of leaching ($H_2CO_3 = 0.5 m$, $NaCl = 1.0 m$, $HCl = 0.1 m$).

Rocks. The compositions of the rocks were assumed to be the average compositions of the supposedly unaltered granites from the Kholst and Verkhonii Zgid deposits [3, 6]. The background concentrations of ore-forming elements in the granites were deter-

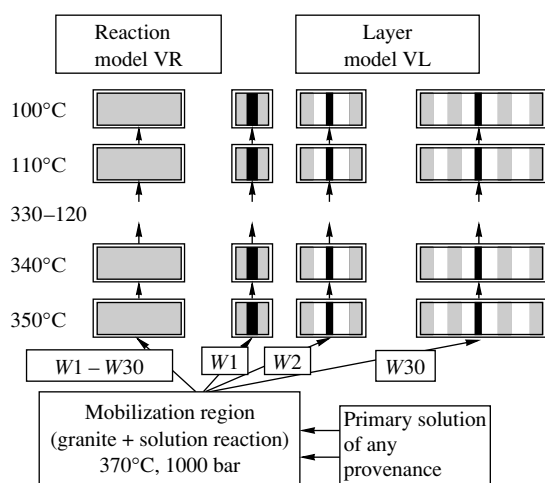


Fig. 1. Simulation scheme and the structures of the layer (VL) and reaction (VR) mechanisms producing filling veins (W are solution waves in the mobilization zone).

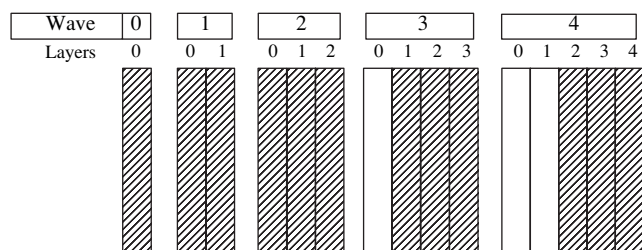


Fig. 2. Simulation scheme of the development of a vein according to the reaction-layer mechanism (RL): an example of two recycled layers. Shaded areas correspond to the layers that occur within the recycling area of this wave.

mined to be as follows: 0.004 wt % Zn, 0.003 wt % Pb, and 0.002 wt % Cu.

The thermodynamic computations were conducted with the use of the HCh program package for the calculation of models of dynamic processes in systems of optional complexity. The package consists of three parts: the MAIN computer program, which organized the computational routine; the GIBBS computer program, whose algorithm makes use of the principle of minimization of the free energy of the system; and the UNITHERM thermodynamic database. The granite-fluid system is described by 15 independent components: H–O–K–Na–Ca–Mg–Al–Si–Fe–C–Cl–S–Zn–Pb–Cu. The model aqueous fluid contains 78 species, including 26 species of Cu, Zn, and Pb. The list of possible solid phases comprises 50 minerals of constant composition (main rock-forming, metasomatic, and ore minerals) and 4 multisite ideal solid solutions (Fe–Mg chlorite, epidote, actinolite, and Ca–Fe–Mg carbonate).

The computational model for a vein comprises 26 successive flow reactors (Fig. 1), the first of which (vein “inlet” from below) has a temperature of 350°C (20°C below the temperature in the mobilization zone,

the zero reactor). The solution comes to this reactor from the zone of metal mobilization. In each reactor, the temperature 10°C is lower than in the previous one. The last reactor (upper termination of the vein) has a temperature of 100°C. Waves (discrete batches) of leaching solution from the mobilization zone successively pass through all reactors, in which thermodynamic equilibrium is achieved (thereby the newly formed minerals remain in the reactor, while the equilibrium solution enters the next reactor “updip the vein”). The calculations were conducted for waves 30–40 of the leaching solution from the mobilization zone. The numbers of discrete solution batches (waves) can be treated as a relative time scale.

For the purposes of analysis, we examined two marginal and a number of intermediate mechanisms responsible for the filling of the free fracture space and the development of veins. The mechanisms (models) were as follows:

The model of *layer-by-layer deposition* (referred to as the **layer model, VL**; Fig. 1).

The *model of reactional deposition (reaction model, VR*; Fig. 1).

Intermediate cases or reaction-layer models (recycling of a given number of already-formed layers in each reactor, **RL**; Fig. 2).

A layer is understood as a certain amount of material (consisting of minerals) that can be produced by a given batch (wave) of the solution over the time period of its residence in this reactor. In considering cross sections of veins at certain depth levels (temperatures) updip, layer 0 corresponds to the very first mineral assemblages deposited at the vein selvages.

Information on the realistic character of these mechanisms is quite extensive. These are the results of our research and data on the mineralogy of filling veins [5, 6, 10, 11, and others].

The possibility of using the HCh program package and introducing solid solutions into the calculations required the recalculation of the results obtained for the mobilization zone and for the layer and reaction models with the aim of comparing the simulation results. The change in the chemistry of the mineralizing solution in the mobilization zone when the calculations were made with regard for solid solutions is demonstrated in Fig. 3 (only data on ore-forming elements and sulfide sulfur are shown). As in our earlier models [3–6], the reference model of mobilization (IS-2) deals with the interaction of 10 kg of granite from the Kholst deposit with 30–40 successive batches (waves) of the primary solution (0.5 m H₂CO₃, 1 m NaCl, 0.1 m HCl, 55.51 m or 1 kg H₂O) at a temperature of 370°C and a pressure of 1 kbar. These data indicate that the differences are insignificant and do not principally modify the earlier conclusions. All of the results reported below refer to the cooling of exactly this mineralizing solution.

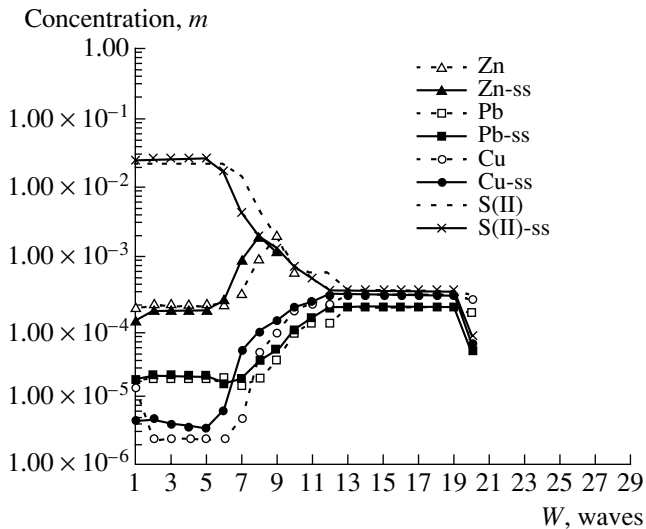


Fig. 3. Comparison of the simulation results at 370°C, 1 kbar for ore-forming components in the solution leaching them in the mobilization region in accordance with the model with phases of constant composition [Zn, Pb, Cu, and S(II)] and with the model involving four multisite solid solutions [Zn-ss, Pb-ss, Cu-ss, and S(II)-ss].

RESULTS OF THERMODYNAMIC SIMULATIONS

The following six simulation series were conducted: the development of a vein in compliance with the layer mechanism (VL); reaction-layer mechanism with the recycling of 1, 2, 5, and 10 layers (denoted as RL-5 layers or RL-5 for simplicity, etc.); and the reaction mechanism (VR). The situation in these model veins after the passage of 30 solution waves is portrayed in Fig. 4. From left to right in each of the four plots, the temperature (“vein coordinate”) decreases updip the vein: 350°C corresponds to the “roots” of the model vein, and 100°C is attained in the upper portion of the vein. The diagrams of Fig. 4 demonstrate only Zn, Pb, and Cu sulfides, which are always accompanied, in natural veins, by quartz (the principal gangue mineral, 40–90%), pyrite or pyrrhotite (0–45%), and minor amounts of Fe–Mg chlorite and muscovite or sericite (~1%). For each temperature (discrete reactor in Fig. 1), the plots of Fig. 4 demonstrate only the overall composition of the vein at certain levels of its depth (updip the vein) but not the relations between minerals in a given vein cross section (from selvages to the central part) at this interval. To analyze these relations, one should reproduce the layered structure of the vein for each temperature, which shall be given below. The exception is the vein reproduced according to the reaction mechanism, because its mineralogical composition is constant at each temperature and moment of time (or “during” a given solution wave) throughout the whole vein cross section.

As the number of reworked layers increases, the character of ore deposition changes from that close to the layer mechanism (when up to 5 layers are recycled) to a near reaction mechanism (when >5 layers are

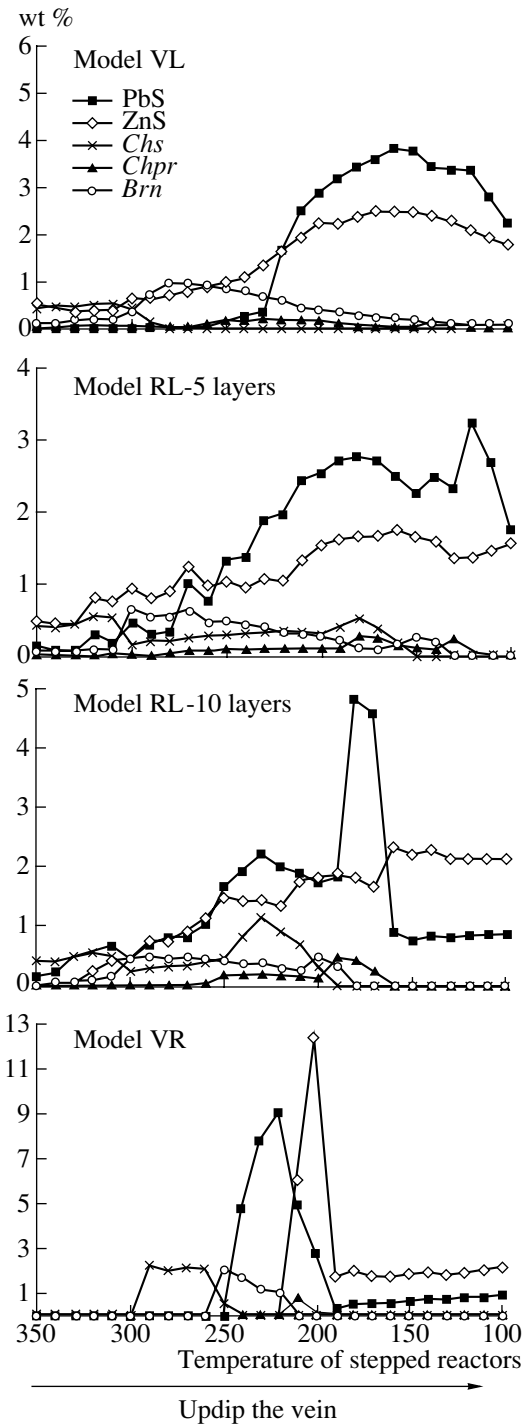


Fig. 4. Structure of a filling vein (generalized data updip the vein, wave 30) that developed according to the reaction-layer mechanism (recycling of 5 and 10 layers) and the reaction mechanism. Only ore minerals are shown. Mineral symbols: PbS = galena, ZnS = sphalerite, Chpr = chalcopyrite, Brn = bornite, Chs = chalcocite.

reworked). Let us consider the principal tendencies in the evolution of the mineralogical composition of the ores with the transition from the layer to the reaction mechanism (Fig. 4).

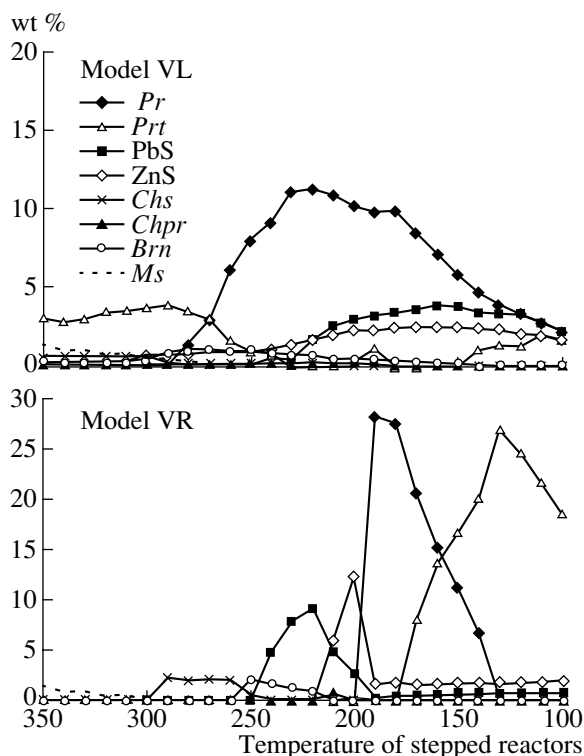


Fig. 5. Structure of a filling vein (generalized data up dip the vein, wave 30), which developed according to the layer and reaction mechanisms. All minerals except quartz are shown. Mineral symbols: *Pr* = pyrite, *Prt* = pyrrhotite, *PbS* = galena, *ZnS* = sphalerite, *Chpr* = chalcopyrite, *Brn* = bornite, *Chs* = chalcocine, *Ms* = muscovite.

(1) The region with the quantitative domination of galena deposition over sphalerite is shifted toward higher temperatures (100–200°C for VL, 100–250°C for RL-5 layers, 150–250°C for RL-10 layers, and 220–240°C for VR with the differentiation between galena and sphalerite maxima).

(2) The region of sphalerite dominance widens at low temperatures (in VL and RL-5 layers, galena dominates at low temperatures; in RL-10, sphalerite dominates from 100 to 150°C; in VR, sphalerite dominates from 100 to 200°C with a 13% maximum at 200°C).

(3) Galena and sphalerite are simultaneously deposited at all temperatures in the range 100–350°C only in reaction–layer models. In the pure layer model, the only ore minerals in veins at high temperatures are sphalerite, minor copper minerals (less than 1%), and pyrrhotite (up to 3%); the veins also contain muscovite (up to 1.5%) (Fig. 5). In a pure reaction model at 300–350°C, the vein consists of quartz with subordinate amounts of muscovite (approximately 1%).

(4) The distribution of sulfides in a vein produced according to the reaction mechanism is rigorously determined by the temperature: chalcocine is deposited at 300–250°C and gives way first to bornite and, at 210–200°C, to chalcopyrite; 240–220°C corresponds

to a maximum of galena (up to 9%), whose concentration does not exceed 1% at lower temperatures; 210–200°C is marked by a maximum of sphalerite (12–13%), whose concentration decreases to 2% at lower temperatures; 190–150°C corresponds to the dominance of pyrite; and 150–100°C is marked by the dominance of pyrrhotite (Figs. 4, 5). An analogous, but much less clearer, differentiation occurs in model RL-10 (galena and chalcocine maxima and other features).

(5) In the models of veins produced in compliance with the near layer mechanism, the bulk of galena and sphalerite deposited at 150–200°C is associated with the precipitation of pyrite (for example, model VL; Fig. 5). With increasing contribution of the reaction mechanism, the fraction of pyrrhotite in the low-temperature region increases (an extreme case of this dominance is demonstrated in Fig. 5 for model VR).

It should be mentioned that the distribution of minerals up dip the vein during earlier stages of the evolution of the vein (with the number of waves <30) can be remarkably different. Earlier [5, 6], we discussed the variations in the mineralogical composition of a vein with the transition from the 1st to 5th, 10th, 15th, and 20th waves, i.e., during discrete evolutionary intervals of the hydrothermal system. As was demonstrated, the early stages (up to wave 20) are marked by the predominance of sphalerite (among the ore minerals), which can be associated with up to 40% pyrite. Here we present only one illustration. Figure 6 shows the inner up dip structures of the model veins (RL-5 layers and RL-10 layers) for the time moment corresponding to the wave 20. As can be seen from comparison with Fig. 4, the galena maximum falls onto higher temperatures, and there are individual sphalerite maxima at lower temperatures and other differences.

The inner structures of the veins in some cross sections up dip the veins can be visualized using the data in Figs. 7a and 7b (only for ore sulfides), which demonstrate the structures of the model veins from the selvage (layer 0) to their central parts (i.e., from layer 0 to layer 30) for temperatures of 150, 200, and 250°C. Obviously, there are the following regularities:

(1) Models similar to layer models (VL and RL-5 layers) are characterized by the absence of high galena and sphalerite concentrations near the selvages (from layer 0 to layers 4–5 and to layers 10–12), and only model RL-10 is characterized by high (up to 10%) sphalerite concentrations, which appear in this region at temperatures of 250°C and higher.

(2) The layer and reaction–layer models are characterized by single deposition maxima of galena and sphalerite, with an increase in the contribution of the reaction mechanism associated with the extension of the field of the simultaneous crystallization of these sulfides at all temperatures (see Fig. 8 for additional information).

(3) The maximum galena deposition is shifted toward the inner parts of the model veins (VL and RL)

relative to the sphalerite maximum, i.e., massive sphalerite deposition occurred earlier than the massive deposition of galena.

(4) The central portions of the veins (models VL and RL) are dominated by quartz, whereas their near-sel-vage parts consist of quartz and pyrite or pyrrhotite with 2–3% sphalerite and up to 1% galena (Fig. 9).

(5) The structure of the vein that developed in accordance with the purely reaction mechanism can be readily visualized based on Figs. 4 and 7b. It is an evenly filled fracture conduit, with mineral assemblages differing only as a function of time (wave) and temperature (updip depth level). For example, the significant dominance of ZnS over PbS may occur at the level of 200°C (Fig. 7b), while galena dominates over other ore minerals at the level of 220°C (Fig. 4).

DISCUSSION OF THE RESULTS AND THEIR COMPARISON WITH NATURAL OBSERVATIONS

Factual materials on the deposits can be subdivided into two groups: (1) those of general character typical of all deposits in the district and (2) specific features of certain veins at their updip sections.

First of all, we compared our simulation results with the **general regularities**.

At the Pb–Zn deposits of the Sadon district, the Pb/Zn ratio varies from <1 in the lower portions of veins to 1–2 and, more rarely, 4–5 at their upper levels [9–12 and others]. This is consistent with the results yielded by model VL (see [5, 6] for details) and model RL with the recycling of only a few layers (Fig. 10). Evidently, in model RL-1 layer, the upper parts of the veins (temperatures of 150–100°C) are characterized by PbS/ZnS ratios as high as 2.5 or more. The model more smoothly describes the increase in the Pb/Zn ratio updip the veins than the purely layer model does, in which this ratio goes no higher than 1.4–1.5. When a greater number of layers is recycled (RL-5), high PbS/ZnS ratios can also be achieved, but the overall increase tendency is complicated by significant fluctuations that violate the smooth character of variations in this parameter. In models close to purely reaction ones (when more than five layers are recycled), no dependence of this kind was observed (Fig. 4 demonstrates that galena dominates in higher temperature parts of the veins).

A similar regularity was identified in the pyrite/pyrrhotite ratio at the deposits of this district. Again, only models close to the layer type can reproduce a correlation of this ratio with depth (compare data on models VL and VR in Fig. 5).

All deposits are characterized by the deposition of the bulk of their sphalerite before the massive crystallization of galena. Relations of exactly this kind are reproduced by the layer and reaction–layer models at all temperatures (Figs. 7a, 7b). However, only the reac-

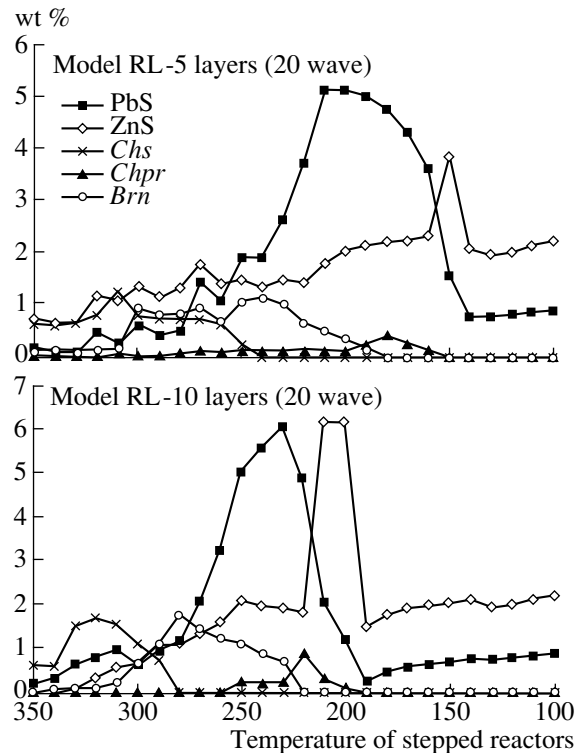


Fig. 6. Structure of a filling vein (generalized data updip the vein, wave 20), which developed according to the reaction–layer mechanism (recycling of 5 and 10 layers). Only ore sulfides are shown. Mineral symbols are the same as in Figs. 4 and 5.

tion–layer models yield intervals with the simultaneous crystallization of both minerals in significant amounts. Their simultaneous crystallization is typical of all veins in the district.

Temperatures highly consistent with the observed values were calculated for models close to the layer type, when the bulk of galena and sphalerite is deposited from 200–250 to 100–150°C (Fig. 4). Galena and sphalerite are unevenly distributed in veins at the deposits, and the concentrations of these minerals vary within very broad ranges, from trace amounts to 19–20% (rarely, even more), but the average values for Pb and Zn in integral samples are usually 3–5%. Exactly these ZnS and PbS concentrations were yielded by our models for the closing stages of the evolution of a vein in the region of the maximum deposition of Zn and Pb (models VL and RL-5, Fig. 4).

The facts listed above suggest that the orebodies were formed mostly with a relatively insignificant role played by redeposition. Of course, the degrees of redeposition or the contribution of the reaction mechanism may have varied from place to place within the fracture conduit owing to fluctuations in the hydrodynamic conditions of the hydrothermal flow or the overprinting of later ore minerals on earlier ones during tectonic reactivation and the recurrent brecciation of the filling

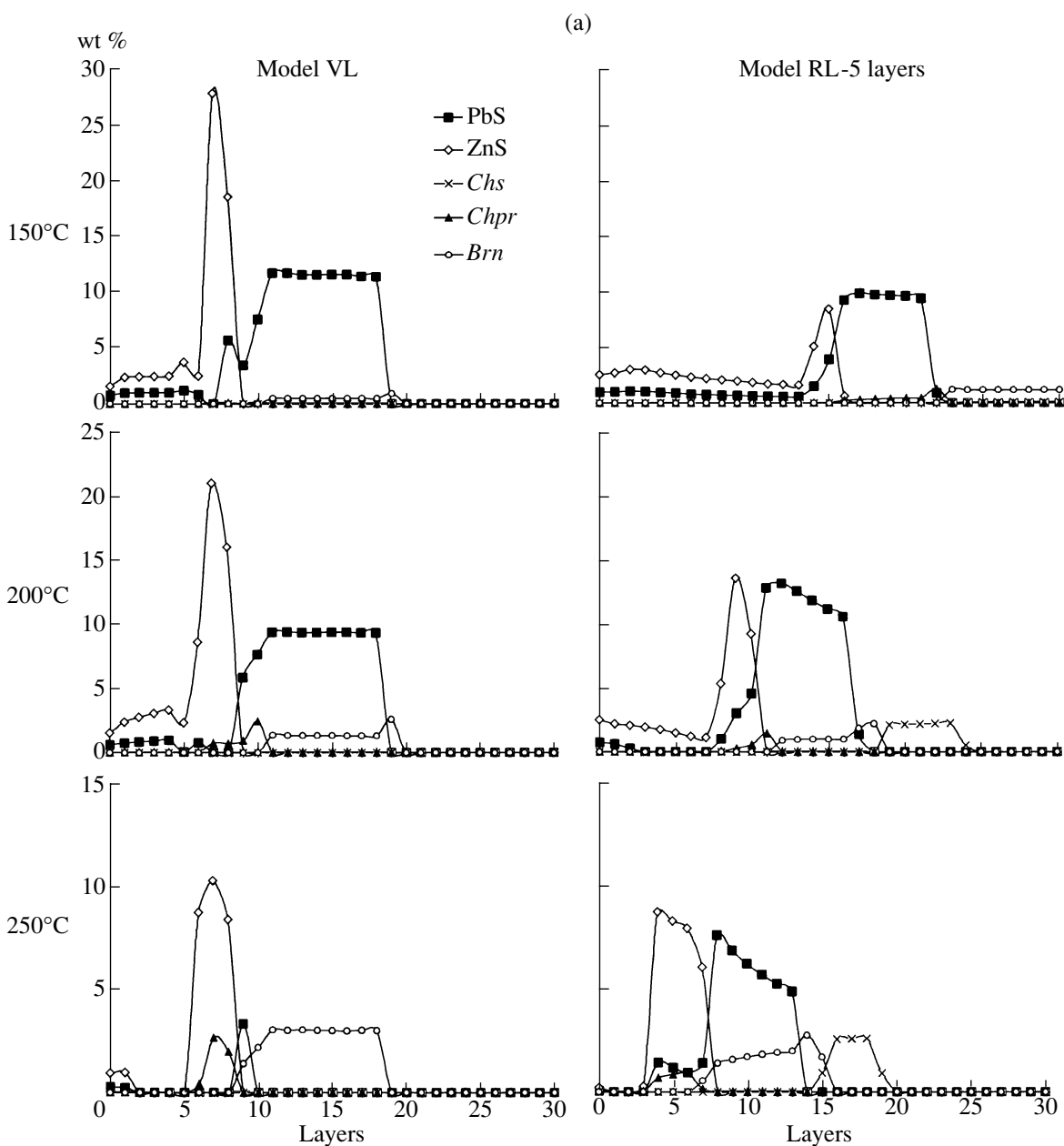


Fig. 7. Structure (cross section) of model filling veins for wave 30 at different updip levels: 150, 200, and 250°C. Only ore sulfides are shown. (a) The reaction and reaction-layer (5 layers) mechanisms. (b) The reaction-layer (10 layers) and reaction mechanisms.

material of the veins. In the latter situation, the role of the mineral-stage metasomatism or the reaction mechanism may have significantly increased.

Let us consider some **examples of local regularities**.

The literature most often contains only qualitative descriptions of the structures of vein bodies at certain depth levels (sketches of veins, general trends in the mineralogy, etc.) but no geochemical data on the regularities in the distribution of elements. We focused on the selection of such data during the 2000 fieldwork

with the aim of testing our modeling results. One of the orebodies of the Bozang ore zone at the Dzhimi deposit (at the level of Adit 3 in the eastern part of the Sadon mining district; it will be referred to as the Bozang vein hereafter) was continuously sampled along two profiles. The thickness of the vein reached 70 cm; the profiles were spaced 1 m apart. We failed to sample one or two rock blocks representing the vein as a whole. Both profiles were run mostly in the form of small samples across the whole vein with 10-cm sampling intervals. We are aware that some of the samples could not be

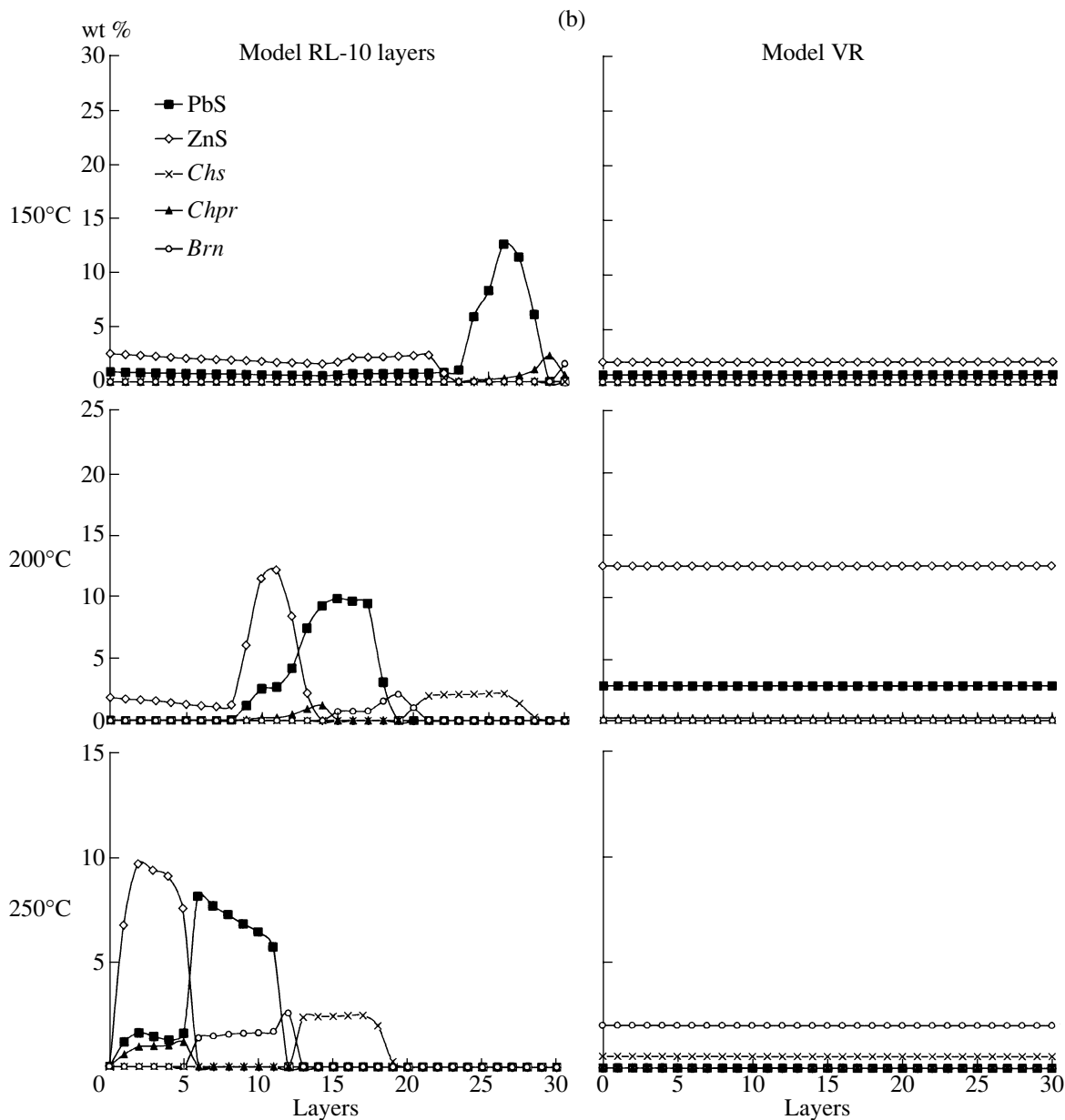


Fig. 7. (Contd.)

fully representative because of the relatively small mass of material in them (100–300 g, whereas representative samples of vein material should be as large as a few kilograms). The samples were analyzed for Zn, Pb, and Cu concentrations by X-ray diffraction techniques at the laboratory of the Department of Geochemistry at Moscow State University (the excitation source was ^{109}Cd). Figure 11 summarizes data on both profiles. As can be seen, ore-forming components in cross section of the Bozang vein are strongly dominated by Zn (10–20%) at much lower concentrations of Pb (1–4%) and Cu (0.3–1%). Similar relations ($\text{Zn} > \text{Pb} > \text{Cu}$) are typical of most of the 14 vein orebodies that were sampled at different levels of four deposits in

the district (up to 60% of the 37 bulk-ore samples) [2, 6] at usually lower Zn concentrations. The plots in Fig. 11 demonstrate the following systematic tendency: the Zn concentrations decrease and those of Pb increase from the selvages of the vein to its central part (interval of 20–30 cm). Indeed, this interval is characterized by the lowest $\text{Zn}/\text{Pb} \approx 4$, while this ratio in the marginal parts is 8–16.

Our calculation models can be employed in explaining the observed distribution patterns and provide a clue to the genetic mechanism that produced the vein. The most satisfactory description of the regularities is provided by the purely reaction model (model VR at 200°C, Fig. 7b), in which the ore components are

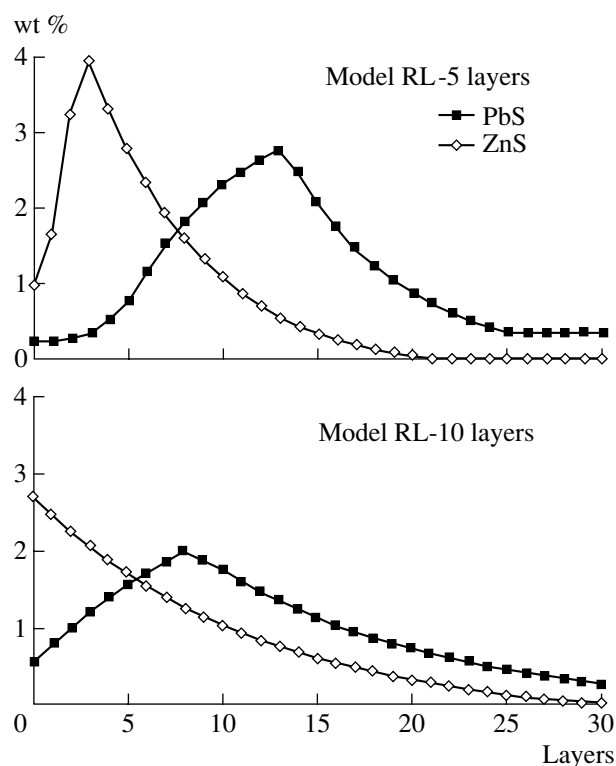


Fig. 8. Generalized galena and sphalerite distribution in discrete cross sections of a vein (at all temperatures) for the RL-5 and RL-10 models.

homogeneously distributed throughout the vein at ~12% ZnS, ~3% PbS, and 0.2% CuFeS_2 . This isothermal model distribution coincides with the distribution observed in a naturally occurring vein in both the ratios of ore-forming components and the relatively high concentration of sphalerite. A quite similar character of distribution (at higher ZnS concentrations) was documented during earlier evolutionary stages of the model vein development according to the reaction mechanism (220°C at wave 20, 210°C at wave 25). These relations did not occur either during earlier evolutionary stages or at higher or lower temperatures. The deposition of such great masses of sphalerite takes place at the front of pyrite reaction dissolution, as is shown in Fig. 5 (model VR). It should be mentioned that the reaction isothermal model cannot explain the tendencies of a decrease in the Zn and an increase in the Pb concentration toward the vein central portion, because only homogeneous reaction filling is permitted (at any moment of time, the proportions of minerals are constant over a given vein section and may vary only with time). These tendencies may, perhaps, be caused by a slight decrease (or an increase) in the temperature toward the vein central part during the reaction-layer mechanism of its development with a significant role played by the reaction mechanism (recycling of >10

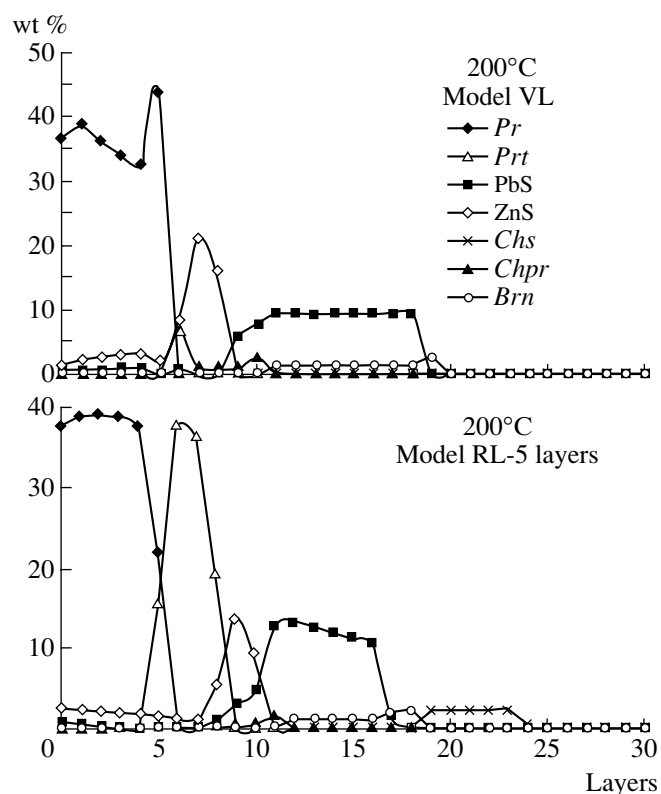


Fig. 9. Structures of model filling veins developing according to the layer and reaction-layer (5 layers) mechanisms; wave 30, 200°C. Data on ore sulfides, pyrite, and pyrrhotite are shown.

layers), but we have not carried out calculations of this kind.

When the reaction-layer filling mechanism acts (low concentrations of ore-forming components near vein selvages that give way first to a strong increase in ZnS and, later, to a drastic increase in PbS; Figs. 7a, 7b), which seems to have been the prevalent mechanism, one should be admitted that the vein developed as a spur branching from a larger vein during a brief period of time within the overall span of the evolution of the hydrothermal system (regions of simultaneous sphalerite and galena crystallization at 200–250°C in Figs. 7a, 7b). However, considering the significant thickness of the vein and the absence of other large bodies nearby, this assumption seems to be hardly probable.

At the same time, this evolutionary scenario and the action of the reaction-layer mechanism fits the Vostochnaya vein quite well (level VI at the Verkhniy Zgid deposit). Data on this vein, whose thickness at the sampling site was 18–19 cm, are presented in Fig. 12. The vein is dominated by quartz and contains significant amounts of chlorite. In contrast to the Bozang vein, this vein is asymmetric. Visually, the zone of sulfide mineralization is spatially restricted only to part of intervals 1 and 2, and the last interval consists of monomin-

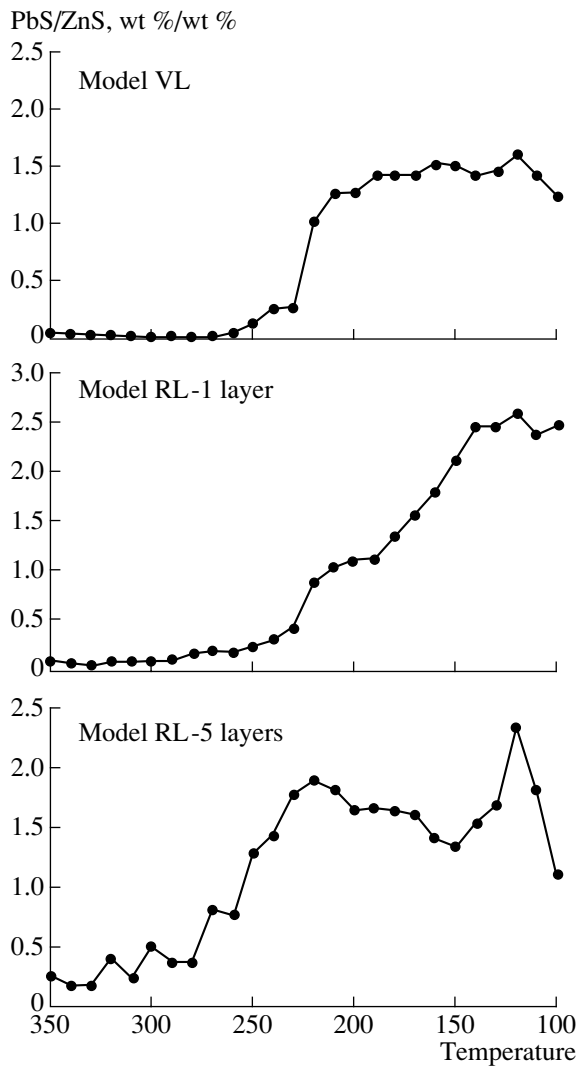


Fig. 10. Variations in the PbS/ZnS ratio up dip the model vein (layer and reaction-layer mechanisms).

eralic quartz. Conceivably, at smaller sampling intervals (as those during sampling five years ago, which was conducted with other purposes), the maxima of Zn and Pb could be differentiated, and an increase in the concentrations of the metals within the maxima could be revealed. The general configuration of the distributions of elements is compatible with the model of the reaction-layer mechanism. The low concentrations of metals in the vein can be accounted for by two distinct causes: (1) some depletion of the source of the ore components in the mobilization zone (for example, due to the origin of the thick Glavnaya vein at the same deposit) and (2) the vein developed as the temperature in the mobilization zone decreased to 300–320°C. We discussed models with a relatively low-temperature source in [5, 6] and demonstrated that the vein (or a vein interval) developing thereby should be characterized by ore-sulfide concentrations no higher than 0.2–0.4%.

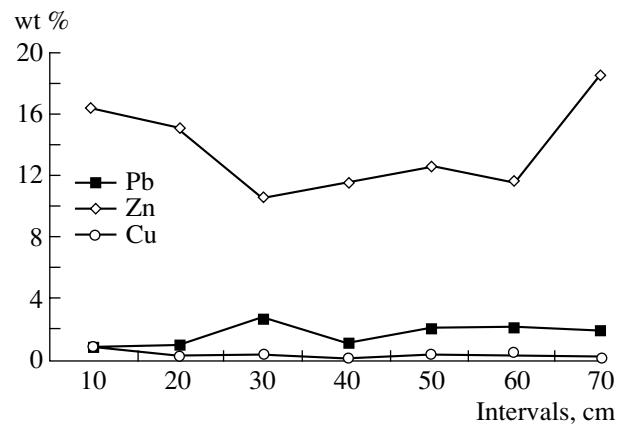


Fig. 11. Distributions of Zn, Pb, and Cu in a cross section of the Bozang vein (generalized data on two profiles, continuous sampling intervals are 10 cm).

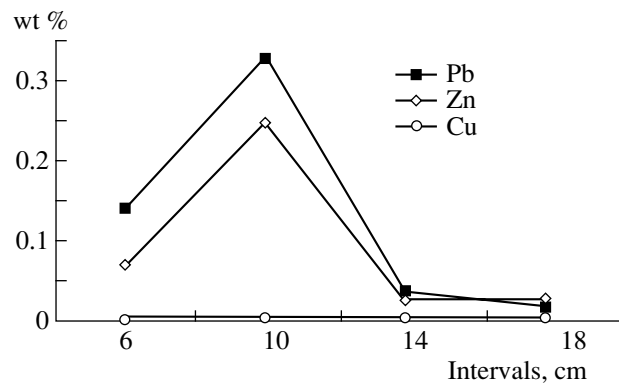


Fig. 12. Distributions of Zn, Pb, and Cu in a cross section of the Vostochnaya vein (continuous sampling intervals are unequal: interval 1 = 6–8 cm, intervals 2–4 = 4 cm on average).

CONCLUSIONS

The models discussed in this paper allow the following principal conclusions to be made:

(1) New techniques were designed for the simulation of processes producing base-metal ore mineralization.

(2) The development of mineralized veins with relatively insignificant redeposition (reaction-layer model) was the main mechanism of the mineralizing process with a subordinate role (but ubiquitous occurrence) played in mineral metasomatism (reaction model).

(3) Our simulation results make it possible to satisfactorily interpret general and local regularities in the distributions of ore-forming elements in natural orebodies.

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REFERENCES

1. Borisov, M.V. and Goreva, Yu.S., Formation Models of the Alteration Halo at Lead–Zinc Ore Veins, *Rudy Metally*, 1994, no. 1, pp. 30–37.
2. Borisov, M.V., Regularities in the Distribution of Elements in Wall Rocks at Vein-hosted Pb–Zn Hydrothermal Deposits, *Geochemistry International*, vol. 35, no. 11, 1997, pp. 985–996.
3. Borisov, M.V. and Shvarov, Yu.V., Mobilization of Ore Components during the Formation of Pb–Zn Hydrothermal Lodes: A Thermodynamic Model, *Geochemistry International*, vol. 36, no. 2, 1998, pp. 134–149.
4. Borisov, M.V. and Kudryavtsev, K.Yu., Thermodynamic Models for Formation of Lead–Zinc Lodes, *Dokl. Akad. Nauk*, 1999, vol. 368, no. 1, pp. 87–90.
5. Borisov, M.V., Thermodynamic Models for Deposition of Pb–Zn Veins, *Geochemistry International*, vol. 38, no. 8, 2000, pp. 750–771.
6. Borisov, M.V., *Geokhimicheskie i termodinamicheskie modeli zhil'nogo gidrotermal'nogo rudoobrazovaniya* (Geochemical and Thermodynamic Models for Formation of Hydrothermal Ore Veins), Moscow: Nauchn. Mir, 2000.
7. Shvarov, Yu.V., Algorithmization of the Numeric Equilibrium Modeling of Dynamic Geochemical Processes, *Geokhimiya*, 1999, no. 6, pp. 646–652.
8. Laz'ko, E.M., Lyakhov, Yu.V., and Piznyur, A.V., *Fiziko-khimicheskie osnovy prognozirovaniya postmagmaticheskogo orudneniya* (Physicochemical Principles for Forecasting Post-Magmatic Ore Mineralization), Moscow: Nedra, 1981.
9. Lyakhov, Yu.V., Pozdeev, K.M., Tibilov, S.M., and Lavrenkov, A.P., A Thermobarogeochemical Model of Ore Zoning and Economic Horizons of the Sadon Lead–Zinc Ore Region, *Rudy Metally*, 1994, no. 2, pp. 45–54.
10. Zlatogruskaya, I.P., The Mineralogy of the Zgid Base-Metal Deposit and Its Comparison with the Sadon Deposit, Northern Caucasus, *Cand. Sci. (Geol.–Mineral.) Dissertation*, Moscow: Moscow State Univ., 1960.
11. Dobrovolskaya, M.G., *Svintsovo-tsinkovoe orudnenie (rudnye formatsii, mineral'nye paragenезisy, osobenosti rudoobrazovaniya)* (Lead–Zinc Ore Mineralization: Ore Types, Mineral Assemblages, and Ore Formation), Moscow: Nauka, 1989.
12. Nekrasov, E.M., *Strukturnye usloviya lokalizatsii zhil'nykh svintsovo-tsinkovykh mestorozhdenii* (Structural Conditions of Localization of Lead–Zinc Lodes), Moscow: Nedra, 1980.