

3.6. *Synthesis and Conclusions*

The models discussed in this chapter led us to make the following conclusions pertaining the genesis of hydrothermal vein deposits as a whole.

(1) Physicochemical simulation techniques were used for the first time to validate the geochemical role of hydrodynamic barriers, which are certain segments of fracture-vein systems where the structure of the hydrothermal flow maintains the most active deposition of gangue and ore minerals. It is established that the barriers are marked by the most intense chemical interaction between mixing fracture and pore solutions, the highest pH and Eh differences, and the main jumps in the concentrations of components in the solution and, correspondingly, the most active deposition of minerals in the free space of fractures. Since hydrodynamic barriers are formed in relation to the heterogeneity of filtration characteristics of the geologic environment, a feature characteristic of all natural objects, the occurrence of such barriers in natural hydrothermal processes is also universal.

(2) The simulation of hydrothermal processes on the basis of the self-mixing mechanism indicates that this mechanism is able to fulfill three essential conditions needed to compose mineral deposits from metals originally disseminated in the country rocks: extraction ore-forming elements from large rock volumes (often from below the mineralized zones), focusing the migration of the extracted metals practically "to a point," and the concentrated deposition of the metals at this point. This process can proceed efficiently under practically isothermal conditions and without any changes in the composition of the barren solution coming from the outside into the hydrothermal system.

(3) The spatially uneven development of syngenetic ore and metasomatic wall-rock mineral assemblages is a natural result of the self-mixing of hydrothermal flows, a process controlled by tectonic structures. Our models indicate that the inflow of solutions of the same composition into an ore deposition region can result in the synchronous formation of different vein mineral assemblages and metasomatic columns of diverse structure and composition in the altered country rocks, as well as in the compositional evolution of hydrothermal solutions within the developing orebody. The weak wall-rock alterations or even the absence of any alterations of the country rocks cannot be regarded as evidence that there was no active mass exchange between the country rocks and solution in the fracture.

(4) Our simulations establish that the infiltration-controlled acid leaching of rocks is coupled with a significant redistribution of ore elements contained in the rocks, with the redistribution aureoles often having complicated structures. The aureoles in the wall rocks can be subdivided into a number of regions with different behaviors of the metals: complete dissolution, redeposition in the form of solid phases (region of above-background concentrations or disseminated ores), and

unperturbed background concentrations in the unaltered country rock. Analysis of U and Pb redistribution in the liparite as a function of diverse factors, such as the composition of the solutions affecting the rock and the background concentrations of metals in the rock, indicates that the ore potential of pore solutions is independent of the redistribution of ore elements in the wall-rock aureole, the presence or absence of redeposition maxima, their magnitude and position relative to the boundaries of the metasomatic rocks, etc., and is controlled only by the composition of the solutions themselves.

(5) The spontaneous evolution of the hydrothermal alterations of the wall rocks and, particularly, filling of the fractures with vein material predetermines inevitable structural transformations of the hydrothermal flow even within a single mineral stage. Our simulations indicate that these purely hydrodynamic phenomena cause the more homogeneous filling of the veins with vein material and the progressive growth of wall-rock alteration aureoles. It was established that metasomatism in the fractures can be brought about not only by the superposition of processes of different stages within the vein but also by intrastage local disturbances in the hydrodynamic conditions under which the veins developed. Continuous spontaneous transformation of the hydrodynamic structure of the hydrothermal flow can cause local inversion in the pH of the solutions and successive metasomatic "stages" without any changes in the composition and alkalinity of the solutions before they came into the deposit.

(6) In hydrothermal flows controlled by fractures and faults, mass exchange between the fracture solutions and wall rocks is mediated by mechanisms of three types: (a) reactions between the fracture solutions and the solid phases of the wall rocks at sites where the solutions spread away from the fracture, (b) reactions caused by the diffusion of components at sites with suppressed filtration-controlled mass exchange between the fracture and pore solutions, and (c) reactions controlled by the mixing of pore and fracture solutions at sites where the hydrothermal flow returns to the fracture. These mass exchange mechanisms repeatedly alternate en route of hydrothermal flows in nature.

CHAPTER 4

ORIGIN OF ORE MINERALIZATION DURING THE MIXING OF THERMAL SOLUTIONS THAT PERCOLATE THROUGH ROCKS OF CONTRASTING CHEMICAL COMPOSITION

In our model for the genesis of ore mineralization at the Chauhi deposit, all analyzed processes related to an ascending solution flow occurred in the same medium: an ore-hosting liparite sequence. However, the model for the Chauhi deposit also explicitly involved another type of rocks: pyritized andesites underlying the ore-hosting unit, with the hydrothermal flow coming into the latter unit from these andesites.

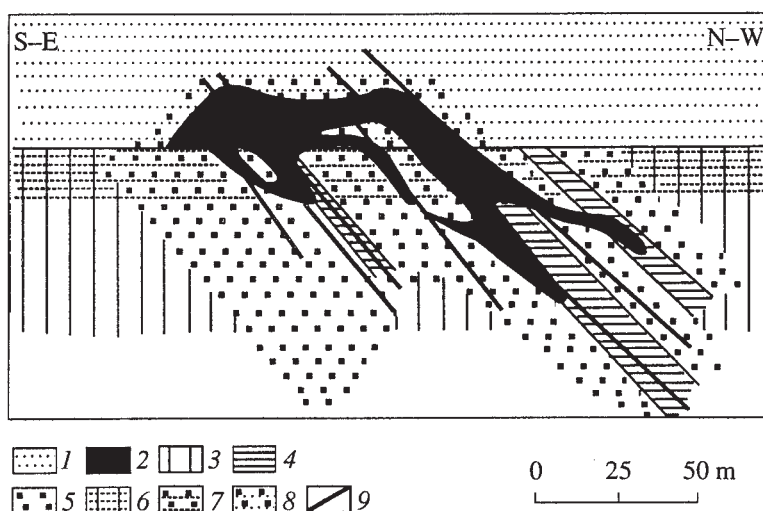


Fig. 31. Cross section of the Dailmann orebody at the Key Lake deposit [Raffensperger and Garven, 1995b]. (1) Athabasca Group rocks; (2) orebody; (3) unaltered basement rocks; (4) graphite-bearing metapelites; (5) altered basement rocks; (6) regolith; (7) altered regolith; (8) altered rocks of the Athabasca Group; (9) faults.

The past two decades witnessed the discovery and the beginning of mining of large and giant uranium deposits (and, simultaneously or shortly after them, gold, nickel-cobalt, and copper deposits) in Archean shields in Australia (Jabiluka, Koongarra, and Ranger) and Canada (Cigar Lake, Key Lake, Midwest, and others). All of these deposits show amazing similarities between their geological settings and structures. They consist of metasomatic bodies of rich (up to 10 wt %) U or complex ores, which developed near the mobile surface of a stratigraphic unconformity between layered Archean and Early Proterozoic high-grade metamorphic rocks of the basement and overlying low-grade Middle Proterozoic sandstones. Bodies with U mineralization are spatially restricted to places where graphite- and pyrite-bearing metapelitic schists of the basement approach the surface of the unconformity (see profile across the Key Lake deposit in Fig. 31). It is also worth noting that the formation of the ore mineralization usually was not coupled with the inflow and deposition of common gangue hydrothermal minerals: the U ores consist of U oxides and variable amounts of secondary aluminosilicates (illite, sericite, chlorite, and others), which were formed by the replacement of pristine rocks near the unconformity.

The genesis of these deposits, which are classed, based on their geologic settings, with the so-called unconformity-type formations (or deposits) was a matter of discussions, with some researchers calling them diagenetic, others believing them to be infiltration, and still others classing them with the hydrothermal group, in spite of the fact that there are no nearby intrusions, whose presence is often considered mandatory for ascribing a deposit to the classic hydrothermal type. Now most researchers are prone to believe that these deposits were produced by a hydrothermal process that

was not directly related to intrusive magmatism and spanned a considerable geologic time (occurred in several repeating pulses).

Some researchers argue that the deposits were formed with the participation of a "mobile reducer," a solution that filtered through the graphite-bearing sulfidized basement rocks [Raffensperger and Garven, 1995a, 1995b]. This follows not only from the usual shifts of the orebodies relative to the exposures of these rocks in the unconformity surface, as is seen in Fig. 31, but also from the relative stability of graphite and sulfides, a fact suggesting that these solid phases themselves did not actively participate in redox reactions. All schemes proposed for the hydrodynamic conditions under which all unconformity-type U deposits were formed take into account the filtration of the mineralizing solutions through both rocks of granitic composition (acid gneisses and arkoses) and graphite-bearing pyritized metapelites (for brevity, they will be referred to as black schists below). The average temperature of ore formation was estimated at 150–160°C (with a scatter from 110 to 200°C), the pressure was lower than 1 kbar [Raffensperger and Garven, 1995a, 1995b].

Hence, a characteristic feature of deposits of this type is the intercalation of compositionally contrasting rocks: acidic and basic gneisses and schists, graphite- and pyrite-bearing schists, etc. Whatever the diverse functions fulfilled by the structural features to which the deposits are spatially restricted, these features definitely mediated interactions between compositionally diverse rocks during the development of the ore mineralization and, hence, also between different geochemical environments and solutions that occurred in them.

Most metamorphic rocks commonly show a strong anisotropy in several of their physical characteristics, such as their permeability. Its values along the schis-

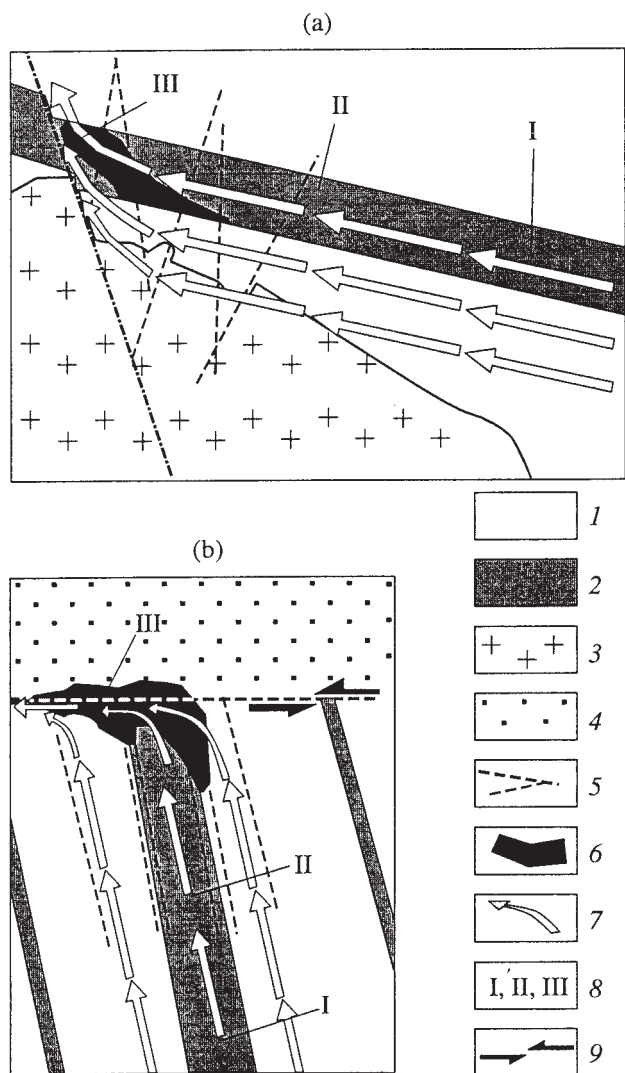


Fig. 32. Principal scheme of the simulated ore formation. (a) Model vein deposit; (b) model unconformity-type deposit. (I) Leucocratic rocks of granitoid composition; (2) metamorphic black schists, often with conformable (formation) tectonic dislocations; (3) granite; (4) overlying rocks, which are separated from the lower rocks by a stratigraphic unconformity surface; (5) regional crosscutting (draining) fault and a system of its splay fractures; (6) ore-bodies developing in the zone of solution mixing; (7) direction of solution filtration; (8) model regions with different types of mass exchange (sequential steps of the modeled process); (9) conformable fault. (I) Region where the initial solution separately reacts with the leucocratic rock and black schists, which tend to equilibria in the solution-rock system; (II) region where unmixing solution flows filter through different rocks and are in relative equilibria with respective rocks; (III) region where solutions coming from the leucocratic rocks mix with the solutions from the black schists and where ore mineralization is precipitated.

osity (layering or banding) could be one to many orders of magnitude higher than in the perpendicular direction. Furthermore, by the time of ore formation, the contacts between compositionally distinct rocks

were often complicated by conformable (formational) shear joints and fractures, whose slickensides and fault gouges were less permeable to solutions filtering from one layer of metamorphic rocks to another. If conditions were created for solution filtration through the metamorphic rocks, it occurred most probably in the form of flows that did not mix and filtered through different layers of metamorphic rocks under the same or similar P - T conditions. In this situation, large structural features transverse relative to the vector of solution movement (unconformities or fault zones with anastomosing fracture arrays) disturbed the "independence" of the solution flows through different rocks and created prerequisites for their interactions.

The geochemical implications of this phenomenon make it possible to model the principal possibility of mass exchange and the deposition of ore mineralization in hydrothermal systems characterized by independent filtration flows through contrasting geochemical media [Barsukov and Borisov, 1992; Borisov and Barsukov, 1992].

4.1. Structure of the Models and Boundary Conditions

Main structure of the model. It is assumed that an initial solution from a source (whose nature is not discussed) filters independently through two layers of metamorphic rocks and interacts with them. One of the layers consists of carbonaceous black schists, and the other is made up of carbon-free leucocratic metamorphic rocks (Fig. 32). Upon reacting with these rocks and attaining equilibrium with them, both solution flows mix in a zone of transverse tectonic structures, react with each other, and, as a consequence, deposit the load of dissolved minerals.

The dimensions of the models, such as the thickness of the layers, length of the paths of solutions through them, the final masses of the reacting solutions and rocks, are not specified. It is implicitly assumed that they are sufficient for attaining equilibrium with the rocks of both layers.

The *temperature and pressure* are 150°C and the saturated water vapor pressure, which are assumed to be constant in the model (analogously to the models in chapter 3). Because of this, the inclination of the general movement vectors of the flows relative to the Earth's surface in the gradientless P - T field is of no concern.

Rock compositions. Metamorphic black schists show broad variations in the chemical and mineralogic composition, for example, different carbon contents. For our models, we selected five black schist samples from Outokumpu, Finland, and the Erzgebirge, Germany. Inasmuch as the organic matter contained in rocks is usually replaced by graphite during their metamorphism [Laverov and Vinokurov, 1988], the concentration of C_{org} in the analyses were assumed to be the concentration of graphite.

Table 32. Chemical composition (wt %) of rocks used in the calculations

Component	BS	GS	CS-1	CS-2	CS-3	L
SiO ₂	61.36	49.14	55.88	90.79	52.93	70.50
Al ₂ O ₃	21.24	13.22	14.08	2.75	16.21	13.75
Fe ₂ O ₃	–	–	0.80	0.48	1.60	3.10
FeO	0.51	1.47	6.25	0.07	9.48	1.07
Fe _(s)	5.05	6.80	0.03	0.28	0.67	–
MgO	3.14	5.62	1.61	1.25	4.55	0.42
CaO	2.04	3.62	3.87	–	2.75	0.58
Na ₂ O	2.95	2.48	0.12	–	3.10	2.10
K ₂ O	2.79	1.89	4.80	0.85	3.11	7.87
S	3.60	5.26	0.03	0.32	0.83	–
CO ₂	–	–	4.62	–	0.09	–
C _{graphite}	3.82	7.26	3.12	1.57	2.61	–
H ₂ O	2.20	3.24	4.19	1.54	2.07	0.16

Note: The concentrations of TiO₂, MnO, P₂O₅, and other minor components were subtracted from the rock analyses together with the equivalent concentrations of CaO in apatite and sphene, and the remainder was renormalized to 100%. Fe_(s) is Fe in sulfides, C_{graphite} is carbon of graphitized organic matter.

The Outokumpu black schists [Peltola, 1960], which host a large copper sulfide deposit, are compositionally quite close to basic igneous rocks (Table 32, BS and GS). These are diopside-bearing pyritized schists consisting of ~20–35% mafic minerals, 20–40% *Fsp*, 25–35% *Qtz*, 8–14% *Ms*, 7–10% *Py*, 3–7% graphite, and <1% *Crb* (carbonate).

The black schists from the Erzgebirge (Table 32, CS-1, CS-2, and CS-3) compositionally approach intermediate and acid rocks. Banded schist CS-1 contains ~17% *Mc*, Fe-*Chl* (*Dph*), and *Ms* each, ~35% *Qtz*, carbonate layers (up to 10% of the rock by mass), trace amounts of *Py*, and ~3% graphite. CS-2 is black quartzite (80% *Qtz*) with ~8% Fe–Mg chlorite, 1.6% graphite, and <1% sum of *Mc*, *Py*, and *Crb*. CS-3 is dominated by *Fsp* (26% *Ab* and 18% *Mc*), 27% Fe–Mg chlorite, ~17% *Tr*, 8% *Qtz*, and minor amounts of *Py* (1.5%), *Crb* (0.2%), and graphite (2.5%).

The leucocratic rocks hosting black schists at natural deposits vary in composition and are generally close to granitoids. Here they are approximated by the composition of liparite (Table 32, L).

The background concentrations of U and Pb are assumed to be the same in the black schists and leucocratic rocks and equal to, respectively, 5×10^{-4} and 2×10^{-3} wt %.

Solution compositions. The anions of naturally occurring hydrothermal solutions are dominated by CO₂ and Cl, because of which our models are based on carbonate-rich solutions W2, W5, W8, and W10 and a chloride-rich solution W13 (Table 33).

Methods of model calculations. In each variant of the model, we analyze processes that occur in two regions of a single hydrothermal system (Fig. 32). In one of them, solution + rock reactions describe phenomena coupled with the filtration of the initial solution separately through the carbonaceous and leucocratic rocks, which separately attain equilibrium with the solution. In the other region, solution + solution reactions reproduce the interaction of the solutions that enter transverse fractures from both the black schist and the leucocratic rock, at different mixing proportions of these solutions in the fractures.

The reactions of both types are imitated by series of local equilibria in the heterogeneous 14 component system K, Na, Ca, Mg, Fe, Al, Si, H, O, C, Cl, S, U, Pb (analogously to the description in Chapter 3).

We constructed more than 30 variants of this model with various combinations of the compositions of the rocks and solutions. Below, we discuss the principal features of processes that are triggered by the filtration of solutions through metamorphic rocks and the mixing of these solutions in a zone of transverse fractures.

4.2. Origin of Solutions with Different Properties

Compositions of pore solution in black schists

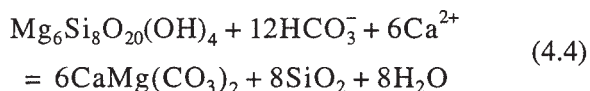
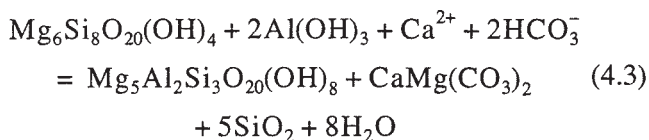
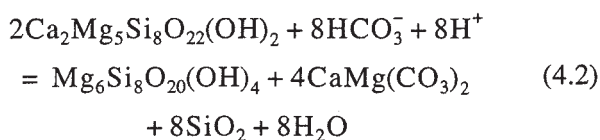
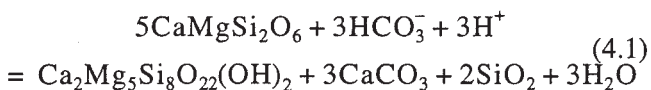
Entering black schist and filtering through it, solutions initially bearing carbon dioxide produce acid leaching columns in which the intensity of rock metasomatic recycling depends on the integral mass of the solutions percolating through a unit volume of the rock over the interaction time (i.e., the integral water/rock

Table 33. Compositions (mol/kg H₂O) of the initial solutions

Component, parameter	W2	W5	W8	W10	W13
H ₂ CO ₃	1.0	1.0	1.0	1.0	0.1
HCl	–	0.001	–	–	–
NaCl	0.1	0.1	0.1	0.1	1.0
KCl	0.01	0.01	0.01	0.01	0.1
CaCl ₂	0.1	0.01	0.01	0.001	0.01
H ₂ S	0.01	–	–	0.01	–
PbCl ₂	–	0.001	(0.001)	–	(0.001)
U	–	0.0001	(5e–5)	–	(1e–6)
O ₂	–	0.001	5e–5	–	–
pH	3.25	3.04	3.28	3.32	3.70
Eh	–0.108	+0.872	+0.809	–0.114	+0.435
Ionic strength	0.2330	0.1110	0.1104	0.0957	0.6453

Note: Shown in parentheses are the U and Pb concentrations introduced into solutions W8 and W13 in one calculation series and excluding one another. U was specified by introducing UO_{2(cr)} and oxide dissolution until the specified U concentration was attained.

ratio). In the outer zones of the column, in schists CS-1 and CS-2 (analogues of acid rocks), the following replacements take place: first, $Fsp \leftarrow Ms + Qtz$, then $Ms \leftarrow Kln$ (at the same level of quartz content). In the rear zone, if the water/rock ratio attains 10000, $Kln + Qtz \leftarrow Dsp$ (Fig. 33a). In black schists of basic or intermediate composition (BS, GS, and CS-3), these reactions proceed along with transformations of the mafic minerals, such as $Di \leftarrow Tr + Cal + Qtz$, $Tr \leftarrow Tlc + Dol + Qtz$, $Tlc \leftarrow Chl + Qtz + Dol$, $Tlc (Chl) \leftarrow Dol + Qtz$ (Fig. 33b), part of which also proceeds with the consumption of the H⁺ ion:



Acid leaching columns developing in black schists under the effect of chloride solution W13 differ from the columns considered above only in that they contain no kaolinite field (or this field dramatically decreases in size, Figs. 33c, 33d).

Pyrite is not stable in the rear zones of all columns in black schists. Fe-chlorite (daphnite) and graphite are transzonal, although graphite starts to partly decompose in the rear diaspore–daphnite zone. Here, the graphite fraction in the insoluble residue even somewhat increases (as is shown in Figs. 33a–33d), but this process is associated with the dissolution of 70% of the reacting rock mass, including graphite (Fig. 33i showing the inner portion of the column of Fig. 33b, but here 100% on the ordinate is not the mass of the newly formed phases but the mass of reacting schist GS).

Interacting with black schists and altering them, the solution filtering through these rocks also changes in composition: it loses part of its CO₂, which is spent on secondary carbonates, leaches some components (which were previously absent from this solution) from the rocks, and changes its pH, Eh, and ionic strength (Fig. 34). These changes continue until relative equilibrium is attained between the changing solution and unchanging rock. The composition of the pore solutions, which are derivatives of initially carbonate solution W10 and initially chloride solution W13 and are in equilibrium with the black schists, are given in Table 34. As can be seen from this data, these are potassic–sodium chloride (or carbonate–chloride) solutions bearing hydrogen sulfide and methane, having pH 6.6–7.6, a

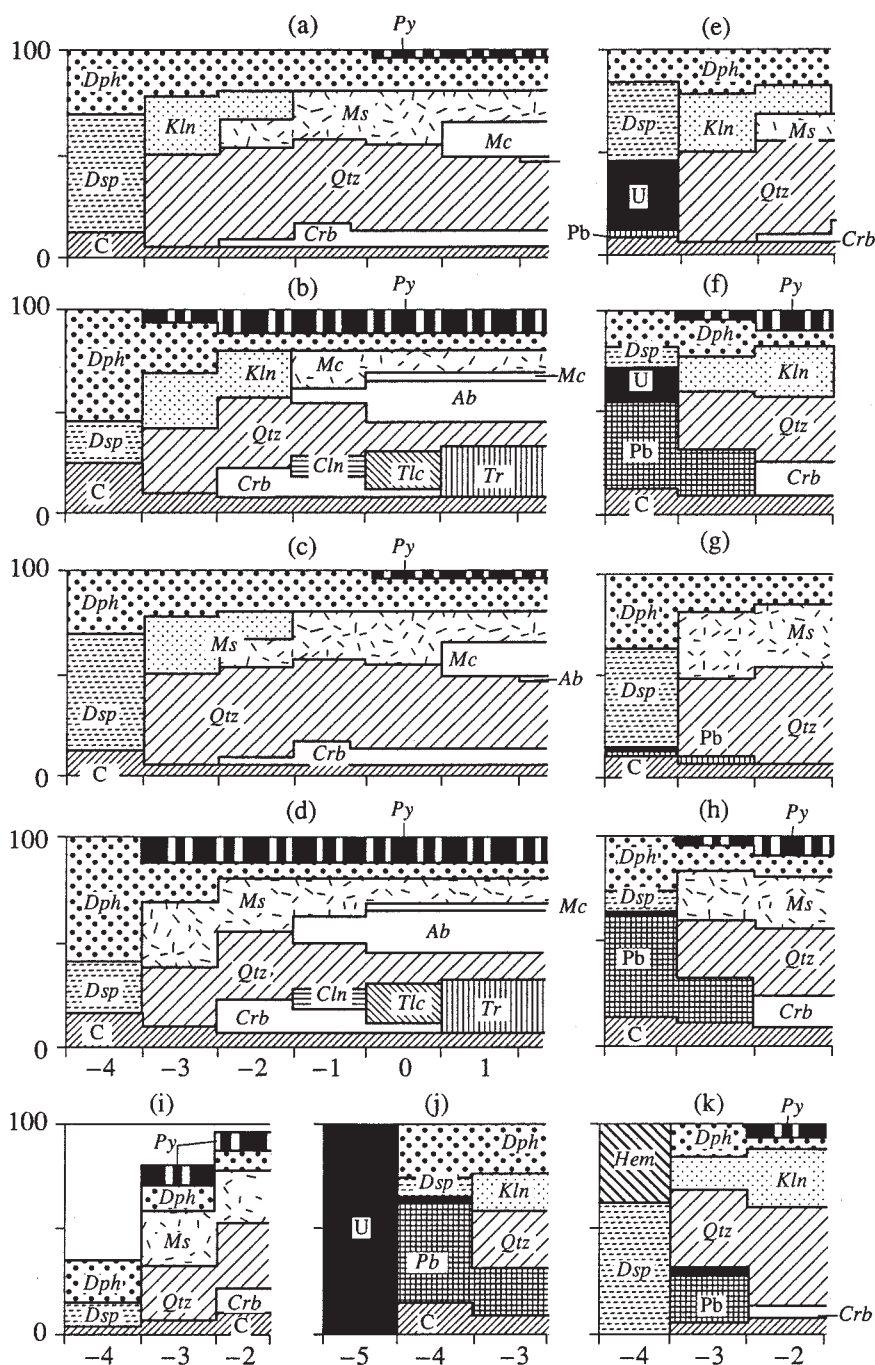


Fig. 33. Infiltration metasomatic columns produced in black schists CS-1 and CS-2 by carbonaceous (W8) and chloride (W13) solutions. Plot on the abscissa are the logarithms of the ratios of the rock mass to the H_2O mass of the solutions; plot on the ordinate are the wt % of the solid phases. Mineral symbols are the same as used above. U—uraninite (pitchblende), Pb—galena, and C—graphite.

low redox potential (from -0.45 to -0.48 V), and an ionic strength from 0.2 to 0.8. Equilibrium concentrations in these solutions are as high as $\sim 4 \times 10^{-5}$ for CH_4 and $(6-11) \times 10^{-7}$ mol/kg H_2O for H_2^0 . Virtually all S (96–99% of its bulk concentration) is contained in them

in the form of S(II), but Fe(II) accounts for as little as one-third of the overall Fe concentration.

The variations in the black schist composition (for Table 34 we specially selected CS-1 and CS-3, which are of acidic and basic composition, respectively) and in the Ca, H_2S , and O_2 concentrations in the initial solu-

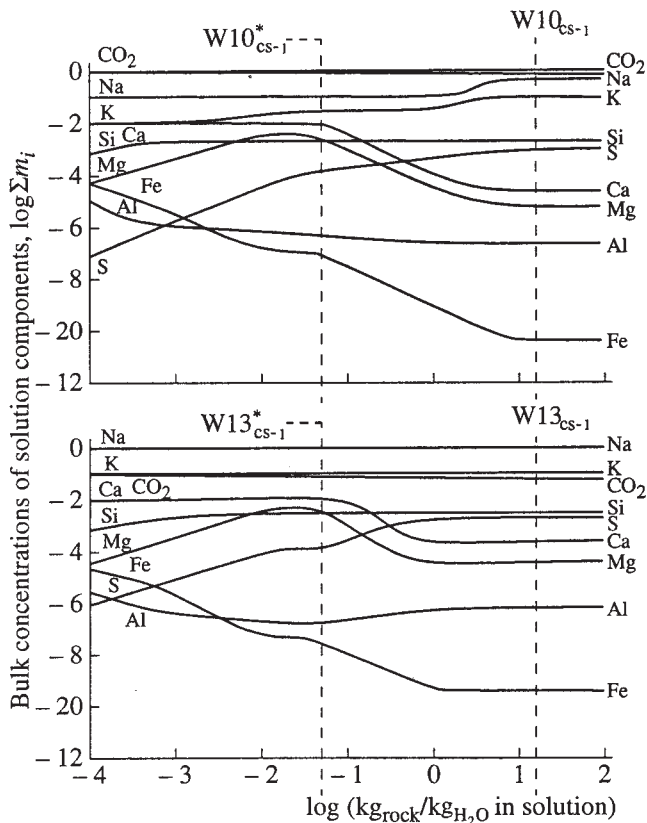


Fig. 34. Systematic variations in the bulk concentrations of components in initially carbonaceous solution W10 (as well as W2, W5, and W8) and initially chloride solution W13 when they form infiltration columns in black schist CS-1. Vertical dashed lines indicate the composition of solutions that are in local equilibria with the quartz–muscovite zone of the metasomatically altered schist ($W10_{CS-1}^*$ and $W13_{CS-1}^*$) and attained equilibrium with the unaltered schist ($W10_{CS-1}$ and $W13_{CS-1}$).

tions only insignificantly affect the composition of the pore solutions in equilibrium with the schists.¹⁰

Solutions can filtrate through black schists not only via rock pores in the “rock-dominated” regime [Fyfe *et al.*, 1981] but also along actively washed conformable dislocations if they are partly open in the “fluid-dominated” regime. In this situation, the solution is relatively isolated from the unaltered rocks by the products of their partial transformations (for, example, the assemblages of the quartz–muscovite zone of the metasomatic column) and cannot attain equilibrium with the black schist as a whole. This solution, filtering along conformable fractures in equilibrium with the quartz–

muscovite zone of schist alterations, has the composition $W10_{CS-1}^*$ and $W13_{CS-1}^*$ (Figs. 34, 35). It is more acidic than the solution in equilibrium with the schist as a whole, is much richer in Ca, Mg, Fe, and CO_2 , and for the most part contains H_2S up to 10^{-3} and CH_4 (10^{-5}).

Uranium and lead contained in black schists in background concentrations cannot be extracted from these rocks by any solutions of those used in our models. Only in the rear diaspore–Fe-chlorite zone of the columns, where pyrite is fully decomposed, is Pb dissolved to be redeposited in the next, quartz–kaolinite or quartz–muscovite zones, but this addition practically does not change the Pb concentration either in this zone or in the schist as a whole. Uranium is not transported even over such a short distance and is stable in the solid phase in all zones of these metasomatically altered rocks. It follows that, under conditions analogous to those in our model, carbon- and pyrite-bearing schists could not serve as a source of metals for hydrothermal solutions regardless of the metal concentrations in the rocks.

Pore solution compositions in the leucocratic carbon-free rocks

Filtering through the leucocratic rocks, the solutions form acid-leaching infiltration columns with different rear zones (quartz, quartz–kaolinite, kaolinite, or even diaspore at a water/rock ratio of >10000) and show systematic changes in their own composition.

The solutions that achieved equilibrium with the leucocratic rock in the model ($W2_L$, $W10_L$, and $W13_L$, see Table 34) have concentrations of several components different from those in the pore solutions of black schists, although these differences are within the same order of magnitude. Major differences are detected between the bulk concentrations and modes of occurrence of elements with variable valences. For example, the Fe concentration in the pore solutions is three orders of magnitude higher than in the solutions in black schists, with all iron contained in the form of ferrous oxide. The sulfur concentration is slightly lower, entirely in the form of sulfate sulfur. The CO_2 concentration is equal to that in the pore solutions in black schists, but these solutions contain no methane. The pH and ionic strength values vary within roughly the same limits as in the solutions of black schists, but the Eh values are higher.

Particularly worth noting is the following: filtering through the leucocratic rocks and extracting their clarke concentrations of U and Pb, the solutions are enriched in these elements and, upon attaining equilibrium with the rocks, contain up to 2×10^{-5} mol U and 8×10^{-5} mol Pb (in pore solution $W10_L$) or up to 10^{-6} mol U and 9×10^{-5} mol Pb (in pore solution $W13_L$). Such concentrations of U are thought to be typical of hydrothermal solutions [Naumov, 1978], including those of presumably magmatic origin [Rybalov and Omel'yanenko,

¹⁰An increase in the O_2 concentration in the solution to 10^{-3} (Table 33, W5) caused the formation of hematite (together with diaspore) in the rear zone of the column (Fig. 33k) but also did not affect the final composition of the pore solution equilibrated with the schists.

Table 34. Compositions (mol/kg H₂O) of pore solutions

Component	W2			W10			W13		
	CS-1	CS-3	L	CS-1	CS-3	L	CS-1	CS-3	L
CO ₂	6.58e-1	8.37e-2	1.12e-1	7.57e-1	1.05e-1	1.39e-1	8.4e-2	6.08e-2	8.14e-2
Cl	0.31	0.31	0.31	0.112	0.112	0.112	1.12	1.12	1.12
K	1.33e-1	5.34e-2	5.75e-2	1.09e-1	3.12e-2	3.57e-2	1.47e-1	1.40e-1	1.45e-1
Na	7.4e-1	3.29e-1	3.53e-1	6.65e-1	1.76e-1	2.04e-1	1.04	1.03	1.04
Ca	3.05e-5	4.3e-5	3.35e-5	1.98e-5	1.3e-5	1.19e-5	3.31e-4	4.19e-4	2.94e-4
Mg	7.05e-6	1.13e-5	1.12e-5	4.28e-6	3.01e-6	3.49e-6	9.83e-5	1.25e-4	1.11e-4
Al	6.93e-7	6.73e-7	9.45e-7	8.4e-7	1.0e-6	1.35e-6	5.9e-7	4.01e-7	4.54e-7
Si	2.52e-3	2.01e-3	2.32e-3	2.54e-3	2.07e-3	2.38e-3	2.46e-3	1.88e-3	2.16e-3
Fe	1.18e-10	2.8e-11	6.6e-8	5.4e-11	1.0e-11	6.73e-8	4.64e-10	5.87e-10	6.38e-8
S	9.69e-4	1.69e-3	3.75e-4	1.14e-3	2.4e-3	3.79e-4	1.39e-3	9.77e-4	-
H ₂	5.86e-7	6.94e-7	3.46e-14	6.43e-7	7.78e-7	1.52e-29	1.91e-6	1.48e-6	1.73e-13
CH ₄	3.29e-5	1.62e-5	-	3.59e-5	2.50e-5	-	3.76e-4	2.94e-4	-
U	n × e-13	n × e-13	7.60e-6	-	-	2.02e-5	n × e-14	n × e-14	1.42e-6
Pb	n × e-11	n × e-12	7.29e-5	-	-	8.49e-5	n × e-10	n × e-11	8.91e-5
Fe(II)	1.02e-10	2.46e-11	4.88e-11	4.81e-11	3.17e-12	3.78e-19	4.54e-10	5.79e-10	2.88e-15
Fe(III)	1.60e-11	3.58e-12	6.00e-8	3.58e-11	7.05e-12	6.73e-8	9.94e-12	7.65e-12	6.36e-8
S(II)	9.36e-4	1.67e-3	n × e-32	1.10e-3	2.40e-3	n × e-32	1.39e-3	9.77e-4	-
S(VI)	3.31e-5	1.63e-5	3.75e-4	4.44e-5	2.19e-5	3.79e-4	6.00e-7	3.12e-7	-
pH	7.00	7.08	7.22	7.10	7.29	7.40	6.92	6.85	6.89
Eh	-0.459	-0.47	-0.173	-0.468	-0.488	-0.188	-0.472	-0.466	-0.296
I	0.456	0.312	0.295	0.370	0.182	0.182	0.655	0.770	0.704

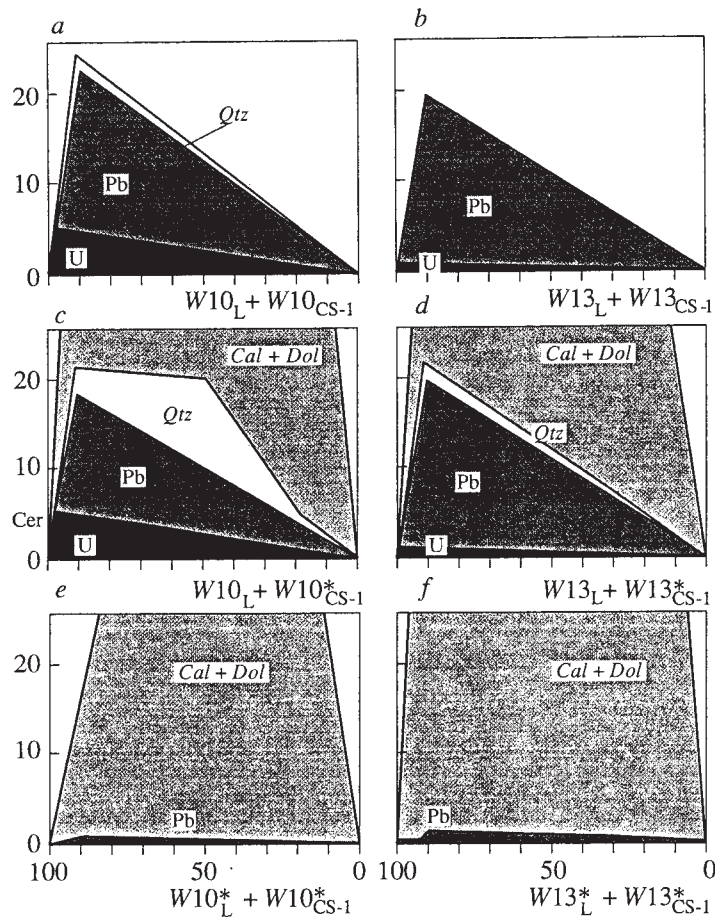


Fig. 35. Assemblages of solid phases formed during the mixing of pore solutions from the leucocratic rock (L) and black schist (CS-1) depending on the proportions of mixing solutions. Plotted on the abscissa is the percentage of pore solution coming from the leucocratic rock, plotted on the ordinate is the normalized yield of solid phases in mg/kg H₂O in the mixing solution; Cer—cerussite (35c).

1989]. The obtained concentrations of Pb are also close to the values determined in hydrothermal solutions [Roedder, 1984]. The predominant U species in the pore solutions from the leucocratic rocks are bi- and tricarbonates of uranyl, while Pb is contained mostly in the form of carbonate complexes (W13_L contains up to 35% of Pb in chloride and hydroxyl complexes).

4.3. Development of Orebodies During the Mixing of Pore Solution Flows in Transverse Fractures

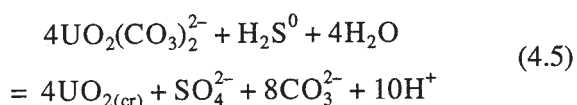
The mixing of pore solution flows that arrive at transverse fractures (tectonic structures cutting across the flow directions) from black schists and leucocratic rocks produces a solution of new composition and a solid phase precipitate, which is formed by reactions between the two mixing solutions.

Because the solutions from metamorphic black schists and leucocratic rocks are in equilibrium with nearly the same assemblages of rock-forming minerals, the mixing solutions also should not show any significant oversaturation in terms of these minerals. Indeed, the

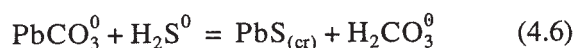
normalized yield of quartz does not exceed 1 mg/ per kg of H₂O in the mixing solution. For other gangue minerals (carbonates, muscovite, chlorite, feldspars) and pyrite, it ranges from 0.0n to 0.00n mg at any mixing proportions.

The situation with U and Pb is different. Two solutions that meet in the space of a draining fracture have majorly different concentrations of these elements. One of the solutions, which comes from the leucocratic rocks is mineralized and contains U and Pb concentrations comparable with those of natural ore-forming hydrothermal solutions. The other solution (from black schists) is barren but contains sulfide sulfur, a component that can precipitate both metals. Reactions between these solutions (without the participation of the solid phases of the rocks) lead to the precipitation of U and Pb in the form of pitchblende (uraninite) and galena. These two minerals comprise the main mass of the precipitate produced during the mixing of the two solutions, for example, such as W10_L + W10_{CS-1} or W13_L + W13_{CS-1} (Figs. 35a and 35b, respectively).

The formation of ore minerals is described by the reactions



and



If the H_2S concentration is higher than the sum of the bulk U and Pb concentrations, both minerals precipitate simultaneously, with the U and Pb concentrations in the mixing solutions drastically decreasing by a few orders of magnitude (with nearly 100% precipitation of both ore elements). However, if the concentration of sulfide sulfur is equal to or lower than $m_{\text{U}}/4$, it is spent solely on the reduction of U by the reaction (4.5) and causes the deposition of pitchblende alone, although, if the system contains no U, the amounts of H_2S and Pb are high enough to exceed the galena solubility product. The point is that reaction (4.5), in which 1 mol of dissolved sulfide sulfur precipitates 4 mol of uranium, is energetically preferable to reaction (4.6).

An example of control calculation for a solution with $m_{\text{U}} = 7.6 \times 10^{-6}$, $m_{\text{Pb}} = 7.3 \times 10^{-5}$, and $m_{\text{S(II)}} = 5 \times 10^{-7}$ indicates that 2×10^{-6} mol of $\text{UO}_{2(\text{cr})}$ is precipitated in this system, and the S(II) concentration in solution equilibrated with pitchblende decreases to $n \times 10^{-31}$. If the constraint imposed on this system is that pitchblende formation is prohibited, the mixing solution precipitates 5×10^{-7} mol of PbS and the solution in equilibrium with galena still contains $n \times 10^{-11}$ mol of S(II). This solution is strongly oversaturated with respect to pitchblende [for reaction (4.5) $\Delta rG = -170.14$ kJ], and if the constraint prohibiting its crystallization is eliminated, $\text{PbS}_{(\text{cr})}$ is dissolved and $\text{UO}_{2(\text{cr})}$ precipitates.

Hence, galena precipitation during the mixing of pore solutions from two rocks can begin only after the H_2S concentration in the mixture becomes higher than that needed to precipitate all dissolved U(VI). This regularity was noted earlier and described above (Chapter 3). In the model it accounts for the fact that the mixing of the pore solution from the leucocratic rocks and the minimum amount of the pore solution from the black schists (for example, solutions W10_{L} and $\text{W10}_{\text{CS-1}}$ in a proportion of 99 : 1) causes the precipitation of almost alone pitchblende (its content in the precipitate is 99.6%, with 0.4% falling onto chlorite), although the Pb concentration remaining in the solution is higher than the U concentration previously contained in this solution (Figs. 35a, 35b).

The maximum normalized yield of pitchblende during the interaction between the solution equilibrated with the leucocratic rock and the solution equilibrated with the black schist is as high as 5.4 mg/kg H_2O of the mixing solution, and the galena yield is 19.2 mg. This

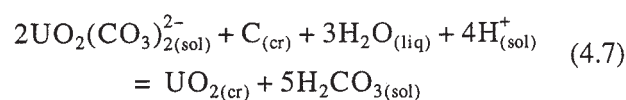
highlights the high ore potential of hydrothermal systems similar to this model.

In the free space of draining fractures, solutions can mix whose filtration regimes were different or varied with time. For example, if the solutions entering a draining fracture from black schists filtered through these rocks in a fluid-dominated regime and were in equilibrium with the quartz–muscovite zone of the hydrothermally altered schists (solutions $\text{W10}_{\text{CS-1}}^*$ or $\text{W13}_{\text{CS-1}}^*$, Fig. 34), the mixing of these solutions with solutions in equilibrium with the leucocratic rock results in the same yields of pitchblende and galena but also in the precipitation of comparable amounts of quartz and much greater masses of carbonates (up to ~1 g/kg H_2O) and, hence, leads to a drastic decrease (by a factor of 4–8) in the content of ore minerals among the newly formed solid phases (Figs. 35c, 35d), i.e., the development of much leaner ores. If the solutions filter through the black schists and the leucocratic rocks only in the planes of actively watered shear fractures, i.e., in a fluid-dominated regime, and these solutions locally attain equilibrium only with the quartz–muscovite alteration zone of both rocks, the mixing of these solutions also gives rise to a polymineralic precipitate, which is commonly dominated by carbonates, contains minor amounts of quartz, muscovite, and chlorite, and smaller amounts of deposited pitchblende and galena (Figs. 35e, 35f) than those in the situations discussed above, because solutions W10_{L}^* and W13_{L}^* , which enter the fracture from the leucocratic rocks, extract small amounts of U and Pb from them.

Another situation is also possible. If the U- and Pb-bearing pore solutions from acidic rocks enter into black schists and react with the mineral matrix of these rocks, pitchblende and galena can also precipitate. This process is particularly efficient if the solution–rock reactions proceed in a fluid-dominated regime.

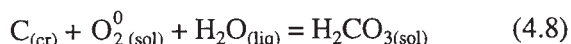
When the initial solutions contained introduced U and Pb, these were almost completely precipitated in the rear zones of the column in the form of pitchblende and galena (Figs. 33e–33h), and the concentrations of these metals decreased in the solutions to nearly zero (10^{-11} to 10^{-13} m).

This takes place because U, which was transported by the solution as uranyl carbonate complexes, was reduced by carbon (graphite) contained in the rocks to $\text{UO}_{2(\text{cr})}$ by the reaction

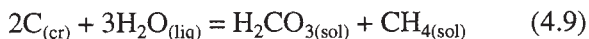


A separate series of calculations for the “titration” of solution W8 by pure C (graphite) indicate that car-

bon is first spent only on the binding of dissolved free oxygen¹¹



As soon as all free oxygen is exhausted (its concentration in the solutions decreases from 10^{-5} to $10^{-35} m$), U is reduced by reactions like (4.5) and only after this, when excess graphite is added, is part of this graphite dissolved to form CH_4 and CO_2 :



It follows that, as U-bearing solutions filtrate through black schists in the fluid-dominated regime, intensely washed surfaces can be marked by the formation of rich (up to monomineralic) U ores if the water/rock ratio ensures the complete dissolution of the schist components (Fig. 33j).

The origin of $PbS_{(cr)}$ is caused by reactions between the lead of the solutions and the sulfide sulfur of pyrite, which is decomposed in the rear zones of acid leaching columns in black schists. The efficiency of Pb precipitation is thus controlled by the amount of S(II) used in the calculation of the rocks, i.e., the total mass of the reacting black schist and its pyrite content. The latter becomes obvious when the rear zones of the columns developing after nearly pyrite-free rock CS-1 (Figs. 33e, 33g), in which galena is disseminated over all three inner zones and part of the Pb is deposited in the form of cerussite (up to 2% in the *Qtz + Ms* zone because of the deficit in sulfide sulfur), are compared with the column after extensively pyritized schist GS (Figs. 33f, 33h), when even small masses of this rock are sufficient to completely precipitate galena in the rear diaspore zone of the columns. Hence, for Pb-rich assemblages to be formed, the Pb-bearing solutions should react, in the fluid-dominated regime, with black schists with high pyrite concentrations.

However, the conditions under which the black-schists components can be completely dissolved seem to be fairly rare and local in nature, if they occur at all, so that significant reserves of rich ores could hardly be formed in such a manner.

4.4. Geochemical Implications of the Model

Our simulations demonstrate that U–Pb hydrothermal ores can be formed by pore solution flows that independently filter through rocks contrastingly differing in composition. In a relatively oxidized environment, a pore solution flow through rocks of the same composition is gradually saturated in metals (U and Pb in this model). In a reduced environment and in rocks

of other composition, another flow becomes simultaneously saturated in components that precipitate U and Pb from solutions. Reactions between such flows in a structurally favorable environment result in the deposition of the ore minerals.

There seem to be no major obstacles that could preclude processes of this type in nature, and, hence, it seems expedient to discuss their main characteristics.

Hydrothermal systems of this type can precipitate only ore (or predominantly ore) minerals in ore-hosting structures and form rich ores, which are not impoverished by the coprecipitation of quartz, fluorite, carbonates, and other gangue minerals. This is caused by the fact that the solutions producing the ore mineralization are in equilibrium with practically all gangue minerals or are equilibrated in terms of nearly all major elements.

There are widely known “monometallic” uranium or predominantly uranium (without gangue minerals) ores at deposits of the unconformity type [Laverov and Vinokurov, 1988; Ypma and Fuzikawa, 1980; Hoeve and Sibbald, 1978; Hoeve and Quirt, 1987; Jones, 1980; Wright, 1979; Powers and Stauffer, 1988; Raffensperger and Garven, 1995a, 1995b; Komminou and Sverjensky, 1996] that could, perhaps, be produced under such relative equilibrium. Of course, if solutions of this kind mix in other structural environments, vein orebodies can also be formed.

Where the pore solutions mix, graphite, pyrite, and Fe-bearing aluminosilicates contained in the rocks do not participate in redox or exchange reactions that result in the precipitation of ore minerals in the zone of transverse fractures, whatever the duration and intensity of these reactions (the extent of which could be tremendous, judging from the ore reserves at large and unique deposits). Instead, these minerals remain stable in the solid phase. This “inertness” of the minerals near the contacts of the orebodies and even within them was often described at uranium deposits in northern Australia and elsewhere [Wright, 1979; Laverov and Vinokurov, 1998].

In the models, as, perhaps, during the development of several unconformity-type deposits in nature, a mobile U reducer (and a mobile Pb precipitator) acts. As follows from the results of our simulations, this is H_2S (or CH_4^0) of pore solutions in the black schists. The mixing of these and metalliferous solutions can occur (owing to a variety of hydrodynamic reasons) outside the contours of carbon-bearing rock layers at a distance from the principal structures that cut across the pathways of pore solution flows, as has been observed in nature [Laverov and Vinokurov, 1988; Ypma and Fuzikawa, 1980; Wright, 1979; Hoeve and Sibbald, 1978; Powers and Stauffer, 1988; Raffensperger and Garven, 1995a, b; Komminou and Sverjensky, 1996].

Hydrothermal systems similar to our model system are able to produce deposits not only of U–Pb ores and not only when the sequence consists of rocks with contrastingly different redox parameters. For example, it was noted that reactions between solutions percolating

¹¹Here we mean equilibrium states of the system and do not discuss the kinetics of reactions between graphite and aqueous solution. Graphite oxidation was reproduced experimentally at higher parameters than in our models [Zeigenbein and Johannes, 1980]. Traces of such reactions in nature are bleaching stripes (halos) in black schists along contacts with hydrothermal veins, including those at low- and medium-temperature U deposits [Sokolova *et al.*, 1972, 1979].

through acid rocks and leaching U and Bi from them and solutions that filtered through basic rocks and extracted Ni, Co, Ag, and Cu from them seem to have played the leading part in the genesis of U–arsenide, U–Cu–Ag, and the so-called five-metal ore types [Malyshev and Savinova, 1979]. In principle, other combinations of ore elements typical of contrastingly different country rocks can also be regarded as indirect evidence that these ores were produced by the interactions between solutions that had filtered through such rocks. Conceivably, these could be the mechanisms that produced many fluorite and scheelite orebodies, which contain significant masses of W and F (elements characteristic of acid rocks), Ca (a component of more basic rocks or those without aluminosilicates), and others.

Changes in the mineral assemblages of ores produced by the hydrothermal systems in question is controlled (at constant T , P , and the initial solution composition) by hydrodynamic factors, such as variations in the proportions of the mixing solutions and their filtration regime through certain rock layers. For example, an increase in the inflow of pore solutions equilibrated with black schists leads, in our models, to a switch from the deposition of pitchblende-rich ore mineralization to the precipitation of galena-dominated ores or, as can be expected in other geologic situations, to an increase in the concentrations of sulfides or arsenides in the precipitate. If the inflow of pore solutions equilibrated with black schists terminates and, instead, solutions that did not completely attain equilibrium with these black schists start to come (for example, in response to the tectonic opening of conformable fractures in the black schists and the enhancement of solution filtration through them), the precipitation of mineral assemblages in the orebodies is changed more sharply, with the deposition of ore minerals alone (development of rich ores) giving way to the predominate precipitation of carbonates, even if the inflow of metalliferous solutions remains unchanged, etc.

The hypothesis of “hydrodynamic regulation of the hydrothermal process” [Pek and Piloyan, 1975] seems to have a more general application, for example, to analysis not only of the temperature regime of the hydrothermal process but also of the causes of the systematic variations in the composition of the mineral load deposited by the solutions.

In hydrothermal systems analogous to the models, the overall time span of ore deposition is not limited by the duration of certain fast geologic processes, such as the emplacement and cooling of magmatic intrusions or volcanic eruptions, and can span significant time intervals if there are replenishable fluid resources and a long-lived regional thermal anomaly. Of course, the gradual cooling of the hydrothermal system can affect some characteristics of the transported and deposited mineral load, but the general principles of the development of ore mineralization discussed above remain valid even if the mass-exchange temperature varies.

Analogously, interludes in the process of ore deposition as a consequence of the clogging of fluid filtration pathways through layers of compositionally contrasting rocks or the discharge structures of the solutions do not modify the essence of the process. The tectonic rejuvenation of solution channels after interludes of any duration reactivates the same “permanent” factors, such as solution filtration through the same compositionally contrasting rock layers, establishment of equilibrium between the solutions and rocks in each of the layers, mixing of pore solutions (which remain the same) in transverse fracture zones, and deposition of the same (or similar) ore mineralization. Phenomena of this type or “telescoping” were documented at several unconformity-type U deposits [Jones, 1980; Powders and Stauffer, 1988].

The recurrent action of the same or closely similar processes can account for “the obvious polychronous character of economic U ore mineralization with systematic multistage U accumulation in ore-controlling structures” [Laverov and Vinokurov, 1988, p. 166], which was, according to these researchers, a necessary prerequisite for the origin of large and unique U deposits in northern Australia and Canada.

4.5. Conclusions

Analysis of the models for ore formation in hydrothermal systems with independent filtration flows of, originally, the same fluids through compositionally contrasting rock layers led us to the following conclusions.

(1) The interaction of the initial solutions with graphite- and pyrite-bearing black schists brings about barren pore reducing solutions containing H_2S and CH_4 , which can be efficient precipitators of ore elements under favorable hydrodynamic conditions.

(2) The mixing of barren reducing pore solutions and metalliferous solutions, which are in equilibrium with the granitoids, in the zones of regional unconformities or transverse fractures and faults, which perturb the independent filtration flows through geochemically distinct rocks, results in the precipitation of the mineral load of the solutions (as is demonstrated in the models by the examples of U and Pb mineralization in vein orebodies and unconformity-type deposits).

(3) Hydrothermal systems of this type can deposit only ore minerals in ore-hosting structures and form rich ores practically devoid of gangue minerals (this is exemplified by the ore mineralization of unconformity-type deposits).

(4) Our models demonstrate the effect of a mobile hydrodynamic barrier on the precipitation of ore elements: the role of this barrier is played by the filtration flow from the black schists. Due to hydrodynamic reasons, solutions can mix outside the contours of the carbonaceous rocks at a distance from the main structures that intersect the pathways of pore solution flows.

(5) The changes in mineral assemblages in the ores are controlled (under constant P - T conditions and solution composition) by hydrodynamic factors. Changes in the filtration regime (increase in one of the flows) results in the precipitation of different mineral associations in the volume of the draining fractures: calcite veins with ore mineralization, mono- and polymineralic ores, or barren gangue material.

(6) Hydrothermal systems of this type can operate over significant time spans if there are replenishable solution resources and a long-lived regional thermal anomaly. Interruptions in the deposition of ore minerals and reactivation of the system in response to tectonic rejuvenation of solution pathways results in the telescoping of ore edifices.

PART 3:

GENESIS OF ORE MINERALIZATION UNDER A TEMPERATURE (PRESSURE) GRADIENT

After simulating ore-forming processes under isothermal conditions, we developed and analyzed a model for the genesis of ore mineralization under a gradient in the temperature field. As illustrative examples, we selected vein base-metal (Pb-Zn) deposits typical of the Sadon mining district in North Ossetia: Kholst, Verkhni Zgid, Arkhon, and Dzhimi.

Base-metal ore deposits in North Ossetia have been studied since the beginning of their active mining in the 20th century. The descriptions of some of these deposits (Sadon and Zgid) became classic and were included in textbooks and fundamental monographs [Smirnov, 1976, 1978]. There are hundreds of volumes of deposited materials containing detailed descriptions of the structures, mineralogy, geochemistry, data on fluid inclusions, and metallogeny of deposits of the Sadon group. Much of this information was published in monographs, reviewing papers, and dissertations and included the structural setting of the deposits [Nekrasov, 1980], the metallogeny of the area and the ore zoning [Geology and Mineral Resources of North Ossetia, 1969; Lyakhov *et al.*, 1994], data on fluid inclusions [Lyakhov *et al.*, 1994; Laz'ko *et al.*, 1981], geochemistry and primary aureoles [Kuikin, 1966; Gorzhevskii *et al.*, 1987; Grigoryan, 1987; Trofimov and Rychkov, 1979, 1988]. The amount of the currently available primary information seems to be sufficient for developing a generalized genetic model of the genesis of these deposits. Synthesis and generalizations of this type were carried out, within the scope of certain geological schemes, by Smirnov [1976]. However, it is now quite obvious that no quantitative collected theory of geochemical processes can be constructed purely intuitively, i.e., based on geologic observations alone, without reference to the laws of physical chemistry. However, no quantitative physicochemical modeling of the genesis of these deposits has been conducted as yet.

Most steeply dipping veins at these deposits are hosted by Middle-Upper Paleozoic granites. The granite massif is localized near the axial part of the Sadon-Unal anticline. The main rock-forming minerals of the granite are quartz (25-45 wt %), plagioclase (25-40%, oligoclase An_{22-26}), orthoclase and microcline (20-25%), and muscovite and biotite (<7%). The massif is dominated by medium-grained granite. The metasomatic alterations of granite near the veins involve its silification, chloritization, serpentization, and carbonatization. Granite outcrops are surrounded by thick zones of tuff, fine-grained tuff-breccia, and, more rarely, andesite-dacitic porphyry lavas and Jurassic sedimentary rocks. The ore mineralization is concentrated more in granites than in porphyritic lavas [Nekrasov, 1980]. At the deposit, a significant role is played by the Sadon-Unal fault of pan-Caucasian trend, which truncates the granite in the south. The orebodies fill shear and detachment fractures trending NE and NW and branching from the footwall of the fault. Large east-west-trending faults could serve as ore conduits [Nekrasov, 1980].

According to the data of most researchers, the deposit is of pre-Callovia age, which corresponds to the postkinematic stage of the Cimmerian metallogenic epoch [Khetagurov *et al.*, 1992]. All veins are nearly vertical and vary from 0.1 to 5.0 m or more in thickness. Mining work has exposed veins over length intervals of more than 1100 m downdip (Verkhni Zgid) and more than 4000 m along strike (Sadon). The ores consist of galena, sphalerite, pyrite, chalcopyrite, and pyrrhotite with gangue quartz, chlorite, carbonates, and others. Available geological-mineralogical data and results obtained by studying fluid inclusions [Laz'ko *et al.*, 1981; Lyakhov *et al.*, 1994] indicate that the processes that formed ore mineralization at these deposits were quite uniform and proceeded under similar physicochemical parameters: the overall temperature range was 415-65°C (345-120°C for the quartz-galena-sphalerite mineral stage) at pressures of 230-11 MPa. Numerous analyses of gas-liquid inclusions [Lyakhov *et al.*, 1978, 1994] point to their chloride-dominated composition (>50% chlorides). Schematic geological profiles across the Kholst, Arkhon, and Verkhni Zgid deposits are shown in Fig. 36.

The primary aureoles of the deposits were examined by several researchers [Kuikin, 1966; Gorzhevskii *et al.*, 1987], who pointed out that the thicknesses of near-vein aureoles only occasionally exceed a few dozen meters. However, the lack of detailed data on the aureoles forced us to conduct additional geochemical examinations in order to identify regularities in the distribution of elements in the nearest space around the veins, where it is reasonable to expect that the effect of chemical interaction between the host granite and hydrothermal fluid should have been at a maximum.