

## INTRODUCTION

The reconstruction of the conditions and mechanisms controlling the genesis of hydrothermal ore mineralization and the physicochemical processes that took part in the development of hydrothermal deposits is a fundamental geochemical problem. Advances in thermodynamic simulation demonstrate that the application of this approach is very efficient in studying the processes of the origin and evolution of ancient ore-forming hydrothermal systems from the areas where the mineralized solutions formed to those of ore deposition and the development of aureoles.

The ore-forming hydrothermal process inevitably involves two main reagents: a hydrothermal fluid and rocks that host the developing mineral deposit, with the results of their interaction discernible at any hydrothermal deposit. A rock–water interaction is most often regarded as a process associated with ore formation but not resulting in the origin of the ores and controlling their genesis. Reproducing the genetic conditions at certain deposits and elucidating the role of water–rock interactions during the origin of hydrothermal orebodies determines the importance and topical character of this research.

The aim of this work was to reconstruct the mechanisms and processes of the origin and evolution of orebodies and related distribution aureoles of metals at low- and medium-temperature hydrothermal vein deposits based on the application and further development of techniques employed in geochemical studies and thermodynamic simulation.

The research was centered on the following principal problems:

(1) To develop techniques for estimating the composition of hydrothermal solutions.

(2) To examine the role of the host rocks in the genesis of the ore mineralization.

(3) To work out techniques for the equilibrium–dynamic simulation of hydrothermal ore-forming systems at vein deposits with regard for dynamical elements and the evolution of mass transfer and exchange processes.

(4) To develop a generalized model for the genesis of vein uranium and base-metal deposits with an analysis of processes and mechanisms in the hydrothermal system from the mobilization regions of the ore components by solutions to the regions of ore deposition and the development of aureoles.

The materials and generalizations presented in this publication make it possible to highlight the following groups of newly obtained principal results:

(1) This research is among the first to lay the foundation for the further development of a new avenue research in geochemistry, namely, the computer physicochemical simulation of hydrothermal ore-forming processes. The monograph presents the first equilibrium–dynamic models for low- and medium-temperature hydrothermal systems.

(2) A complex of methods and approaches is developed for estimating the composition of hydrothermal solutions on the basis of numerical physicochemical simulation. By studying the ore-forming role of the rocks hosting the deposit, new data are obtained on the systematic variations in the composition of the hydrothermal solution with time.

(3) The role of hydrodynamic barriers is first demonstrated by means of physicochemical simulation. These barriers are local portions of fracture–vein systems where the structure of the hydrothermal flow ensures the maximum intensity of solution–solution interactions, resulting in the deposition of ore and gangue minerals.

(4) The first application of studying the fine structure of the distribution aureoles of ore elements in the country rocks around veins is described with reference to hydrothermal vein base-metal deposits, and the possibility is demonstrated for the utilization of such data as the basis of genetic models for ore formation and the development of aureoles.

(5) Based on simulation data, the evolution of the hydrothermal ore-forming system at vein base-metal deposits is first analyzed.

(6) The first generalized models are developed for ore-forming hydrothermal systems at vein base-metal and uranium deposits. The models involve the mobilization regions of ore components and the areas where ore is deposited and aureoles develop. The simulation results are demonstrated to be in agreement with natural analogues.

Most of the models discussed below were developed for Pb–Zn vein base-metal and U deposits.

The author studied Pb–Zn deposits of the base-metal ore type (Kholst, Verkhniy Zgid, Arkhon, and Dzhami in North Ossetia) during ten field seasons (1991–1995 and 1997–2001) and headed a field team of students and postgraduates at the Department of Geochemistry, Moscow State University. This research is based on the materials of 37 detailed profiles (at different topographic levels) across the host rocks of 14 veins at 4 deposits. The primary materials include more than 1900 samples (host and vein rocks), 300 hand specimens, and approximately 700 petrographic thin and polished sections.

The author did not study mineral deposits of the U–Mo type (Chauli and the like) in field, but his fruitful long-term cooperation with Vikt.L. Barsukov enabled him to examine a vast volume of primary geological and geochemical information gathered at these deposits and to use this information in the thermodynamic simulations.

The first part of the monograph (Chapters 1 and 2) are devoted to general problems of the methodology, thermodynamic basis of the models, techniques applied to the estimation of solution compositions, etc.

The second part contains descriptions of models for the origin of mineral deposits under isothermal or

nearly isothermal conditions (vein U deposits and unconformity deposits).

The third part deals with models of ore formation under temperature and pressure gradients, as is typical of medium-temperature (Pb–Zn) deposits.

The formulated problems were resolved using two main approaches: *geochemical* and *thermodynamic*.

The *geochemical approach* involved studying the regularities in the distribution of elements in the veins themselves and the neighboring country rocks based on information on the detailed inner structure of the orebodies and primary aureoles. Geochemical data were formed the basis of the geological model of the process and were utilized for verifying the thermodynamic simulation results.

The *thermodynamic computer simulation* was aimed at developing equilibrium–dynamic models for the genesis of orebodies and primary distribution aureoles of metals in wall rocks. The new methodological aspect of this approach was the analysis of models for the origin and evolution of a hydrothermal system from the region where the ore components are mobilized to where the ore mineralization is deposited and aureoles develop as interrelated self-regulating phenomena. Hundreds of thousands of individual calculations were conducted.

PART 1:  
GENERAL SIMULATION PROBLEMS  
AND ESTIMATING THE COMPOSITION  
OF HYDROTHERMAL SOLUTIONS

CHAPTER 1  
INTRODUCTION TO THE PROBLEM

Now a vast and ever increasing volume of physicochemical information has accumulated about various aspects of hydrothermal ore formation, possible sources of water and ore material, the composition of solutions at different temperatures and their different metallogeny, speciation of ore and nonore components in the solution, possible chemical reactions in ore deposition zones, the mineralogy of orebodies and its spatiotemporal evolution, composition of the host rocks and their alterations in the course of the ore-forming process, physical properties of these rocks (permeability, thermal conductivity, etc.), temperatures and pressures of ore formation, vertical and lateral gradients of these parameters, and other factors and phenomena. Each of these aspects providing for the understanding of the ore-forming process was elucidated by specialists dealing with certain characteristics of the processes, because data of this kind can be obtained only by highly qualified researchers after lengthy specialized training, with the use of precision equipment. Nowadays research is focused not as much as on obtaining new information, although, of course, it is also needed, as on the synthesis of all or at least most of these lines of evidence. It is quite clear that only by tak-

ing into account all available information is it possible to develop a scientifically justified description of ore-forming processes at natural deposits or a single mineral occurrence. Obviously, this task could not be accomplished until a new approach to geologic problems had been worked out: the computer simulation of physicochemical equilibria in complex multicomponent heterogeneous systems. Since our research was launched as early as 1978–1979, it was among the first to apply this approach to studying the genesis of mineral deposits of different types.

*Scope of Geochemical Problems Attacked  
in This Research*

The main task of this work is to reconstruct the mechanisms and processes giving rise to and maintaining the evolution of orebodies and associated aureoles at hydrothermal vein deposits on the basis of newly developed methods of geochemical investigation and thermodynamic simulation.

This analysis is focused on the following geochemical problems:

- \* The role of water–rock interactions in the hydrothermal process, when the composition of hydrothermal solutions is formed; in the ore-generating potential of the host rocks (we do not discuss the genesis of the water and the main anionic components of solutions: chlorine and carbon dioxide); and in the origin of orebodies and wall-rock aureoles.

- \* The occurrence of geochemical barriers, when mineral deposits are generated under nearly isothermal conditions.

- \* The behavior of elements during different evolutionary stages of vein hydrothermal deposits.

These problems were solved with the purpose of developing generalized models for the genesis of vein uranium and base-metal mineralization and the analysis of the interdependent processes and mechanisms taking place in the system from its mobilization regions of ore-forming components to the areas of ore deposition and the development of aureoles. The solution of this problem required the development of a method for the equilibrium–dynamic simulation of ore-forming systems on the basis of local and partial equilibria and dynamic elements in the form of hydrodynamic models and descriptions of evolving mass transfer and mass exchange.

The field research was carried out mostly at hydrothermal deposits about which the author had geochemical information and certain experience in fieldwork.

The models of ore generation are discussed below in order of progressively more complicated physicochemical conditions in the ore-forming systems:

- \* a model for uranium mineralization in a host medium with unequal filtration properties and homogeneous chemical composition under constant  $P$ – $T$  conditions (as exemplified by the Chauli deposit);

\* a model for uranium mineralization in areas with rocks of chemically contrasting composition under constant  $P$ - $T$  conditions (unconformity deposits);

\* a model for vein base-metal mineralization under thermo- and barogradient conditions (deposits in the Sadon mining district).

#### *Water–Rock Interaction in the Hydrothermal Ore-Generating Process*

This research is underlain by the following three self-evident postulates:

(1) A hydrothermal solution continuously occurring in contact with crustal rocks cannot have an arbitrary composition but, conversely, the latter is controlled by water–rock interactions (equilibria).

(2) In conformity with hydrodynamic laws, the hydrothermal solution occurs in continuous motion, which is the main hydrodynamic prerequisite for the hydrothermal process and which affects physicochemical equilibria in the water–rock system.

(3) A distinctive feature of the hydrothermal process is the fact that it enables the mobilization, transportation, and concentration of elements disseminated in the Earth's crust, including ore-forming elements. The behavior of the latter throughout the whole evolutionary course of hydrothermal systems is controlled by water–rock interactions in their various manifestations.

The genetic problems of hydrothermal mineralization cannot be solved without exhaustive analysis of water–rock interactions. The ore-forming hydrothermal process inevitably proceeds with the participation of two main groups of reactants: a hydrothermal fluid and rocks hosting the developing mineral deposit. The result of their interaction can be discerned at any hydrothermal deposit or body in the form of metasomatized wall rocks, zones of leaching and introduction of components, zones of hydrothermal alterations, etc. The problem of water–rock interaction during the hydrothermal ore-forming process is usually discussed in its two principal aspects: (1) the possible source of the ore material and (2) the cause of its deposition. The analysis and generalization of data pertaining to the former problem (the source of ore-forming components) indicates that any rock can serve as a source of geochemically rare metals if the hydrothermal solution is able to extract them during its interaction with the rock [*Geochemistry of Hydrothermal...*, 1979]. When the causes of ore deposition are analyzed, reactions between the hydrothermal solution and rocks through which it filters are usually thought to be of particular importance.

It follows that rock–water (solution) interactions are among the most important factors controlling the hydrothermal process, including that resulting in ore mineralization. However, in spite of the importance of these processes, there are still practically no publications in which interactions of this kind are considered

not separately for discrete parts of the newly-formed and evolving geothermal system but in interrelations of all of its parts. This is quite understandable, because such an analysis cannot be accomplished based on geological data alone (given the “different scales” of information on different parts of the hydrothermal system).<sup>1</sup> Because of this, research usually ends with the proposition of a probabilistic geological scheme. Some parts of this scheme (commonly this is only the region of commercial ore mineralization) are covered with extensive factual information, while others are either not described at all or data on them are indirect and, instead, are “predicted” or “extrapolated” (usually this pertains to the region of the mobilization and transport of ore-forming components). Analogously, it is impossible to describe the whole hydrothermal system by experimentally obtained data, alone because the researcher is left only with the possibility of speculating about “links” between different experiments (which were most often static and conducted at different laboratories). At the same time, the number of papers on the experimental study of the interaction of rocks with water is vast [Zaraiskii, 1989; Rafal'skiy, 1993; and several others].

The researcher is faced with even more problems, he tries to take into account some dynamic characteristics of the hydrothermal process or describe the evolutionary dynamics of the whole ore-forming system. “In essence, these problems are underlain by the fact that ore-forming systems evolve irreversibly in space and time, and the original structure of the geologic environment is thereby complicated: the chemical composition of certain portions of rock sequences appears to be modified, as are the physical properties of these rocks, while certain chemical elements become enriched in some parts of the system and depleted or disseminated in others.” [Sharapov, 1992].

Thermodynamic or, at the present state of the art, equilibrium–dynamic simulation makes it possible to obviate these difficulties, because relations between discrete parts of a hydrothermal system can be immediately incorporated into the model. The structure of an equilibrium–dynamic model for a hydrothermal system involves a region in which ore-forming and other components are mobilized (this can be a simple or a composite source), a region in which the components are transported, and that in which ore mineralization is produced (if necessary, the system can also include a region where the components are disseminated). All of these model regions are interconnected by a mobile hydrothermal flow, whose characteristics can vary with time in response to interaction with the environment or changes in the external conditions (such as temperature

<sup>1</sup> “Parts of endogenic deposits that are the most interesting from the standpoint of the genesis of these deposits commonly appear to have been studied the least thoroughly, if at all, so that available materials on them are the scarcest” [Sharapov, 1992].

and pressure). Models of this type are discussed in this publication.

The terms used in this chapter and below can, in principle, be interpreted in somewhat different ways; because of this it is pertinent to clarify their meaning as understood here.

An "ore-forming system is a physical system that includes the sources of the material, its migration pathways, and sites of localization" [*Geological Dictionary*, 1973]. As was pointed out by V.N. Sharapov, neither this nor other definitions "specify the region in which the system exists, neither do they elucidate the causes of the ore deposition in the system; i.e., although the organization elements of the system are listed, its specific features remain obscure" [Sharapov, 1992]. Because of this, V.N. Sharapov proposed another, physicochemically more accurate, definition of an ore-forming system as "a lithospheric volume where hot fluids are generated, brought to the Earth's surface, and disseminated and where energy dissipation coupled with mass transfer within a certain subvolume brings about anomalous concentrations of mineral resources" [Sharapov, 1992]. Here the concept of an endogenous hydrothermal system (or simply a hydrothermal system) is used in a similar sense.

In various sections of this publication, the concepts of fluid- and rock-dominated regimes are used, which were first introduced by Fyfe *et al.* [1978]. When the solution/rock ratio is high, the rock is extensively recycled metasomatically, while the solution composition changes only insignificantly. This regime can be referred to as fluid-dominated. Conversely, if the masses of the solid phases are much greater than the solution mass, the rock composition remains virtually unchanging and the solution composition is significantly modified and "adjusts" to new equilibrium conditions. This regime can be termed rock-dominated [Korotaev *et al.*, 1992].

#### *Methodology of Hydrothermal Processes Simulation*

Simulation is a method of studying a process or phenomenon when, instead of examining a process or phenomenon itself, an auxiliary, artificially developed system is studied, which is referred to as a model. The model should be adequate and adaptable for the processes in question in terms of certain specified criteria.

The development of a physicochemical (thermodynamic) model starts with the construction of a *quantitative geological* (geochemical or other) *model* of the process that embodies theoretical concepts of the process with regard for factual natural and experimental data. A geological model can describe a process as a whole or some of its aspects and phenomena. However, it is impossible to develop a quantitative theory for geochemical processes and solve applied geochemical

problems based on purely inductive speculations (based on geologic observations alone) without employing laws of physical chemistry.

A *physicochemical model* describes relations between the constituents of the geological model by means of thermodynamic relations (including the conditions of chemical equilibria), the dynamics of heat and mass transfer, and the kinetics of chemical interactions.

A *mathematical model* describes the relations of the physicochemical model by equations and constraints (conditions of the minimum value of the thermodynamic potential, heat and mass transfer equations, kinetic constraints, etc.) and involves calculation techniques and algorithms.

A convenient scheme of a research underlain by the model approach was published by D.V. Grichuk [2000a].

Each of the models can evolve relatively independently, but only their synthesis can result in a *quantitative model for an object or process*. Numerical simulation makes it possible to examine a physicochemical model of a process and, if there are more than one alternative models, to select a model that can most adequately describe the regularities observed. Inconsistencies between the numerical simulation results and data on the natural phenomena and processes force the researcher to correct the physicochemical model or consider possible changes in the geological model of the process.

The type of modeling currently most actively being developed is based on equilibrium thermodynamic principles and requires fast computers. This type of simulations will be referred to below as thermodynamic modeling (simulation). To obtain quantitative information with the aid of a thermodynamic model, the researcher should (1) develop a geological model for the process or phenomenon,<sup>2</sup> (2) possess sufficient input of thermodynamic information for description of the system, and (3) know a mathematical algorithm and the means of its realization in the form of a computer program. The past three decades witnessed the intense amassing of diverse thermodynamic information on various natural compounds, such as minerals, aqueous solute species, and gases. The need for exploring complex multicomponent heterogeneous systems, the appearance of fast computers, and progress in mathematical simulation techniques were prerequisites for a qualitative breakthrough and the design of highly efficient computer programs able to calculate equilibria in complex chemical systems.

An important methodological issue in studying geochemical systems is relations between an experimental research and quantitative thermodynamic simulation. It is now quite clear that almost no direct exper-

<sup>2</sup> Inasmuch as we discuss hydrothermal ore formation, the geological model should involve a hydrodynamic model (dealing with the structure of hydrothermal flows at the object in question).

imental modeling of complex natural processes is possible, mostly because of the multicomponent character of natural systems, their long lifetimes, metastable character of many reactions in experiments, inevitability of simplification and modification of the actual systems, the need for obtaining numerous experimental points, vast times required for this, etc.

Computer thermodynamic simulations are devoid of these limitations and offer an alternative to a model experiment. At the same time, experimental research serves as a "nutrient" for thermodynamic simulation. The experimental study of simple systems with precisely controlled parameters provides required data for reliable thermodynamic characteristics of minerals, species in aqueous solutions, gases, etc. Much importance is also attached to the reference experimental study of relatively complex systems, whose results, if proved undoubtedly reliable, serve as good checkpoints for thermodynamic calculations.

The methodological foundation for the modeling of geochemical phenomena by means of equilibrium thermodynamics is the concept of partial or local equilibria in geochemical systems. The concept of *partial equilibrium* implies that in a geochemical system that is not in equilibrium as a whole and is characterized by multitudes of chemical reactions, chemical equilibrium may be attained by one (or many) of them. This means that this reaction relaxes with respect to the chemical equilibrium state more quickly than the external variables vary and that other reactions can adjust to this state. The concept of partial equilibrium is temporal. *Local equilibrium* in a system is attained when phases in contact with one another interact in a reversible manner (for example, equilibrium of this kind can be achieved at grain boundaries). Proceeding from the concept of local equilibria, a generally unequilibrated geochemical system can be subdivided into a series of volumes which meet the conditions of local chemical equilibrium at a specified instant of time. These volumes within the system are not in equilibrium with one another, and this ensures the generally disequilibrated state of the geochemical system. The concept of local equilibrium is spatial.

The probabilities of the existence of partial and local equilibria are unequal in homogeneous and heterogeneous systems. Reaction rates in homogeneous systems are so fast that the systems can approach chemically equilibrated states when the external conditions vary quickly enough. For example, solute carbon dioxide species relax with respect to equilibrium states almost instantly. Even for redox processes, the relaxation rates are geologically quite fast.

Heterogeneous systems with phase interactions are more complex, but partial and local equilibria can also occur in them. These equilibria are attained when groundwater filtration velocities decrease and the times of phase interaction are large at unchanging external conditions.

Thermodynamic modeling starts with the specification of the system. Natural geologic systems are open in principle; i.e., they can exchange material and energy with their environments. However, problems of thermodynamic modeling can sometimes be formulated for both open and closed systems (which cannot exchange material with the environments) depending on the research task. The outlining of a system and distinguishing of its boundaries predetermines the approaches utilized in the interpreting the results of thermodynamic modeling.

The modeling of a process on the basis of equilibrium thermodynamics with the use of the local and partial equilibrium concepts means that the state of the system in which a specified process occurs is described by a certain succession of equilibrium states of the system. The dynamics and kinetics of natural processes, which reflect the unequilibrated and irreversible character of the spatiotemporal evolution of the natural systems, should be expressed, in the context of the adopted modeling technique, as regularities in the variations of the overall chemical compositions and conditions of existence of the successive equilibrium states.

Even during the simplest interaction of water with a congruently dissolving mineral, the evolution of the system passes through a succession of stages. A certain scope of problems of the irreversible evolution of systems can be solved by calculating equilibria based on the partial and local equilibrium principles. There is a series of methodological approaches to the calculation of the irreversible evolution of systems.

The most widespread technique of the thermodynamic simulation of natural processes is referred to as the *method of reaction progress* ( $\xi$  method), which was proposed by H. Helgeson in 1969 and further developed by I.K. Karpov and his colleagues. In its original form, this method was designed for describing processes in a closed system (and in systems with a perfectly mobile component, whose chemical potential is determined externally). The method was utilized by certain researchers (S.A. Kashik, I.K. Karpov, V.A. Kopeykin, M. Reed, and others) to model metasomatic zoning without any specified limitations. However, analysis of the essence of the  $\xi$  techniques indicates that this can not always be justified [Borisov and Grichuk, 1998; Grichuk, 2000a]. If the processes of solution filtration through rocks are modeled, secondary minerals in such a process can occur out of contact with the solution portion with which they were in equilibrium (this cannot be realized in the  $\xi$  method). As was demonstrated by theoretical analysis and numerical simulation, the  $\xi$  method can yield accurate information on the solution composition and a realistic list of secondary minerals only if a simple metasomatic zoning is simulated, i.e., when the numbers of minerals increase by one in every successive zone and none of the deposited minerals is dissolved. These conditions are usually fulfilled if the starting solution contains no

components passing into a solid phase (except H<sub>2</sub>O itself). The  $\xi$  method can be safely applied to simulating metasomatic zoning in these models. However, if the aforementioned condition is not met, the  $\xi$  method gives unrealistically extended stability fields of secondary minerals, inaccurate solution compositions, and even nonexistent mineral assemblages.

The  $\xi$  method received further development in works by B. Fritz, C. Fouillac, and others, who represented a metasomatic column in the form of a succession of boxes. In calculating the evolution of this composite system, the system composition during each log  $\xi$  step changes because the solution portion produced in the previous box during the previous step is transferred to a given box (replenished system). As was demonstrated, this technique gives results different from those of the classic  $\xi$  method if the mass transfer (filtration velocity) is much higher than the interaction rate.

In order to analyze dynamic systems with the introduction and removal of components, the method of stepwise flow reactors was proposed. In this technique the system is subdivided into a series of discrete subsystems (reactors), with the starting solution beginning to react with the rock in the first reactor and the resulting solution transferred to the next reactor, in which it reacts with the rock contained in it, and so on. Thus, each solution portion changes its composition when passing through a series of reactors, and the rock compositions in them also change simultaneously. The successive passage of solution portions produces metasomatic zoning in the rock (series of reactors). The amount of rock in each reactor is determined by relations between the solution filtration velocity and solution-rock interaction.

The method of stepwise reactors marks the transition to equilibrium-dynamic models. A system of reactors can be designed in different ways: the rock masses in the reactors can be equal or different; the system itself can be isothermal or polythermal, isobaric or polybaric, etc. The choice between the system types is dictated by the task of the research and the adopted geological model of the object.

#### *Current State of Computer Simulation of Hydrothermal Processes*

The physicochemical computer simulation of hydrothermal systems (including ore-forming systems) has been actively developed over the past two decades. These researches are being conducted in Russia, the United States, France, Australia, Canada, and other countries [Karpov *et al.*, 1976; Helgeson, 1976; Fritz, 1981; Reed and Spycher, 1985; Heinrich, 1990; *Thermodynamic Modeling...*, 1992]. Methods for the simulation of hydrothermal processes, algorithms of computer programs, and databases have been designed and worked out, with the participation of the author, at the Department of Geochemistry, Moscow State Univer-

sity, starting from the early 1980s [Ivanov and Borisov, 1980; Barsukov and Borisov, 1980, 1982c, 1987b, 1989a; Grichuk and Borisov, 1983; Borisov *et al.*, 1984; Kraynov *et al.*, 1988; Borisov and Khodakovskiy, 1989; Borisov and Shvarov, 1992, 1996].

The GIBBS computer program, developed at the Department of Geochemistry, Moscow State University, can be used in calculating thermodynamic equilibria in systems of arbitrary complexity [Shvarov, 1982]. GBFLOW, a specialized version of this program, was designed by Yu.V. Shvarov, M.Yu. Korotaev, and D.V. Grichuk, as adapted for IBM PC compatibles with the purposes of calculating models for dynamic processes in the hydrothermal region. The HCh program package, developed later for analogous systems [Shvarov, 1992, 1999; Shvarov and Bastarkov, 1999], consists of the MAIN computer program, which organizes the whole computational process; the GIBBS program; and the UNITHERM thermodynamic database. The UNITHERM thermodynamic database (Yu.V. Shvarov, M.V. Borisov, and D.V. Grichuk) includes thermodynamic constants for more than 600 compounds in its basis version and can be readily expanded by the experienced user. The data on aqueous solutions contained in UNITHERM are consistent with the SUPCRT92 database [Johnson *et al.*, 1992], which is currently the most popular among geochemists. The GIBBS computer program shows technical characteristics comparable to those of the SELECTOR [Karpov, 1981] and EQ3/6 [Wolery, 1979; Woley and Daveler, 1992] programs and is now widely used both in Russia (at the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences; the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences; St. Petersburg University; and Moscow State Geological Prospecting Academy; the Joint Institute of Geology, Geophysics, and Mineralogy, Siberian Division, (Russian Academy of Sciences) and abroad (US Geological Survey and at several universities in the United States, Australia, Switzerland, and Canada).

The software and thermodynamic information mentioned above were used at the Department of Geochemistry of the Moscow State University to design, with the participation of the author, thermodynamic models capable of describing various aspects of ore-forming systems, such as at deposits of Sn [Volosov *et al.*, 1981; Sushchevskaya and Borisov, 1992] and Hg [Voitsekovskaya *et al.*, 1990; Ozerova *et al.*, 1988; Shikina *et al.*, 1985, 1993], mineralized U-bearing veins [Barsukov and Borisov, 1987c, 1989a; Borisov and Barsukov, 1992], and the genesis of modern mineralization at the seafloor [Grichuk and Borisov, 1983; Grichuk *et al.*, 1985; Grichuk, 2000a; Bychkov, 1995].

Obviously, the simple calculation of equilibria alone, even when conducted for complex multicomponent systems, is insufficient for understanding the process if its dynamics is not taken into account. The equi-

librium–dynamic approach, in which a process is described with a succession of thermodynamically stable systems interrelated through certain dynamic characteristics, has been developed starting from the mid-1980s [Ivanov and Borisov, 1980; Barsukov and Borisov, 1982c, 1989a, 1989b, 1992; Kraynov *et al.*, 1988; Grichuk and Borisov, 1982, 1983; Grichuk *et al.*, 1985; Borisov and Barsukov, 1985a, 1989; Borisov and Goreva, 1994; Borisov *et al.*, 1995, 2002; Borisov, 2000a]. To implement the equilibrium–dynamic approach, the GBFLOW computer program for IMB compatibles was created at the Department of Geochemistry, Moscow State University. The principal simulation procedure of the program is underlain by the method of multiwave stepwise flow-through reactors (MSFR). In the MSFR procedure, a hydrothermal system is represented in the form of a succession of reactors, which contain some amounts of rocks at specified *P–T* parameters, and solution portions, which successively pass through the reactors, with thermodynamic equilibrium between the rock and solution attained at each step of the passage.

The MSFR method exhibits high performance in application to the modeling of ore formation and aureole development at vein Pb–Zn deposits [Borisov and Goreva, 1994; Borisov, 2000a; and others], as well as ore formation in convective hydrothermal systems [Abramova and Grichuk, 1994; Grichuk, 1996, 2000a].

Nowadays there seem to be still no papers devoted to the equilibrium–dynamic modeling of the origin and evolution of hydrothermal systems and the resultant ore formation, with the system encompassing regions ranging from mobilization areas to those of ore formation and aureole development. Of papers most closely approaching our research, it is pertinent to mention works by C. Heinrich [1990], conducted at the Swiss Federal Technological Institute in Zurich. The paper presents thermodynamic analysis of ore formation and the development of aureoles at Sn and W deposits. It is also worth mentioning and a paper by Bowers and Taylor [1985], whose research was devoted to modern oceanic hot hydrotherms and was carried out at MIT.

The devising and analysis of quantitative equilibrium–dynamic models for ore-forming hydrothermal systems makes it possible to further develop the physicochemical theory of the hydrothermal process and clarify the causes, conditions, and mechanisms resulting in concentrated and disseminated ore mineralization, which, in turn, facilitates the elaboration of new criteria for searches for mineral deposits.

*Hydrodynamic Elements in Models  
for Hydrothermal Ore-Forming Systems: Main  
Concepts and Definitions*

Along with thermodynamic conditions, hydrodynamic conditions are among the principal factors pre-

determining the ore-forming potential of hydrothermal ore-forming systems. The main cause of hydrothermal solution motions is gradients of the hydrodynamic pressure (differences between the physical and equilibrium hydrostatic pressures). The development of hydrodynamic pressure gradients could be caused by (1) variations in the volumetric proportions in the system of fluid and fracture–pore space of rocks, which brings about the *induced convection* of fluids; (2) variations in the fluid density, which results in its *free convection*; and (3) deviations of the surface from the horizontal, which gives rise to *gravitational convection* [Pek, 1989].

*Induced convection* is fluid flow under the effect of external forces. The main processes that result in induced convection are the generation of solutions during the crystallization of water-bearing silicate melts or the dehydration of rocks in diagenetic or metamorphic processes and the expulsion of aqueous solutions during rock compaction. Magmatic hydrothermal solutions are believed to be able to exert pressures higher than the lithostatic pressure at depths where the parental intrusions solidify.

*Free convection* is caused by an unequilibrated distribution of solution density. In the hydrothermal process, the main role is played by the thermal expansion of solutions. According to A.A. Pek, “the thermal convection mechanism in the genesis of hydrothermal ore mineralization is controlled mainly by the fracture permeability of the geological environment” [Pek, 1989] (the typical permeability of fractured rock massifs is from  $10^{-14}$  to  $10^{-16}$  m<sup>2</sup>). A pressure gradient that maintains fluid motions in a thermal-convection hydrothermal systems is caused by the differences between the fluid densities in the low-temperature descending and high-temperature ascending convection branches. The average gradient of hydrodynamic pressure is estimated as 0.5–1 MPa/km [Pek, 1989].

*Gravitational convection* appears owing to the unhorizontal position of the Earth’s surface, when the source areas of infiltration flows are restricted to topographical highs, and their discharge areas are in topographical lows. The infiltration flows pass through highly permeable aquifers and fault zones.

All hydrothermal systems discussed below seem to belong to systems with predominantly induced, thermal, and possibly, gravitational types of convection. The models themselves can well permit the limited involvement of the magmatic constituent in the composition of the initial hydrothermal solutions (for example, in the concentrations of chlorine and carbon dioxide).

An important concept of the theory of ore formation is that of the necessity of hydrodynamic focusing mineralized solutions. This follows from comparison of the volumes of mineral deposits themselves and the volumes of the alimentation areas of their hydrothermal ore-forming systems. The significant differences

between the alimentation and ore-deposition volumes justifies the statement that the hydrodynamic focusing of mineralized solutions within the ore deposition area is an inevitable condition of ore formation [Pek, 1989]. It is also important that the problem of solution deficit in hydrothermal systems with free convection is resolved by conjuring solution circulation. The resources of infiltration waters in systems with gravitational convection can also be considered limitless.

The hydrodynamic focusing of mineralized solutions within the ore deposition volume is maintained mostly by the heterogeneity in the filtration characteristics of the geologic environment. The results of hydrodynamic modeling, which specify the mechanisms of solution focusing in characteristic structural environments in which hydrothermal ore mineralization is localized, were summarized by Safonov *et al.* [1982] and are partly listed in Chapter 3 of this publication. These data lay the hydrodynamic foundation for the main model of ore formation under nearly isothermal conditions (Chapters 3 and 4).

*Thermodynamic Basis of Modeling:  
Programs, Data, etc.*

All thermodynamic calculations described below were conducted with the GIBBS program [Shvarov, 1976, 1982] during the early stages of this research and, afterwards, with the GBFLOW program (a modification of the GIBBS program), whose algorithm is based on the minimization of the system energy and the approach of multiwave stepped flow-through reactors (devised at the Department of Geochemistry by Yu.V. Shvarov, M.Yu. Korotaev, and D.V. Grichuk). Some calculations were carried out using the modern HCh program package [Shvarov, 1995, 1999; Shvarov and Bastrakov, 1999].

The input information for the calculation of the equilibrium state within a local volume (part of or interval, point within the hydrothermal system) included a list of independent components of the system (chemical elements); a list of dependent components (minerals of constant composition or solid solutions, and aqueous solute species); the bulk starting composition of the rock; the initial composition of the primary solution; the number of stepped reactors describing the system; the number of solution portions (waves) passing through the reactors; the proportion of the rock and solution masses in each reactor (the rock mass in a reactor can be equal to zero); the temperature and pressure in each reactor; the Gibbs free energies for all of the minerals and aqueous species at any temperature and pressure (in HCh they were calculated automatically when the UNITHERM database was addressed); parameters for the calculation of the activity coefficients of the aqueous species (Debye-Hückel equation in the form of the third approximation or its modification).

For each reactor during each stage (wave) of interaction, the calculations yielded the bulk compositions of the equilibrium solution and the solid phase; the list and amounts of minerals produced as equilibrium was attained (numbers of moles, weight or volume percentages); equilibrium solution composition (molal concentration and activity coefficient for each species). The possible additional information included pH, Eh, ionic strength, etc.

The models for uranium mineralization were explored using the technique of flow-through stepped reactors and the GIBBS computer program, in which the movement of solutions within the space of the ore-forming medium had still not been represented in a computerized form and was calculated manually. In this part of the research, we analyzed the heterophase 14-component system H-O-K-Na-Ca-Mg-Fe-Al-Si-C-Cl-U-Pb-S, which was described by 69 solute species (including 17 species of ore-forming elements—Pb<sup>2+</sup>, PbOH<sup>+</sup>, PbCl<sup>-</sup>, PbCl<sub>2</sub>, PbCl<sub>3</sub><sup>-</sup>, PbCl<sub>4</sub><sup>2-</sup>, PbCO<sub>3</sub>, Pb(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, UO<sub>2</sub><sup>2+</sup>, UO<sub>2</sub>(OH)<sup>+</sup>, UO<sub>2</sub>(OH)<sub>2</sub>, (UO<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub><sup>2+</sup>, UO<sub>2</sub>SO<sub>4</sub>, UO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup>, UO<sub>2</sub>CO<sub>3</sub>, UO<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, and UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub><sup>4-</sup>)—and 36 solid phases. Their list, assumed Gibbs free energy values, and references to thermodynamic information sources are summarized in a table in Chapter 3. This part of the work had been carried out before the UNITHERM thermodynamic database was prepared.

The models for base-metal ore formation were examined using the GBFLOW computer program and the HCh computer package. The rock-fluid system was described by 15 independent components: H-O-K-Na-Ca-Mg-Al-Si-Fe-C-Cl-S-Zn-Pb-Cu. The model aqueous fluid contained 79 solute species, including 26 species with ore-forming elements. The list of the possible solid phases included 52 minerals (principal rock-forming, metasomatic, and ore minerals). The list of solid phases and solute species, references, and the means of free energy calculations are given in Tables 1 and 2. The thermodynamic data were calculated using the UNITHERM database (Yu.V. Shvarov, M.V. Borisov, and D.V. Grichuk, Department of Geochemistry, Moscow State University).

*UNITHERM: calculation of the free energy for minerals.* The  $\Delta g^0(T, P)$  for minerals were calculated by the equation

$$\Delta g^0(T, P) = \Delta f G^0(298) - S^0(298)(T - 298) + \int_{298}^T C_p^0(T) dT - T \int_{298}^T C_p^0(T)/T dT + V^0(298)(P - 1),$$

where  $S^0(298)$ ,  $V^0(298)$ , and  $\Delta_f G^0(298)$  are, respectively, the entropy, volume, and free energy of formation of the mineral at a temperature of 25°C and a pres-



**Table 1.** Sources data (UNITHERM database) for the calculation of thermodynamic properties of solid phases (minerals) potentially possible during the origin of vein base-metal ore mineralization and included in the model

Mineral	Formula	Symbol	Reference
Quartz	SiO <sub>2</sub>	Qtz	Helgeson <i>et al.</i> , 1978; SURCRT92
Hematite	Fe <sub>2</sub> O <sub>3</sub>	Hem	IVTANTERMO, 1983
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	Mag	
Tenorite	CuO	Tn	Robie <i>et al.</i> , 1978
Cuprite	Cu <sub>2</sub> O	Ct	
Zincite	ZnO	Zt	
PbO	PbO	PbO	Glushko, 1979
Pyrite	FeS <sub>2</sub>	Py	IVTANTERMO, 1983
Marcasite	FeS <sub>2</sub>	Mrs	
Pyrrhotite (troilite)	FeS	Po	
Galena	PbS	Gn, PbS	Glushko, 1979
Sphalerite	ZnS	Sp, ZnS	Robie <i>et al.</i> , 1978
Chalcocite	Cu <sub>2</sub> S	Cc	Robie <i>et al.</i> , 1978; Ferrante <i>et al.</i> , 1981
Covellite	CuS	Cv	
Chalcopyrite	CuFeS <sub>2</sub>	Ccp	Helgeson <i>et al.</i> , 1978
Bornite	Cu <sub>5</sub> FeS <sub>4</sub>	Bn	
Diaspore	AlO(OH)	Dsp	Kuyunko <i>et al.</i> , 1983
Portlandite	Ca(OH) <sub>2</sub>	Prt	Glushko, 1979
Brucite	Mg(OH) <sub>2</sub>	Brc	Robinson, Haas, 1982
Calcite	CaCO <sub>3</sub>	Cal	Robie <i>et al.</i> , 1978; Glushko, 1979
Magnesite	MgCO <sub>3</sub>	Mgs	
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	Dol	Helgeson <i>et al.</i> , 1978; SURCRT92
Siderite	FeCO <sub>3</sub>	Sd	Robie <i>et al.</i> , 1978; Naumov <i>et al.</i> , 1971
Cerussite	PbCO <sub>3</sub>	Cer	Volkov <i>et al.</i> , 1982
Smithsonite	ZnCO <sub>3</sub>	Sm	Robie <i>et al.</i> , 1978
Anhydrite	CaSO <sub>4</sub>	Anh	
Anglesite	PbSO <sub>4</sub>	Ang	CODATA, 1978; Robie <i>et al.</i> , 1978
Zinkosite	ZnSO <sub>4</sub>	Zks	Robie <i>et al.</i> , 1978
Andalusite	Al <sub>2</sub> SiO <sub>5</sub>	And	Hemingway <i>et al.</i> , 1982
Wollastonite	CaSiO <sub>3</sub>	Wo	
Enstatite	MgSiO <sub>3</sub>	En	Helgeson <i>et al.</i> , 1978; SURCRT92
Tremolite	Ca <sub>2</sub> Mg <sub>5</sub> Si <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	Tr	Kiseleva, Ogorodova, 1983
Actinolite*	Ca <sub>2</sub> Mg <sub>4</sub> FeSi <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub>	Act	Grichuk, 1996
Muscovite	KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	Ms	Pokrovskii, 1984
Phlogopite	KMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	Phl	Sidorov, 1983
Annite	KFe <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	Ann	
Kaolinite	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Kln	Hemingway <i>et al.</i> , 1982
Pyrophyllite	Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	Prl	
Talc	Mg <sub>3</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>	Tlc	Dorogokupetz, Karpov, 1982, 1984
Chrysotile	Mg <sub>3</sub> Si <sub>4</sub> O <sub>5</sub> (OH) <sub>4</sub>	Ctl	
Prehnite	Ca <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	Prh	Haas <i>et al.</i> , 1981
Epidote	Ca <sub>2</sub> FeAl <sub>2</sub> Si <sub>3</sub> O <sub>12</sub> (OH)	Ep	Sidorov, 1983
Epidote-60**	Ca <sub>10</sub> Fe <sub>3</sub> Al <sub>12</sub> Si <sub>15</sub> O <sub>65</sub> H <sub>5</sub>	Ep-60	Grichuk, 1996
Epidote-75**	Ca <sub>8</sub> Fe <sub>3</sub> Al <sub>9</sub> Si <sub>12</sub> O <sub>52</sub> H <sub>4</sub>	Ep-75	
Clinochlore	Mg <sub>5</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub>	Cln	Dorogokupetz, Karpov, 1982
Daphnite	Fe <sub>4</sub> Al <sub>4</sub> Si <sub>2</sub> O <sub>10</sub> (OH) <sub>8</sub>	Dph	Karpov <i>et al.</i> , 1976; Sidorov, 1983
Chlorite-50***	Mg <sub>5</sub> Fe <sub>4</sub> Al <sub>6</sub> Si <sub>5</sub> O <sub>20</sub> (OH) <sub>16</sub>	Chl-50	Grichuk, 1996
Chlorite-75***	Mg <sub>5</sub> Fe <sub>12</sub> Al <sub>14</sub> Si <sub>9</sub> O <sub>40</sub> (OH) <sub>32</sub>	Chl-75	
Albite	NaAlSi <sub>3</sub> O <sub>8</sub>	Ab	Robie <i>et al.</i> , 1978
Microcline	KAlSi <sub>3</sub> O <sub>8</sub>	Mc	Helgeson <i>et al.</i> , 1978; SURCRT92
Anorthite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	An	Hemingway <i>et al.</i> , 1982
Lawsonite	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>6</sub> (OH) <sub>4</sub>	Lws	Dorogokupetz, Karpov, 1982, 1984

Note: Minerals of intermediate composition: \* actinolite 80 = tremolite/Fe-tremolite as 4/1, \*\* epidote 60 = epidote/zoisite as 3/2, epidote 75 = epidote/zoisite as 3/1, \*\*\* chlorite 50 = clinochlore/daphnite as 1/1, chlorite 75 = clinochlore/daphnite as 1/3.

**Table 2.** Sources data (UNITHERM database) for the calculation of thermodynamic properties of solute species included in the model of vein base-metal ore mineralization

Aqueous species	Calculation technique for $\Delta_f G^0(T, P)$ and (variant)	Reference
H <sub>2</sub> O		Haar-Gallagher-Kell model
H <sup>+</sup>		
OH <sup>-</sup>	pK (H <sub>2</sub> O)	Marshall, Frank, 1981
CO <sub>3</sub> <sup>2-</sup>	HKF**	SUPCRT92
HCO <sub>3</sub> <sup>-</sup>	HKF	
H <sub>2</sub> CO <sub>3</sub>	HKF	
H <sub>3</sub> SiO <sub>4</sub> <sup>-</sup>	Ryzhenko equation (A)*	Busey, Mesmer, 1977
H <sub>4</sub> SiO <sub>4</sub>	HKF	SUPCRT92
O <sub>2</sub>	HKF	
H <sub>2</sub>	HKF	
H <sub>2</sub> S	HKF	
HS <sup>-</sup>	HKF	
SO <sub>4</sub> <sup>2-</sup>	HKF	
HSO <sub>4</sub> <sup>-</sup>	Ryzhenko equation (A)	Naumov <i>et al.</i> , 1971
Cl <sup>-</sup>	HKF	SUPCRT92
HCl	Ryzhenko equation (A)	Sretenskaya, 1992; Pearson <i>et al.</i> , 1963; Frank, 1956
Na <sup>+</sup>	HKF	SUPCRT92
NaOH	Ryzhenko equation (B)	Baes, Mesmer, 1981
NaCO <sub>3</sub> <sup>-</sup>	Ryzhenko equation (C)	Smith, Martell, 1976
NaHCO <sub>3</sub>	Ryzhenko equation (C)	
NaSO <sub>4</sub> <sup>-</sup>	Ryzhenko equation (A)	Smith, Martell, 1976; Grichuk, Shvarov, 1985
NaCl	Ryzhenko equation (B)	Pearson <i>et al.</i> , 1963; Quist, Marshall, 1968
K <sup>+</sup>	HKF	SUPCRT92
KOH	Ryzhenko equation (A)	Frank, 1956; Baes, Mesmer, 1981
KSO <sub>4</sub> <sup>-</sup>	HKF	SUPCRT92
KHSO <sub>4</sub>	HKF	
KCl	Ryzhenko equation (B)	Naumov <i>et al.</i> , 1971
Mg <sup>2+</sup>	HKF	SUPCRT92
MgOH <sup>+</sup>	Ryzhenko equation (A)	McGee, Hostetler, 1975
MgCO <sub>3</sub>	Ryzhenko equation (A)	Siebert, Hostetler, 1977
MgHCO <sub>3</sub> <sup>+</sup>	Ryzhenko equation (B)	Bauman, 1981
MgSO <sub>4</sub>	Ryzhenko equation (B)	Marshall, 1967; Malinin, 1979; Larionov, 1985
MgCl <sup>+</sup>	Ryzhenko equation (D)	Saccocia, Seyfried, 1989
MgCl <sub>2</sub>	Ryzhenko equation (B)	Luce <i>et al.</i> , 1985; Frantz, Popp, 1981
MgOHCl	Ryzhenko equation (B)	Sinitsyn, 1986
Ca <sup>2+</sup>	HKF	SUPCRT92
CaOH <sup>+</sup>	Ryzhenko equation (C)	Baes, Mesmer, 1981
CaCO <sub>3</sub>	Ryzhenko equation (A)	Plummer, Busenberg, 1982
CaHCO <sub>3</sub> <sup>+</sup>	Ryzhenko equation (A)	Bauman, 1981; Malinin, 1979
CaSO <sub>4</sub>	Ryzhenko equation (A)	Malinin, 1979; Grichuk, Shvarov, 1985
CaCl <sup>+</sup>	HKF	SUPCRT92
CaCl <sub>2</sub>	HKF	
Al <sup>3+</sup>	HKF	Pokrovskii, Helgeson, 1989, 1995

Table 2. (Contd.)

Aqueous species	Calculation technique for $\Delta_f G^0(T, P)$ and (variant)	Reference
AlOH <sup>++</sup>	HKF	
Al(OH) <sub>2</sub> <sup>+</sup>	HKF	
Al(OH) <sub>3</sub>	HKF	
Al(OH) <sub>4</sub> <sup>-</sup>	HKF	
NaAl(OH) <sub>4</sub>	HKF	Pokrovskii, Helgeson, 1989, 1995
Cu <sup>+</sup>	HKF	SUPCRT92
CuOH	Ryzhenko equation (A)	Smith, Martell, 1976; Variash, Rekharskii, 1981
Cu(HS) <sub>2</sub> <sup>-</sup>	Ryzhenko equation (B)	Crerar, Barnes, 1976
Cu(HS) <sub>2</sub> H <sub>2</sub> S <sup>-</sup>	Ryzhenko equation (B)	
CuOHCl <sup>-</sup>	Ryzhenko equation (A)	Grichuk, 1996, 1998
CuCl	Ryzhenko equation (A)	
CuCl <sub>2</sub> <sup>-</sup>	Ryzhenko equation (A)	
CuCl <sub>3</sub> <sup>-</sup>	Ryzhenko equation (A)	
Cu <sup>++</sup>	HKF	SUPCRT92
Zn <sup>++</sup>	HKF	
ZnOH <sup>+</sup>	Ryzhenko equation (A)	Plyasunov, 1989; Khodakovskiy, Elkin, 1975
Zn(OH) <sub>2</sub>	Ryzhenko equation (B)	Plyasunov, 1989
ZnHCO <sub>3</sub> <sup>+</sup>	Ryzhenko equation (A)	Bauman, 1981
Zn(HS) <sub>2</sub>	Ryzhenko equation (B)	Wood <i>et al.</i> , 1987
ZnCl <sup>+</sup>	Ryzhenko equation (A)	Ruaya, Seward, 1986
ZnCl <sub>2</sub>	Ryzhenko equation (A)	Plyasunov, Ivanov, 1990
ZnCl <sub>3</sub> <sup>-</sup>	Ryzhenko equation (A)	Ruaya, Seward, 1986
ZnCl <sub>4</sub> <sup>-</sup>	Ryzhenko equation (A)	Plyasunov, Ivanov, 1990
ZnSO <sub>4</sub>	Ryzhenko equation (C)	Naumov <i>et al.</i> , 1971
Pb <sup>++</sup>	HKF	SUPCRT92
PbOH <sup>+</sup>	Ryzhenko equation (A)	Tugarinov, 1976
Pb(HS) <sub>2</sub>	Ryzhenko equation (B)	Wood <i>et al.</i> , 1987
PbCl <sup>+</sup>	Ryzhenko equation (A)	Seward, 1984
PbCl <sub>2</sub>	Ryzhenko equation (A)	
PbCl <sub>3</sub> <sup>-</sup>	Ryzhenko equation (A)	
PbCl <sub>3</sub> <sup>-</sup>	Ryzhenko equation (A)	
Fe(OH) <sub>2</sub> <sup>+</sup>	Ryzhenko equation (C)	Baes, Mesmer, 1981
Fe(OH) <sub>3</sub>	Ryzhenko equation (A)	Naumov <i>et al.</i> , 1971; Sinitsyn, 1986; Zeng <i>et al.</i> , 1986, 1989
Fe(OH) <sub>4</sub> <sup>-</sup>	Ryzhenko equation (A)	Baes, Mesmer, 1981; Zeng <i>et al.</i> , 1986
FeOHCl	Ryzhenko equation (A)	Grichuk, 1996, 1998 (by experiment Sinitsyn, 1986)
FeOHCl <sub>2</sub> <sup>-</sup>	Ryzhenko equation (A)	Grichuk, 1996, 1998 (by experiment Hemley <i>et al.</i> , 1992)

\*The dissociation constant was calculated by Ryzhenko's equation. Shown in parentheses is a variant of the calculation (see text). The energy of the complex was calculated from the dissociation constant and energy values of the reference ions.

\*\*The energy values of the aqueous species were calculated with the Helgeson–Kirkham–Flowers (HKF) model.

sure of 1 bar,  $C_p^0(T)$  is the heat capacity equation for this mineral for a pressure of 1 bar. The relations between  $\Delta_f G^0(T)$  and  $\Delta g^0(T)$  are determined by the equality

$$\Delta g^0(T) = \Delta_f G^0(T) + \text{SUM}\{n(i)\Delta g(i)\},$$

where  $n(i)$  is the stoichiometric coefficient of element  $i$  in its stable state and  $\Delta g(i)$  is the free energy of this element at a given temperature [Borisov and Shvarov, 1992].

The heat capacity equation is given as a polynomial in  $T$  (it is possible to represent it in the form of a ten-term equation with  $T$  in powers of 0, 1, -2, -0.5, 2, 3, 4, -3, 0.5, and -1). If there are phase transitions in a mineral,  $C_p^0(T)$  equations are given separately for each temperature interval corresponding to one modification. The last "phase transition" can specify the boundary of the stability field of this mineral.

*UNITHERM: calculation of the free energy for reference ions.* The calculations of  $\Delta g^0(T, P)$  for reference ions (these are usually simple ions with which it is possible to describe the full dissociation reaction of a complex species) were conducted by the modified Helgeson-Kirkham-Flowers (HKF) equation [Helgeson *et al.*, 1981; Shock and Helgeson, 1988; Shok *et al.*, 1989]. Coefficients for most reference ions were borrowed from the SUPCRT92 database [Johnson, Oelkers, and Helgeson, 1992] or later papers by Helgeson *et al.* and other researchers. Now, the coefficients for the direct calculation of  $\Delta g^0(T, P)$  with the HKF equation for many solute species are still absent, but there are experimental data involving the determined constant of electrolytic dissociation over certain temperature and pressure intervals. Because of this, in developing the UNITHERM database, we utilized a combined technique for obtaining the thermodynamic data of solute species (it was briefly described by Borisov and Shvarov [1992]), which synthesizes the HKF model and modified Ryzhenko equation [Ryzhenko, 1981; Bryzgalin and Rafal'skiy, 1982; Bryzgalin, 1989].

*UNITHERM: calculation of the free energy for complex ions.* This part of the UNITHERM database was prepared by Yu. V. Shvarov, M. V. Borisov, and D. V. Gri-chuk, who developed a technique for the calculation by a semiempirical equation, selected experimental data, assessed their quality, conducted auxiliary calculations, treated the data to attain their consistency, etc.

The  $\Delta g^0(T, P)$  for complex ions was calculated by the equation for the dissociation reaction

$$\Delta g^0(T, P) = \text{SUM}\{n(i)\Delta g^0(i)\} - 2.302RTpK_{(\text{diss})}^0,$$

where  $i$  are simple (reference) ions, and  $n(i)$  are the stoichiometric coefficients of the dissociation reaction.

The dependence of  $pK_{(\text{diss})}^0$  on  $T$  and  $P$  was calculated by the modified Ryzhenko equation

$$\begin{aligned} pK_{(\text{diss})}^0(T, P) \\ = (298.15/T)pK_{(\text{diss})}^0(298, 15 \text{ K}, 1 \text{ bar}) \quad (*) \\ + B(T, P)(zz/a)_{\text{eff}}, \end{aligned}$$

where  $B(T, P)$  is taken to be independent of the character of the ion and can be calculated from  $pK^0(\text{H}_2\text{O})$  [under the assumption that  $(zz/a)_{\text{eff}}(\text{H}_2\text{O}) = 1.0107$ ] and  $(zz/a)_{\text{eff}}$  is a characteristic of the complex ion for which the following approximation is assumed:

$$(zz/a)_{\text{eff}} = A + B/T.$$

In comments on each complex ion, characters A through D denote the calculation variant utilized to determine the parameters of this ion. The choice between the variants for the calculation of parameters for Eq. (\*) was dictated by the available input information as follows:

(A) If there was a reliable  $pK_{(\text{diss})}^0$  (298.15 K, 1 bar) value for the ion, and there were a few determinations of its  $pK$  under other conditions, the value of the  $(zz/a)_{\text{eff}}$  was calculated by least-square fitting (LSF) with Eq. (\*).

(B) If the  $pK_{(\text{diss})}^0$  (298.15 K, 1 bar) for the ion was unknown or unreliable but its  $pK$  was determined under other conditions (for instance, at elevated  $T$ ), the  $pK_{(\text{diss})}^0$  (298.15 K, 1 bar) and  $(zz/a)_{\text{eff}}$  parameters were calculated by LSF with Eq. (\*).

(C) If a reliable  $pK_{(\text{diss})}^0$  (298.15 K, 1 bar) value was available but there were no  $pK$  determinations under other conditions, the  $(zz/a)_{\text{eff}}$  value was calculated as theoretical, following the method of Bryzgalin and Rafal'skiy [1982].

(D) If no  $pK_{(\text{diss})}^0$  (298.15 K, 1 bar) value was available but there was at least one  $pK$  determination at other  $T$  and  $P$  (or a few such values for a narrow interval of  $P$ - $T$  parameters), the  $(zz/a)_{\text{eff}}$  value was calculated as theoretical, following the method of Bryzgalin and Rafal'skiy [1982], and  $pK_{(\text{diss})}^0$  (298.15 K, 1 bar) was then calculated by Eq. (\*).

The reliability of the  $pK_{(\text{diss})}^0$  (298.15 K, 1 bar) values thus obtained diminishes from variant A through D. The wider the  $P$ - $T$  interval for which the experimental data on  $pK$  were used, the more reliable the extrapolations in variants (A) and (B). Very reliable data were obtained by interpolating experimental data in compliance with the modified Ryzhenko equation.

## CHAPTER 2 ESTIMATION OF THE COMPOSITION OF HYDROTHERMAL SOLUTIONS

The assessment of the composition of hydrothermal solutions is one of the most important and limitless problems of research, which is discussed in thousands