*ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 6, pp. 1345–1359. © Pleiades Publishing, Ltd., 2011.*
*Original Russian Text © I.N. Kigai, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 2, pp. 87–98.*

# Some Chemical Aspects of Hydrothermal Mineralization[1]

**I. N. Kigai**

*Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences,*
*Staromonetny per. 35, Moscow 119017, Russia*
*e-mail: kigai@igem.ru*

Received January 1, 2010

**Abstract**—A modern state of the following problems of magmatogene hydrothermal mineralization are considered in this paper: Dependence of ore types from a redox state of ore producing magmas; D.S. Korzhinskii's principle of acid–base interaction as a possible variety of Le Chatelier's principle; the structural features of zonal near-ore alkaline and acidic metasomatites and related revised formula of the mineralogical phase rule; dependence of acidity-alkalinity of fluids from NaCl and KCl hydrolysis at different *P*–*T* environments, as well as from subcritical fluid's heterogenization; the features and reason of general evolution of mineralization within a single metallogenic cycle; mineralization from heterophase fluids at the postorogenic deposits of W, Sn, Au, Ag, Cu, Pb, Zn, and Hg related to acidic metasomatites; evidence and reason of intermittent (multi-stage) mineralization on the background of general evolution of composition and properties of fluids; as well as (8) some guidelines for local ore prediction based on above analysis.

**DOI:** 10.1134/S1070363211060399

## INTRODUCTION

“Hydrothermal” are hot natural solutions of a deep-seated origin and mineral accumulations (minerals, rocks, ores), formed at their participation. The solutions consist mainly of water and the salts dissolved in it (with prevalence of chlorides and, far less, sulfates or carbonates, of Na, K, less often Ca and Mg, at subordinated role of $SiO_2$) and gases (more often $CO_2$, but sometimes also $CH_4$, $NH_3$, $H_3BO_3$, $H_2S$and $SO_2$). Solutions can have temperature 100–750°C, sometimes higher, and to be in subsurface under pressure up to 3 kbar, seldom more. Their phase state can be supercritical or subcritical and, in the latter case, liquid and/or gaseous. When the actual phase state of a liquid, solution or gas is not known or (for a particular consideration) is insignificant, then, by proposal of American geologist L. Graton [1], they are named *fluids*. Ascending up to a realm of hydrothermal mineralization (to a depth usually from 7 up to 1 km, and sometimes to terrestrial surface) through fractures and pores in surrounding rocks, the fluids are interacting with them, producing the hydrothermal alterations. In case when such changes are observed around or near ore bodies and in relation with them, they are called near-ore alterations. If the fluids are enriched with ore components, they can under certain environment precipitate ore substances in open (or in opening under fluid's pressure) fractures or also by replacement of country rocks beside fluid-conducting faults. Transformation of one mineral or rock into a mineral or mineral aggregate of different composition, under influence of solutions interacting with the rocks, is called metasomatose or metasomatism, and the process itself is metasomatic one [2]. The rock being metasomatized keeps, as a whole, a solid state, and its total volume does not change during hydrothermal rock alteration.

Mountain ridges arising on the Earth are destroyed with the time, and the rock fragments, being accumulated on the bottom of river valleys, lakes and the seas, form the sedimentary rocks. During accumulation of new sediments, the older ones are buried and get to the bottom horizons of the Earth's crust, up to 20–80 km deep, where greater pressure and temperatures dominate. The sediments are converted there into metamorphic rocks. Such transformation is known as a regional metamorphism. At a later time (and partially already during metamorphism), the sedimentary and metamorphic rocks are folded, penetrated by bodies of granites and other magmatic rocks and participate in

---

[1] The text was submitted by the author in English.

formation of new mountain ridges. In the Earth's development history these processes have been repeated many times in its continental areas.

In relation to the mentioned consecutive processes of a geological cycle (sediments accumulation, metamorphism and folding), the mineral deposits can be subdivided into three groups: (1) deposits formed in sedimentary basins and predating the folding; (2) metamorphic and metamorphosed deposits; and (3) postorogenic (postkinematic, postcollisional) deposits located in fold belts. Deposits of these groups considerably differ by $P$–$T$ environments of formation, regularities of distribution, morphology of ore bodies, wall-rock alterations and mineral composition of ores. This paper deals mainly with the last group, i.e. with the postorogenic deposits. This group comprises numerous magmatogene ore deposits of ferrous, rare, small, radioactive, base and precious metals.

The geochemistry of hydrothermal processes and deposits became a large and important division of geology, but some its achievements and results could be probably useful for development of theoretical inorganic chemistry of high temperatures and pressures, and some processes of chemical technology.

## Ore-Forming Magmatism of Hydrothermal Deposits

Ore-producing granitoid complexes and related mineral deposits have the age from Archean to Cenozoic and are located in the very diverse geotectonic environments, with the exception of areas of oceanic crust occurrence. The last allows assuming just the continental crust to be the main source for granite magmas and for many metals in them. Really, the highest average contents of such typical granite-related elements as Sn, W, Mo, F and B, by one–two orders of magnitude and more exceeding their concentrations in mantle (subcrustal) rocks are observed in clayey sediments which can be considered as the main source of these elements for palingenic granitoid magmas. Besides, for W, Sn and of some other metals, a distinct increase of specific productivity in consecutive geological epochs is characteristic. It is, most likely, related to escalating thickness and area extent of the continental crust from Archean up to Cenozoic and to the processes of global recycling, resulted in progressive enrichment of younger sedimentary rocks and palingenic granite magmas (melted from them) with the ore components most stable against weathering under environment of terrestrial surface [3]. All postorogenic hydrothermal deposits of Mo, W, Sn, Be, Li are obviously or implicitly related to so-called homodromous[2] granitoid complexes. Their earliest phases are low-silica and enriched with Mg and Fe, i.e. are close in composition to diorites and granodiorites. The subsequent phases during differentiation (due to submersion of earlier crystallized Mg–Fe enriched phases like olivine, pyroxenes, amphibole and biotite) become more "acid" (silica rich), more and more enriched in alkali components and depleted in Mg and Fe. As a result, the intrusive complexes form, for instance, a typical homodromous series (from early to late): diorite–granodiorite–biotite granite–alaskite–lithium-fluorine granite. The more "acid" (silica rich) is a melt, the lower is temperature of rock crystallization and the later is its solidification during general cooling.

There is also a simultaneous gradual enrichment of residual melts with water (that also reduces the temperature of rock crystallization). The reason consists in primary undersaturation of granitoid melts with water. According to estimates of P. Wyllie [4], W. Burnham [5] and I.D. Ryabchikov [6], the initial average content of water in melts makes 1.5–3.0 wt %, whereas a potential solubility of water in them on typical depths of crystallization of ore-producing magmas (3–0 km), from various experimental data, is above 4–7%. During crystallization of melanocratic magmas (containing many dark-colored water-bearing minerals, amphibole and biotite), a residual melt cannot form a large enough volume of free water phase, therefore no significant hydrothermal deposits are related to such intrusions (for example, diorites and granodiorites). F.G. Reif [7] as a result of determining water content in melt inclusions in minerals from granitoids of Transbaikalia and the Central Kazakhstan has shown, that granitoid massifs with the initial water content below 4% are not ore-productive ones, barren.

Thus, hydrothermal deposits of Mo, W, Sn, Be and Li are genetically related only to the most felsic and water-rich final differentiates of multiphase granitoid complexes of fold regions.

Hydrothermal deposits of a majority of other metals: Au, Ag, Pt, Cu, Pb, Zn, As, Sb, and Hg are

---

[2] This typical Russian and not used abroad term means successive magmatic phases emplacement from the most melanocratic rocks (enriched with Fe-Mg minerals) to most leucocratic, felsic granitoid rocks. A reverse series is usually named antidromous one.

genetically related to basic magmas of mantle (subcrustal) origin.

Beside all that, a very important role in formation of industrial accumulations of all above listed metals is played by an oxidation-reduction state of potentially ore-bearing magmas. The reason is that some metals are transported in fluids from magmas in their highest valency and are precipitated in ores, in a lowest one, or reverse. As the Japanese geologist S. Ishihara [8] has shown by an example of magmatism and ore mineralization of South-East Asia and other regions, the ore-producing granitoids according to their redox state can be subdivided into two series: ilmenite (reduced) and magnetite (oxidized) ones. A boundary between them is made by oxygen fugacity $fO_2$, provided by FMQ (fayalite–magnetite–quartz) mineral buffer. For division of these series it is possible to use a magnetic susceptibility of rocks (which can be simply measured with a portable kappa meter), a chemical composition and optical properties of biotite, features of accessory minerals of rocks. For division of leucocratic ("acid," or felsic) differentiates of both series, the weight ratio $Fe_2O_3$: FeO = 0.5 in chemical analyses of rocks can be used.

Tin deposits are exclusively related to granitoids of ilmenite series (IL type) that proves tin transfer from magmas in a bivalent state. In ores Sn is precipitated in the form of cassiterite $SnO_2$ or stannite $Cu_2$ (Fe, Zn) $SnS_4$, i.e. as $Sn^{4+}$. Hence, for deposition in ores Sn, unlike the majority of other metals, requires oxidation. Mo deposits, on the contrary, are related to granitoids of magnetite series (MT type). It means that Mo is transferred in the form of $Mo^{6+}$, and as it is precipitated in the form of molybdenite $Mo^{4+}S_2$, it demands reduction. Tungsten is transported and precipitates in $W^{6+}$ form and it is not limited by magmas $fO_2$, therefore it associates as with cassiterite in the form of wolframite (Fe, Mn) $WO_4$ and with molybdenite in the form of molybdoscheelite (or powellite) Ca (W, Mo) $O_4$.

The other mentioned metals are related to basic magmas of magnetite series, represented in the ore fields in the form of intersecting granites dikes of various composition, vein-like magmatic bodies of variable thickness. Gold and silver are transferred, most likely, in the univalent form, being bound in bisulfide or chloride complexes, and are precipitated preferentially in a native form, $Au^0$ and $Ag^0$, therefore they require reduction for precipitation. Copper, lead and zinc during transport and deposition, as a rule, preserve their valency (1+, 2+), but precipitate mostly in the form of sulfides and consequently require presence of sulfide anions in solutions, if they are not transported in the form of bisulfide complexes of $Zn(HS)_2$, $Zn(HS)^+$, $Zn(HS)_3^-$ etc. type. Reduction for gold, silver and sulfur (if the last is transported in more oxidized sulfate form) is usually provided by black shale, enriched with bitumen, or by dissolved in fluids methane, the product of bitumen pyrolysis. If tellurium and (or) selenium are present in fluids, gold and silver can precipitate directly as tellurides and/or selenides or undergo dismutation (disproportionation) and precipitate simultaneously in the form of both native metals and telluride and selenide, for example:

$$2Au(HS) + 2H_2Te = Au^0 + AuTe_2 + 2H_2S + H_2.$$

Therefore gold and calaverite $AuTe_2$ (and other tellurides) are frequently associated in epithermal gold-silver deposits. However, a problem of gold valency in calaverite it is not simple. Gold looks as bivalent (by analogy to iron in pyrite $FeS_2$ where sulfur forms "dumb-bell"[3] of two tightly pulled together atoms, and iron is bivalent), but Au, as is known, does not form bivalent cations, therefore in the calaverite structure there is probably a complex combination of mono- and trivalent forms of gold.

## On Acidity of Mineralizing Fluids

A problem of acidity-alkalinity of hydrothermal fluids is considered as one of the most important parts of the theory of mineral formation. The papers devoted to it (in the chronological order) have been written by R. Bunzen (1847), C. Fenner, N. Bowen, W. Lindgren, T. Bart, D.S. Korzhinskii, J.J. Hemley, N.I. Khitarov, V.A. Zharikov, B.N. Ryzhenko, I.P. Ivanov, J.W. Shade, I.D. Ryabchikov, W.D. Gunter and H.P. Eugster, G.B. Naumov, G.R. Kolonin, R.P. Rafal'skii, I.N. Kigai, and B.R. Tagirov (2010) and many other researchers. Especially great importance to influence of fluid's acidity on mineral formation, in particular, on ore precipitation, was given by D.S. Korzhinskii.

### *A Principle of Acid–Base Interactions by D.S. Korzhinskii*

When estimating acidity of fluids responsible for any wall-rock alteration, a Principle of Acid–Base Interactions developed by D.S. Korzhinskii [9] is widely used. According to this principle, *an increase of acidity of a solution favors reactions of replac*ement

---

[3] The term by Academician N.V. Belov.

*of stronger bases by weaker ones and weaker acids by stronger ones. Symmetrically, an increase of solution alkalinity favors reactions of replacement of stronger acids by weaker ones and weaker bases by stronger ones.* This principle can be considered, in our opinion, as one of new varieties of Le Chatelier's Principle of equilibrium displacement or as an important addition to this principle. Really, an inhibition of a process is also provided here: an increase of acidity of a solution rises activity of acid components and promotes their preferred introduction into a solid phase that leads as a result to decrease of solution acidity, and, reverse, an increase of solution alkalinity rises activity of the bases and leads to alkaline metasomatism of country rocks, which results in drop of solution alkalinity. Similarly to Le Chatelier's Principle, the Korzhinskii's principle of acid-base interactions (ABI) can be applied only to equilibrium conditions and, for example, to saturated solutions of components under consideration. ABI Principle has been successfully applied by D.S. Korzhinskii in analysing not only hydrothermal, but also magmatic processes.

For effective application of ABI Principle in defining direction of acid–base interactions in the nature, it is necessary to have an opportunity to estimate relative acidity-basicity of minerals. With this purpose, some researchers have been using an electronegativity of the main components (D.S. Korzhinskii, A.A. Marakushev). Proceeding from data on ionization energy, D.S. Korzhinskii has shown that, with rare exceptions, univalent metals are more basic than bivalent, and bivalent, more basic than trivalent, and so on. In each row of equal valency, the basicity of metals drops with the atomic weight decrease [10].

Main rock-forming elements, according to increase of average energy of atom ionization per valency electron, form the following series corresponding to decrease of basicity and increase of acidity of the elements [11]:

$$K^+–Na^+–Ba^{2+}–Ca^{2+}–Mg^{2+}–Mn^{2+}–Fe^{2+}–Al^{3+}–Fe^{3+}–Ti^{4+}–B^{3+}–Si^{4+}.$$

But such relations can be used rather simply only when comparing minerals of similar structure differing only by one element, for example, potassium and sodium feldspars: $KAlSi_3O_8$ and $NaAlSi_3O_8$. As potassium is stronger base than sodium, a replacement of albite by K-feldspar is indicative of fluid's alkalinity rise. But it is much more difficult to estimate ABI direction when comparing minerals of more complex composition and large chemical difference. For them, the attempts to develop a system of acidity-basicity of minerals on the basis of the weight-average ionization potentials of elements for a mineral [12] or with the use of solid state physics approach [13] also have been done. But they still have appeared to be unsuccessful, so far as in both systems the orthoclase (K-feldspar) has been shown as more acidic than muscovite, one of the principal minerals of greisens (acidic metasomatites), that is absurd.

A considerable assistance in estimates of relative basicity of minerals and direction of fluid's acidity shift is rendered by study of zoning of metasomatic columns.

### *A Structure of Metasomatic Columns*

According to D.S. Korzhinskii's theory of metasomatic zoning [14], the number of minerals, in zones of near-fracture metasomatic columns of diffusion type, decreases from front of replacement to rear zone by one mineral in each sequential zone due to transition of one of the components into a perfectly mobile state. Typical columns of alkaline and acid metasomatites formed in the hydrothermal processes related to postorogenic calc-alkaline magmas, are shown in Tables 1 and 2. In the nature, such columns can have thickness from tens cm up to several meters. But for Transbaikalia the columns of albitization with a rear monoalbite zone up to 20 m thick are known (they were described in P.V. Koval's papers). Zones of tourmalinization in Komsomol'sk district of Khabarovsk territory reach thickness of 20–40 m. At the tin deposits of Primorye territory studied by the author, the rear zones of monotourmaline or monosericite composition are from 1 to 20 cm thick, and total thickness of columns reaches several meters. The thickness of zones always increases from a rear zone to a frontal one in a geometric progression. But all zones of metasomatic columns appear at once, simultaneously, already in a microscopic scale, and further they only proportionally expand, similarly to extension of accordion bellows, that has been confirmed by detailed study of metasomatites at mineral deposits [15, 16] and by experiments [17].

Presence of monomineral zones in metasomatic columns allows identifying easily a direction of acid-base interaction responsible for their formation.

The following reactions in systems $K_2O–Al_2O_3–SiO_2–H_2O$ and $Na_2O–Al_2O_3–SiO_2–H_2O$, important for

**Table 1.** Typical structure of alkaline metasomatic columns[a]

| Zone | Unaltered rock: Qtz-Pl-Kfs-Bt ± Mu ± Kaol | | |
|---|---|---|---|
| 5 | Qtz -Kfs-Pl-Mu-Chl | Qtz -Kfs-Pl-Mu-Chl | Qtz -Kfs-Pl-Mu-Chl |
| 4 | Qtz-Kfs-Ab-Chl | Qtz-Kfs-Ab-Chl | Qtz-Kfs-Ab-Chl |
| 3 | Qtz-Kfs-Ab | Qtz-Kfs-Ab | Qtz-Kfs-Chl |
| 2 | Qtz-Kfs | Qtz -Ab | Qtz- Chl |
| 1 | Kfs | Ab | Chl |
| Fluid conducting fracture, later – ore vein | | | |

[a] (Ab) albite or oligoclase; (Bt) biotite; (Chl) chlorite; (Kaol) kaolinite; (Kfs) K-feldspar (microcline, orthoclase or adularia); (Mu) muscovite or sericite; (Pl) plagioclase; (Qtz) quartz.

**Table 2.** Typical structure of acid metasomatic columns of greisen type[a]

| Zone | Unaltered rock: Qtz-Pl-Kfs-Bt ± Mu ± Kaol | | |
|---|---|---|---|
| 6 | | Qtz-Kfs-Pl-Mu-Chl | Qtz-Kfs-Pl-Mu-Chl |
| 5 | Qtz-Kfs-Pl-Mu-Chl | Qtz-Kfs-Pl-Mu | Qtz-Kfs-Mu –Chl |
| 4 | Qtz-Kfs-Pl-Mu | Qtz- Kfs-Mu | Qtz- Kfs-Mu |
| 3 | Qtz-Kfs-Mu | Qtz-Mu | Qtz-Mu |
| 2 | Qtz-Mu | Qtz-Toz | Qtz-Tur |
| 1 | Mu | Toz | Tur |
| Fluid conducting fracture, later – ore vein | | | |

[a] (Ab) albite or oligoclase; (Bt) biotite; (Chl) chlorite; (Kaol) kaolinite; (Kfs) K-feldspar (microcline or orthoclase); (Mu) muscovite, lepidolite, sericite, zinnwaldite or siderophillite; (Pl) plagioclase; (Qtz) quartz; (Toz) topaz; (Tur) tourmaline.

the analysis of natural mineral associations and processes have been experimentally studied by J.J. Hemley with colleagues [18, 19]:

$$\underset{\text{K-feldspar}}{3KAlSi_3O_8} + 2HCl = \underset{\text{Muscovite}}{KAl_3Si_3O_{10}(OH)_2} + \underset{\text{Quartz}}{6SiO_2} + 2KCl \qquad (1)$$

and

$$\underset{\text{Albite}}{3NaAlSi_3O_8} + 2HCl = \underset{\text{Paragonite}}{NaAl_3Si_3O_{10}(OH)_2} + \underset{\text{Quartz}}{6SiO_2} + 2KCl. \qquad (2)$$

The equilibria of feldspars (K-feldspar and albite) with micas (muscovite or paragonite) and quartz in reactions (1) and (2) correspond to a mineral buffer of granitic composition and, in mineralogical respect, they can be conventionally accepted as the assemblages corresponding to neutrality of solutions (actually the solutions in these equilibria are really weakly acid). Replacement of feldspars by quartz plus muscovite assemblage corresponds to acidic leaching of granite and it is an exothermic reaction, and reverse process of quartz and micas replacement by feldspars is of endothermic nature and corresponds to alkaline metasomatism.

Thus, the rear zones, consisting of K-feldspar or albite in metasomatic columns, indicate to relation of such columns to alkaline metasomatism, so far as silica at their formation was extracted from granites down to full removal of quartz. And, as is known from experiments, a solubility of quartz in acidic solutions is low and practically does not depend on acidity of solutions, but sharply increases with the rise of alkalinity [20]. It was a reason to admit quartz as an acid mineral. In columns of Table 2, the replacement of bases-rich alkaline feldspars first by the assemblages of quartz with mica, topaz or tourmaline also points to increase of solution acidity, though it is difficult to explain the formation of quartz-absent rear zones at a single-phase liquid state of a solution.

The problem is that if a liquid solution is being filtered through units of silicate rocks, it should become saturated with silica. And if, according to D.S. Korzhinskii's hypothesis of an overtaking (or advancing) wave of acidic components [21], a filtration of solution results in rise of its acidity, the bases should be extracted from the rocks at the front of replacement, starting from the strongest ones, to be substituted for more acidic components, and in such case, the rear monomineral zones should be composed of quartz. And, according to the specified ideology, the monoquartz rear zones have been, as a matter of fact, shown in all columns of acidic leaching presented in a paper by V.A. Zharikov and B.I. Omel'yanenko [22]. Though such columns really can be seen at some mineral deposits, but the detailed studies of real columns [15, 23] have shown that the rear monoquartz zones in them are of secondary origin. Rear zones, as is shown in Table 2, are formed first by micas, topaz or tourmaline and only subsequently, during precipitation of ores and quartz in veins, are replaced by silica. For tourmaline and sericite, it was found as a result of detailed studies of tin deposits at Primorye territory where a distinct loss of silica from country rocks has been revealed at formation of tourmaline and sericitic metasomatites, accordingly, in quartz-cassiterite and arsenopyrite-pyrrhotite-chalcopyrite stages of mineralization [15]. A primary nature of muscovite in greisens relative to quartz of rear zones clearly follows from O.D. Levitskii [24] descriptions of greisens of East Transbaikalia, the primary nature of sericite relative to quartz in typical columns of beresites has been described in [25] monograph for reference beresites from the Berezovskii gold deposit, Urals. Primary nature of albite and K-feldspar relative to quartz in rear zones of columns of alkaline metasomatism has been shown in [26, 27].

The fact that rear zones of columns of acidic leaching are composed by other minerals than quartz, did not find an explanation until it has been understood that the acid solutions necessary for formation of acid metasomatites, form only under environment of fluid's heterogenization [16]. But in more detail it will be considered in due course a little bit later.

### *A Revised Mineralogical Phase Rule*

It has been a study of metasomatic zoning that has formed a basis for development of a Principle of Differential Mobility of Elements (DME) in natural processes by D.S. Korzhinskii [28]. According to this DME Principle, the elements can behave as inert components, whose mass defines mineral composition of zones, and as perfectly mobile components, for which the system is open. For example, for high-temperature phlogopite and lazurite deposits of Cisbaikalia, D.S. Korzhinskii [28] has defined a following series of relative mobility of components from the most inert to the most mobile (it is shown here with some abridgements):

$$Al_2O_3–TiO_2–SiO_2–MgO–BaO–P_2O_5–Fe–CaO–F–Na_2O–K_2O–Cl–S–CO_2–H_2O.$$

Relative mobility of elements is influenced by many conditions: temperature, pressure, redox state, acidity-alkalinity of environment, porosity of rocks and intensity of solution circulation. But Al and Ti, as a rule, appear to be the most inert components. It can be seen that the behavior of K-feldspar and albite in real columns of acidic leaching (Table 2) does not agree with the relative basicity (alkalinity) of sodium and potassium. But D.S. Korzhinskii has explained it by a greater solubility of albite in comparison with K-feldspar.

Without taking into account a real zoning of metasomatites, the well known physico- chemical Gibbs' Phase Rule cannot be applied to metasomatic columns in which the number of minerals is being regularly reduced from a frontal zone to a rear one down to formation of monomineral zones.

The classical Gibbs' Phase Rule, as it is known, relates a number of phases (in our case, of minerals) in a system ($m$), a number of components ($k$) and a number of freedom degrees, or variance of the system ($f$) by a relation:

$$m = k + 2 - f. \quad (3)$$

One of Geochemistry founders, Norwegian scientist Professor V.M. Goldschmidt [29], with reference to the closed systems of contact hornfelses, whose variance is not higher than two (temperature and pressure), has deduced a Mineralogical Phase Rule:[4]

$$m \leq k. \quad (4)$$

D.S. Korzhinskii has corrected this equation with reference to metamorphic rocks and to open systems which are closed only for inert components:

$$m \leq k_{\mathrm{in}}, \quad (5)$$

where $k_{\mathrm{in}}$ is a number of inert components in a system (for instance, in a zone of a metasomatic column). Meanwhile, he has entered an amendment for metasomatic rocks, which admittedly form with preservation of volume, i.e. under isochoric condition (in this case, the variance of a system is decremented

---

[4] Prof. V.M. Goldschmidt's formulation of his Mineralogical Phase Rule has been as follows: "From ***n*** components (at arbitrary pressure and temperature), not more than ***n*** minerals can exist stably."

by unity and, accordingly, the number of stable phases is augmented by this unity):

$$m \le k_{\text{in}} + 1, \tag{6}$$

when it follows that one or two minerals can be kept stable in a rear zone of a metasomatic column comprising only one inert component [10].

But actually, a Rule of Rock's Volume Preservation at Metasomatism, which has been formulated by W. Lindgren [2], refers to a total volume of a metasomatized rock whereas its physical volume really changes. Thus, at active alkaline metasomatism (K-feldspathization, albitization, chloritization) and acidic leaching (greisenization, tourmalinization, phyllic alteration etc.), the effective porosity of rocks noticeably (from initial 0.5–1.5% to final 10% and more) increases, hence, its physical volume (volume of a solid skeleton of a rock minus pore space) evidently decreases. On the contrary, during the ore deposition and silicification, the effective porosity of rocks always decreases [30]. Hence, for the rock metasomatism, a New Mineralogical Phase Rule should be written as follows:

$$m = k_{\text{in}}, \tag{7}$$

i.e. *the number of minerals in a zone of a metasomatic column is always equal to a number of inert components and cannot be less than it*. Such conclusion is based on the fact that all typical completely developed columns of metasomatites have monomineral rear zones. Their stability is ensured by $Al_2O_3$–the most inert component in many metasomatic processes. More intensive acidic leaching or alkaline metasomatism should lead to transition of all components in a perfectly mobile state, i.e. to formation of open leaching cavities (because if there are no inert components–there are also no minerals).

During the subsequent cooling, the solution becomes oversaturated with silica, that earlier has been leached from country rocks, and that leads to quartz precipitation in veins and to silicification of monomineral rear zones of metasomatic columns.

An original feature of columns of acidic metasomatites with participation of topaz and tourmaline is formation of paired bimineral zones–quartz-muscovite and quartz-topaz, in the first case, quartz-sericitic and quartz-tourmaline in the second one (Table 2). D.S. Korzhinskii has explained this anomaly by a change of equilibrium factors at transition from external (frontal) bimineral zones to internal (rear) ones: according to his opinion, a constant pressure condition is changed in this direction to a constant volume one (i.e. there a change happens from isothermal-isobaric condition to isothermal-isochoric one, which allows to increase a number of status variables and, accordingly, a number of minerals in a rear bimineral zone by unity). But such explanation looks like a quite artificial one. As a matter of fact, nothing similar occurs in a simpler column of muscovitization under the same conditions. A real explanation of the anomaly is that the fluorine (at topaz metasomatism) and boron (at tourmalinization), introduced into rocks by fluids in large quantities, start to play in rear zones a role of virtual inert components and increase the number of inert components in rear bimineral zones by unity. Therefore a second bimineral zone forms here. It is interesting, that the possibility of such behavior of perfectly mobile components has been earlier supposed by D.S. Korzhinskii himself [28].

### *Evolution of Acidity of Mineralizing Fluids*

Among the Russian geologists, D.S. Korzhinskii's *hypothesis about an overtaking (or advancing) wave of acidic components in a flow of ascending liquid solution filtered through rock units* [21] was popular until rather recent time. Being based on this hypothesis, D.S. Korzhinskii has been denying a multistage, intermittent nature of hydrothermal mineralizetion. He has considered that one phase of magmatic intrusion can be, in a typical case, followed only by one wave of fluid's acidity with a gradual change from alkaline solutions to acidic ones, then to late alkaline and subneutral, with this wave corresponding to one stage of mineralization. To follow this idea, V.A. Zharikov and B.I. Omel'yanenko [22] have tried later to lay down all complex suite of diverse and sequentially arising assemblages of metasomatites and related ores into the Procrustean bed of one acidity wave, that has been challenged by I.N. Kigai [23].[5]

Some students of ore deposits already in 1950–60th have described multiple alternations of assemblages comprising near-ore metasomatites and related ore parageneses (B.L. Flerov, A.D. Shcheglov, I.N. Kigai, G.Yu. Grigorchyuk).

---

[5] Though B.I. Omel'yanenko has introduced later some corrections into a chronological system of metasomatites and related ores [31].

**Table 3.** Evolution of hydrothermal mineralization related to a postorogenic calc-alkaline magmatism within a single metallogenic epoch (modified after Kigai, 1974, 1989)[a, b, c, d]

| Type of magmatic rocks | Main components of ore fluids | Succession of ore-metasomatic assemblages, shown upwards | | |
|---|---|---|---|---|
| | | Initial pH of fluids | Metasomatites | Main commodities |
| Basic dikes | The fractures grown up to the Earth's surface | Acid fluids at the top → and alkaline fluids at the bottom → | 9. Argillization, alunitization ("high-sulfidation", oxic type) | Fluorite; Hg, or Au, Ag in unoxic environment |
| | | | Adularia, chloritiza-tion, carbonatization ("low sulfidation" type) | Au, Ag, or Pb–Zn, (Sn) |
| | $CO_2 < H_2O$, $MeCl_n$, $Me(HS)_n$, $H_3BO_3$, $H_2S$, $\pm H_2SO_4$, $\pm SO_2$ | Acid | 8. Beresites-listvenites, fillic alteration | Au, W, or U<br>Cu, Pb-Zn, As, Sb, Hg |
| Granitoids and felsic dikes | | | 7. Tourmalinites | Sn ± W, or Au |
| | | | 6. Greisens | W ± Sn, Be, Li |
| | | Alkaline | 5. Albitites | Be, (W), or U |
| | | | 4. K-feldspathic metasomatites | Mo or (Sn) |
| | $H_2O > CO_2$, $MeCl_n$ $\pm H_3BO_3$ | Subneutral-alkalescent | 3. Calcic skarns | Fe, B, W, Cu, Sn, Pb–Zn |
| | | | 2. Scapolitization | Fe |
| | $CO_2 \geq H_2O$, $\pm$ $MeCl_n \pm H_3BO_3$ | | 1. Magnesian skarns | Fe, B |

[a] In the environment of high pressures and temperatures, all above shown assemblages can be predated by pegmatites. [b] Not all, but several (from 2 to 6) of shown ore-metasomatic assemblages can form at a single ore field or deposit, their order of formation being always preserved, though there can be some gaps in a particular succession. [c] The latest two types of metasomatic alterations (no. 9) form simultaneously at different levels of epithermal systems. [d] Metals shown within brackets correspond to some rare types of mineralization.

Especially convincing are the cases when the ore-metasomatic assemblages with a similar trend of acid-base interaction appear consecutively being related to one magmatic phase–for example, greisens with tungsten (±Sn) ore and then tourmalinites with tin (±W) mineralization (such combination of ore-metasomatic assemblages is typical of tin deposits of Yakutia and Primorye territory, and also of Cornwell and Malaysia). At the Pervomayskii molybdenum deposit in Dzhida district of Transbaikalia, a triple repetition of K-feldspathization with the subsequent formation of metasomatic quartz-molybdenite veins was detected, additionally emphasized by injection of intramineralization granitoid dikes. In other words, the repeated "waves" of alkalinity, and acidity are registered at many different hydrothermal deposits [15, 16].

Detailed studies of temporal relationships of metasomatites and ores has allowed to establish the following general sequence of ore-metasomatic assemblages (OMA), related to postorogenic granitoids and to overprinting them basic dikes of mantle origin (Table 3). The OMA sequence shown in the Table represents a synthesis of data from many ore fields and all these OMA are never met at one particular deposit. A single deposit can comprise only 2–5 OMA, but their relative sequence indicated in Table 3 is always preserved within a deposit, ore field or ore region.

Analyzing this Table, it is possible to notice, that the general tendency of fluid's acidity evolution has been correctly guessed by D.S Korzhinskii,–the fluids have been evolving from subneutral and alkalescent through highly alkaline to very acidic with the further neutralization and transition to late low-temperature alkaline and subneutral solutions. But such evolution was not defined by a filtration of fluids and proceeded intermittently, in multi-stage manner.

### *A Chemical Nature of the Evolution of Acidity of Magmatogene Fluids and Some Geological Constraints upon itsIinfluence on Natural Processes*

Studies of fluid inclusions in minerals of hydrothermal magmatogene deposits that have been

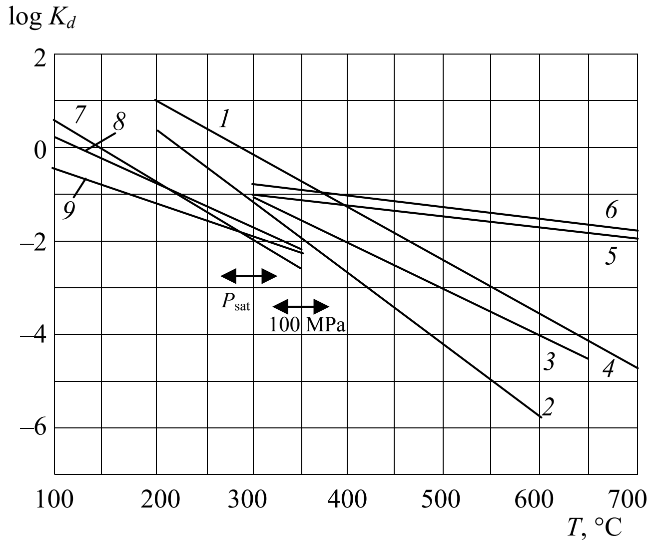

**Fig. 1.** $T$–$P$ dependence of dissociation constants of HCl and Na and K hydroxides in diluted supercritical fluids at 250–100 MPa and at vapor saturated fluid's pressure ($P_{sat}$). The double-pointed arrows show no-hydrolysis temperature intervals for solutions of intermediate composition at different pressures. (*1*) HCl, 250 MPa, (*2*) HCl, 100 MPa, (*3*) NaOH, 100 MPa, (*4*) KOH, 100 MPa, (*5*) NaOH, 250 MPa, (*6*) KOH, 250 MPa, (*7*) HCl, $P_{sat}$, (*8*) KOH, $P_{sat}$, and (*9*) naOH, $P_{sat}$. Data sources for calculations are referred in the text.

carried out by numerous Russian and foreign researchers show that a leading role in composition of magmatogene fluids is played by $H_2O$, $CO_2$, NaCl and KCl. Subordinate role belong to $H_3BO_3$, $CaCl_2$, $MgCl_2$, $CH_4$, $NH_3$, $H_2S$ and $SO_2$. In low-temperature conditions the relative share of carbonates and bicarbonates increases. As far as the chlorides of other metals have properties rather close to those of NaCl, a typical hydrothermal fluid with a sufficient accuracy for genetic interpretations can be approximated by a system NaCl–$CO_2$–$H_2O$.

Among the listed minor components there are no strong acids, and even such weak acid as $H_2CO_3$ is practically completely associated at elevated temperatures. Therefore the basic contribution into acidity-alkalinity of fluids should be made by alkali chloride hydrolysis, which is capable to proceed in two directions:

$$\begin{aligned} &Na^+ + OH^- + HCl \leftrightarrow \mathbf{NaCl + H_2O} \\ &\leftrightarrow NaOH + H^+ + Cl^-. \end{aligned} \tag{8}$$

Thus, the acidity of a fluid should depend on a relative dissociation degree of alkali hydroxides and HCl. Figure 1 shows the dependence of NaCl and KCl hydrolysis product dissociation on temperature and

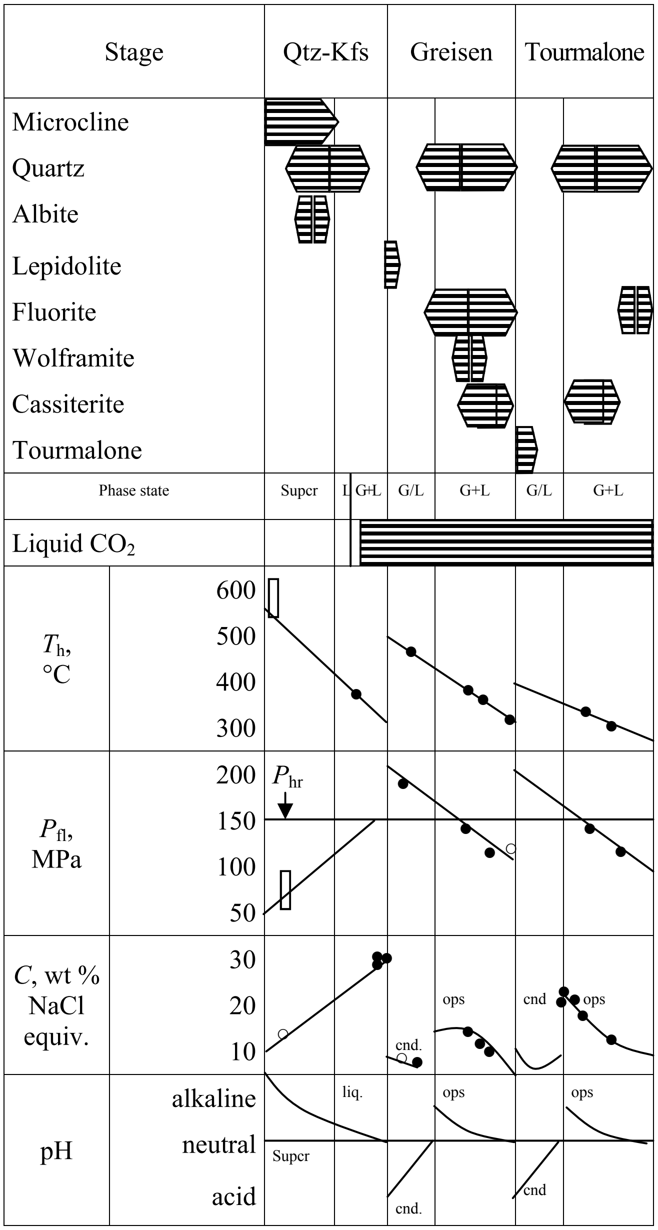

**Fig. 2.** Evolution of mineralization at the Trudovoye tin-tungsten deposit, Kirghizia [34]. Legend: (●) measured values; (○) minimal values; (□) values estimated from indirect data (the vertical size corresponds to probable limits); At the line of "liquid $CO_2$", the oblique hatching shows the range of heterogeneous fluids existence. A phase state of fluids: (Supcr) supercritical; (L or liq) liquid; (G +L) vertically unseparated gas and liquid bubbles randomly coexisting in pore space of a rock; (G/L) gravity separated gas and liquid in open faults; (cnd) condensate of the gas phase; (ops) ore precipitating solution; ($T_h$) filling (homogenization) temperature; ($P_{fl}$) fluid's pressure; ($P_{hr}$) fluid's pressure sufficient for the hydrorupture; ($C$) concentration of KCl+NaCl or NCl-equiv., wt %.

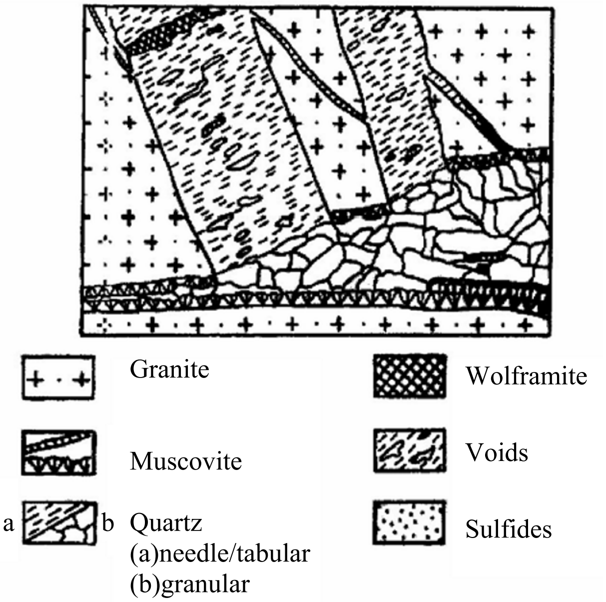

**Fig. 3.** The open space filling vein typical of greisen type tungsten deposits. A drawing of ore vein structure, the Bukuka deposit, Western Transbaikalia, Russia.

pressure of fluids in supercritical region and in a vapor saturated solution. This diagram was created by I.N. Kigai and B.R.Tagirov with the use of recently published experimental data [32]. As it can be seen, the isochors for HCl have more steep inclination and crosscut the flat isochors of alkalies in points of hydrolysis inversion, where dissociation constants ($K_d$) for HCl and alkalies are equal, and both NaCl and KCI solutions should be neutral. To the left of these points the solutions are acid, to the right–alkaline.

At pressure decrease, and also at increase of solution concentration, the inversion points are displaced to lower temperatures, and the area of alkaline solutions extends. Fluid's alkalinity of this period is proved by mineral assemblages of metasomatites where the rear monomineral zones composed of K-feldspar or albite are always observed.

As it is seen on Fig. 1, a temperature decrease converts the earlier alkaline NaC1 and KCl solutions to weakly acid. With the similar alkaline to acidic shift of solutions pH revealed by their calculations, G.B. Naumov and V.A. Dorofeyeva [33] have been explaining a change from alkaline metasomatism to acidic leaching, but it is impossible to agree with such suggestion. In a presence of muscovite-quartz-feldspar buffer (which can be represented practically by any granitoid or arkose rock), such high acidity, that is necessary for formation of greisens or tourmalinites, most likely, cannot be attained by a simple cooling of Na–K-chloride solutions. The example of the Trudovoye tin-tungsten deposit in Kirghizia (Fig. 2), whose ore bodies occur in granites, is typical enough. At this deposit, according to results of fluid inclusion studies, the temperature, during the first quartz-feldspar stage, has been decreasing down to 290°C, but no greisens or typical acidic minerals like topaz, muscovite or tourmaline were formed [34].

### *Formation Conditions of Solutions Responsible for Acidic Leaching*

The author has noticed long ago that there are no typical filling veins related to skarns and high-temperature feldspar metasomatites [15]. Additional observations at many dozens mineral deposits allow to be convinced that there are no exceptions from the following *rule of greisens relation to secretion* (the filling of open cavities): in a consecutive series of ore-metasomatic assemblages, related to granitoids, the earliest of them (ore-bearing skarns and feldspar-ore assemblages) are characterized by only metasomatic ore bodies. The first filling veins appear only in connection with greisens, and, in the sequel, the metasomatic and secretional ores are combined within the same ore bodies. A typical example of quartz-wolframite filling veins related to greisens is shown on Fig. 3. The existence of veins of such structure testifies that, during greisenization and ore deposition, the highly pressurized fluids existed whose pressure was sufficient for opening vein-controlling faults, i.e. it was higher than a hydrorupture pressure, $P_{\text{hr}}$. The last generally exceeds a lithostatic pressure by rock strength which is usually ranging between 100 and 300 bars.

Thus, the temporal boundary between only metasomatic and combined metasomatic-secretional mineral precipitation precisely coincides with the moment of transition from alkaline metasomatism to acidic leaching, and that points out at the existence of a causal relationship between these two phenomena.

The analysis of the specified geological data and results of fluid inclusion studies has led the author to a conclusion that the solutions necessary for formation of acid metasomatites appear only at a combination of two conditions: the heterophase state of a fluid and the presence of open or getting open fault cavities [16, 3, 34]. The heterophase state of fluids have been revealed by fluid inclusion studies for minerals of greisen-ore and other acid metasomatites related ore assemblages at many deposits of tin, tungsten and copper in Bolivia, the USA, the USSR, Mongolia, Portugal and Czech Republic (W. Kelly and F. Turneaure, E. Roedder, V.Naumov et al., R. Bussink et al., J. Durišova et al.).

However, the above mentioned authors, as a rule, have been referring to boiling of fluids. But it is necessary to distinguish a bubble boiling from a long-term heterophase gas-liquid equilibrium. Boiling arise in endogenous environment as a result of short-term depressurization (opening) of so far closed endogenous fluid systems under influence of a high pressure of fluids or tectonic deformations with the faults opening and sometimes extending up to terrestrial surface. But the heterophase equilibrium in closed endogenous systems can be kept during long enough time–tens and hundreds thousand years, being only occasionally interrupted by boiling when intensive faulting occurs or fluid system intermittently opens to terrestrial surface. It is possible to judge it, at least, from duration of modern thermal systems in volcanic areas. For one of them in Japan, the isotope carbon age over 10 000 years has been determined.

The model of vapor-dominated hydrothermal systems has been developed by D. White with co-authors [35] for volcanogenic geothermal areas of Geysers in California and Larderello in Italy. Applicability of the model to ore deposits proper was problematic for the authors, with the exception of mercury and, with some doubts, of porphyry-copper deposits. But two important criteria ascertained in our studies, loss of silica from silicate country rocks during acidic leaching and close relation of greisenization to formation of the first open faults filling veins, have made possible to develop further the model of mineralization with the participation of heterophase subcritical fluids and extend it to the large group of endogenous hydrothermal deposits of W, Sn, Be, Li, Au, Ag, Cu, Pb, Zn, and Hg, i.e. practically to all vein-type deposits associated with acid metasomatites [36, 16].

Later, the possibility of long coexistence of gas and saline solution in the system NaCl–$CO_2$–$H_2O$ has been confirmed by M. Gehrig's experiments [37] in Germany and T. Bowers and H. Helgeson's thermodynamic calculations in the USA for all *P–T–C* environments typical of hydrothermal deposits [38].

In a subcritical fluid at its heterogenization, due to different volatility of solutes, the gas phase becomes enriched with acidic components ($CO_2$, HCl, HF, $SO_2$, $H_2S$, $H_3BO_3$) whereas a residual liquid comprises less volatile $SiO_2$, NaCl, KCl, NaOH, KOH, and also species of ore-forming metals, and gets alkaline [35, 16].[6]

At the absence of open faults, the gas and the liquid have a random spotted distribution through all pore volume of a rock and are unable to make acidic leaching: a liquid because of its high pH, and gas–by virtue of its insignificant dissolving ability at pressure considerably below a critical one [34].

After opening the fractures under pressure of a fluid (hydrorupture, or hydrofracturing), the opportunity of gravitational separation of gas and liquid is being created, especially in hydrodynamically closed conditions typical of endogenous ore-forming systems [40, 16]. Due to influence of a superficial tension, the gas in capillaries of country rocks will be condensed to form an acid solution. Such style of acid solutions formation is proved by leaching of $SiO_2$ from silicate rocks during formation of acid metasomatites: the acid solution, unsaturated with silica, could form only at condensation of a gas phase, where saturation concentration of silica is much less than in a coexisting liquid phase.

Because of low volatility of alkali chlorides and ore metal compounds, the condensate is poor in them. For this reason, there are no ore minerals in “pure” greisens, beresites and tourmalinites devoid of superimposed ore mineralization. A single well known exception is only pyrite which forms in greisens and beresites due to reaction of volatile $H_2S$ with the Fe borrowed directly on-site from country rocks that underwent the acidic leaching. The ore deposition probably is made primarily from alkaline, then subneutral solutions with a substantially higher initial concentration of chlorides than in condensates responsible for greisenization (Fig. 2).

As it is seen on Fig. 2, a concentration of chlorides in a solution of each stage of mineralization usually decreases on the background of temperature and pressure drop. It is, most likely, caused by dilution of magmatogene fluids with meteoric water that in many

---

[6] According to experimental data by M.A. Styrikovich [39], the concentrations of components $C$ in coexisting gas and liquid phases and the densities ρ of these phases are related by expression: $C_g : C_{liq} = (\rho_g : \rho_{liq})^n$, where $n = 1.9$ for $SiO_2$ and 4.0 for NaCl. So, if $\rho_g : \rho_{liq} = 1 : 2$, then concentrations of $SiO_2$ and NaCl in a gas phase will be correspondingly 4 and 16 times less than in a liquid one.

published cases has been convincingly proved by the data on oxygen and hydrogen isotopes.

Formation of low-temperature adularia, chlorite and carbonate metasomatites of the late alkaline period can be explained by alkalization of solutions in hydrothermal systems where it was possible an irreversible removal of a gas phase. Such conclusion is prompted, in particular, by vertical spatial association of deep-seated near-vein adularization with near-surface areal argillization and alunitization at epithermal gold-silver deposits and at modern geothermal areas. These relationships has been long ago considered by V.V. Averyev in his paper on the Pauzhetka thermal springs of Kamchatka [41]. Recently such epithermal gold-producing systems and their possible relation to deep-seated porphyry-copper ore types have been a subject of numerous interesting papers by J. Hedenquist, R. Sillitoe, Ch. Heinrich and many other scientists discussing a problem of tops and bottoms of gold-silver epithermal systems.

At tin deposits of the Far East Russia, this late period of evolution of ore-forming systems, most likely, corresponds to formation of the late Pb–Zn sulfide mineralization associated with pre-ore chloritization of country rocks. Later, the barren quartz-calcite veins sometimes containing minor fluorine and boron minerals (fluorite, axinite) form without any appreciable related wall rock alterations. This mineralization can be attributed to the last subneutral stage of solution acidity evolution.

Thus, the evolution of acidity of magmatogene fluids can be subdivided into four periods, or phases (Table 3):

(1) Early subneutral period in which the skarns form with conjugated or overprinted on them ores of magnetite and ludwigite, scheelite and chalcopyrite or galena and sphalerite, i.e. the skarn-ore OMA. Solutions during this period are supercritical alkaline, but their effective alkalinity at temperatures above 600°C is very low because of low dissociation degree of alkalies (see Fig. 1), so they behave practically as subneutral ones.

(2) Early alkaline period when the feldspar-ore OMA, K-felspathization with the subsequent formation of metasomatic quartz-molybdenite veins or gold-uranium ores; or albitization with Be or U mineralizetion. Temperatures here are lower than in previous case, and the initial alkalinity of fluids is rather high.

(3) Acidic period (OMA with greisens, tourmalinites, beresites-listwenites). During this period, the supercritical fluids, opening cracks and breaking into surrounding rocks with the abrupt adiabatic drop of both temperature and pressure, become subcritical and undergo vertical gravity stratification in open fractures.

(4) A period of conjugated rather low-temperature acidic and alkaline alterations (near-surface areal argillization or alunitization and synchronous near-fracture adularization, chloritization or carbonatization ± ore mineralization on deeper horizons). These processes are related to breakthrough of ore-controlling faults up to terrestrial surface, with the resulting heterogenization of fluid and mixture of acidic gas phase with meteoric underground waters rich in oxygen at the top parts of systems and alkalization of liquid solutions due to acid gases loss at the bottom parts.

Thus, a magmatogene hydrothermal process is both evolutional and pulsational (multi-stage) one. Intrinsically integrated in it are: the general evolution of chemical composition and properties of magmatic distillates (caused, most likely, by change of magmatic sources of fluids and different solubility of components in melts) and intrastage evolution of mineralization parameters ($P$, $T$, pH, $fO_2$, composition and salinity of fluids) caused mainly by mass and heat exchange of the fluid with the country rocks and formational waters. The reasons of intermittence of the process consist in the limited solubility of $CO_2$ and $H_2O$ in silicate melts, in the importance of fracture opening by hydrorupture for migration of endogenous fluids and in plugging fluid-conducting faults by precipitated ore and vein minerals at the end of each stage of mineralization.

## Possible Spatial Relationships between Metasomatites and Ores and Their Importance for Prospecting and Forecasting Hidden Mineralization

The detailed proofs of asynchronous formation of metasomatites and related ores of the same stage of mineralization have been brought forward above. Development of mineralization occurs on a background of permanent tectonic and mineralforming processes leading to growth of old fractures in various directions, their pinch down or plumbing by mineral substance. In such environments, the following combinations of spatial relationships between the zones of intensive pre-ore alteration of country rocks and the sites of maximum ore deposition are possible.

(1) Ore-controlling fault had no significant upwards growth. The water table of heterogeneous fluid also did not rise essentially due to limited influx of meteoric waters from surrounding rocks. Then the zone of pre-ore alterations will be located above the ore body and can be used as indicator of possible ore occurrence at depth. The Akchatau tungsten deposit in Central Kazakhstan is an example of such interrelations: there the zone of ore deposition has risen only up to a top of topaz greisen zone, but has left barren the muscovite greisens located above [39].

(2) After pre-ore wall rock alterations, the ore-controlling fault has extended far upwards, and meteoric waters influx into the system has been intensive enough. Then ores can occupy a much greater vertical interval in comparison with the pre-ore metasomatites, and the top parts of ore bodies can appear in practically unaltered (until the end of a given stage) country rocks. In this case, the ore can be found during prospecting earlier than the pre-ore metasomatites of the productive stage. A typical example of such case is the Dubrovskii tin deposit in Kavalerovo district of Primorye territory, Russia, where the ores of tin-productive first stage have been discovered with the help of trenches, whereas the pre-ore tourmaline metasomatites have been met only within the depth range of 160-320 m in underground workings. At the surface, the tin ores were accompanied by chlorite metasomatites, which were formed long after tin ores, in relation to late sphalerite-galena stage of mineralization [15]. At the Deputatskii deposit in Yakutia, a similar zoning was developed both from deep levels upwards and laterally from the center of the ore field to western and eastern flanks. The assemblage of tourmaline + cassiterite is changed in those directions to assemblage of chlorite + cassiterite + base-metal sulfides [40, 41].

(3) In more typical case, the ore-forming solutions are well supplied with the meteoric waters and usually rise, after termination of metasomatism, up to a level of pre-ore acidic metasomatites location. Then the ore mineralization develops not only in veins, but replaces greisens, tourmalinites and others metasomatites, sometimes essentially expanding the limits of industrial ore bodies.

(4) But sometimes the pre-ore metasomatites are developed much wider than related ores, though at the same hypsometric levels. In this case, the metasomatites could not serve as ore indicators at prospecting. Thus, at Komsomol'sk ore district of Khabarovsk territory, the very thick (to 20–40 m wide) submeridional zones of tourmaline metasomatites stretch out to many tens km, but the ore bodies only 1–1.5 km long are confined only to sites of the greatest structure loosening, being located at places of metasomatites zones intersection with the sublettitudinal fractured zones. In such cases (as well as in many other ones), during prospecting, it is more convenient to use zones of alkali metals fixation in near-ore metasomatites, which are spatially and temporally most close to productive ore mineralizetion. Due to amphoteric properties of many typical ore metals, their sulfides and hydroxides, the solubility of majority of ore minerals is minimal in subneutral area and increases with the rise of both acidity and alkalinity of a solution.[7] Therefore one of the principal conditions of ore deposition is the decrease of alkalinity of a residual solution, which has grown after gas phase removal from it during fluid's heterogenization [48]. And decrease of alkalinity is reached by interaction of a solution with the country rocks resulting in strongest bases transfer into a solid phase to form there a halo of alkaline metals (K, Na, Li, Rb, Cs). Such haloes were found by geochemical studies at deposits of different metals, in particular, tin, gold, uranium, copper, lead and zinc.

The above presented modernized theory (or integrated genetic model) of formation for postorogenic magmatogene hydrothermal ore deposits is in accord with all data accumulated up to a recent time. It has been proved in detail in a number of author's publications and was reported at many large domestic and international [49–51] conferences.

## REFERENCES

1. Graton, L.C., *Nature of the Ore-Forming Fluid, Paper no. 63, Supplement to Econ. Geol.*, 1940, vol. 5, pp. 197–358.
2. Lindgren, W., *Bull. Geol. Soc. Am.*, 1925, vol. 36, pp. 247–262.
3. Kigai, I.N., *The Genesis of Hydrothermal Deposits of Non-Ferrous and Rare Metals, Related to Granites*, Moscow: IGEM RAS, 1989.

---

[7] This pH dependence of metallic species solubility has been well shown in G. Charlot [42] monograph on qualitative analysis for standard conditions and in [43, 44] for $Ag_2S$, ZnS and $SnO_2$ at elevated temperatures.

4. Wyllie, P.J., Huang, W.-L., Stern, Ch.R., et al., *Canad. J. Earth Sci.*, 1976, vol. 13, pp. 1007–1019.
5. Burnham, C.W., *Geochemistry of Hydrothermal Ore Deposits*. Barnes, H.L., Ed., John Wiley & Sons, 1979, pp. 76–136.
6. Ryabchikov, I.D., *Thermodynamics of a Fluid Phase of Granitoid Magmas*, Moscow: Nauka, 1975.
7. Reif, F.G., *Ore-Forming Potential of Granites and Conditions of Its Realization*, Moscow: Nauka, 1990.
8. Ishihara, S., *Econ. Geol. 75th Annivol. Volume*, 1981, pp. 458–484.
9. Korzhinskii, D.S., *Geochemistry,* 1956, no. 7, pp. 3–10.
10. Korzhinskii, D.S., *Izv Akad. Nauk SSSR, Ser.: Geol.*, 1976, no.6, pp. 5–13.
11. Korzhinskii, D.S., *Metasomatic Alterations of Country Rocks and Their Role in the Ore Formation*, Moscow: Nedra, 1966, pp. 133–140.
12. Zharikov, V.A., *Geology of Ore Deposits*, 1967, no. 5, pp. 26–31.
13. Rakcheyev, A.D., *A New Physico-Chemical Methods of Studying Minerals, Rocks, and Ores*, Moscow: Nedra, 1989.
14. Korzhinskii, D.S., *Theory of Metasomatic Zoning*, 2nd ed. Moscow: Nauka, 1982.
15. Kigai, I.N., *Lifudzin Tin-Ore Deposit and Some Problems of Hydrothermal Mineralization*, Moscow: Nauka, 1966.
16. Kigai, I.N., *Key Parameters of Natural Processes of Endogenous Ore Formation*, Novosibirsk: Nauka, 1979, vol. 2, pp. 7–34.
17. Zharikov, V.A. and Zaraiskii, G.P., *Geology of Ore Deposits*, 1973, no. 4, pp. 3–18.
18. Hemley, J.J., *Am. J. Sci.*, 1959, vol. 257, pp. 241–270.
19. Montoya, J.W. and Hemley, J.J., *Econ. Geol.*, 1975, vol. 70, pp. 577–583.
20. Balitskii, V.S. and Zubkova, E.I., *Hydrothermal Mineralforming Solutions of Areas of Active Volcanism*, Novosibirsk: Nauka, 1974, pp. 114–119.
21. Korzhinskii, D.S., *Dokl. Akad. Nauk SSSR*, 1958, vol. 122, no. 2, pp. 267–270.
22. Zharikov, V.A. and Omel'yanenko, B.I., *Studies of Regularities of Mineralization Distribution at Metallogenic Investigations of Ore Districts*, Moscow: Nedra, 1965, pp. 119–194.
23. Kigai, I.N., *Zoning of Hydrothermal Ore Deposits*, Moscow: Nauka, 1974, vol. 2, pp. 164–195.
24. Levitskii, O.D,. *Tungsten Deposits of Eastern Transbaikalia*, vol. 2, Moscow: Akad. Nauk SSSR, 1939.
25. Borodaevskii, N.I. and Borodayevskaya, M.B., *The Berezovskoye Ore Field (a Geological Structure),* Moscow: Metallurgisdat, 1947.
26. Lisitsynam, G.A. and Raudonis, P.A., *Problems of Metasomatism*, Moscow: Nedra, 1970, pp. 162–170.
27. Danilevskii, V.I. and Alexandrov, G.V., *Problems of Geology and Genesis of Mineral Commodities*, Leningrad: Len. Univol. Publ., 1966, pp. 67–81.
28. Korzhinskii, D.S., *Zapiski Rus. Mineralog. Soc.*, 1942, nos. 3–4, pp. 160–167.
29. Goldschmidt, V.M., *Z. Anorg. Chem.*, 1911, vol. 71, pp. 313–322.
30. Kigai, I.N. and Nikolaev, S.V., *Geology of Ore Deposits*, 1965, no. 2, pp. 25–37.
31. Omel'yanenko, B.I., *Metasomatites and Metasomatic Rocks*, Moscow: Nauchnyi Mir, 1998, pp. 207–219.
32. Kigai, I.N. and Tagirov, B.R., *Evolution of Acidity of Hydrothermal Fluids Related to Hydrolysis of Chlorides. Petrology,* 2010, vol. 18, no. 3, pp. 270–281.
33. Naumov, G.B. and Dorofeyeva, V.A., *Geochemistry*, 1975, no. 2, pp. 248–258.
34. Kigai, I.N. and Samovarov, Yu.V., *Zapiski Rus. Mineralog. Soc.*, 1989, vol. 118, no. 2, pp. 8–24.
35. White, D.E., Muffler, L.J.P., and Truesdell, A.H., *Econ. Geol.*, 1971, vol. 66, pp. 75–97.
36. Kigai, I.N., *Metasomatism and the Ore Formation*, Leningrad: VSEGEI, 1976, pp. 183–184.
37. Gehrig, M., *Hochschul Sammlung Naturwissenschaft, Chemie*, Freiburg: Hochschul Verlag, 1980.
38. Bowers, T.S. and Helgeson, H.C., *Geochim. Cosmochim. Acta*, 1983, vol. 47, pp. 1247–1275.
39. Styrikovich, M.A., *Thermodynamics and a Structure of Solutions*, Moscow: Akad. Nauk SSSR., 1959, pp. 158–166.
40. Kigai, I.N., *Metallization Associated with Acid Magmatism*. Prague, 1978, vol. 3, pp. 343–348.
41. Averyev, V.V., *Trudy Lab. of Volcanology,* vol. 19, 1961, pp. 80–98.
42. Bogolepov, V.G., Kuznetsova, V.D., and Gulyaev, A.P., *Criteria of Ore Potential of Metasomatites*, vol. 1, Alma-Ata, 1972, pp. 220–255.
43. Lir, Yu.V., *Geology of Ore Deposits*, 1968, no. 5, pp. 91–95.
44. Dubrovskii, V.N. and Kigai, I.N., *Zoning of Hydrothermal Ore Deposits*, Moscow: Nauka, 1974, vol. 1, pp. 19–88.
45. Charlot, G., *L'analyse qualitative et les réactions en solution*, Paris: Masson et Cie, 1957, vol. VIII.
46. Melent'ev, B.N., Ivanenko, V.V., and Pamfilova, L.A., *A Solubility of Some Ore-Forming Sulfides in Hydrothermal Conditions,* Moscow: Nauka, 1968.
47. Jackson, K.J. and Helgeson, H.C., *Geochim. Cosmochim. Acta*, 1984, vol. 49, pp. 1–22.
48. Kigai, I.N., *Geochemistry in a Local Metallogenic Analysis*, Novosibirsk: Inst. Geol. Geophys., 1986, pp. 10–11.

49. Kigai, I.N., Abstract of Papers, *9th IAGOD Symp.*, Beijing, China, 1994, vol. 1, pp. 346–347.
50. Kigai, I.N., *Int. Mineralogical Assoc. 16th General Meeting*, Pisa, Italy, 1994, pp. 203.
51. Kigai, I.N., Abstract of Papers, *Goldschmidt Conference*, Geochem. Soc. Publ., Pennsylvol. State Univol. Press, 1995, pp. 61.
52. Ho, P.C., Palmer, D.A., and Mesmer, R.E., *J. Solut. Chem.*, 1994, vol. 23, pp. 997–1018.
53. Ho, P.C. and Palmer, D.A., *Geochim. Cosmochim. Acta*, 1997, vol. 61, pp. 3027–3040.
54. Ho, P.C., Palmer, D.A., and Wood, R.H., *J. Phys. Chem. B.*, 2000, vol. 104, pp. 12084–12089.
55. Oelkers, E.H. and Helgeson, H.C., *Geochim. Cosmochim. Acta*, 1990, vol. 54, pp. 727–738.
56. Shock, E.L., Oelkers E.H., Johnson J.W., et al., *J. Chem. Soc. Faraday Trans.*, 1992, vol. 8, pp. 803–826.
57. Shvarov, Yu.V., *Geochem. Intern.*, 2008, vol. 46, pp. 834–839.
58. Sweeton, F.H., Mesmer, R.E., and Baes, C.F., *J. Solution Chem.*, 1974, vol. 3, pp. 191–214.
59. Tagirov, B.R., Zotov, A.V., and Akinfiev, N.N., *Geochim. Cosmochim. Acta*, 1997, vol. 61, pp. 4267–4280.