БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ • BULGARIAN ACADEMY OF SCIENCES

ГЕОХИМИЯ, МИНЕРАЛОГИЯ И ПЕТРОЛОГИЯ • 34 • СОФИЯ • 1998
GEOCHEMISTRY, MINERALOGY AND PETROLOGY • 34 • SOFIA • 1998

The crystallochemical - structural and energetic - aspect of metasomatism

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Abstract. The paragenetic trend in the crystallization sequence of silicate minerals is deduced for the wallrock alteration and metasomatite formation related to the granitoid magmatism. The sequence of occurrence of mineral parageneses with decreasing temperature and increasing acidity of the medium is traced with respect to the energy index and structural type of mineral. The energy index of the minerals in the parageneses characterizing the different wallrock alterations increases from 1.42-1.46 for the K-silicate alteration to 1.46-1.58 for the propylitization, 1.55 for the sericitization, 1.70-1.75 for the argillitization and 1.73-1.75 for the advanced argillitization. The structure type changes from predominantly pseudoisometric for the greisenization to axial for the high temperature advanced argillization with andalusite and from predominantly axial for the K-silicate alteration and propylitization to planar for the lower temperature and more acidic wallrock alterations.

The crystallochemical aspect of studying the metasomatic processes allows to find common features in the classifications of wallrock alterations and formation-based metasomatites. It supplements and contributes essentially to the physico-chemical aspect of these studies.

Key words: crystallochemical aspect, metasomatism, paragenetic trend, wallrock alteration, metasomatic formations

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Каназирски, М. 1998. Кристалохимичен аспект на метасоматичните процеси (структурен и енергиен). - *Геохим., минерал. и петрол.*, **34**, 73-81

Изведен е парагенетичният тренд в последователността на кристализация на силикатните минерали при околорудните изменения на скалите и при образуването на метасоматитите на формации, свързани с гранитоидния магматизъм. Проследена е последователността на образуване на минералните парагенези при намаляване на температурата и увеличаване на киселинността на средата в зависимост от енергийния индекс и структурния тип на минералите. Енергийният индекс на минералите в парагенезите, характеризиращи различните околорудни изменения, нараства от 1,42-1,46 за К-силикатния тип изменение до 1,46-1,58 за пропилитизацията, 1,55 за серицитизацията, 1,70-1,75 за аргилизацията и 1,73-1,75 за интензивната аргилизация. Типът структура се изменя от преобладаващо псевдоизометричен за грайзенизацията до аксиален за високотемпературната интензивна аргилизация с андалузит и от преобладаващо аксиален при К-силикатния тип изменение и пропилитизацията до планарен при по-нискотемпературните и по-киселинни околорудни изменения.

Ключови думи: кристалохимичен аспект, метасоматични процеси, парагенетичен тренд, околорудно изменение, метасоматични формации

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Crystal chemistry and paragenetic trend of the silicate minerals - previous studies

The metasomatic processes occur with reactions which are related to ion migration accomplished by diffusion (diffusion metasomatism) or infiltration (infiltration metasomatism) and is determined by the physicochemical properties of minerals and their crystal structures.

Most studies devoted to the theory of metasomatic processes treat only the thermodynamic aspects of the replacement reactions. Undoubtedly, a combination of the achievements in physico-chemical metasomatic petrology presenting the geochemical association of the minerals in corresponding parageneses and assemblages with the crystallochemical features and properties of minerals is of particular interest.

There are very few fundamental studies on crystal chemistry and paragenetic tendencies in the sequence of forming metasomatic silicate minerals. They suggest some ideas in a comparatively new direction of research in the field of metasomatism.

Gruner's publication (1950) treats the sequence of forming (order of stability or energy of reactions) of silicate minerals. The minerals are presented in a table in the order of decreasing their energy index introduced by the author. Gruner's energy index (E_i) characterizes the energy of the crystal lattice and is deduced on the basis of the electronegativity (E) of the chemical elements after Pauling and so-called bridging factor (f). The increase in the energy index is correlated with a decrease in the temperature of metasomatic mineral formation. Special attention is paid to the silicates formed in the hydration of higher temperature minerals as well as to the alumosilicates produced from the hydrothermal alterations without deducing the mineral parageneses which determine the various types of wallrock alteration (Meyer, Hemley, 1967). The energy indices presented in the table allow to study the relationship between this basic energy crystallochemical feature and the paragenetic trend in the sequence of forming silicate minerals as a result of wallrock alterations.

A study of this kind, which emphasizes the crystallochemical structural aspect, i.e. the types of crystal structure and sequence of forming the minerals and crystal habits, is that of Kostov (1981). The general tendency in the sequence of crystallization of silicate minerals is deduced depending on their structure type, i.e. from isometric I, pseudoisometric (I), to axial A and planar P, respectively, with a decrease in temperature and increase in the mobility of components, despite the peculiarities of the geological processes. The following characteristics are analyzed: a) the mineral formation sequence in the mafic branch of magmatic mineral forming (Bowen's reaction series); b) the influence of the temperature of the structure type on the progressive metamorphism of carbonate rocks in the systems CaO-MgO-SiO_2 and MgO-Al_2O_3-SiO_2; c) the I-A-P trends in dominating pegmatite associations with Be and Zr-bearing mineral assemblages and d) the I-A-P trends in the low temperature metasomatic hydrothermal minerals of the zeolite groups in the diagram H_2O/Al_2O_3 - E_i involving epidote and prehnite. The study proposes types of crystal structure for basic minerals in metasomatic mineral forming (biotite, amphibole, anorthite, albite, K-feldspar, larnite, wollastonite, diopside, enstatite, forsterite, monticellite, merwinite, andalusite, corundum, periclase, wustite, garnet, talc, serpentine, zeolites, epidote, etc.). The author also points out the sequence in the alteration of the crystal habits as an I-A-P trend of the second order indicating the temperature and mobility of components in the mineral formation process, especially in the cases when the newly formed mineral assemblages have the same structure types. Meanwhile, the sequence of forming zeolites depending on the relation Al/Si and energy index (E_i) was described in an earlier paper (Kostov, 1959).

The combination of crystallochemical and physico-chemical factors in metasomatic mineral forming reveals basic regularities in the formation of monomineral and polymineral pseudomorphs as well as in the free space crystallization. According to Zaraisky (1993) the realization of each of these three ways of forming new minerals in the experimental metasomatic columns is determined by the degree of similarity between the crystal structures of the source and newly formed mineral and by the relationship between the mobilities of the components participating in the chemical reactions. The formation of silicate mineral pseudomorphs takes place as a result of the high inertia of the aluminosilicate chain (Al_2O_3 and SiO_2) of the primary mineral and the delivery of mobile components from the solution, mostly potassium and sodium. Calcium, magnesium and iron occupy an intermediate position.

The replacement reactions, which determine the formation of pseudomorphs in the wallrock alterations, take place at several levels, each having its own energy characteristic: transportation of the substances necessary for the reaction, sorption, desorption of the ions on the crystal surface, diffusion in the crystal lattice, breaking the old chemical bonds and forming new ones. Therefore the reaction velocity, which is an important parameter for the various reactions of pseudomorphism, is determined by the different levels of these reactions.

Undoubtedly, the type of crystal structure, crystal habits and stable mineral assemblages give genetic information on the physico-chemical conditions of their formation. The basic regularities should be sought in this relationship between the physico-chemical conditions and crystallochemical properties of minerals, as well as in the processes of metasomatic mineral forming.

Crystallochemical aspect of the wallrock alteration in the classification of Meyer and Hemley and their genetic analogues the metasomatites in the formation classification of Zharikov and Omelyanenko

There is no generally accepted classification of wallrock alterations and metasomatites. This is due to the complexity and diversity of metasomatic processes and their products. Most preferable are the genetic classifications which take into account the relationship between the chemical composition and the new mineral formations, the latter being stable under certain physico-chemical conditions of metasomatic mineral forming. These are: 1) the classification of wallrock alterations given by Meyer and Hemley (1967), which is used by researchers in the USA, Australia, Japan, New Zealand, UK, Spain, France, Italy, etc., and 2) the classification on a formation-facial basis given by Zharikov and Omelyanenko (1978), which is used in the East and Central European countries, Sweden, China, etc.

On a physico-chemical basis (physico-chemical analysis of mineral parageneses, thermodynamic modelling, experimental modelling and facial analysis) the theoretical foundations have been analyzed and unifying characteristics of the two genetic classifications have been deduced (Kanazirski, Ivanov, 1992; Kanazirski, 1992a, 1992b; Kanazirski, 1994; Kanazirski et al; 1996; Kanazirski, 1996). It is particularly interesting to trace the genetic analogues in the two classifications on a crystallochemical basis in their structural and energy aspect.

Taking into account the physico-chemical nature of metasomatic processes, Meyer and Hemley (1967) propose a classification of wallrock alterations based on a group of minerals forming simultaneously under conditions similar to thermodynamic equilibrium. The analysis of the theoretical foundations of the classification shows that the authors propose some major methods of the physico-chemical petrology: 1) physico-chemical analysis of the mineral parageneses based on the classical thermodynamics for reaching local equilibrium in the system rock-hydrothermal solution and 2) experimental modelling of the sequence of hydrothermal alterations in acid metasomatism (Hemley, Jones, 1964), which shows the equilibrium ratios of the minerals K-feldspar - K-mica - kaolinite - pyrophillite. When identifying the types of wallrock alteration in the proposed classification, the equilibrium mineral associations are taken into account (Fig.1). In their discussion of the mineral associations and types of wallrock alteration, Meyer and Hemley (1967) assume a possibility that the observed mineral phases in the hydrothermally altered rocks reflect the process of adaptation of the rocks to the new conditions leading to a stable equilibrium.

In his monographic generalization Pirajno (1992) proposes an updated characterization of the types of wallrock alteration in the hydrothermal mineral deposits indentified by Meyer and Hemley.

The characteristic minerals for the K-silicate type of alteration (Fig.1) in the porphyry copper deposits are K-feldspar and biotite. Common assemblages are K-feldspar-biotite-quartz, K-feldspar-chlorite, K-feldspar-biotite-magnetite, in combination with varying amounts of minerals such as albite, sericite, anhydrite, apatite.

The typical minerals for the propylitization are epidote, chlorite, carbonates, albite, K-feldspar and pyrite. The mineral composition of propylitized rocks is supplemented by sericite and rarely by montmorillonite and zeolites.

The equilibrium mineral association quartz-sericite-pyrite (QSP) is typical of sericitization and the mineral paragenesis defining the greisenization is quartz-muscovite with possible varying amounts of topaz, tourmaline and a rich variety of ore minerals.

The moderate argillization is determined by the presence of montmorilonite, sericite (illite), chlorite and clay minerals of the kaolinite group (kaolinite, dickite, halloysite).

The associations of advanced argillization are characterized by a particularly rich variety of minerals which in different paragenetic relations determine the following types of wallrock alteration (Kanazirski, 1996): a) acid-chloride (dickite, kaolinite, pyrophillite, andalusite, corundum, diaspore, sericite); b) acid-sulphate (alunite, barite) and c) alterations related to higher activity of B (tourmaline, dumortierite) and F (topaz, zunyite).

The hydrothermal alterations involve a series of metasomatic processes and basic chemical exchange reactions, including hydrogen ion and alkali metasomatism which are of particular importance. Most hydrothermal processes are related to the alkali and hydrogen ion activities. The variations in the ratio a_{K^+}/a_{H^+} result in a change in the chemistry of hydrothermal solutions and determine the character of wallrock alterations. A decrease in this ratio causes an increase in the acidity of solutions and determines the following sequence (Pirajno, 1992) of the basic types of wallrock alteration: 1) alkali metasomatism and, in particular, K-silicate type of alteration in the porphyry-copper deposits; 2) propylitization; 3) sericitization and greisenization; 4) moderate argillization; 5) advanced argillization.

This paper studies the crystallochemical (structural and energy) aspect of the metasomatic processes. The paragenetic trends of the equilibrium silicate mineral associations are deduced on the basis of bench mark measurements made by Gruner (1959) and Kostov (1981) taking into account the well-expressed basic regularity of the relationship between the crystallochemical and physico-chemical properties of minerals.

Fig.1 presents an idealized development of the wallrock alterations (Meyer, Hemley, 1967) and the corresponding formations (Zharikov, Omelyanenko, 1978). The sequence of forming the minerals is traced with their typical structure and energy index, depending on two major factors of the acid metasomatic mineral forming - the activities of potassium and hydrogen cations. The potassium and hydrogen cation activities and the temperature are the main physico-chemical factors of the metasomatic processes in the acid stage of the hydrothermal cycle. Especially varied are the metasomatic formations and facies of the acid stage involving almost all major types of wallrock alteration (Zharikov, Omelyanenko, 1978).

In the coupled ACF/AKF for each type of wallrock alteration (Meyer, Hemley, 1967) the most typical minerals for the respective alterations are given in bold and the type of mineral structure and mineral

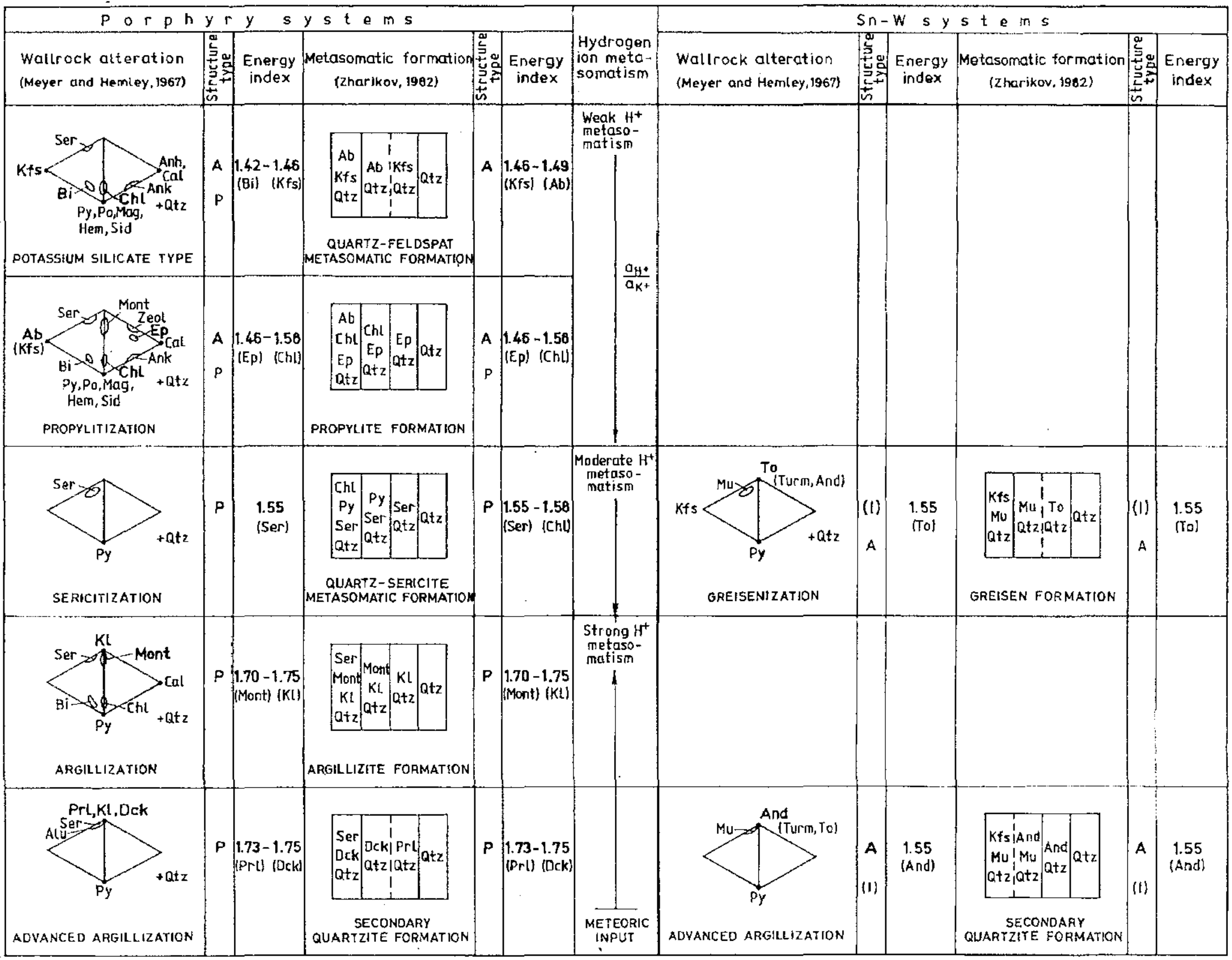

Fig.1. Scheme of idealized evolutionary wallrock alteration sequence and corresponding formations with the stucture type and energy index of their characteristic minerals as a function of K^+ and H^+ activities. Structure type: (I) - pseudoisometric; A - axial; P - planar; Ei - energy index

Minerals: Ab - albite, Alu - alunite, And - andalusite, Anh - anhydrite, Ank - ankerite, Bi - biotite, Cal - calcite, Chl - chlorite, Dck - dickite, Ep - epidote, Hem - hematite , Kfs - K-feldspar, Kl - kaolinite, Mag - magnetite, Mont - montmorillonite, Mu - muscovite, Po - pyrrhotite, Prl - pyrophillite, Py - pyrite, Qtz - quartz, Ser - sericite, Sid - siderite, To - topaz, Turm - tourmaline, Zeol - zeolite minerals

Фиг. 1. Схема на идеализираното развитие в последователността на околорудните изменения на скалите и отговарящите им формации, с характерните за техните минерали тип структура и енергиен индекс, в зависимост от активностите на калиевите и водородните катиони. Тип структура: (I) - псевдоизометричен, A - аксиален, P - планарен; Ei - енергиен индекс

energy indices (E_i) are shown. For the metasomatic formations corresponding to the wallrock alterations are given unified metasomatic columns following Zharikov (1982), designating part of the intermediate and all internal zones in the columns, the latter being significant for the facial-formation appurtenance of the metasomatites.

The diagram depicts clearly the sequence of forming silicate minerals with a definite structure type and energy index in mineral parageneses characterizing different types of wallrock alterations and their corresponding metasomatic formations depending on the increase in the acidity of hydrothermal solutions, which is expressed by the ratios of the hydrogen and potassium cation activities. The structure type changes from predominantly axial for the K-silicate alteration and propylitization to planar for sericitization, argillization and advanced argillization. There is a correspondence with the change in the structure type for metasomatic formations - genetic analogues of the wallrock alterations.

With increasing the acidity of the mineral forming medium, the values of the energy indices (E_i) also increase: 1.42-1.46 for the K-silicate alteration (1.46-1.49 for the quartz-feldspar metasomatic formation), 1.46-1.58 for the propylitization (1.46-1.58 for the propylite formation), 1.55 for the sericitization (1.55-1.58 for quartz-seritite metasomatic formation), 1.70-1.75 for the argillization (1.70-1.75 for the argillisite formation) and 1.73-1.75 for advanced argillization (1.73-1.75 for the medium- and low temperature facies of the secondary quartzite formation).

A sharp increase in the energy index E_i from 1.55 for the sericitization up to 1.70-1.75 for the argillization and 1.73-1.75 for the advanced argillization indicates a considerable increase in the acidity of the solution, most probably due to the strong predominance of the meteoric solutions in the mixed meteoric-magmatic system.

The identification of the porphyry system and Sn-W system follows Pirajno's scheme (1992) which summarizes the types of alteration at different depths. The minerals in the equilibrium mineral associations for the greisenization (greisen formation) and in the andalusite parageneses of the advanced argillization (quartz-andalusite facies of the secondary quartzite formation), chracteristic of deep intrusives and high temperature conditions, have the pseudoisometric and axial structure types typical of these conditions and an average energy index E_i = 1.55. The minerals in parageneses characterizing the corresponding low temperature wallrock alterations, formations and facies - sericitization (the quartz-sericite metasomatic formation) and advanced argillization (medium- and low temperature facies of the secondary quartzite formation) show only a planar structure type.

The crystallochemical aspect in the formation of wallrock metasomatites depending on the total acidity and temperature can also be studied by means of Zharikov's diagram (1982) - Fig.2. The diagram shows the distribution of the fields of the metasomatic formations identified by the author, which are connected with the granitoid magmatism depending on the temperature and acidity of the metasomatic mineral forming. The structure types and energy indices E_i of the minerals in the different parageneses typical of the formations are plotted in the fields and allow to trace the sequence of their formation with changing the temperature and acidity.

The increase in the acidity in the high temperature part of the diagram results in increasing the energy index E_i from 1.45-1.46 for the quartz-feldspar-amphibole (chlorite)-epidote metasomatic formation up to 1.46 for the quartz-feldspar-metasomatic formation, 1.55 for the greisen formation and the high temperature quartz-andalusite facies of the secondary quartz formation. The predominant structure type is the axial one.

Under medium temperature conditions, with increasing the acidity, the axial structure type typical of minerals of the quartz-feldspar-amphibole (chlorite)-epidote metasomatic and propylite formations, turns into an axial type (the quartz-tourmaline metasomatic formation) and planar type (the quartz-sericite metasomatic formation) as well as into an axial and planar type for the andalusite-pyrophilite facies and planar type for the diaspore-pyrophillite facies of the secondary quartzite formation. The values of the energy index E_i change from 1.45-1.46 (the quartz-feldspar-amphibole (chlorite)-epidote metasomatic formation) and 1.46-1.58 (the propylite formation) up to 1.55 (the quartz-tourmaline metasomatic formation) and 1.55-1.58 (the quartz-sericite metasomatic formation) and 1.55-1.73 and 1.73 (for the andalusite-pyrophillite and diaspore-pyrophillite facies of the secondary quartzite formation, respectively).

At low temperatures, with increasing of the acid metasomatism, the axial structure type (the gumbeite formation) turns into a planar structure type (the beresite and argillizite formations). The energy index E_i increases from 1.46 (the gumbeite formation) up to 1.55 (the beresite formation) and 1.75 (the argillizite formation).

At low acidity metasomatic formations have typically the axial structure type and similar energy indices E_i despite the different temperature stability conditions of the characterizing mineral parageneses. This

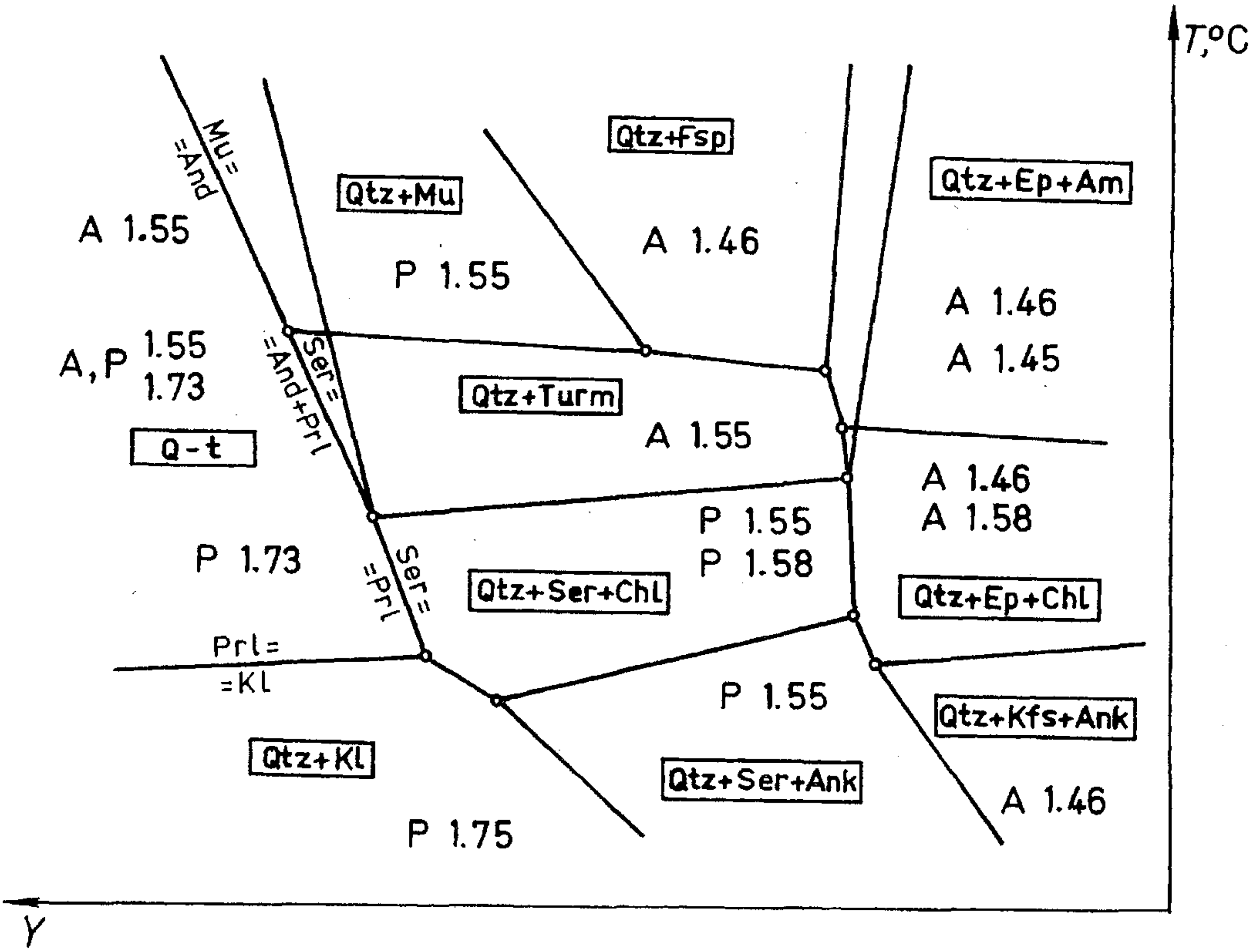

Fig.2. Schematic diagram of the conditions of occurrence of the wallrock metasomatic formations depending on the total acidity and temperature (Zharikov, 1982). The designations of wallrock metasomatic formations: (Q + Fsp) - quartz-feldspar metasomatites, (Q + Mu) - greisens, (Q-t) - secondary quartzites, (Q + Ep + Am) - quartz-feldspar-amphibole (chlorite)-epidote metasomatites, (Q + Ep + Chl) - propylites, (Q + Ser + Chl) - quartz-sericite metasomatites, (Q + Tu) - quartz-tourmaline metasomatites, (Q + Ksp + Ank) - gumbeites, (Q + Ser + Ank) - beresites, (Q + Kl) - argillizites

Фиг. 2. Схематична диаграма на условията за образуване на формациите на околорудните метасоматити в зависимост от общата киселинност и температурата (Zharikov, 1982). Означения на формациите на околорудните метасоматити: (Q + Fsp) - кварц-фелдшпатови метасоматити, (Q + Mu) - грайзени, (Q-t) - вторични кварцити, (Q + Ep + Am) - кварц-фелдшпат-амфибол(хлорит)-епидотови метасоматити, (Q + Ep + Chl) - пропилити, (Q + Ser + Chl) - кварц-серицитови метасоматити, (Q + Tu) - кварц-турмалинови метасоматити, (Q + Ser + Ank) - гумбеити, (Q + Ser + Ank) - березити, (Q + Kl) - аргилизити

emphasizes the dominance of acidity as a factor of equilibrium under such conditions.

At medium acidity, with decreasing the temperature, the axial type (the quartz-feldspar metasomatic and quartz-tourmaline metasomatic formations) is transformed into a planar structure type (the quartz-sericite metasomatic formation), related also to a slight increase in the energy index E_i from 1.46 up to 1.55.

The high acidity conditions are characterized by an AP sequence of the structure type with decreasing the temperature and by a sharp increase in E_i from 1.56 for the high temperature quartz-andalusite facies up to 1.73 for the medium temperature facies of the secondary quartzite formation and 1.75 for the argillizite formation.

The relationships obtained between the crystal structure type, the energy index E_i and the sequence of forming the mineral parageneses depending on basic equilibrium factors, namely the acidity of the medium (the ratio between the hydrogen and potassium cation activities) and the temperature, confirm the significance of the established connections and the actuality of studying the metasomatic processes in combination with crystallochemical and physico-chemical theoretical investigations.

The crystalochemical characteristics, structure type and energy index permit genetic interpretations. The same structure types and indices in greisenization and high temperature secondary quartz forming suggest the predominance of temperature as a factor of equilibrium and of the crystallochemical characteristics under high temperature conditions. The greisenization and sericitization have similar energy indices but different structure types - pseudoisometric and axial for the greisenization and planar for the sericitization. The extreme increase in the energy index for minerals in the parageneses of the advanced argillization from the Sn-W system, for minerals in the porphyry system, indicates a sharp increase in the acidity of the medium and its dominance as a factor of equilibrium over temperature.

The ideas launched by Gruner (1950) and Kostov (1981) about the energy and structural aspect in the sequence of forming the silicate minerals (depending on the temperature and mobility of the components in the process of mineral forming) are also corroborated in the metasomatic processes characterized by their complexity, diversity and multiple effect of various equilibrium factors. Obviously this refers to a basic regularity on a physico-chemical and crystallochemical basis concerning the geochemical relation of the minerals in the respective parageneses and associations to the crystalochemical properties of the minerals. This general theoretical contribution allows to make a modern interpretation of the metasomatic processes on a crystallochemical basis with the resulting enriched genetic information on the nature of these processes.

The crystallochemical aspect of studying the metasomatic processes makes it possible to find unifying features in the classifications of wallrock alterations and metasomatites on a formation basis. It supplements the physico-chemical aspect of these studies and makes a considerable contribution to them.

Acknowledgements. I am particularly indebted to Acad. Kostov who suggested to me the idea of studying the crystallochemical (structural and energy) aspect of the wallrock alterations. The study was financially supported by the National Science Fund, Grant H3-437.

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Accepted April 13,1998

Одобрена на 13.04.1998 г.