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CRYSTALLOCHEMICAL PECULIARITIES Of METASILICATES STRUCTURES FORMATION

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This work is represented by results of crystallochemical study concerning the role of metal cation, parent structural minals and structural units during formation of metasilicates structures. Study of metasilicates structure allowed to define: 1) if chemical composition meets the requirement of definite structure in this case there is no need to crystallize it in the form of other phase; 2) if there are small and large cations in composition of metasilicates in this case trade-off appears, i.e. chain consists of sorogroups and triorthogroups; 3) if different type structural units form in the same structure in this case they can form crystalline structure with mixed structural types; 4) if (OH)-group includes silicon coordination in this case by temperature increase Si-O radical complicates at first stage and further it becomes simpler; 5) there are K, Ho-triorthosilicates and Ca-hydrosilicate-afwillite in hard phase reaction in this case their derivatives remain inheritance of structural peculiarities.

Keywords: *crystal chemistry, metasilicates, formation of structures*

In work (Chiragov M.I, 2002), the method of comparative crystal chemistry first identified the parent structural minerals: in the ortho- and diortosilicate structures discrete Ca and TR and polyhedra (coordination number) bound along the edge of the SiO_4 tetrahedron, in the structures of silicates with condensed radicals isolated Ca and TR octahedra bound along the vertices with triorthogroups of Si_3O_{10}. The revealed crystallochemical regularities are used for controlling the processes of phase transformation, phase formation and modeling of new mineral structures.

Goal of research-revealing by method of comparative crystal chemistry the following: role of metallic cation, parent structural minal and structural unit during metasilicates formation. It is known formation of silicates structures mainly depends on M_mO_n: SiO_2 correlation, ionic radiuses of metallic cations and physicochemical conditions of phase formation. To define dependence between stoichimetric composition and structure of different phases it is necessarily to study their structures formed in particular physicochemical systems. On examination the silicate phases formed in system M_mO_n-SiO_2 it was defined that atoms of Na, Ca, Mg, Fe, Co, Ni, TR are typical for metasilicates. In structure Na-metasilicate (McDonald and Cruickshank, 1967) - Na_2SiO_3 and Li - metasilicate (Hesse, 1977) - Li_2SiO_3 values of ionic radiuses Na^+ (0.99 Å) and Li^+ (0.68 Å) reflects as oxygen silicon chains. In structure Na-metasilicate distance between the same oxygen 4.81Å corresponding distance in structure Li-metasilicate ~ 4.67 Å. These two structures differ according to zigzagging Si-O chains. Deformation of Si-O radical in structure Li-metasilicate shows that oxygen has maximum density which reflects in values V_0 (the volume of one oxygen ion) for Na-metasilicate $V_0 = 25.40$ Å^3 ($\rho_{\text{Na-form}} = 2.68$ g/cm^3), for Li metasilicate $V_0 = 19.6$ Å^3 ($\rho_{\text{Li-form}} = 2.52$ g/cm^3).

Crystallochemical formula for pyroxene – Mg / $MgSi_2O_6$ / or M2 / M1 Si_2O_6 / shows that part of magnesium atoms substitutes by cations of other size. In position M1 magnesium atom substitution is followed by change of form and composition of Si-O radical and therefore structural unit with / $M1Si_2O_6$ / composition can be distinguished here. This explains the existence of double salts with composition $CaSiO_3 \times MgSiO_3 \rightarrow$ Ca /Mg Si_2O_6/ (Shirinova and Chiragov, 2012). In this case crystallographic positions of cations differ sharply. Mentioned structural peculiarities can be observed in structure of wollastonite – Ca_2 / $CaSi_3O_9$ / (Hesse, 1984) as well where two atoms of calcium can be substituted by other cations.

It is known in structure of pyroxene-johannsenite $CaMnSi_2O_6$ (Freed and Pealov, 1967) cations of calcium and manganese don't form pyroxene chains separately. In these structures Si-O radical distinguishes according to its activity which doesn't depend on ionic radiuses of metallic cations, but connects with particular conditions providing radical existence. This can be observed in structures of clinopyroxene. For instance, in structures of spodumene – $LiAlSi_2O_6$ or jadeitie – $NaAlSi_2O_6$ Li^+ and Al^{3+} or Na^+ and Al^3 together meet a demand of pyroxene radical.

In nature Ca, Mn containing metasilicates form minerals of two structural types – pyroxene-johannsenite – $CaMnSi_2O_6$ and pyroxenoid – bustamite – Mn_3Ca_3 /Si_3O_9/$_2$ (Aksenov et al., 2015). In the first a structural unit is represented by pyroxene structural block with composition /$Mn_2(Si_2O_6)_2$/, in the second – wollastonite structural block with composition - /Ca_2 $(Si_3O_9)_2$ /. In structure of johannsenite there are calcium atoms between structural units and in structure of bustamite three atoms of manganese and one atom of calcium distribute in four positions and this is followed by reduction of structure symmetry.

Distribution of metallic cations concerning chains is taken into account by observation of dependence of ionic radiuses values upon parameters of chains. In pyroxene chain general oxygen of two tetrahedral are in the same line and octahedral of metallic cations create zigzag columns. This connects with the following: the component part of chains is sorogroup Si_2O_7, height of which correspond to ribs of octahedral and equal ~ 3 Å and period of chains is 5.2 Å. Unlike the pyroxenes in structure Li and Na metasilicates zigzag-formation is found in Si-O chain and in distribution of metallic cations. In structure of wollastonite the chain of wollastonite forms from triorthogroup Si_3O_{10}. Inasmuch height of sorogroup out of proportion concerning ribs of calcium octahedra in this case triorthogroups as U-shaped adjust to borders of calcium octahedra and wollastonite chain with period 7.2 Å forms from equivalent triorthogroups.

Dependence of ionic radius value on temperature (qualitatively and quantitatively) is understudied during phase-forming. In the same structural types according to temperature deviation from gravity centre for different atoms will be various, i.e. dependence of effective ionic radiuses upon temperature will be different. The following crystallochemical features mainly affect it: 1) atom radius during ordinary temperature; 2) crystallochemical position of atom; 3) structure and weight of atom; 4) coordination number of atom: 5) energy of structure.

These features affect greatly on temperature expansion of effective ionic radiuses. By temperature increasing atoms oscillation occurs around its own gravity centre. In this case each atom has corresponding temperature of oscillation sphere. It's difficult to connect these structural features with atoms specific character. However, one can correlate ionic radiuses of two atoms being in different crystallochemical positions.

Atoms of manganese and ferrum are between atoms of magnesium and calcium according to radiuses values. By crystallization of manganese and ferrum silicates a compromise derivative appears – chains consist of sorogroup and triorthogroup as in structures of rhodonite – $CaMn_4Si_5O_{15}$ (Leverett et al., 2008) and pyroxmangite – $Fe_7Si_7O_{21}$ (Zanazzi et al., 2008). It's noteworthy there are octahedra of two types in octahedra column within structures of these minerals, they are: octahedral the ribs of which are connected with three similar octahedra and their general tops tie with sorogroup. The second type – octahedra connected with two octahedral, i.e. octahedra connected with triorthogroup. It shows according to temperature atoms oscillation sphere will be different, i.e. values of effective ions of cations radiuses connected with triorthogroup will be more than radiuses of metallic cations connected with sorogroup. Therefore crystallochemical formula of minerals can be represented as rhodonite $CaMnSi_{3+2}$ O_{15} and pyroxmangite – $Fe_7Si_{3+2+2}O_{21}$. Probably rhodonite and pyroxmangite with structural type of wollastonite can appear by high temperatures.

These patterns are not found in silicates where value of ionic radius of metallic cation is more than calcium size. For instance, strontium (R_{Sr}^{2+} =1.18 Å) regardless of temperature doesn't form structural type of calcium metasilicate. In structures of silicates with more condensate Si-O radicals calcium are not substituted by strontium ions.

Additional anions or anionic groups play an important role in structure of silicates. Structures of hydrosilicates according to structural peculiarities are divided into two different groups: the first (OH) includes coordination of metallic cation and silicon, and H_2O includes coordination of metallic cation. The second group oxygens of tetrahedral substitute (OH) group. For instance, in structure of afwillite – Ca_2 / Ca $(SiO_3\ OH)_2$ / × $2H_2O$ (Malik and Jeffery, 1976); synthetic K, Ho – triorthosilicate Ho - $K_3H_0Si_3O_8\ (OH)_2$ (Chiragov et al. 1979). In structure K, Ho – triorthosilicate Ho – octahedral and triorthogroups $Si_3O_8\ (OH)_2$ form holmium oxygen silicon heterogenetic layer which connects with hydrogen bond where in O - H … O' distance O - O' between adjusting layers 2.9 Å and length O - H=0.98 Å forms structure Ho-silicate, and potassium atoms are in its cavities. By temperature 580-650°C and as a result of $OH^{-}\rightarrow O^{2-}$ substitution mixed layer condensates and triorthogroup transforms to wollastonite chain. As a result of it a composite frame appears and potassium atoms with chemical composition K_3 / Ho $Si_3\ O_9$ / (Chiragov and Ragimov, 1986) fill its empties.

It is seen from crystallochemical formula of afwillite that its composition possesses water molecules of two types: as $(OH)^{-}$ group and H_2O. There are (OH) groups in tetrahedra in silicon coordinations and $(OH)^{-}$ and H_2O – in calcium coordinations. Therefore, in afwillite structure water molecules are lost within wide temperature range 250-450°C by low temperatures water molecules are lost and by high temperatures $(OH)^{-}$ groups transform to O^{2-}, i.e. 2 / SiO_3OH / transforms to / Si_2O_7 / as a result of it rankinite structure appears which finally transforms to mennonite – γ-Ca_2SiO_4.

Chemical activity of transformation can be represented as: $4Ca_3(SiO_3OH)_2 \times 2H_2O) \rightarrow 4Ca_3\ (SiO_3OH)_2 + 8H_2O \rightarrow Ca_{12}Si_8O_{28} + 4(OH) = 4\ Ca_3Si_2O_7 \rightarrow \gamma\text{-}4Ca_2SiO_4 + 4SiO_2$.

It is found that during solid-state reaction K, Ho triorthosilicate and Ca – hydrosilicate-afwillite inheritance of structural peculiarities remains in the products of transformation.

Thus, studying structures of metasilicates we can conclude: 1) cations with onion form coordination polyghedra and parent structural minals form from it and further structural unit, by its different polymerization different structural types form; 2) if chemical composition meets demand of particular structure there is no need of its crystallizing as another phase; 3) if different type structural units form in the same structure in this case crystalline structure with mixed structural types forms; 4) if in tetrahedra (OH)-group includes silicon coordination in this case Si-O radical complicates by temperature increase at first stage and further it will be simplified.

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METASİLİKAT QURULUŞLARININ FORMALAŞMASININ KRİSTALLOKİMYƏVİ XÜSUSİYYƏTLƏRİ

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İşdə metallik kationların, ilkin quruluş minallarının və quruluş vahidlərinin rolunun kristallokimyəvi araşdırmasının nəticələri əksini tapmışdır. Müəyyən edilmişdir: 1) əgər kimyəvi tərkib müəyyən quruluşun tələblərini ödəyirsə, onun başqa fazada kristallaşması mümkün olmur; 2) əgər metasilikatın tərkibində kiçik və iriölçülü kationlar iştirak edirsə, bu halda kompromis yaranır – tetraedr radikalları diortoqrup və triortoqruplardan təşkil olunur; 3) bu və digər quruluşlar müxtəlif quruluş vahidlərindən əmələ gəlirsə, bu halda qarışıq quruluş tipli kristal quruluşları formalaşır; 4) əgər tetraedrdə (OH)-qrupu silisiumun koordinasiyasına daxil olursa, bu halda temperaturun artması ilə Si-O radikalı mürəkkəbləşir və sonra sadələşir; 5) bərkfaza reaksiyasında K, Ho –triortosilikat və Ca –hidrosilikat – avfillitin quruluş xüsusiyyətlərində irslilik prinsipi saxlanılır.

Açar sözlər: *kristallokimya, metasilikatlar, quruluşun formalaşması*

КРИСТАЛЛОХИМИЧЕСКИЕ ОСОБЕННОСТИ ФОРМИРОВАНИЯ СТРУКТУР МЕТАСИЛИКАТОВ

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В работе представлены результаты кристаллохимического исследования роли металлических катионов, родоначальных структурных миналов и структурных единиц в процессе формирования структур метасиликатов. Установлено, что: 1) если химический состав удовлетворяет требованию определенной структуры, тогда нет необходимости ее кристаллизации в форме другой фазы; 2) если в составе метасиликатов имеются и мелкие, и крупные катионы, то появляется компромисс – цепочка состоит из диортогрупп и триортогрупп; 3) в одной и той же структуре образуются разнотипные структурные единицы, из которых формируется кристаллическая структура со смешанными структурными типами; 4) если в тетраэдре (OH)-группа входит в координацию кремния, то с увеличением температуры на первом этапе Si-O радикал усложняется и далее упрощается; 5) в твердофазной реакции K, Ho – триортосиликата и Ca – гидросиликата - авфиллита в их продуктах превращения сохраняется унаследование структурных особенностей.

Ключевые слова: *кристаллохимия, метасиликаты, формирование структур*