

## THE ESSAYS ON FUNDAMENTAL AND GENETIC MINERALOGY: 5. MINERAL SPECIES AND THE METASTABLE MINERALIZATION

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The problems of the valid mineral species definition are discussed: in case of the metastable and convergence mineralization.

4 figures, 41 references.

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In the previous articles (Borutzky, 2005; 2006; 2008; 2009) the author made an attempt to convince the readers that mineralogy is in need of systematization of the *real objects* of investigation (minerals), and not their conceptual abstract character (*minerals concept*). Secondly, as far as mineralogy studies mineral matter within *geology*, the *mineral species* should be determined and systematized according to the laws of geology – *natural-history* science unlike that of chemical or crystallochemical approaches implanted nowadays. Since minerals are geological bodies which are formed in *nature*, i.e. independent, conditions and later occur in specific physical-chemical conditions, the totality of individuals with variations in chemical composition and structure should be merged into species according to the *natural* criteria discovered during investigation of geological objects and processes, and not to the *formal* features accepted in chemistry and crystallochemistry and dissimilar to *real* correlations, complicated and diverse, observed in nature.

In the first essay (Borutzky, 2005), using correlation between another natural-history science – biology, the author indicated, that despite the importance of such fundamental characteristics as chemical composition and crystal structure, the basic *species-forming* criterion for mineral species, by analogy with biology, should be their *genetic* characteristic, which defines the possibility of forming and the existence of certain chemical compound and crystal structure in certain physical-chemical parameters in certain geological conditions. The author believes that such a criterion for instance should be *confidence* that the candidate that is to become a valid mineral species has its *own stability field*, separated from the others' by *natural bounds*. In this field the chemical composition and some

structural features can vary *continuously* within this or another limits. The bounds of the stability field (and hence – this mineral species) are determined as the phase boundaries – solidus, phase transformations, solvus, where the features and composition of the mineral matter change dramatically: the individuals of the mineral species get destroyed, transformed or replaced by another mineral species.

The application of these ideas was developed in the second essay (Borutzky, 2006) on the example of "*natural-genetic*" nomenclature and systematization of alkali feldspars. It was indicated that the term "mineral species" is not set in a rigid convention and constant; the composition and features of its individuals vary according to the changes in character of mineral-forming conditions. Thus, the high-temperature sanidine and anorthoclase are the members of the practically *complete* isomorphic series between potassium and sodium feldspars. These species are separated by the boundary of reconstructive phase transformation with the change in symmetry  $C2/m \rightarrow C\bar{1}$  in  $Ab_{63}Or_{37}$  (room temperature) and nearly  $Ab_{80}Or_{20}$  (on the solvus curve, at approximately 650°C) respectively; and not in  $Ab_{50}Or_{50}$  according to the "chemically" proven "50% rule", recommended by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA). The low-grade feldspars – microcline and "low" albite, on the contrary, are divided by a field of solvus, and sodium admixture in microcline is under 10 relative %, and potassium admixture in albite – under 5 relative % (there is no question of applying the "50% rule"). The fundamentally important issues here are: evidence by mineralogists-geologists and improvement of some common misunder-

standings. Thus, I totally agree with Evgeny K. Lazarenko (Lazarenko, 1963) that *continuous* isomorphic series should not be divided into formal species, corresponding to its end-members, exactly due to this continuity – this is one (single) valid mineral species. In alkali feldspars the isomorphic series between  $\text{KAlSi}_3\text{O}_8$  and  $\text{NaAlSi}_3\text{O}_8$  becomes not only complete, but continuous – above the point of phase transformation at temperatures greater than  $980^\circ\text{C}$  and water pressure 1 kbar; the feldspars in this series remain monoclinic. On the other hand we cannot disagree with Andrey G. Bulakh (Bulakh, 2004), that both microcline and sanidine are one and the same mineral species, because they differ only by a degree of Si and Al ordering in tetrahedral framework (minerals which are formed due to orderings are not approved by the CNMNC IMA as mineral species). This is misunderstanding, because the process of Si/Al ordering in this case is followed by the phase transformation  $C2/m \rightarrow C\bar{1}$ , resulting in two separate stability fields: the microcline and the sanidine one. Taking into account genetic information – considerable differences in formation conditions, one has no doubt that these are different mineral species.

The correlation of mineral species and *varieties* were thoroughly discussed earlier (Borutzky, Urusov, 2008). Their differences are in estimation of *importance* of the features observed in totality of the mineral species compared. According to the principle of "Ockam's razor" one should not proliferate terms as happens in the modern mineralogy, unless there is an urgent necessity. It is obvious to everyone that amethyst or morion are varieties of quartz. In more complicated cases, for example, in eudialyte or labuntsovite "groups" we should be more careful in formal application of the "rule of dominance" ("50% rule") implanted by CNMNC IMA, but use more considerable criteria. Formal statement of change in symmetry (space group) without reasoned explanation for change is of concern. Reasons can be various. Quite often this is slight, insignificant displacement of atoms, as observed, for example, in anorthite. In other cases, the differences in symmetry are "set" by the scientific researcher during the crystal structure refinement, according to a number of reflexes involved in the analysis, especially the weak ones from "loose" weakly fixed atoms. It is common that the scientists do not understand this and it leads to further

speculation around space groups and the discovery of "new" mineral species. Finally, for appropriate comparison of the minerals the scientists deliberately diverge from the strict analysis and choose the largest unit or the high-symmetry space group. The example, again, can be feldspars, in which the primitive units of triclinic albite or microcline are compared with the primitive unit of monoclinic sanidine and doubled body-centered unit of anorthite. Considering the above-said, Vadim S. Urusov believes that the most important, i.e. species-forming, structural feature should be *structural type*, which reflects the structural identity of the mineral crystal lattice and not its space group.

It is noticeable that in the time of pandemic of "proliferation" of mineral species in mineralogy, the imaginary pseudo-isomorphic series are also considered. The glaring example is eudialyte, considered in detail earlier (Borutzky, 2007; 2008; 2009). Thus, aggressively implanted "*eudialyte-kentbrooksites*" (instead of traditional classic *eudialyte-eucoleite*) isomorphic series (Johnsen *et al.*, 1998; Johnsen, Grice, 1999; Johnsen *et al.*, 2003) is based on substitution of an *additional* Si atom for an additional Nb atom in the silicon-oxygen frame of *kentbrooksites*. The substitution occurs in one of 22 additional positions of the crystal structure (oxygen and frame silicon sites are not considered); it is substituted for only 55% of 1 formula unit, but it did not stop the authors "deduced" the formula of a hypothetical end-member with  $\text{Nb} = 1.00$ . However, even conceding total substitution (although in all known structural analyses it is below  $\text{Nb} = 0.80$ ), which corresponds to  $\text{Nb}_2\text{O}_5$  3.60–3.80 wt.%, and does not exceed 1 at.% from the total chemical composition of a mineral, I could agree with Andrey G. Bulakh (Bulakh, 2004) saying that this micro-impurity has no effect on the structural topology and features of the mineral. It should be noted that this additional position also usually shows simultaneous substitution by titanium and zirconium, i.e. the supposed isomorphic series is not binary but complex:  $\text{Si} \leftarrow \text{Nb, Ti, Zr}$ . An identical situation occurs with new eudialyte mineral – *khomyakovite*, in which silicon in this position is substituted by tungsten for 56%. In general, eudialyte is a complex analogue of zeolites, ion-exchanger, where up to one third of the Periodic Table can be involved in the composition as micro-impurities at any one time. However this is

not followed by the formation of individual pure isomorphic series. The complex simultaneous substitution of various components in one and the same sites leads to distortion of the structure, transformation of co-ordination polyhedra, displacement of atoms and therefore lowering of symmetry, doubling of  $c$  parameter in a cell and change in physical and spectroscopic features of the mineral. However all these changes could be considered within the single stability field of one mineral – eudialyte. Unlike the decisions of CNMNC IMA, the character of these chemical and crystallochemical features of eudialyte does not qualify as significant characteristics for a discovery of individual valid mineral species. Eudialyte and minerals similar to it are considered here as *minerals of variable composition with variable structure (MVCVS)* – i.e. one (single) mineral species.

It well may be so, that some of these compounds (which are considered as chemical and structural varieties of eudialyte) with time will “deserve” the status of mineral species but in order to be so, the general basic condition should be fulfilled – their individual stability field should be proven to exist in a certain mineral-forming processes. We believe, that investigation of typomorphism of eudialyte varieties are the most perspective in this respect (Borutzky, 2009).

### Metastable state and metastable crystallization of minerals

*“The mighty nature is full of wonders!”*  
Alexander N. Ostrovsky

As we saw above, the presence of a stability field is in general a compulsory condition for the separation of the mineral species. But a stability field is inherent in only *equilibrium* crystallization of a mineral, and mineral-forming processes in nature are not always in equilibrium. Does this mean that we have to “sustain a defeat”, refuse the *genetic species-forming* criteria and return to the chemists’ “formality”? By no means. Mineralogy should investigate real natural minerals, and not their “made-up” images. One should take into account all the peculiarities of mineral formation in nature and try and find their place in mineralogical nomenclature and systematization.

Generally speaking, the *metastable state* – is not an exception, but the *usual* form of

existence in nature. Almost everything we are able to observe at present (possibly despite the products of the modern mineral-forming process) does not correspond to the primary equilibrium conditions that existed when the mineral was formed. It did not achieve equilibrium with its present environment so far, hence is in a metastable state.

The typical and most simple example of such correlations are polymorphs of  $\text{SiO}_2$  (Putnis, McConnell, 1980; Putnis, McConnell, 1983). A priori, the position of atoms at a high temperature has a higher thermodynamic probability, than at a low temperature; the internal energy decreases during cooling and any transformations. That is, in order to achieve equilibrium with the new low-temperature conditions, the structure should attain reconstructive change with commensurate internal energy decrease. However, this reconstruction happens differently: in one cases – with considerable re-organizing of the structure (*structural-reconstructive*, “spasmodic” transitions), in other cases – only with the minor atom displacements and structure distortions (*gradual* transitions). The first type is comparable with thermodynamic transformations of the first type – when at the temperature of transformation we observe the gap between the change in the first-order derivative of the free energy function: entropy, volume and enthalpy (a hidden heat effect of transformation) at the temperature of transformation. The second type corresponds to *thermodynamic transformations of the second type* – all the above-mentioned functions are continuous, and the gaps are typical only for second-order derivatives of the free energy function (this, for instance, specific transformation heat). The structural-reconstructive transitions are more energy-intensive; in order for such a transition to take place the matter should be supplemented by additional *energy of activation*, some *energy barrier* should be overcome – therefore the real processes are strongly dependant on the *kinetics* of the mineral-forming process. When the energy barrier is not overcome, the matter can remain in the other’s stability field, i.e. be in metastable state.

#### Silica polymorphs

The polymorphs of  $\text{SiO}_2$  depend both on temperature and pressure (Fig. 1, 2). We will not describe here the high-pressure modifications: coesite (monoclinic,  $C2/c$  or  $Cc$ ) and stishovite (tetragonal,  $P4_2/mnm$ ) with their

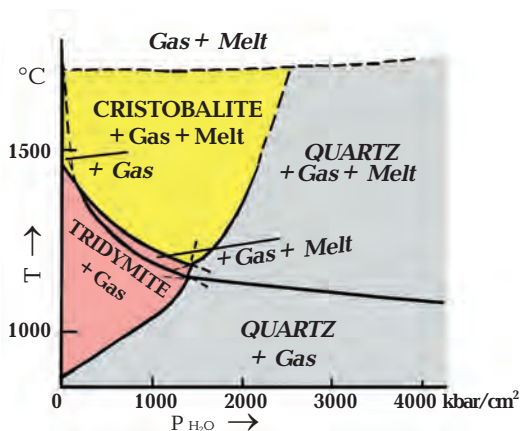
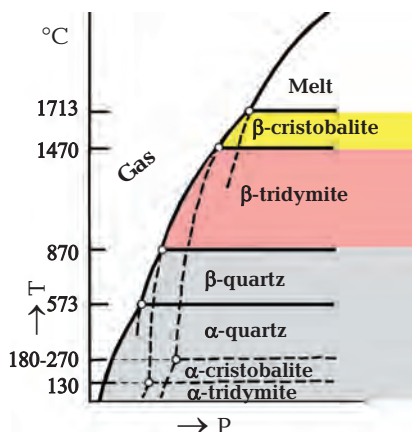


Fig. 1.  $\text{SiO}_2 - \text{H}_2\text{O}$  system by increased pressure. After I.A. Ostrovskiy et al., 1959.

Fig. 2. The scheme of polymorphic transformation of  $\text{SiO}_2$  in dry conditions, by normal pressure. After K.N. Fenner (Classic works..., 1937).



dense structures, probably typical only for abyssal zones of the Earth. Quartz occurs in the wide area of temperatures and pressures: at  $P = 40$  kbar and  $T = 1300^\circ\text{C}$ ,  $P = 40 - 80$  kbar and  $1000 - 700^\circ\text{C}$ , at  $100$  kbar and  $T = 1200^\circ\text{C}$  it transforms into coesite, at  $100 - 140$  kbar and  $1000^\circ\text{C}$  it transforms into stishovite. Cristobalite and tridymite are unstable at the high pressures. High-temperature  $\beta$ -cristobalite at normal pressure exists within the temperatures  $1710 - 1470^\circ\text{C}$ . Under cooling till  $1470^\circ$  it transforms into high-temperature  $\beta$ -tridymite, stable to  $870^\circ$ , which at this temperature transforms into high-temperature  $\beta$ -quartz.

The structure of cubic  $\beta$ -cristobalite ( $Fd\bar{3}m$  or  $P2_13$ ;  $a = 7.11 \text{ \AA}$ ) (Wyckoff, 1925) can be presented as succession of two-dimensional tetrahedral layers, parallel to (111). The tetrahedra are tilted to different sides from this plane; the atoms of oxygen form closest packing  $ABCABC\dots$ . The structure of hexagonal  $\beta$ -tridymite ( $P6_3/mmc$  or  $P62c$ ;  $a = 5.04$ ,  $c = 8.24 \text{ \AA}$ ) is a three-dimensional frame with the hexagonal rings of  $\text{SiO}_4$  tetrahedra. The baselines of tetrahedra in all these rings are parallel to (0001), and the apexes are oriented alternately up and down. Thus they form a two-layered structure  $ABAB\dots$  parallel to (0001). The structure of hexagonal  $\beta$ -quartz ( $P6_22$  - right and  $P6_422$  - left;  $a = 4.999$ ,  $c = 5.457 \text{ \AA}$ ) is also presented by a frame, but  $\text{SiO}_4$ -tetrahedra are located on different layers and are twisted right or left along hexagonal two-way spiral axis. The transitions

between the high-temperature modifications are structural-reconstructive, because considerable additional energy is required. For instance, the heat of transformation of  $\beta$ -cristobalite into  $\beta$ -quartz is  $29 \text{ cal/g}$  - slightly less than the heat of melting of  $\beta$ -quartz ( $39 \text{ cal/g}$ ). Metastable crystallization of the high-temperature forms of  $\text{SiO}_2$  outside their stability fields has been observed. The further partial transitions  $\beta$ -cristobalite  $\rightarrow \beta$ -tridymite and  $\beta$ -cristobalite  $\rightarrow \beta$ -quartz are activated by the presence of different mineralisers. However, under reverse dry annealing at  $1000 - 1200^\circ\text{C}$  (i.e. in the stability field of tridymite), metastable cristobalite was formed, and then partially transformed into tridymite.

Besides the high-temperature modifications of these minerals, there are the low-temperature ones. The most abundant and well-known is trigonal low-temperature  $\alpha$ -quartz ( $P3_121$  - right and  $P3_221$  - left;  $a = 4.913$ ,  $c = 5.405 \text{ \AA}$ ). At normal pressure the transformation  $\beta \rightarrow \alpha$  quartz occurs at  $573^\circ\text{C}$ . The temperature of transformation rises with increasing pressure: to  $599^\circ\text{C}$  ( $1000$  bar) and  $704^\circ\text{C}$  ( $5000$  bar). This  $\beta \rightarrow \alpha$  transition is reversible and extended in the temperature range  $555 - 574^\circ\text{C}$  depending on the type of quartz-bearing rocks and impurities in quartz: germanium increases the temperature of transition, aluminium and lithium - decrease it. Atoms of Si misplace insignificantly, i.e. this is the transformation that could be characterized as of the second type. On the other hand, this transition is evidently not gradual: the

thermal capacity of quartz increases (with peak in interval 550–577°C and maximum at 574.1°), and then gradually decreases. The temperature of transition in this interval is 9.2 cal/g, although it is only 1.5 cal/g at  $\beta \rightarrow \alpha$  transition. The unit cell parameters also change unevenly (at 575–570°:  $a = 4.993 \rightarrow 4.983$ ,  $c = 5.430 \rightarrow 5.400$  in  $\beta$ -quartz;  $a = 5.027 \rightarrow 4.983$ ,  $c = 5.580 \rightarrow 5.400$  in  $\alpha$ -quartz). Taking into account the aforesaid and the importance of the low-temperature quartz for the analysis of geological objects, it is reasonable to consider it as a valid mineral species of a silica group.

The low-temperature modifications of cristobalite and tridymite are more problematic; as they are an example of an *alternative behavior* of silica minerals (Putnis, McConnell, 1980; Putnis, McConnell, 1983).  $\beta$ -cristobalite can transform into  $\beta$ -tridymite, but alternatively can transform into the low-temperature  $\alpha$ -cristobalite (tetragonal  $P4_12_12$  or  $P4_22_12$ ;  $a = 4.9709$ ,  $c = 6.9278 \text{ \AA}$ , see Pluth *et al.*, 1985). The transition  $\beta \rightarrow \alpha$  cristobalite is also reversible, at temperatures of 180–270°C with maximum at nearly 220°C, depending on crystallinity. Microimpurities, stabilizing the high-temperature  $\beta$ -phase, also affect the character of transition resulting in:  $\text{SiO}_2 \rightarrow \text{Si}_{1-x}\text{Al}_x\text{M}_{x/n}^{n+}\text{O}_2$ , where  $\text{M} = \text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{La}^{3+}$  (Perrotta *et al.*, 1989; Saltzberg *et al.*, 1992; Thomas *et al.*, 1994). This transition is also characterized by significant hysteresis, i.e. difference between the temperatures of transformation at heating ( $\alpha \rightarrow \beta$ ) and cooling ( $\beta \rightarrow \alpha$ ). Thus, for instance, in the vanadium-containing system ( $\text{Si}_{0.85}\text{V}_{0.15}\text{Na}_{0.15}\text{O}_2$ ) the  $\alpha \rightarrow \beta$  transition was observed at  $T = 246^\circ\text{C}$ , and  $\beta \rightarrow \alpha$  – at  $231^\circ\text{C}$  (Bruhns, Fischer, 2000), although it is unclear whether vanadium is occupies a site in the cristobalite structure or only acts as a catalyst. The heat of  $\alpha \rightarrow \beta$  transformation of cristobalite is even less than that of quartz (4.4 cal/g). But the most alerting fact is that  $\alpha$ -cristobalite has no stability field of its own, more precisely – it is within the stability field of  $\alpha$ -quartz. i.e. both  $\beta$ - and  $\alpha$ -cristobalite can be metastably formed within the stability field of  $\alpha$ -quartz.

The crystal structures of  $\alpha$ - and  $\beta$ -cristobalite and their  $\beta \rightarrow \alpha$  transformation were studied in detail by Wyckoff, 1925; Nieuwenkamp, 1937; Peacor, 1973; Wright, Leadbetter, 1975; Hatch, Ghose, 1991. The scientists were not satisfied with the *ideal* cubic model

of "C9-type"  $\beta$ -cristobalite (Wyckoff, 1925). It was later designated as  $Fd\bar{3}m$ , because otherwise it could not be interpreted in detail compression of the structure with rigid angle  $\text{Si-O-Si} = 180^\circ$  along [111] axis and interatomic distance  $\text{Si-O} = 1.540 \text{ \AA}$  under its transformation into the structure of  $\alpha$ -cristobalite with  $\text{Si-O-Si} = 146^\circ$  and  $\text{Si-O} = 1.609 \text{ \AA}$ . In the new hexagonal model (Nieuwenkamp, 1937; Peacor, 1973; Wright, Leadbetter, 1975) the 16 atoms of oxygen occupy a 96(h) system with 1/6 occupancy in each sixth site, which is related to a rotation of  $60^\circ$  around the Si-Si axis along a small circle with radius  $0.45 \text{ \AA}$ , resulting in  $\text{Si-O} = 1.609 \text{ \AA}$  and an  $\text{Si-O-Si}$  angle =  $146^\circ$ . The structure of  $\beta$ -cristobalite is interpreted as the average of 6 domains around [111] axes of the cubic phase "C9". The total symmetry of these twins was presumed to decrease from  $Fd\bar{3}m$  to  $\bar{I}42d$ , which is not a super-group  $P4_32_12$  or  $P4_12_12$  (Wright, Leadbetter, 1975; O'Keefe, Hyde, 1976). The transition into  $\alpha$ -phase ( $\bar{I}42d \rightarrow P4_12_12$ ) is a further rotation of the  $\text{SiO}_4$ -tetrahedra. Finally, Dorian M. Hatch and Subrata Ghose (Hatch, Ghose, 1991) noted that the  $a$  parameter in  $\beta$ -cristobalite at  $205^\circ\text{C}$  ( $7.195 \text{ \AA}$ ) is slightly less than in the initial cubic structure  $Fd\bar{3}m$  ( $7.432 \text{ \AA}$ ), and although the  $\text{Si-O-Si}$  angle is still  $180^\circ$ , the distance  $\text{Si-O}$  is  $1.609 \text{ \AA}$ , i.e. corresponding to  $\alpha$ -cristobalite. Applying formalization of Landau, they showed the possibility of formation of 12 domes during  $\beta \rightarrow \alpha$  transition: 1) transformation twins, with loss of  $L_3$  along [111], 2) enantiomorphous twins, with loss of symmetry centre, and 3) anti-phase domains, with loss of translation vector  $1/2[110]$  ( $F \rightarrow P$ ). This structural model correlates with the X-ray model by Donald R. Peacor (Peacor, 1973), although the true inner symmetry of these domes in the high-temperature  $\beta$ -phase is  $P4_32_12$  (or in enantiomorphous group –  $P4_12_12$ ) and not  $\bar{I}42d$ , as the other researchers assumed (Wright, Leadbetter, 1975; O'Keefe, Hyde, 1976). In a  $\beta$ -phase these  $P$ -domains are both microscopic and dynamic, imitating higher symmetry, and in  $\alpha$ -phase they are macroscopic and static.

Thus such a complicated mechanism of  $\beta \rightarrow \alpha$  transformation is interpreted as fluctuating-caused transition of the first type. During transformation into  $\alpha$ -cristobalite,  $\text{SiO}_4$ -tetrahedra rotate simultaneously and translate along  $x$  and  $y$  axes, which is related to a gradual  $\text{Si-O-Si}$  angle divergence from  $180^\circ$  in an ideal structure (Pluth *et al.*, 1985).



However, the displacement leap is strictly limited by temperature ( $\sim 220^\circ\text{C}$ ), whereas fluctuations and ordering are observed in a larger range, entailed by changes in such features as, for instance, elastic parameters  $C_{11}$ - $C_{12}$ . Thus, we have a combination of thermodynamic transitions of the first and second type.

Similar effects are typical for the transition  $\beta \rightarrow \alpha$  tridymite, in the interval  $117 - 163^\circ\text{C}$ . Three phases of  $\alpha$ -tridymite, stable at the room temperature, were discovered: orthorhombic (or triclinic, but with  $\alpha = \beta = \gamma = 90^\circ$ ) with  $a = 9.932$ ,  $b = 17.216$ ,  $c = 81.854 \text{ \AA}$  (Konnert, Appleman, 1978), monoclinic  $Cc$  (Dollase, Baur, 1976) and monoclinic with unrequited superstructure MX-1 (Graetsch, Topalovich-Dierdorf, 1996). Besides, two "intermediate" structures were established (Wennemer, Thompson, 1984; Pryde, Dove, 1998). The heat of transformation  $\beta \rightarrow \alpha$ , calculated in total ( $\alpha \rightarrow \beta_1$  0.43 cal/g;  $\beta \rightarrow \beta_1$  0.23 cal/g) does not exceed 0.66 cal/g. Similar to  $\alpha$ -cristobalite,  $\alpha$ -tridymite has no stability field of its own and is formed in the stability field of  $\alpha$ -quartz.

The low-temperature forms of cristobalite and tridymite are typical for the opal, chalcedony, agate deposits among volcanic rocks. They occur as overgrowths on zeolite crystals in cavities in basalts, in sedimentary rocks – opokas, tripoli, diatomites.  $\alpha$ -cristobalite often occurs along with opal globules and micro-globules (Fig. 3). Sometimes  $\alpha$ -cristobalite is observed together with  $\beta$ -cristobalite, which indicates the metastable crystal-

lization of a high-temperature form outside its stability field, with a further partial transformation into a low-temperature form. The attempt to classify opals in mineralogical terms was made by Jones and Segnit (1971, 1972). They highlight three main types: 1) "opal-C" – with an ordered  $\alpha$ -cristobalite forming horizontal layers in the bottom parts of agates and geodes of Uruguay type, 2) "opal-CT" – with a disordered  $\alpha$ -cristobalite and tridymite as flaky-spherulitic aggregates and cristobalite as pencil aggregates of lussatite, and 3) "opal-A" – as an amorphous non-crystallized hyalite. In "opals CT", V.G. Balakirev *et al.* (Balakirev *et al.*, 1977) determined three types of particles: (1) hexagonal or pseudo-hexagonal platelets  $100 - 200 \text{ \AA}$  forming tracery aggregates, (2) flattened fibers  $100 - 200 \text{ \AA}$  thick (in transparent opals), and (3) large fibers  $300 - 1000 \text{ \AA}$  across (in milky opals). Using micro-diffraction cristobalite and tridymite were determined in the samples. The experiments on hydrothermal sedimentation of cristobalite (Flörke *et al.*, 1990) showed, that various forms of  $\text{SiO}_2$  (hyalite, quartz, cristobalite) form together, although tridymite crystallized only at high temperature ( $750^\circ\text{C}$ ) as  $\beta$ -modification. Cristobalite also crystallized at the temperatures over  $250^\circ$  and later transformed into the  $\alpha$ -modification at various times depending on the level of ordering in specimens.

Considering the above said, one should admit that the nomenclature of low-temperature cristobalite and tridymite is unclear. The

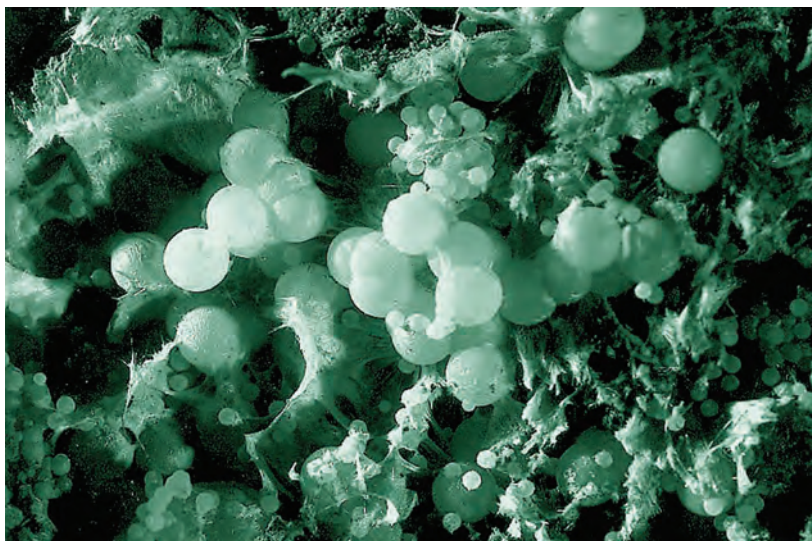


Fig. 3. Globular and microglobular opal with cristobalite at Pomachskoye agate deposit, Georgia.  $\times 30$ . After L.M. Lebedev, 1965.

absence of individual stability fields, uncertain character of complicated "uneven-extended" transitions which cannot be classified as thermodynamic ones of the first or second types, weak energy effects — leads us to consider them as *varieties*, depending on gradual changes, and not as individual *mineral species*. However, the situation might change with further investigation, as happened with  $\alpha$ -quartz which is obviously more stable and abundant in nature.

### Alkali feldspars

Restoring the conditions of crystallization and post-crystallization transformation using physical-chemical simulation, we face the totality of kinetically different parallel processes. The case with  $\text{SiO}_2$  polymorphs was relatively simple as only structure was subject to change with constant chemical composition. In the minerals with variable composition both can change.

As an example I will use well-studied alkali feldspars (Fig. 4), which for I suggested natural-genetic nomenclature of minerals (Borutsky, 2006). Under lava quenching their relic state, which is close to their initial state, remains. Whereas under slow crystallization of a melt, both the structural state and chemical composition of a feldspar change, attaining equilibrium with the later low-temperature stages of a rock. In the latter case the components can re-distribute and order in the feldspar framework, as a result of diffusion. The diffusion of Na and K in the hollows is more rapid than Si and Al in the frame. In the next stage the ordering of alkali reaches the first stages of "exsolution": first — spinodal, then — coherent. The phase exsolution was deliberately mentioned in quotes, because these phases are rather peculiar. The spinodal exsolution results in undulating fluctuations of a composition, from K- to Na-feldspar without phase interfaces. Coherent "phases" are essentially potassic and essentially sodium within a single Si/Al framework, they are detectable in X-ray diagrams as cells with a different  $a$  parameter, equal  $b$  and  $c$  parameters, and angles distinctly different from the angles of albite and K-feldspar cells. Such morphology of the cells enables them to adapt to each other whilst still within the single crystal space, as a result the lattice is tensed, i.e. has surplus internal energy. Si/Al ordering has the same results. For instance, in K-feldspar (i.e. without influence of a sodium component) a pseudo-microcline lattice ap-

pears that is visible under SEM — *tweed* structure of *orthoclase*; it is both monoclinic and triclinic with gradual transformations in between, i.e. even without phase interfaces.

The general principles of the behavior of feldspars are written in the fundamental work (Putnis, McConnell, 1980; Putnis, McConnell, 1983). We know that the stable low-temperature forms of alkali feldspars are *microcline* (below  $500\pm 50^\circ\text{C}$ ) and low albite ( $680\pm 20^\circ\text{C}$ ). However, according to kinetic limitations, the direct transition of sanidine and anorthoclase (or analbite) into these modifications is not always possible as the activation energy of transformation into the stable form cannot be overcome as one or another temperature conditions. Thus, the mineral matter will remain as metastable or will transform into the stable form gradually, via a number of intermediate close states, according to the "Ostwald Step Rule". An equilibrium can be reached for kinetically faster processes but not for the slower, therefore the exsolution of K- and Na- phases outstrips the process of exsolution of Si/Al-ordering in exsolved phases, and the Na-phase will always be better ordered and purer than the potassic one. If we use the equilibrium phase diagrams insufficiently critically, for, say, the estimation of the temperature conditions of postcrystallizing history of the feldspars, then we will get lower temperatures "by sodium" than "by potassium".

The stable low-temperature forms of alkali feldspar are nevertheless formed, due to the relatively high temperatures required for the heat fluctuations to overcome the energy barriers. It is known, that depending on geological history, either homogeneous microcline and low albite, or their conforming co-growths as crypto-, micro- or macro-perthites form. They are formed not only under the process of phase exsolution, but under their *collective re-crystallization*, which takes place with an increased role of water — post-magmatic solutions in the primary-magmatic system. In the range of stability fields of microcline and albite, variations in chemical composition keep on changing in response to changes in the physical-chemical parameters until almost pure  $\text{KAlSi}_3\text{O}_8$  with impurity of Na-component under 10 relative %, and  $\text{NaAlSi}_3\text{O}_8$  with impurity of K-component under 3–5 relative %, with distinct phase interfaces and change in the internal morphology of the exsolved phases: from peri-

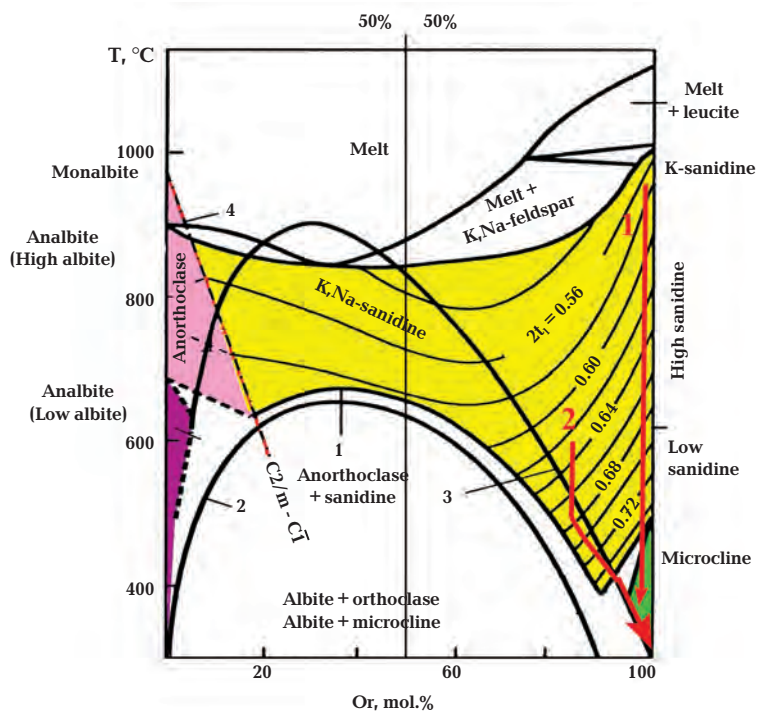


Fig. 4. Diagram "T-x" by E.E. Senderov (1990), composed for  $P = P(H_2O) = 1$  kbar, considering degree of Si/Al-ordering of the phases; for explanation the natural-genetic nomenclature of alkali feldspars (Borutzky, 2006).

The explanation the natural-genetic nomenclature of alkali feldspars: 1 – the true-equilibrium coexistence curve (after Senderov), 2 – analbite (high albite)-sanidine solvus, 3 – albite (low albite)-microcline solvus, 4 – non-tempering phase transition between monoclinic and triclinic feldspars. Red arrows indicate: 1 – metastable crystallization of adularia, 2 – metastable formation of a "tweed" orthoclase.

cline to albite twins in Na-phase and to albite-pericline (*twin lattice*) in K-phase.

Thus, along with "alkali K,Na-feldspar", "sanidine", "anorthoclase", "microcline" and "albite" having their own stability fields with natural boundaries – there are minerals which we can specify as valid mineral species which in nature include a number of metastable states of feldspar matter that cannot be ignored but whose status in mineralogical nomenclature and classifications is less determined.

These, first of all, are *adularia* and *orthoclase*.

It is well-known, that *adularia* forms under low-temperature hydrothermal conditions – in the "alpine" veins, deposits of gold, during zeolite stage of pegmatite-forming process etc. Judging by the character of mineral associations and immediate co-occurrence with low albite and microcline, it crystallizes metastably within the stability field of microcline. Its sterility regarding micro-impurities and specific crystal morphology is confirmed. Nevertheless, the structural state of *adularia* corresponds to sanidine, even "high sanidine". This fact even amazed scientists, because "high sanidines" (the most Si/Al-disordered potassic feldspars) were described not from volcanic rocks, but from *adularia*-bear-

ing veins. It also should be noted, that "sanidine", being formed during diagenesis of marine sediments, strictly speaking should be identified as *adularia* and not as sanidine. Thus, we again face the well-known problem of crystallization of the high-temperature modification outside its stability field, or rather – its absence. At the same time, genetically, *adularia* is a fully determined mineral with distinctive typomorphic features and is important for geological investigation. So, can one determine *adularia* as a valid mineral species? We believe not: it is only a variety of feldspar. Genetically important variety! In this connection we have to remind once again we previously wrote (Borutzky, 2005; 2006): the term *variety* is no less important a category for mineral systematization, than *mineral species*, and it is time to stop the mass action for transforming known mineral varieties into individual species.

*Orthoclase* was mentioned before. *Orthoclase* is not a synonym of potassic feldspar, but its specific modification, which is optically (and sometimes X-ray) monoclinic but built of triclinic blocks, i.e. intermediate between sanidine and microcline. Apparently, *orthoclase* should not be determined as a valid mineral species, but, strictly speaking it is nei-



ther variety, nor mineral aggregate — mineralogists did not conceive how to systematize such a natural mineral objects.

### On convergence of the mineral-forming processes and "convergent" minerals

In view of the problem examined, one should dwell on convergence of mineral-forming processes, i.e. forming one and the same minerals or mineral associations under different geological conditions. The detailed overview of such a convergence and convergence of typomorphic features of minerals, was made by Fedor V. Chukhrov in the book "Typomorphism of minerals and its application" (1972). According to academician Chukhrov, the "convergence of the first order" can be determined when the minerals of one and the same species (or association) occur both in endogenic and supergene processes; and the "convergence of the second order" — when they occur either in endogenic or supergene processes. The convergent minerals can also differ by a range of thermodynamic conditions of formation — the wider or narrower. The convergence of the 1<sup>st</sup> type is more typical for quartz. Pyrite and chalcopyrite are formed from the early magmatic crystallization stage ending with the supergene processes. Titanium oxides — rutile, brookite and anatase crystallize both at high temperatures and under supergene conditions by leucogenisation of the primary titanium-bearing minerals. Minerals with complex chemical composition can also be convergent, such as alkali feldspars, aegirine, riebeckite, reedmergnerite, elpidite, labuntsovite etc. Although they are typical of alkaline granites, syenites and pegmatites, they were discovered in association with authigenic minerals in the limnic sediments of the Tertiary formation Green-River in the USA. In the book mentioned above there are multiple examples of minerals from different classes, with a smaller range of conditions of formation. There are also examples of convergent minerals of the 2<sup>nd</sup>-type given, but in my opinion, they are less convincing because they are not mineral species but varieties, which obviously occur at narrower variations of temperature, pressure and chemism of a mineral-forming environment. Comparison of convergence of supergene and hypogene mineral-forming processes is presented in the later papers by

Fedor V. Chukhrov (Chukhrov, 1979; 1980). He analyses not so much the differences in physical-chemical conditions, as in the sources of solutions: "the same minerals, typical for supergene processes, can be formed from cooled thermal solutions; it enables one to talk about convergence of mineral formation from both ascending thermal solutions and solutions of supergene zone, which were not affected by hypogene heat" (Chukhrov, 1980, p. 102).

Analysing the data on convergence of typomorphic features of minerals (introduction to the book "Typomorphism...", 1972"), Fedor V. Chukhrov precisely defined the problem (p. 14): "The important question is similarity or coincidence of the features of minerals, which were formed in different conditions. This phenomenon can be named the convergence of typomorphic features". In fact, there are no "convergent minerals" — there are *convergent* (coincident) features, whose nature should be understood prior to naming them typomorphic — i.e. being typical for a certain geological conditions. Fedor V. Chukhrov cites literature examples of colloform aggregates of cassiterite and framboidal aggregates of pyrite that were crystallized from gels — both in near-surface zones and hydrothermal deposits of abyssal zones, when solutions entered open fissures and cavities. It was shown that the isotopic composition of sulphur, oxygen and carbon can be one and the same in minerals from igneous, sedimentary, metamorphic and some diagenetic rocks; the same can be applied to polytypism of micas, molybdenite etc. However, it does not mean that the minerals are identical, convergent by other features too.

Trying not to be persistent, we will discuss this fact using the example of alkali feldspars, which, as is known, occur under various combinations of temperature and pressure. Initially, at high temperature, monoclinic sanidine with maximum disordered distribution of Si and Al within four tetrahedral positions of a crystal structure: 0.25:0.25:0.25:0.25 (% Al per unit) crystallizes from a melt; this is the "high sanidine" with stoichiometry Si:Al = 3:1. Upon cooling, Al is re-distributed in the feldspar framework and predominantly segregated in two tetrahedral positions (T<sub>1</sub>) out of four: 0.50:0.50:0:0; this is "low sanidine". This is the reason that we do not observe high sanidine in nature — it does not

remain even in quenched volcanic rocks, and was only grown experimentally. However, as it was mentioned above, K-feldspars with such a high grade of Si/Al-disorder were discovered in alpine veins and diagenetically altered sediments, often in association with maximum ordered K-feldspar – triclinic *microcline*, where all Al is concentrated in only one position ( $T_1O$ ). As we clarified such “sanidines” are metastable, formed within the stability field of microcline. Their convergent feature is Si/Al-disorder. They fundamentally differ from “real” sanidine by other features: their pure, almost sodium-free chemical composition and dissimilar crystal morphology with dominant (110) prism. These feldspars are known as *adularia*. Genetically it is clearly an individual mineral with a specific combination of the main features – chemical composition, structure and morphology, which are typomorphic for a certain geological conditions. It would be incorrect to equate *adularia* with such mineral species of the K-feldspar group, as sanidine or microcline.

A similar example was described by Fedor V. Chukhrov (Typomorphism..., 1972). Thus, he gave an example of the similarity of “dipyramidal” quartz – high-temperature hexagonal-dipyramidal from some effusive rocks, and falsely-dipyramidal (with two equally developed rhomboherda) – from low-temperature deposits, as *false* convergence. It is possible to consider this feature as false or true, but it is obvious that their other features differ; in particular, these minerals belong to different structure modifications:  $\alpha$ - and  $\beta$ -quartz. Partial convergence, the convergence of separate features, i.e. actually *false* regarding to a term mineral species, gives individual names for such a minerals. For example, fibrous low-temperature quartz is *chalcedony*, colloidal-amorphous molybdenite is *jordisite*, sedimentary fluorite – *ratofkite*, supergene cassiterite – *varlamoffite*.

### Mineral or mineral aggregate?

Discussing my suggestion to consider an individual *stability field* as a major species-forming criterion for a potentially new mineral species, Vadim S. Urusov suggested substituting the term *stability field* for the term *existence field* (Urusov, 2009). In principle we agree with this, although in general it makes the term mineral species undesirably less specific. The Russian equivalent for “stability” is

“steadiness”. Substitution of “steadiness” for “existence” unwittingly support our opponents criticism, who substantiate the approved by CNMNC IMA multiple *cloned* “new” mineral species by their real *existence* in nature (and who never wonder whether they are new species or varieties of the known species). On the other hand, this suggestion enables one to consider in the scientific systematization of mineralogical objects both stable and metastable minerals, and also some minerals which have lost stability with geological time (having in mind that mineralogy is a natural-historical science). We discussed unstable and metastable minerals above. Examples of minerals which have lost stability are perthites and their plagioclase analogues that were mentioned casually above.

In the previous papers (Borutzky, 2006), it was shown, that the diagrams  $NaAlSi_3O_8$ - $KAlSi_3O_8$ - $T$  has an area of immiscibility (solvus) between anorthoclase and sanidine and (at a lower temperature) between albite and microcline. It seems that there is nothing to speak about: in this field there are two coexisting minerals (two mineral species) with distinct phase interfaces, i.e. mineral aggregate. Yes, but this concerns only macro- and micro-perthites – the co-growth of low albite and microcline, with appropriate chemical compositions and cell parameters. However, in crypto-perthites the inter-grain boundaries are absent: perthitic “aggregate” is represented by the integrated aluminosilic framework with identical *b* and *c* unit cell parameters for Na- and K-phases and variable *a* parameter, which reflects the site occupancy by these alkaline metals. The inter-axis angles distort in order that the cell volume has a minimum deviation from the volume of unexsolved K,Na-feldspar. For this case, within the field surrounded by equilibrium solvus, one could draw an area limited by coherent solvus. Finally, at the earlier stage of exsolution in a homogenous K,Na-feldspar there occurs undulatory fluctuations of composition – coherent spinodal; the X-ray data is not dissimilar to homogenous, i.e. we have all the reasons to identify this “aggregate” as a monomineral and refer it to a certain mineral species.

A similar situation is observed in plagioclases. In the so-called, intermediate plagioclases (from oligoclase to bytownite) the crystal structure is built from co-existing domains

of albite and anorthite, which can be detected only by additional ("over-structural") reflexes. In practical mineralogical-petrological research such plagioclases are considered as homogenous and described by the summary X-ray diagrams. Even their heterogeneity can be detected on the electron-microscopic level using SEM/EMPA. When the intermediate plagioclases reveal iridescence ("moonstones" – peristerites, labradorites), i.e. exsolution becomes obvious, they still are considered as homogeneous, corresponding to relevant minerals species or (according to some scientists) – varieties. In this respect how can we not reconcile it with similar structural effects seen in more complicated mineralogical objects, such as eudialyte or labuntsovite, which are used for speculative multiplication of new mineral species.

## Conclusions

1. It is normally believed that the reason for all terminology and classification misunderstandings in mineralogy is the absence, carelessness or artificiality (formality) of species-determining criteria. They are discussed by various commissions, where different opinions, approaches and scholarships conflict, and where the majority approve decisions, obscure to the scientists who deal with the natural matter, or suit only the minority who use them to speculative purposes. We suppose, that one of the important reasons for such misunderstanding is "disregard" for the objects of mineralogical research – the minerals, which are considered only "snatched out" of a certain geological environment. Therefore one classifies not certain objects, but ideas about them. The objects themselves are more complicated and diverse, and their chemical composition, structural features and other characteristics depend directly on variations in formation conditions, that should be considered in systematization.

2. In the previous papers on the subject we indicated that, in general, for determination of a new mineral species proof is required of its individual stability field. Within this field, the chemical composition, structural peculiarities and features of the mineral might change gradually, depending on conditions of formation (and retaining), without abrupt changes resulting in formation of a new mineral species.

3. However, under certain conditions in nature there occur unstable phases, meta-

stable phases, minerals which have lost equilibrium relationship with the mineral-forming (or mineral-retaining) environment, "mineralogical hybrids" – several mineral species "mixed", "quenched" "intermediate" states etc. On one hand, we cannot recognise them as non-minerals, and on the other – cannot properly equate them with the known species.

4. The question about approval of such minerals as valid species is open, and apparently should be solved individually. In one cases, the crystallization of a mineral outside its stability field can be described by one or another existence area, in another cases – the stability field can be determined for this certain modification, and thirdly – there is insufficient experimental data and observation in nature. The term "spasmodic" transition itself is not quite determined: besides distinct transformations of the "first" and "second" types, for which energy difference is not a strong criterion, there evidently are more complex transformations inheriting features of the first and second transition types.

5. The term convergence of minerals is not fully determined. Probably, it is more correct to speak about convergent features of minerals and not about convergent minerals, because either similar structures of compositions are repeated. But at the same time the compared objects differ essentially by their morphology and other features, which can be considered as typomorphic for their recognition and understanding of their relation with geological environment.

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