

Mechanisms of Isomorphous Substitution in Quartz

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Abstract—Mechanisms of the incorporation of isomorphous impurities of Al, Ti, and Ge into quartz were studied by EPR techniques. For this purpose, laboratory experiments were carried out on quartz annealing, which allowed us to model the processes of impurity atom introduction into the quartz lattice. The investigation of the kinetics of these processes showed that they are described by diffusion-controlled reactions. In many samples, a proportional relationship was observed between the concentrations of Al and Ti impurities incorporated into the quartz structure during laboratory annealing. A comparison of the experimental results with the character of the natural distribution of isomorphous impurities in quartz revealed their similarity. Based on the analysis of the results of our investigations, two main mechanisms were proposed for isomorphous substitutions in quartz. One of them is referred to as the capture mechanism and corresponds to the incorporation of isomorphous impurities during mineral formation. The second, diffusion mechanism operates after the crystallization of quartz. The isomorphous impurities incorporated into the quartz structure by this mechanism are either formed through the decomposition and transformation of composite complexes or as a result of diffusion from crystalline and gas–liquid inclusions. It was suggested that both mechanisms are responsible for the incorporation of Al and Ge impurities into the mineral lattice, whereas Ti is introduced mainly by the diffusion mechanism. The accounting for the mechanisms of isomorphous substitutions provides a means to significantly increase the reliability of the interpretation of genetic information recorded in the distribution of structural impurities in quartz.

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INTRODUCTION

Isomorphous substitutions in quartz, like in any other minerals, are controlled by many factors: temperature, rate of mineral formation, pressure, acidity–alkalinity of the mineral-forming solution, etc. The role and degree of the influence of each of these factors on the extent of isomorphous substitution can be estimated only after the identification of mechanisms responsible for the incorporation of natural impurities into the quartz structure. In this study we attempted to determine how impurities enter the quartz crystal lattice under natural conditions and how their composition and concentration can be related to the fundamental parameters of mineral formation.

The possibility to carry out laboratory experiments modeling the processes of impurity atom transition from a nonstructural (nonisomorphous) form into the quartz structure is favorable for the solution of this problem. It was found that the concentrations of some isomorphous impurities in quartz may increase during its thermal treatment [1–6]. This fact was established by the investigation of quartz by the method of electron paramagnetic resonance (EPR). This method registers a number of paramagnetic defects related to the isomorphous substitution of Si^{4+} in the quartz lattice by the ions of aluminum, titanium, and germanium [3, 7–9].

It is well known that the quartz structure is based on a three-dimensional framework of silicon–oxygen tet-

rahedra $[\text{SiO}_4]^{4-}$. The ion Al^{3+} forms bonds with three oxygen atoms, while the charge of the fourth oxygen remains uncompensated. The excess negative charge of the tetrahedron is balanced by Li^+ or Na^+ . Under the influence of irradiation, the oxygen ion not connected to aluminum captures a hole forming an $\text{Al}-\text{O}^-$ paramagnetic center [3, 7]. The univalent ion (Li^+ or Na^+) moves away from the $\text{Al}-\text{O}^-$ paramagnetic center toward another defect.

The tetravalent ions Ti^{4+} and Ge^{4+} form bonds with all four oxygen ions of a silica–oxygen tetrahedron. However, these ions capture electrons during irradiation, probably because the shielding of titanium and germanium nuclei is different from that of silicon [3]. The compensation of the excess negative charge is achieved by Li^+ , Na^+ , or H^+ diffusing from other defects. Depending on the type of the charge compensating ion, different types of Ti and Ge centers are observed in quartz [8, 9]. Ti–Li centers and Ge(C) centers with charge compensating Li^+ are most common in natural quartz. The concentration of Ge(C) is usually as high as 80% of the total concentration of paramagnetic defects related to isomorphous Ge [10].

It was shown that the EPR method provides a means for the quantitative estimation of the concentration of structural impurities of Al, Ti, and Ge (N_{Al} , N_{Ti} , and N_{Ge}) in polycrystalline quartz samples [11]. The experimental procedure includes the irradiation of quartz by

optimum doses necessary for the transformation of all structural impurity ions into the paramagnetic state.

The concentration of isomorphous impurities in quartz may increase considerably after thermal treatment. For instance, the concentration of structural aluminum, N_{Al} , in quartz annealed at $t = 800^\circ\text{C}$ may increase by an order of magnitude or even more compared with the initial value [12]. Such a considerable increase in N_{Al} suggests that thermal treatment may cause a dramatic redistribution of aluminum and other impurities in the mineral.

It should be noted that the increase of N_{Al} during quartz annealing was explained in a number of studies by the existence of structural Al^{3+} ions associating with protons, which compensate the excess negative charge of $[\text{AlO}_4]^{3-}$ tetrahedra [3]. In contrast to other compensating ions (Li^+ and Na^+), protons do not migrate away from the aluminum–oxygen tetrahedra during quartz irradiation and prevent the formation of Al–O^- centers. However, according to these authors, H^+ escapes from the $[\text{AlO}_4]^{3-}$ tetrahedron and is replaced by Li^+ and Na^+ during high-temperature annealing. Therefore, the irradiation of annealed quartz samples transforms all structural aluminum into the paramagnetic state, which results in an increase in N_{Al} .

In our opinion, this process does occur but exerts a minor influence on the concentration of structural aluminum during quartz annealing. First, the temperatures corresponding to the most extensive increase in N_{Al} are much higher than any reasonable temperature of the decomposition of aluminum–oxygen tetrahedra with compensating protons. It was shown that the concentration of structural Al increases monotonously during the isochronous annealing of quartz up to temperatures of $1200\text{--}1300^\circ\text{C}$. Second, the thermal treatment of quartz results in an increase in the concentration of both structural Al and Ti and Ge isomorphous impurities. Therefore, the main reason for the N_{Al} increase during high-temperature annealing is probably the incorporation of aluminum admixture into the quartz crystal lattice.

KINETICS OF THE PROCESSES OF ARTIFICIALLY STIMULATED INCORPORATION OF IMPURITIES INTO THE QUARTZ STRUCTURE AT HIGH TEMPERATURES

In order to determine the main characteristics of the transition of nonstructural impurities into the isomorphous state, changes in N_{Al} , N_{Ti} , and N_{Ge} induced by the laboratory annealing of quartz were investigated.

Quartz samples were collected for this study from pegmatite and rock crystal deposits. The former were represented by samples from the crystal-bearing chamber pegmatites of Kent (Kazakhstan), and the latter included a number of vein quartz deposits of the Nether-Polar and Central Urals (Dodo, Puiva, Nestor-

Shor, Astaf'evskoe, Svetlorechenskoe, Ol'khovskoe, etc.). Overall, 11 samples of natural quartz were investigated.

Experiments on the artificial annealing were carried out using polycrystalline quartz samples. This allowed us to minimize the influence of the heterogeneity of the material on the results of investigations and reliably measure the concentrations of structural impurities in quartz. The samples were crushed in an agate mortar to a grain size of $0.5\text{--}0.25$ mm before annealing.

The quartz samples were heated in air using a muffle furnace. The samples were preliminarily divided into several charges, each of which was heated at a certain temperature over a certain time interval. Combining the temperature and time of annealing, two regimes of the thermal treatment of samples were simulated, isochronous and isothermal. During isochronous annealing, each sample was kept for 15 min at some temperature between 300 and $(950\text{--}1250)^\circ\text{C}$. Isothermal annealing included heating of several charges at the same temperature for different time periods, from 5 to $150\text{--}240$ min.

After thermal treatment, the quartz charges were irradiated with various doses of gamma-quanta using ^{60}Co as a source. This provided the complete conversion of each type of isomorphous impurities into a paramagnetic state and allowed its correct measurement by the EPR method. The optimum irradiation dose was 10^8 rad for Al impurities, 10^6 rad for Ti, and 6×10^5 rad for Ge [11]. The EPR spectra were recorded on a Bruker ER-420 spectrometer with a wavelength of $\lambda = 3$ cm at temperatures of $T = 77$ and 300 K.

We investigated the character of changes in the normalized contents of structural impurities (N/N^{max} , where N is the current absolute content of the impurity in the heated quartz sample, and N^{max} is the maximum content for the given temperature or time interval) during the isochronous or isothermal annealing of quartz. The absolute contents of admixtures were determined using reference samples and recalculated to conditional units (c.u.), which were equal to 5 ppm for Al, 1 ppm for Ti, and 0.1 ppm for Ge. The relative error of determinations was no higher than 15%.

The obtained experimental results revealed complex and diverse processes accompanying the transition of an impurity between nonstructural and structural forms. Their occurrence is controlled by many factors. Nonetheless, it is possible to distinguish general features characteristic of these processes.

One of these features is the existence of two segments on the $N_{Al}/N_{Al}^{\text{max}}(t)$ curves for structural Al established during isochronous annealing. It is illustrated by Fig. 1, which shows the respective dependencies for quartz samples 1172 and 1393 from the Kent pegmatite field. It can be seen from these diagrams that Al is most intensely incorporated into the quartz structure at $t < 550^\circ\text{C}$

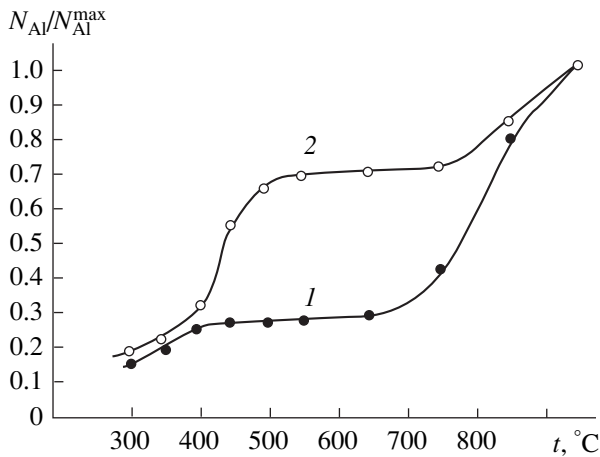


Fig. 1. Dependence of the normalized concentration of structural aluminum, N_{Al}/N_{Al}^{max} , in samples (1) 1393 and (2) 1172 (Kent) on the temperature of isochronous annealing, t .

and $t > 650^\circ\text{C}$, and the $N_{Al}/N_{Al}^{max}(t)$ curves rise rapidly in these temperature regions. Within the intermediate temperature segment between 550 and 650°C , the $N_{Al}/N_{Al}^{max}(t)$ curves show either a plateau or an inflection point.

An increase in the normalized concentrations of structural Al in the low-temperature and high-temperature segments is usually different for different samples. It was found that N_{Al}/N_{Al}^{max} may increase abruptly at $t < 550^\circ\text{C}$ at a low concentration of structural Al. In contrast, if the initial content of structural Al in quartz is high, the main contribution into its thermally stimulated growth is due to annealing at $t > 650^\circ\text{C}$. As can be seen from Fig. 1, this relation is observed for samples 1172 and 1393. The absolute concentrations of structural Al in these samples are 1.3 and 4.8 c.u., respectively.

The experimental isothermal annealing of quartz samples showed that under certain temperatures and annealing times (t), the normalized concentrations of structural Al and Ti impurities in quartz increase proportionally to $t^{1/2}$. These relationships are clearly manifested in the temperature ranges of sufficiently active processes of impurity incorporation into the quartz structure. Figure 2 shows the $N/N^{max}(t^{1/2})$ dependencies for Al and Ti impurities in sample 1172 at a temperature of $t = 400^\circ\text{C}$. It can be seen that these dependencies are linear within the whole time range or its significant part for isothermal annealing. A similar character has the $N_{Al}/N_{Al}^{max}(t^{1/2})$ dependency for sample 1393 in the high-temperature region.

Among the established regularities, of special importance is the linear correlation between the abso-

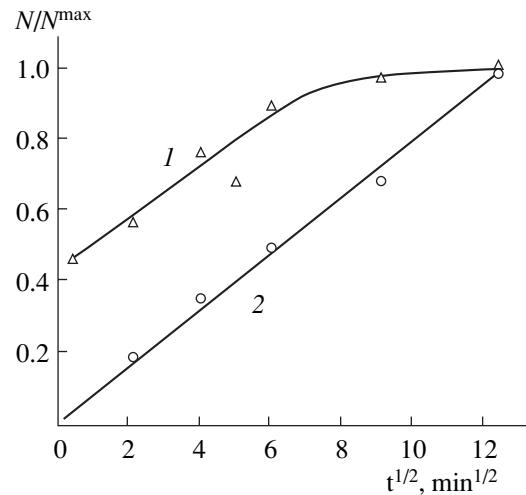


Fig. 2. Normalized concentrations, N/N^{max} , of isomorphous (1) Al and (2) Ti in sample 1172 as functions of the time of isothermal annealing at $t = 400^\circ\text{C}$.

lute concentrations of Al and Ti impurities incorporated into the quartz structure during isochronous annealing. This correlation was repeatedly observed in many samples and can be considered typical of the processes of the thermally stimulated transition of a nonstructural impurity into an isomorphous state.

Figure 3 shows covariations between the absolute concentrations of Al and Ti during the isochronous annealing of sample 1172 (curve 1). For the sake of comparison, also shown is the $N_{Al}(N_{Ti})$ dependency for the isothermal annealing of this sample at $t = 400^\circ\text{C}$ (curve 2). Points on the curve indicate N_{Al} and N_{Ti} values corresponding to annealing times of (from left to right) 5 min, 15 min, 35 min, etc. It can be seen that curve 2 mimics the shape of line 1, only if the time of isothermal annealing is less than 35 min. The incorporation of nonstructural Al into the quartz lattice is sharply depressed at $t > 35$ min, whereas nonstructural Ti continues to transform into the isomorphous form at a constant rate.

Some features in the behavior of the $N_{Al}(N_{Ti})$ dependency during the isochronous annealing of quartz were observed in samples from quartz crystal vein deposits of the Urals (Fig. 4). This dependency appeared to be linear and similar to that of quartz sample 1172 (line 1) only for sample A-2-2 from the Astaf'evskoe deposit, whereas nonlinear $N_{Al}(N_{Ti})$ dependencies were obtained for samples from the Dodo, Puiva, and other deposits (curves 2 and 3).

Compared with isomorphous Al and Ti, the structural Ge impurity shows a more complex behavior during quartz annealing. In the majority of samples, its concentration increases proportionally to the concentration of isomorphous Ti during isochronous annealing. In other samples, the values of N_{Ge} increased but showed

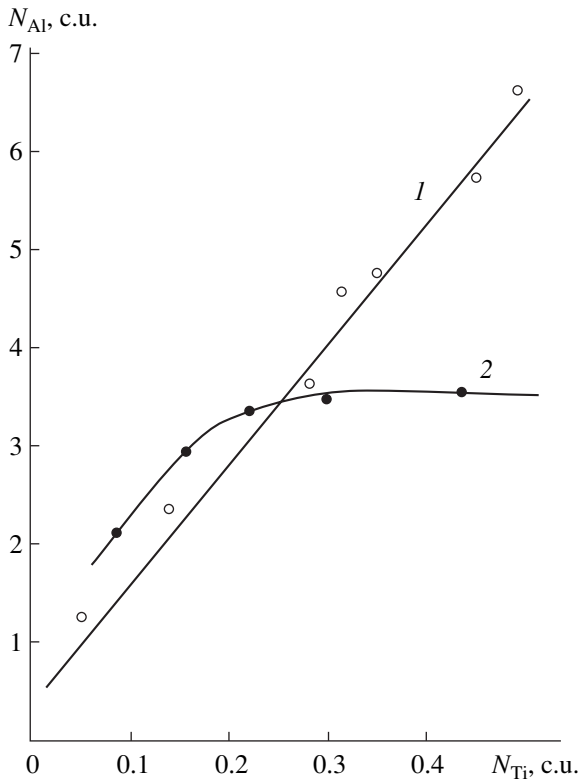


Fig. 3. Correlations of the concentrations of isomorphous Al (N_{Al}) and Ti (N_{Ti}) in sample 1172 during (1) isochronous and (2) isothermal annealing at $t = 400^\circ\text{C}$.

no linear correlation with N_{Ti} . Finally, there are quartz samples (mainly rock crystals) showing a decrease of structural Ge impurity with increasing annealing temperature.

RADIATION-STIMULATED INCORPORATION OF IMPURITIES INTO THE QUARTZ STRUCTURE

The investigation of electron-irradiated quartz samples allowed us to detect phenomena of radiation-stimulated incorporation of impurities into the quartz structure.

Figure 5 presents the dose dependence of the concentration of Al-O⁻ centers in quartz from the Yur gold deposit, which was irradiated in sequence by gamma-quanta (dose of 10^8 rad) and electrons (dose of 1.2×10^7 rad). It can be seen that gamma irradiation by a saturating dose of 10^8 rad resulted in the transition of all structural Al into a paramagnetic state. However, the additional electron irradiation of quartz by a relatively small dose of 1.2×10^7 rad increased the concentration of Al-O⁻ centers by almost 30%.

The sharp increase in the concentration of Al-O⁻ centers after the electron irradiation of quartz could be caused by the transition of part of nonstructural Al into the structural form. This effect was never observed in the quartz samples that were preliminarily annealed at high temperatures.

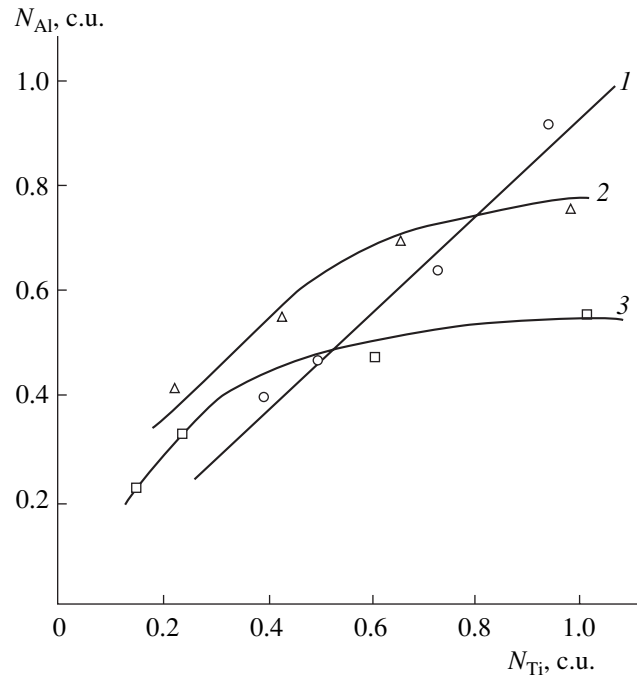


Fig. 4. Correlations of the concentrations of isomorphous Al (N_{Al}) and Ti (N_{Ti}) for the isochronous annealing of samples from the quartz vein deposits of the Urals: (1) Astaf'evskoe (rock crystals), (2) Dodo (vein 490), and (3) Puiva (vein 153/38).

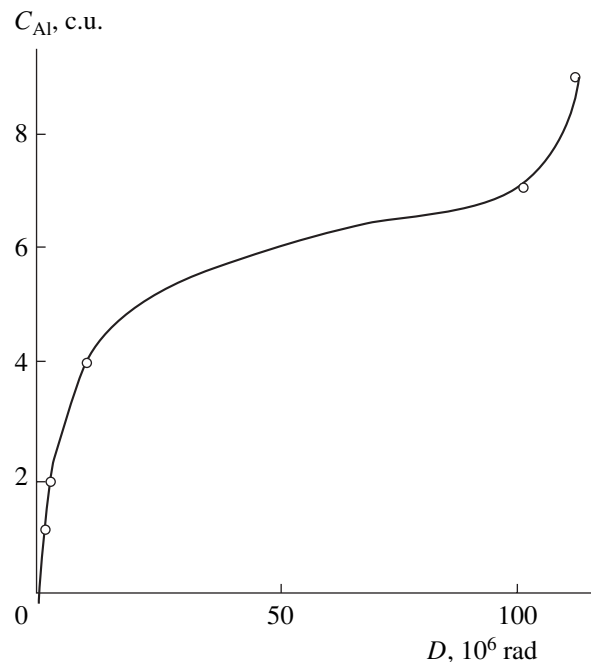


Fig. 5. Kinetics of an increase in the concentration of Al-O⁻ centers in quartz from the Yur gold ore deposit during its sequential irradiation by gamma rays and electrons. The doses lower than 100×10^6 rad correspond to gamma irradiation. The excess doses above 100×10^6 rad were provided by additional electron irradiation.

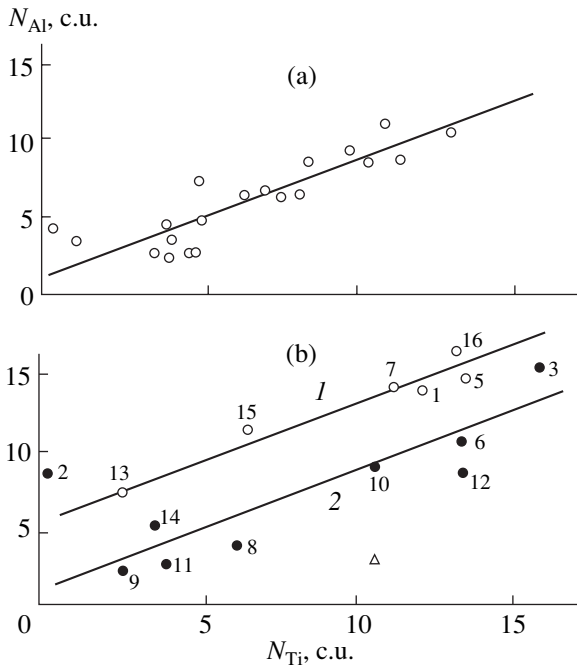


Fig. 6. Relationships between the concentrations of isomorphic Al (N_{Al}) and Ti (N_{Ti}) in quartz samples from sites (a) I and (b) II of the Kyzyl Tau tungsten deposit.

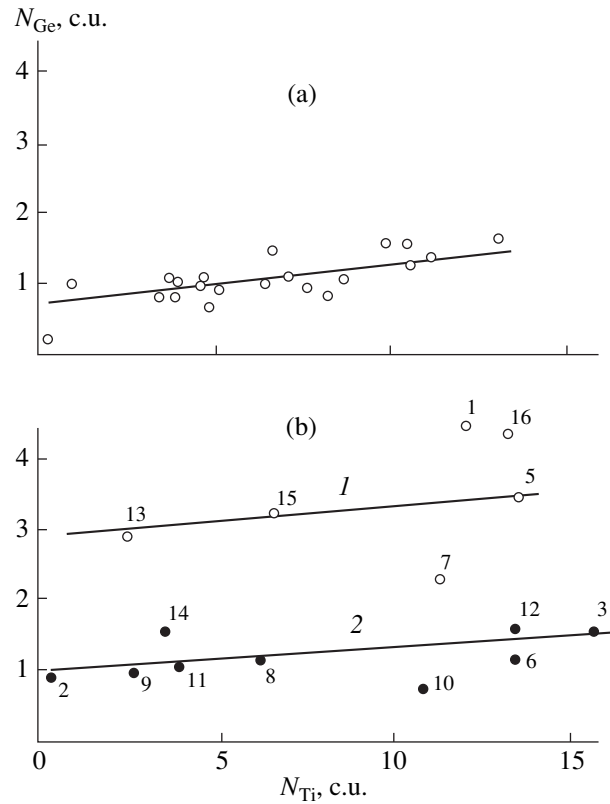


Fig. 7. Relationships between the concentrations of isomorphic Ge (N_{Ge}) and Ti (N_{Ti}) in quartz samples from sites (a) I and (b) II of the Kyzyl Tau tungsten deposit.

MECHANISMS OF IMPURITY INCORPORATION INTO THE QUARTZ STRUCTURE UNDER NATURAL CONDITIONS

The investigation of impurity incorporation into the quartz lattice under natural conditions encounters severe difficulties related to the influence of a number of factors and uncertainties in the conditions under which they could affect the process. The only way to obtain reliable and reasonably interpretable information for the reasons of isomorphic substitutions in quartz is to study the simplest cases of their occurrence. They commonly correspond to the sequential evolutionary development of mineral formation described by the minimum number of monotonously changing parameters. The existence of relatively simple experimentally reproducible relationships in the distribution of structural impurities in quartz can be used as a criterion for the occurrence of isomorphic substitutions by such a simplified mechanism. The distinguishing and analysis of such regular relationships help in the determination of the main mechanisms of isomorphic substitutions in quartz.

Taking into account the above considerations, it is interesting to evaluate the distribution of structural impurities in quartz from the Kyzyl Tau tungsten deposit (Kazakhstan), which was assigned to the vein-greisen type (mineralized cupolas). The material for our investigation was collected at two sites, I and II, which probably differed in the conditions of mineral formation. The investigation of quartz from this

deposit was carried out in cooperation with Getmanskaya [12].

Figures 6 and 7 portray general features in the distribution of isomorphic impurities in quartz from the Kyzyl Tau deposit. Figures 6a and 7a show the relationships of N_{Ti} , N_{Al} , and N_{Ge} in quartz from site I. These data suggest that the concentration of isomorphic Ti is linearly correlated with the concentrations of structural Al and Ge. Similar relationships were observed in quartz from site II, but two groups of samples were distinguished at this site with different characters of this dependency (lines 1 and 2 in Figs. 6b and 7b). Samples 1, 5, 7, 13, 15, and 16 form linear dependencies $N_{Al}(N_{Ti})$ and $N_{Ge}(N_{Ti})$, whose slopes correspond to those obtained for samples from site II but vertical position is shifted toward higher N_{Al} and N_{Ge} values (lines 1). The distribution of structural impurities in quartz of the other group (samples 2, 3, 6, 8–12, and 14) is identical to their distribution in samples from site I (lines 2).

Formally, the linear dependence of N_{Al} and N_{Ge} on N_{Ti} must imply a linear correlation between N_{Al} and N_{Ge} . The analysis of the $N_{Al}(N_{Ge})$ diagram for quartz from the Kyzyl Tau deposit supports this suggestion. However, the correlation coefficient is much lower than those for the $N_{Al}(N_{Ti})$ and $N_{Ge}(N_{Ti})$ dependencies.

Correlations between the concentrations of structural admixtures of Al and Ge in quartz were previously noted in a number of studies [13, 14]. Therefore, the relationships obtained for the Kyzyl Tau deposit can be considered as additional evidence for the existence of such correlations. On the other hand, the results of our investigations indicate a special role of structural Ti in isomorphic substitutions in quartz. Indeed, while the character of distribution of isomorphic Al and Ge impurities in quartz was different at sites II and I, the distribution of structural Ti was practically invariant. This may indicate that the incorporation of impurities of Ti, on the one hand, and Al and Ge, on the other hand, into the quartz lattice is governed by different laws.

DISCUSSION

In order to elucidate the mechanism of isomorphic substitutions in quartz, we compared the characteristics of artificially stimulated and natural processes of impurity incorporation into the mineral structure.

The existence of two segments in the $N_{\text{Al}}/N_{\text{Al}}^{\text{max}}(t)$ curves (Fig. 1) indicates that there are two variants of the process of Al incorporation into the quartz structure during isochronous annealing. One of them dominates at temperatures $t < 550^\circ\text{C}$ and the other at $t > 650^\circ\text{C}$. It should be pointed out that the temperature interval between these segments includes the temperature of α - β phase transition, $t_{\alpha-\beta} = 573^\circ\text{C}$.

The linear dependency $N/N^{\text{max}}(t^{1/2})$ for Al and Ti impurities (Fig. 2) indicates that the process of their incorporation into the quartz structure is connected with diffusion processes. Indeed, assuming that the incorporation of impurity ions into the quartz structure is related to the interdiffusion of these ions and silicon vacancies, the rate of accumulation of isomorphic impurities during isothermal annealing can be described by the following expression:

$$dN/dt = 4\pi r_0 D N_{\text{v}} b [1 + r_0/(\pi D t)^{1/2}] (N_a - N), \quad (1)$$

where N is the concentration of the nonstructural admixture transforming into the isomorphic form after sample heating to temperature t for time t ; N_a is the initial concentration of the nonstructural admixture in the unheated sample; N_{v} is the equilibrium concentration of silicon vacancies at temperature t ; $D = D_0 \exp[-E/k(t + 273)]$ is the coefficient of interdiffusion of the impurity ions and silicon vacancies; E is the activation energy for diffusion; D_0 is the preexponent factor; k is the Boltzmann constants; r_0 is the radius of interaction between the impurity ion and the silicon vacancy; and b is the probability of migration of the impurity ion from an interstitial position into a lattice node occurring at the distance r_0 .

Equation (1) is based on the main principles of the theory of diffusion-controlled reactions [15]. Its solution can be given in the form [16]

$$N = N_a \{1 - \exp[-f(t)]\},$$

where

$$f(t) = 4\pi r_0 D N_{\text{v}} b [1 + 2r_0/(\pi D t)^{1/2}] t.$$

It is clear that at small times of annealing when $2r_0/(\pi D t)^{1/2} \gg 1$, the concentration of the impurity incorporated into the quartz structure is

$$N = 8r_0^2 N_a N_{\text{v}} b (\pi D)^{1/2} t^{1/2}. \quad (2)$$

Equation (2) implies that N varies as $t^{1/2}$ during the isothermal annealing of quartz.

The major role of diffusion in the process of impurity transition from a nonstructural form into structural one can be invoked to explain the existence of two temperature segment with a rapid increase in N_{Al} .

It is known that the diffusion mobility of Al^{3+} in β -quartz is much higher than in α -quartz [17]. Therefore, the considerable increase of the concentration of isomorphic Al after the isochronous annealing of quartz at temperatures of $t > 650^\circ\text{C}$ appears to be quite understandable. In our opinion, Al^{3+} diffusion at temperatures below $t_{\alpha-\beta}$ occurs owing to the presence of clusters of the β phase in quartz. Such clusters can be formed in the mineral during low-temperature polymorphic transformations [18]. However, Al^{3+} may penetrate and destroy these clusters, converting them into a state outside their stability field. The further diffusion of Al^{3+} is possible after the formation of new clusters of the β phase. Thus, nonstructural Al ions prevent polymorphic transformations in quartz. On the other hand, owing to the polymorphic transformations, Si^{4+} can efficiently diffuse in the mineral, interact with silicon vacancies, and substitute for Si^{4+} . The role of Al impurity in the decomposition of clusters of the β phase was noted previously [18]. It was shown that such clusters can exist in quartz under natural conditions, if the concentration of aluminum impurity is low. In our opinion, this is why the incorporation of Al into the quartz structure at $t < 550^\circ\text{C}$ is characteristic of samples with low concentrations of this impurity.

It is worth noting that the initial linear segments of the $N/N^{\text{max}}(t^{1/2})$ curves for Al and Ti impurities have identical slopes (Fig. 2). This experimental observation provides additional insight into the process of impurity incorporation into the quartz structure. According to Eq. (2), the slope of this segment is $8r_0^2 N_{\text{v}} (N_a/N^{\text{max}}) b (\pi D)^{1/2}$. Therefore, the identity of slopes for the incorporation of Al^{3+} and Ti^{4+} is only possible when a number of conditions are met.

First, within the segments of the linear dependence of N/N^{max} on $t^{1/2}$ for Al^{3+} and Ti^{4+} , equilibrium must be

maintained between the concentrations of nonstructural and structural impurity forms. The similarity of N/N^{\max} values for Al^{3+} and Ti^{4+} implies that this balance is maintained for these ions in identical proportions. Since the balance can be maintained by the occurrence of the process to both directions, it is clear that thermal treatment can cause both impurity incorporation into the quartz structure and transition of isomorphous impurities into a nonstructural form. The occurrence of such a transition was previously experimentally established for some quartz samples [19]. It can be supposed that the distribution of structural and nonstructural impurities in quartz reflects the distribution of larger ("primary") defects. The latter can be represented by defect microscopic zones, clusters of polymorphic modifications, microscopic pores, nanometer-sized minerals, etc. The distribution of primary defects forms a common environment for the existence of many other defects, which are forced to adjust their organization patterns to minimize the potential energy of the atomic system of the mineral. Primary defects form a continuum of nonstructural impurities in quartz.

Second, the slopes of the linear segments of $N/N^{\max}(t^{1/2})$ dependencies for Al and Ti can be identical, if the diffusion processes controlling their incorporation into the quartz structure are governed by similar diffusion coefficients. However, Al^{3+} and Ti^{4+} are too different to show identical diffusion parameters. Most likely, before meeting silicon vacancies, they pass only a small portion of the diffusion path, which involves defect zones in quartz and terminates in ordered domains. The major portion of the diffusion path is passed by silicon vacancies. The activation energy for diffusion related to the incorporation of impurities into quartz was roughly estimated as 0.4–1.0 eV, which is similar to $\varepsilon = 0.6$ eV reported previously in [20]. The

obtained ε values are small and may correspond to the surface rather than volume diffusion of vacancies or atoms. Hence, it can be supposed that Al^{3+} and Ti^{4+} interact with vacancies on the surface of quartz grains, which result in the enrichment of impurities in the near-surface layer.

It cannot be ruled out that the diffusion of alkali ions (Li^+ and Na^+) is the main control on the process of impurity incorporation into the quartz structure. Alkali ions are needed for the compensation of excess negative charge formed by the isomorphous substitution of Al^{3+} for Si^{4+} . Furthermore, their presence significantly increases unit-cell parameters [21], which may be favorable for the incorporation of relatively large Ti^{4+} ions into the quartz structure.

If the amount of alkali ions is not sufficient, part of incorporated Al remains without compensating ions and can probably transform into a metastable state (state of an activated complex) [22]. The formation of such complexes in thermally treated quartz was established by X-ray luminescence (band $\lambda = 345$ nm). Their components are defects of the $[\text{AlO}_4]^-$ type, which are unstable and decompose upon irradiation [22].

The significance of alkali ions for the processes of impurity incorporation into the quartz lattice was supported by experimental results. It was found that the preliminary boiling of polycrystalline quartz samples in carbonate solutions results in an increase in the amount of impurity incorporated into the mineral lattice during subsequent high-temperature annealing. After boiling in LiCO_3 and NaCO_3 solutions, the concentration of Ti- and Ge-centers in quartz increased, and Li^+ and Na^+ served as charge compensating ions, respectively [22]. This fact additionally supports the suggestion that impurities incorporated into the crystal structure are localized in the surface layer of quartz microblocks.

Figure 3 illustrates the linear correlation between the concentrations of structural Al and Ti impurities, which was observed during the isochronous annealing of sample 1172. The time of annealing in these experiments (15 min) provided compliance with Eq. (2) at any temperature. An increase in the time of annealing can considerably change the initial distribution of defects in quartz, such that Eq. (2) is violated and the linear relation between N_{Al} and N_{Ti} is disturbed (Fig. 3, curve 2). The main reason for the nonlinearity is a decline in the rate of Al impurity incorporation into the quartz structure, which can be caused by a decrease in the content of β phase in quartz. This is suggested by a decrease in the concentration of T centers, which are localized in the domains of the high-temperature polymorph (Fig. 8).

Approximately the same quantitative relationships between the concentrations of structural Al and Ti impurities were observed in samples from the vein quartz deposits of the Urals (Fig. 4). In this case, the probable reason for the nonlinear relationships between

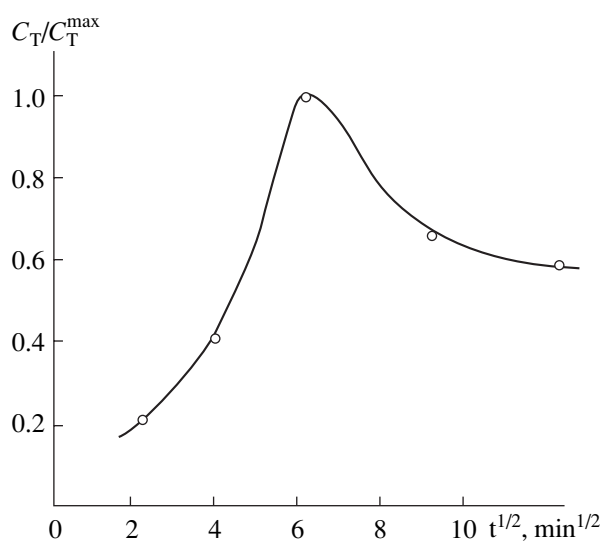


Fig. 8. Variations in the normalized concentrations of T-centers with time for the isothermal annealing of sample 1172 at $t = 400^\circ\text{C}$.

N_{Al} and N_{Ti} for samples from the Dodo and Puiva deposits at high annealing temperatures is the exhaustion of the continuum of nonstructural Al impurities. It is known that samples from these deposits are conspicuously pure and the concentration of Al impurity in them is much lower than in other quartz samples. The nonlinearity of the relationships between N_{Al} and N_{Ti} during quartz annealing can also be caused by the deficit of Ti impurity. In particular, such nonlinearity was detected in some samples with no more than 1 ppm Ti from the Astaf'evskoe and Ol'khovskoe deposits. In contrast to the quartz of the Dodo and Puiva deposits, these samples showed an anomalous slight increase in N_{Ti} rather than N_{Al} . This implies that the $N_{\text{Al}}(N_{\text{Ti}})$ dependency may be linear in quartz with a sufficiently large inventory of nonstructural Al and Ti impurities.

The character of distribution of isomorphous Al and Ti impurities in quartz from the Kyzyl Tau deposit is, in principle, identical to their distribution in thermally annealed quartz. This suggests that isomorphous substitutions in natural quartz can occur by the same mechanism as operated during artificial quartz annealing. Since this mechanism is controlled mainly by diffusion processes, it is referred to as the diffusion mechanism.

The viability of this mechanism of isomorphous substitutions was previously discussed in [23]. It was noted that a significant fraction of impurities can be incorporated into the quartz structure after crystallization. These impurities could be supplied by composite complexes forming during crystallization and decomposing during quartz cooling. It is obvious that the amount of impurities incorporated in such a manner into the quartz structure must increase with increasing temperature of mineral formation and time of its cooling. In contrast, an increase in external pressure must decrease the concentration of isomorphous impurities incorporated by the diffusion mechanism, because it decreases the equilibrium concentration of silicon vacancies (N_{v}) in quartz [24].

It should be pointed out that the term "composite complex" is used to refer to various nanometer-sized structures in equilibrium with the crystal lattice of quartz. Trace elements may occur as components of such complexes or at the interface boundary between the crystal lattice and complexes, which is favorable for their preservation. It is supposed that a considerable fraction of composite complexes may occupy a leading place in the hierarchy of defects; i.e., they may play a role of primary defects.

In addition to composite complexes, small crystalline and gas-liquid inclusions may significantly contribute to the development of diffusion-controlled structural impurities. Having a large contact surface with quartz, they can also serve as an efficient source of impurities in its crystal lattice. Both composite complexes and small crystalline inclusions are localized mainly on the surface of quartz microblocks.

The inspection of diagrams in Fig. 6 shows that the segment of a linear relationship between N_{Al} and N_{Ti} extends to the zero N_{Ti} value. Consequently, practically all isomorphous Ti in quartz from the Kyzyl Tau deposit is related to the diffusion mechanism. It is possible that this observation reflects a general feature of the incorporation of Ti impurity into the quartz structure. Obviously, Ti^{4+} cannot be captured by the quartz lattice during mineral formation because of its large radius. The only way to introduce it into the mineral is through the formation of Ti-bearing composite complexes at the frontal surfaces of quartz growth. Subsequently, Ti^{4+} can be incorporated into the mineral lattice during the transformation of these complexes.

The suggestion of the diffusion mechanism of Ti incorporation into the quartz structure under natural conditions is corroborated by the correlation between N_{Ti} and the temperature of mineral formation [25]. Among all structural impurities, the concentration of isomorphous Ti most adequately reflects the temperature conditions of mineral formation. The efficiency of the diffusion mechanism for the isomorphous substitution of Ti is supported by the results of our experiments on the laboratory annealing of quartz. It was shown that Ti is usually incorporated into the quartz lattice at lower temperatures compared with Al and Ge.

Points with $N_{\text{Ti}} \approx 0$ in Fig. 6 correspond to the samples showing the minimum contribution of the diffusion mechanism of isomorphous substitutions. However, rather significant concentrations of structural Al were detected in some of them. This impurity was probably captured by quartz directly during mineral formation. The incorporation of impurities into the quartz structure during its growth is referred to as the capture mechanism. The main factors controlling the efficiency of the capture mechanism are, evidently, the composition, acidity-alkalinity, and temperature of mineral-forming solution. These factors affect primarily the concentration of captured isomorphous impurities and the possibility of the compensation of their excess charges with alkali ions. It is interesting that the points approaching $N_{\text{Ti}} \approx 0$ tend to deviate from the general linear trends (e.g., point 2 in Fig. 6b). Such behavior supports the conclusion that the diffusion and capture mechanisms are controlled by different factors.

All the above considerations are also valid for the diagrams of Fig. 7, which suggest that, similar to Al, Ge impurity is incorporated into the quartz lattice by both the diffusion and capture mechanisms. However, the role of the diffusion mechanism for Ge impurity is less important than for Al. Indeed, the slope of the $N_{\text{Ge}}(N_{\text{Ti}})$ lines in Fig. 7 is much lower than that of $N_{\text{Al}}(N_{\text{Ti}})$ (Fig. 6), which suggests a significantly lower accumulation rate of isomorphous Ge during quartz cooling.

These considerations provide an explanation for the existence of two limbs on the $N_{\text{Al}}(N_{\text{Ti}})$ and $N_{\text{Ge}}(N_{\text{Ti}})$ curves for site II of the Kyzyl Tau deposit (Figs. 6b and 7b). Per-

haps, lines *I* in these diagrams correspond to the zone where the process of mineral formation occurred at the same temperature as at site I, but the composition and acidity–alkalinity of the solution were different.

Strictly speaking, the existence of two mechanisms of Al and Ge incorporation into the quartz structure leads to an ambiguity in the interpretation of the distribution of these impurities in natural samples. Given the total concentrations of these elements, the contributions due to different mechanisms cannot be determined, and the conditions of mineral formation cannot be reliably estimated. Fortunately, this problem can be circumvented using the distribution of isomorphous Ti, which is incorporated into the quartz crystal lattice mainly by the diffusion mechanism. The fractions of structural Al and Ge incorporated into quartz via the diffusion and capture mechanisms can be determined by analyzing the $N_{Al}(N_{Ti})$ and $N_{Ge}(N_{Ti})$ diagrams. The concentrations of impurities captured by quartz during crystallization (N^{capt}) can be determined from the points where the $N_{Al}(N_{Ti})$ and $N_{Ge}(N_{Ti})$ lines intersect the N_{Al} and N_{Ge} axes. The concentrations of impurities incorporated into the mineral structure during cooling are estimated as the differences between the bulk concentrations (N_{Al} or N_{Ge}) and N^{capt} . The discrimination of isomorphous impurities with respect to the mechanism of their incorporation strongly increases the genetic significance of the character of their distribution in quartz.

In addition to the Kyzyl Tau deposit, linear relationships between the concentrations of structural Ti, Al, and, to a lesser extent, Ge were detected in quartz samples from several quartz vein deposits of the Nether-Polar Urals (samples of G.I. Krylova) and the Bainazar, Inkur, and Kholton tungsten deposits (samples of Getmanskaya). Although only some preliminary data were obtained, their general agreement with the conclusions of this paper can be noted. However, the genetic significance of these data can be fully evaluated on the basis of a more comprehensive investigation of their relation to the genesis of deposits.

Thus, the results of our investigations provide an explanation for the linear relationships between the concentrations of various isomorphous impurities, which were observed in quartz from rare-metal pegmatites [13], hydrothermal metamorphic quartz from the Nether-Polar Urals [14], and quartz samples from the Kyzyl Tau tungsten deposit and other deposits. These relationships are related to the diffusion mechanism of isomorphous substitution in quartz. Each of such dependencies corresponds to a process of mineral formation within a single hydrothermal system. Therefore, genetically related samples may have significantly different concentrations of isomorphous impurities, but, if the inventories of nonstructural impurities are sufficiently large, they will lie along a single line in the $N_{Al}(N_{Ti})$ and $N_{Ge}(N_{Ti})$ space. The interrelations of the concentrations of structural impurities defining such behavior compose a peculiar genetic code of quartz. Genetically dif-

ferent samples show no correlations between these concentrations [26].

In addition to the two main mechanisms of isomorphous substitutions in quartz, our investigations revealed a third mechanism, referred to as the radiation mechanism. Most likely, electron irradiation is capable of destroying some defect complexes, which associate with the nonstructural form of impurity occurrence in the mineral, and transforming them into the isomorphous form. The importance of this mechanism of isomorphous substitutions and conditions of its occurrence in natural quartz can be estimated by future studies.

Finally, it should be pointed out that the concept presented in this paper reflects the most important, but not the only, tendency in the behavior of isomorphous impurities in quartz. In fact, a number of factors may operate and complicate the distribution patterns of isomorphous impurities in quartz: their association with other defects, for instance, with oxygen vacancies [27, 28]; introduction of an impurity into the quartz structure from relatively large mineral grains [5]; contribution of Ge to the preservation of polymorphic modifications [18]; natural diffusion of impurities from quartz into the environment and vice versa [29]; crystallization of the mineral in dissipative systems experiencing repeated transitions into new regions with nonlinear properties [30]; partial or complete recrystallization of quartz resulting in a fundamental redistribution of impurities; etc. Furthermore, the capture and diffusion mechanisms of isomorphous substitutions may superimpose on each other. For instance, impurities incorporated into the quartz structure during its crystallization can subsequently participate in diffusion processes providing the balance between the concentrations of isomorphous and nonstructural impurities. In this regard, the concept presented here can be used for the analysis of available phenomenological data and serve as a basis for the more comprehensive understanding of the genetic meaning of the distribution of structural impurities in quartz.

CONCLUSIONS

(1) The results of our investigations suggest that there are two main mechanisms of isomorphous substitutions in quartz: capture and diffusion ones.

The former mechanism is related to the capture of isomorphous impurities during quartz growth. Its efficiency is probably controlled by the composition, acidity–alkalinity, and temperature of mineral-forming solutions. The latter mechanism is related to the implementation into the quartz structure of impurities formed through the decomposition and transformation of composite complexes and diffusing from crystalline and gas–liquid inclusions during mineral cooling. Its occurrence must depend primarily on the temperature of quartz formation, external pressure, and the time of quartz cooling. Isomorphous admixtures related to the

diffusion mechanism are localized mainly in the surface zones of quartz microblocks.

(2) The data obtained for quartz from the Kyzyl Tau and some other deposits suggest that Al and Ge impurities are incorporated into the quartz structure under natural conditions by both the capture and diffusion mechanisms, whereas the isomorphic impurity of Ti is mainly connected with the diffusion mechanism.

(3) It is supposed that the analysis of relationships between the concentrations of Al, Ge, and Ti structural impurities in quartz can be used in many cases for the estimation of the contributions of particular mechanisms of isomorphic substitutions into the concentrations of isomorphic Al and Ge. This provides a means to significantly increase the information content of the characteristics of structural impurity distribution in quartz and apply them in genetic mineralogy.

(4) Summing up the above, it can be stated that our results prompted us to revise the well-known concepts on the unequivocal connection between the distribution of isomorphic impurities in quartz and conditions of its formation. In general, the isomorphic impurity can be considered as consisting of two components, initial and superimposed. The former is related to the capture of impurities during quartz formation and the latter is a product of the relaxation of disequilibrium states arising in quartz during crystallization. The maximum intensity of relaxation processes providing the balance between the concentrations of isomorphic and non-structural impurities is observed at the highest temperatures, i.e., usually during quartz cooling. Each of these components provides important information on the prehistory of the mineral and must be accounted for during genetic information analysis. The initial and superimposed concentrations of isomorphic impurities in quartz record the conditions of mineral formation and its subsequent residence in a rock, respectively.

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REFERENCES

1. F. W. Mitchell and E. G. Paige, "The Optical Effects of Radiation Induced Atomic Damage in Quartz," *Philos. Mag.* **46**, 1383–1397 (1955).
2. M. I. Samoilovich and L. I. Tsinober, "Color Centers in Quartz," in *Scientific Results (Geochemistry, Mineralogy, and Petrography)*, No. 19, 119–138 (1968) [in Russian].
3. Sh. A. Vakhidov, E. M. Gasanov, M. I. Samoilovich, and U. Yarkulov, *Radiation Effect in Quartz* (FAN, Tashkent, 1976) [in Russian].
4. L. E. Halliburton, N. Koumvakalis, M. E. Markes, and J. J. Martin, "Radiation Effects in Crystalline SiO₂: The Role of Aluminum," *J. Appl. Phys.* **52**, 3565–3574 (1981).
5. N. G. Stenina, L. Sh. Bazarov, M. Ya. Shcherbakova, and R. I. Mashkovtsev, "Structural State and Diffusion of Impurities in Natural Quartz of Different Genesis," *Phys. Chem. Miner.* **10**, 180–186 (1984).
6. L. T. Rakov, "Behavior of Paramagnetic Centers at the Thermal Annealing of Quartz," *Kristallografiya* **34** (1), 260–262 (1989).
7. M. S. M. Brien, "The Structure of the Colour Centers in Smoky Quartz," *Proc. R. Soc. London* **A231**, 410–414 (1955).
8. P. M. Wright, J. A. Weil, and J. H. Anderson, "Titanium Colour Centers in Rose Quartz," *Nature* **197**, 246–248 (1963).
9. J. H. Mackey, "ESR Study of Impurity-Related Color Centers in Germanium-Doped Quartz," *J. Chem. Phys.*, No. 1, 74 (1963).
10. L. T. Rakov, N. D. Milovidova, K. A. Kuvshinova, and B. M. Moiseev, "EPR Study of Ge Centers in Natural Polycrystalline Quartz," *Geokhimiya*, No. 9, 1339–1344 (1985).
11. L. T. Rakov, N. D. Milovidova, and B. M. Moiseev, *Rapid Determination of Isomorphic Impurities in Samples of Quartz Raw Material Using the EPR Method* (VIMS, Moscow, 1991) [in Russian].
12. T. I. Getmanskaya and L. T. Rakov, "Distribution of Impurities in Quartz from Plutonogenic Greisen Tungsten Deposits," in *Proceedings of International Seminar on Quartz-Silica, Syktyvkar, Russia, 2004* (Syktyvkar, 2004), pp. 97–98 [in Russian].
13. N. D. Milovidova, A. G. Mikhailov, N. I. Stepanenko, and L. G. Fel'dman, "Concentration of Ge and Al Centers in Blocky Quartz of Rare-Metal Pegmatites As Indicator of Their Ore Potential," *Mineral. Zh.* **6** (4), 26–32 (1984).
14. E. N. Kotova, S. K. Kuznetsov, and V. P. Lyutov, "Concentration Ranges of Aluminum and Germanium in the Structure of Hydrothermal-Metasomatic Quartz from the Nether-Polar Urals," in *Proceedings of International Seminar on Quartz and Silica, Syktyvkar, Russia, 2004* (Syktyvkar, 2004), pp. 115–118 [in Russian].
15. T. R. Wait, "Theoretical Treatment of the Kinetic of Diffusion-Limited Reactions," *Phys. Rev.* **107** (2), 463–470 (1957).
16. L. T. Rakov, "Radiation Properties of Crystal Defects in Quartz," No. 6, 637–643 (1997) [*Geochem. Int.* **35**, 557–562 (1997)].
17. R. Pankrath and O. W. Florke, "Kinetics of Al-Si Exchange in Low and High Quartz: Calculation of Al Diffusion Coefficients," *Eur. J. Mineral.* **6**, 435–457 (1994).
18. L. T. Rakov and G. I. Krylova, "Role of Structural Impurities in Polymorphic Transformations in Quartz," *Geokhimiya*, No. 12, 1277–1284 (2001) [*Geochem. Int.* **39**, 1172–1178 (2001)].
19. L. T. Rakov and T. I. Getmanskaya, "Regularities in the Distribution of Impurities in Quartz from Plutonogenic Tungsten Deposits," in *Proceedings of International*

- Conference on New Ideas in Earth Sciences* (Moscow, 2003), p. 52 [in Russian].
20. V. P. Lyutoev, "Incorporation of Trace Aluminum in the Lattice of Silica Minerals," in *Proceedings of International Seminar on Quartz and Silica, Syktyvkar, Russia, 2004* (Syktyvkar, 2004), pp. 28–31 [in Russian].
 21. I. E. Kamentsev, "Variations in Unit Cell Parameters and Content of Structural Aluminum Impurity in Quartz of Different Genesis," in *Proceedings of International Seminar on Quartz and Silica, Syktyvkar, Russia, 2004* (Syktyvkar, 2004), pp. 31–32 [in Russian].
 22. L. T. Rakov, A. A. Rogozhin, and V. A. Rasulov, "Activated Complex in a Thermally Treated Quartz," in *Proceedings of International Seminar on Quartz and Silica, Syktyvkar, Russia, 2004* (Syktyvkar, 2004), pp. 237–238 [in Russian].
 23. L. T. Rakov, "General Aspects of the Formation of Structural Defects in Quartz," *Geokhimiya*, No. 11, 1196–1207 (2005) [*Geochem. Int.* **43**, 1098–1107 (2005)].
 24. B. S. Bokshtein, S. Z. Bokshtein, and A. A. Zhukhovitskii, *Thermodynamics and Kinetics of Diffusion in Solids* (Metallurgiya, Moscow, 1974) [in Russian].
 25. L. V. Bershov, M. D. Krylova, and A. V. Speranskii, "Electron–Hole Centers O^- – Al^{3+} and Ti^{3+} in Quartz As an Indicator of Temperature Conditions of Regional Metamorphism," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 10, 113–117 (1975).
 26. E. N. Kotova and S. K. Kuznetsov, "Content of Impurity Paramagnetic Centers in the Vein Quartz from Some Deposits of the Urals, Kazakhstan, and Karelia," in *Proceedings of International Seminar on Quartz and Silica, Syktyvkar, Russia, 2004* (Syktyvkar, 2004), pp. 193–194 [in Russian].
 27. D. Maschmeyer, K. Niemann, and H. C. A. Hake, "Two Modified Smoky Quartz Centers in Natural Citrine," *Phys. Chem. Miner.* **6**, 145–146 (1980).
 28. F. J. Feigl and J. H. Anderson, "Defects in Crystalline Quartz: Electron Paramagnetic Resonance of E Vacancy Centers Associated with Germanium Impurities," *J. Phys. Chem. Solids* **31**, 575–596 (1970).
 29. L. T. Rakov, "Natural Diffusion of Structural Impurities in Quartz from Sedimentary Rocks," *Dokl. Akad. Nauk SSSR* **323**, 756–760 (1992).
 30. G. I. Krylova, V. G. Balakirev, A. A. Mitrofanov, and L. S. Skobel', "Experience in Studying Multi-Level Quartz Defects," in *Proceedings of International Seminar on Quartz and Silica, Syktyvkar, Russia, 2004* (Syktyvkar, 2004), pp. 27–28 [in Russian].