Synthesis and properties of minerals

Kotelnikov A.R.[1], Tschekina T.I.[2], Gramenitskiy E.N.[2], Zubkov E.S.[1], Kovalsky A.M.[1], Suk N.I. [1], Kotelnikova Z.A. [3] Synthesis of fluorine-bearing sodalite and its properties study

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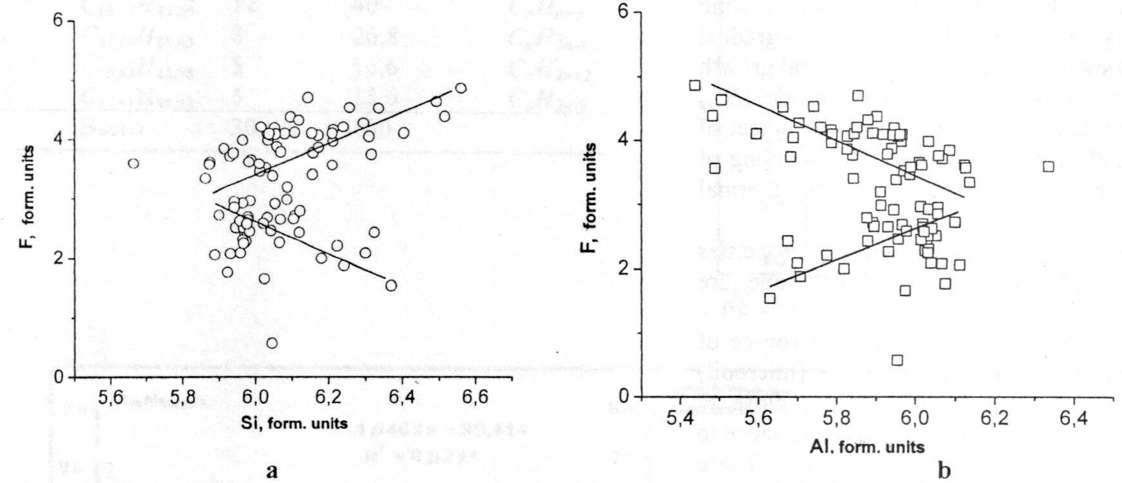
Key words : Synthesis, fluorine-sodalite, cell parameters, isomorphism

Synthesis of fluorine-beating sodalite was carried out in temperature interval 400÷750°C and pressure 1.0÷2.0 kbar in presence of NaF solutions of different concentrations. It is shown that sodalite is stable when sodium fluoride concentration is more than 5 wt % (at 400°C), 10 wt % (at 500 and 650°C). Compositions of synthetic F-sodalites have been studied by microprobe analysis. Earlier [*Yakubovich et al.*,2010] it has been shown that fluorine incorporates into the structure as "cryolite" anion – AlF_6^{3} group. Based on a lot of microprobe analyses of fluorine-bearing sodalites (recalculation of sodalite analyses to crystal-chemical formula was produced using the sum Al+Si=12) it has been indicated that when fluorine concentrations are up to 3 formula units (f. un.) his content in sodalite linearly correlates with Al amount (f. un.); and when F content is 3.5 ÷ 5 (f. un.) it linearly correlates with Si amount (f. un.) (fig. 1). This fact gives evidence of possibility of fluoride incorporation to sodalite as malladrite anion (SiF_6^{2-}). Based on the x-ray data the specification of cell parameters of synthetic fluorine-bearing sodalites has been produced. The average cell parameters are shown to be following: a=9.045(±0.006) [A]; V=740.0(±1.5) [A]^3. Based on the data [*Epelbaum et al.*, 1970] the correlation dependence of parameter "a" of synthetic sodalites on anion radius has been obtained: a, [A] = 8.6795 + 0.13187*(R) [A] ± 0.025 [A] (calculation for n=8; S_x = 0.29); where (R) – anion radius, [A]. This dependence is shown at fig. 2. Based on these data the size of anion group AlF_6^{3-} is estimated, it is 2.7± 0.2 [A] approximately. AlF_6^{3-} radius is comparable with the size of SO_4^{2-} (2.98 A) anion group. So, it is possible to wait for good miscibility in the fluorine- and sulphate-bearing sodalites sequence. The isomorphism between chlorine- and fluorine-bearing sodalites has been studied at 650°C and 2 kbars. It is shown that the disintegration field of sodalites solid solution exists, the boundary lines are following: X_F^{Sod}=0.09 and X_F^{Sod}=0.945. Based on the immiscible borderlines the parameters of Margules model for solid solutions of chlorine- and fluorine-bearing sodalites are estimated, they are W1=24.7(±4.2) and W2=21.3(±3.8) kJ/mol. By these parameters the excess mixing energies of chlorine- and fluorine-bearing sodalites solid solutions have been calculated (fig. 3). The excess mixing energies of (Na, K)-Fsp are presented at fig. 3 too.



a

b

Fig. 1. Dependence of fluorine content on the amount of silicon (a) and aluminum (b).

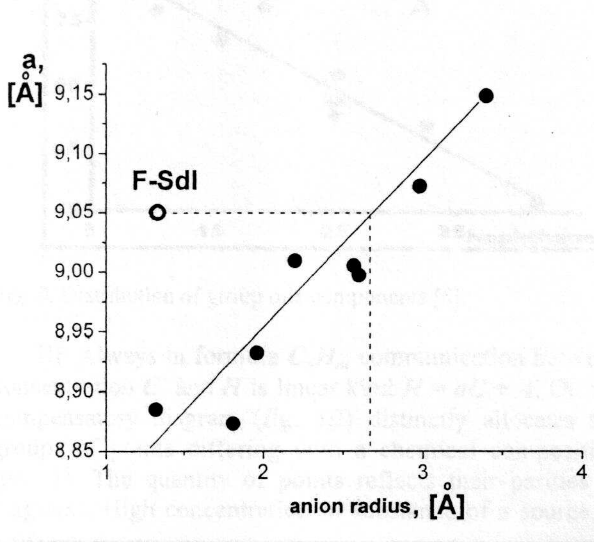


Fig. 2. Dependence of sodalite cell parameter on the anion radius.

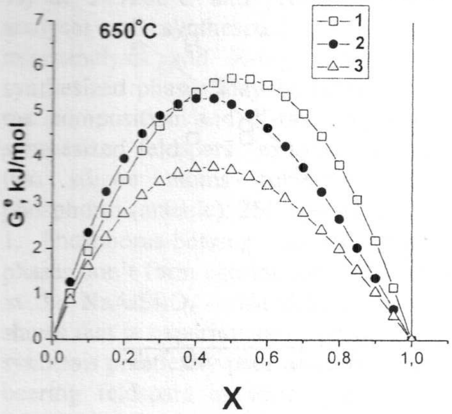


Fig. 3. The excess mixing energies of solid solutions: 1 – (Cl, AlF_6)-Sdl; 2 – (Cl, SO_4)-Sdl; 3 – (Na, K)-Fsp.

Table 1. Mineral paragenesis of pegmatites of Lovozerskii massif containing F-sodalite.

Paragenesis: (Cl,S,F)-Sdl + Williomite + K- feldspar + Amf1 + Amf2 + Ussingite + Natrolite + Lomonosovite + Eudialite + Stenstrupine + (Na,Ce)- Apatite	
Mineral	Formula
(Cl,S,F)- sodalite	$Na_{8.28}Al_{6.03}Si_{5.96}O_{23.57}(Cl)_{1.41}(SO_4)_{0.61}(F)_{0.48}$
Williomite	NaF
K- feldspar	$KAlSi_3O_8$
Amf(1)	$(Na_{2.35}K_{0.75})_{3.10}(Mg_{0.70}Fe^{2+}{}_{1.92}Mn_{0.70})_{3.32}(Al_{0.20}Fe^{3+}{}_{0.78})_{0.98}[Si_{8.00}Ti_{0.33}]\ O_{22}(OH)_2$
Amf(2)	$Na_{3.80}(Mg_{0.16}Mn_{0.08}Fe^{2+}{}_{1.63})_{1.87}Ti_{0.34}(Al_{0.23}Fe^{3+}{}_{1.47})_{1.70}Si_8O_{22}(OH)_2$
Ussingite	$Na_{1.97}Al_{0.99}Si_{3.04}O_8[OH]_{1.10}$
Natrolite	$Na_{1.95}Al_{2.00}Si_{3.05}O_{10.07}*2H_2O$
Lomonosovite	$Na_{8.47}(Mg_{0.11}Fe_{0.25}Mn_{0.27})_{0.63}Si_{3.89}P_{1.96}Ti_{2.19}Nb_{0.84}O_{24}$
Eudialite	$Na_{6.56}Ca_{0.73}K_{0.14}Mn_{0.53}Fe_{0.2}Zr_{0.95}Ti_{0.19}Si_{9.05}Nb_{0.08}O_{24}[SO_4]_{0.11}Cl_{0.15}(OH)_{2.4}$
Stenstrupine	$Na_{6.49}Mn_{0.48}Ca_{1.14}(La_{0.15}Ce_{0.50}Nd_{0.23})_{0.88}Th_{0.05}Si_{5.47}P_{2.70}O_{24}$
(Na,Ce)- Apatite	$Na_{8.15}(Ca_{0.31}Sr_{0.46}Ba_{0.05})_{0.82}(La_{0.46}Ce_{1.31}Pr_{0.15}Nd_{0.73})_{2.65}P_{6.45}O_{24}(OH)_2$

The paragenetic associations of minerals from Lovozerskii alkaline massif containing sodalite and williomite have been studied. The minerals from this paragenesis are presented in the table 1. It has been shown the fluorine intromission to the sodalite represented by the solid solution of nozeane and chlorine-sodalite. Mole fraction of fluorine-sodalite is 0.15 approximately.

References

1. Yakubovich O.V., A.R. Kotelnikov, T.I. Tschekina, E.N. Gramenitskiy, E.S. Zubkov (2011) New agent in structural type of sodalite with [AlF6]3- anions in micropores of tetrahedral frame. Crystallography. T. 56, N 2, pp. 217–224.
2. Epelbaum M.B., Yu.E. Gorbaty, V.F. Gusynin, I.P. Ivanov (1970) The study of sodium sodalites with different frame anions. Sketch-book of physics-chemistry petrology. T. II, pp. 269-280.

Kotelnikov A.R.[1], Tschekina T.I.[2] Albite ordering under hydrothermal conditions

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Key words: synthesis, feldspar, structural ordering of albite

Structural state of albite is a good indicator of mineral genesis conditions. Earlier it has been shown [McKenzie, 1957; Taylor, 1967] that aluminum distribution between unequivalent positions in albite structure depends on the temperature. Quite disordering "high" albite contains ¼ aluminum atoms in every alumosilicic tetrahedron $(Al,Si)O_4$. But in quite ordering "low" albite all aluminum places in tetrahedron $T_1(0)$ [Taylor, 1967; Deer et al, 1966]. Cell parameters of albite change depending on structural condition [Kroll&Ribbe, 1980]. It has been shown [Bambauer et al, 1967a, b] the connection between albite structural state and distance between 131 and 1-31 peaks which is usual to mark as Δ131. For high albite Δ131 is 2.01 (Cu-K_α) and for low albite Δ131 is 1.06(Cu-K_α). The dependence of Δ131 parameter of synthetic albite on temperature was studied in works of different authors [McKenzie, 1967; Mason, 1979; Martin, 1969; Senderov et al, 1971]. It has to mark the works of Martin and Senderov in which the high alkalinity of solution is shown to essentially influence to the structural condition of albite: the increase of solution pH promoted the forming of more ordering albites. The experimental data connected the Δ131 parameter and temperature have been obtained in temperature interval 350-1000°C. But because of some causes estimated by kinetics of ordering processes the experimental data obtained at the temperature >400°C are in better agreement. The purpose of our work was to study the processes of ordering albite synthesis at low temperature (200-500°C) and to obtain the dependence of Δ131 on temperature at T<500°C. Albite synthesis was carried out under hydrothermal conditions at temperature 200÷500°C and pressure 0.5÷1.0 kbar. Gel mixtures of albite composition with addition of 10 wt% amorphous

SiO_2 were used as initial mixtures. Synthesis was carried out in NaOH and $Na_2SiO_3*9H_2O$ solutions with the concentration of 2÷10 wt%. The alkaline solutions activate the synthesis of ordering feldspars as it has been previously shown [Martin, 1969; Senderov et al, 1971]. Experimental duration was up to 65 days.The natural low albite was added to initial mixture (1÷2 wt% of charge mass). Low albite and quartz (and sometimes sodium silicates) were detected in run products. Microprobe analysis has shown a good correspondence of synthetic albites to $NaAlSi_3O_8$ formula. Cell parameters of albites were calculated by X-ray study data. The data obtained are presented in tabl. 1 and fig. 1. These high degree ordering albites with Δ131=1.087 (for Cu-K_α) were synthesized first at 200°C and 0.5 kbar.

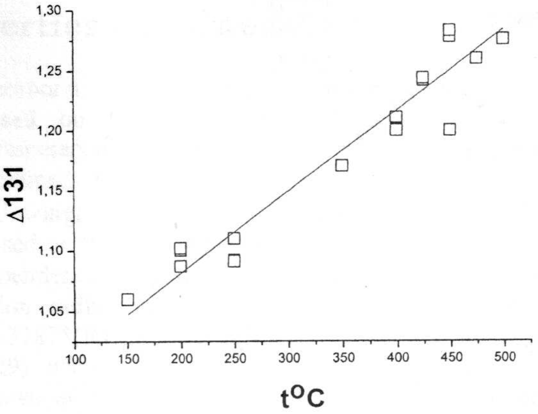

Fig. 1. Temperature dependence of Δ131 parameter of synthetic albite.

Table 1. Cell parameters of albite synthesized under hydrothermal conditions (t= 200 ÷ 500°C; P=0.5-1.0 kbar) in solutions of sodium hydroxide and sodium silicate

N	t/p[1)]	a,[A][2)]	b, [A]	c, [A]	α, [°]	β, [°]	γ, [°]	V, $[A]^3$	Δ131[3)]
6311	200/0.5	8.136	12.786	7.159	94.26	116.59	87.69	664.1	1.10
6312	200/0.5	8.137	12.788	7.159	94.25	116.60	87.71	664.2	1.087
6313	200/0.5	8.137	12.787	7.159	94.26	116.60	87.69	664.2	1.102
6338	250/0.5	8.137	12.787	7.159	94.27	116.60	87.70	664.2	1.107
6339	250/0.5	8.139	12.786	7.159	94.26	116.61	87.70	664.2	1.092
6340	250/0.5	8.136	12.783	7.160	94.29	116.59	87.65	664.0	1.091
5703	400/1	8.141	12.795	7.154	94.21	116.60	87.96	664.6	1.211
5834	400/1	8.140	12.793	7.154	94.20	116.60	87.97	664.4	1.210
5840	425/1	8.140	12.795	7.152	94.16	116.58	88.08	664.4	1.242
5841	425/1	8.140	12.791	7.151	94.12	116.57	88.11	664.3	1.244
5846	450/1	8.141	12.802	7.148	94.11	116.57	88.20	664.5	1.278
5746	450/1	8.141	12.802	7.146	94.09	116.55	88.23	664.5	1.283
5850	500/1	8.141	12.801	7.147	94.08	116.55	88.24	664.6	1.281

1) t/p – temperature (°C)/pressure (kbar);
2) parameters means are presented in angstrom, angles – in degree;
3) Δ131 – distance between 131 and 1-31 peaks (Cu-$K_{\alpha1}$).

The analytical dependence of albtite ordering degree on temperature has been calculated. This dependence may be used as geothermometer for albite-bearing mineral paragenesis:

$$t,(^\circ C)=[-1255.2+1356.6*(\Delta131)] \pm 20^\circ C.$$

This equation is worked adequately in temperature interval 100÷500°C.

References

1. McKenzie W.S. (1957) The crystalline modification of $NaAlSi_3O_8$. Amer.J.Sci., V. 255, N7, pp. 481-516.
2. Taylor U.H. (1967) Framework silicates: feldspar. In: W. L. Bragg, G.F. Claringbull. Crystalline structures of minerals. M., Mir, 391 p.
3. Deer W.A., R.A. Howie, J. Zussmann (1966) Rock forming minerals. Bd. 4 Framework silicates. M., Mir, 481 p.
4. Kroll H., P.H. Ribbe (1980) Determinative diagrams for Al, Si order in plagioclases. Amer.Miner., v. 65, N 5-6, pp.449-457.
5. Bambauer H.U., M. Corlett, E. Eberhard (1967a) Diagrams for the determination of plagioclases using X - ray powder methods. Schw. miner.petrogr. Mitt., Bd. 47, N1, pp. 333-350.
6. Bambauer H.U., E. Eberhard, K. Viswanathan (1967b) The lattice constants and related parameters of plagioclase (low). Schw. miner. petrogr. Mitt., Bd.47, N 1, pp.351-364.
7. Mason R.A. (1979) The ordering behaviour of albite in aqueous solutions at 1 kbar. Contrib.Mineral.Petrol., v. 68, pp. 269-273.
8. Martin R.F. (1969) The hydrothermal synthesis of low albite. Contrib. Mineral.Petrol., v. 23, pp. 323-339.
9. Senderov E.E., T.I. Tschekina, K.I. Tobelko (1971) The investigation of low albite crystallization. Geochimia, N 8, pp. 963-973.

Kotelnikov A.R.[1], Ananiev V.V.[2], Kovalsky A.M.[1], Suk N.I.[1] Synthesis of phosphorus- and arsenic-bearing framework silicates similar to feldspar

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Key words :synthesis, feldspar, phosphorus- and arsenic-bearing framework silicates

The finds of phosphorus- and arsenic-bearing feldspars in natural complexes are described in literature [*London et al.*, 1990; *Vergasova et al.*, 2004]. Phosphorus-bearing feldspars synthesis has been successfully produced in the works [*Simpson,* 1977; Bychkov et al., 1989]. But the problems of isomorphic substitution and synthesis of solid solutions $(Na,K)(Al,Si,P)_4O_8$ и $(Na,K)(Al,Si, As)_4O_8$ remain insufficiently studied by experiment. So, we have carried out the synthesis of phosphorus- and arsenic-bearing sodium (potassium) feldspars in hydrothermal conditions at T=400÷600°C, P=1.5 kbar. The mixtures of salts and gels: $NaPO_3$ + Al_2SiO_5 (sillimanite gel); Na_3AsO_4 (or NaOH + As_2O_5) + Al_2SiO_5 (sillimanite gel) + SiO_2 were the initial mixtures. Sometimes glass of $NaAl_2SiPO_8$ composition obtained by melting of Al_2SiO_5 gel and sodium metaphosphate ($NaPO_3$) and water (10 wt

%) at T=1200°C and pressure 2 kbar was used. The analyses of synthesized phases were produced by microanalysis and X-ray analysis. It is shown that synthesized phases may be related to feldspars based on the composition and X-ray properties. Isomorphism in synthesized feldspars exercises according to scheme of two silicon atoms substitution to aluminum and phosphorus (arsenic): $2Si^{4+} \leftrightarrow Al^{3+} + P^{5+}(As^{5+})$.

1. Phosphorus-bearing phases Apparently, synthesized phases don't form continuous sequences of solid solutions in the $NaAlSi_3O_8$ – $NaAl_2SiPO_8$ systems. The figure 1 shows that in experiments of phosphorus-bearing feldspars synthesis practically pure albites coexist with phosphorus-bearing feldspars in which $NaAlSi_3O_8 \leftrightarrow NaAl_2SiPO_8$ substitution is up to 50 or more mol% of $NaAl_2SiPO_8$ minal. Moreover, in some experiments phosphorus practically entirely replaces silicon and phase $Na_{0.76}Al_{2.33}P_{1.65}O_8$ is formed. Substitution of $2Si^{4+} \leftrightarrow Al^{3+} + P^{5+}$ in synthesized phases is described by following regression equation: (Al+P)= 3.956 – 0.488*(2Si); (n=40; r=0.998; S_x=0.07; E_x=0.02).

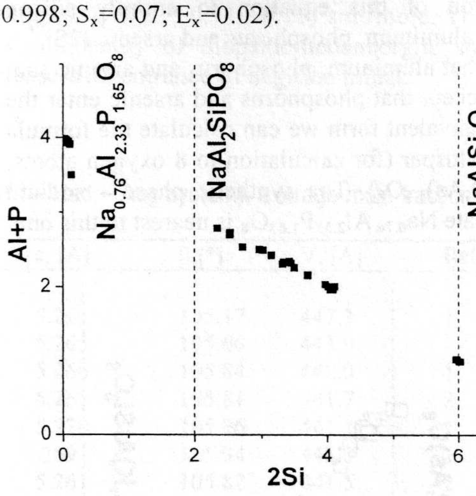

Fig. 1. Isomorphic interrelations in synthetic phosphorus-bearing feldspars.

Table 1. Cell parameters of synthetic phosphorus-bearing feldspars

N	a, [A]	b, [A]	c, [A]	α, [°]	β, [°]	γ, [°]	V, [A]^3
6378	8.179	12.992	7.168	94.39	116.67	89.47	677.9
6379	8.166	13.036	7.139	93.90	116.48	89.63	678.4
Sim*	8.164	13.019	7.139	94.00	116.61	89.85	676.4
l-Ab**	8.135	12.785	7.158	94.27	116.60	87.68	663.8

* Cell parameters of synthetic phosphorus-bearing feldspar [*Simpson*, 1977].
** Cell parameters of low albite [*Kroll, Ribbe*, 1987].

Table 2. Formula and atomic interrelations in phosphorus- and arsenic substituted feldspars

Formula to 8 atoms (O)	(Na+K)/Al	[Al+P(As)]	Al/[P(As)]
$Na_{0.76}Al_{2.33}P_{1.65}O_8$	0.326	3.98	1.412
$(Na,K)_{1.64}Al_{1.89}As_{1.74}O_8$	0.868	3.63	1.104
$(Na,K)Al_2SiP(As)O_8$	0.5	4.00	1.00

X-ray study of synthesized phases has allowed correcting the cell parameters of phosphorus-bearing feldspars (tabl. 1). These data show that cell parameters of phosphorus-bearing feldspars are close to ones described in work [*Simpson*, 1977].

2. Arsenic-bearing phases. Synthesis of arsenic-bearing feldspars has allowed obtaining As- substituted phases with compositions: $NaAl_{1.5}Si_2As_{0.5}O_8$ and $NaAl_2SiAsO_8$. $2Si^{4+} \leftrightarrow Al^{3+} + As^{5+}$ substitution in synthesized phases is described by following regression equation:

(Al+As)= 3.754 – 0.448*(2Si); (n=40; r=0.989; S_x=0.12; E_x=0.04).

Moreover, in some experiments the phase corresponding to composition of entirely silicon substitution to aluminum and arsenic $2Si^{4+} \rightarrow Al^{3+} + As^{5+}$ has been synthesized. The composition of this phase is following: $(Na,K)_{1.64}Al_{1.89}As_{1.74}O_8$. The comparison of this phase with the phase of phosphorus feldspar (entirely substituted by aluminum and phosphorus) is presented in tabl. 2. From tabl. 2 it follows that entirely substituted phosphorus and arsenic phases differ in interrelation of isomorphic elements; it seems to connect with geometric, dimension factors. Isomorphic interrelations in arsenic-bearing feldspars are presented by fig. 1. It is shown that solid solutions from albite to $(Na,K)Al_2SiAsO_8$ exist. Figure 2 demonstrate the entirely substituted by arsenic and aluminum phase $(Na,K)_{1.64}Al_{1.89}As_{1.74}O_8$, too.

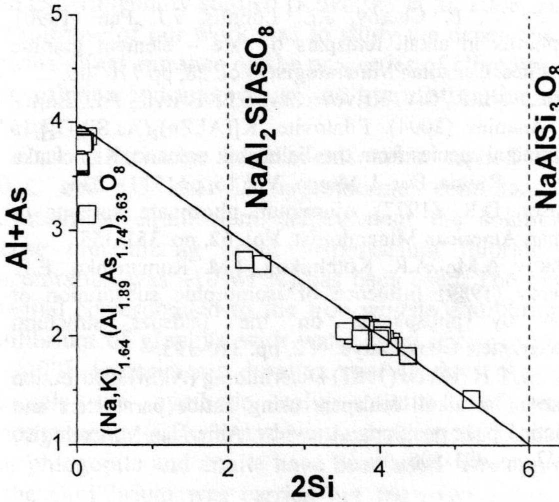

Fig. 2. Isomorphic interrelations in synthetic arsenic-bearing feldspars.

Isomorphic interrelations in natural P, As-bearing feldspars are presented in fig. 3. All natural As-bearing feldspars are shown to correspond to solid solutions of $(Na,K)AlSi_3O_8$ – $(Na,K)Al_2Si(As,P)O_8$ system. $2Si^{4+} \leftrightarrow Al^{3+} + (P^{5+}, As^{5+})$ substitution in synthesized phases is described by following regression equation:

[Al+(As,P)]= 4.057 – 0.508*(2Si); (n=40; r=0.996; S_x=0.05; E_x=0.02).

Extrapolation of this equation to entirely silicon substitution by aluminum, phosphorus and arsenic ($2Si^{4+} = 0$) contributes that aluminum, phosphorus and arsenic sum must be 4. If accept that phosphorus and arsenic enter the structure in pentavalent form we can calculate the formula of hypothetic feldspar (for calculation to 8 oxygen atoms: $(Na,K)_{1.0}Al_{2.5}(P,As)_{1.5}O_8$). The synthetic phase – sodium aluminophosphate $Na_{0.76}Al_{2.33}P_{1.65}O_8$ is nearest to this one.

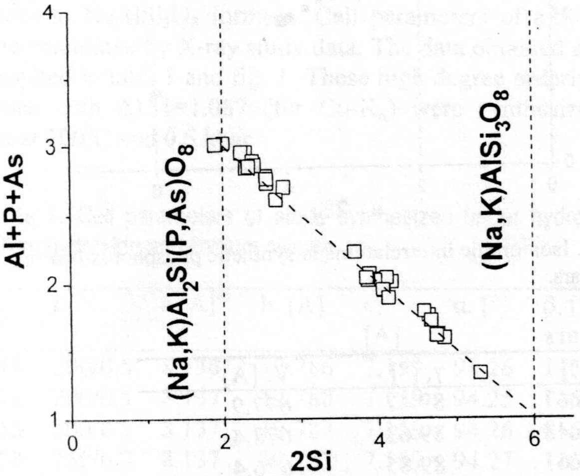

Fig. 3. Isomorphic interrelations in natural P, As-bearing feldspars (volcano Tolbachik).

The existence of phases with entirely silicon substitution to aluminum, phosphorus and arsenic in natural phosphorus- and arsenic-bearing feldspars is not noted. In natural conditions the chemical activity of phosphorus and arsenic is likely to be less than in our experiments.

References

1. London D., P. Cherny, J.L. Loomis, J.J. Pan (1990). Phosphorus in alkali feldspars of rare – element granitic pegmatites. Canadian Mineralogist, Vol. 28, pp.771-786.
2. Vergasova L.P., S.V. Krivovichev, S.N. Britvin, P.C. Burns, V.V. Ananiev (2004). Filatovite, $K[(Al,Zn)_2(As,Si)_2O_8]$, a new mineral species from the Tolbachik volcano, Kamchatka peninsula, Russia. Eur. J. Miner., Vol.16, pp. 533 – 536.
3. Simpson D.R. (1977) Aluminum phosphate variants of feldspar. American Mineralogist, Vol. 62, pp. 351-355.
4. Bychkov A.M., A.R. Kotelnikov, I.M. Romanenko, E.E. Senderov (1989) Influence of isomorphic substitution of silicon by phosphorus on the feldspar structural characteristics. Geokhimiya. N 2, pp. 310-313.
5. Kroll H., P.H. Ribbe (1987) Determining (Al,Si) distribution and strain in alkali feldspars using lattice parameters and diffraction-peak positions: A review. American Mineralogist, Vol. 72, pp. 491-506

Kotelnikov A.R., Kovalskaya T.N., Kovalsky A.M. Solid solutions of triangle clinopyroxenes: synthesis and cell parameters refinement

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Key words : clinopyroxene, solid solutions, cell parameters

Clinopyroxenes are the minerals widespread in metamorphic and magmatic rocks. As a general rule clinopyroxenes are solid solutions of three or more minales. The study of alkaline clinopyroxene solid solutions represented by the diopside – hedenbergite – aegirine system was the purpose of our work. In previous papers the binary solid solutions aegirine – diopside [Nolan, Edgar, 1963], diopside –hedenbergite [Nolan, 1969], aegirine – hedenbergite [Redhammer et al, 1998] have been investigated. These studies show insignificant deviation of clinopyroxenes solid solutions from ideality. At the same time the Nolan`s results [Nolan, 1969] concerned with synthesis of clinopyroxenes in triangle system (Di-Hed-Aeg) demonstrate the existence of valuable deviations from ideality in spite of great data dispersion. To estimate the influence of aegirine intromission to the clinopyroxene solid solutions systematically it has been necessary to synthesize the triangle solid solutions with constant content of aegirine minal (20 mol.%). The synthesis of clinopyroxene triangle solid solutions (in the system diopside – hedenbergite – aegirine) was carried out at the temperature 750oC and pressure 1.5 kbar; experiment duration was 45 days. The initial materials were gel mixtures of corresponding compositions in mole proportions. Hedenbergite gel was previously deoxidizing in hydrogen flow at 600oC during 2 hours. We select mixtures with mole part of aegirine 0.2 in every one. Synthesis of clinopyroxene was carried out in solution of potassium fluoride which is good mineralizer. Herewith potassium doesn't penetrate into clinopyroxene composition. Oxygen potential was preseted by iron-wustite (or wustite-magnetite) buffer. The ratio test charge:fluid was 12÷15. Microanalysis shows correspondence of synthetic clinopyroxenes to theoretical formula. Aegirine content in synthetic clinopyroxenes is according to mole fraction $X_{Aeg}^{CPx3}=0.22\pm0.03$. Based on the x-ray study the cell parameters refinement has been produced. Estimation of cell parameters was realizing for c2/c space group (tabl. 1).

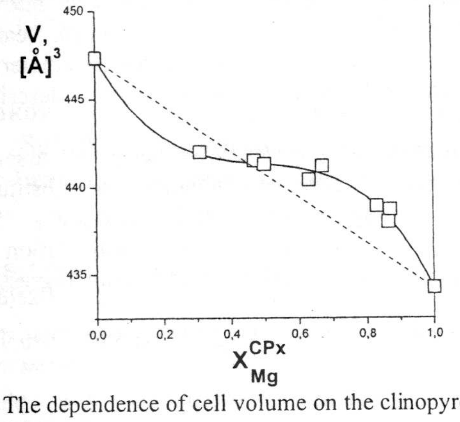

Fig. 1. The dependence of cell volume on the clinopyroxenes composition.

For analytical description of clinopyroxene cell parameters it has been used the polynom as:

$$P = A_0 + A_1*x + A_2*(x^2) + A_3*(x^3) \qquad (1)$$

where x is the mole fraction of magnesium in clinopyroxenes.

The values of coefficients of the equation (1) for the estimation of clinopyroxene cell parameters with aegirine mole fraction whose value is 0.2, are presented in the table 2.

The dependence of cell volume on the composition is shown at the fig. 1. It is observed that triangle solid solutions are characterized by alternating deviation from ideality. To describe the clinopyroxenes excess volumes of mixture the Margules approximation was used. For the triangle solid solutions of clinopyroxenes (aegirine – diopside – hedenbergite system) following values of Margules equation parameters were obtained: W1 = 3.59(±12); W2 = -2.66(±8) sm^3/mole. These parameters essentially exceed the values of analogical parameters for the binary hedenbergite-diopside solid solution: W1 = 0.34(±0.03); W2 = 0.71(±0.15) sm^3/mole. This evidences that nonideality of diopside-hedenbergite solid solution increase with entrance of aegirine minal.

Table 1. Cell parameters of triangle solid solutions of clinopyroxenes (Di – Hed – Aeg system); average mole fraction of aegirine is 0.22±0.03

Mol.% Aeg	Mol.% Hed	Mol.% Di	X_{Mg}^{CPx} 1)	a, [A]	b, [A]	c, [A]	β,[°]	V, [A]^3	References 2)
20	80	0	0	9.821	8.984	5.253	105.17	447.3	1
20.6	57.5	21.9	0.276	9.777	8.957	5.265	105.66	443.9	2
33	46	21	0.31	9.767	8.933	5.266	105.84	442.0	1
25.4	47.3	27.3	0.366	9.764	8.937	5.262	105.81	441.7	2
22	41	37	0.47	9.763	8.925	5.270	105.96	441.5	1
20	40	40	0.50	9.758	8.926	.269	105.94	441.3	1
20	37.7	42.3	0.529	9.761	8.937	5.261	105.82	441.5	2
22	29	49	0.63	9.752	8.923	5.263	105.93	440.4	1
25	25	50	0.67	9.758	8.930	5.262	105.82	441.2	1
24.6	22.9	52.5	0.696	9.747	8.919	5.264	106.00	439.9	2
23	13	64	0.83	9.744	8.906	5.262	106.03	438.9	1
14.5	13.5	72	0.842	9.746	8.924	5.263	105.92	440.1	2
12	12	76	0.87	9.740	8.912	5.256	105.94	438.7	1
29	9	62	0.873	9.728	8.902	5.261	106.15	437.6	2
20	0	80	1	9.723	8.919	5.220	106.43	434.2	1

X_{Mg}^{CPx}= Mg/(Mg+Fe^{2+}); 2) References: 1 – our data; 2 – data of Nolan [Nolan, 1969].

Table 2. Polynom coefficients for the estimation of cell parameters of clinopyroxene triangle solid solutions (aegirine mole fraction is 0.2)

Parameters, (P)	A_0	A_1	A_2	A_3	S_x 1)	E_x 2)
a, [A]	9.821	-0.27155	0.42079	-0.24709	0.005	0.002
b, [A]	8.983	-0.15733	0.0979	-0.007406	0.007	0.003
c, [A]	5.253	-0.012382	0.18647	-0.20505	0.007	0.003
β,[°]	105.16	4.10935	-7.95421	5.07771	0.08	0.04
V, [A]^3	447.3	-30.1444	57.2286	-40.04632	0.57	0.31

1) S_x – root-mean-square deviation of experimental data approximation by polynom; 2) E_x – approximation accuracy.

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References

1. Nolan J., A.D. Edgar (1963) An X-ray investigations of synthetic pyroxenes in the system acmite- diopside – water at 1000 kg/cm^2 water pressure. Min.Mag., V. 33, pp. 625-634.
2. Redhammer G.J., G. Amthauer, G. Roth, G. Tippelt, W. Lottermoser (2006). Single-crystal X-ray diffraction and temperature dependent ^{59}Fe Moessbauer spectroscopy on the hedenbergite – aegirine (Ca,Na)(Fe^{2+}Fe^{3+})Si$_2$O$_6$ solid solutions. Amer.Mineral., V. 91, pp.1271-1292.
3. Nolan J. (1969) Physical properties of synthetic and natural pyroxenes in the system diopside –hedenbergite – acmite. Min.Mag., V. 37, pp. 216-229.

Kotelnikov A.R., Kovalsky A.M., Suk N.I. Mg and Fe distribution between ternary solid solutions of clinopyroxenes and bioite

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Key words: Clinopyroxene, biotite, solid solutions, excess energy of mixing

To construct the mineral thermometer using CPx-Bi association the data of magnesium and iron distribution between these minerals are necessary. This equilibrium for binary clinopyroxenes of diopside-hedenbergite range has been experimentally studied [Kovalsky et al, 2008, 2009]. The purpose of our work was to study the dependence of aegirine minal entrance on the properties of clinopyroxene solid solution and magnesium and iron distribution in Bi-CPx pair.

Cation exchange experiments were carried out at 750oC and 1.5 kbar in hydrothermal conditions. For activation of equilibrium achievement the solution of intense mineralizing agent – potassium fluoride (KF concentration was ~10 wt %) has been used. The oxygen potential corresponded to the iron-wustite equilibrium or equilibrium of graphite with water fluid [Gramenitsky et al, 2000]. Experiments duration was 45 days. As initial materials the synthetic solid solutions of ternary clinopyroxenes (CPx-3) and synthesized at 650°C and 1.5 kbar phlogopite and annite have been used. The approach to the equilibrium was carried out from two sides. The initial minerals compositions and results of cation exchange experiments are presented in table 1.

Based on the cation exchange experiments the isotherm of Mg and Fe distribution between CPx-3 and Bi has been obtained (fig. 1). Mg distribution coefficient between clinopyroxene and biotite (KD) is described by equation of third order: ln(KD) = 0.65 + 3.30*x -5.763*x2 -1.0911*x3 (±0.40), where x is magnesium mole fraction in clinopyroxene (x=Mg/(Mg+Fe2+)). Used this equation the energy parameters of nonsymmetrical Margules model for description of excess energy of mixing of clinopyroxene solid solutions (Aeg – Di – Hed system, aegirine mole fraction is 0.2±0.04) have been calculated: W1 = -48.5 (16.2) and W2 = 24.1 (2.5) kJ/mole. Earlier the equilibrium CPx-Bi for binary clinopyroxene solid solutions was studied [Kovalsky et al, 2008, 2009] and practically ideal miscibility in diopside-hedenbergite range was shown. So, we can conclude that nonideality of diopside-hedenbergite solid solution increases with entrance of aegirine minal. Based on the Perchuk`s data [Perchuk, 1970] of natural clinopyroxene and biotite paragenesis the excess energies of mixing of clinopyroxenes have been calculated for 750oC isotherm (fig. 2). Based on our experimental data, calculations using Perchuk`s [Perchuk, 1970] and Kovalsky`s [Kovalsky et al, 2008, 2009] works we estimated the integral excess energies of mixing (tabl. 2).

Table 1. The experimental results of Mg and Fe exchange between clinopyroxene (CPx-3) and biotite (Ann – Phl range) at 750°C and 1.5 kbar. $K_D=[X_{Mg}^{CPx3}*(1-X_{Mg}^{Bi})]/[(1-X_{Mg}^{CPx3})*X_{Mg}^{Bi}]$

№	X_{mg}^{CPx3} until/exp	X_{mg}^{Bi} until/exp	X_{mg}^{CPx3} after/exp	Variation	X_{mg}^{Bi} after/exp	Variation	K_D	ln(K_D)
6424	0.50	1.0	0.73	0.70÷0.75	0.91	0.90÷0.93	0.267	-1.319
6431	0.83	0.0	0.65	0.62÷0.66	0.42	0.40÷0.43	2.565	0.942
6433	0.80	0.0	0.43	-	0.22	0.20÷0.23	2.675	0.984
6489	0.83	0.5	0.66	0.63÷0.77	0.63	0.59÷0.67	1.140	0.131
6490	0.05	1.0	0.68	0.64÷0.72	0.63	0.62÷0.63	1.248	0.221
6491	0.05	0.5	0.55	0.47÷0.55	0.42	0.42÷0.45	1.689	0.523
6492	0.60	1.0	0.68	0.65÷0.69	0.82	0.81÷0.83	0.466	-0.762
6499	0.50	0.00	0.43	0.41÷0.45	0.22	0.21÷0.23	2.675	0.984
6501	0.83	0.00	0.45	0.38÷0.46	0.29	024÷0.30	2.003	0.695
6505	0.5	1.0	0.74	0.60÷0.74	0.80	0.80÷0.82	0.711	-0.340

$$\ln(K_D) = 0.65 + 3.30*x - 5.763*x^2 - 1.0911*x^3\ (\pm 0.40) \quad (1)$$

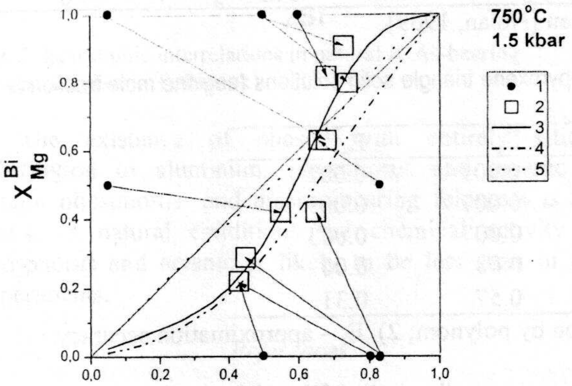

Fig. 1. Mg, Fe distribution between ternary solid solution of CPx (Aeg-Di-Hed, X_{Aeg}=0.2) and biotite. 1– initial compositions of CPx and Bi; 2 – equilibrium compositions of CPx and Bi after experiments; 3 – isotherm of Mg, Fe distribution between CPx and Bi (our data); 4 – isotherm of Mg, Fe distribution between CPx and Bi (natural paragenesis [*Perchuk,* 1970]); 5 – isotherm of Mg, Fe distribution between binary CPx and Bi [*Kovalsky et al*, 2008].

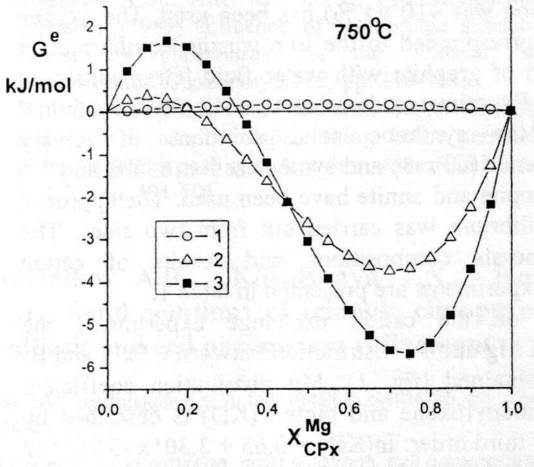

Fig. 2. Concentration dependences of excess mixing energies of clinopyroxenes solid solutions. 1 – binary CPx (Di-Hed range); 2 – natural CPx [Perchuk, 1970]; 3 – ternary solid solutions of CPx (Aeg-Di-Hed, XAeg=0.2).

Table 2. Dependence of values of integral excess energies of mixing G^e_{int} (kJ/mol) (750°C) of diopside-hedenbergite clinopyroxenes on the content of third minal (jadeite or aegirine)

№	Average composition of CPx	(Aeg+Jd), mol %	G^e_{int} (kJ/mol) (750°C)	Note
1	$(Aeg+Jd)_{0.2}(Di+Hed)_{99.8}$	0.2	0.11	Kovalsky et al (2008, 2009)
2	$Aeg_{5.6}Jd_{8.4}(Di+Hed)_{86}$	14	1.85	Perchuk, 1970
3	$Aeg_{17.4}Jd_{1.1}(Di+Hed)_{81.5}$	18.5	2.76	This work

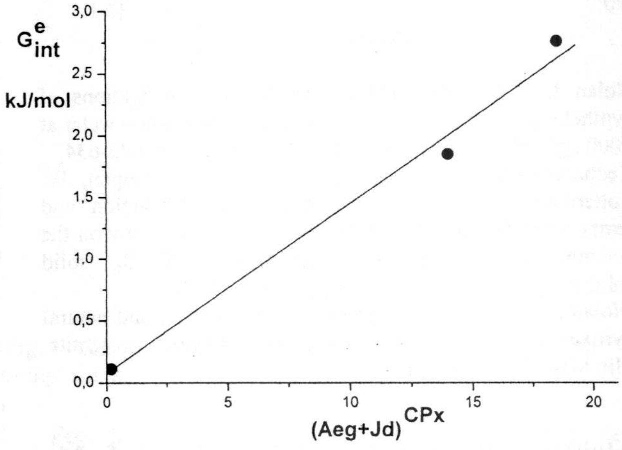

Fig. 3. Dependence of CPx integral excess energies of mixing on the jadeite and aegirine minals content.

It has been shown that values G^e_{int} of diopside-hedenbergite solid solutions depend on entrance of third minal (jadeite or aegirine) linearly (fig. 3.).

Conclusions

1. The Mg and Fe distribution between clinopyroxene (ternary solid solution of Di-Hed-Aeg system; X_{Aeg}^{CPx}=0.2) and biotite (binary solid solution of Phl-Ann)

has been studied at 750°C and 1.5 kbar in hydrothermal conditions.

2. It has been shown that Mg, Fe^{2+} distribution between clinopyroxene and biotite is unideal; when there is low X_{Mg}^{CPx} , Fe^{2+} enriches biotite, when $X_{Mg}^{CPx} > 0.7$, the inversion takes place and Fe^{2+} redistributes to the CPx.

3. Based on the data of Mg, Fe^{2+} distribution between clinopyroxene and biotite the Margules parameters of clinopyroxene mixing model have been calculated; it has been shown that value of integral excess energies of mixing directly correlate with mole fraction of third clinopyroxene minal (aegirine and jadeite).

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References

1. Kovalsky A.M., T.N. Kovalskaya, A.R. Kotelnikov (2008) Calibration and application of mineral thermometer based on the study of clinopyroxene-biotite equilibrium. Abstracts of Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry. Moscow, GEOKHI RAS, 22-23 april 2008, pp. 36-37.
2. Kovalsky A.M., T.N. Kovalskaya, A.R. Kotelnikov (2009) Experimental study of Mg and Fe distribution in the system clinopyroxene-biotite, thermometry of natural paragenesis. Abstracts of Russian youth scientific conference “Minerals: structure, properties, investigation methods”. Miass, IM Ural D. RAS, p. 38.
3. Gramenitsky E.N., A.R. Kotelnikov, A.M. Batanova, T.I. Shchekina, P.Yu. Plechov (2000) Experimental and technological petrology. M., Scientific World, 415 p.
4. Perchuk L.L. (1970) Equilibria of rock forming minerals. M., Science, 392 p

Makarov V.P. At the two mechanism of garnets allocation

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Key words: garnet, the allocation mechanism, minerals, magmatic melt, kimberlite, mafics, eclogites, granites, the acidic rocks,

Under the mechanism of allocation of minerals is a chemical reaction, leading to the deposition of mineral. The solution of this problem helps identify the conditions of the formation of garnets, and, hence, and host mineral rock. Thus, the problem of the mechanism of allocation of mineral is one of the inverse problems of geology, directed to the establishment of conditions for the formation of rocks (ores).

Base solving the problem are the laws of chemistry and physical chemistry. Considerable information about the mechanism of allocation of minerals represent a variety of experiments, carried out by domestic and foreign researchers practically for all time of existence of geology, as a branch of scientific knowledge. These studies include a wide range of minerals, both soluble in water (fluid) in a wide interval of temperatures (T) and pressure (P), as well as minerals, spun off from the magmatic melts.

Solution of the problem is based on the axiom: 1) in the reactions of the natural mineral formation is always maintained the state of thermodynamic isotope and geochemical equilibria between the explored mineral M and some connection $\dot{C}$. It is generalization of the point of view of E.M. Galimov [1]. 2) geochemical system M- $\dot{C}$ is formed as a result of the collapse of some initial parent substance.

In general solution of the problem is divided into two stages: 1) determination of the composition of connection $\dot{C}$, equilibrium studied mineral; 2) on the basis of the determination of the composition of the parent compounds, decomposition of which formed compounds M and $\dot{C}$.

Procedure for solving tasks of the first stage is an analysis of the isotherms of the relations of elements in a mineral or minerals. For these minerals methods of the analysis of gas-liquid or melt inclusions determine taken for the standard temperature (T_{et}) education of these minerals. That are prepared pairwise relations of the three elements. Method of culling for the selection of sampling is described in [12, 13]. According to this new charts of isotopes (elements) in one or more minerals, having the angular coefficient of S_{watch} [2, 6].

According to literary data the isotopic composition of quartz Qw, biotite Bio, and muscovite Mus, feldspars Kf, albite Al, adularia, plagioclase Pl_{40}, garnet Grn, diopside, hornblende. Set the sequence of allocation of minerals in the form of sequences [3, 5]

(Qw, Bio) >
> (Mt, Il) > Al_1> Mus > Al_2 > Grn, (A, magmatites)
(Qw, Bio) >
>(Mt, Il) > Pl_{40} > Mus > Grn. (B, metamorphites)

This is the most rich in the number of silicate analyses mineral. He is from the granites, peridotites, pyroxenite, lherzolites, kimberlite, gneisses, schists, enderbites, eclogites different regions of the world. On it are the chemical exchange reactions elements of Ca, Mg, Fe and Mn between connections Grn -$\dot{C}$. As a $\dot{C}$ taken: Ca, Mg, Fe, Ca^{+2}, Mg^{+2}, Fe^{+2}, CaO, MgO, Fe, Fe_2O_3, Al_2O_3, pyroxenes, biotite, olivines, cordierites, sillimanites (for a couple of Fe^{+3}-Al^{+3}), spinels (including maghetites), corundum, hematite. In terms of education all sample garnets are conditionally divided into two parts:

A. Garnets of a) kimberlite; b) ultrabasic rocks (mafic, pyroxenite, peridotites, lamproites) and c) of eclogite. In the group of kimberlites sample garnets in the vast majority are selected from the diamond-bearing tubes of Yakutia. From melt inclusions single definition T_{form} garnets range from 1150°C (kimberlite, tube Berry; N. I. Zinchuk, etc., 1999) to 1230°C (eclogite, Mugojari, V.B. Naumov, 1979). The same T_{form} a garnets on geochemical barothermometers: Pyr 1000-1200°C, Cpx- 980-1400; P= 40-75 kbar (A.I. Ponomarenko, 1977; E.E. Lazko, 1976; L.I. Panina and others., 1973; J.E.N. Pike, 1976, etc.). The average T_{form} of pyroxenes, olivine and plagioclase is approximately 1250°C, it is taken as a reference; minerals are in equilibrium CO_2 and together with it stand out [2]. On garnets isotopic data are not available. According to geological data Grt (Pyr- pyrope) are together with clino- (Cpx, diopside) and ortopiroxenes (Opx, enstatite), rarely - kyanite [9 - 11].

The available geochemical data pyrope thermodynamically is equilibrium pyroxenes. Communication Grt with pyroxene is genetic: they are formed from the decomposition of protomatter. Assessment of its composition is based on data for quantitative measurements of the Pyr/Cpx in real objects, often Pyr/Cpx ≈ 1.0. Then $Mg_3Al_2Si_3O_{12}$ + $CaMgSi_2O_6$= $CaMg_4Al_2Si_5O_{18}$ is cordierite, initially formed, perhaps, by the reaction of (An)= (Mg-Ol) + 2(Mg-Opx) (considered J.M. Mclelland and P.R. Whitney (1980)).

For pyroxenes (diopsides) together with olivine and plagioclase on the isotope data set equilibrium with CO_2 to oxygen. Then the equation of garnet and pyroxene should has the form ... = ... **{Gr + [Px} + CO_2]** + ..,here brackets reflect: [...] - isotope; {...} - geochemical equilibrium.

Thus, the supplier ^{18}O in minerals is CO_2, consistent with good solubility of CO_2 in the ultrabasic melts of high pressures (A.A. Kadik and etc. 1982). When analyzing the impact of CO_2 on the melting of the silicates in the literature were considered reaction carbonatization pyroxenes (enstatites Ens) and olivine under pressure: (1) Ol + Dio +CO_2 → Ens + Dol; (2) Ol + Dol + CO_2 → Ens + Mgt (magnesite). The obtained results show doubtfulness of these equations. These data can be understood, if we consider, for example, the equation (1) in the form of Ens + Dol → Ol + Dio +CO_2. This leads to the hypothesis that the ultrabasic rocks – transformation product of the pyroxene (enstatite) - dolomite (or magnesite) rocks.

B. On the isotope data all biotites are formed at T ≈ 700°C, plagioclases ≈ 500°C. On the isotope data [4 - 6] and the analysis of gase-liquid inclusions garnet is allocated at 300-450°C. On the official point of view - ≈ 700°C, but it relies heavily on the geochemical thermometers, the use of which there are significant errors [7]. Biotite and garnets are in equilibrium with water. About cordierite information is not available. In experiments of L.L. Perchuk and etc. (1983) at T= 550-1000°C ion exchange between garnet and cordierite at joint crystallization is absent.

The results of calculations and comparisons have shown that the best agreement is observed in equilibrium of garner with cordierite, biotite, and pyroxene. According to geological data in the studied rocks pyroxene is not identified. Biotite also under suspicion, as between it and pomegranate there is a significant difference in T_{form}. The basic version is equilibrium with cordierite, often present in gneisses in association with a garnets. Thus, the probable equation of education garnets has the form

... = {Cor + [Grn }+ H_2O]+ ....

The results of interpretation of the obtained results are based on the work [8, p. 284]. Transition of rocks of green-schist facies, rocks epidote amphibolites is carried out on the basis of reaction Chl + Qw → Grn + H_2O (Chl-chlorite). But, explaining isotopic equilibrium garnet with water, this reaction does not reflect the geochemical equilibrium of mineral with other components of gneisses. In describing the origin of garnets, N.A. Eliseev [8] also writes about the reaction of Chl + Qw → Cor + Ant + H_2O (Ant - anthophyllite). These reactions occur at different P-T conditions. But their unification in the central areas of P-T conditions leads to the reaction of formation of minerals: Chl + Qw → {Cor + [Grn} + H_2O], the scheme of allocation received by isotope-geochemical data.

Thus, in the history of the formation of garnets are two different mechanism of its formation. In the acidic rocks garnet is in equilibrium with water and cordierite, corresponding conditions, characteristic facies of epidote amphibolites.

In ultrabasic rocks, forming at high values of T and P, the garnets are together with pyroxene in equilibrium with CO_2. Here already protomatter substance, perhaps, is the cordierite; the primary products can also be pyroxene (enstatites) - dolomite (or magnesite) rock (marbles or skarns).

References

1. Galimov E.M. Isotopes of carbon in the oil and gas geology. M: Nedra, 1973.
2. Makarov V.P. Method of definition of temperature of the natural compounds. Avt.cert.1312504. // Bull. inventions and discovery.1987. N19. P.192.
3. Makarov V.P. The sequence of rock-forming minerals on the isotope data./All-union conference. "Geochemistry of magmatic rocks. Alkaline magmatism of the Earth". Tez. dokl. M.: GEOKHI, 1991, C.98.
4. Makarov V.P. The temperature of formation of rock-forming minerals. /Vseros. conference. "Geochemistry of magmatic rocks. Alkaline magmatism of the Earth". Tez. dokl. M.: GEOKHI, 2002. p.66. URL: http://alkaline2002.narod.ru.
5. Makarov V.P. About the mechanism of allocation of minerals of igneous and metamorphic rocks./The annual seminar on the Exper. miner., petrol. and geochemistry. Tez. dokl. M.: GEOKHI, 2004. Electronic science .information journal " Office of division of science about earth RAN ".2004. (1,). URL: www:geokhi.ru/conference/ annotat-05-05/ doc. URL: www:scgis.ru/russion/cp1251/h_dgggms/1-2004/ informbul-1_2004/izotop-2.pdf.
6. Makarov V.P. Isotope geothermometers./The 13-th scientific seminar "System "Planet Earth".- M.: Moscow, state university, NGO "Harmony of a structure of the Earth and planets", 2005, C. 228- 253.
7. Makarov V.P. Comparison of results of formations temperature of minerals. /VII International. Conf. "New ideas in Earth sciences", M.: RSGRU, 2005, V.2. P.155.
8. Eliseev N.A. Metamorphism. M.: Nedra, 1963.
9. Makarov V.P. On the mechanism of formation of minerals in kimberlites. 2. The nature of garnets and spinel. /Seminar "Geochemistry of magmatic rocks. Alkaline magmatism of the Earth". GEOKHI, 2002. URL: www.alkaline2002. narod.ru.
10. Makarov V.P. On certain conditions of crystallization of minerals mafic rocks and meteorites. /Seminar "Geochemistry of magmatic rocks. Alkaline magmatism of the Earth". GEOKHI, 2005. URL: www.alkaline2005. narod.ru.
11. Makarov V.P. On the mechanism of allocation of minerals. 3. Some of the conditions of crystallization of minerals of mafic rocks and meteorites./Tez. dokl. M.: GEOKHI, 2006. Electronic science information journal. "Office of division of science about earth RAN". №1(24)'2006. URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2006/informbul-1_2006/izotop-3.pdf
12. Makarov V.P. "The phenomenon of compensation - a new form of communication between the geological objects./ Materials of I International scientifically-practical conference "Formation of the contemporary science - 2006". V.10. Dnepropetrovsk: Science and education, 2006. P.85- 115.
13. Makarov V.P. "Compensation equation" - a new method of study of petrochemical peculiarities of high-temperature formations (by the example of biotite)./Materials of the all-Russia meeting "Geochemistry, petrology, mineralogy and genesis of alkaline rocks". Miass: izd. institute of mineralogy UrO RAN, 2006. P.137-139.

Marina E.A., Marin A.A., Bublikova T.M., Balitsky V.S. Synthesis of eulytite ($Bi_4Si_3O_{12}$) crystals in the hydrotermal solutions with different compositions.

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Eulytite ($Bi_4Si_3O_{12}$) is one of the rarest minerals in a nature. It occurs in the albitized pegmatites in the tetrahedral crystals form and crust around tantalum grain in the Caucasus, find out together with quartz and native bismuth in the Shneeberg and Johanngeorgenstadt (Germany), in the Banat (Rumania), single finding – in the France and Western Australia [Semenov E.I. at al.,1981; Frey K. at al. 1985; Chukhrov F.V. at al., 1972].

Crystals of eulytite are uses for scintillator in the high-energy physics, computer tomography, dosimetry. One of the most promising materials for these purposes is a single crystal bismuth orthogermanate with the structure of eulytite. However, eulytite has better scintillation properties compared with bismuth orthogermanate (e.g., its decay time (0.1 ms) is 3-fold higher), but because of the difficulty of growing eulytite single crystals from the melt (due to high viscosity) the problem remains unsolved. It is well known that in modern science and technology there is a clear trend to replace the single crystal materials with the ceramic ones obtaining in fact the same or even improved functional characteristics. The technology of optical ceramics, compared with the technology of single crystals grown from the melt, has several additional advantages. A breakthrough in technology of oxide ceramics has been achieved only in the last decade. This was facilitated mainly by the use in their manufacturing powders as initial oxide components.

It is known that the ceramics of optical quality are produced by pressing small natural or synthetic crystals [Basiev T.T. at al., 2008]. We believe that the ceramics obtained from crystals of bismuth orthosilicate that we grow, will have better scintillation characteristics than the ones obtained by direct sintering of the initial oxide components.

Previously eulytite was synthesed in NaOH [Litvin B.N. at al., 1968], but subsequent researches in this field don't carried out. Eulytite crystals in ammonium fluoride and hydrogen peroxide we grown in a first time in the world. The analysis of the results of our researches has shown that hydrogen peroxide is the most perspective solvent for eulytite synthesis. So long as in the system unavailable elements, which incoming in composition of eulytine, these automatically solve a problem of impurities of dissolvent in obtained crystals. The given problem faced rather critical, so far us very difficult to separate obtained crystals from environment of growth, not allowed their contamination of dissolvent elements (Na or F).

Synthesis of the eulytite was carried out by hydrothermal method at temperature of 250 - 260°C and pressure 500 bars. High-temperature autoclaves have volume of 250 ml. Use of contact Teflon fettle was feature of the technique applied by us, allowing to exclude ingress of the elements containing in a steel of autoclaves in a solution. Starting material was stoichiometric mix of Bi_2O_3 и SiO_2. The fine crystalline eulytite got in experiments with duration from 10 to 60 days. We carried out experimental researches to crystals of eulytite in the alkaline (NaOH), fluoride (NH_4F), hydrogen peroxide (H_2O_2) solutions. The best results have been received at growth of crystals in solutions NaOH with concentration from 5 to 20 wt %, NH_4F concentration 1 and 2 wt % and H_2O_2 concentration from 2 to 5 wt %. X-ray patterns show the presence of eulytine eumorphic crystals virtually without admixtures of other minerals. It is especially pronounced at growth of eulytite in a solution of hydrogen peroxide since in the system absent elements strange in composition to eulytite.

The research of obtained crystals by means of electronic-scanning microscope has showed that eulytite crystals grown in different solutions have tetrahedral habitus, but generally that's crystals aggregates with vague marked faces. Habit which is similar to natural one at the most has patterns grown in hydrogen peroxide. (Fig.1, 2)

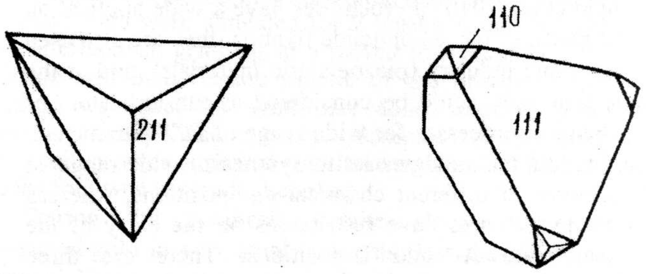

Fig.1. Crystals habit of eulytite is from field Shneeberg (Germany) [Shulgin V.V. at al., 1992]

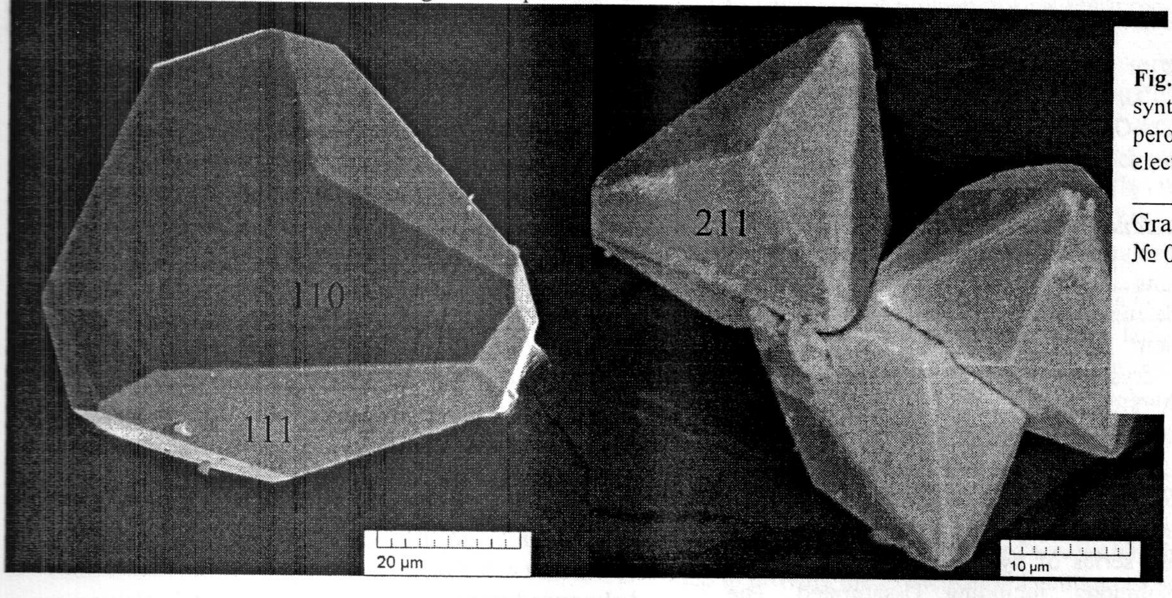

Fig.2. Eulytite crystals synthesized in hydrogen peroxide. (By scanning electron microscopy)

Grant from RFBR
№ 09-02-00647

References

1. Edited by Semenov E.I. (1981) Mineralogical tables. Moscow, Nedra, 400 p.
2. Edited by Frey K. (1985) Mineralogical encyclopedia. Leningrad, Nedra, 512 p.
3. Edited by Chukhrov F.V., E.M. Bronshtedt-Kupletskaya, N.I. Smolyaninova (1972) Minerals, Reference book, Moscow, Nedra, 883 p.
4. Shulgin V.V., T.I. Polupanova, A.V. Kruzhalov, V.M. Skorikov (1992). Bismuth orthogermanate. Ekaterinburg, Vneshtorgizdat, p.8.
5. Basiev T.T., M.E. Doroshenko, V.A. Konushkin, V.V. Osiko, P.P. Fedorov, K.V. Dukelskiy, I.A. Mironov, V.A. Demidenko, A.N. Smirnov (2008) Fluoride optical nanoceramics. Izv. RAS, №5, p.863-873.
6. Litvin B.N., U.V. Shaldin, I.E. Pitovranova (1968) Crystallography, vol. 13, № 6, p.1106.

Redkin A.F., Borodulin G.P. Pyrochlores: hydrothermal synthesis, composition, properties

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Keywords: hydrothermal synthesis, pyrochlore, microlite, betafite, perovskite, uranium, zirconium, vanadium

According to the present day classification, minerals and artificial substances which have chemical formula $A_{2-m}B_2O_6(O,OH,F)_{1-n}\cdot pH_2O$ (where A – cations with charge (Z) from +1 to +4 and $r_A = 1.1–1.5$Å, B – cations, Z from +3 to +5 and $r_B = 0.7–0.9$Å, $m = 0.0–1.7$, $n = 0.0–1.0$ and $p = 0.0–2.5$) and crystal structure correspond to space group *Fd*3*m* are named pyrochlores (Hogarth, 1977, Atencio et al., 2010). Pyrochlores have a wide application as the matrixes for radionuclide fixation, they are also used in electronic industry (piezoelectric materials), and at the same time they could be considered as the indicators of geochemical processes for wide range of *PTX* parameters. The modern technologies let to synthesize wide range of pyrochlores of different chemical compositions, whereas natural pyrochlores have restrictions on the entry of the elements into A- and B-positions. There are three widespread groups of pyrochlores: the pyrochlores-group if Nb>Ta+2Ti, microlite group if Ta>Nb+2Ti, and betafite group if 2Ti≥Nb+Ta (in moles). Thus, the estimation of maximum acceptance of other cations into pyrochlores formed in the appropriate geochemical conditions is of scientific interest.

The synthesis of pyrochlores was carried out in Pt capsules at $T = 800$°C, $P = 2000$ bars, and oxygen fugacity appropriated to Co–CoO, Fe_2O_3-Fe_3O_4, and Cu_2O–CuO buffers. Initial materials were represented by well ground artificial mixtures of NaF (or Na_2CO_3), $CaCO_3$, Nb_2O_5, Ta_2O_5, TiO_2, ZrO_2, V_2O_5, U_3O_8, and $UO_4\times2H_2O$. Saturated at $T = 22$°C NaF solution was used as a medium for the synthesis. The runs duration was 7 days. The phase composition of the run products was studied with XRD powder diffraction analyses, while the chemical composition of crystals was defined on electron microscope VEGA–TESCAN.

The run products were represented by the fine crystal grains of 0.2-20 μm. The mixture with excess of Nb and Ta produced pyrochlores, whereas Ti, Zr and V enriched mixtures gave rise to perovskites (space group *Pm*3*m*). We synthesized the full series of pyrochlores of pyrochlore-microlite solid solutions, including U-saturated. The maximum U^{4+} concentration in this pyrochlores reached 0.2-0.3 f.u. Run products of pyrochlore-microlite solid solutions have a constant $a_0=10.42\pm0.01$Å. The pictures of the typical pyrochlores and perovskites from our experiments are shown on the Fig. 1 and Fig. 2.

When uranium was added into the betafite mixture, the pyrochlore crystal structure stabilized. The compositions of 0.25–0.4 $X(U^{4+})$ gave the 100 % yield of betafite $(Na_{0.79}Ca_{0.91}U_{0.38})(Nb_{1.04}Ti_{0.96})O_{6.19}F_{0.78}$ ($a_0 = 10.30\pm0.01$Å), but a cubic perovskite $(Na_{0.92}Ca_{0.96})(Nb_{0.98}Ti_{1.02})O_{5.88}F_{0.06}$ ($a_0 = 3.851\pm0.003$Å) grew in U-free mixtures. It was observed a straight relation between uranium content in an initial mixture and total titanium in pyrochlore and inverse one between a_0 and $X(Ti^{4+})$. Betafites synthesized in UO_2 and CaF_2 saturated conditions have 0.4–0.5 of U^{4+} and $a_0 = 10.27\pm0.01$Å.

As at betafite synthesis, we could not get the Zr-rich & U-free pyrochlores. Zr^{4+} entering into pyrochlores and microlites is limited because value of ionic radius of $r(Zr^{4+}) = 0.98$ (c.n.=8) – 0.86 (c.n.=6) Å is situated between limited values of radii of cations in A and B positions. The perovskites $(Na_{1.62}Ca_{0.36})(Nb_{1.9}Zr_{0.1})O_6$ and pyrochlores $(Na_{0.36}Ca_{1.36})(Nb_{1.93}Zr_{0.07})O_{6.33}F_{0.34}$ were formed at T=800°C and P=2000 bars from the mixture of composition $NaF+CaCO_3+0.5Nb_2O_5+ZrO_2$. The introduction of 30 wt. % of U_3O_8 into the initial mixture lead to increasing of yield of pyrochlore $(Na_{0.86}Ca_{0.69}U_{0.46})(Nb_{1.55}Zr_{0.45})O_{6.73}F_{0.16}$ with $a_0=10.45\pm0.01$Å.

In the condition of Hem-Mt oxygen buffer, the pyrochlores and microlites with $X(V^{3+}, V^{4+})=0.18$-0.19 ($a_0=10.39$-10.40Å) mixed with VO_2 were obtained from the mixtures of composition $(NaCa)(NbV)O_6F$ and $(NaCa)(TaV)O_6F$. In uraninite saturated system we synthesized pyrochlores $(Na_{0.66}Ca_{0.99}U_{0.26})(Nb_{1.67}V_{0.33})O_{6+x}F_{0.52}$ ($a_0=10.35\pm0.01$Å). In spite of V-bearing pyrochlores were synthesized in conditions of VO_2 stability, the valance of vanadium in pyrochlores remain unsolved. The analysis of composition influence to the a_0 parameter indicates that V^{4+} (r=0.72Å) and V^{3+} (r=0.78Å) might be present in B position, while V^{5+} (r=0.68Å) presence would be improbable.

Thus, pyrochlore and microlite could be synthesized at 800°C and 2000 bars. There is an continuous Nb and Ta composition row in pyrochlore-microlite solid solutions. The data obtained show that Nb^{5+} and Ta^{5+} crystal radius are close indeed, they also have full isomorphic miscibility in pyrochores.

Uranium entrance does not effect to the size of the elementary cell in pyrochlores of the pyrochlore-microlite group, obtained in 1*m*NaF solutions. The maximum uranium content in pyrochlores of the pyrochlore-microlyte group does not exceed 0.2-0.3 f.u.

Replacement of 50 mol % Nb by Ti in pirochlores leads to unit cell changing from 10.42 to 10.27 Å, and also to the increasing of U^{4+} isomorphic capacity up to 0.4-0.5 f.e.

Some features of cations from A-position replacement (i.e. Ca^{2+} and Na^+ by U^{4+}) are noted. Ca^{2+} was replaced by U^{4+} in pyrochores of pyrochlore-microlite solid solutions, while in betafites and Zr-bearing pyrochlores the Na^+ was replaced by U^{4+}. Obtained data allow to believe that such replacements in A position do not lead to the change of pyrochlore unit cell size.

Acknowledgments: We acknowledge A.N.Nekrasov for the help in microprobe analyzes, T.N.Dokina and

O.L.Samokhvalova for the XRD analyzes of synthetic pyrochlores.

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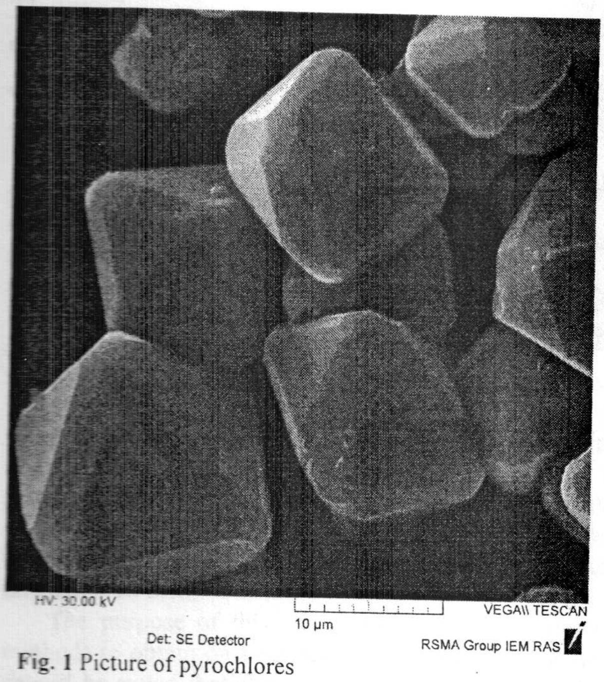

Fig. 1 Picture of pyrochlores

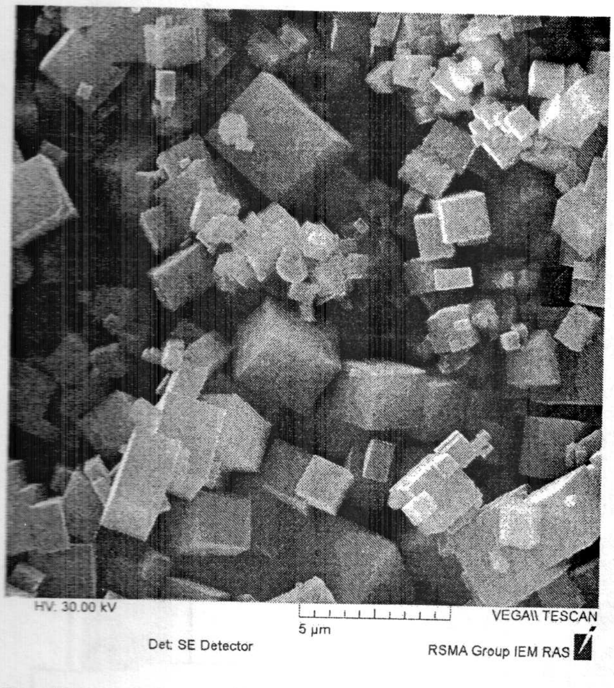

Fig. 2 Picture of perovskites

References

1. *Hogarth D.D.* Classification and nomenclature of the pyrochlores-group. Amer. Min. 1977, v. 62, p. 403–410.
2. *Atencio D., Andrade M.B., Christy A.G. et al.* The pyrochlores supergroup of minerals: nomenclature. The Canad. Mineral., 2010, v.48, p. 673-698

Korepanov Ya.I., Osadchii E.G. Anionic solid solution uytenbogaardtite-petzite

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In the systems Ag-Au-chalcogenide, where X = S, Se, Te [Osadchii, Rappo, 2004], [Osadchii, Echmaeva, 2007], there are three isotypic compounds Ag_3AuX_2, known as minerals yutenbogaardtite (Ag_3AuS_2), fishesserit (Ag_3AuSe_2) and petzite (Ag_3AuTe_2). Minerals and their synthetic analogues have a cubic structure. Minerals exhibit limited miscibility, and their synthetic analogues may form a continuous series of solid solutions.

To investigate the solid solution for continuity and the definition of the lattice parameter dependence on the composition of six samples $Ag_3Au\ (Te_xS_{1-x})_2$ were synthesized with in increments of 0,2*x*. Synthesis of solid solutions was carried out by dry method in evacuated quartz glass ampoules of pre-synthesized end-members. In experiments on the synthesis using gold (99.9%) and silver (99.9%) foil, S (99.9%) and Te (99.9%) powder.

End-members, yutenbogaardtite and petzite, were synthesized from the alloy Ag_3Au and corresponding chalcogen. Alloy required composition was obtained by melting a mixture of small pieces of gold and silver foil (~ $1mm^2$) in an evacuated ampoule in the gas flame. Appropriate stoichiometric amounts of tellurium and sulphur were loaded into the ampoule. For the elimination of the gas phase in the ampoule was placed a well-fitting rod of quartz glass, after which the ampoule was evacuated to ~ 10^{-4} bar. and sealed in a gas flame.

Synthesis occurred in a horizontal resistance furnaces. End-members were annealed for 2 weeks at 600 ^{0}C with two intermediate grinding in a mortar to homogenize the mixture and increase the kinetic of the process. Same method was used to synthesise solid solutions from yutenbogaardtite and petzite. Samples of a given composition were annealed simultaneously at 500 ^{0}C for 2 weeks followed by gradual cooling.

During the synthesis petzite always remained unreacted gold in very small amounts (less than 0.5% by volume).This fact we can see in the photos given from the microprobe. Fig.1. Showing photos of two samples with different sulphur and tellurium density. Presence of similar particles of unreacted gold was noted in [Smit et al., 1970]. During the synthesis was obtained Ag_3AuS_2 phase, in which were found unreacted gold.

X-ray studies of the samples were carried out on a diffractometer Bruker-8 (Cukα1 radiation). To investigate the dependence of the lattice parameter were selected 3 peaks, present in the radiographs of each sample, sufficiently distant from each other. In the table are averaged over them((110), (431) and (222)).

x, $Ag_3Au(Te_xS_{1-x})_2$	0	0.2	0.4	0.6	0.8	1
a(Å)	9.72	9.88	10.02	10.15	10.28	10.38

For the other X-ray peaks of the lattice parameter deviation from the following data is not more than 0,01 Å. Results of the determination of the lattice parameter of the composition of the reflections (110) (431) and (222) are shown on the graph

From the data shown in the graph we can see that the solid solution yutenbogaardtite -petzite has a slight positive deviation from Vegard's rule, which is the first step to proving the existence of a continuous series of solid solutions.

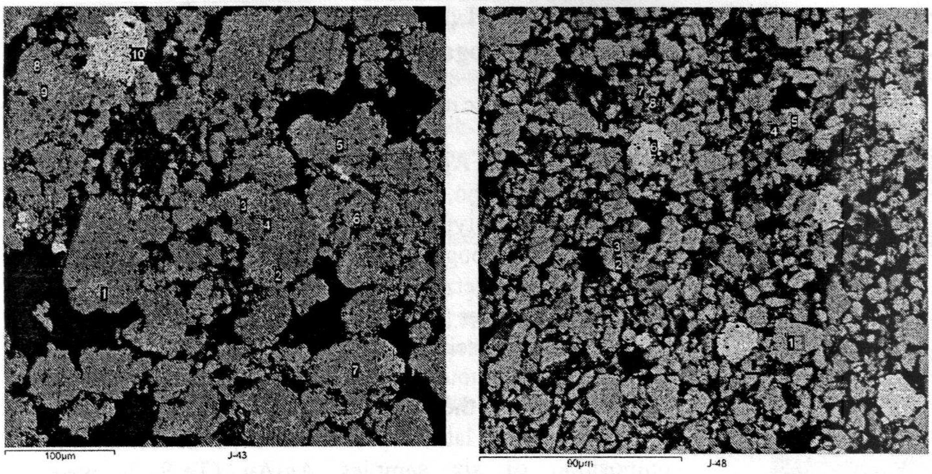

Fig.1. Photo of compositions $Ag_3Au\ (Te_{0.2}S_{0.8})_2$ on the left and $Ag_3Au\ (Te_{0.8}S_{0.2})_2$ on the right. A bright area in the photographs is a phase composition close to pure gold.

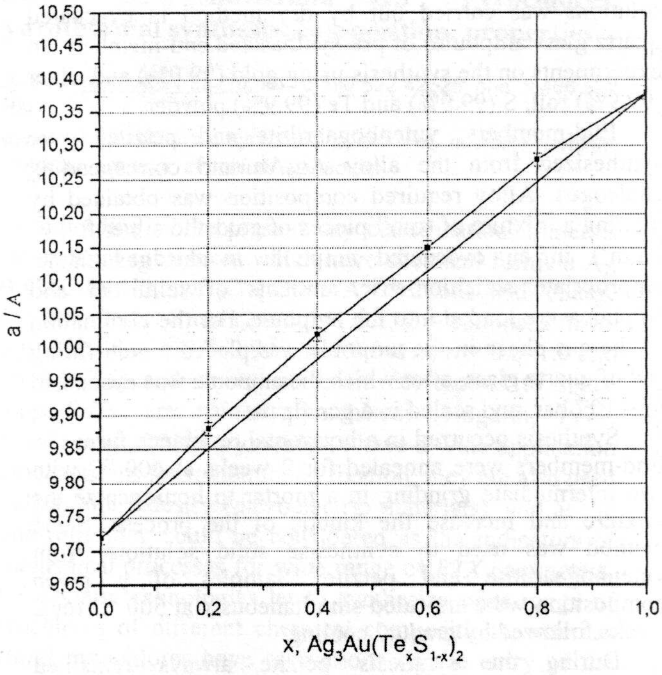

Fig.2. Graph of the lattice parameter of solid solution on composition

The quality of the samples was checked by XRD, using a microscope in reflected light and the microprobe. Lattice parameters of the end-members correspond to the data base MinCryst.

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References

1. Osadchii E. G. and O. A. Rappo, (2004) “Determination of Standard Thermodynamic Properties of Sulfides in the Ag–Fe–S System by Means of a Solid-State Galvanic Cell,” Am. Mineral., 89, 1405–1410.
2. Osadchii E. G, E.A. Echmaeva . (2007) “The system Ag-Au-Se: Phase relations below 405 K and determination of standard thermodynamic properties of selenides by solid-state galvanic cell technique” American Mineralogist, Volume 92, pages 640.647.
3. Smit T. J. M., E. Venema, J. Wiersma, and G. A. Wiegers, (1970) “Phase Transitions in Silver Gold Chalcogenides” JOURNAL OF SOLID STATE CHEMISTRY 2, 309-312.

Thermodynamics of minerals

Osadchii E.G.[1], Korepanov Ya.I.[1], Ionov K.A.[2]. Thermodynamic properties of Ag_x-Au_{1-x} solid solution at 298K- 673K and pressure of 1 atm

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The most important work on the thermodynamics of gold - silver alloy is an article [White et al., 1957] and references therein. This remarkable work has not lost its significance and in the present. Suggested by the authors interpretation of uncoordinated and often conflicting literature data in combination with their own experimental data on the enthalpy of formation of alloys in the framework of the quasi-regular solid solution proved to be very persuasive. Resulting equations describe well the solution in the solid state from 273 K to melting temperatures and further in the liquid state. However, the scatter of literature data used is so large that the absolute values of the selected values of thermodynamic functions in the article [White et al., 1957] can be regarded as a talented predicted.

The purpose of this study was to find experimental methods to obtain data on activity in the alloys Ag-Au. It should be noted that the most common electrolyte (AgI, $RbAg_4I_5$), used for EMF measurements, contains iodine which reacts with the gold of the alloy that makes it impossible to interpret results. This reaction is described by [White et al., 1957]:

Au(alloy) + Ag^+(electrolyte) = Ag(alloy) + Au^+(electrolyte)

and which also observed in our experiments with iodine-containing solid electrolytes. Application of AgCl solid electrolyte allows to avoid this reaction.

Activity of silver for the five compositions Ag_x-Au_{1-x} solid solution $Ag_{0.1}Au_{0.9}$, $Ag_{0.3}Au_{0.7}$, $Ag_{0.5}Au_{0.5}$, $Ag_{0.7}Au_{0.3}$, $Ag_{0.9}Au_{0.1}$ were determined by solid-state galvanic cell in the temperature range 298K -673K and atmospheric pressure of argon. Experiments used gold (99,9%) and silver(99,9%) foil. Alloys of the desired composition were obtained by melting a mixture of small pieces of gold and silver foil (~ 1mm2) in an evacuated ampoule in the gas flame. Fig.1. shows the scheme of a galvanic cell. Silver electrode (reference electrode) was made from a silver rod 3-4 mm in length and 6 mm in diameter. Solid electrolyte tablet was cut from a block of AgCl, obtained by zone melting. Elements of the cell (Fig. 1) were placed in the cell holder (6.5 mm internal diameter) and pressed against a spring for better contact. Finally, the holder of the cell was placed in a container, cells body, made of quartz glass with pipes for input and output of the gas. The measurements were performed in a dry argon flow (flow rate 0.5–1 cm3 per minute). Cell's design and methodology of the experiment are described in detail in the article [Osadchi, Rappo, 2004].

The measurements were made by temperature titration in increments of 50 K. Achieving equilibrium EMF takes from 10 hours to 10 days at different temperatures and compositions. Equilibrium was considered reached when the EMF remained constant within ± 0,003 V for several hours. Temperature dependence of the EMF determined in a reversible galvanic circuit

(+) Pt|C(graphite)|Ag|AgCl|Ag_xAu_{1-x}|C(graphite)|Pt (-)

with AgCl as a solid electrolyte. Activity of silver in the alloy is defined as:

$\lg(a_{Ag}) = -nFE/RT\ln(10)$ (n=1), where n – the number of electrons involved in the reaction, F – Faraday constant, E – EMF in volts, R – universal gase constant, T – temperature in Kelvin.

The data obtained are well described by linear equations $E = a + b(x) * T$, which allowed us to refine the model [White et al., 1957].

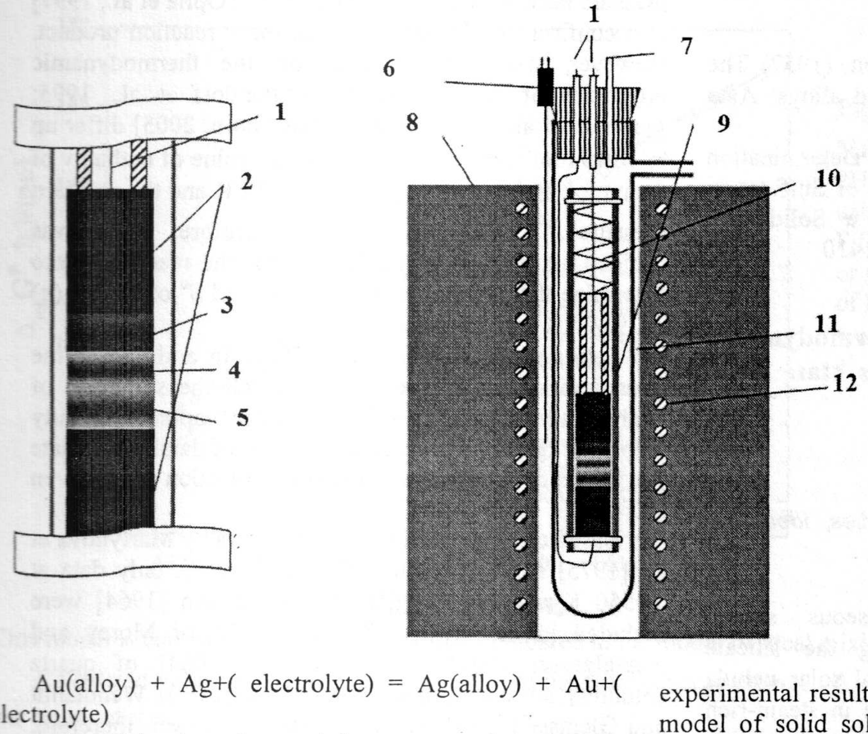

Fig. 1. The scheme of solid-state galvanic cell. (1 - Au-wire, 2 - Graphite, 3 – sample system, 4- solid electrolyte (AgCl), 5 - reference system, 6 - thermocouple, 7 – gas input, 8 – resistance furnace, 9 – cell's holder 10 – spring, 11 - cell body, 12 -heating element.)

The results of our measurements (Fig. 2) show a systematic deviations in the EMF in the direction of decreasing compared with those calculated by the model [White et al.,1957] for all compositions. The experimental results describes in the terms of subregular model of solid solutions, borrowed from [White et al., 1957].Thermodynamic activity of components as a function of (x - mole fraction of silver) and the absolute temperature by the equations:

$$a_{Ag}= x\cdot\exp[-(2190 - 430(1-x) -0.873T)\cdot(1-x)^2/T] \quad (1)$$

$$a_{Au}= (1-x)\cdot\exp[-(1960 -430x - 0.873T)\cdot x^2/T] \quad (2)$$

The original model of [White et al., 1957] we have adopted formula expression look like:

$$a_{Ag}= x\cdot\exp[-(2840 - 810(1-x) - 0.691T)\cdot(1-x)^2/T]$$

$$a_{Au}= (1-x)\cdot\exp[-(2440 - 810x - 0.691T)\cdot x^2/T]$$

These equations (1) and (2) applicable in the temperature range 273K - 773K.

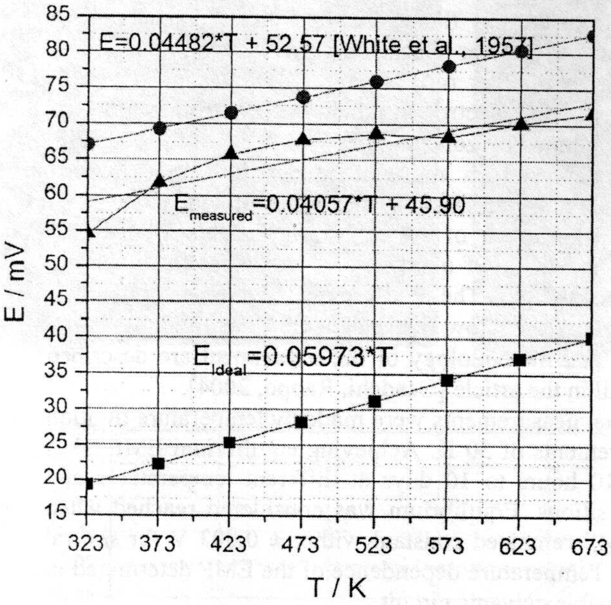

Fig.2. Comparison of the values of EMF of composition $Ag_{0.5}Au_{0.5}$, the experimental data, data [White et al., 1957] and for an ideal solid solution

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References

1. White, J. L., R. L. Orr and R. Hultgren, (1957) The thermodynamic properties of silver-gold alloys: Acta Metallurgica, v. 5, p. 747-760.
2. Osadchii E. G. and O. A. Rappo (2004) Determination of Standard Thermodynamic Properties of Sulfides in the Ag–Fe–S System by Means of a Solid-State Galvanic Cell. Am. Mineral., 89, 1405–1410

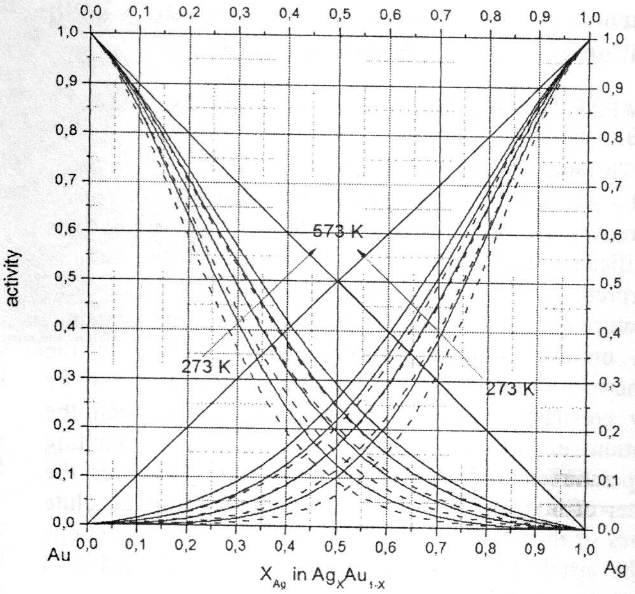

Fig. 3. Activity isotherms of silver and gold in the alloy. (dashed lines denote the data [White et al., 1957], solid one experimental data.)

Plyasunov A.V. Evaluation of thermodynamic properties of h_4sio_4 in the ideal gas state from experimental data

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Keywords: H_4SiO_4, thermodynamic properties, ideal gas state.

Thermodynamic properties of gaseous silicon hydroxides are necessary for analyzing the silicate condensation phenomena in the primordial solar nebula [Hashimoto, 1992], the silica precipitation in steam-rich geothermal systems and recent concerns with the corrosion or deposition of SiO_2-containing alloys and ceramics in high-temperature moist environments.

Experimental transpiration studies (i.e. studies of the partial pressures of Si over solid phases in the presence of steam) of the reaction of water vapor with cristobalite [Hashimoto, 1992; Jacobson et al., 2005] agree that at 1100-1650 K and water pressures close to 0.1 MPa the vapor phase concentration of Si is determined by the reaction

$SiO_2(s) + 2H_2O(g) = H_4SiO_4(g)$. (1)

Mass spectrometric data on the volatile species formed from $SiO_2(s)$ and water at 1473-1773 K and water vapor pressure between 0.018 and 0.094 MPa [Opila et al., 1997] also confirm that H_4SiO_4 is the primary reaction product. However, the literature data on the thermodynamic properties of gaseous H_4SiO_4 [Allendorf et al., 1995; Jacobson et al., 2005; Rutz and Bockhorn, 2005] differ up to 18 $kJ\cdot mol^{-1}$ and 9 $J\cdot K^{-1}\cdot mol^{-1}$ in the value of enthalpy of formation and the entropy at T_r=298.15 K and the standard pressure $P^{\otimes} = 0.1$ MPa. Therefore, it was decided employ all available data for the reaction (1) to determine the optimal values of $\Delta_f G^o$ and S^o of $H_4SiO_4(g)$ at 298.15 K and 0.1 MPa.

Selection of experimental data In addition to the transpiration data we accepted data on the solubility of quartz and amorphous silica in water vapor of density below 15 $kg\cdot m^{-3}$. The accepted data set of data to calculate the values of equilibrium constant of reaction (1) is given in Table.

Based on critique of Heitsmann' data by Martynova et al. [1975] and Harvey and Bellows [1997], only data at T>550 K and P>0.6 MPa from Heitmann [1964] were included in the set. At 773 K results of Morey and Hesselgesser [1951] and Heitmann [1964] of quartz solubility are comparable, however, values of Wendlandt and Glemser [1963] are up to 3-4 times lower, therefore, the latter data at this temperature were excluded.

Data treatment The expression for $\ln K^o$ of the reaction (1) with a good approximation is given by

$$\ln K^o = \ln\frac{Y\cdot\phi^{\infty}_{H_4SiO_4}\cdot P^{\otimes}}{P\cdot\left(\phi^{*}_{H_2O}\right)^2} - \frac{V(SiO_2(s))\cdot(P-P^{\otimes})}{RT} \qquad (2)$$

where Y stands for the mole fraction of silica in the vapor phase, $\phi^{*}_{H_2O}$ is the fugacity coefficient of water, $\phi^{\infty}_{H_4SiO_4}$ is the partial molar fugacity coefficient of dissolved silica at infinite dilution in water, V stands for the molar volume of solid silicon dioxide phase. The values of the fugacity coefficient of water, $\phi^*_{H_2O}$, are accurately known over very wide T and P ranges [Wagner and Pruß, 2002], however, $\phi^\infty_{H_4SiO_4}$ is not known.

2 models for the fugacity coefficients were used in our data treatment:

1). An ideal mixture of ideal gases, i.e. $\phi^*_{H_2O}=1$ and $\phi^\infty_{H_4SiO_4}=1$.

2). An approximation, based on preliminary results for boric acid and H_4SiO_4 that $B_{12}(T) \approx n \cdot B_{11}(T)$, where n is close (within ±1) to the number of OH groups in the molecule of a hydroxide, i.e $B_{12}(T)=4 \cdot B_{11}(T)$ for the interactions between molecules of H_2O and H_4SiO_4. Here B_{11} is the well-known second virial coefficient of water [Harvey and Lemmon, 2004], B_{12} is the second cross virial coefficient for interactions between molecules H_2O and H_4SiO_4. According to thermodynamic textbooks [Prausnitz et al., 1999]: $\ln \phi^*_{H_2O} = \frac{B_{11}(T) \cdot P}{RT}$ and

$$\ln \phi^\infty_{H_4SiO_4} = \left(2B_{12}(T) - B_{11}(T)\right)\frac{P}{RT}\cdot$$

Table. Data sets used in the determination of $\Delta_f G^o$ and S^o of $H_4SiO_4(g)$ at 298.15 K and 0.1 MPa.

Reference	Solid Phase[a]	T range, K	P range, MPa	Number of points	$\overline{\lvert\Delta\rvert}$ [b] J·mol^{-1}
Straub and Grabowski (1945)	AS	533.2-616.5	0.345-2.76	32	579
Morey and Hesselgesser (1951)	Q	673.2-773.2	3.45-6.89	3	4322
Wendlandt and Glemser (1963)[c]	Q	673.2	2.128	1	3497
Heitmann (1964)[d]	AS	572.2-776.2	0.88-4.90	21	871
Heitmann (1964)[d]	Q	624.2-865.2	0.88-4.90	6	907
Martynova et al. (1975)	AS	424.25-496.06	0.49-2.45	3	417
Hashimoto (1992)[e]	CR	1375-1661	≤0.1	10	182
Jacobson et al. (2005)	CR	1074-1375	≤0.1	26	946

(a) AS, Q, CR designates amorphous silica, quartz, cristobalite, respectively

(b) $\overline{\lvert\Delta\rvert}$ is the average of the absolute values of the difference between experimental and calculated $G^o_{T,P^\otimes}(H_4SiO_4(g))$.

(c) The numerical values are quoted from the review of Harvey and Bellows [1997].

(d) Weight of data points is taken equal to 0.5.

(e) Primary data are not reported in the paper, however, most data points are tabulated in Jacobson et al. [2005].

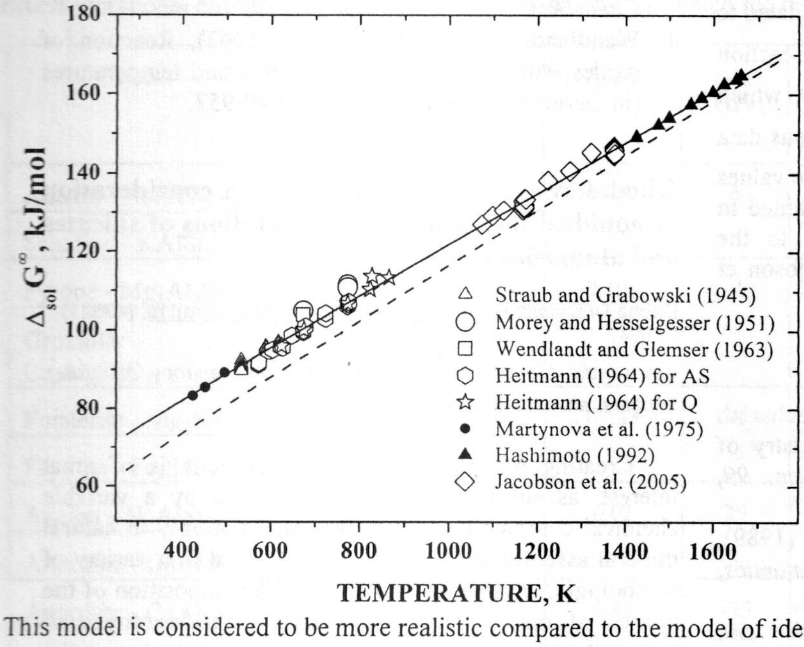

Fig. Values of $\Delta_{sol}G^o$ at $P^\otimes = 0.1$ MPa for the reaction SiO_2(quartz) + $2H_2O(g) = H_4SiO_4(g)$, calculated using values of the auxiliary function F from various sets of data (symbols), or using the thermodynamic functions of $H_4SiO_4(g)$ recommended in this work (solid line) or by [Jacobson et al., 2005] (dashed line).

This model is considered to be more realistic compared to the model of ideal mixing of ideal gases.

Calculated values of $\ln K^o$ were converted to the Gibbs energy change, $\Delta_r G^o(T)$, for the reaction (1) at the ideal gas standard state pressure of 0.1 MPa according to:

$$\Delta_r G^o(T) = -RT\ln K^o = G^o_T(H_4SiO_4(g)) - 2G^o_T(H_2O(g)) - G^o_T(SiO_2(s)) \qquad (3)$$

The value of $\Delta_r G^o(T)$ is the stoichiometric sum of the Gibbs energies, G^o_T, of the reaction (1) participants at the standard state pressure of 0.1 MPa, which are given by

$$G^o_T = \Delta_f G^o_{T_r} - S^o_{T_r}(T - T_r) + \int_{T_r}^{T} C^o_p dT - T\int_{T_r}^{T}\frac{C^o_p}{T}dT\cdot \qquad (4)$$

Then, for each experimental point the values of the auxiliary function F were calculated as follows:

$$F = \Delta_r G^o + 2G^o_T(H_2O(g)) + G^o_T(SiO_2(s)) - \int_{T_R}^{T} C^o_p(H_4SiO_4(g))dT + T\int_{T_r}^{T}\frac{C^o_p(H_4SiO_4(g))}{T}dT\cdot \qquad (5)$$

It follows that

$$F = \Delta_f G^o_{T_r}(H_4SiO_4(g)) - S^o_{T_r}(H_4SiO_4(g)) \cdot (T - T_r). \quad (6)$$

In total, 102 values of F over the temperature range 424-1661 K were collected. The weighted least-squares fit of all data resulted in the following values at 298.15 K for $H_4SiO_4(g)$:

1). An "ideal mixture of ideal gases" model: $\Delta_f G^o$=-1239.74±0.53 kJ·mol^{-1}; S^o=346.65±0.75 J·K^{-1}·mol^{-1}.

2). An approximation $B_{12}=4 \cdot B_{11}$: $\Delta_f G^o$=-1238.51±0.51 kJ·mol^{-1}; S^o=347.78±0.72 J·K^{-1}·mol^{-1}, with uncertainties given as 2σ. This result is considered more realistic.

Taking into account the effect of uncertainty of thermodynamic functions of solid phases and, what is most important, the uncertainty in the heat capacity of $H_4SiO_4(g)$ (data of Allendorf et al. [1995] and Rutz and Bockhorn [2005] differ from 2 to 8%), the final recommendations of the thermodynamic properties of H_4SiO_4 are as follows: $\Delta_f G^o$=-1238.51±3.0 kJ·mol^{-1}; S^o=347.78±6.2 J·K^{-1}·mol^{-1}; $\Delta_f H^o$=-1340.68±3.5 kJ·mol^{-1}, with necessary values of S^o for $H_2(g)$, $O_2(g)$, Si(c) taken from Cox et al. [1989]. The heat capacity of $H_4SiO_4(g)$ at 250-2000 K from data of Allendorf et al. [1995] was approximated by a polynomial: $C^o_p/R = a_o + a_1 \cdot 10^{-2} \cdot T + a_2 \cdot 10^{-5} \cdot T^2 + a_3 \cdot 10^{-8} \cdot T^3 + a_4 \cdot 10^{-11} \cdot T^4 + a_5 \cdot 10^{-15} \cdot T^5$, where a_o=2.87914; a_1=5.89126; a_2=-9.47715; a_3=7.84564; a_4=-3.15382; a_5=4.89073.

For graphical presentation all data were recalculated to the Gibbs energy change, $\Delta_{sol}G^o$, of the reaction SiO_2(quartz) + $2H_2O(g) = H_4SiO_4(g)$, see Figure, which shows the values of $\Delta_{sol}G^o$ calculated from various data sets (symbols). The solid line is calculated using the values of the thermodynamic functions of $H_4SiO_4(g)$ obtained in this study, while the dashed line corresponds to the thermodynamic functions of $H_4SiO_4(g)$ from Jacobson et al. [2005].

References

1. Allendorf M. D., C. F. Melius, P. Ho, M. R. Zachariah (1995), Theoretical study of the thermochemistry of molecules in the Si-O-H system, *J. Phys. Chem., 99*, 15285-15293.
2. Cox J. D., D. D. Wagman, V. A. Medvedev (1989), *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corporation, New York.
3. Harvey A. H., J. C. Bellows (1997), *Evaluation and correlation of steam solubility data for salts and minerals of interest in the power industry,* NIST Technical Note 1387, 88 pp.
4. Harvey A. H., E. W. Lemmon (2004), Correlation for the second virial coefficient of water, *J. Phys. Chem. Ref. Data, 33*, 369-376.
5. Hashimoto A. (1992), The effect of H_2O gas on volatilities of planet-forming major elements: I. Experimental determination of thermodynamic properties of Ca-, Al-, and Si-hydroxide gas molecules and its application to the solar nebula, *Geochim. Cosmochim. Acta, 56*, 511-532.
6. Heitmann H. G. (1964), Solubility of silicic acid in water and steam and its effect on silica deposits in turbines (in German), *Chemiker-Zeitung, 88*, 891-893.
7. Jacobson N. S., E. J. Opila, D. L. Myers, E. H. Copland (2005), Thermodynamics of gas species in the Si-O-H system, *J. Chem. Thermodyn., 37*, 1130-1137.
8. Martynova O. I., A. S. Popov, V. F. Fursenko (1975), Boundary lines of phase equilibrium diagrams of the silicon dioxide - water system (in Russian), *Teploenergetika*, No.5, 66-68.
9. Opila E. J., D. S. Fox, N. S. Jacobson (1997), Mass spectrometric identification of Si-O-H(g) species from the reaction of silica with water vapor at atmospheric pressure, *J. Am. Ceram. Soc., 80*, 1009-1012.
10. Prausnitz J. M., R. N. Lichtenthaler, E. G. de Avezedo (1999), *Molecular Thermodynamics of Fluid-Phase Equilibria.* 3rd Edition, Prentice-Hall, New York, 860 p.
11. Rutz L. K., H. Bockhorn (2005), Theoretical studies on the mechanism of formation of silicon dioxide (SiO_2), *Fourth Joint Meeting of the U.S. Sections of the Combustion Institute*: Western States, Central States, Eastern States, Philadelphia, PA, United States, Mar. 20-23, 2005, F38/1-F38/6. Publisher: Combustion Institute, Pittsburgh, Pa.
12. Straub F. G., H. A. Grabowski (1945), Silica deposition in steam turbines, *Trans. ASME*, 67, 309-316.
13. Wagner W., A. Pruß (2002), The IAPWS formulation for the thermodynamic properties of ordinary water substances for general and scientific use, *J. Phys. Chem. Ref. Data, 31*, 387-535.
14. Wendlandt H. G., O. Glemser (1963), Reaction of oxides with water at high pressures and temperatures (in German). *Angew. Chem., 75*, 949-957.

Khodakovsky I.L. , Mukhina I.V A consideration of nonideal formation of solid solutions of silicates and alumosilicates

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Key words: thermodynamics, solid solutions, entropy of mixing, silicates, aluminosilicates

Creating a database on solid solutions is of great interest, as solid solutions, characterized by a variable chemical composition, are widespread not only in natural mineral assemblages, but are often formed in a variety of technological systems. To estimate the composition of the phases of many chemical systems in wide ranges of temperatures a nd pressures it is necessary to know the thermodynamic properties of various solid solutions. It is important to identify the relationship of the microscopic picture of atomic interactions with macroscopic thermodynamic characteristics of the end of the series [Navrotski 1992], [Avchenko 2009].

Contribution of ΔG ° mix for the thermodynamic properties of solid solutions consists of two parts - the enthalpy and entropy terms:

$$\Delta G^o_{mix} = \Delta H^o_{mix} - T\,\Delta S^o_{mix} \quad (1),$$

$$\text{and } \Delta S^o_{mix} = \Delta S^o_{id} + \Delta S_{vib}^{ex} \quad (2)$$

[Urusov 1987],

where, ΔS°_{id} - the entropy of mixing of ideal solutions and ΔS°_{vib} - vibrational contribution, arises because of the nonadditivity of the specific heat capacity of solid solution.

$$\Delta S^{\circ}_{id} = -R[x\cdot \ln x + (1-x)\cdot \ln(1-x)] \qquad (3).$$

In the literature, reliable values of ΔH°_{mix} were determined using calorimetric methods for many solid solutions of silicates and aluminosilicates, while the value of ΔS°mix, defined by the classical method of low-temperature adiabatic calorimetry, until recently, only limited by results of the study of binary solid solutions of garnets series of pyrope-grossular ($Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$) [Hazelton and Vestrum, 1980], disordered feldspars $NaAlSi_3O_8$-$KAlSi_3O_8$ (analbit-sanidine) [Hazelton et al, 1983] and scapolites [Komada et al., 1996]. It was shown that for the garnets there are positive excess heat of mixing at temperatures below 300 K, A study of binary solid solutions of garnets series of pyrope-grossular ($Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$) and disordered feldspars $NaAlSi_3O_8$-$KAlSi_3O_8$ (analbit-sanidine) by low-temperature adiabatic calorimetry (Hazelton and Vestrum, 1980, Hazelton et al, 1983) have shown that there are positive excess heat capacity of mixing for disordered feldspars at temperatures below 300 K, which leads to excess vibrational entropy of about 3 J/mol K at 298.15 K.

Creating a relaxation calorimeter (measuring the physical properties of the system Quantum Design) allowed measurements of low-temperature heat on milligram quantities of sample materials (Dachs and Bertoldi 2005; Dachs and Geiger 2006). Comparison of results of specific heat measurements of the same sample of hematite (Fe_2O_3), and performed by the classical methods [7] showed that the error in heat capacity measurements of samples in the milligram quantities of ± 1%.

Recently, the method of relaxation calorimetry measured the low-temperature specific heat for steam analbit-sanidine [5], pyrope-grossular [8], forsterite-fayalite [9], analbit-anortite [10], anortite-sanidine [11], CaTs-diopside [12] and estimates are made ΔS_{vib}^{ex}. Recently, in [Benisek 2011] it was shown that the excess vibrational entropy (ΔS_{vib}^{ex}) for several silicate solid solutions are linearly correlated with the difference of molar volumes (ΔV_i) and compressibility (Δk_i) end members of solid solutions. Empirical relationship between ΔS_{vib}^{ex}, ΔV_i and Δk_i, described by the expression $\Delta S_{vib}^{ex} = (\Delta V_i + m\Delta k_i)\, f$, was calibrated for the six silicate solid solutions (analbid-sanidine, pyrope-grossular, forsterite-fayalite, analbit-anortite, anortite-sanidine, CaTs-diopside), where m = 0.0246 and f = 2.926.

In the Table 1 shows the theoretical values of molar volumes and bulk moduli for the above series of solid solutions.

Table 1. Molar volume (V), bulk modulus (k), their differences between the end members (ΔV_i and Δk_i), and maximum excess vibrational entropy (ΔS_{vib}^{ex}) silicate solid solutions, for which the necessary data

Name	V, J/bar	*k*, GPa	ΔV_i, J/bar	Δk_i, GPa	ΔS_{vib}^{ex}, J/mol·K		
					ΔS_{vib}^{ex} (exp.)	ΔS_{vib}^{ex} (eq. 5)	ΔS_{vib}^{ex} (eq. 6)
Analbit - $NaAlSi_3O_8$	10.06	52	0.85	6	2.6	2.9	2.9_9
Sanidine - $KAlSi_3O_8$	10.91	58					
Pyrope - $Mg_3Al_2Si_3O_{12}$	11.32	171	0.403	-1	1	1.1	1.1_4
Grossular - $Ca_3Al_2Si_3O_{12}$	12.53	170					
Forsterite - Mg_2SiO_4	4.365	128	0.133	-6	0	0	-0.0_4
Fayalite - Fe_2SiO_4	4.631	122					
Analbit - $NaAlSi_3O_8$	10.06	52	0.03	29	2.6	2.2	2.5_1
Anorthite - $CaAl_2Si_2O_8$	10.09	81					
Anorthite - $CaAl_2Si_2O_8$	10.09	81	0.82	-23	1	0.7	0.76_3
Sanidine - $KAlSi_3O_8$	10.91	58					
CaTs - $CaAlAlSiO_6$	6.37	127	0.25	-13	0	-0.2	-0.2_1
Diopside - $CaMgSi_2O_6$	6.62	114					

__Note:__ Empirical relationship between ΔS_{vib}^{ex}, ΔV_i and Δk_i, was calibrated for the six silicate solid solutions. In this case, the sign for Δk_i chosen to be positive if the final term with a large volume has a larger bulk modulus. Negative values arise when the final term solution with a large volume has a lower compressibility.

In the paper [Benisek 2011] obtained the equation:

$$\Delta S_{vib}^{ex} = (\Delta V_i + m\Delta k_i)\cdot f \qquad (4),$$

where *m* = 0.0246 и *f* = 2.926.

Equation (5) can be simplified by fixing the ratio f = 3 (exactly). The result is a linear dependence on ΔS_{vib}^{ex} Δk_i:

$$\Delta S_{vib}^{ex} - 3\Delta V_i = 3m\Delta k_i. \qquad (5)$$

Using the experimentally determined thermodynamic parameters for solid solutions, given in the paper [Benisek 2010] and fixing $\Delta S_i - 3\Delta V_i = 0$ for $\Delta k_i = 0$, we find the numerical value of empirical coefficient m in equation (6) and its error: $m = 0.0228 \pm 0.003$.

Table 1 shows the theoretical values of molar volumes and bulk moduli for the aforementioned pair of solid solutions. In the last three columns show the values ΔS_{vib}^{ex}, obtained experimentally by the authors, and calculated by equations 4 and 5, respectively.

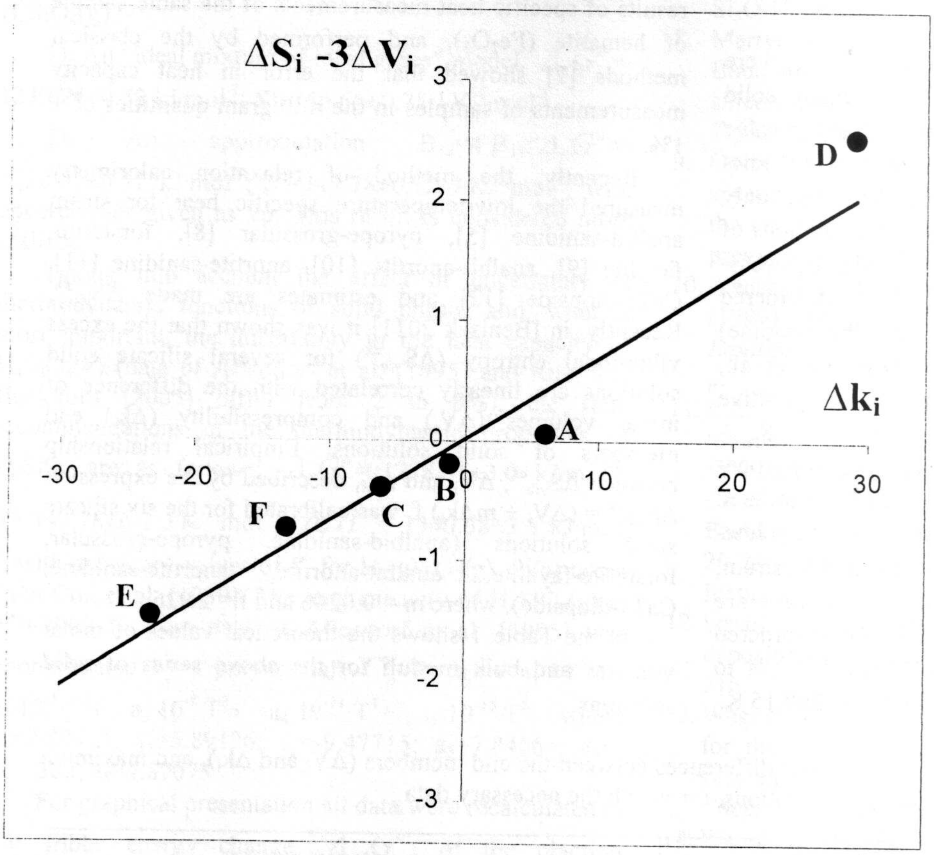

Fig. 1. The relationship of parameters of mixing of solid solutions for the pairs: A – analbit-sanidine; B – pyrope-grossular, C – forsterite-fayalite; D – high structural state plagioclases; E – high structure state (K,Ca)feldspars-diopside;
F – CaTs-diopside.

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References

1. A. Navrotsky (1992). Models of crystalline solutions. Thermodynamic modeling in geology. Publ. “Mir”, pp. 49-81.
2. O.V. Avchenko, K.V. Chudnenko, I.A. Aleksandrov 92009). Fundamentals of physical-chemical modeling of mineral systems. Publ. Nauka, pp. 35-78.
3. V.S. Urusov (1987). Theoretical crystallochemistry. Publ. MSU, 275p.
4. Haselton H.T. Jr., Westrum E.F. Jr. (1980) Low-temperature heat capacities of synthetic pyrope, grossular, and pyrope60grossular40 // Geochim Cosmochim Acta, Vol 44, N 5, 701–709.
5. Haselton H.T. Jr., Hovis G.L., Hemingway B.S., Robie R.A. (1983) Calorimetric investigation of the excess entropy of mixing in analbite-sanidine solid solutions: lack of evidence for Na, K short-range order and implications for two-feldspar thermometry // Amer. Mineral., Vol. 86, N 3-4, 398–413.
6. Komada N., Moecher D.P., Westrum E.F., Hemingway B.S., Zolotov M.Yu, Semenov Y.V., Khodakovsky I.L. (1996). Thermodynamic properties of scapolites at temperatures ranging from 10 K to 1000 K // J. Chem. Thermodyn., Vol. 28, N 9, 941-973.
7. Shi Q., Snow C.L., Boerio-Goates J., Woodfield B.F. (2010). Accurate heat capacity measurements on powdered samples using a Quantum Design physical property measurement system // J. Chem. Thermodynam., Vol. 42, N 9, 1107-1115.
8. Dachs E, Geiger CA (2006) Heat capacities and entropies of pyropegrossular ($Mg_3Al_2Si_3O_{12}$–$Ca_3Al_2Si_3O_{12}$) garnet solid solutions: a low-temperature calorimetric and a thermodynamic investigation. // Amer. Mineral., Vol. 91, N 5-6, 894–906.
9. Dachs E, Geiger CA, von Seckendorff V, Grodzicki M (2007) A low temperature calorimetric study of synthetic (forsterite plus fayalite) (Mg_2SiO_4 – Fe_2SiO_4) solid solutions: an analysis of vibrational, magnetic, and electronic contributions to the molar heat capacity and entropy of mixing // J. Chem. Thermodyn., Vol 39, 906–933.
10. Benisek A, Dachs E, Kroll H (2009) Excess heat capacity and entropy of mixing in the plagioclase solid solution // Amer. Mineral., Vol 94, N 8-9, 1153–1161.
11. Benisek A., Dachs E., Kroll H. (2010) Excess heat capacity and entropy of mixing in the high-structural state (K, Ca)-feldspar binary // Phys. Chem. Minerals, Vol. 37, 209–218.
12. Etzel K., Benisek A., Dachs E., Cemic L. (2007) Thermodynamic mixing behavior of synthetic Ca-Tschermak-diopside pyroxene solid solutions: I. Volume and heat capacity of mixing // Phys. Chem. Minerals, Vol. 34, 733–746.
13. Benisek A., Dachs E. (2011) On the nature of the excess heat capacity of mixing // Phys. Chem. Minerals, Vol. 38, N 3, 185-191

Stolyarova T.A., Osadchii E.G. Enthalpies of formation of tellurides of palladies from elements

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Key words: palladium, tellurium, enthalpy, thermochemistry

Palladium as other platinum metals belongs to the group of transitive metals of the VIII-th group of the periodic system. Their electronic structure is rather complicated, mainly due to the closeness of d and s-energetic levels. Thus, a transition from one level to another is easily realized there. According to the type of interaction with the other elements of the periodic system platinum metals are divided into three groups: - Ru, Os, II-Ir, Rh, III-P, Pd is characterized by the largest reaction capacity, especially Pd due to a specific structure of its electronic levels. In contrast to Pt and other platinum metals Pd has three electronic levels (4s, 4p an 4d) filled, but two (5s and 5p) are free, what explains its increased reaction capacity.

In nature tellurides of platinum and palladium are most widely spread. They usually contain bismuth, however, no pure binary compounds are found.

Tellurides of platinum and palladium are typical for ores of complex copper-nickel deposits. It is very important to reveal geochemical factors of separation of platinum and palladium in the processes of depth mineral formation what is impossible without knowledge of thermodynamic properties most widely-spread on the deposits of compounds (minerals).

Due to the above - mentioned facts the researchers of the laboratory of thermodynamics of minerals of IEM, Russian Academy of Sciences have thermochemical investigations of the compounds of platinum metals with halcogenites. The object of this study are tellurides of palladium.

Two stable compounds PdTe and $PdTe_2$ [Groeneveld, 1955] are found in the palladium-tellurium system.

Both tellurides are easily obtained while heating stochiometric mixtures. The latter are placed into the capsules made from melted quartz, pumped to pressure 10^{-4} mm, sealed in the flame of the oxygen burner and heated at T=800°C.

It was determined by the preliminary investigations that the synthesis of tellurides took place completely under the above-described conditions for 5-6 min. The X-ray analysis of the synthesis products confirmed the presence of substances of only given composition there. Calorimetric definitions were performed at a high-temperature vacuum-block calorimeter, made in the laboratory of thermodynamics of minerals, IEM, Rus. Acad. Sci. and described earlier [Soboleva and Vasil'ev, 1962, Fleisher and Stolyarova, 1978]. The capsule with the charge processed as above was put into the furnace of the calorimetric bomb which was then filled by argon: pressure 5 atm. The calorimetric bomb was put into the vessel; the latter was pumped to the remnant pressure 10^{-2} mm. The temperature of the isothermic cover was 25±0,02°C. The electric energy was measured with the accuracy to 0,02 %.

Temperature rise during the run was measured by a copper resistance thermometer (-865 Om at T=25°C), located along the calorimetric bomb. The calorimeter was calibrated by the electric energy.The accuracy of determination of the thermal value was 0,02%. The reactions of synthesis in the calorimeter took place completely during the first heating, the second heating gave no additonal effect what confirmed our conclusion on a total reaction during the first heating.

The X-ray phase analysis of products of calorimetric runs confirmed the presence of only given substances PdTe and $PdTe_2$ there, respectively. The results of the calorimetric definitions are given in Tables 1 and 2.

The average square error was calculated at the level of valuability of 95% [Nalimov, 1960].

The following values were obtained:

For PdTe $\Delta_f H^o_{298.15}$ = -51,93±0,49 кJ/mol

For $PdTe_2$ $\Delta_f H^o_{298.15}$ = -75,75±0,68 кJ/mol

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References

1. Groeneveld Meijer W.D.J. Synthesis, structures and properties of platinum metal tellurides /Amer.Mineralogist. B40. 1955. pp.646-57.
2. Soboleva M.S., L.V. Vasil'ev Enthalpy of formation of Ni tellurides $NiTe_{1,00}$-$NiTe_{1,5}$/ Vestn.Leningrad Univ. 1962. Ser.physics and chemistry. V16. P.153.
3. Fleisher L.L., T.A. Stolyarova. Automatization of the process of measurement of electric energy of high-tmperature calorimetric vessel // Measur.Technique. 1978. N2. P.60.
4. Nalimov V.V. The use of mathematics statistics at substance analysis. M: Nauka, 1960.

Table 1. Enthalpy of formation from elements of palladium tellurides PdTe (MM 234,02 $g{\cdot}mol^{-1}$)

Characteristics of heater work									Heat number in the run, Q/J			
Runs	Charge, g	t, sec	V, V	J, A in switchig on	$\int_{t_H}^{t_k} Jdt$ on device, A·sec	$\int_{t_H}^{t_k} Jdt$ in the run, A·sec	Speed cooling, 10^{-5}, $K{\cdot}min^{-1}$	ΔR + δ, Om [*]	Total	on the heater	in the run	$-\Delta H^o_{peak} f_{298.15}$ kJ/mol in unique run
1	1,8200	360,472	35,478	3,079	1118,576	1119,665	38	6,1148	40123,6	39723,5	400,1	51,44
2	2,0550	361,716	35,481	3,074	1119,364	1121,201	36	6,1336	40246,8	39781,3	465,5	53,01
3	2,9020	361,649	35,501	3,070	1122,579	1124,207	40	6,1796	40548,7	39910,5	638,2	51,46
4	2,1200	360,690	35,596	3,078	1117,308	1119, 067	40	6,1418	40300,7	39843,3	466,4	51,48
5	2,7205	360,298	35,518	3,072	1117,709	1118,262	41	6,1667	40329,0	39718,4	610,6	52,52
6	2,0252	360,516	35,524	3,073	1112,882	1114,105	37	6,1193	40019,0	39577,5	441,5	51,02
7	2,5109	360,087	35,624	3,083	1118,411	1118,314	40	6,1767	40394,4	39834,3	466,4	51,48
8	2,0449	361,154	35,657	3,080	1119,518	1119,626	35	6,1749	40382,6	39922,5	460,1	52,68
						Result						51,93±0,49

Note: Thermal value of calorimeter in the runs 1-4 W=6561,7±2 J/Om; in runs 5-8 W=6539,8±2 J/Om

[*] (ΔR + δ) – A change of thermometer resistence with the correction for thermal exchange

Table 2. Enthalpy of formation from elements of palladium ditellurides from elements (MM 361,627 $g{\cdot}mol^{-1}$)

Characteristics of heater work									Heat number in the run, Q/J			
Runs	Charge, g	t, sec	V, V	J, A in switchig on	$\int_{t_H}^{t_k} Jdt$ on device, A·sec	$\int_{t_H}^{t_k} Jdt$ in the run, A·sec	Speed cooling, 10^{-5}, $K{\cdot}min^{-1}$	ΔR + δ, Om [*]	Total	on the heater	in the run	$-\Delta H^o_{peak} f_{298.15}$ kJ/mol in unique run
1	3,6057	360,500	35,719	3,086	1117,870	1119,049	33	6,1934	40722,0	39971,3	751,1	-75,37
2	3,1576	360,938	35,751	$3,087_5$	1120,262	1122,795	37	6,2051	40799,8	40141,0	658,8	-75,45
3	1,3959	360,983	35,485	3,077	1116,747	1119,409	41	6,0827	40021,7	39722,2	299,5	-77,59
4	1,4080	360,957	35,517	$3,072_5$	1115,240	1117,817	39	6,0791	39998,0	39701,5	296,5	-76,15
5	3,1636	361,618	35,473	3,062	1118,237	1119,766	35	6,1379	40384,9	39721,4	663,5	-75,84
6	1,4910	361,283	35,510	$3,072_5$	1115,470	1115,975	37	6,0703	39940,1	39628,3	311,8	-75,62
7	1,5041	360,671	35,497	3,073	1111,554	1113,253	34	6,0533	39828,3	39517,1	311,2	-74,82
8	1,4982	361,627	35,518	3,0765	1116,768	1116,851	36	6,0733	39979,6	39668,3	311,3	-75,14
						Result						75,75 ±068

Note: In the runs 1-2 - – thermal value of the calorimeter - W = 6575,2±2 $J{\cdot}Om^{-1}$; In the runs 3-8 - W = 6579,6 ±2 $J{\cdot}Om^{-1}$.

[*] (ΔR+δ) - change of thermometer with the correction for thermal exchange