

## Synthesis of minerals

**Balitsky V.S., Setkova T.V., Balitskaya L.V., Nekrasov A.N., Bublikova T.M. Germanium distribution in high-germanium quartz crystals (HGQ), grown in hydrothermal solutions at temperatures of 240–720 °C and pressures of 5–150 MPa.**

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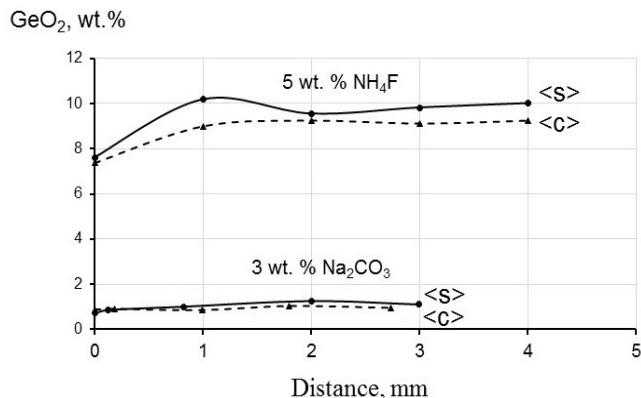
**Abstract.** The article presents new experimental data of influence of various growth and physico-chemical factors (growth direction, size and shape of seeds, growth rate, temperature, composition of solutions, etc.) on the capture and zonal-sectorial distribution of germanium impurities in crystals of high germanium quartz.

**Keywords:** quartz, germanium, hydrothermal solution

Crystals of high-germanium quartz (HGQ) are a promising piezoelectric material because they have higher piezoelectric characteristics than conventional quartz. We present new experimental data that determine the influence of various growth and physico-chemical factors on the capture and distribution of germanium impurities in grown HGQ crystals. The crystals growth was carried out in hydrothermal solutions, according to earlier

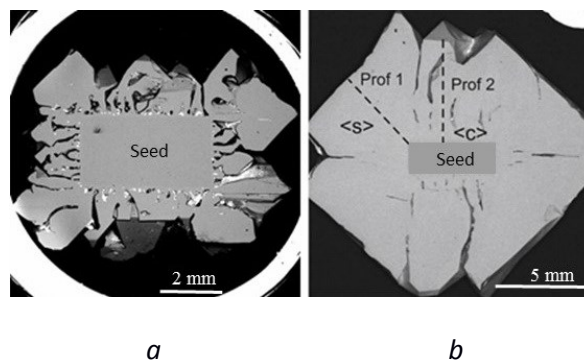
developing method (Balitsky et al., 2004; Balitsky et al., 2005; Balitsky et al., 2017). The content and distribution of silicon and germanium in crystals was measured on a carbon coated samples by electron probe micro analysis on CamScan MV2300. As a result, the following dependencies were established.

**Influence of the solution composition.** Traditional highly alkaline solutions of sodium hydroxide and sodium carbonate, which apply in the industrial growth of piezoelectric and optical quartz, cannot be used to grow of HGQ crystals. First of all, this is due to the formation of stable, hardly soluble sodium germanates in such systems that reduce the activity of germanium in the solution. As a result, the germanium content in crystals grown in alkaline solutions, even at temperatures of 540-650°C and pressures of 120-150 MPa, is no more than 4-5 wt %, and only 1.2-2.5 wt % at temperatures of 350-380°C and pressures of 70-100 MPa. (Fig. 1). In addition, sodium germanates are deposited on the fragments of the nutrient quartz and on the surface of seed plates (Fig. 2a). This leads to blocking the dissolution of the nutrient quartz and the defective crystal growth on the seeds.



**Fig. 1.** Distribution of germanium in the sectors <+ s> and <c> of HGQ crystals grown on XY-seed in solutions of 3 wt % Na<sub>2</sub>CO<sub>3</sub> and 5 wt % NH<sub>4</sub>F.

A different situation is observed when we use the ammonium fluoride as a starting solution. Quartz has a high solubility in these solutions comparable to its solubility in equimolar solutions of sodium carbonate. The temperature coefficient of solubility (TCS) of quartz in NH<sub>4</sub>F solutions is characterized by positive values and increases with increasing temperature and solution concentration. As a result, in the lower, hotter zone of the autoclave the intensive dissolution of nutrient quartz occurs to form the highly soluble penta- and hexa-silicon-fluoride complexes (SiF<sub>5</sub><sup>-</sup> and SiF<sub>6</sub><sup>-2</sup>). The condition of a direct temperature gradient in the autoclave

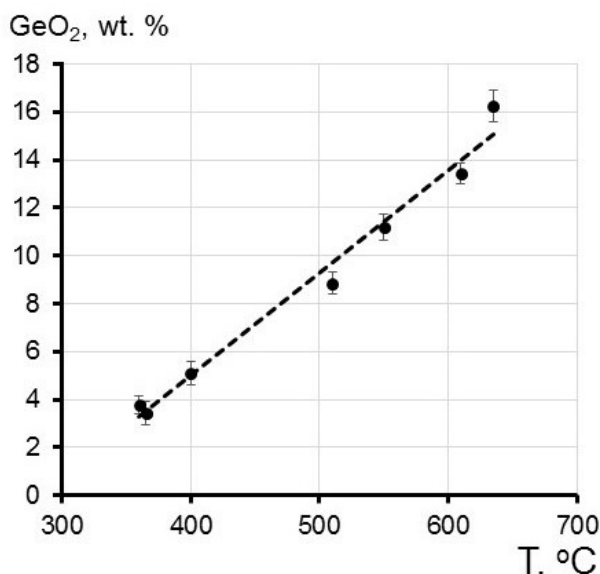


**Fig. 2.** SEM images of HGQ crystals sections grown on XY-seed in solutions (a) 3 wt % Na<sub>2</sub>CO<sub>3</sub> and (b) 5 wt % NH<sub>4</sub>F.

results in the transfer of silica and the growth of quartz crystals on seeds in the less hot upper zone of the autoclave. Probably the quartz-like germanium oxide added to the nutrient has a similar dissolution and transport chemistry in NH<sub>4</sub>F solutions. Nevertheless, germanium concentration in the solution is tens of times lower than the silicon concentration to temperatures of 340-370°C. The well-soluble metastable quartz-like germanium oxide loaded into the autoclave undergoes a transition to a stable rutile-like modification already at 180°C. The rutile-like modification has a very low solubility above this temperature. Only at temperatures of 540-

650 °C and pressures of 120-150 MPa, the solubility of rutile-like germanium oxide in the solutions of ammonium fluoride has sufficient value to capture of 10-15 wt % GeO<sub>2</sub> by quartz crystals. Attempts to grow HGQ crystals in solutions of alkali metal fluorides (NaF, KF and LiF) and their mixtures did not lead to positive results. The growth rates of quartz in these solutions are substantially lower than the growth rates in NH<sub>4</sub>F solutions. In this case, the overgrown layer is has numerous macro and microdefects, and the germanium oxide content does not exceed 5 wt % even at a temperature of 540°C. All this allows us to consider that solutions of ammonium fluoride with a concentration of 5 to 10 wt % are most suitable for growing homogeneous HGQ crystals.

**Influence of the temperature.** The temperature is most important among the growth factors which influence germanium content in HGQ crystals. A patently linear dependence of the GeO<sub>2</sub> content in quartz on the temperature for solutions of the same concentration was established as a result of numerous experiments (Fig. 3).



**Fig. 3.** Temperature influence on the content germanium dioxide in HGQ crystals (solution of 5 wt % NH<sub>4</sub>F, pressure 100-160 MPa).

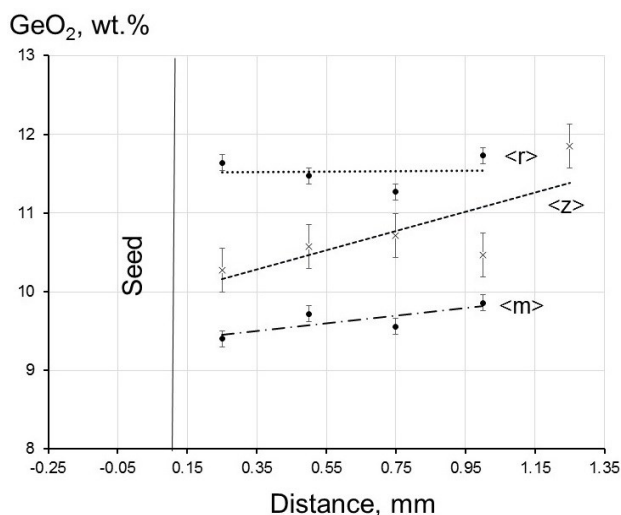
**Influence of nutrient composition.** The selection of nutrient material is very important for the growth of HGQ crystals. Несмотря на относительно небольшое разнообразие опробованных шихт, ряд полученных результатов могут иметь в будущем принципиальное значение для их выбора.

In most of the experiments, a mixture of crush synthetic quartz and powder of quartz-like germanium oxide crystals was used in a quantitative ratio of SiO<sub>2</sub>:GeO<sub>2</sub> from 20:1 to 1:1. In some runs, relatively large fragments (transverse size up to 10-

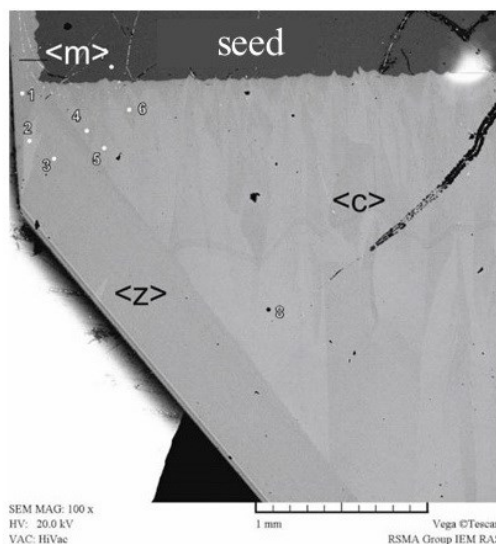
15 mm) of germanium oxide single-crystal of the same modification were used instead of powdered quartz-like germanium oxide. These crystals were grown by a special previously developed method (Balitsky et al., 2000). In some cases, the nutrient was prepared from fragments previously grown and cracky HGQ crystals with a high content 9-16 wt % GeO<sub>2</sub>. In several experiments, large-crystal elemental germanium was added to the quartz nutrient.

As a result, it was found that when the content of quartz in the nutrient exceeds 10 times the content of powdered GeO<sub>2</sub>, the content of germanium in grown crystals, remained practically unchanged all other things being equal. In crystals grown at 540-570°C with a nutrient from fragments of HGQ crystals containing not less than 9-15 wt % of germanium oxide, are observed a steady tendency to the germanium content rise in the overgrown layer as the duration of the experiments increases. At temperatures of 355 and 334°C and pressures of 70-80 MPa the germanium oxide content in crystals increases up to 5 wt %, whereas in crystals grown with ordinary nutrient, the GeO<sub>2</sub> content does exceed 1.2 wt %. The replacement of the quartz-like germanium oxide in the nutrient with elementary large-crystal germanium did not lead to success. Germanium oxidize rapidly to the oxide form of rutile-like modification. Its content in grown crystals does not exceed 4.5 wt %, even at temperatures close to 600°C.

**Influence of the seed crystallographic orientation.** As known the crystallographic orientation, size, shape of seeds, largely determine the habit and internal structure of the crystals and the capture of various impurities and the formation of other macro- and microdefects also. Different growth sectors of smooth faces of positive  $r$  {10 $\bar{1}$ 1} and negative  $z$  {0 $\bar{1}$ 11} rhombohedra, and further - rough faces of the prism -  $x$  {11 $\bar{2}$ 0}, dipramids  $s$  {11 $\bar{2}$ 1} and base pinacoid  $c$  {0001} capture germanium in different ways. The difference in the GeO<sub>2</sub> content in different growth sectors of the same crystal varies from 5 to 10 wt % (Fig. 4, 5). The so-called "Honeycomb" cleavage was one of the problems of seeds made from ordinary quartz. Such cracks appear in seeds with a germanium oxide content in the overgrown layer more than 5 wt %. Some of them penetrate into the overgrown layer by tens of microns. Such cleavage may be due either to the difference in unit cell parameters of the seed and the Ge-containing layer that has grown up ( the phenomenon of heterometry) or to the alpha-beta transformation of seed quartz, whose growth was carried out at temperatures, close or exceeding the temperature of its alpha-beta inversion (i.e., 573 °C).



**Fig. 4.** The germanium oxide content in various growth sectors of HGQ crystals grown in high-temperature fluoride solutions.



**Fig. 5.** SEM image of the internal structure of HGQ single crystal grown in high-temperature fluoride solutions and the germanium oxide distribution in various growth sectors.

As a result, the optimal conditions for the reproducible growth of perfect HGQ single crystals with germanium oxide content of 10-15 wt % were determined. Growth of such crystals is carried out at temperatures of 540-650°C and pressures of 120-150 MPa in supercritical ammonium fluoride solutions with a concentration  $\text{NH}_4\text{F}$  of 5-8 wt %.

Cuts parallel to the trigonal prism  $x \{11\bar{2}0\}$  and the trigonal

pyramid  $s \{11\bar{2}1\}$  as well as narrow (no more than 3-4 mm) ZY-cuts known as Y-rods are used as the seeds. The weight of HGQ crystals which grown in 280 ml autoclaves with a diameter of 30 mm amounts 80g with a layer thickness of 7-8 mm on one side of the seed. At the same time, the very high thermobaric growth conditions of such crystals do not allow us to carry out their industrial growth at present.

This work was support RFBR (Grant № 17-05-00976).

#### References:

- Balitsky V.S., Balitsky D.V., Nekrasov A.N., Balitskaya L.V., Bondarenko G.V., Samokhvalova O.L. Growth, structural and morphological features and some properties of single crystals of quartz and germanium solid solutions with quartz structure. 2004. DAN, V. 396. No. 1. P. 89-92.
- Balitsky V.S., Balitsky D.V., Pushcharovsky D.Yu., Setkova T.V., Balitskaya L.V., Nekrasov A.N. Growth and morphology of single crystals of high-germanium quartz // Doklady Earth Sciences. V. 477. No2. P. 1437-1440.
- Balitsky D.V., Balitsky V.S., Pisarevsky Yu.V., Silvestrova O.Yu., Pilippo E. Growth and piezoelectric properties of germanium dioxide single crystals with quartz structure. Crystallography. 2000. V.45. No. 1. C.151-153.
- Balitsky V.S., Balitsky D.V., Nekrasov A.N., Balitskaya L.V. Growth and characterization of  $\text{SixGe}_{1-x}\text{O}_2$  solid solution single crystals with quartz structure. Journal of Crystal Growth. 2005. T. 275. P. 807-811.

#### Redkin A.F., Nekrasov A.N. Hydrothermal synthesis of Ba-bearing romeites.

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**Abstract.** Using dependence of lattice parameter ( $a_0$ ) of pyrochlore on the chemical composition, structures of "stable" romeite of  $\text{A}_2\text{Sb}_2\text{O}_7$  containing in position  $^{[8]}\text{A}$  bivalent cations of  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  are calculated and synthesis of them in water at 800 °C and 200 MPa is carried out. It is established that the Ba-bearing romeite aren't synthesized at the specified parameters, and the compound  $\text{BaSb}_2\text{O}_6$  of a hexagonal system steadily is formed of all considered mixes. The  $\text{BaSb}_2\text{O}_6$  is also formed on the mixture consisting  $\text{NaF}$ ,  $\text{BaO}$ ,  $\text{Sb}_2\text{O}_5$ , and  $\text{NaF}$  completely passes into solution.

**Keywords:** experiment, pyrochlore, romeite, hydrothermal synthesis

The lattice parameter ( $\text{LP} \equiv a_0$ ) of pyrochlores is the main crystallochemical parameter that determines not only the position of the cations in the structure, but also gives special properties to this class of compounds. Pyrochlores are oxide compounds of the type  $\text{A}_2\text{B}_2\text{O}_6\text{Y}$  (where Y is O, OH, F) having a structure  $Fd\bar{3}m$ . They widely were used as catalysts in organic synthesis; electrical and optical properties of pyrochlores were used in the electronics industry. Isomorphic substitution of cations can also serve as an indicator of the conditions of pyrochlores formation in natural conditions. Therefore, any attempts to predict LP by chemical composition are relevant for the synthesis of pyrochlores with unique properties.

For synthetic oxide compounds with pyrochlore structure, no less than 6 analytical equations (Table 1) were proposed, based on experimental data from 100 to 440 compounds of different chemical



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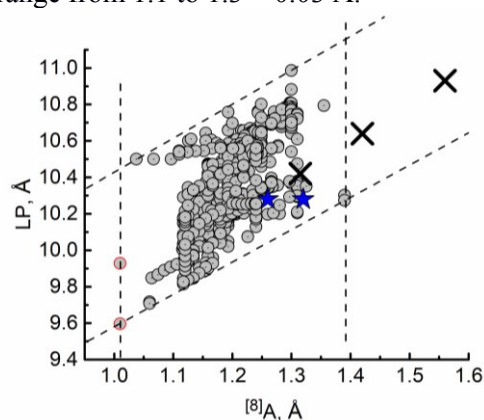
composition. The averaged values of ionic radii of cations and oxygen ( $R_A$ ,  $R_B$ ,  $R_O$ ) or crystal ionic radii ( $r_A$ ,  $r_B$ ) according to Shannon [Shannon, 1976] as well as the averaged values of electronegativity by Pauling [CRC, 2005] were used in the equations (1) - (6) for the estimation of LP of complex composition

pyrochlores. The averaged radii were calculated as the sum of the numbers obtained as a result of multiplying the radius by the mole fraction of this cation in the corresponding position  $^{[8]}A$  or  $^{[6]}B$ . Similarly, the averaged values of electronegativities were calculated.

**Table 1.** Effect of cation radii  $^{[8]}A$  or  $^{[6]}B$  on the lattice parameters of pyrochlores.

Eq	Analytical expression	Author
1	$a_0 (\text{Å}) = 1.914R_A + 2.910R_B + 6.422$	Chakoumakos, 1984
2	$a_0 (\text{Å}) = \frac{1}{2}(4.6188r_{YA} + 5.3333r_{BO})$	Siday & Shteyfan, 2011
3	$a_0 (\text{Å}) = 1.99818(R_A+R_O)+2.64756(R_B+R_O)-0.02238(\chi_A-\chi_O)-0.06215(\chi_B-\chi_O)-0.07432$	Brik & Srivastava, 2012
4	$a_0 (\text{Å}) = 4.6188 \cdot (R_A+R_O) \cdot t; t = 1.43373 - 0.42931 \cdot \left( \frac{R_A + R_O}{R_B + R_O} \right)$	Mouta et al., 2013
5	$a_0 (\text{Å}) = 6.035263 + 2.298669R_A + 2.872774R_B$	Nickolsky, 2015
6	$a_0 (\text{Å}) = 7.24534 + 0.4953 \times r_A + 0.547587 \times r_B + 2.173033 \times r_A \times r_B$	Redkin et al., 2015

The statistical analysis performed by us [Redkin, 2015] for a selection of more than 800 data, showed that the two-parameters nonlinear equation (6) gives a better fit to the experimental values of LP. Therefore, the equation (6) was used to estimate LP depending on the composition. Pyrochlores are characterized by a synthesis limited region. There is, so-called *tolerance factor* ( $t$  - permissible index), limiting the ratio of the distance between cations A and B with anion (oxygen). According to the statistical calculation [Mouta et al., 2013], the pyrochlore structure is stable with a probability of 95%, if  $t = 0.91 \pm 0.03$ . The compounds having a pyrochlore structure are shown in Fig. 1 in the coordinates of lattice parameters - averaged crystalline ionic radii of the cation  $^{[8]}A$ . For the most compounds, the cation radius in the eight-position is in the range from 1.1 to  $1.3 \pm 0.03 \text{ Å}$ .

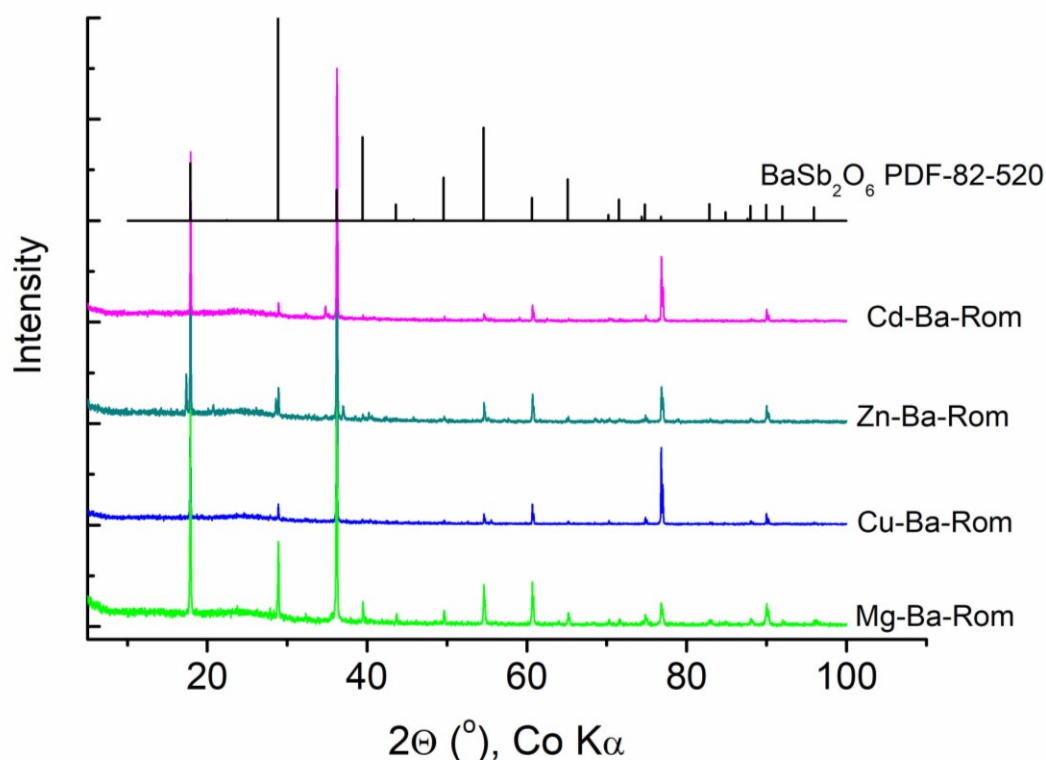


**Fig.1.** The dependence of LP and the stability region of the pyrochlore structure on the crystalline ionic radii of the cation  $^{[8]}A$ . Legend: -oxide pyrochlore (869 samples);  $\zeta$ -romeites (NaCa)Sb<sub>2</sub>O<sub>6</sub>F and Ca<sub>2</sub>Sb<sub>2</sub>O<sub>7</sub>;  $\square$ -Ba-containing mixtures used in the experiments.

In this study, we attempted to synthesize Ba-containing romeite or a compound of the Ba<sub>2-x</sub>A<sub>x</sub>Sb<sub>2</sub>O<sub>7</sub> type, where A are the cations Mg<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, ( $r=1.03\text{Å}$ ), Cd<sup>2+</sup> ( $1.24 \text{ Å}$ ) are the substituents of Ba<sup>2+</sup> ( $r_{Ba^{2+}}=1.56\text{Å}$ ) in position  $^{[8]}A$ . The reaction mixtures were prepared from BaO<sub>2</sub>, MgO, ZnO, CuO, CdO, and Sb<sub>2</sub>O<sub>5</sub>. The average ionic radius of the cations in position A and the expected LP values (calculated from Eq. 6) are shown in Fig. 1. Synthesis was carried out in Pt capsules on a hydrothermal line at 800 °C and 200 MPa. The run duration was 24-48 hours, so that Sb<sup>5+</sup> did not have time to reduce to Sb<sup>3+</sup>.

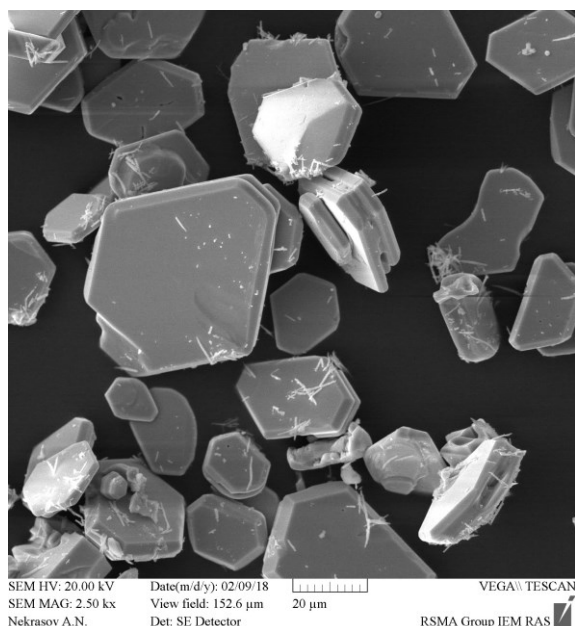
The run products were carefully washed from water-soluble compounds and examined by X-ray diffraction and electron microscopy. XRD analyses of the run products was carried out on Dron-7 apparatus at room temperature in the interval (2 $\theta$ ) 8 to 100° in steps of 0.02° with Ni-filter, Co K $\alpha$  radiation. The composition of individual, small crystals was determined by scanning electron microscopes CamScan MV2300 (Tescan VEGA 5130MM), Tescan VegaIIXMU (SEM).

Of all the mixtures (2BaO<sub>2</sub>+Sb<sub>2</sub>O<sub>5</sub>; 1.47BaO<sub>2</sub>+0.53MgO+Sb<sub>2</sub>O<sub>5</sub>; 1.47BaO<sub>2</sub>+0.53CuO+Sb<sub>2</sub>O<sub>5</sub>; 1.47BaO<sub>2</sub>+0.53ZnO+Sb<sub>2</sub>O<sub>5</sub>; 1.13BaO<sub>2</sub>+0.87CdO+Sb<sub>2</sub>O<sub>5</sub>; 1.058BaO<sub>2</sub>+0.942ZnO+Sb<sub>2</sub>O<sub>5</sub>; 0.47BaO<sub>2</sub>+1.53CdO+Sb<sub>2</sub>O<sub>5</sub>, BaO<sub>2</sub>+NaF+Sb<sub>2</sub>O<sub>5</sub>) there was formed BaSb<sub>2</sub>O<sub>6</sub> compound of hexagonal system with the unit cell parameters  $a_0 = 5.3036$ ,  $c_0 = 5.7602 \text{ Å}$ , analog PDF82-0520 or 46-1494.



**Fig. 2.** X-ray diffraction patterns of the run products of synthesis from mixtures containing BaO<sub>2</sub>, MgO, ZnO, CuO, CdO, and Sb<sub>2</sub>O<sub>5</sub> at  $t = 800\text{ }^{\circ}\text{C}$ ,  $P = 200\text{ MPa}$ .

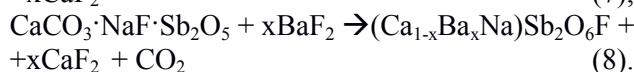
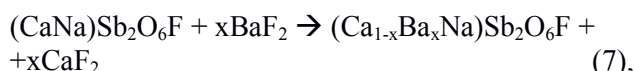
The runs products are represented by hexagonal crystalline formations (Fig. 3). Depending on the initial composition of the mixture, a different degree of erosion of the vertices of the faces of hexagonal plates was noted. None of the experiments showed octahedrons being typical to pyrochlores.



**Fig. 3.** The SEM image of the run products from a mixture of  $1.47\text{BaO}_2+0.53\text{MgO}+\text{Sb}_2\text{O}_5$ .

Of interest are experiments on the isomorphous substitution of cations A in the pyrochlore structure. It is known that such substitution is limited, as by the charges of cations (preservation of electroneutrality),

and by their ionic radii (Grimm-Goldschmidt rule). To replace Ca<sup>2+</sup> or Na<sup>+</sup> for Ba<sup>2+</sup> in romeite, synthetic romeite and a mixture of oxides were used. The studied reactions were:



According to XRD and SEM analyzes, romeite and BaF<sub>2</sub> were detected in the run products. The parameter of the elementary cell of romeite, both the initial and after the runs, did not change and was  $a_0 = 10.283 \pm 0.003\text{ \AA}$ . The occurrence of significant amounts of BaF<sub>2</sub> in the romeitic structure was not observed.

Thus, the romeites containing significant amounts of Ba<sup>2+</sup> are not stable. The stable phase at  $800\text{ }^{\circ}\text{C}$  and  $200\text{ MPa}$  is the compound BaSb<sub>2</sub>O<sub>6</sub>. The conducted studies indicate that there are restrictions for the ionic radius of the cations in position <sup>8</sup>A of pyrochlores.

This work was supported by the grant of RFBR 18-05-01001-a

#### References:

- Brik M.G. and Srivastava A.M. (2012). Pyrochlore structural chemistry: predicting the lattice constant by the ionic radii and electronegativities of the constituting ions. *J. Am. Ceram. Soc.*, v. 95 (4), p. 1454–1460.
- Chakoumakos B.C. (1984). Systematics of the pyrochlore structure type, ideal A<sub>2</sub>B<sub>2</sub>X<sub>6</sub>Y. *J Sol State Chem* 53: 120–129.

Mouta R., Silva R.X., Paschoal C.W.A. (2013). Tolerance factor for pyrochlores and related structures. *Acta Cryst.* B69: 439-445.

Nickolsky M.S. (2015). Predicting the lattice constants of the ternary pyrochlores  $A_2B_2O_6$ . *Acta Cryst.* B71: 235–240.

Shannon R.D. (1976). Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* A32: 751-767.

Redkin AF, Ionov AM, Nekrasov AN, Mzhchil RN (2015). Effect of chemical composition on the parameter of the unit cell of pyrochlore. Theses XVII All-Russian Conference on Experimental Mineralogy. Section II. Growth and properties of crystals. Novosibirsk, 2015, p. 73.

Siday V.I., Shteyfan A.Ya. Predicting the structures of pyrochlores  $A_2B_2X_6Y$ : The bond valence model. Scientific. Vesnyk Uzhhorod University (Set of Chemistry). 2011. No 1(25). C. 17-21.

CRC Handbook of Chemistry and Physics (2005) (Lide D.R., ed.) 86th Edition-CRC Press. P. 1299. Internet Version 2006, <<http://www.hbcnpnetbase.com>>, Taylor and Francis, Boca Raton, FL, 2006.

### Simakin A.G.<sup>1</sup>, Salova T.P.<sup>1</sup>, Gabitov R.I.<sup>2</sup>, Tutunnik O.A.<sup>3</sup> Contrast distribution of Au and Pt deposited from the fluid of the C-O-S system: observations by various methods

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**Abstract.** Platinum and gold do not form liquid or gaseous carbonyls at low pressure. We have first obtained data on the stability of carbonyls at a pressure of 200 MPa. The mechanism of reaction of platinum and gold with a fluid containing CO at high PT parameters it is necessary to studied experimentally.

**Keywords:** reduced carbonic fluid, Au, dry fluid, solubilities, sulfur.

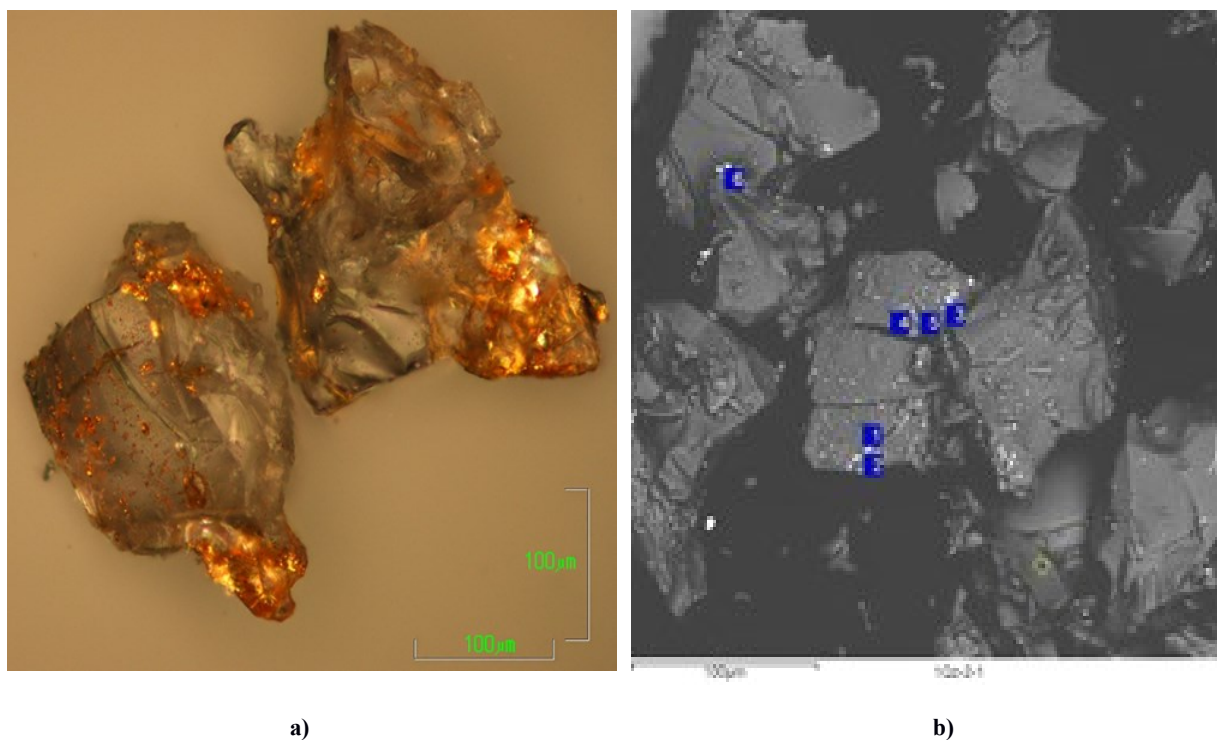
In this paper presents the first experimental results confirming the significant solubility of gold and platinum in the reduced carbonic fluid at temperatures close to magmatic and  $P = 200$  MPa. Experiments on the solubility of Pt and Au in the fluids of the composition of CO-CO<sub>2</sub> and C-O-H-S showed that the metals dissolve well in these fluids and are precipitated upon quenching. To obtain quantitative estimates of solubility, it is required to relate the amount of precipitated metal to the volume of the fluid. For this purpose, we used various glass traps: albite, sodium-silicate and quartz glass powders. Sulfur was introduced in the form of pyrite (FeS<sub>2</sub>), decomposing at temperatures above 450-650°C on pyrrhotite and elemental sulfur. The source of the fluid was iron and magnesium carbonates ( $2FeCO_3 = Fe_2O_3 + CO_2 + CO$ ;  $3FeCO_3 = Fe_3O_4 + 2CO_2 + CO$ ), and magnesium oxalate ( $MgC_2O_4 =$

$MgO + CO + CO_2$ ). The source of metals is the capsule walls. The experiments were carried out at  $P = 200$  MPa and  $T = 950$  ° C using the two-capsule technique (Simakin et al., 2016). The experimental samples were studied on a microprobe (CamScan MV2300 and Tescan Vega TS5130MM with an energy dispersive attachment INCA Energy 450) at the IEM RAS. The water contents in the experimental glasses were measured in a Karl-Fisher titration apparatus (KFT) on an Aqua 40.00 unit with a high temperature HT 1300 attachment (IEM RAS). Local analyzes of gold in glasses were performed using the LA-ICP-MS method on an Agilent 7900 quadrupole mass spectrometer equipped with a CETAC excimer laser (193 nm) at the University of Rochester (USA). The gross analysis of the samples for gold was carried out at the Vernadsky Institute RAS using the method of electrothermal atomic absorption spectroscopy (ETAAS). In the experiments with platinum, to absorb liquid by a glass trap, we used albite glass (Simakin et al., 2018). In the experiments with gold, we tried to use sodium silicate glass, which is more readily melted than albite glass. The sodium-silicate glass could not be completely freed from absorbed water, therefore, in the sulfur-containing system, in addition to COS, many sulfur compounds were formed. The residual water content in this glass after calcination was 0.93 mass% (determined by the KFT method). Formation of salt melts containing Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> was noted. The study of albite glass by X-ray tomography has shown that in the glass volume, platinum particles of a few microns size are evenly distributed, also there are separate large particles of platinum (fig.1).



**Fig.1.** The X-ray tomography data on the distribution of Pt in albite glass.





**Fig.2.** The Optical and BSE images of redeposited gold and platinum: a) Au - optical image; b) Pt-BSE image

It can be assumed that the large particles of Pt were separated from the walls of the ampule at an early stage, and many fine particles were redeposited during the experiment. The height of the sample is 1.65 mm. The quartz pieces do not meld and one can observe particles of platinum and gold redeposited on their surface on BSE and optical images. (Fig.2). On the optical images of quartz pieces after the experiment, it is possible to distinguish the thin translucent Au shell giving the surface a red color (Fig. 2a). In the corners of the cleavage cracks, large gold pieces measuring about 5  $\mu\text{m}$  are seen. The platinum pieces are clearly visible on BSE images (FIG. 2b). The smallest pieces of gold have a size of a few microns, close to the resolution limit of the image. Gold distribution is non-uniform, with concentration of visible particles on separate parts of quartz glass. The gold content in the fluid can be estimated from the initial porosity of the powder and the phase densities given the mass balance ratios (described in detail in Simakin et al., 2016). To this end, three sodium-silicate glass traps after the experiments were analyzed by the LA-ICP MS method on gold, sulfur and a number of other elements at the University of Rochester (USA).

Metal-organic compounds of gold and platinum at high temperatures are stable only at high pressure. They are formed during the experiment and are destroyed during quenching. We observe only native metals, in quenching products. The large metal particles enter the glass powder before melting, as a result of chemical corrosion of the capsule walls caused by fluid reactions. The metal dissolved in the fluid falls during hardening. It sets the background

distribution, which can be measured by local methods (LA-ICP-MS). The gross analysis of glass traps samples gives platinum content of 100 to 1300-1400 ppm. The gross contents depend little on temperature and grow with time.

The application of x-ray tomography method showed that sufficiently large submicron platinum particles are evenly distributed in the volume of the albite glass trap. This can be interpreted as: 1) platinum particles grow rapidly in the fluid phase with an effective transfer in a porous medium over distances of tens of microns; 2) a two-phase fluid with microcaps of a platinum-concentrated phase.

**Acknowledgements.** This study was supported by RFBR grant #18-05-00597a

#### References:

- Simakin A.G., Salova T.P, Gabitov R.I. and Isaenko S.I. Dry  $\text{CO}_2$ - $\text{CO}$  fluid as an important potential deep Earth solvent // *Geofluids*, 2016. Vol. 16, pp. 1043–1057.  
 Симакин А.Г., Салова Т.П., Кислов Е.В., Некрасов А.Н. Восстановленный углекислый флюид как фактор рудогенеза на примере аподоломитовых скарнов Йокондовыренского массива. // *Петрология*. 2018 (в печати).