

Hydrothermal equilibria and ore formation

Berkovsky E.M.¹, Tarnopolskaya M.E.¹, Nikolaeva I.Yu.¹, Lubkova T.N.¹, Bychkov A.Yu.¹ Experimental study of titanium fluoride complexes in hydrothermal solutions at 300°C and saturated water vapour pressure. UDC 550.4.02

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Abstract. The experimental study of rutile solubility in fluoride solutions at 300°C and saturated water vapor pressure was carried out. A mixture of HF + HNO₃ solutions with different HF content and TiO₂ powder were used. The titanium content in the experimental solutions was measured by ICP-MS. The results showed that, under the experimental conditions, the titanium solubility does not depend on pH; therefore, uncharged complexes are formed. The ratio of fluorine and titanium in the solutions under study indicates the predominance of Ti(OH)₂F₂⁰.

Keywords: hydrothermal solution; fluoride complexes; titanium

Titanium is an inactive element in the hydrothermal process and does not migrate in the composition of chloride complexes due to their low stability. To date, various forms of titanium in hydrothermal solutions are known.

Purtov and Kotelnikova (1993) investigated the solubility of rutile (TiO₂) at $T = 400\text{--}700^\circ\text{C}$, $P = 1$ kbar in pure water and aqueous solutions of HCl ($m_{\text{HCl}} = 0.1\text{--}0.25$ mol/kg) and HF ($m_{\text{HF}} = 0.001\text{--}0.02$ mol/kg). The experiments were carried out in vessels made of a heat-resistant alloy with sealed gold capsules inside, containing solutions and powder of rutile. It was found that the solubility of rutile increases with an increase in the concentration of fluorine and chlorine in acidic solutions and the complexes Ti(OH)₃F⁰ and Ti(OH)₃Cl⁰ are formed. However, at $m_{\text{HCl}} = m_{\text{HF}}$, the titanium content was higher in fluoride solutions and did not exceed $5 \cdot 10^{-5}$ mol/kg.

Knauss et al. (2001) studied the rutile solubility in buffer solutions, composed of HNO₃, HCO₂CH₃–NaCO₂CH₃, NaH₂PO₄–Na₂HPO₄, B(OH)₃–NaOH and NaOH. Each of solutions contained 0.1M NaNO₃ as a background electrolyte and had pH = 1–13. The experiments were carried out at $T = 100\text{--}300^\circ\text{C}$, $P = 200$ bar in Au–Ir autoclaves. In this case, titanium complexes Ti(OH)₃⁺, TiO₂⁰(aq), Ti(OH)₅[–] were formed and the hydrolysis constants were calculated. The solubility of titanium at $T = 300^\circ\text{C}$, $P = 200$ bar, pH = 1–4 and pH = 7–13 was $10^{-4}\text{--}10^{-7}$ mol/kg, and at pH = 4–7 it was close to $10^{-7}\text{--}10^{-8}$ mol/kg.

Ryzhenko et al. (2006) investigated the solubility of rutile in HCl, HF, NaF, NaOH and H₂SO₄ at $T = 500^\circ\text{C}$, $P = 1$ kbar and hydrogen fugacity $8 \cdot 10^{-12}\text{--}10.3$ bar. The experiments were carried out in

hydrogen-permeable gold ampoules placed in heat-resistant steel autoclaves, the lower parts of which contained buffer mixtures Mn₃O₄/Mn₂O₃ and Ni/NiO. The authors concluded that titanium migrates best in fluorine-enriched acidic aqueous solutions within the complexes Ti(OH)₂F₂⁰, Ti(OH)₃F⁰, Ti(OH)₄F[–], and the titanium concentration reaches several fractions of a milligram per kilogram of water.

Table 1. Thermodynamic parameters of titanium complexes.

TiO ₂ ⁰ (aq)			
$\Delta_r G^\circ_{298}$, cal/mol	S°_{298} , cal/mol·K	$a_1 \cdot 10$, cal/mol·bar	$a_2 \cdot 10^{-2}$, cal/mol
-200309	-10.318	6.20	-27.11
a_3 , cal·K/mol·bar	$a_4 \cdot 10^{-4}$, cal·K/mol	c_1 , cal/mol·K	$c_2 \cdot 10^{-4}$, cal·K/mol
40	-1.66	42.01	-45.51
$\omega \cdot 10^{-5}$, cal/mol		-0.0342	
Ti(OH) ₃ ⁺ = TiO ₂ ⁰ (aq) + H ₂ O + H ⁺		Ti(OH) ₅ [–] + H ⁺ = TiO ₂ ⁰ (aq) + 3H ₂ O	
pK(298)	(zz/a) _{eff}	pK(298)	(zz/a) _{eff}
1.94	0.57	-12.57	-0.27
Ti(OH) ₂ F ₂ ⁰ = TiO ₂ ⁰ (aq) + 2H ⁺ + 2F [–]			
pK(298)	(zz/a) _{eff}	pK(300°C, sat. water vap. press.)	
19.25	1.74	17.21	

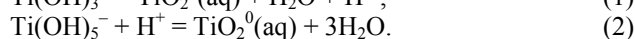
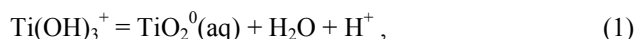
Table 2. Solubility of rutile in acidic fluoride solutions at 300°C and saturated water vapor pressure.

HF, mol/kg	HNO ₃ , mmol/kg	Ti, 10 ⁻⁶ mol/kg
0.0992	0.90	105
0.0498	0.95	75.5
0.0249	0.98	3.64
0.0125	0.99	14.4
0.0062	0.99	1.39
0.0034	1.0	0.38
0.0016	1.0	0.31

In this work, experiments were carried out on the solubility of rutile in fluoride solutions at 300°C and the pressure of saturated water vapor. Rutile powder was placed on the bottom of autoclaves made of VT8 titanium alloy, solutions obtained by mixing in various proportions of 10^{-3} mol/kg HNO₃ (to reduce corrosion of autoclaves and regulate pH) and 0.1M HF were poured. The autoclaves were kept in an oven for 7 days at a temperature of 300°C. Then the autoclaves were quenched in water, solutions were taken from them and filtered through a Vladipor 0.45 μm membrane filter. The samples were analyzed by the ICP-MS method on an Element-2 mass

spectrometer at the Department of Geochemistry of the Geological Faculty of Lomonosov Moscow State University.

Based on data from Knauss et al. (2001) and Antignano, Manning (2008) using the Helgeson-Kirgham-Flowers (HKF) model in the OptimB program, the thermodynamic parameters for the complex were calculated: $\text{TiO}_2(\text{s}) = \text{TiO}_2^0(\text{aq})$ (Table 1). And using data of Liberti et al. (1963) and Knauss et al. (2001) according to the Ryzhenko-Bryzgalin model in the OptimC program, thermodynamic data for the following reactions were calculated:

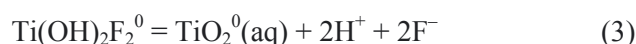


The obtained values are presented in Table 1 and Fig. 1. The experimental data obtained in this work were processed in the OptimA program.

It was found that at $T = 300^\circ\text{C}$ and the saturated vapor pressure of water, the $\text{Ti}(\text{OH})_2\text{F}_2^0$ complex dominates in solutions, and the following complexes

are also present: $\text{Ti}(\text{OH})^{3+}$, $\text{TiO}_2^0(\text{aq})$, $\text{Ti}(\text{OH})^{5-}$. With an increase in the fluorine content, the titanium solubility increases sharply (Table 2). That is, the hydroxo complexes become hydroxofluoride complexes and the content of the latter in solutions becomes higher. This is expressed in the change of the flat section of the graph (Fig. 2) to a steeply inclined one.

In the OptimC program for the reaction:



thermodynamic parameters under experimental conditions were calculated (Table 1). Using the Gibbs formation energies for $\text{Ti}(\text{OH})_2\text{F}_2^0$ and F^- given by Ryzhenko et al. (2006) at $T = 500^\circ\text{C}$, $P = 1$ kbar, the stability constant of the complex was calculated (Table 1). The stability data of mentioned complex, obtained in this work at the pressure of saturated water vapor, and the data (Purtov and Kotel'nikova, 1993) were extrapolated to lower temperatures (Fig. 3).

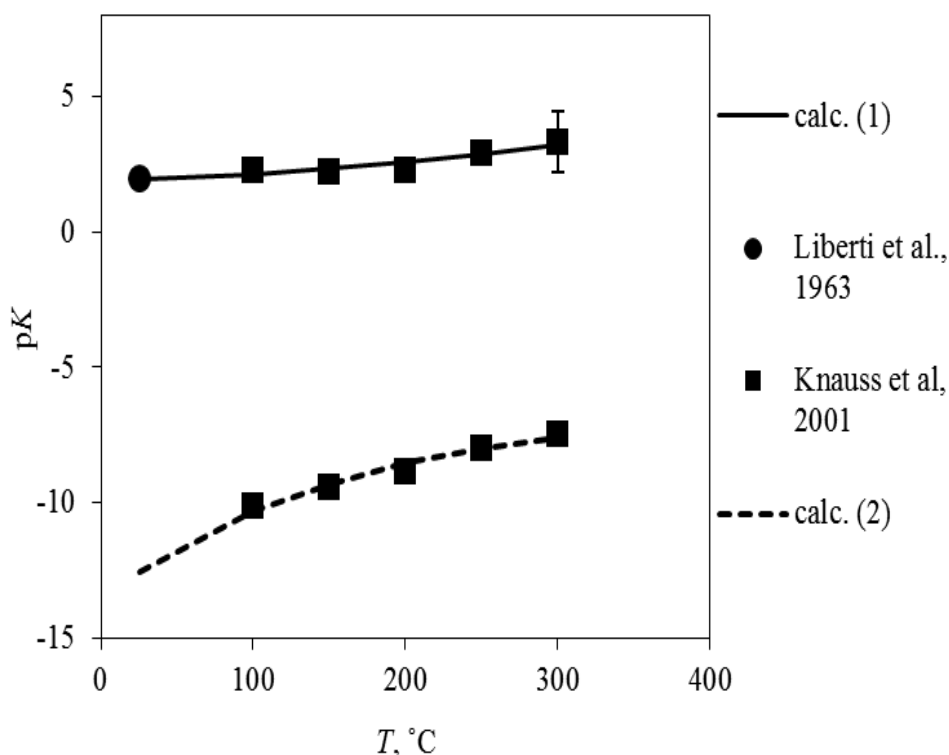


Fig. 1. Dependence of pK reactions (1) – solid lines and (2) – dotted lines on temperature at the pressure of saturated water vapor.

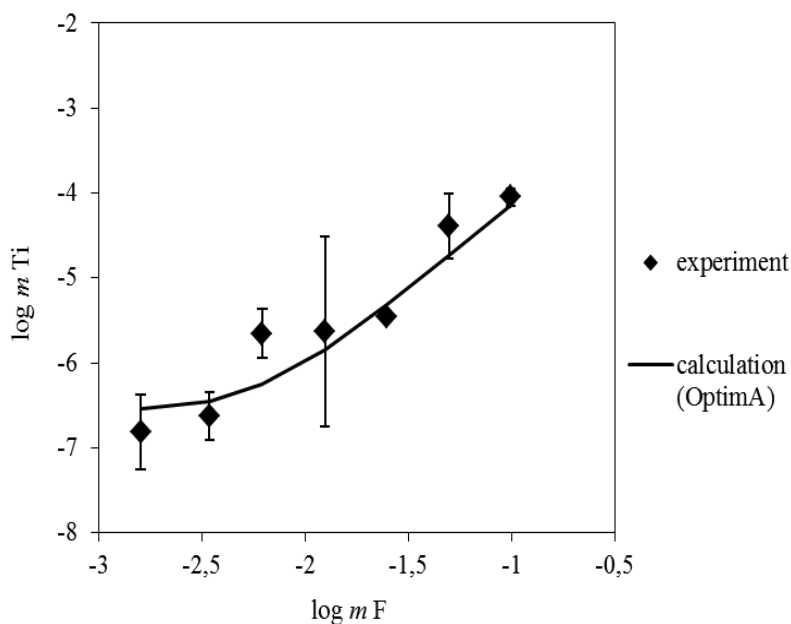


Fig. 2. Solubility of rutile at 300°C and saturated water vapor pressure.

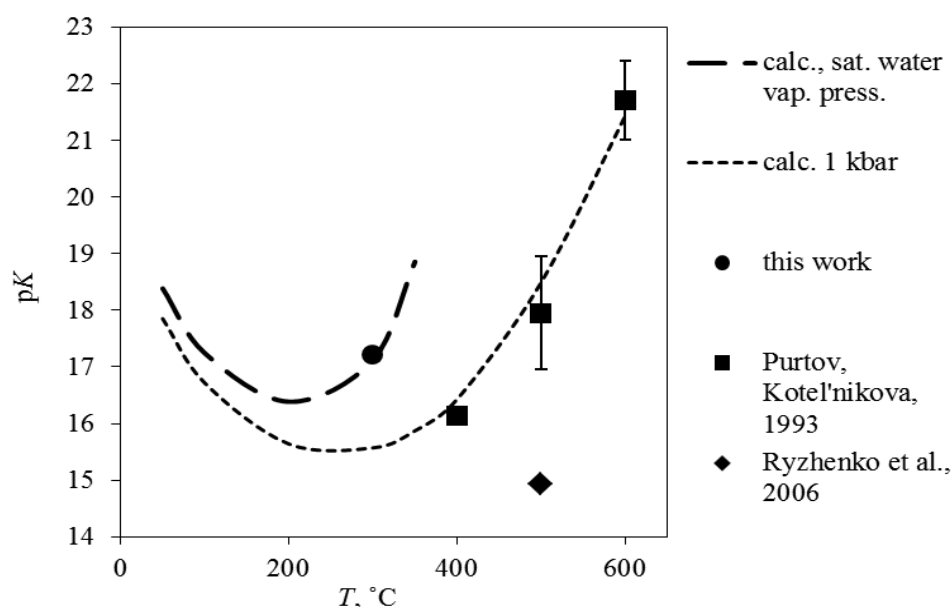


Fig. 3. Dependence of the reaction constant (3) on temperature.

Conclusions

1. The study of rutile solubility in fluoride hydrothermal solutions showed that at 300°C and the pressure of saturated water vapor, the following complex is stable:

$$\text{Ti}(\text{OH})_2\text{F}_2^0 = \text{TiO}_2(\text{s}) + 2\text{H}^+ + 2\text{F}^-, -\lg K = 17.21.$$

2. Due to the stability of the titanium fluoride complexes, the solubility of rutile sharply increases with an increase in the concentration of fluoride. If in solutions with $m(\text{HF}) \leq 0.001$ mol/kg the solubility does not exceed the first ppb, then at $C(\text{HF}) = 0.1\text{M}$ it reaches 3.7 ppm.

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Bublikova T.M., Setkova T.V., Balitsky V.S. Theoretical calculation of the solubility of tenorite and malachite in water and ammonia solutions at temperatures up to 100 °C. UDC 549.743.1:546.06

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Abstract. The stability of solid phases of tenorite and malachite when interaction with water and aqueous solutions of ammonia have been studied theoretically. Calculations were carried out using the HCh geochemical modeling software package. The solubility of tenorite and malachite is calculated in pure water and ammonia solutions 0.01 and 2.0 *m* NH₄OH. It was shown that malachite dissolves in water and aqueous ammonia solutions incongruently, with the formation of tenorite. The tenorite content in the solution increases with increasing temperature. Possible forms of the presence of copper during the dissolution of tenorite and malachite have been determined. The dependence of the solubility of minerals on the temperature in the range of 20 – 100 °C is found. Theoretical calculations are confirmed experimentally. Crystalline tenorite and malachite phases were obtained by recrystallization of basic copper carbonate in 2.0 *m* NH₄OH.

Keywords: *geochemical modeling, phase formation, tenorite, malachite, copper, ammonia solutions*

The study of phase formation in aqueous copper-carbonate systems is actual now. Since it is directly related to the solution of important theoretical and practical problems such as: (1) clarification of the formation conditions of copper-containing minerals in nature, (2) assessment of environmental risks in the areas of mining and processing plants, (3) the creation of new technologies for the synthesis of oxide minerals copper, (4) determination of the forms of copper in the process of corrosion at water interaction. The main objective of this study was the theoretical and experimental study of stability conditions, determination of solubility and the ratio of solid phases (tenorite and malachite) when interacting with water and aqueous ammonia containing solutions.

The theoretical analysis of the phase relationships and tenorite and malachite solubility in pure water and aqueous solutions of ammonia was carried out using HCh geochemical modeling software package (Shvarov, 1999). Tenorite (Ten) and malachite (Mal)

solubility was calculated in pure water and ammonia solutions of 0.01 and 2.0 *m* NH₄OH. The choice of solutions concentration is due to the following. Tenorite and malachite are widespread minerals in the oxidation zone of copper sulfide and polymetallic deposits. It seemed important to reveal stability of minerals in near-surface conditions close to the conditions of their formation at atmospheric pressure ($p_{\text{CO}_2} \approx 10^{-3.45}$ atm) and low (up to 100 °C) temperatures. The study of tenorite and malachite solubility in ammonia solutions of low concentration is fundamental importance for ensuring the safe storage of spent nuclear fuel in copper canisters placed in granite rocks. Chemical environment in canisters area can have both a negative effect on the walls of containers, increasing copper corrosion, and a positive one, making a passivation film. Copper oxidation in humid air occurs with the formation of basic copper carbonate (copper green), which covers the external walls of canisters and interacts with pore water of granites. The established nitrogen content in deep groundwater in the form NO₃⁻, NO₂⁻ и NH₃ was fixed up to 0.5 mmol/kg (Puigdomenech, 2000). The form in which copper is found in the interaction of basic copper carbonate with ammonia solutions plays an important role in assessing the mechanism and degree of corrosion of canisters. To calculate the solubility of malachite and tenorite, we took the concentration value of 0.01 *m* NH₄OH and the temperature from 20 to 100 °C, since the expected temperature on the canisters surface can reach ≈ 80 °C, and after the storage is closed, it gradually decreases to temperatures of about 15 °C. Concentrated ammonia solutions (1.0 – 3.0 *m* NH₄OH) are an integrant part of complex solutions used in hydrometallurgical processes of ammonia leaching of copper from poor oxidized, native ores and waste from primary ores (Nadirov et al., 2017).

The results of theoretical calculations of malachite and tenorite solubility in water and aqueous ammonia solutions at temperatures up to 100 °C are shown in Figure 1.

The solubility of tenorite and malachite in pure water increases with temperature raise. Copper concentration in solution increases from $2 \cdot 10^{-5}$ to $6 \cdot 10^{-5}$ mol/kg for malachite and from $9 \cdot 10^{-8}$ to 10^{-6} mol/kg for tenorite. The calculated data are in good agreement with the experimental data of Scaif (Scaif, 1957), obtained by dissolving basic copper carbonate in water at a temperature of 30 °C (see Fig. 1a). Tenorite solubility in water is two orders of magnitude lower than the malachite solubility in the temperature range under consideration. The temperature dependence of tenorite solubility is more pronounced than that of malachite (see Fig. 1a).

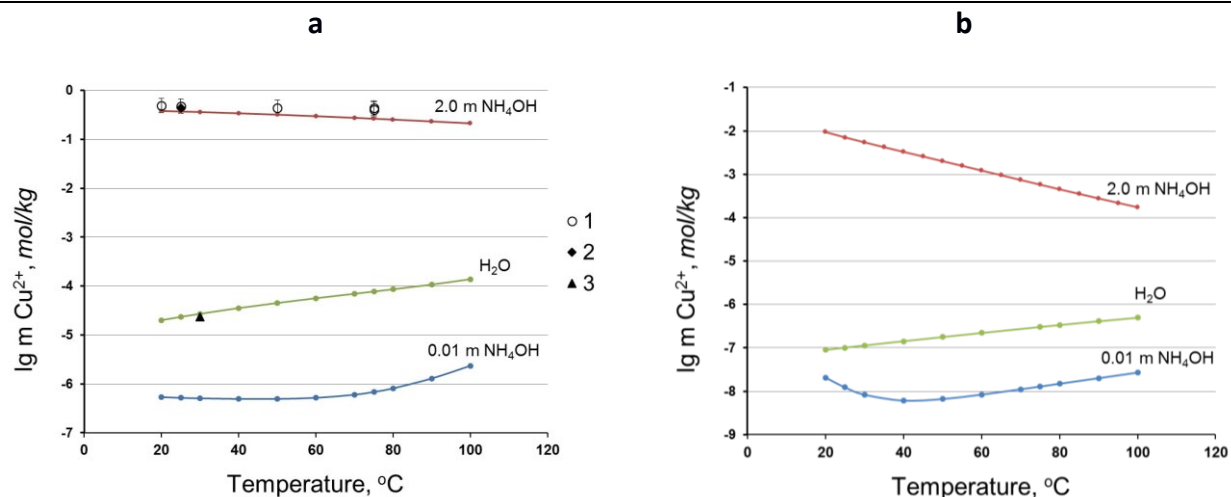


Fig. 1 Temperature dependence of malachite (a) and tenorite (b) solubility in pure water and solutions of ammonium hydroxide. 1 – our experimental data; 2 – calculated and experimental data of Xi Wang et al. (2009); 3 – experimental data from Scaif (1957).

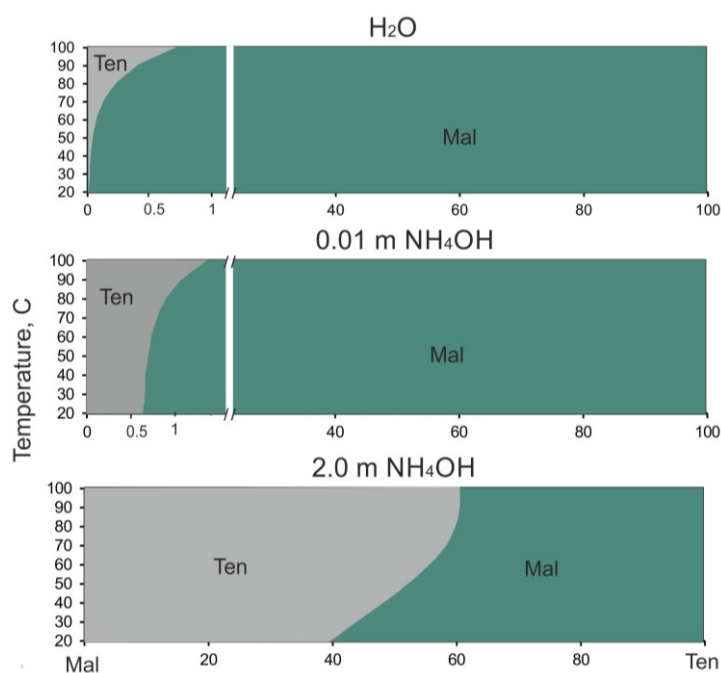


Fig. 2 Temperature dependence of ratios of crystalline phases of tenorite (Ten) and malachite (Mal) when malachite is dissolved in water and ammonium hydroxide solutions.

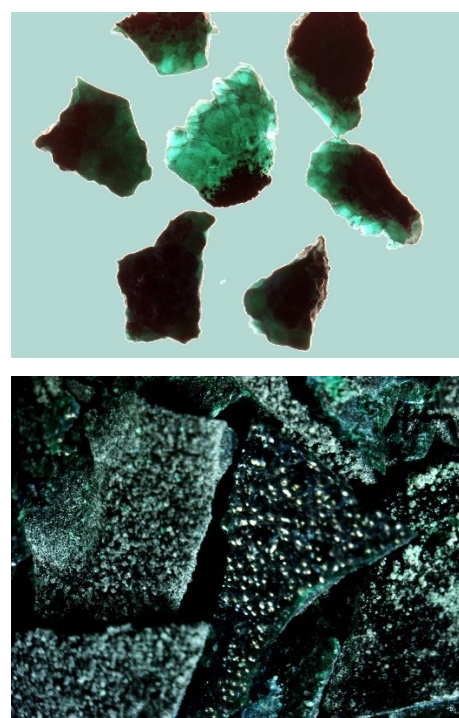


Fig. 3 Malachite and tenorite obtained by recrystallization of basic copper carbonate in 2.0 m NH_4OH . (x5).

It is obvious that tenorite is more stable in the near-surface conditions of the oxidation zone than malachite. At deeper horizons of the oxidation zone at a constant partial pressure of carbon dioxide this advantage persists with temperature increase, since the tenorite formation requires a lower concentration of copper in aqueous solutions. The ions Cu^{2+} , CuHCO_3^+ , CuCO_3^0 present in the water is make largest contribution to formation of the malachite phase. Decrease in the partial pressure of CO_2 in the

atmosphere and a decrease in the saturation with carbon dioxide of solutions circulating in the near-surface part of the oxidation zone leads to a decrease in the content of carbonate-bicarbonate copper ions. This results in the replacement of malachite with tenorite. Malachite dissolves incongruently in water, with tenorite formation and tenorine content slightly increases with temperature increase. (Fig. 2).

Dependence of tenorite and malachite solubility in 0.01 m NH_4OH is more complex and nonlinear. In

the temperature range 20 – 40 °C, the total copper concentration at CuO dissolution determines the total amount of complexes: $\text{Cu}(\text{OH})_2^0$, $\text{Cu}(\text{NH}_3)_3\text{OH}^+$, $\text{Cu}(\text{NH}_3)_n^{2+}$. Copper-ammonia complexes become less stable with temperature increase, their content in the solution decreases, and the $\text{Cu}(\text{OH})_2^0$ content increases over the all temperature range under consideration and becomes decisive at $T > 40$ °C. The general character of quantitative changes in species and complexes in an equilibrium solution upon dissolution of malachite remains the same. CuHCO_3^+ , CuCO_3^0 species make a significant contribution to total copper concentration in solution at temperatures above 60 °C. In a solution in equilibrium with malachite there is a significant amount of free ammonia ($1.1 \cdot 10^{-3}$ mol/kg), which decreases with temperature increase ($7.5 \cdot 10^{-4}$ mol/kg at 100 °C). Malachite solubility in the temperature range of 20 – 100 °C is higher than that of tenorite by one and half – two orders. Tenorite is more stable than malachite in 0.01 m NH_4OH solutions. Malachite dissolves incongruently with tenorite formation, which proportion is higher than when dissolving in water malachite under the same conditions (see Fig. 2).

Incongruent dissolution of malachite in water and 0.01 m ammonia solutions, shown in our calculations and experiments, as well as the thermodynamic calculation of the chemical composition of a solution in equilibrium with solid phases, have a great practical importance for understanding the mechanism of corrosion of copper canisters. In case of possible contact of clean water or groundwater containing low-concentration ammonium hydroxide, the surface of the canisters is covered with malachite layer. Then this layer begins to dissolve with the formation of a more stable tenorite phase, which in this case passivates the surface. As the temperature rises to 100 °C, the stability of tenorite increases due to malachite. However, under mechanical stress on the metal, a special form of localized corrosion can occur. This is the so-called stress corrosion cracking, which is usually associated with a specific environment. Typical media leading to stress corrosion cracking of copper alloys and pure copper are solutions containing nitrite or ammonia (Beavers, 1992). At 70 °C, the critical concentration of NH_4OH is 0.05 mol/kg (Puigdomenech, 2000), and it increases with temperature decreases. Our calculations showed that when the ammonia solution interacts with malachite with a decrease in temperature from 100 to 20 °C, the fraction of free ammonia in the solution increases from 0.00075 to 0.0010 mol/kg, increasing its negative effect on the container surface. Thus, the risks of stress corrosion cracking increase, which is concordant with Suzuki and Hisamatsu (1981).

When malachite and tenorite are dissolved in concentrated 2.0 m NH_4OH solution, copper in an equilibrium solution is predominantly in the form of complexes $\text{Cu}(\text{NH}_3)_4^{2+}$, $\text{Cu}(\text{NH}_3)_5^{2+}$, $\text{Cu}(\text{NH}_3)_3^{2+}$, $\text{Cu}(\text{NH}_3)_3\text{OH}^+$ (in descending order) which lose their stability with increasing temperature. The solubility of malachite and tenorite in solution decreases with temperature increases (see Fig. 2). The temperature dependence of tenorite solubility is pronounced with temperature increases to 100 °C, it decreases by almost two orders. As can be seen from Figure 1a, the previously obtained experimental data on the solubility of basic copper carbonate at temperatures of 20, 25, 50 and 75 °C are in good agreement with our calculated data, as well as Xi Wang experimental and calculated data at $T = 25$ °C (Wang et al. 2009).

The calculated change in the ratios of solid phases during dissolution of malachite depending on temperature is shown on Figure 2. Experimentally, crystalline phases of malachite and tenorite were obtained in experiments on recrystallization of basic copper carbonate ($T_{\text{solubility}} \approx 50 - 55$ °C; $T_{\text{crystallization}} = 75$ °C) according to the method developed in IEM RAS (Bublikova et al., 2018). The overgrown layer at the bottom of the crystallizer is composed by a mixture of crystalline phases of malachite and tenorite (Fig. 3), which was confirmed by the X-ray phase analysis. Although it is rather difficult to estimate the quantitative ratio of malachite and tenorite in the products of experiments, it is obvious that the results of calculation and experiment do not contradict each other.

The high solubility of malachite in concentrated ammonia solutions is widely used in hydrometallurgical processes for extracting copper from depleted ores and secondary waste. The results of study showed that under atmospheric conditions, when malachite is dissolved in equilibrium (2.0 m NH_4OH) solutions with solid phases presents 40 – 45% tenorite. The tenorite solubility in these solutions is lot lower, which makes it difficult to leach completely copper from the ore in hydrometallurgical process. The recyclable ore also contains copper oxides, sulfides, phosphates, which are less soluble in ammonia solutions. To achieve the highest possible degree of copper leaching, it becomes necessary to add additional components to the solution composition that lead to their solubility: chloride, carbonate, ammonium nitrate (Xi Wang et al., 2009). With a high percentage composition of basic copper carbonates in rocks, concentrated solutions of ammonium hydroxide remain promising for its leaching due to their high efficiency, low toxicity and cost. The data on the solubility of tenorite and malachite in ammonia solutions make it possible to model the composition of the working solution and variate it with a change in the composition of the initial ore.

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Kotelnikov A.R.¹, Damdinov B.B.², Suk N.I.¹, Akhmedzhanova G.M.¹, Van K.V.¹
Experimental study of the transport of sulfide and silicate minerals under gradient conditions in connection with the problem of genesis of telethermal deposits UDC 553.21/.24

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Abstract. The modeling of the processes of metamorphic transformation of the substance of oceanic basalts and sulfide ores of black smokers under the influence of hydrothermal fluids of complex composition in gradient conditions is carried out in relation to the problem of the genesis of telethermal deposits. The experiments were carried out using the ampoule technique in high gas pressure vessel at T = 650–680°C and P = 4.5 kbar in concentrated water-salt solutions under conditions of a temperature gradient of 0.5°C/mm for 12–14 days. It is shown that at T = 680–650°C, intense recrystallization and precipitation of sulfide minerals (sphalerite, galenite, chalcopyrite, pyrite) occurs together

with feldspars, micas and quartz. For the first time, data on the joint formation of quartz-feldspar-sulfide associations were obtained.

Keywords: experiment, sulfide and silicate minerals, telethermal deposits, genesis

It has previously been shown that sulphide ores common in ophiolite of Eastern Sayan are analogues of the ancient black smokers, metamorphosed under the conditions of the epidot-amphibolite phase of metamorphism (Damdinov et al., 2019). However, ores from ophiolites have a substantially pyrrhotine composition, unlike modern black smokers, where, along with Fe sulphides (pyrite, marcasite), copper and zinc sulfides (chalcopyrite, sphalerite, kubanite, etc.) are widespread. Therefore, it was necessary to study the transport and deposition of the sulfide substance under the conditions of conflict transformation of the rocks of the earth's crust.

The purpose of this study was to model the processes of metamorphic transformation of the substance of ocean basalts and sulfide ores of black smokers under the influence of hydrothermal fluids of the complex composition in gradient conditions in relation to the problem of the genesis of telethermal deposits.

EXPERIMENTAL METHOD The experiments were carried out using the ampoule technique in high gas pressure vessel (HGPV-10000, designed by IEM RAS) in concentrated water-salt solutions under the conditions of a temperature gradient: the bottom of the ampoule is 680°C, the top is 650°C at a pressure of 4.5 kbar. We used platinum ampoules with a diameter of 7 mm and a length of 60 mm. Water-salt solutions were set with a mixture (100 mg NH₄Cl + 100 mg NaCl + 50 mg NaOH + 600 mg H₂O) or (100 mg NH₄Cl + 100 mg KCl + 50 mg KOH + 600 mg H₂O). Basalts of the East Pacific Rise, as well as sulfide minerals that are part of the associations of “black smokers” (ZnS + FeS₂ + PbS + CuFeS₂) were used as initial materials. The duration of the experiments was 12–14 days.

The composition of the experimental products was determined by the method of local X-ray spectral microanalysis using a Tescan Vega II XMU scanning electron microscope (Tescan, Czech Republic) equipped with an INCA Energy 450 X-ray spectral microanalysis system with energy-dispersive (INCAx-sight) and crystal-diffraction (INCA wave 700) X-ray spectrometers (Oxford Instruments, England) and the INCA Energy + software platform.

EXPERIMENTAL RESULTS As a result of the experiments, almost complete transfer of the substance (both silicate and sulfide) to the upper part of the ampoule was observed. In this case, both intergrowths of sphalerite crystals and intergrowths of sphalerite crystals with feldspar and quartz crystals were synthesized (Fig. 1). When the ampoules were opened, the smell of hydrogen sulfide

was often observed, which indirectly indicates that the transport of the sulfide substance was carried out by hydroxyl-sulfide complexes. To simulate the transport of substances in black smokers, a fluid with

an alkaline specificity was chosen. The issues of ore deposition and transport of ore matter are considered in the works of academicians D.S. Korzhinsky, V.A. Zharikov and others.

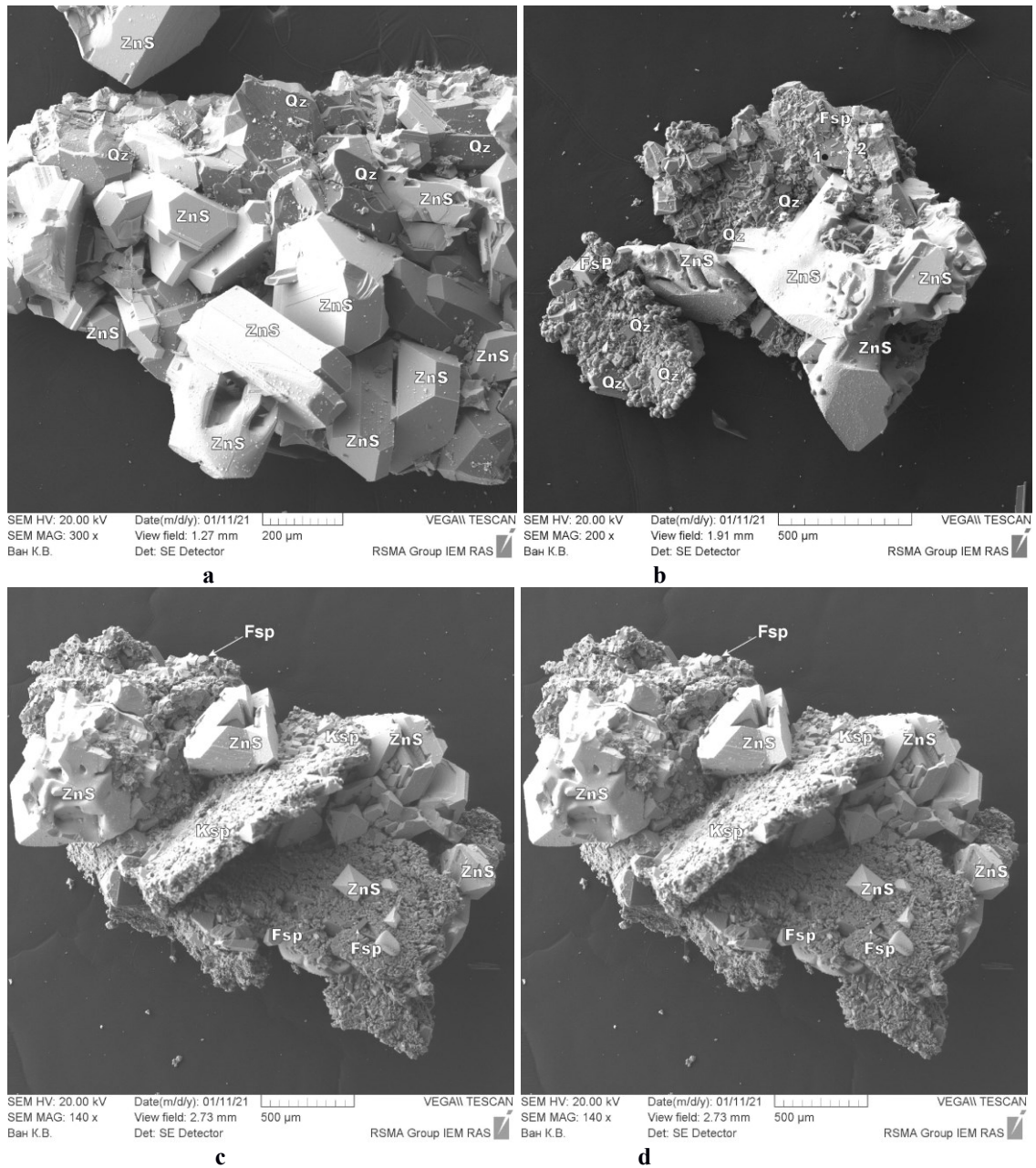


Fig. 1. Intergrowths of quartz and sphalerite (sample 7369-16) (a); intergrowths of quartz, potassium feldspar, and sphalerite (sample 7369-10) (b); intergrowths of potassium feldspar and sphalerite (sample 7369-11) (c); sphalerite intergrowths (sample 7369-9) (d). Q – quartz, Fsp – potassium feldspar, ZnS – sphalerite.

They showed that the movement of a fluid in a porous medium under decompression conditions leads to its heterogenization into two phases (in the simplest case, into vapor and liquid). A redistribution of elements occurs between these phases, as a result, the vapor phase is acidified, and the liquid phase is made alkaline. Most of the salts are concentrated in the liquid phase. As the fluids rise (especially in a porous medium), these phases are separated in space. The vapor phase is ahead of the liquid one; therefore,

in the works of D.S. Korzhinsky suggested a primary "wave of acidic fluid", which is superimposed on a later alkaline one. The process of ore deposition is associated with the alkaline stage of the process (Korzhinsky, 1982). This process is considered in detail as applied to fluid-magmatic systems in the works of Kotelnikov et al. (2018, 2019), Shapovalov et al. (2019). Many researchers note the potassium specificity of ore-forming fluids. The metamorphosing effect of fluids during periods of

tectonic-magmatic activation and collisional processes in the earth's crust most strongly manifested. This is determined by an increase in the temperature gradient during the rise of mantle plumes and by the flows of deep fluids. Therefore, the conditions for modeling metamorphic transformations of submarine sulphide sediments are: (1) relatively high PT-parameters – temperatures of 500–650°C, pressures of 3-5 kbar; (2) fluids of alkaline specificity with a high content of salt components; (3) temperature gradient. The assumed values of the PT- parameters of metamorphism of submarine sulfide ores and the composition of fluids (its salinity) were previously estimated by various methods of mineral thermobarometry and the study of fluid inclusions in minerals (Damdinov et al., 2019). We carried out experiments under these conditions and obtained a high speed of transportation of both ore and silicate minerals.

CONCLUSIONS

1. The possibility of transport of sulfide matter of "black smokers" in collisional conditions of tectonic-magmatic activation of the earth's crust has been shown experimentally.

2. The process of substance transfer requires a combination of certain conditions: (1) temperature gradient; (2) fluids with a sufficiently high salt concentration; (3) relatively high pressures.

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Novikov M.P., Nerkasov A.N., Gorbachev P.N. About zonality of kularite UDC 552.11:553.21:550.89:552.351.2

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Abstract. Kularite-orthophosphate of rare earths of the Ce-subgroup was found in mass quantities in the Kular Ridge in the North-East of Yakutia within the Verkhoyansk fold system of Permian and Triassic black shale deposits enriched in phosphate matter (Nekrasova and Nekrasov, 1982). The very name of the mineral still raises controversial questions, but according to a number of signs it differs markedly from the magmatic monazite of granitoids proper and isostructural with it. In this regard, we will consider some issues related to the composition and distribution of rare earth elements, as well as the nature of the mineral zoning.

Keywords: *kularite, huttonite, solubility, deposit, rare earths, sample, mineral.*

Experimental procedure

For a detailed study of natural material, we selected three types of kularite, differing in color: gray, dark gray, and black. In all cases, kularite is ellipsoid grains no more than 1 mm in size. All samples were studied in detail using a microprobe. Despite the difference in color, the average content of REE oxides (rare-earth elements) of all studied samples is almost the same, or more precisely, is within the error of the method for their determination (see Table 1). Electron-probe microanalysis, including obtaining images of the studied object in secondary and reflected electrons, as well as X-ray spectral local microanalysis, was performed on a digital scanning electron microscope Tescan VEGA TS 5130MM (CamScan MV2300) TPPT equipped with YAG detectors of secondary and reflected electrons and energy dispersive X-ray spectrometer INCA Energy 350 with semiconductor Si(Li) detector INCA PENTAFet x3. Calculations of the results of X-ray spectral microanalysis were performed using The Microanalysis Suite Issue 18d +SP3 (INCA Suite version 4.15) software package. Standards for rare earth elements were previously obtained by us in the form of orthophosphates TRPO₄ (Nekrasova et al., 1985) and, as reference samples for quantitative X-ray spectral analysis, are described in detail in (Lavrent'ev et al., 2011).

Despite the difference in color, the average content of oxides of rare-earth elements in all studied samples (more than 50) is practically the same, more precisely, it is within the error of the method for their determination (Table 1). Note that, in the same separately selected sample, fluctuations in the REE distribution are observed (see Table 2). Most likely, the distribution of rare earths is of a cluster nature. As an example (Fig. 1), the distribution of cerium on one of the sections of the mineral grain is shown.

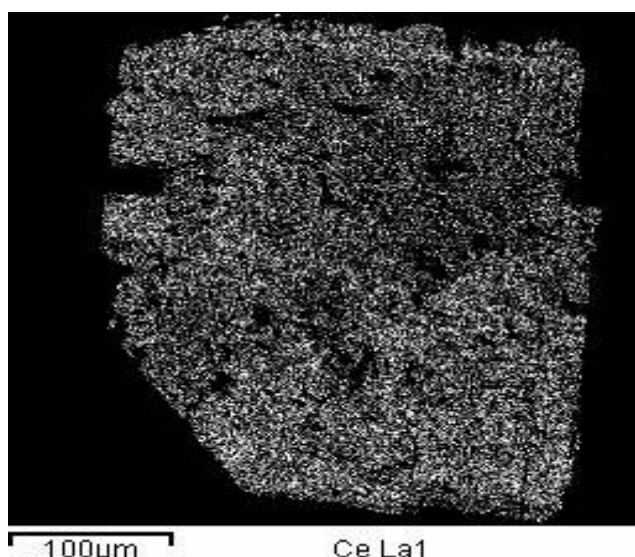


Fig.1. Ce distribution in one of the kularite grains

Table 1. Results of the X-ray spectral analysis of kularite. Average composition of kularite based on 10 measurements and 15 samples.

Oxide	black	dark gray	gray
P ₂ O ₅	30.67	30.61	30.15
La ₂ O ₃	9.08	11.54	6.13
Ce ₂ O ₃	31.37	34.33	27.30
Pr ₂ O ₃	4.07	4.06	4.43
Nd ₂ O ₃	18.30	14.95	21.52
Sm ₂ O ₃	2.67	1.80	3.18
Eu ₂ O ₃	1.01	0.45	0.40
Gd ₂ O ₃	1.89	1.46	1.71
ThO ₂	0	0.18	3.60
UO ₂	0.33	0.19	0
Total	99.39	99.57	98.34

Table 2. Distribution pattern of rare earth oxides in kularites.

Oxide	Content, wt.% Scatter range
La ₂ O ₃	5.55÷18.54
Ce ₂ O ₃	21.68÷35.78
Pr ₂ O ₃	2.39÷4.53
Nd ₂ O ₃	8.32÷24.74
Sm ₂ O ₃	0.23÷7.70
Eu ₂ O ₃	0.40÷1.52
Gd ₂ O ₃	0.48÷3.77
ThO ₂	0.10÷3.60

For the first time, attention was paid to the zonal structure of kularite in the work (Nekrasova, Nekrasov, 1990). It is important to note at Th distribution (Fig. 1) in one of the kularite grains in the kularite samples, where the ThO₂ content is about 4 wt%, there is a direct correlation between Th and SiO₂. This circumstance gives reason to assert that an independent ThSiO₄ phase is formed in the form of

hattonite (Pabst et al., 1951). Thus, the actual microconcretions of kularite are polycrystal. Hattonite crystallizes in a monoclinic system, which makes it easy to enter an identical structure, such as kularite. The unit cell parameters of both minerals practically coincide. So for kularite $a = 6.77 \text{ \AA}$, $b = 7.04 \text{ \AA}$, $c = 6.46 \text{ \AA}$, and for hattonite $a = 6.77 \text{ \AA}$, $b = 6.96 \text{ \AA}$, $c = 6.49 \text{ \AA}$, respectively. The similarity of space groups and parameters of unit cells allows us to speak about the isotopy of these compounds. The same picture is observed in natural monazites with an increased content of thorium, which, regardless of their genesis, also have a zonal structure. Some researchers associate the cluster character in the distribution of rare earths with the crystal chemical factor or explain the zoning of kularite and monazite by a thermodynamic model of different geochemical mobility of lanthanides (Kolonin et al., 2010). However, as will be shown below on the basis of experimental data, these statements are not justified.

The constancy of the composition and the quantitative content of rare earth elements in kularites, monazites and rhabdophanes (Fig. 2.)

indicates their common original source. To prove this statement, a series of experiments on the synthesis of monazite was carried out, where all REEs from La to Gd were initially assigned in equal amounts. Crystallization was carried out from a $K_2Mo_3O_{10}$ solution-melt in air at $T = 1200^\circ C$, as a model of an open magmatic system. In this case, all REEs entered the growing crystal in the same amount (see Table 3).

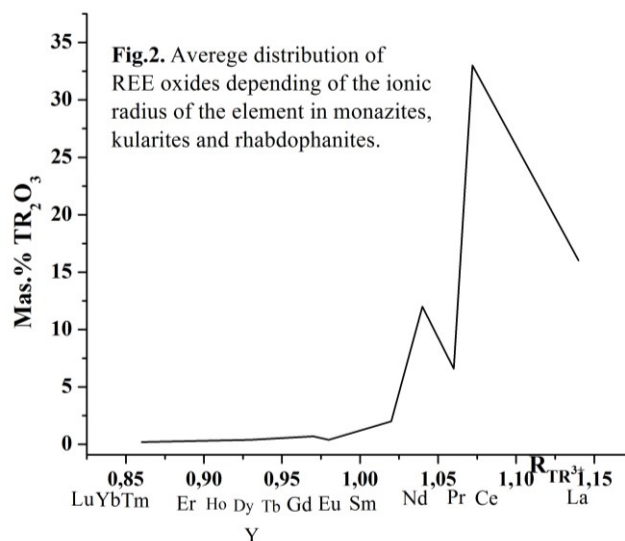


Fig.2. Average distribution of REE oxides depending of the ionic radius of the element in monazites, kularites and rhabdophanites.

We have previously described the isomorphic capacity of rare earth elements in synthetic monazite in detail in our work (Nekrasov and Novikov, 1991). These circumstances confirm the fact that there is a single original natural source for REEs in the above minerals and their obvious clarke content. Thus, the opinion that existed for a long time that the composition of lanthanides in rare earth orthophosphates is controlled to a large extent by the crystal chemical factor, and is also associated with the spatial differentiation of rare earths during their deposition, is unjustified. The zoning of kularite, like that of monazite, is most likely associated with different growth rates of both polycrystalline components of the $TRPO_4$ proper monoclinic phase and hattonite - $ThSiO_4$ also with a monoclinic structure.

Conclusion. Based on the above, we can conclude that the average content of rare earth elements in natural orthophosphates such as rhabdophanite, kularite, and monazite is the same, and therefore confirms the fact about a single original natural source in relation to REE in the above minerals and their obvious clarke content. Thus, the opinion that existed for a long time that the composition of lanthanides in rare earth orthophosphates is controlled to a large extent by the crystal chemical factor, and is also associated with the spatial differentiation of rare earths during their deposition, is unjustified. The zoning of kularite, as well as of monazite, is most likely associated with different growth rates of both components of the

polycrystal of the $TRPO_4$ proper - the monoclinic phase and the hattonite - $ThSiO_4$ with an identical structure.

Table 3: Results of synthetic monazite samples with a set of REE from La to Gd according to RSMA X-ray spectral microanalysis.

Oxide	Initial composition	Found in crystals (average of 10 samples)
La_2O_3	10.0	10.12
Ce_2O_3	10.0	10.15
Pr_2O_3	10.0	9.13
Nd_2O_3	10.0	10.22
Sm_2O_3	10.0	10.00
Eu_2O_3	10.0	10.90
Gd_2O_3	10.0	10.87
P_2O_3	30.0	29.52
Total	100	100.91

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