

Engineering of experiment

Molchanov V.P. Development of a method for extracting titanium dioxide with ammonium sulfate from ilmenite ores and placers of the Ariadne intrusion of ultrabasites (Primorye).

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Abstract. A new promising type of complex titanium-bearing ores and placers associated with ultramafic intrusions has been discovered in the south of the Far East. The possibilities of extracting titanium from ilmenite concentrate using ammonium sulfate are considered. It has been established that the reactions of the main components of the concentrate with $(\text{NH}_4)_2\text{SO}_4$ begin when the thermal decomposition temperature of $(\text{NH}_4)_2\text{SO}_4$ (300-360°C) is reached and proceed with the formation of a mixture of double salts readily soluble in water - ammonium sulfate and iron of the compositions $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_3$ and $\text{NH}_4\text{Fe}(\text{SO}_4)_2$ and ammonium sulfate and titanyl of composition $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2$. It is shown that an increase in the interaction temperature above 400°C leads to thermal decomposition of the resulting double salts to sulfates and then oxides. The experience gained in the deep processing of ilmenite mineral raw materials will help to more easily outline the ways for the development of Far Eastern titanium deposits in compliance with the principles of rational nature management and environmental protection.

Keywords: Primorye, ultrabasites, ilmenite ores and placers, titanium, processing technology, ammonium sulfate.

In the south of the Russian Far East, within the Sikhote-Alin orogenic belt, with the participation of the authors (Khanchuk et al., 2020; Molchanov et al., 2020), a new promising type of ore-placer manifestations of complex mineralization has been identified, in which strategically important metals (Ti and Au) act as the main industrial components, and a wide range of high-tech elements (V, Nb, Nd, Co, Hf, Ce, Y) – as passing ones. The presence of acutely deficient types of solid minerals in ores and placers indicates the need to create a concept for the industrial development of these objects based on the principles of rational nature management and environmental safety, which predetermined the direction of our research. The possibilities of processing their main industrial mineral – ilmenite using pyro-hydrometallurgy methods have been studied using the example of placers of the Ariadne junction (the central part of the Primorsky Territory).

Ilmenite is a source of titanium dioxide, one of the most popular titanium-containing products on the world market. (U.S. Geological Survey, 2018). It is a mineral species of variable composition FeTiO_3 , where Fe^{2+} can be isomorphically replaced by Mg^{2+}

and Mn^{2+} (Donohue P.H. et al., 2012). The stoichiometric composition of ilmenite is characterized by the presence of Ti (31,6 wt. %), or in terms of oxygen 52,6 % TiO_2 . The Ariadne Ilmenites are characterized by (mas. %) rather close to the stoichiometry of the content of TiO_2 (49,5), relatively high concentrations of V_2O_5 (1,8), moderate magnesia (1,5), insignificant limited impurities of SiO_2 (1,02) and Cr (0,2), as well as a specific set of trace elements (up to 800 g/t) Nb, Nd, Co, Si.

Two methods are widely used in industry to produce titanium dioxide – chloride and sulfuric acid. Chloride includes primary chlorination of titanium-containing raw materials, heat treatment of the resulting titanium tetrachloride with the formation of free chlorine and titanium dioxide and subsequent multi-stage surface treatment of the latter. The sulfuric acid method consists in the decomposition of titanium-containing raw materials with sulfuric acid to form soluble titanium sulfates and their subsequent processing into titanium dioxide. The whole process takes place in the liquid phase at a temperature of 110-120 °C. The use of these technologies is associated with significant environmental pollution due to the appearance of free chlorine in the first case in the technological scheme, and in the second - the formation of significant volumes of sulfate wastewater (Baibekov M.K. et al., 1980; Gerasimova L.G. et al., 2015; Achimovicova M. et al., 2014; Zhang W. et al., 2011).

To solve this problem, quite a lot of pyrohydrometallurgical methods of technological conversion have been developed (Zhang Y., 2014; Pashnina E.V. et al., 2017). In the case of the Ariadne dressing material, we previously used the most environmentally safe, but at the same time quite simple and effective method of opening ilmenite with ammonium sulfate when heated in the range of 360-400°C (Molchanov V.P. et al., 2020; Medkov M.A. et al., 2020). The objectives of this study included the study of the possibilities of firing ilmenites, according to experimental data (Vodopyanov A.G. et al., 2015; Valiev H.R. et al., 2018; Garcia-Valverde M.T. et al., 2014; Rajakumar G. et al., 2012; Santhoshkumar T. et al., 2014; Jalill A. et al., 2016; Subhapiya S. et al., 2018; Su H., et al., 2016), at temperatures from 300 to 360 °C.

The selected large-volume sample of the initial concentrates (up to 2.5 tons) was divided using gravity and electromagnetic separation methods into magnetic (up to 93% of the total mass) and non-magnetic (7%) concentrates. The first of them is almost completely represented by ilmenite, the

second includes the bulk of the associated components. For effective opening, a sample of ilmenite concentrate (2,7 kg/l) was mixed with ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$. Attachments with a mixture of ilmenite concentrate and ammonium sulfate weighing 10-40 g in glass-carbon crucibles with a lid were placed in a muffle furnace controller from Nabertherm GmbH (Germany) and heated at a rate of 2,5 degrees /min to a predetermined temperature. The changes occurring with the substance during heating were controlled by the decrease in the mass of the initial mixture, as well as using the X-ray phase analysis method. X-ray images of the samples were taken on an automatic D-8 ADVANCE diffractometer with sample rotation in $\text{CuK}\alpha$ radiation. X-ray phase analysis was performed using the EVA search program with a PDF-2 powder data bank.

The leaching process of the ilmenite concentrate treated with ammonium sulfate was carried out at room temperature by dissolving the resulting product in water for 15-30 minutes and then filtering through a blue ribbon filter. The content of elements in the obtained filtrates was determined by atomic absorption analysis on a Solaar 6 M spectrometer along the analytical lines of the elements-components of the concentrate. Thermogravimetric studies were performed on a Q-1500 derivatograph in an open platinum crucible in air at a heating rate of 5 deg/min and a suspension of 100-200 mg.

During the experiment, chemical treatment of ilmenite concentrate with ammonium sulfate was carried out using a 10% excess $(\text{NH}_4)_2\text{SO}_4$. The concentrate weights were 10-40 g. The resulting charge was heated to a temperature of 360 °C and kept at this temperature for up to 4-4,5 hours. An increase in the duration of exposure (up to 5-6 hours) did not significantly affect the composition of the resulting product, only the phase ratio and the appearance of the sample changed: an increase in the duration of heating made it possible to obtain a loose sample. After heat treatment, the concentrate was a homogeneous bulk product of a lilac color and, according to X-ray phase analysis, contained a mixture of mainly $\text{NH}_4\text{Fe}(\text{SO}_4)_2$, $(\text{NH}_4)_2\text{Fe}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2$. The color of the resulting product is most likely due to the appearance of crystallohydrates of double iron salt, colored from light green to light purple shades, due to air cooling.

An increase in the interaction temperature above 400°C was accompanied by the decomposition of the formed double ammonium sulfates with titanium and iron. So, on the radiograph of the product obtained by heating the charge above 400°C, in addition to the reflexes of double salts, the reflexes of TiOSO_4 also appeared, and on the radiograph of the product

obtained by heating the charge to 480 °C, the reflexes of the double salt of ammonium sulfate and titanium were absent. The titanium product was presented only by TiOSO_4 , which allows the endothermic effect to be attributed to the process of thermal decomposition of the double salt of ammonium sulfate and titanium to titanium sulfate. A further increase in temperature was accompanied by the decomposition of the double salt of ammonium and iron to iron sulfate, and titanium sulfate to TiO_2 . Thus, heating a mixture of ilmenite concentrate with ammonium sulfate to a temperature of 580°C and holding at this temperature for 2 hours led to the formation of a product containing a mixture of mainly two phases: TiO_2 in the form of anatase and FeSO_4 with a small admixture of quartz present in the concentrate under study and not reacting with $(\text{NH}_4)_2\text{SO}_4$. The resulting product was a loose substance of light gray color. In some cases, inclusions of red powder were observed on the surface of the resulting product. According to X-ray phase analysis, this product was hematite Fe_2O_3 , which is formed by the interaction of FeSO_4 with air oxygen under conditions of a decrease in the reducing atmosphere with a decrease in the intensity of ammonia release at the final stage of thermal decomposition of double salts and ammonium sulfate. The addition of $(\text{NH}_4)_2\text{SO}_4$ made it possible to convert the Fe_2O_3 oxide formed on the surface back into double ammonium and iron sulfate at a temperature of 360°C. A further increase in the processing temperature of ilmenite concentrate with ammonium sulfate to 850-900 °C led to the formation of iron and titanium oxides. At the same time, titanium dioxide precipitated in the form of an acid-insoluble rutile form.

Thus, the interaction of Ariadne ilmenite concentrate with ammonium sulfate occurred in the temperature range of 300-360°C and was accompanied by the destruction of the structure of ilmenite and the formation of a mixture of well-soluble in water double ammonium and iron sulfates, as well as double ammonium sulfate and titanium. During water leaching, the product of the interaction of ilmenite concentrate with ammonium sulfate almost completely passed into solution, only a little dark sediment remained at the bottom. According to X-ray phase analysis, this dark precipitate was a mixture of iron oxides Fe_2O_3 and FeOOH . The aqueous leaching solution had an acidic reaction with a pH of ≈ 2 . The content of elements in the resulting filtrate was determined by atomic absorption analysis. At the same time, it was found that the aqueous leaching of the product of the interaction of ilmenite concentrate with $(\text{NH}_4)_2\text{SO}_4$ at a temperature of 360 °C made it possible to transfer almost all

titanium and the bulk of iron into solution. With a slight heating (up to 50–60 °C), the resulting solution became cloudy and a white precipitate formed. X-ray phase analysis of the resulting sediment indicated the course of the process of thermo-hydrolysis of titanium salt with the formation of titanium dioxide in the form of anatase. With a slight acidification of the leaching solution (when the pH of the solution was brought from 2 to 1 with a solution of H₂SO₄), the crystallization of titanium dioxide proceeded faster, the precipitate was easily separated by filtration through a blue ribbon filter. This method allows you to completely isolate titanium from the leaching solution. The resulting filtrate, evaporated to dry salts, is, according to X-ray phase analysis, a mixture of only two phases - NH₄Fe(SO₄)₂ and NH₄H₂SO₄.

As a result of the work carried out, the fundamentals of the processing technology of the main placer-forming mineral of the Ariadne node - ilmenite were established. It is shown that the interaction of ilmenite concentrate with ammonium sulfate begins when the temperature of thermal decomposition (NH₄)₂SO₄ reaches 300 °C and proceeds up to 360 °C with the formation of a mixture of double salts – ammonium sulfate and iron compositions (NH₄)₂Fe₂(SO₄)₃ and NH₄Fe(SO₄)₂, as well as ammonium sulfate and titanyl composition (NH₄)₂TiO(SO₄)₂. The aqueous leaching of the product of the interaction of ilmenite concentrate with (NH₄)₂SO₄ makes it possible to transfer almost all titanium into solution.

The proposed technical solutions for the extraction of titanium dioxide in compliance with the principles of rational nature management and environmental safety are only the first step in the development of ilmenite placers in the south of the Russian Far East. It is obvious that further research needs to be carried out in the direction of deepening the degree of processing of gold-titanium-bearing sands, which will reduce the cost of obtaining individual products and ensure higher production efficiency.

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Zinovieva N.G.¹, Shchekina T.I.¹, Rusak A.A.², Khvostikov V.A.³, Kotelnikov A.R.⁴, Bychkov A.Y.¹, Alferyeva Y. O.¹ Experience in applying several types of substance analysis in studies silicate and fluoride phases in the system Si-Al-Na-K-Li-F-O-H containing rare earth elements. UDC: 552.11

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Abstract. Diagnostics, study of the phases composition formed in the model granite system Si-Al-Na-K-Li-F-O-H, and the distribution of REE between them required the application of several analytical methods. Energy-dispersive microanalysis (SEM: Jeol JSM-6480LV + EDS: Oxford X-MaxN) was used to determine the content of rock-forming elements, fluorine, and oxygen; analysis of REE, yttrium, and scandium was performed on a Superprobe JXA-8230 electron probe microanalyzer. Due to the need to determine the content of lithium in silicate and fluoride phases, as well as the fact that the concentration of REE in some phases was very low, it was necessary to use mass spectrometry methods. In a number of cases, the experimental material was transferred into solution and studied on an Element-2 mass spectrometer of the Department of Geochemistry, Moscow State University. Polished samples were studied using the local laser ablation method at the Institute for Microelectronics Technology and High-Purity Materials of the Russian Academy of Sciences. The paper compares and discusses the results obtained by various analytical methods at different shooting parameters, and offers

recommendations for their use to solve experimental problems.

Keywords: scanning electron microscopy, electron probe microanalysis, mass spectrometry, laser ablation, aluminosilicate and aluminofluoride melts, residual salt melts, fluorine, lithium, rare earth elements

The study of phase relationships in the model granite system Si-Al-Na-K-Li-F-O-H required the use of several analytical methods due to the need to determine the composition of a large set of phases formed in a wide range of physico-chemical parameters from 1250 to 400°C and pressures 1-5 kbar. The phases were represented by aluminosilicate and salt aluminofluoride melts formed at temperatures (700 - 1250°C), their crystallization products at lower temperatures, up to 400°C, and fluid. The complexity of studying the composition of the phases was that they contained the entire range of rare earth elements and lithium. To determine their contents, it was necessary to involve not only the methods of electron microanalysis, but also mass spectrometry. The phase composition of the system and the contents of rock-forming elements, fluorine, and oxygen were determined using a Jeol JSM-6480LV scanning electron microscope (Jeol, Japan) with an Oxford X-MaxN energy-dispersive spectrometer (Oxford Instrument Ltd., UK) at an accelerating voltage of 20 kV and current 0.7nA. The glasses were analyzed over an area of at least (7.5 x 7.0 µm) to avoid the migration of alkaline elements. With such parameters, the accuracy of estimating the content of the main elements was 2-5 rel.%, and the error in measuring fluorine was ±1 rel.%.

To determine the content of REE, Y, and Sc, glasses (quenched silicate melts) and salt phases were additionally analyzed on a Superprobe JXA-8230 electron probe microanalyzer (Jeol, Japan) in the Laboratory of High Spatial Resolution Analytical Techniques for studying matter of the Department of Petrology and Volcanology, Faculty of Geology, Moscow State University. To prevent the migration of alkalis, the analyzes were carried out in the defocused beam mode (up to 10 µm) at an accelerating voltage of 15 kV and a current of 10 nA. Standards and studied samples were taken under the same conditions. The position of the characteristic X-ray peaks in the standards and samples was determined as a result of preliminary detailed scanning of the ranges of interest. For the main elements, the pulse accumulation time at the peak was 30 s, against the background, 15 s. Under these conditions, the dispersion value in the measurement of Si, Al and O did not exceed 0.8 rel.%, K - 1.5 rel.%, Na - 2 rel.%, F - 2 rel.%. For small elements, the measurement time for the intensity of the peak and background (peak/background) was selected

depending on the concentration of the element in order to ensure its detection limit of no more than 0.01 wt.%. To avoid underestimation of the REE content, the samples were additionally analyzed at an accelerating voltage of 25 kV and a current of 50 nA.

The complexity of determining REE elements by electron probe microanalysis is associated with the superposition of their X-ray spectral lines not only in energy-dispersive, but also in crystal-diffraction microanalysis. To solve this problem, a series of experiments was set up in which the ratio of the main elements was kept the same, and the combination of REE elements was set in such a way that their sequence lines did not overlap. For each temperature, five experiments were carried out with the same ratio of the main elements and a different set of REE - (Y + La), (Sc + Gd), (Nd + Tm), (Ce + Eu + Ho) and (Dy). The survey parameters F, Na, Al, Si and K, in cases where their lines overlapped with the serial lines of REE elements, were selected in such a way as to cut off the overlap of the Dy-Mb (2) and Y-Lb1,3,4 serial lines, 6 (3) on the F-K α peak; order lines Y-Lb3 (2) on the Na-Ka1,2 peak; sequence lines Sc-Kb1.3 (3) and Sc-Kb5 (3) to the Al-Ka1.2 peak; order lines Nd-La1 (3) and Nd-La2 (3) peak Si-

Ka1,2 and order lines Nd-Lg1 (2) peak K-Ka1,2. This helped to avoid overestimation of the content of F, Na, Al, Si, and K in the corresponding experiments.

The table 1 lists the analyzes of glasses performed by both the energy dispersive and crystal diffraction methods. It can be seen that both methods for the main rock-forming elements give well comparable results. The situation with the analysis of residual alkali-aluminum fluoride salt melts enriched in rare earth elements is more complicated. And, if the results of the crystallization of aluminosilicate melts can be analyzed both by the energy-dispersive and crystal-diffraction methods, then only the crystal-diffraction method is suitable for the analysis of salt melts with rare earth elements, since in the energy-dispersive analysis, X-ray lines of rare earth elements overlap each other. Unfortunately, the crystal-diffraction analysis of rare earths cannot avoid superposition of their X-ray spectrum lines. This fact forced us to set up five experiments for each temperature with the same ratio of the main elements and a different set of REE, the spectra of which do not overlap.

Table 1. Average compositions of aluminosilicate glasses (in wt. % of elements) obtained at 500°C and 600°C, analyzed on energy dispersive (EDS: Jeol JSM-6480LV with Oxford X-MaxN EDS spectrometer) and crystal diffraction (WDS: Superprobe JXA) -8230) spectrometers.

Elements	T=500°C				T=600°C			
	WDS		EDS		WDS		EDS	
	Aver(10)	Sd	Aver(18)	Sd	Aver (20)	Sd	Aver(21)	Sd
Si	28,60	3,62	29,70	1,32	29,97	1,11	29,61	1,00
Al	7,38	0,27	7,25	0,32	6,88	0,35	7,05	0,36
Na	1,37	0,32	1,95	0,52	1,39	0,23	1,69	0,27
K	6,10	0,59	7,31	0,30	7,09	0,80	7,09	1,13
Li*	3,54	3,26	h.o.	h.o.	3,11	1,72	h.o.	h.o.
F	6,15	0,48	6,45**	0,49	6,48	0,58	7,06	0,88
O	46,84	1,54	46,61	3,72	44,96	1,56	45,67	0,64
Total	99,98		99,28		99,88		98,18	

* the Li contents given in the WDS analyzes were calculated from the deficit of the sum; ** if we include data on the F content in glasses for experiments with Ce, Eu, and Ho, then the F content will be overestimated. This is understandable, since the Ce-MZ line energy is superimposed on F-Ka in the EDS analysis, which leads to F content. Therefore, the data on the F content for experiments with Ce, Eu, and Ho were excluded from the averaging.

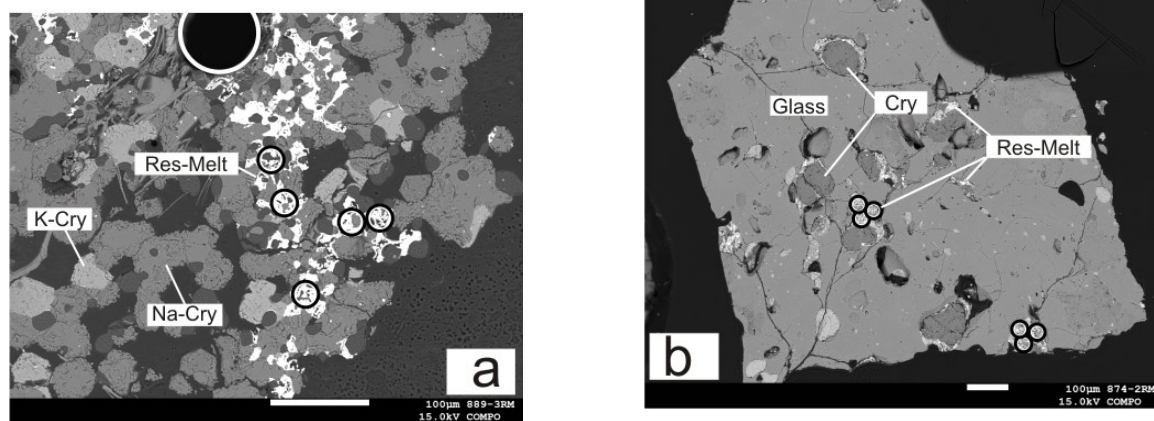


Fig.1. The relationship of the phases obtained as a result of the melting of the Si-Al-Na-K-Li-F-O-H system at $T=800^{\circ}\text{C}$ and their subsequent crystallization at 500°C (a) and 600°C (b). Images in the back-scattered electron mode (Res-Melt - residual melt, Cry - cryolites (rich in K or Na), Glass - glass)

The experiments were carried out as follows: the ampoule with the initial charge was heated to 800°C and held for 3 days, while the system was separated into 2 melts - aluminosilicate and alkaline aluminofluoride. Then the ampoule was cooled to lower temperatures, crystallization from both silicate and salt melts took place in the system. In salt melts, aluminum fluorides crystallized and a residual salt melt enriched in REE was formed. It still remained in the form of a liquid phase, the quenching products of which we were able to analyze, at 600°C and 500°C .

Figure 1a shows the segregation of the residual alkaline-rare-earth salt melt (composed mainly of white REE phases in BSE), which occupies an interstitial position with respect to the already crystallized part of the salt melt globule, composed of crystals of the KNa- and NaK-cryolite-like phase. The circles show areas of the quenched residual alkali-rare-earth melt, analyzed by a beam defocused to $10\ \mu\text{m}$, and in the upper part of the photograph one can see a trace (a black area in a white circle, about $100\ \mu\text{m}$ in diameter) left by the laser beam. Figure 1b clearly shows the stage of separating into silicate and saline alkaline-rare-earth melts, followed by crystallization of alkaline aluminum fluorides in salt melt globules and the formation of a residual essentially rare-earth melt.

Methods of X-ray spectral analysis, both energy-dispersive and crystal-diffraction, do not allow one to analyze Li. With crystal diffraction analysis, it is possible to estimate the Li content only from the deficit of the sum. The determination of lithium content in silicate and fluoride phases became possible using the local method of laser ablation in polished samples. This method also makes it possible to locally determine the contents of rare earth elements in quenched silicate (with a beam diameter of $100\ \mu\text{m}$) and salt melts (with a beam diameter of

$20\text{--}50\ \mu\text{m}$) in those experiments in which almost all REE, Y, and Sc were introduced into the initial composition.

The studies were carried out at the analytical certification testing center of the Institute for Problems of Microelectronics Technology and High-Purity Materials of the Russian Academy of Sciences. The measurements were carried out on an X Series II inductively coupled plasma quadrupole mass spectrometer (Thermo Scientific, USA) with an UP266 MACRO laser ablation attachment (New Wave Research, USA) with the following operating parameters: mass spectrometer - RF generator output power 1200 W, the flow rate of the plasma-forming flow of argon is 13 l/min, the auxiliary flow is 0.90 l/min, the flow rate of the carrier gas is 0.6 l/min, followed by mixing with Ar 0.6 l/min, the resolution is 0.4M and 0.8M; attachment for laser ablation - laser wavelength 266 nm, pulse repetition rate 10 Hz, pulse energy 3 mJ, pulse duration 4 ns, crater diameter $60\ \mu\text{m}$. The time of one measurement was 10 s. External calibration was performed using NIST SRM-610 ÷ 616 silicate glass standard samples. Silicon was used as an internal standard.

The use of the laser ablation method made it possible to determine the contents of Li and REE in all phases. However, we had to face the difficulty of interpreting some data in cases where the size of the analyzed phase with REE was less than $20\ \mu\text{m}$ (beam diameter). In this case, the capture of nearby phases occurred, resulting in underestimated REE concentrations.

To study the bulk composition of silicate and salt quenched melts and quench fluid containing Li, REE, Y, and Sc, mass spectrometry was applied using the Element-2 instrument of the Department of Geochemistry, Faculty of Geology, Moscow State University.

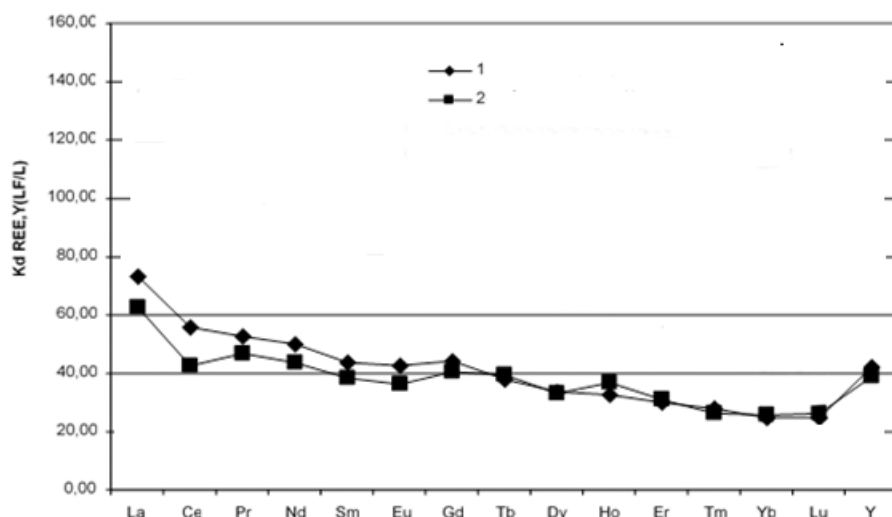


Fig.2. Comparison of REE and Y separation factors between saline LF and silicate L melts (K_d (LF/L) at 800°C, 1 kbar: 1- ICP MS from solution, 2 - La-ICP MS La-ablation

The measurements were carried out on an Element-2 inductively coupled plasma ionization mass spectrometer with double focusing. Ion detection is performed by an electron multiplier that maintains linearity in the range of $1 \dots 1 \cdot 10^{10}$ ions per second. To calculate the concentrations of elements, we used a series of calibration solutions with concentrations of 0.03 ng/g, 0.3 ng/g, 3 ng/g, and 10 ng/g, prepared from a standard 68-element solution ICP-MS-68A, HPS (A and B). The detection limits for elements ranged from 0.01 ng/g for heavy and medium-weight elements, increasing to 1 ng/g for light elements. The measurement error was 1–3 rel.%. This method, the only one possible for studying the composition of quenched fluid in experiments, was widely used to analyze glass and homogeneous salt globules obtained at high temperatures of 1000-700°C. Good agreement (convergence) of the results of both ICP MS methods is demonstrated in the graph (Fig. 2). However, the last mentioned method is not applicable to the analysis of inhomogeneous phases or multi-phase objects, such as our salt, partially crystallized globules.

Comparing the results of the REE analysis obtained by the above methods, it can be seen that with some difference in absolute values, the distribution coefficients are comparable. This indicates the need to combine different methods of substance analysis in the study of silicate and fluoride phases in the Si-Al-Na-K-Li-F-O-H system containing rare earth elements.

Conclusions

1. Due to the use of four analytical methods in the study of the silicate-salt granite system with rare elements (Li, REE) and fluorine, it became possible to comprehensively study the composition of all

phases - aluminosilicate, salt and fluid, formed at various P-T parameters during the experiment.

2. Methods of electron probe microanalysis, both energy-dispersive and crystal-diffraction, are absolutely necessary for all petrological, including experimental studies, since they allow diagnosing phases and determining their composition in relation to petrogenic and volatile components (F, Cl) and oxygen. They give good data convergence, but have different capabilities.

3. The method of energy-dispersive analysis makes it possible to obtain both analyzes at a “point” and bulk compositions of phases, but, unlike crystal diffraction analysis, it does not allow analyzing rare-earth elements of the entire series and estimating the Li content even approximately (by the deficit of).

4. It is shown that the absolute values of the content of Li, REE, Y, Sc in quenched silicate and fluoride melts, obtained on mass spectrometers with an attachment for laser ablation and from solutions, as well as the partition coefficients of lithium and rare earth elements between the phases, are close or comparable quantities.

5. The differences between these methods are as follows: the La-ablation method, being local, can be applied to solid phases in polished samples, but only the ICP MS method (from solution) can be used in the analysis of trace amounts of elements contained in fluid or liquid phases.

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