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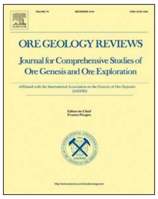

Review

Physicochemical conditions of formation of hydrothermal titanium mineralization on the Murunskiy alkaline massif, western Aldan (Russia)

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ABSTRACT

The unique Aldan ore-magmatic province in Yakutia is characterized by Mesozoic alkaline magmatism and related ore deposits (Cu-Au porphyry, gold-quartz vein and gold-brannerite). The Murunskiy alkaline massif occurs in the western part of this province.

This massif includes the world's largest volcanic-plutonic complex of potassium-alkaline rocks and has no analogs in the world. High agpaitic indexes are common for all magmatic rocks of the massif. Moreover, the massif is well known for its unique Ba-Sr carbonatite and charoite rocks. We have studied the fluid regime of a post-magmatic formation of rutile and anatase-brookite quartz veins with pyrite, galena, sphalerite, chalcopyrite, native gold and the titanium mineralization. Fluid inclusions study shows that the titanium mineralization was formed at the temperature range of 475–440 °C and pressure between 150 and 125 MPa from heterogeneous chloride-carbonate-sulfate fluid. The immiscible fluid fractions were represented by gaseous phase, low- and middle-concentrated solutions, as well as highly concentrated salt brine. Mineral-forming fluids were characterized by high redox-potential, due to the high concentration of sulfates. The immiscible fluid fractions differ in the content of ore elements. Highly concentrated fluid fractions contain increased concentrations of S, Cu, Mo, Fe, Pb, Zn, U, and Au, and low-concentrated fluid fractions containing U, Th, As, and Au.

1. Introduction

Titanium mineralization represented by anatase, brookite and rutile crystals in hydrothermal quartz veins occurs only at the Murunskiy massif. In these veins vanadium, uranium and thorium minerals, sulfides and native gold are common. Studying the fluid regime of the hydrothermal ore formation at the Murunskiy massif is one of the important problems in revealing the factors governing the ore-bearing potential of alkaline massifs.

The Murunskiy massif consists of compositionally diverse alkaline rocks: from alkaline ultramafic rocks to alkaline granites with all intermediate varieties included (Vladykin, 2009). The study of melt inclusions in the minerals of olivine-monticellite rocks from the Murunskiy massif revealed the carbonate–silicate liquid immiscibility at the high-temperature magmatic stage (1280–1260 °C). In addition, melt inclusions demonstrate the evolutionary pathways of parental alkaline-ultramafic magmas from silicate melts to carbonate-sulfate-phosphate salt melt fractions (Panina and Motorina, 2008). The further evolution of salt and silicate-salt magmatic melts generated by parental alkaline magmas might have led to the generation of metal-bearing hydrothermal fluids, which could take part in the formation of post-magmatic and hydrothermal ore deposits associated with alkaline magmatism (Bilibina et al., 1963; Maximov et al., 2010; Borisenko et al., 2011). Physicochemical parameters and the metal-bearing potential of fluids generated during the formation of K-alkaline massifs can be obtained by studying the fluid regime of various postmagmatic mineralization in the Murunskiy alkaline massif, including quartz veins with REE-titanium and sulfide mineralization.

2. A brief geological outline

2.1. Geology of Murunskiy massif

The Murunskiy massif is located to the west of Aldan (northeast of the Irkutsk region), which borders Yakutia (Fig. 1). It consists of two large outcrops of Mesozoic alkaline rocks, known as Big Murun and Small Murun massifs. A relatively small alkaline granite massif – Kedroviy stock located to the southeast of these large massifs, also belongs

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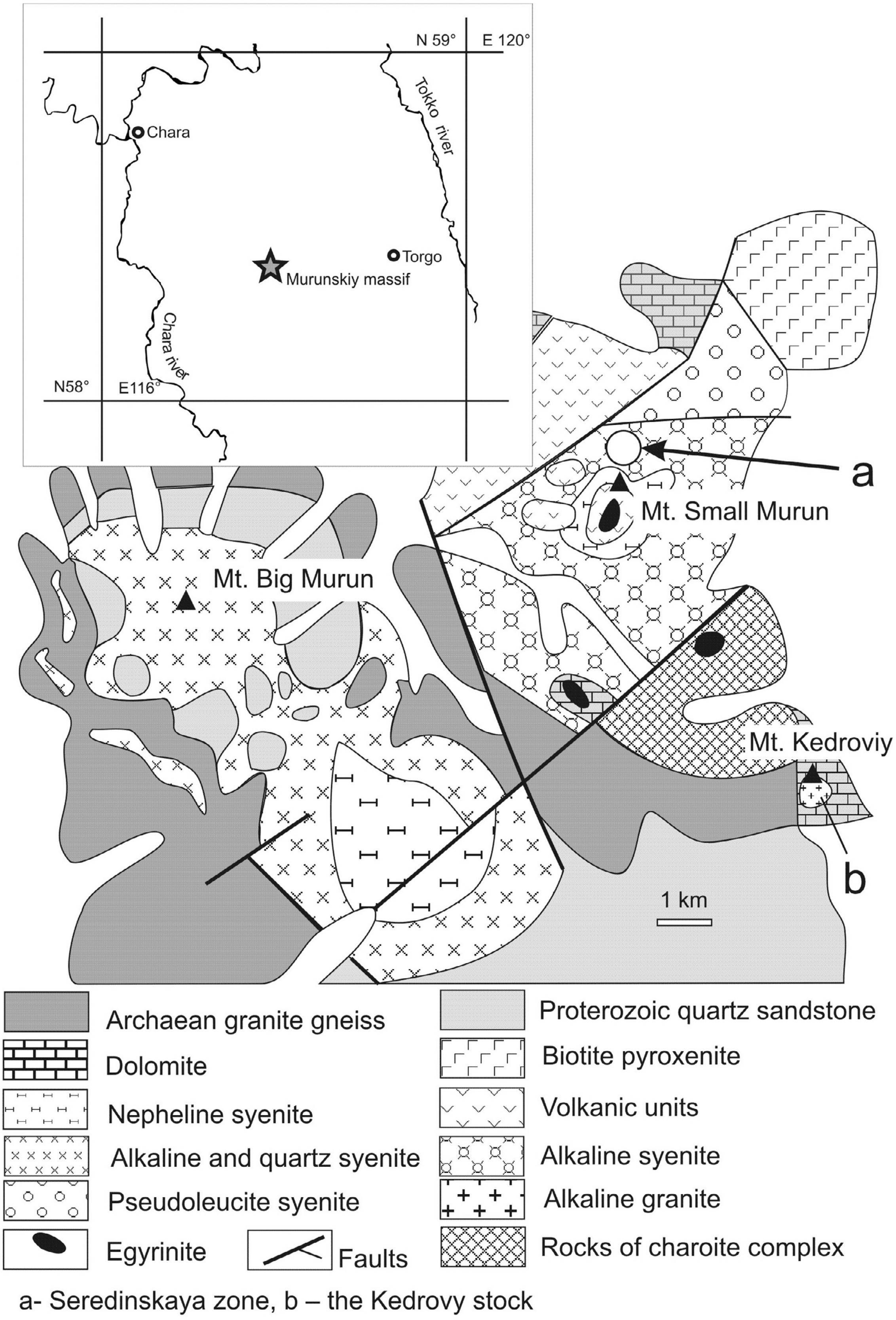

Fig. 1. Simplified geology of the Murunskiy alkaline massif Vladykin (2009).

to the magmatic rocks of the Murunskiy massif. The total outcrop area of alkaline rocks is about 150 km^2. The age of the massif was previously reported as 145 Ma (Vladykin, 2009). The geochemical and isotopic data suggest a deep-seated EM-1 source for the Murunskiy massif (Vladykin, 2009). The following model of the magmatic system was proposed for this massif (Vladykin, 2009):

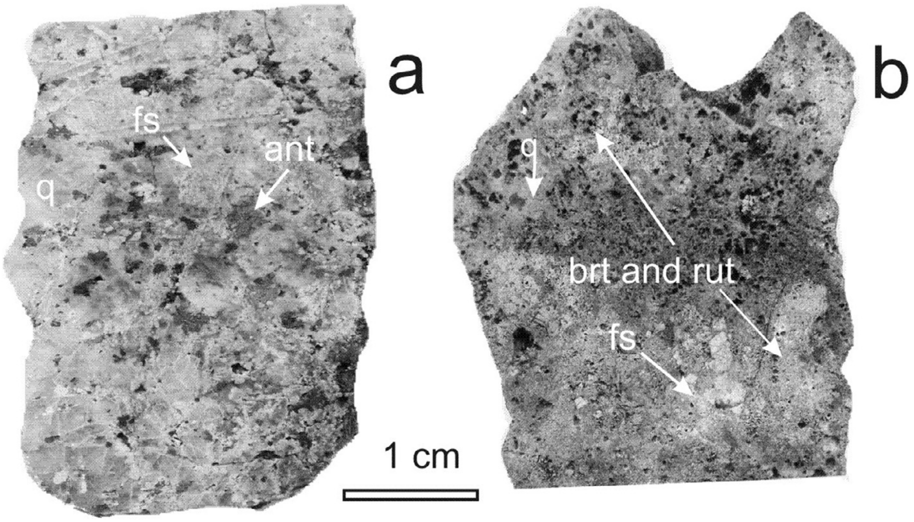

Fig. 2. Samples of REE-Ti veins. (a) The Kedroviy stock and the; (b) according to Small Murun massif (Seredinskaya zone). q – quartz, fs – microcline, ant – annatase, brt – brookite, rut rutile.

(1) Early intrusion phase includes the layered complex consisting of biotite-pyroxenites, K-ijolites, olivine lamproites, feldspar-schonkinites, leucitic shonkinites. Xenoliths of cumulative olivine-spinel and olivine-pyroxene-monticellite-micaceous rocks are also found.
(2) Main stage comprises horizontally layered complex of diverse pseudoleucitic, feldspar-calcilitic, biotite-piroxene potassium feldspar syenites. Quartz syenites, dikes and stocks of alkaline granites were intruded at the late stages of crystallization of the layered rock complex.
(3) Volcanic stage consists of layered flow of leucitic melaphonolites, leucitic lamproites, sometimes with tuff-lavas and tuff-breccias. The dike complex of this phase is formed by leucitic tinguaites, richterite-sanidine lamproites, trachyte-porphyries, syenite-porphyries and eudialyte lujavrites.
(4) Late stage includes the layered complex of potassium silicate-carbonate rocks of the following composition: (a) prevailing K-feldspar (white fine-grained rocks composed of K-feldspar with insignificant amount of pyroxene and tinaksite); (b) quartz-calcite-pyroxene-microcline with calcite content varying from 5 to 20%; (c) pyroxene-K-feldspar showing wide variations of both components; (d) benstonite, calcite and quartz-calcite carbonatites; (e) silicate charoite rocks. All the above rocks are subject to intensive hydrothermal alteration through tectonic zones and fractures. The hydrothermal processes result in sulfide alteration and silicification of rocks.

There are other interpretations of the magmatic rock sequence of the Murunkiy massif. The variations between those reflect the researcher's opinion on the conditions of the magmatic melt differentiation. The inconsistency in systematics of alkaline igneous rocks and the role of magmatic and hydrothermal metasomatic processes in the formation of certain rock types also result in different in magmatic models, especially for the final stages of the massif formation (Konev et al., 1996). In particular, the magmatic or metasomatic genesis of the complex of carbonatite and charoite rocks is still under discussions (Rogova, 1980; Bullach, 1984; Vorobyev et al., 1984; Biryukov and Berdnikov, 1992; Konev et al., 1996; Vorobyev, 2008).

Most hydrothermal veins within Murunskiy massif are not well studied, because of the limited outcrops and difficult access to the area. Quartz veins with titanium and sulfide mineralization are traced as quartz fragments in eluvial and colluvial deposits. As outcrops, they are exposed on surface of open excavations and in rare exploration trenches. Quartz veins with brookite and rutile at the Small Murun massif (Seredinskaya zone) are 30 m thick and up to 1 km long. Quartz-sulfide veins with brookite and rutile are common for the area, while quartz-anatase and galena-sphalerite veins with fluorite are found less often. For all types of veins, the hosting rocks are alkaline syenite. The content of titanium in veins ranges from 5 to 30 wt%, but it is uneven, so the economical value of titanium mineralization is not clear. However, unique brookite and anatase crystals found in quartz geodes make these veins mineralogically interesting. In addition to titanium, uranium and thorium mineralization has been found close to the breccia in a fault zones to the south from Small Murun massif. Moreover, large sulfide ore body is located at the contact of the dolomite with syenite of the main phase to the north of the charoite deposit (Fig. 1). It contains massive ore composed of galena, sphalerite, chalcopyrite and pyrite with insignificant amount of pyroxene and microcline. Veins with quartz, smoky quartz, barite, carbonates and manganese oxides are also common. Similar mineralization was found at the Kedroviy stock: quartz veins with anatase and brookite are about 20 m wide and 500 m long.

2.2. Titanium mineralization

Several samples of quartz veins with titanium mineralization from Small Murun massif (Seredinskaya zone) and from Kedroviy stock were investigated. The samples from Kedroviy stock are represented by the massive grey quartz containing pinkish K-feldspar, brown pseudomorphs of iron hydroxides after pyrite, dark blue anatase and black brookite (Fig. 2 a). In these veins, the titanium mineralization is confined to interstitial cavities or cracks. Rare inclusions of sulfides (pyrite, chalcopyrite, and galena) are observed in the vein quartz and anatase crystals.

Quartz veins with sulfide and titanium mineralization from the Small Murun massif are strongly oxidized and consist of spongy quartz aggregate with numerous cavities formed by the leaching of pyrite (Fig. 2b). The titanium mineralization is represented by large rutile crystals and fine disseminated grains of brookite and anatase. There are two morphological types of the vein quartz: the smoky crystal quartz colored in brown and the aggregate of fine-grained quartz grains (Fig. 3). Numerous leaching cavities remaining from the large crystals of cubic pyrite are observed in the fine-grained aggregate of quartz. The cavities are filled with collomorphic jarosite as the pseudomorph after pyrite. Investigations of the fine-grained quartz aggregate under the reflected light reveal disseminated grains (≤ 0.5 mm) of pyrite, chalcopyrite and other minerals (partly oxidized). The SEM-study (Leo 1430VP and an Oxford ISIS EDX, IGM SB RAS, Novosibirsk) of mineral micro-inclusions (10 μm) in the vein quartz reveals the presence of

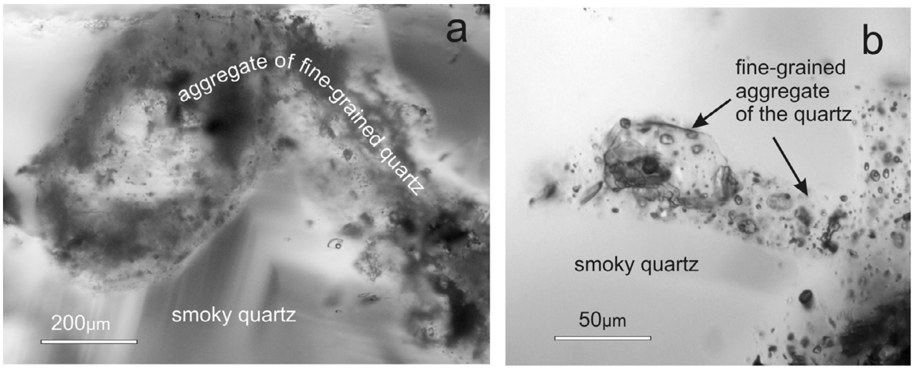

Fig. 3. Two morphological types of quartz in REE-Ti veins (Small Murun massif).

Table 1
Electron microprobe analysis of anatase, brookite and rutile in wt.%.

N	Sample	TiO_2	FeO	Nb_2O_5	V_2O_5	MnO	Ta_2O_5	Total
1[*]	1-1	98,11	0,69	1,04	0,15	0,01	0	100
2	1-2	97,04	1,13	0,92	0,31	0,01	0,02	99,43
3	1-3	98,69	0,45	0,55	0,14	0	0,03	99,86
4	1-4	96,9	1,11	1,29	0,17	0,01	0	99,48
5	1-4	97,16	1,22	0,68	0	0	0,03	99,09
6	1-5	92,76	2,01	4,99	0,14	0	0,06	99,96
7	1-6	97,54	0,85	1,15	0,45	0	0	99,99
8	2-1	99,64	0,54	0,40	0,17	0	0,02	100,77
9	2-1	99,29	0,65	0,35	0,46	0	0	100,75
10	2-1	96,47	1,49	2,5	0,24	0	0	100,7
11	2-2	98,23	0,42	0,86	0,30	0,00	0,00	99,81
12	2-3	99,21	0,57	0,46	0,23	0,00	0,00	100,47
13	2-4	98,29	0,76	0,55	0,39	0	0	99,99
14	2-5	92,71	1,94	4,50	0,08	0	0,07	99,3
15	2-6	97,05	1,1	0,9	0,3	0,03	0	99,38
16	2-7	98,23	0,54	0,46	0,25	0	0,01	99,49
17	3-1	98,52	0,2	1,33	0,09	0	0,03	100,17
18	3-5	99,7	0	0,5	0	0,01	0	100,21
19	3-6	98,29	0,17	1,34	0,31	0	0	100,11
20	3-2	97,63	0,35	1,99	0	0	0	99,97
21	3-3	99,36	0	0,76	0	0	0	100,12
22	3-4	99,23	0	0,61	0,03	0	0	99,87
23	4-1	99,48	0	0,56	0	0	0	100,04
24	4-2	99	0,01	0,6	0	0	0,01	99,62
25	4-3	99,3	0	0,71	0	0	0	100,01
26	4-4	98,93	0	0,77	0	0	0	99,7
27	4-5	99,31	0,01	0,64	0	0	0	99,96
28	4-6	99,58	0,05	0,51	0,13	0	0,01	100,28

Abbreviations:

[*] N 1-16 – rutile (Small Murun massif, Seredinskaya zone); N 17-19 – brookite and N 20-28 – anatase (Kedroviy stock). CAMEBAX-Micro, IGM SB RAS.

phases containing Ti, U, V, Nb, Nd, Ce, La, Th, Zr, P, and Ba. Some of these mineral phases can be identified as anatase, brookite, brannerite, Ce-Th monazite and bastnaesite. Samples with titanium mineralization were investigated using ICP-MS (ELEMENT Finnigan Mat, IGM SB RAS) with sample decomposition (Nikolaeva et al., 2008). Increased concentrations of following elements (in ppm) have been found for samples of the Small Murun massif and Kedroviy stock, respectively: Nb (1374 and 365), Ba (80 and 53), Zr (59 and 470), Ce (3.5 and 9.3), La (1.64 and 6.3), Nd (1.7 and 2.5), Th (6.5 and 10.8), U (2.5 and 2.4). The composition of the rutile (Small Murun) is characterized by common admixtures of Fe 1.94–0.42 wt%, Nb 4.99–0.40 wt%, and V up to 0.46 wt%. Anatase and brookite (Kedroviy stock) contain niobium from 1.99 to 0.51 wt% (Table 1). Gold content in veins revealed by atomic absorption analysis reaches 0.1 ppm (detection limit of 0.002 ppm), whereas several Au grains are found in ore concentrates from crushed samples (Thermo Scientific Thermo Solaar M6, IGM SB RAS, Novosibirsk).

3. Fluid inclusion, study

3.1. Fluid inclusion, petrography

Numerous secondary multiphase, two-phase and gas fluid inclusions were found in quartz from anatase-brookite quartz veins of the Kedroviy stock. Rare multiphase and two-phase fluid inclusions in recrystallized quartz associated with anatase, K-feldspar, and sulfides can be related to the primary inclusions. Quartz of this generation often has crystal faceting and contains needle-like mineral inclusions, fluid inclusions tracing the growth zones or forming cloudy accumulations in the central parts of crystal. In anatase small primary inclusions of the same composition as the primary inclusions in quartz are observed very rarely. Crystal-bearing fluid inclusions observed in quartz are arranged as isolated compact groups independently of the system of microfractures. These are likely to be syngenetic with early quartz of the main matrix. Crystalline quartz of rutile-brookite quartz veins of Small Murun massif contains primary two-phase and multiphase water-salt inclusions tracing the growth zones and forming cloudy accumulations in the central parts of zoned quartz crystals. Fine-grained quartz contains the same set of fluid inclusions which are distributed irregularly (Fig. 3 b).

According to phase filling at room temperature, the following types of fluid inclusions can be distinguished in quartz from the veins with titanium mineralization:

Type 1. Crystal-bearing fluid inclusions (Fig. 4a) characterized by the prevalence of solid salt phases over salt solution and gas. Solid phases exhibit anisotropy and tightly fill the vacuole of inclusion; a portion of water-salt solution and gas bubble are located in the interstitial space of the solid phases. Liquid CO_2 usually is absent in crystal-bearing fluid inclusions. Localized in isolated groups with no connection to crack these inclusions are likely to be related to one of the earliest generations of vein.

Type 2. Multiphase inclusions (Fig. 4b) are usually characterized by the presence of one or more relatively large anisotropic salt phases and 1–3 smaller solid phases. The gas phase of these inclusions often contains liquid CO_2.

Type 3. Two-phase inclusions (Fig. 4c) contain mainly salt solution, gas bubble and often 1–2 small solid anisotropic soluble salt phases. Sometimes liquid CO_2 is present in these inclusions.

Type 4. Gas inclusions (Fig. 4d) contain gas and comparatively small portion of water-salt solution. Usually liquid CO_2 is present. Often small solid phases floating on the interfaces of the solution – liquid CO_2 – gas can be observed.

The presence of primary inclusions with contrasting phase composition in vein quartz (two-phase, multiphase and gaseous) allows to suggest heterogeneous aggregative state of the mineral-forming fluid.

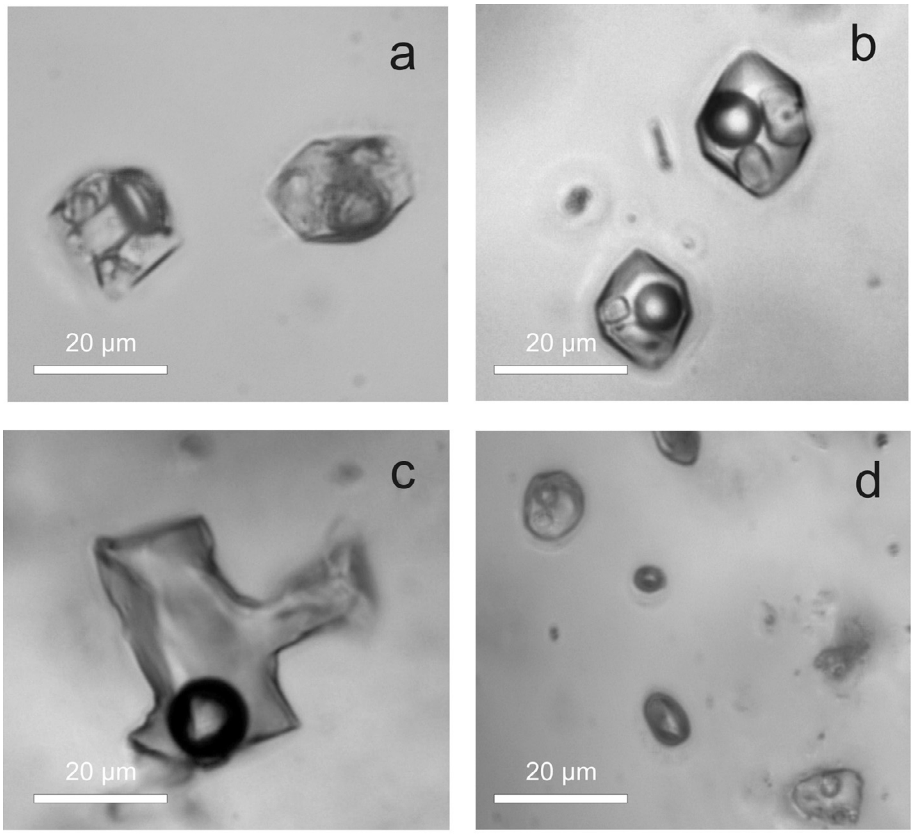

Fig. 4. Fluid Inclusions in quartz of the REE-Ti veins from the Small Murun massif and the Kedroviy stock. (a) Crystal-fluid inclusions; (b) multiphase inclusions; (c) two-phase inclusions; (d) multiphase and essentially gaseous inclusions.

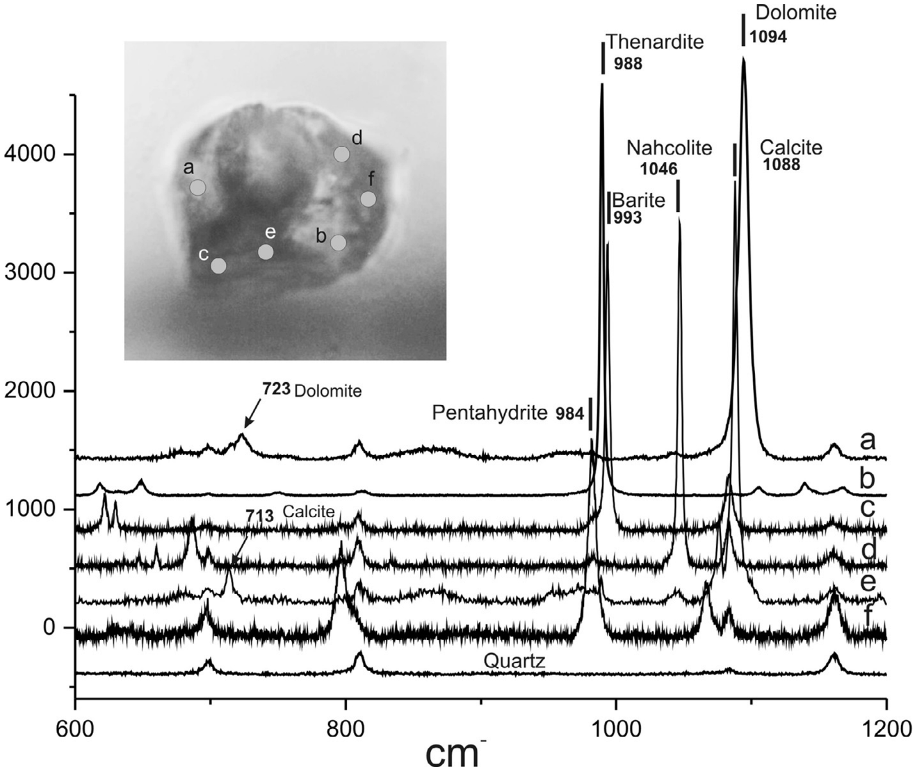

Fig. 5. Raman spectra of representative solid phases in the multiphase fluid inclusion.

3.2. Fluid inclusion study methods

Water-salt solutions of fluid inclusions in quartz were studied using cryo- and thermometry (heating stage Linkam THMSG-600 with measuring range from −196 to +600 °C). Raman spectroscopy was applied to determine the composition of the gas and to identify solid phases in the inclusions (spectrometer JobinYvon LabRAM HR800 IGM SB RAS, Novosibirsk). The Raman spectra database RRUFF (http://rruff.info/) was used to identify separate daughter phases in multiphase inclusions. The elemental composition of individual inclusions was studied using quadrupole mass-spectrometer with inductively coupled plasma ICP-MS NexION 300D in combination with laser ablation system New Wave UP 213 (Irkutsk, Vinogradov Institute of Geochemistry, SB RAS). The set of elements analyzed included B, Na, S, K, Ca, Mn, Fe, Cu, Rb, Sr, Mo, Sn, Sb, Cs, W, Pb. To assess the contents of these elements in the inclusions, NIST 612 glass was used as an external standard, and Na was used as an internal standard. The element concentrations in melt inclusions were calculated based on the algorithm by Henry Longerich for the calculation of LA-ICP-MS analysis results (Longerich et al., 1996). Element concentrations (wt.% and ppm) were determined by normalizing the absolute results to the ratio of Na concentration at the interval of inclusion opening to Na concentration in the inclusion, obtained by another analysis. A similar calculation algorithm is used in numerous publications reporting the LA-ICP-MS analysis of fluid inclusions (Günther et al., 1997, 1998; Audétat et al., 1998; Ulrich et al., 2001; Günther and Heinrich, 1999; Heinrich et al., 2003; Borovikov et al., 2015, 2016). The salt concentration in liquid phase of fluid inclusions was determined from the data of Bodnar and Vityk (1994) in wt.% NaCl eq. Sodium concentrations obtained directly by cryo- and thermometry were then corrected by using ratios of Na and K absolute abundances determined by LA-ICP-MS (Borovikov et al., 2016). Contents of major salt components (Na_2SO_4 and $NaHCO_3$) in sulfate multiphase inclusions from quartz of veins were calculated using the determinations of the volume of separate phases in multiphase inclusions, and the densities of thenardite, nahcolite and saturated aqueous solution of Na_2SO_4 and $NaHCO_3$ at 20 °C of known composition (Kogan et al., 1969).

3.3. *Result of fluid inclusion study*

3.3.1. *Raman spectroscopy*

Crystal-bearing inclusions contain thenardite and nahcolite as the main phases as well as dolomite, calcite, barite, pentahydrate (Fig. 5). Low-density CO_2 was only established in the gaseous phase. According to their Raman spectra the multiphase inclusions enclose the largest solid phases represented by thenardite and nahcolite (Fig. 6). The gaseous phase of multiphase inclusions contains CO_2 (98.9–91.9 mol.%) and N_2 (8.1–1.1 mol.%). However, H_2S was not detected in multiphase inclusions. Raman spectroscopy reveals two-phase inclusions containing CO_2 (96 mol.%) and H_2S (4 mol.%) in the gaseous phase. The salt solution contains BHO_3^-, HCO_3^-, HS^- and SO_4^{-2} anions (Fig. 7).

3.3.2. *Microthermometric study of fluid inclusions*

The results of the microthermometric study are shown in the Table 2.

Anatase-brookite quartz veins (Kedroviy stock). Heating experiments with crystal-fluid inclusions showed homogenization of vapor bubbles at the temperatures from 390 to 415 °C and partial dissolving of the solid phase. Further temperature rise led to inclusion decrepitation for many large (20–10 µm) fluid inclusions in quartz. Homogenization was achieved in some smallest (> 5 µm) crystal-fluid inclusions. Solid phases were completely dissolved at the temperature range from 605 to 615 °C.

In isolated inclusion groups small (> 5 µm) primary multiphase inclusions completely homogenized in the temperature interval 450–475 °C (dissolving of solid phases), while vapor bubbles were dissolved within temperature range 150–236 °C. During cooling down to the room temperature, the vacuole of multiphase inclusions got the initial shape; fine-grained aggregate of salts and rounded gas void appeared in inclusions. Pseudo-secondary multiphase inclusions in quartz of anatase-brookite veins from the Kedroviy stock completely homogenized during heating at temperature range from 168 to 210 °C, dissolving of the gas phase happened at 87–100 °C, nahcolite and thenardite were dissolved at 141–152 °C and 168–210 °C, respectively. During cooling of multiphase inclusions, ice phase and hydrates were formed in the solutions. The first melting of frozen phases observed in the range −23.3 to −21.7 °C. The ice in the solutions of multiphase inclusions melted at the temperatures from −11 to +9.5 °C.

Two-phase inclusions homogenized in the temperature range of 150–260 °C. When cooling the predominant ice phase forms in solutions of two-phase inclusions. Also, one-two weakly anisotropic small phases were crystallized. In two-phase inclusions the melting starts at a temperature range from −23.3 to −21.7 °C. The ice melts completely between −16 and −4 °C, which corresponds to the salt concentration from 16.5 to 6.5 wt% in NaCl eqv. Small solid anisotropic phases formed during cooling were dissolved between +6 and +10 °C. Raman

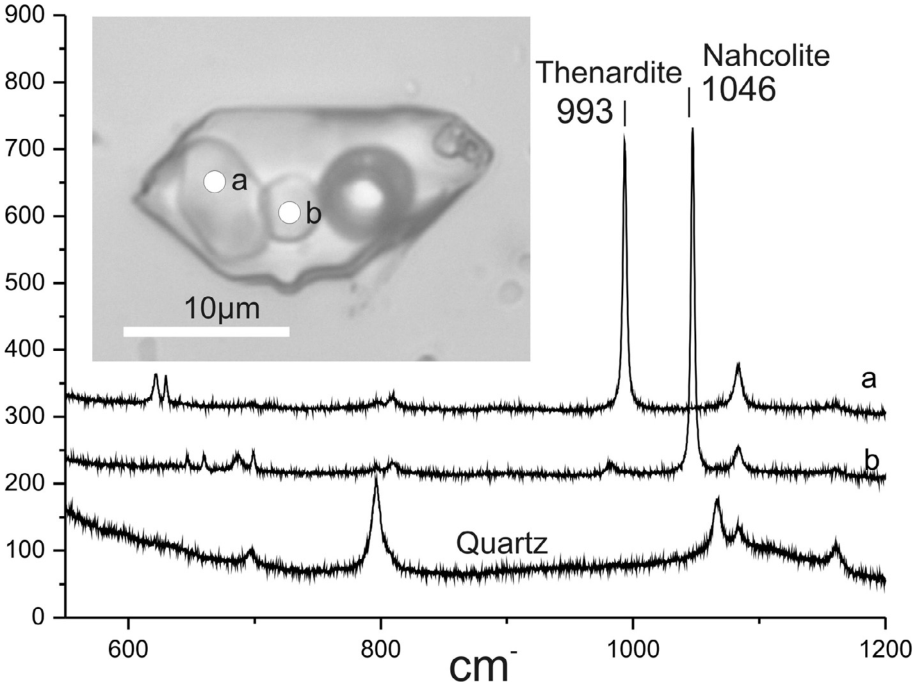

Fig. 6. Raman spectra of representative solid phases in the multiphase fluid inclusion.

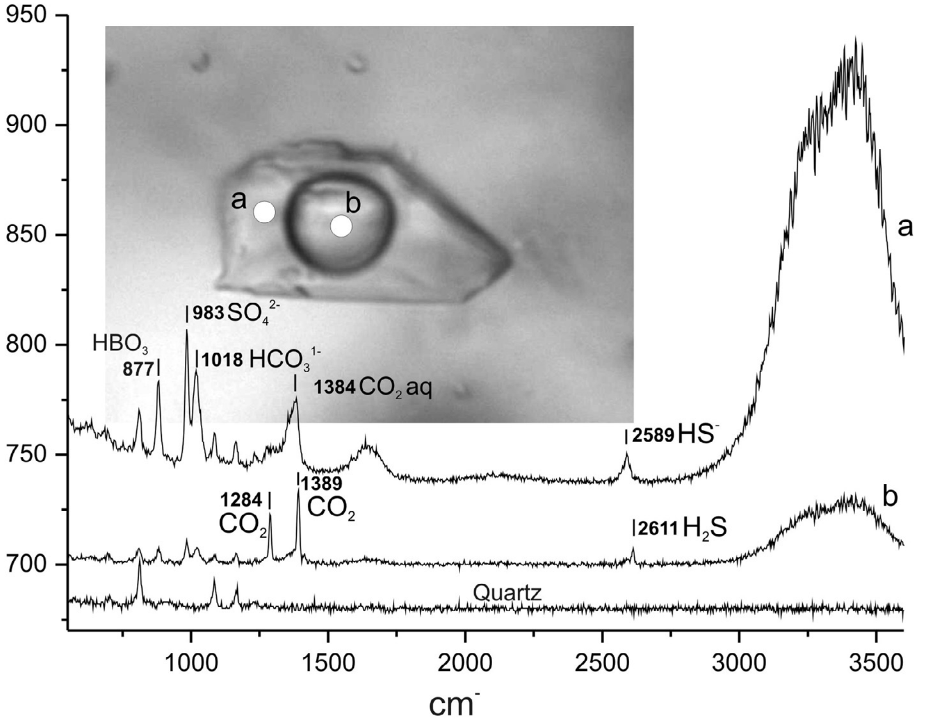

Fig. 7. Raman spectra of representative liquid and vapor phases in the two-phase fluid inclusion.

Table 2
Summary of the fluid inclusions microthermometry data.

Sample	Inclusion type	T_m eu (°C)	T_m ice ore CO_2 (°C)	T_m hydrated (°C)	T_m tenardite (°C)	T_m nahcolite (°C)	T_h vapor ore CO_2 (°C)	Salinity (wt.% NaCl eq/) ore density CO_2
Anatase quartz vein	I	–	–	–	615–605	–	390–415	80–70*
	II		–	–	475–450	–	150–236	67–62**
		−23.3/−21.7	–	–	168–175	152–141	210–168	64–55**
	III	−23.3/−21.7	−16/−4	10–6		–	250–150	21–8***
	IV(CO_2)		−56.9				+9…+6 in liquid	0.9
Rutile-brookite Quartz veins	II	−41/−38	–	–	112–110	100–95	280–210	38**
	III	−25/−21.5	−11/−3.8	57–32	–	–	255–210	29–10***

Notes:

* The rough estimate according to visual examination of volume ratios of the individual phases of crystal-rich inclusions.

** According to volumetric measurements and calculations.

*** According solubility (Kogan et al., 1969).

spectroscopy shows the presence of HCO_3^- and SO_4^{2-} in the solutions, and the solid phases formed during cooling may be regarded as $Na_2SO_4 \cdot 10H_2O$ hydrate and nahcolite. In two-phase and essentially gaseous inclusions vapor bubbles often contain CO_2 which melts in cooled inclusions at the temperature of −56.9 °C. The CO_2 homogenizes to the liquid phase at temperature between +6 and +9 °C. The density of CO_2 is estimated as 0.9 g/cm^3.

Rutile-brookite-quartz veins with sulfides (Small Murun massif). In rutile-brookite quartz veins multiphase inclusions homogenized completely. The vapor bubbles disappeared between 280 and 210 °C. Thenardite and nahcolite phases dissolved at 112–110 °C and 100–95 °C, correspondingly. In multiphase inclusions of rutile-brookite quartz veins the first melting of frozen phases happens at temperatures between −41 and −38 °C, which are lower than those in anatase-quartz veins the Kedroviy stock. This temperature interval includes the eutectic melting points of water-salt systems containing K_2CO_3 and may reflect the presence of noticeable amounts of salt component these multiphase inclusions (Roedder, 1984).

Two-phase inclusions homogenize between 255 and 210 °C. After being cooled two-phase inclusions contain the prevailing ice and small weakly anisotropic solid phases. In solutions of two-phase fluid inclusions the beginning of melting is clearly recognized within the temperature range from −25 to −21 °C. These first melting temperatures of two-phase inclusion solutions are close to eutectic melting temperatures of NaCl-KCl-H_2O and NaCl-H_2O systems. The ice melting is observed between −11 °C and −3.8 °C. Small anisotropic phases dissolve between +57 and +32 °C.

3.3.3. Approximate estimate of salt concentration in fluid inclusions

Multiphase inclusions in anatase-brookite quartz veins (Kedroviy stock). The approximate estimation of concentrations of Na_2SO_4, $NaHCO_3$ and NaCl (NaCl + KCl as NaCl eqv.) in the multiphase inclusions can be carried out using the volumetric data on major solids, liquid and vapor phases, the thenardite and nahcolite density and composition data as well as $NaHCO_3 + Na_2SO_4$-saturated solution ($NaHCO_3 + Na_2SO_4 + NaCl + H_2O$) composition data. NaCl is the main component of the eutectic of the water system $NaHCO_3 + Na_2SO_4 + NaCl + H_2O$ ($T_{eu} = -21.48$ °C, NaCl – 22.55 wt%). Other salt components are represented in smaller amounts: Na_2SO_4 – 0.18 wt% and $NaHCO_3$ – 0.66 wt% (Table 3,

Table 3
Composition and concentration (wt.%) of the saturated solutions of the $Na_2SO_4 + NaHCO_3 + NaCl + H_2O$ system (Kogan et al., 1969).

	The composition of the solid phase	NaCl	Na_2SO_4	$NaHCO_3$	T °C
1	Eutectic	22.55	0.18	0.66	21.48
2	$Na_2SO_410H_2O + NaHCO_3$	19.63	0.63	1.12	−5
3	$Na_2SO_410H_2O + NaHCO_3$	12.47	0.75	2.4	−5
4	$Na_2SO_410H_2O + NaHCO_3$ + ice	5.23	1.07	3.40	−5
5	$Na_2SO_410H_2O + NaHCO_3$	22.38	1.09	0.80	0
6	$Na_2SO_410H_2O + NaHCO_3$	20.15	1.16	1.02	0
7	$Na_2SO_410H_2O + NaHCO_3$	18.66	1.09	1.17	0
8	$Na_2SO_410H_2O + NaHCO_3$	14.44	1.17	1.51	0
9	$Na_2SO_410H_2O + NaHCO_3$	11.26	1.30	2.00	0
10	$Na_2SO_410H_2O + NaHCO_3$	8.57	1.42	2.57	0
11	$Na_2SO_410H_2O + NaHCO_3$	5.88	1.62	3.21	0
12	$Na_2SO_410H_2O + NaHCO_3$	4.94	1.78	4.10	0
13	$Na_2SO_410H_2O + NaHCO_3$	3.65	1.88	3.86	0
14	$Na_2SO_410H_2O + NaHCO_3$	2.41	2.19	4.47	0
15	$Na_2SO_410H_2O + NaHCO_3$	14.31	5.38	2.17	15
16	$Na_2SO_410H_2O + NaHCO_3$	7.48	6.89	3.91	15
17	$Na_2SO_4 + Na_2SO_410H_2O + NaHCO_3$	18.38	8.91	1.43	20
18	$Na_2SO_4 + Na_2SO_410H_2O + NaHCO_3$	19.42	9.22	1.47	20
19	$Na_2SO_4 + NaHCO_3$	16.87	11.31	1.30	25
20	$Na_2SO_4 + NaHCO_3$	12.38	15.58	1.85	30
21	$Na_2SO_4 + NaHCO_3$	12.66	14.46	2.30	45
22	$Na_2SO_4 + NaHCO_3$	12.86	12.83	3.48	45

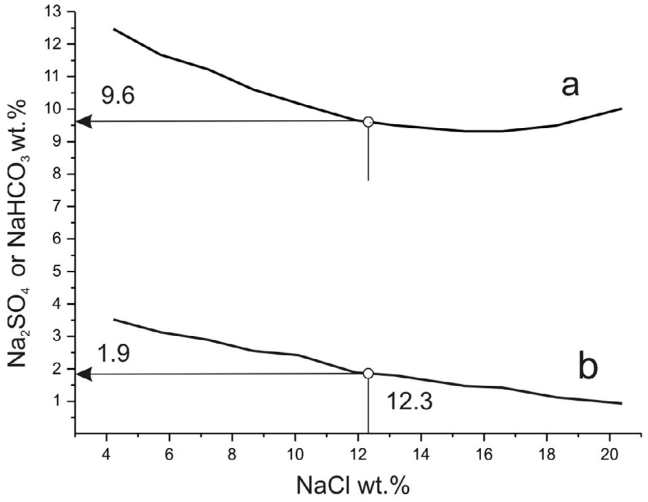

Fig. 8. The ratio of Na_2SO_4 and $NaHCO_3$ to NaCl in the $NaHCO_3 + Na_2SO_4$ saturated solution for $NaHCO_3 + Na_2SO_4 + NaCl + H_2O$ system. According to data of Sukmanskaya G.V. and Bogoyavlenskiy P.S. 1960 (Kogan et al., 1969).

Kogan et al., 1969). NaCl can be the predominant salt component in the Na_2SO_4 and $NaHCO_3$ saturated solutions in the range from the eutectic temperature to 20 °C (Table 3). According to cryometric data, the liquid phases of the multiphase inclusions are characterized by average salinity of 12.3 wt% in NaCl eqv. for Na and K chlorides. At 20 °C and 12.3 wt% NaCl, the Na_2SO_4 and $NaHCO_3$ saturated solution can contain about 1.9 wt% $NaHCO_3$ and about 9.6 wt% Na_2SO_4 (Fig. 8). The known contents of $NaHCO_3$, Na_2SO_4 and NaCl in phases of multiphase inclusions and the known phase volumes and densities allowed us to calculate the concentrations of $NaHCO_3$, Na_2SO_4 and NaCl in the multiphase inclusions. The calculation includes the following steps:

1) Determination the volumes of solid, liquid and vapor phases in multiphase inclusions according to the method by Reyf (1997).
2) Determination of the mass of every phase and the total weight of the inclusion content using known density and volume values for every phase.
3) Calculation of salt components masses in solid and liquid phases and the total weight of every salt component.
4) Calculation of the weight percentage for every salt component in fluid inclusion.

The phase volumes have been determined for five multiphase inclusions. The data obtained indicate that multiphase inclusions contain on average 6.2 wt% of NaCl, 38.1 wt% Na_2SO_4 and 12.1 wt% $NaHCO_3$. The total average salt concentration is 56.4 wt%.

Two phase inclusions. The available data on compositions and concentrations of NaCl-undersaturated solutions of $NaHCO_3$ and Na_2SO_4 at different temperatures are very limited (Table 3). The composition of two-phase inclusions is in agreement with the $NaHCO_3 + Na_2SO_4 + NaCl + H_2O$ salt-water system. Thenardite (or Na_2SO_4 hydrate) and nahcolite phases are presented in the two-phase inclusions as small particles at the room or lower temperature. Following conclusions can be made based on these facts:

1) NaCl is the dominant component in the compositions of two-phase inclusions;
2) Inclusion solutions are Na_2SO_4 and $NaHCO_3$ saturated at the temperature of the dissolution of the small solid phases (thenardite or the Na_2SO_4 hydrate and nahcolite).

NaCl concentrations and the melting temperatures of the solid phases in two-phase inclusions compared with the available data (Table 3) allows to assess the Na_2SO_4 and $NaHCO_3$ concentrations in two-phase inclusions. Thus, the compositions of two-phase inclusions can be estimated from the data on the solubility of halite, thenardite and nahcolite in $NaHCO_3 + Na_2SO_4 + NaCl + H_2O$ solutions. According to cryometric data, the NaCl concentration in two-phase inclusions varies between 19.5 and 6.5 wt% (average 13 wt%). At the melting temperature of solid phases between +6 and +10 °C, the solutions may contain no more than 5.4 wt% Na_2SO_4 and 2.2 wt% $NaHCO_3$ (Table 4, line 15). The total salt concentrations of the two-

Table 4
Results of LA-ICP-MS analysis of fluid inclusions, average concentrations are given in ppm.

	Multiphase inclusions (5)*	*I* σ	Two-phases inclusions (4)	*I* σ
B	1750	865	140	6.8
Na	186000	–	97200	–
Mg	280	126	20	7.9
P	60	36	0.6	0.15
K	16300	3840	7300	2310
Ca	2	0.6	20	6
Mn	260	157	0.2	0.05
Fe	1560	950	15	3.0
Co	9	2.5	3	1.2
Ni	220	116	1.5	0.98
Cu	1030	629	50	13
Zn	270	121	30	14
As	50	4.6	50	25
Rb	210	51	950	221
Sr	15	3.0	750	470
Mo	60	36	1	0.3
Ag	3	1.6	5	3.3
Sn	50	30	5	2.3
Sb	10	2.7	6	1.7
Cs	21	2.1	260	29
Ba	20	7.1	1	0.5
W	14	1.6	2	3
Au	2	0.5	4	1.4
Pb	510	327	3.0	0.8
Bi	5.1	3.3	0.4	0.2
Th	9	3.6	38	15
U	15	3.1	8.8	2.8

Notes:
* Number of fluid inclusions

phase inclusions are about 20.6 wt%. This is a very rough estimation, but it is useful for our conclusions.

Rutile-brookite-quartz veins (Small Murun massif). The concentrations of Na_2SO_4, $NaHCO_3$ and NaCl in the multiphase inclusions were defined by the method described above. The multiphase inclusions from the rutile-brookite-quartz veins contain about 25 wt% of Na_2SO_4, 9 wt% of $NaHCO_3$ and 4 wt% of NaCl. The total salt concentration is near 38 wt %. The two-phase inclusions contain 12.9 wt% of NaCl, at least 14.5 wt % of Na_2SO_4 and 2.3 wt% of $NaHCO_3$. (Table 3, line 22). The average concentration of solutions in two-phase inclusion of rutile-brookite-quartz veins is 28.8 wt%.

4. LA-ICP-MS analysis

LA-ICP-MS technique was successfully used to study the composition of one crystal-fluid inclusion, four multiphase inclusions in anatase-brookite veins from the Kedroviy stock, and four two-phase fluid inclusions in quartz-brookite veins from Seredinskaya zone (Small Murun massif) (Table 4). The analyses of crystal-bearing fluid inclusions show the following elements: Na and K as major elements; Rb, Sr, Cs, Fe, Ni, As, W, Zn, Mo, Cu, Mn, Sn, Pb, Bi, U and Th as trace elements. Multiphase inclusions are characterized by high concentrations of Na and K (18.6 and 1.63 wt%), while other elements are determined at ppm level. The average content of Rb is 210 ppm, Cs – 21, Sr – 15, Ba – 10 ppm. Concentrations of metals range from 210 ppm (Ni) to 1560 ppm (Fe). Other trace elements demonstrate the range of concentrations from 2 to 50 ppm. Similar to multiphase ones, two-phase inclusions have high Na (9.7 wt%) and K (0.7 wt%) contents. However, they contain more Rb (950 ppm), Sr (750 ppm) and Cs (260 ppm), but much less metals: only Cu concentration riches 50 ppm, while all others are lower. In addition, all inclusions contain S, Cl and Hg, in some inclusions fluorine was detected as well.

5. Discussion

5.1. Temperature, pressure and salt concentration of ore-forming fluids

The formation of anatase-brookite mineralization (Kedroviy stock) involved two types of fluids. The first type is characterized by a high concentration of Na_2SO_4 and $NaHCO_3$. The NaCl content was not significant in the fluid composition. Fluid temperature was decreasing from 470 to 168 °C during the crystallization of anatase-brookite quartz veins. The concentration and the salt composition of these fluids were not substantially changing as the temperature drops.

The second type of fluid features a predominance of NaCl and small admixture of $Na_2SO_4 + NaHCO_3$ in the salt composition. The temperature of the fluid was in the range of 280–150 °C. Thus, high-concentrated Na_2SO_4 brines evolved to low- and medium-concentrated NaCl-predominantly fluids as the temperature decreases.

High-concentrated fluids of the first type (the Kedroviy stock) feature Na_2SO_4 as the major salt components and high temperature up to 470 °C. The $Na_2SO_4 + H_2O$ solutions belong to the water-salt systems of the P-Q type (Valyashko, 2004). The P-Q systems are characterized by the liquid incompatibility for the region of supercritical P-T-X parameters. The fluid includes two immiscible liquid phases, different in concentration of Na_2SO_4 (Fig. 9). The $Na_2SO_4 + H_2O$ diagram shows figurative concentrations and homogenization temperature points of multiphase inclusions for anatase-brookite mineralization located within the field of liquid immiscibility at a pressure of about 130 MPa (Fig. 9). If these highly concentrated fluids were one of the supercritical fractions, then there should be equilibrium immiscible fractions (Fig. 9 the (f) field) corresponding to these highly concentrated fluids in the heterophase fluid system. Low- and medium-concentrated solutions of two-phase inclusions may correspond to such the equilibrium immiscible fraction in concentration. Thus, the heterophase fluids could be involved at the beginning of anatase-brookite crystallization. The fractions of this heterophase fluid enriched in Na_2SO_4 correspond to multiphase inclusions with tenardite and nakhcolite. The fractions depleted in Na_2SO_4 are consistent in composition with low- and medium-concentrated two-phase inclusions with a predominance of NaCl. The coexistence of such fluids as immiscible fractions was shown in high temperature experiments for the synthesis of fluid inclusions in $Na_2SO_4 + NaHCO_3 + NaCl$ system at the temperature 600 °C (Borovikov et al., 2015).

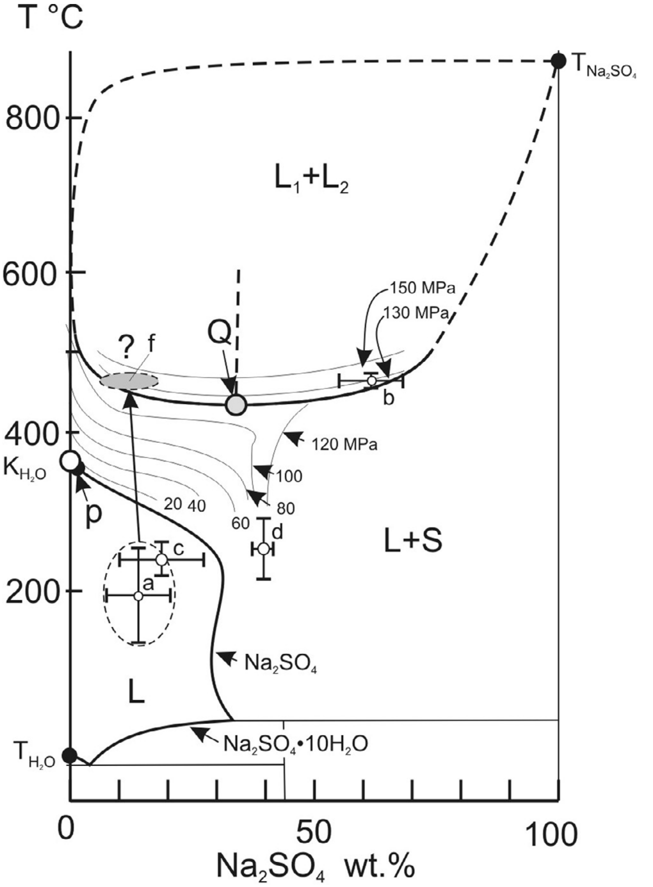

Fig. 9. P-T-X diagram of the $Na_2SO_4 + H_2O$ system by Valyashko (2004) with authors' supplements. T and K are the triple (L-G-S) and critical (L = G) points of pure components; Q and p are the critical endpoints $L_1 = L_2$-S and L_1 = G-S. Heavy lines are the composition of liquid phases in monovariant equilibria L-G-S and L_1-L_2-S; dashed lines show an extension of the studied part of three-phase curves $L_1 = L_2$-S up to the triple point T_{Na2SO4}; dot-dashed lines are the critical curves L = G (originated in K_{H2O}) and $L_1 = L_2$ (originated in Q); solid line are the composition of liquid phases in isobaric cross-sections of two-phase equilibria; thin lines are the tie-lines. Authors' supplements: homogenization temperatures and salt concentrations of (a) two-phase and (b) multiphase inclusions in quartz from anatase-brookite quartz veins (the Kedroviy stock); (c) two-phase and (d) multiphase inclusions in brookite-rutile quartz veins with sulfides (the Small Murun massif, Seredinskaya zone). (f) The hypothetical immiscible fluid fraction is at high temperature and pressure in equilibrium with fluids from multiphase inclusions.

The rutile-brookite-quartz veins were formed at the temperature range from 280° to 210 °C. The mineral assemblage including pyrite, chalcopyrite, galena, native gold occured at the temperature between 255° and 210 °C during cooling of ore-forming fluids. The mineral-forming fluid is characterized by the predominance of Na_2SO_4 in salt composition and the total concentration from 10 to 38 wt%. The temperature decrease was associated with rise of the NaCl concentration in the mineral-forming fluids.

6. Conclusions

1) Quartz veins with titanium mineralization from the Kedroviy stock and Small Murun massif are typical high-temperature post-

magmatic formations. Mineral assemblages with anatase crystallize in the range from 470 to 450 °C, while those with brookite, rutile and sulfides crystallized at temperatures of 280–210 °C. Anatase in the quartz veins of the Kedroviy stock and sulfide-brookite quartz veins of the Small Murun massif seem to represent the sames mineral-forming stage. Identical mineral assemblage of titanium mineralization in both cases and similar compositions of mineral-forming fluids and formation temperatures indicate that they may belong to different facies of the same hydrothermal process. The existence of both TiO_2-bearing minerals (brookite – anatase and brookite – rutile) is unique. The fluid inclusion study shows that they crystallized from the same fluid, but at different temperatures. The mineral paragenesis of the pyrite, chalcopyrite, galena, native gold and REE minerals were formed at the temperatures of between 255° and 210 °C.

2) Quartz veins with titanium mineralization are considered have formed with the involvement of heterophase fluids. Those fluids belong to a complex $(Na_2SiO_3 + NaHCO_3 + Na_2SO_4 + NaCl + H_2O)$ water-salt system. The heterophase state of fluids supported by both the co-existence of gaseous and liquid fluid phases and liquid immiscibility typical of P-Q type water-salt systems under supercritical P-T conditions. Moreover, one "liquid-like" fluid phase contains mainly NaCl and KCl, while another shows high concentration of Na_2SO_4 and $NaHCO_3$. These fluid fractions are characterized by different metal-bearing capacity: highly concentrated fluids are specialized in Fe, Cu, Pb, Zn, Mn, and contain As, Mo, Sn, U, Th, Ag and Au. The major anions are SO_4^{2-} and HCO_3^-; CO_2 and N_2 dominate among dissolved gases. Medium- and low-concentrated fluids are specialized in Cu, As, Zn, Th, U, as well as Ag and Au. The major anion components are HCO_3^- and Cl^-, dissolved gases include CO_2, N_2 and H_2S.
3) According to the salt composition, the hydrothermal fluids forming titanium mineralization of the Murunskiy massif can be compared with magmatic fluids of the final magmatic phase of the massif. These magmatic fluids are characterized by a chloride-sulfate-carbonate composition and the presence of CO_2 and N_2 in the gas phase. The temperature and pressure of magmatic rocks determined at successive crystallization of strontium-barium carbonatite, silicate charoite rock and quartz-calcite carbonatite are relatively low – from 800 to 470 °C and from 5.5 to 0.5 kbar respectively (Prokofiev and Vorobiev, 1991). Thus, these magmatic fluids could be separated from carbonatite melts and participated in the formation of quartz veins with titanium mineralization, wherein the parameters of quartz-calcite carbonatite fluids are closest to hydrothermal conditions.

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