# **Chronology of Hydrothermal and Magmatic Activity in the Dukat Gold–Silver Ore Field**

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**Abstract**—The previously published and newly obtained geological and geochronological (Rb–Sr and Ar–Ar) data show that the igneous rocks and products of hydrothermal alteration in the Dukat ore field pertain to two ore-forming magmatic–hydrothermal systems (OMHSs). The igneous rocks of the Early Cretaceous rift-related OMHS are represented by potassium rhyolites of the Askol'd Formation with Rb–Sr ages of 124  $\pm$  3 and 119.3  $\pm$ 3.4 Ma and intercalating amygdaloidal basalts. The products of the hydrothermal activity of this OMHS are the metasomatic anatase–chlorite assemblage of the root zone, which replaces potassium rhyolites, and shallowseated quartz–adularia and quartz–carbonate–feldspar veinlets retained in rhyolite fragments in Late Cretaceous conglomerate and breccia. The Late Cretaceous OMHS was related to the origination of the Okhotsk– Chukotka volcanic belt and consists of calc-alkaline basaltic andesites of the Tavvatum Formation and moderately silicic K–Na rhyolites of the Nayakhan Formation with a Rb–Sr age of  $84 \pm 4$  Ma. The Late Cretaceous postmagmatic hydrothermal activity in the Dukat ore field resulted in the formation of preore metasomatic rocks and orebodies of the unique Dukat Au–Ag deposit. The first stage of the Late Cretaceous hydrothermal activity gave birth to preore propylites with a Rb–Sr isochron age of adularia samples estimated at  $85 \pm 1$  Ma and quartz–chlorite–sulfide and Ag-bearing quartz–chlorite–adularia orebodies with Rb–Sr isochron ages of adularia estimated at  $84 \pm 1$  and  $86.1 \pm 4$  Ma. The second stage was marked by the formation of garnet-bearing propylites and quartz–rhodonite orebodies with a Rb–Sr age of 73  $\pm$  3 Ma. Further hydrothermal activity occurred after a break related to structural rearrangement of the ore field and was expressed in the replacement of propylites by products of argillin alteration and Ag-bearing Mn hydroxides. Paleogene basaltic dikes and related subeconomic mineralization concluded magmatic and hydrothermal processes in the Dukat ore field.

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#### INTRODUCTION

Ideas about the sequence of mineral formation during magmatic and fluid–magmatic activity in large ore fields are typically based on geological relationships observed at the Earth's surface and in underground workings and borehole cores (Lipman et al., 1978; Rundquist, 1997; Safonov et al., 2000; Ponomarchuk and Sotnikov, 2003). The ages of magmatic bodies and postmagmatic mineral assemblages with an unclear geological position are specified with isotopic methods. However, in some cases, the interpretation of isotopic ages is ambiguous, especially when they come into conflict with geological data, and leads to contradicting genetic models of the same deposit.

Such a situation has arisen at the Dukat gold–silver deposit, the largest in the northeast of Russia. Since the discovery of this deposit in 1967, the age of its orebodies and their relationships with igneous rocks have remained a matter of debate.

On the basis of geological data, Raevskaya et al. (1977), Sidorov et al. (1989), and Konstantinov et al. lived center of endogenic activity in the Cretaceous and Paleogene; the economic orebodies of the Dukat deposit were regarded as formed in the Late Cretaceous. The first K–Ar datings of felsic volcanic rocks,

(1998) considered the ore-bearing area to be a long-

granitoids, and gangue minerals from the orebodies of the Dukat deposit (Volkov et al., 1983) showed that the isotope system of most analyzed samples was disturbed by subsequent impulses of endogenic activity. Volkov et al. (1983) suggested an Early Cretaceous age of the deposit. A different approach to the interpretation of K−Ar and Rb–Sr isotopic data allowed Kotlyar et al. (2001, 2004) and Rozinov et al. (2004) to draw the same conclusion and to suggest that the high-grade orebodies were affected by skarnification in the Late Cretaceous.

The study of the geological setting of preore metasomatic alteration of the volcanic rocks at the Dukat deposit allowed us to distinguish products of Early and Late Cretaceous ore-forming magmatic–hydrothermal systems (OMHSs). The Rb–Sr dating of adularia from Late Cretaceous metasomatic rocks spatially associated

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with the older generation of quartz–chlorite–adularia orebodies, as well as of gangue minerals from the younger quartz–rhodonite orebodies, made it possible to specify the age of particular events of ore-forming hydrothermal activity and to estimate the duration of formation of high-grade orebodies.

Together with the new results, we discuss in this paper the previously published data on the geological relationships between igneous rocks and hydrothermal alteration in the Dukat ore field and their K–Ar, Rb–Sr, and Ar–Ar ages.

## GEOLOGY OF THE DUKAT ORE FIELD AND RELATIONSHIPS BETWEEN IGNEOUS ROCKS THEREIN

The Dukat ore field is localized in the near-meridional riftogenic Balygychan–Sugoi Trough, which is bordered in the north by the Okhotsk–Chukotka volcanic belt (Fig. 1). The Cretaceous volcanic–sedimentary sequences, which are cut through by granitoid intrusions, and the products of hydrothermal activity hosted in these sequences were formed in two geodynamic settings (Raevskaya et al., 1977; Sidorov, 1989; Konstantinov et al., 1998).

The Lower Cretaceous sequence, composed of subalkali potassium rhyolites, amygdaloidal basalts, and coal-bearing continental sedimentary rocks of the Omsukchan Formation characterized by the Aptian, Albian, and Cenomanian floral assemblages (Samylina, 1986; Filipova and Abramova, 1993), was formed under conditions of rifting. In the northern, relatively subsided part of the volcanic structure, the Lower Cretaceous sequence comprises jointly deformed fluidal aphyric rhyolites and coal-bearing sedimentary rocks. Basement rocks and silicified fluidal aphyric rhyolite and rhyolitic porphyry are exposed in the southern, relatively uplifted block bounded in the north by the Buyunda–Gizhiga Fault System.

The Late Cretaceous stage of endogenous activity was related to the formation of the Okhotsk–Chukotka marginal continental volcanic belt. The conglomerate unit at the base of the volcanic sequence unconformably rests upon the deformed Lower Cretaceous rocks exposed in the core of a domal uplift. Calc-alkaline basaltic andesite and andesite of the Tavvatum Formation and K–Na rhyodacite and rhyolite of the Nayakhan Formation build on the section. The rhyodacitic tuffs of the Nayakhan Formation contain Albian and Cenomanian–Santonian floral assemblages (Samylina, 1986; Filipova and Abramova, 1993).

An intrusive body composed of leucogranite and porphyritic biotite granite with granodiorite schlieren was penetrated by boreholes at a depth of 1200–1300 m. The Early Cretaceous potassium rhyolites above the intrusion were converted into andalusite–feldspar and garnet–biotite hornfels for a distance of 500–800 m from the intrusive contact.

The basaltic dikes that cut the Cretaceous volcanic rocks and granitoids are the youngest igneous rocks in the ore field. Like dikes from other ore fields of the Balygychan–Sugoi Trough, they are referred to the Paleogene (Konstantinov et al., 1998).

## ORE MINERALIZATION OF THE DUKAT ORE FIELD AND ITS SPATIAL RELATIONS TO VOLCANIC AND PLUTONIC ROCKS

The data on the Early Cretaceous hydrothermal activity in the Dukat ore field are scanty. Quartz, adularia–quartz, and quartz–carbonate–feldspar veinlets were described by Raevskaya et al. (1977) in fragments of the Early Cretaceous rhyolite incorporated into the Upper Cretaceous coarse-clastic conglomerate and breccia that surround the volcanic dome (Fig. 1). These veinlets are the sole evidence for Early Cretaceous orebodies that were formed in the hypabyssal epithermal system and subsequently eroded.

The bulk of the orebodies of the Dukat Au–Ag deposit are hosted in the Early Cretaceous potassium rhyolites that plunge beneath the coal-bearing clayey rocks of the Omsukchan Formation. At the upper levels of the deposit, the branching ore zones reach 100– 120 m in thickness. They grade into axial veins with depth and pinch out at a depth of 500–700 m. As can be seen in the adits at the western flank of the deposit (the Smely area), the orebodies penetrate into the Upper Cretaceous tuffaceous conglomerate, which is regarded as a screen preventing free percolation of hydrothermal solutions through the overlying Late Cretaceous volcanic rocks (Konstantinov et al., 1998).

Acanthite and native silver are the major silver minerals at the Dukat deposit. The Ag/Au ratio varies from 250 to 550. Two episodes of hydrothermal activity were distinguished on the basis of numerous data on the mineral composition and structure of multistage orebodies at the Dukat deposit (Konstantinov et al., 1998). Disseminated quartz–chlorite–sulfide orebodies and N–S-trending quartz–chlorite–adularia veins with Au-bearing native silver, acanthite, and freibergite were formed consecutively at the first stage. The adularia–chlorite stringer zones continuing orebodies at a depth acquire vague outlines in hornfels of the contact aureole (Kolesnikov et al., 1998).

The younger NW-trending quartz–rhodonite orebodies are related to the rejuvenation of the hydrothermal system during emplacement of the granitic intrusion (Sidorov et al., 1989; Berman et al., 1993; Goncharov and Sidorov, 1979). Native silver, acanthite, and sulfosalts, including fahlore, are ore minerals, while the gangue minerals include rhodonite, rhodochrosite, spessartine, grossular, and pyroxene.

The vein orebodies of both stages exhibit banded structures caused by repeated rhythms of ore deposition (Konstantinov et al., 1998; Sakharova et al., 2000). In the older orebodies, the banded structures are expressed



**Fig. 1.** Geological sketch map of the Dukat ore field and its position (inset) in the Okhotsk–Chukotka volcanic belt (oblique hatching). (1) Triassic–Jurassic metasedimentary rocks of the basement in the outer zone of the volcanic belt; (2–4) Early Cretaceous OMHS: (2) potassium rhyolite, (3) coal-bearing sedimentary rocks of the Omsukchan Formation, (4) metasomatic rocks of the root zone; (5–10) Late Cretaceous OMHS: (5) conglomerate and breccia with fragments of mineralized rhyolites of the Askol'd Formation, (6) K–Na rhyolite of the Nayakhan Formation, (7) basaltic andesite of the Tavvatum Formation, (8–10) preore metasomatic rocks of the (8) outer and (9) inner zones of the Dukat ore field and (10) younger garnet-bearing propylite; (11) faults; (12) zones of hidden transform faults of the near-latitudinal Buyunda–Gizhiga and near-meridional Omsukchan systems.

in a ribbonlike arrangement of fine-grained aggregates of quartz, adularia, chlorite, and sulfides. In the younger orebodies, pink, white, gray, and black bands consist of quartz–adularia–rhodonite and sulfide–sulfosalt assemblages; manganese oxides; and aggregates of comb quartz, chlorite, rhodochrosite, calcite, sericite, and kaolinite.

The regeneration of ore-bearing mineral assemblages is widespread at the deposit. This process was responsible for the formation of some skarn minerals and ore shoots composed of coarse-grained quartz and very high contents of almost Au-free native silver.

Raevskaya et al. (1977), Vargunina and Andrusenko (1983), and some other geologists distinguished still

younger mineralization stages: base-metal stringers with high Pb, Zn, Cu, Ag, Sb, Sn, and Cd contents and deepseated greisen enriched in W, Mo, and Sn and containing fluorite, spessartine, helvite, and tourmaline.

The dikes of Paleogene basalts bear traces of the youngest hydrothermal activity. The cavities and thin veinlets therein are filled with quartz; chlorite; carbonate; zeolites; K-feldspar; and Fe, Zn, Pb, and Mn sulfides (Vargunina and Andrusenko, 1983).

## THE PREVIOUSLY PUBLISHED ISOTOPIC AGES OF OREBODIES AND HOST IGNEOUS ROCKS

The previously published K–Ar, Rb–Sr, and Ar–Ar ages of igneous rocks, metasomatic alteration, and hydrothermal veins in the ore field are summarized in Fig. 2. Some Rb–Sr datings are consistent with the geological position of the analyzed minerals and rocks and the respective isochrons are characterized by low MSWD values.

The potassium rhyolites of the Lower Cretaceous Askol'd Formation are dated at  $124 \pm 3$  Ma (Konstantinov et al., 1998) and  $119.3 \pm 3.4$  Ma (Rozinov et al., 2004). Four rhyolite samples from the Nayakhan Formation yielded an Rb–Sr age of  $84 \pm 4$  Ma (Chernyshev et al., 2005), which practically coincides with the age of  $90.8 \pm 2.3$  Ma determined for volcanic rocks located to the north of the Ken Sn-bearing area (Kolesnikov et al., 1998).

The Rb–Sr isochron age of 12 adularia samples from the older quartz–chlorite–adularia orebodies is  $84 \pm 1$  Ma; the MSWD is low (Konstantinov et al., 1998). This age is consistent with the observed relationships of orebodies with felsic volcanic rocks. The age calculated by Rozinov et al. (2004) for 8 of the 12 aforementioned samples and 2 new samples equals  $86.1 \pm 4$  Ma. These data agree with the Ar–Ar step heating age of adularia (Newberry et al., 2000), which indicates that vein orebodies could have been formed 84– 79 Ma ago.

Some K–Ar datings of felsic volcanics are inconsistent with their geological position and Rb–Sr age. The K–Ar dates of potassium rhyolite from the Askol'd Formation and rhyodacite from the Nayakhan Formation below 90 Ma are regarded as underestimated. As was pointed out for the first time by Volkov et al. (1983), these dates reflect the complete or partial loss of radiogenic Ar from minerals and rocks under the effect of subsequent endogenic events.

The third group of K–Ar and Rb–Sr ages spans too wide a time interval to be helpful for reliable timing of the analyzed samples.

The Rb–Sr isochron calculated by Kotlyar et al. (2001) for six whole-rock tuff and ignimbrite samples from the Nayakhan Formation in the Dukat ore field yielded  $100 \pm 20$  Ma. This rather uncertain result covers both the Early and the Late Cretaceous.

The age of the multiphase granitic intrusion altered by postmagmatic processes remains unclear. The Rb–Sr and Ar–Ar ages of  $82 \pm 4$  (Konstantinov et al., 1998),  $80 \pm 2$  Ma (Plyusnin et al., 1989), and 81–82 Ma (Newberry et al., 2000) do not contradict the observed relationships of quartz–chlorite–adularia stringer zones forming downward extensions of the orebodies dated at  $84 \pm 1$  and  $86.1 \pm 4$  Ma with hornfels. However, the Rb−Sr datings obtained by Rozinov et al. (2004) for chloritized and silicified biotite granite and leucogranite porphyry are older  $(93 \pm 4$  and  $88.5 \pm 3.7$  Ma).

The K–Ar ages of orebodies at the Dukat deposit also show a wide range from the Early Cretaceous to the Paleogene. The possible disturbance of the K–Ar system of adularia in veins can be related to both a loss and a gain of <sup>40</sup>Ar. Excess <sup>40</sup>Ar that results in age overestimation could have been supplied in hydrothermal solutions together with deep gas flows that accompanied hydrothermal activity (Goncharov and Sidorov, 1979; McDougall and Harrison, 1988; Giggenbach, 1997). Similar disturbances of K–Ar isotopic systems were established for intrusions and volcanic rocks in the western United States and Alaska (McDougall and Harrison, 1988; McCoy et al., 1997).

The Rb–Sr ages of quartz–rhodonite orebodies were obtained by Konstantinov et al. (1998), Kotlyar et al. (2001), and Rozinov et al. (2004) for whole-rock samples of mineral aggregates consisting of quartz, rhodonite, and rhodochrosite, as well as for aggregates enriched in carbonates and treated with HCl. The MSWD of the errorchron calculated by Kotlyar et al. (2001) is 24. Based on these data, Kotlyar et al. (2001) and Rozinov et al. (2004) argued that the Rb–Sr age of  $75 \pm 3$  Ma obtained by Konstantinov et al. (1998) for the younger generation of orebodies does not reflect their formation time. As a result, all Late Cretaceous datings of orebodies were estimated as inadequate (Kotlyar et al., 2001; Rozinov et al., 2004). Only the two oldest K–Ar dates of 109 and 104 Ma were considered to be reliable.

## UNSOLVED PROBLEMS OF TIMING THE IGNEOUS ROCKS AND PRODUCTS OF HYDROTHERMAL ACTIVITY AT THE DUKAT ORE FIELD

The available geological data indicate that the magmatic activity within the Dukat ore field and the entire Balygychan–Sugoi Trough took place in the Early and Late Cretaceous. However, the age of the multiphase deep-seated granitic intrusion, the emplacement of which presumably gave rise to the resumption of hydrothermal activity at the Dukat deposit, remains uncertain. In spite of the compositional similarity between biotite granite and Late Cretaceous calc-alkaline rhyodacite of the Nayakhan Formation, some authors suggest that the deep-seated granitoids of the Dukat ore



**Fig. 2.** Isotopic age of igneous rocks and hydrothermal alteration in the Dukat ore field. (1) Rb–Sr, (2) K–Ar, and (3) Ar–Ar methods. The number of samples is shown in square brackets; numbers in parentheses are references listed hereafter: (1) Konstantinov et al. (1998); (2) Rozinov et al. (2004); (3) Volkov et al. (1983); (4) Chernyshev et al. (2005); (5) Kotlyar et al. (2001); (6) Plyusnin et al. (1989); (7) Newberry et al. (2000); (8) original data.

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field belong to the Early Cretaceous plutonic complex. According to this suggestion, the hydrothermal system resumed its activity in the Early Cretaceous (Kotlyar et al., 2004).

The compact placement of most orebodies in potassium rhyolite of the Askol'd Formation also supports their Early Cretaceous age. The adherents of this concept ignore the fact that the orebodies crosscut the Late Cretaceous conglomerate and do not take into account the established Late Cretaceous Rb–Sr age of adularia from the older generation of orebodies (isochron based on 14 samples), giving preference to the sporadic Early Cretaceous K–Ar datings. The age of the younger quartz–rhodonite orebodies remains uncertain. Therefore, no reliable data are available to date on the duration of hydrothermal activity in the Dukat ore field.

#### RESEARCH METHODS

The mapping of preore metasomatic rocks within the ore field was performed with consideration for the abundances of newly formed minerals in the exposed 400-m-thick volcanic sequence and deep-seated granitoids. These minerals occur as amygdules in the groundmass of porphyritic volcanic rocks and fill microfractures and cavities, which are especially typical of subvolcanic fluidal rocks. The internal structure of newly formed mineral aggregates less than 1–2 mm in size and the chemical composition of grains smaller than 0.5 mm were studied under an optical microscope, with a JSM-5300 scanning electron microscope equipped with Link ISIS EDS, and with a Cameca SX-50 microprobe.

The Rb–Sr isotopic study of newly formed minerals in preore metasomatic rocks and quartz–rhodonite orebodies was conducted at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences, using methods developed at the Laboratory of Isotope Geochemistry and Geochronology (Chernyshev et al., 1983). Samples were decomposed in a mixture of  $HNO<sub>3</sub>$  and HF (1 : 3). Rb and Sr were separated by ion-exchange chromatography on a set of quartz columns using 2N HCl and a 3-ml Dowex  $50 \times 8$  resin bed. The total blank during chemical preparation of samples was not higher than 0.1 ng for Rb and 0.15 ng for Sr. The Rb and Sr contents were determined with the isotope dilution method. The Rb and Sr isotope ratios were measured on a Micromass Sector 54 thermoionization mass spectrometer. The analytical precision was controlled by replicate analysis of the SRM-987 standard. The measurement error (2 $\sigma$ ) was not higher than 0.005% for <sup>87</sup>Sr/<sup>86</sup>Sr and 0.5% for 87Rb/86Sr. The errors in Rb–Sr datings and the initial <sup>87</sup>Sr/<sup>86</sup>Sr ratio reported in this paper correspond to a confidence level of 0.95 ( $2\sigma$ ).

## PREORE METASOMATIC ROCKS OF THE DUKAT ORE FIELD AND THEIR RELATIONSHIPS WITH FELSIC VOLCANIC ROCKS AND OREBODIES

As was shown by the mapping, the preore metasomatic alteration of the Dukat volcanic structure, described for the first time by Filimonova (2002, 2004) and Filimonova and Trubkin (2004), embraced an enormous volume of rocks affected by hydrothermal activity related to the evolution of the Early and Late Cretaceous OMHSs. Similar metasomatic rocks are known from other hydrothermal deposits and areas of modern hydrothermal activity (Henley, 1985; Tauson et al., 1987; White and Hedenquist, 1990; Zharikov et al., 1998).

Among preore metasomatic rocks, we distinguish root zones, formed at subore levels of an OMHS under pneumatolytic–hydrothermal conditions with participation of magma-derived fluids, and shallow-seated orebearing propylites and products of argillic alteration, which were formed in an epithermal convective cell with participation of pore solutions and vadose water.

The root anatase–chlorite metasomatic rocks of the Early Cretaceous OMHS replace the Early Cretaceous fluidal potassium rhyolites of the Askol'd Formation in the southern, relatively uplifted block, where the Triassic–Jurassic basement metamorphic rocks are exposed (Fig. 1). Newly formed minerals fill amygdules in the groundmass of rhyolitic porphyry and cavities in silicified porphyries. These minerals are typical of propylitic assemblage (high-Fe chlorite, alkali feldspar) and pegmatites (zircon, anatase, brookite, rutile, Th-bearing REE phosphates). Dispersed grains and nanoparticles of carbonic matter; sulfides; native Ag, Pb, Sn, Bi, Zn, and Cu; and their alloys are noted. Some of these minerals were traced by Kolesnikov (1998) in the ore-bearing aphyric rhyolites of the Askol'd Formation.

The Early and Late Cretaceous rhyolites and deepseated granitoids serve as protoliths for the metasomatic rocks of the Late Cretaceous OMHS. The shallow-seated preore metasomatic rocks, which are spatially conjugated with the older quartz–chlorite–sulfide and quartz–adularia–chlorite orebodies, compose the outer and inner zones of the ore field (Fig. 1). The metasomatic rocks of the outer zone contain newly formed propylitic minerals such as Mn-bearing clinozoisite, Fe-chlorite, calcite, and K-feldspar, as well as dispersed pyrite, chalcopyrite, sphalerite, native silver, and Pband Tl-bearing todorokite. The newly formed minerals of the inner zone comprise Fe-chlorite, Fe-phengite, adularia, dispersed galena, acanthite, native silver, and scorodite. The preore metasomatic rocks of the inner zone are related to the rejuvenation of the hydrothermal system and formation of quartz–rhodonite orebodies. They correspond to allanite–chlorite facies at subore levels and to propylites at near-surface levels. The former are traced in deep-seated granitoids and rhyolites of the Askol'd Formation and contain typical minerals of propylites (Fe-chlorite, alkali feldspar) and

(a)  $2 \text{ cm}$ 2 (b)  $2 \text{ cm}$ 1 2 1 1

**Fig. 3.** (a) Preore metasomatic rock and (b) quartz–rhodonite from the Dukat deposit. (a) Rhombohedral adularias (1), Fe-chlorite (dark), and prismatic quartz (2) fill a lithophysa in fluidal rhyolite; (b) aggregates of rhodonite, quartz, and adularia (1) and aggregates of coarse-grained galena (2).

pegmatites (allanite, fluorite, thorite, carbonates, and REE phosphates), as well as dispersed grains and nanoparticles of sulfides, sulfosalts, and native silver. The shallow-seated propylites contain newly formed spessartine or grossular; Fe-chlorite; high-Ce clinozoisite; adularia; fluorite; collomorph aggregates of cerianite nanoparticles; and Mn hydroxides with admixtures of Pb, Zn, Cu, and Ag.

The study of newly formed minerals in the preore metasomatic rocks showed that the Ca, Fe, and Al contents in chlorites and clinozoisites; the Sr isotope composition of clinozoisite and K-feldspar; and the Pb isotope composition of galena do not depend on the difference in chemical compositions of the protoliths composed of ultrasilicic potassium rhyolilte and less silicic rhyodacite (Filimonova, 2002; Chernyshev et al., 2005). These results suggest that metasomatic minerals, like adularia and galena from orebodies, were precipitated from well-stirred solutions of the magmatic– hydrothermal system.

Newly formed minerals of argillic assemblages are widespread throughout the Dukat ore field. They were formed after uplift and erosion of the ore field when the propylitized ore-bearing sequence was involved in argillic alteration.

Thus, the established relationships of preore metasomatic zones with felsic volcanic rocks are weighty arguments in favor of the formation of high-grade orebodies at the Dukat deposit after accumulation of the entire Cretaceous bimodal volcanic sequence. Younger garnet-bearing metasomatic rocks conjugated with quartz–rhodonite orebodies replace older metasomatic rocks associated with quartz–chlorite–adularia orebodies, thus confirming the two-stage formation of Agbearing orebodies. This is also supported by different contents of Ca, Fe, K, F, Th, P, and REE in gangue minerals from older and younger orebodies and in the newly formed minerals of related metasomatic rocks.

## CHARACTERISTICS OF SAMPLES TAKEN FOR Rb–Sr ISOTOPIC STUDY

Newly formed white rhombohedral adularia crystals were taken from lithophysae in the Early Cretaceous fluidal rhyolites for dating preore metasomatic rocks (Fig. 3a). The milky white and transparent euhedral crystals, up to 1.5–2.0 mm in size, are intergrown with prismatic crystals of transparent quartz and randomly oriented flakes of dark green Fe-chlorite.

Rhodonite grains 0.2–0.3 mm in size with quartz and adularia inclusions were taken for Rb–Sr dating of the younger ore. These grains make up the earliest pinkish orange rhythms of banded quartz–rhodonite orebodies (Fig. 3b). They fringe cockades made up of fragments of early sulfides and host rocks and compose selvages of banded veins. The younger rhythms consist of thin dark bands of silver-bearing sulfosalts and sulfides and thicker bands of comb quartz, carbonates, chlorite, and micas.

The fresh appearance of the analyzed hydrothermal minerals indicates that their Rb–Sr system was not disturbed by secondary processes.

#### DISCUSSION

The results of Rb–Sr studies are presented in the table and Figs. 4 and 5.

In the 87Rb/86Sr–87Sr/86Sr diagram, the data points of adularia from preore metasomatic rocks fit the isochron relationship with a slope corresponding to an age of

Sample	Location			$ Rb, ppm Sr, ppm ^{87}Rb/^{86}Sr $	${}^{87}\mathrm{Sr} / {}^{86}\mathrm{Sr}$	$(87S_r/86S_t$	$\mathbf{M}$ a	SWD
Adularia of preore metasomatic rocks								
1 <sup>b</sup> /86	Left bank of the Iskra River, 800 m upstream from the mouth, 1100 m asl	93.7			$4.06 66.82 \pm 3 $ 0.7880 ± 8 0.7077 ± 3 85 ± 1 0.15			
4/86	Left bank of the Iskra River, 1500 m upstream from the mouth, 950 m asl	511	115		$12.81 \pm 6 \cdot 0.72310 \pm 4$			
12/86	Right bank of the Iskra River, 2000 m from the mouth, 1000 m asl	592	119		$14.46 \pm 7 \mid 0.72506 \pm 3$			
Quartz-rhodonite-adularia aggregates from the younger quartz-rhodonite-rhodochrosite orebodies								
	Dk-419   Ore zone 15, drift 6	2.04			1.58 $3.75 \pm 3 \mid 0.71190 \pm 3 \mid 0.7079 \pm 1 \mid 73 \pm 3 \mid 3$			
	55-1/78 Ore zone 16, drift 22	0.3 <sup>2</sup>	4.7		$0.180 \pm 2 \mid 0.70813 \pm 7$			
	$50-2/87$ Ore zone 15, 450 m from the mouth of drift 6	4.3	6.8		$1.83 \pm 2 \cdot 0.70987 \pm 5$			
3a	Ore zone 8, drift 13	66	22		$8.96 \pm 5 \mid 0.71721 \pm 4$			

Rb–Sr data on minerals from preore metasomatic rocks and quartz–rhodonite–rhodochrosite orebodies at the Dukat deposit

 $85 \pm 1$  Ma:  $(^{87}Sr)^{86}Sr)_0 = 0.7077 \pm 3$  (Fig. 4); MSWD = 0.15. The scatter of experimental data points relative to the calculated regression line is caused only by analytical errors. As was shown above, the newly formed minerals that fill the system of fissures and cavities were formed from homogenized (on the scale of the ore field) hydrothermal solutions. Hence, the isochron parameters calculated for three samples cannot be accidental and should be extrapolated to all adularia associated with Fe-chlorites in metasomatic rocks that are related to the older generation of ore. The calculated age of  $85 \pm 1$  Ma virtually coincides with the Rb–Sr age of the older quartz–chlorite–adularia orebodies  $(84 \pm 1)$ and 86.1  $\pm$  4 Ma). This implies that the hydrothermally altered rocks and precipitation of silver-bearing vein orebodies were related to one impulse of the activity of the ore-forming epithermal system. Furthermore, the similar initial Sr isotope ratios of adularia from orebod-



**Fig. 4.** The Rb–Sr isochron for adularia from the preore metasomatic rocks in the Dukat ore field.

ies  $(0.7079 \pm 4)$  and related metasomatic rocks  $(0.7077 \pm 3)$  indicate that hydrothermal solutions were homogeneous with respect to Sr isotope composition.

The Rb–Sr isotopic data for gangue minerals of quartz–rhodonite orebodies yield an isochron with an age of 73  $\pm$  3 Ma; (<sup>87</sup>Sr/<sup>86</sup>Sr)<sub>0</sub> = 0.7079  $\pm$  2 and  $MSWD = 3$  (Fig. 5). The obtained data are consistent with the geological relationships of these orebodies with the Late Cretaceous volcanic rocks at the western flank of the deposit, as well as with their crosscutting relations with the older quartz–chlorite–adularia orebodies. The Rb–Sr age of the younger orebodies indicates that the rejuvenation of the Dukat hydrothermal system occurred 12 Ma later than the formation of the quartz–chlorite–adularia orebodies.

Thus, the unique silver-bearing orebodies of the Dukat ore field were formed as a result of long-term



**Fig. 5.** The Rb–Sr isochron for quartz–rhodonite–adularia mineral aggregates from the younger quartz–rhodonite orebodies of the Dukat deposit.

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Late Cretaceous hydrothermal activity. The older and younger ores and conjugated propylites were formed 84  $\pm$  1 and 73  $\pm$  3 Ma ago, respectively. The age of argillic alteration developed after propylites remains unclear. Argillic alteration could have been accompanied by redeposition of minerals in high-grade orebodies and formation of local ore shoots of silver-bearing minerals associated with Mn hydroxides.

The similar initial Sr isotope ratios of gangue minerals related to the older and younger orebodies imply a high degree of homogenization of hydrothermal solutions with respect to Sr isotopic composition in the Dukat ore-forming system related to a single, longlived magmatic source.

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