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Fluorite Deposits at Voznesenka in the Khanka Massif, Russia: Geology and Age of Mineralization

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Abstract: A huge fluorite deposit at Voznesenka in the Khanka massif, Far East Russia is concluded to have formed at ca. 450 Ma in Late Ordovician time based on the K-Ar ages for Li-micas in the fluorite ore and greisenized leucogranite within the deposit. This conclusion is inconsistent with the current view of Devonian mineralization that stemmed from widely scattered whole-rock Rb-Sr isotope data for the heterogeneous leucogranite stocks influenced by strong alteration. The Voznesenka and neighboring fluorite deposits may have formed in Cambrian limestone in relation to the intrusion of the Li-F-rich felsic magma which has a similar chemistry to representative Li-F-rich felsic rocks including topaz granite and ongonite or topaz rhyolite; these rocks may be classified as a specific group of highly fractionated felsic magmas.

Biotite granite plutons exposed in the Voznesenka district are divided in age into two groups based on the CHIME age data for zircon, monazite and xenotime: Ordovician and Permian. The Ordovician plutons seem to be coeval to the fluorite deposits and are characterized by F-rich chemistry, reduced nature and association of tin mineralization with the deposition of fluorite and tourmaline. The biotite granite magmas of initially enhanced F contents could have been highly fractionated to form Li-F-rich leucogranite cupolas that provided fluorite deposits within the host limestone. Future prospecting for similar fluorite deposits is to be focused on areas of intersection between Ordovician Li-F-rich granite and Cambrian carbonate sequences.

The Permian granite of southeastern margin of the Grodekovo batholith is characterized by lesser F content, oxidized nature and the lack of tin and fluorite mineralization in contrast to the Ordovician granite. The result of Permian age does not support the current view of Silurian age for the batholith and requires overall chronological reinvestigation in connection with the tectonic history of the Khanka massif because the Grodekovo is a representative of Paleozoic batholiths in Primorie.

Keywords: fluorite deposit, Voznesenka, Khanka massif, Russia, Ordovician, Silurian, Permian, Li-F-rich granite, greisen alteration, Cambrian limestone, K-Ar & CHIME ages, Li-mica, zircon, monazite, xenotime, Grodekovo batholith, metallogeny

1. Introduction

A huge fluorite deposit occurs at Voznesenka near Yaroslavka Village about 120 km north of Vladivostok in Primorie, Far East Russia (Fig. 1). The fluorite deposit was discovered in 1948. It has provided more than 80 per cent of total fluorite production from the former Soviet Union since the beginning of its development in 1964, although recent mining activity has been slow under the difficult economic situation after the collapse of the Soviet system. This deposit is unique in its geology as well as its large size; similar deposit has not been found in the other areas of the Khanka massif, nor in the Mesozoic terranes in Sikhote-Alin.

The Voznesenka fluorite deposit actually consists of three major deposits, Voznesenka, Pogranichny and Lagernoe, and some satellite orebodies (Fig. 3). The largest Voznesenka deposit has been mined by an open-pit method (Fig. 4), though recent mine operation shifted to the Pogranichny deposit from 1998. Thus this district is often called as "Voznesenka Ore District (VOD)" in the Russian literatures after the name of the leading deposit (Ryazantseva, 1998). Major fluorite deposits are hosted in Cambrian limestone close to greisenized leucogranite stocks, and are locally accompanied by Zn-rich skarns, suggesting a close genetic relation to granitoid magmatism.

Age and genesis of the fluorite mineralization have been controversial. Age of the mineralization has been considered to be Devonian on the basis of Rb-Sr ages of 384 Ma or 399 Ma which were obtained for the greisenized leucogranite stocks in the Voznesenka and Pogranichny deposits (Ryazantseva and Gerasimov, 1993; Rub and Rub, 1994; Ryazantseva et al., 1995). Devonian age is significantly younger than the ages of other granitoid plutons in this district which are considered to be Ordovician to Silurian. If these age estimates are correct, the leucogranite intrusions accompanied by the fluorite mineralization may be independent from the Ordovician to Silurian granitoid activity. After the field and preliminary laboratory works, however, we felt that this scenario is to be reviewed based on additional and reliable age data, in consideration of the fact that the older granitoids are partly rich in fluorine, suggesting a possible genetic link to fluorite mineralization, and they are not very good for conventional age dating due to strong weathering. This district is very poor in topographic relief and outcrop, and granitoids on the surface are strongly weathered and sometimes easily broken to sandy materials. Therefore, careful selection of samples and dating techniques are essential for more reliable age data.

As to the source of fluorine, the unusually large volume of the fluorite ores in comparison with small size of the leucogranite stocks attracted attention of some Russian geologists and led them to a two stage model, in which primary stratiform deposits in the Cambrian carbonate sediments or fluorite deposits in the Precambrian basement were remobilized and concentrated to the present position through a magma-hydrothermal system caused by the Devonian granite magmatism (Androsov and Ratkin, 1990; Khanchuk et al., 1996; Ryazantseva, 1998). However, no definite evidence of such primary mineralization has been presented. It is important to note that this model is influenced by the idea that the leucogranite stocks are independent from the large granite plutons exposed on the surface. If they are apical parts of a large batholith enriched in fluorine, the point of too small size of the ore-forming intrusion may be eliminated from the discussion.

As mentioned above, it is very difficult to collect fresh samples on the surface except for the openpit mine. Fortunately, Li-rich mica (Li-mica hereafter) occurs as a ubiquitous and dominant K-bearing mineral not only in the greisenized granite but also in the fluorite ores. This mineral may be the best material for K-Ar dating and is expected to give directly the age of mineralization because subsequent magmatic or thermal event that can disturb K-Ar system seems to be insignificant in this district. We selected two fresh samples collected from the Voznesenka openpit mine: one from the greisenized granite and another from the fluorite ore,

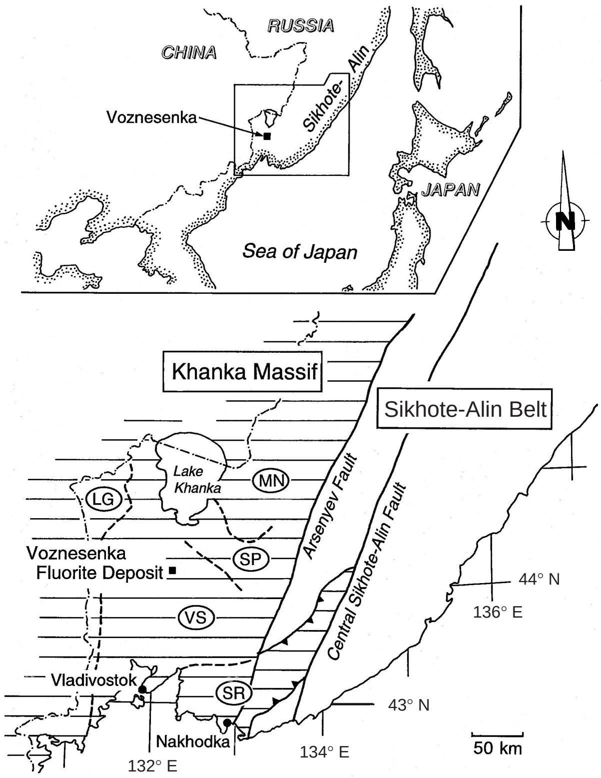

Fig. 1 Map showing location of the Voznesenka fluorite deposit and tectonic division of Primorie, Far East Russia, modified from Khanchuk et al. (1996). Khanka massif is a Precambrian-Paleozoic continental block, which is divided into five tectonostratigraphic subdivisions: Matveevka-Nakhimovka (MN), Spassk (SP), Voznesenka (VS), Sergeevka (SR) and Laoelin-Grodekov (LG) terranes. Sikhote-Alin Belt consists of Jurassic-Early Cretaceous accretionary complexes, Cretaceous turbidite basin deposits, and Cretaceous-Paleogene arc volcanic and plutonic rocks. Eastern Sergeeka terrane to the northeast of Nakhodka is a nappe on a Jurassic accretionary complex within the Sikhote-Alin Belt. Refer to Sato et al. (1993) for details.

and extracted mica concentrates from them. The two samples gave practically the same ages of about 450 Ma, indicating that the fluorite mineralization occurred in Late Ordovician time, in contrast to the current opinion of the Devonian mineralization.

In order to study the genetic link between the mineralization and granitoid activity, we also examined age of granitoids using the CHIME method (Chemical Th-U-total Pb isochron method) which can give reliable and primary magmatic ages even for altered or weathered samples (e.g., Suzuki and Adachi, 1991; Suzuki et al., 1991, 1999). The CHIME data suggest that the examined granitoid plutons in this district are divided into two groups by age, Ordovician and Permian; the former group may have been related to the fluorite min-

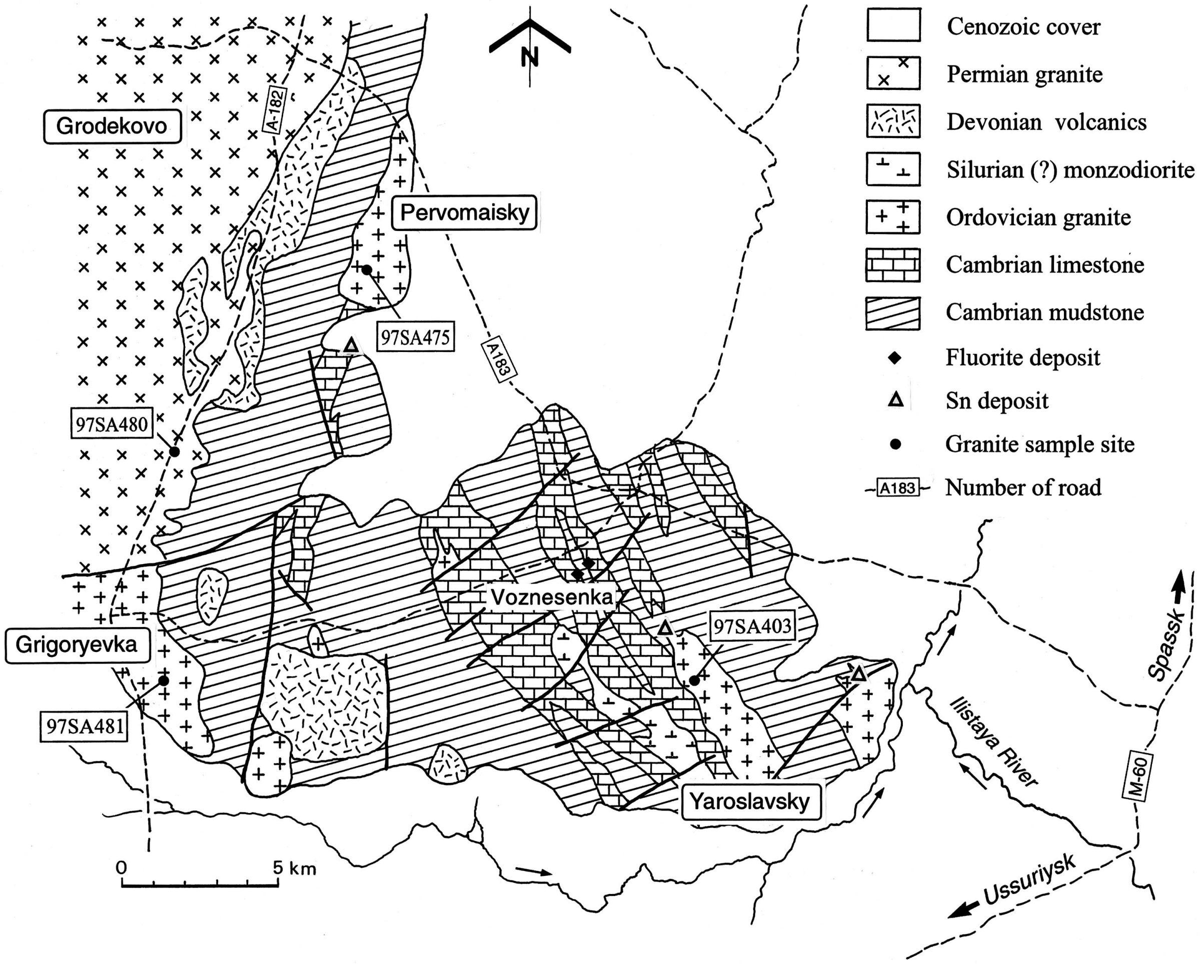

Fig. 2 Geologic map of the Voznesenka district, compiled from Ryazantseva et al. (1995), Kupriyanova and Shpanov (1996), Ryazantseva (1998) and this study.

eralization.

In this paper, we describe the outline of geology of the fluorite deposits and the surrounding area and the results of age dating with some discussions on the genetic relation between granitoids and fluorite deposits.

2. Outline of Geology

2.1. Geology of the Khanka massif

The Khanka massif is a Paleozoic continental block which is composed of Proterozoic to Early Paleozoic metamorphic rocks, Paleozoic sedimentary and volcanic sequences and granitoids (Khanchuk et al., 1996). This massif within Primorie is thought to be an accreted terrane of at least four sub-terranes of different geodynamic origin: Matveevka-Nakhimova (MN), Spassk (SP), Voznesenka (VZ) and Sergeevka (SR) terranes from north to south, and Laoelin-Grodekov (LG) terrane near China border (Fig. 1). These sub-terranes are thought to have amalgamated in the Late Silurian, but their relations need further studies because wide areas are covered by Mesozoic and Cenozoic sedimentary and volcanic sequences.

The Voznesenka fluorite deposit occurs in the Voznesenka sub-terrane, which is characterized by Lower Cambrian terrigenous and carbonate sediments of continental shelf origin (Khanchuk et al., 1996). The Lower Cambrian strata of 500–1,000 m thick have been distinguished, but any Precambrian crystalline basement is not seen in this sub-terrane. Granitoids in the Voznesenka sub-terrane are thought to be various in age from Ordovician to Permian. Devonian to Permian continental deposits and volcanic rocks of bimodal composition unconformably cover the Silurian and older units in the Voznesenka and its neighboring sub-terranes, suggesting a similarity in their geodynamic history in Late Paleozoic since the Silurian amalgamation.

2.2. Geology of the Voznesenka district

Geology around the Voznesenka deposit is shown in Figure 2. The area shown in the map is named the Voznesenka district in this paper. This district consists mainly of Cambrian sedimentary sequences and Paleozoic granitoids and volcanic rocks, but their exposures, if any, are limited in relatively high areas (100–300 m above sea level). Lowlands are totally covered by young sediments and soil.

2.2.1. Sedimentary sequences: Cambrian strata are composed of limestone, dolomite, slate and sandstone which may have been deposited in shallow marine environments on a continental shelf. Fossils of *algae* and *archaeocyathids* from carbonate sediments indicate the age of deposition to be Early Cambrian (Ryazantseva, 1998). The Lower Cambrian strata are strongly folded with axes of NW-SE direction, showing nearly vertical dips in the Voznesenka deposit (Fig. 3), and are intruded by granitic plutons and locally by dioritic plutons (Fig. 2).

2.2.2. Granitic plutons: Characteristics of the granitoid plutons and associated mineralization in the Voznesenka district are summarized in Table 1 together with the results of our field and laboratory observations and age dating. The followings are brief descriptions for major plutons, based mainly on Ryazantseva (1998), Ryazantseva et al. (1995), Rub and Rub (1994), Khetchikov et al. (1996) and Khanchuk et al. (1996).

1) Ordovician biotite granite: Yaroslavsky, Pervomaisky and Chikheza River plutons consist of medium to coarse-grained biotite granite (~72–74 % SiO_2). The reported Rb-Sr whole-rock ages and initial Sr ratios (Sr_0) are as follows; 408 ±47 Ma with Sr_0 of 0.714 for Yaroslavsky, 451±20 Ma with Sr_0 of 0.720 for Pervomaisky and 452±4 Ma with Sr_0 of 0.707 for Chikheza River plutons (Ryazantseva and Gerasimov, 1993; Ryazantseva et al., 1995). This group of granite is practically free of magnetite; the Yaroslavsky and Pervomaisky plutons were confirmed to show very low magnetic susceptibility values less than 0.2×10^{-3} SI during our field work. These plutons are also characterized by the common occurrence of tourmaline-bearing pegmatite pockets and fluorite-tourmaline veinlets (Fig. 5C). They are accompanied by small tin deposits near the contacts with the host Lower Cambrian sediments (Fig. 2). The cassiterite-bearing quartz veins are also enriched in tourmaline and fluorite, and are occasionally accompanied by beryl and wolframite (Ryazantseva, 1998). The veins in limestone are accompanied by skarn alteration. Unfortunately, it is difficult to examine details because the mines were shut down many years ago and the old workings are under water.

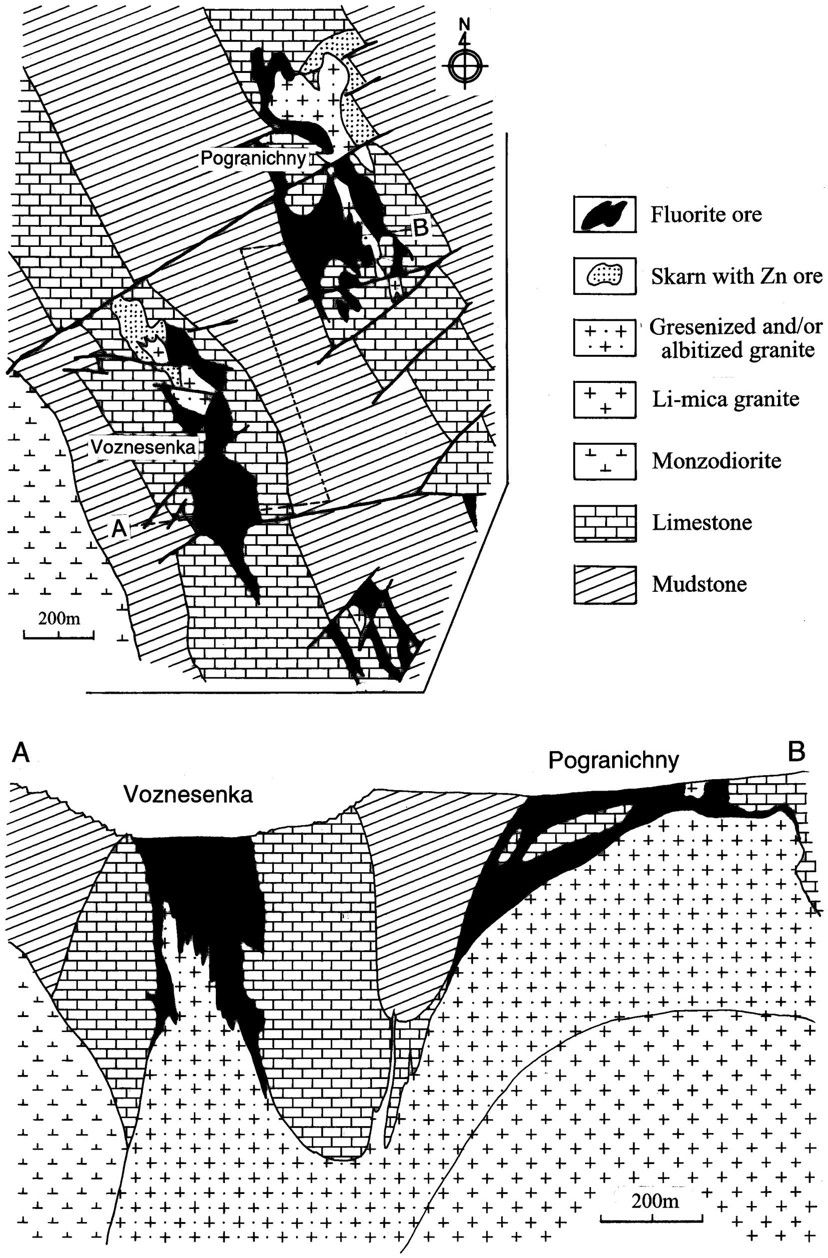

Fig. 3 Geologic map and vertical section showing the mode of occurrence of fluorite ore, Zn-skarn and greisenized granite in the Voznesenka openpit mine and Pogranichny deposit, simplified from Rub and Rub (1994) and Ryazantseva (1998).

Table 1 Summary table for granitoid plutons and associated mineralization in the Voznesenka district.

Name of pluton	Major rock facies (Representative SiO_2 content)	Characteristic accessory mineral	Current age (Rb-Sr age*)	CHIME and K-Ar ages (Sample No.)	Magnetic suscepti-bility**	Associated mineralization (Name of deposit)
Chikheza River***	Biotite granite (74 %)	Tourmaline,	Ordovician (452Ma[3)])			Sn-W qz vein (Chapaevka)
Yaroslavsky	Biotite granite (72 %)	Tourmaline, Fluorite	Ordovician (408Ma[3)])	451±27Ma (97SA403)	0.05–0.1	Sn qz vein with tourmaline fluorite, sulfides and skarns (Yaroslavsky)
Pervomaisky	Biotite granite (72 %)	Tourmaline, Fluorite	Ordovician (451Ma[3)])	439±14Ma (97SA475)	0.05–0.2	Sn qz vein with tourmaline, fluorite and sulfides (Pervomaisky)
Grigorievka	Biotite granite	Fluorite	Devonian (396Ma[3)])	432±24Ma (97SA481)	0.05–1.0	
Voznesenka	Leucogranite (greisenized) (71 %)	Li-mica, Topaz, Fluorite, Columbite, Struverite, Cassiterite	Devonian (441Ma[3)]) (399Ma[4)])	450±11Ma (97SA19a)	<0.1	Fluorite, limestone replacement, with Zn skarn (Voznesenka), 453±11Ma (K-Ar Li-mica)[1)]
Pogranichny	Leucogranite (greisenized) (75 %)	Same as above	Devonian (384Ma[3)]) (399Ma[4)])		<0.1	Fluorite, limestone replacement (Pogranichny)
Grodekovo	Biotite granite (74 %)	Magnetite	Silurian (411Ma[3)])	250±12Ma (97SA480)	0.1–4.0	Fe, Cu-Pb-Zn skarn occurrences
Moskalenkovsky	Monzodiorite (50 %)		Silurian (415Ma[3)])		0.5–0.9	
Data source	2, 3	1, 2, 3, 4	2, 3, 4	1	1	1, 2

*: See text for error and other details; **: Measurement on least weathered outcrops by means of a Kappa Meter KT5 (× 10^{-3}SI)
***: Exposed to the east of Yaroslavsky pluton in Figure 2.
Data source: 1) This study, 2) Ryazantseva (1998), 3) Ryazantseva et al. (1995), 4) Rub and Rub (1994).

Grigorievka pluton was thought to be Permian in age until 1980's. Ryazantseva et al. (1995) reported a Rb-Sr whole-rock age of 396±7 Ma with Sr_0 of 0.709 and identified its age as Devonian. We rather consider that this pluton may also belong to the same group as the Ordovician biotite granite mentioned above, judging from similar petrochemical features especially the occurrence of accessory fluorite and our own age determination (Table 1), although association of tin mineralization is not known.

2) Leucogranite in the fluorite deposits: Small stocks of greisenized leucogranite occur in the major fluorite deposits (Figs. 3 and 4B). Their close spatial relationships with the fluorite ores clearly indicate that the mineralization was related to the intrusion and subsequent greisenization. The intrusion and mineralization have been thought to be Devonian in age (e.g., Rub and Rub, 1994; Ryazantseva et al., 1995), but our study indicates that they are Ordovician in age, probably coeval with the group of Ordovician biotite granite described above (Table 1). Deep drillings (down to 1,200 m) have revealed that the stocks in the Voznesenka and Pogranichny deposits are apical parts of a single leucogranite pluton which is characterized by a Li-F-rich chemistry (Fig. 3). Russian literatures described "protolithionite" granite in the deep levels and variably greisenized and/or albitized granite in the shallower levels (Rub and Rub, 1994; Ryazantseva, 1998). "Protolithionite" is a special name for a Li-mica which has intermediate compositions between siderophyllite and zinnwaldite (Fig. 6) and shows a pleochroism of light brown to pale yellow color in thin sections (Rub and Rub, 1994). They consider that "protolithionite" is a magmatic phase, while Li-mica dated here is a product of greisen alteration. In any case, it should be noted that the stocks are significantly heterogeneous; the heterogeneity may be at least partly due to subsolidus alteration including greisenization and albitization. Chemical analyses of drill cores from the Pogranichny stock to a depth of 1,200 m show a remarkable enrichment of F, Rb, Nb, Ta and Cs toward the top of the intrusive body (Rub and Rub, 1994). F is present mainly in topaz, fluorite and micas. Nb and Ta occur as columbite, tantalite and struverite. Rb and Cs exist mainly in micas as Li does. Other accessory minerals reported from the stocks are apatite, zircon xenotime and cassiterite (Ryazantseva, 1998). Granites like these stocks with enhanced rare-metal contents are often called "rare-metal granite" (e.g., Rub and Rub, 1994).

3) Grodekovo batholith: The Grodekovo batholith is one of the largest batholiths in Primorie; the total exposure exceeds 3,000 km^2. The exposure in the Voznesenka district is its eastern end, which intrudes the Early Cambrian strata (Fig. 2). The exposure extends for more than 50 km to the area near China border, where the batholith intrudes Silurian strata. Khanchuk et al. (1996) indicated that the Grodekovo batholith intrudes Lower Silurian strata and is overlain by Devonian sequences. They thought the batholith to be a Late Silurian collision-related granitoid complex emplaced during the amalgamation of sub-terranes within the Khanka massif. Ryazantseva et al. (1995) reported a Rb-Sr whole-rock age of 411±14 Ma with Sr_0 of 0.707 using four granite samples collected in the Voznesenka district. On the contrary, our CHIME data for a granite sample collected near the Rb-Sr sample sites shows an age of Late Permian to Triassic (250±12 Ma) as described later (Fig. 7).

The Grodekovo batholith consists mainly of medium to coarse-grained biotite granite (~70–75 % SiO_2) and is characterized by high alkali content (Na_2O+K_2O = 7.5–10.6 %) and peraluminous chemistry (Ryazantseva, 1998). Less silicic rocks near the margin contain hornblende. Xenoliths of metamorphosed wall rocks are common and often show gradational transition to gneissose granite, suggesting significant involvement of metamorphic rocks in the generation of granite magmas. Minor occurrences of Fe and base-metal bearing skarns are locally associated with this batholith.

4) Other plutons, dikes and volcanic rocks: Moskalenkovsky monzodioritic pluton is exposed in the central part of the map area (Fig. 2). This pluton is not accompanied by mineralization, and its detailed petrographical data have not been available. It is also thought to be Silurian in age (Ryazantseva, 1998), based on a Rb-Sr whole-rock age of 415±48 Ma. A small gabbroic body near the southeastern end of the Yaroslavka pluton was also dated by Rb-Sr method at 559±87 Ma (Ryazantseva et al. 1995). The large errors for these mafic plutons preclude a definite idea about the real age of intrusion. We also tried to apply the CHIME method to the Moskalenkovsky pluton, but could not obtain any reliable age data because of very low Pb contents.

Another mafic igneous rock unit to be noted here may be dark-colored dikes. Many dark-colored dikes of basaltic composition occur in the Voznesenka openpit mine without any systematic orientation (Rub and Rub, 1994). Abundant occurrences of the dikes have attracted attention and their bearing on the fluorite mineralization has been discussed. They are classified into three groups: (1) pre-ore, (2) syn-ore and (3) post-ore dikes (e.g., Kupriyanova and Shpanov, 1996). So far as our observation is concerned, however, all the basaltic dikes cut fluorite orebodies with chilled margins along the intrusive contacts. We consider that the basaltic dikes are younger than the fluorite deposit and do not have any direct connection with the mineralization. Similar dikes without any fluorite mineralization were observed in a limestone outcrop about 7 km southeast of the Voznesenka mine, implying an independence of the basaltic dikes from the mineralization.

Felsic igneous rocks which are not mentioned above are rhyolitic volcanic rocks and minor granite porphyry stocks; the former was dated at 379±56 Ma by Rb-Sr method (Ryazantseva et al., 1995). Their detailed petrography, age and relation with fluorite mineralization are not known.

2.3. *Geology of the fluorite deposits*

The Voznesenka deposit actually consists of three major fluorite deposits: Voznesenka, Pogranichny and Lagernoe with some satellite orebodies. The fluorite deposits occur in limestone within the Early Cambrian Volkushino Formation, near the greisenized leucogranite stocks which may be apical parts of a single pluton of Li-mica granite (Fig. 3).

Mode of occurrence of the leucogranite stock and surrounding fluorite deposit are well observed in the Voznesenka openpit mine. The size of the pit is about 1.4 km NS, 0.8 km EW in its margin, and the pit bottom is about 200 m below the surface (Fig. 4A). The fluorite deposit shows, as a whole, a nearly vertical and thick lenticular shape of about 1,200 m × 500 m extending in accordance with the host limestone structure and the deposit is centered by the leucogranite stock (Fig. 3). Vertical extension exceeds 400 m (Ryazantseva, 1998); the upper part was eroded away. The leucogranite stock is exposed in the northern part of the pit, where sphalerite-rich clinopyroxene skarn, as well as fluorite ore, is closely associated (Fig. 4B). The stock is actually heterogeneous and strongly greisenized; it is partly pegmatitic and cut by many quartz veins and quartz-albite-topaz veins which commonly contain Li-mica, sericite and fluorite, suggesting successive process of magmatic and multistage hydrothermal activities. Fluorite, topaz and Li-mica are common in the greizenized matrix as well as in the veins. Sulfide minerals are scarce; minor amounts of arsenopyrite, pyrite and sphalerite were identified, and molybdenite veinlets were also observed. Rub and Rub (1994) reported the occurrence of Nb-Ta minerals such as columbite and tantalite in the Voznesenka and Pogranichny stocks.

Fluorite ores are composed mainly of fluorite with lesser amounts of Li-mica, sericite, albite, quartz, calcite and rarely colorless tourmaline, pyrite, arsenopyrite and sphalerite. Be-minerals such as phenakite and chrysoberyl also occur and BeO contents of the ores are generally less than 1 wt%, though CaF_2 contents are 31–52 wt% (Kupriyanova and Shpanov, 1996, 1997). The fluorite ores show purple or black color. The dark color may be partly due to the presence of remnant graphite originated from the host limestone rich in carbonaceous matter. Texture of the ores is various; massive, banded and brecciated. The boundary between the ores and

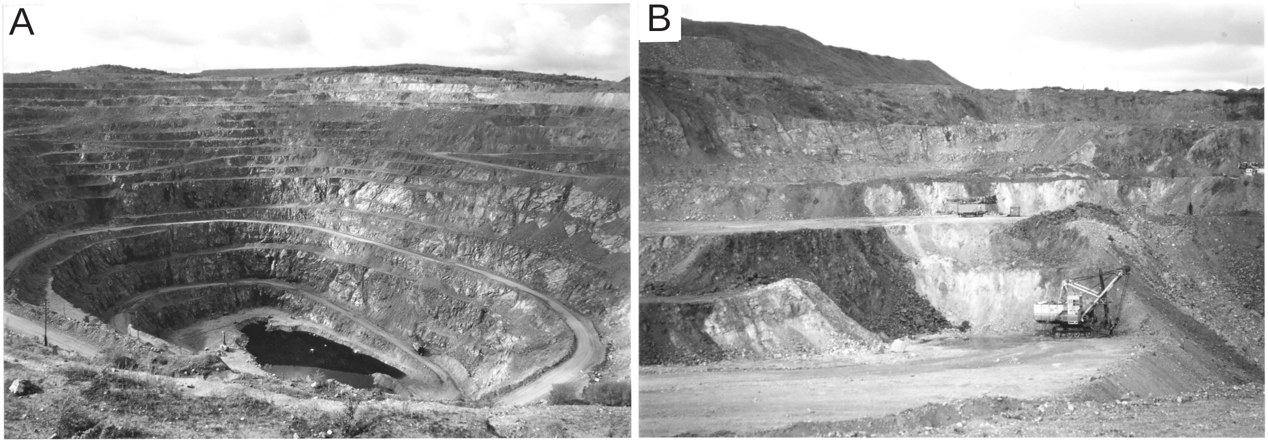

Fig. 4 Photographs of the Voznesenka mine.
A) Panorama view of southern part of the Voznesenka openpit, looking southwest; B) Leucogranite stock (white) accompanied by Zn-rich skarn (black) and fluorite ore (gray) in northern part of the Voznesenka openpit. Both taken in October, 1994.

limestone is sometimes called "fluoritized limestone" (Ryazantseva, 1998), which is a transitional replacement zone where veins of fluorite ores occur in limestone, but the discrimination of ore from limestone is sometimes difficult in the field when they are compact and black in color.

3. Age of Fluorite Mineralization and Granitoid Magmatism

Age of fluorite mineralization can be determined by K-Ar dating on Li-mica which may be the best mineral due to its ubiquitous occurrence in the fluorite ores as well as in the greisenized leucogranite as an essential constituent. On the other hand, K-Ar and other conventional radiometric method seems to be hopeless or unreliable for granitoids from natural outcrops because of strong weathering; we could not find any fresh granitoid sample during our field work in 1994 and 1997. CHIME method applied here is a powerful tool even for altered or weathered samples due to high retentivity of U-Pb-Th system in zircon and monazite (e.g., Suzuki et al., 1991).

3.1. K-Ar dating

3.1.1. Sample and method: Two representative samples were selected for K-Ar dating among many samples collected from the Voznesenka openpit mine. Both samples are quite fresh and practically free of weathering.

94SA19a: This sample was collected from the small leucogranite stock which is exposed in northern part of the pit and surrounded by Zn-rich skarns and fluorite ores (Fig. 4B). As described already, the leucogranite is an apophysis of a large pluton beneath the Voznesenka and Pogranichny deposits (Fig. 3) and is actually heterogeneous and strongly greisenized. The dated sample is a relatively homogeneous and medium-grained rock composed mainly of quartz, albite, K-feldspar, Li-mica, topaz and fluorite with microscopic amounts of sphalerite, pyrite, arsenopyrite and molybdenite (Fig. 5A). Li-mica is observed in thin sections as clear colorless crystals of 0.01–2 mm without apparent secondary alteration; the mineral was misidentified as muscovite in the initial stage of our study.

94SA25a: This sample is a representative high-grade fluorite ore collected in the bottom of the pit center where fluorite ores replace host Cambrian limestone. It shows a brecciated texture; deep purplish fluorite aggregates are cemented by pale greenish to white rock composed of fluorite, topaz, Li-mica, sericite, albite, quartz and minor amounts of sulfides including sphalerite, arsenopyrite and pyrite. Sericite defined here occurs as fine-grained muscovite of 10–50 μm or less and shows X-ray diffraction pattern corresponding to the $2M_1$ type. Mica for age dating was extracted from a monomineralic band which is composed mostly of coarse grained and colorless Li-mica (0.5–1.5 cm) with minor amounts of albite, sericite, fluorite sphalerite and arsenopyrite (Fig. 5B); the mica was also misidentified as muscovite because of its colorless feature in the initial stage.

Li-mica concentrates of 60–80 mesh were prepared by the conventional technique using magnetic separator and heavy liquid with the examination by X-ray powder diffraction. Possible contaminants within the concentrates were estimated under the binocular to be less than 1 per cent in volume. Chemical analyses of the dated specimens by microprobe and wet chemical methods are shown in Table 2 and are illustrated in Figure 6. The two specimens have similar compositions close to the boundary between lepidolite and zinnwaldite, and they are simply named as Li-mica in this paper. K-Ar dating

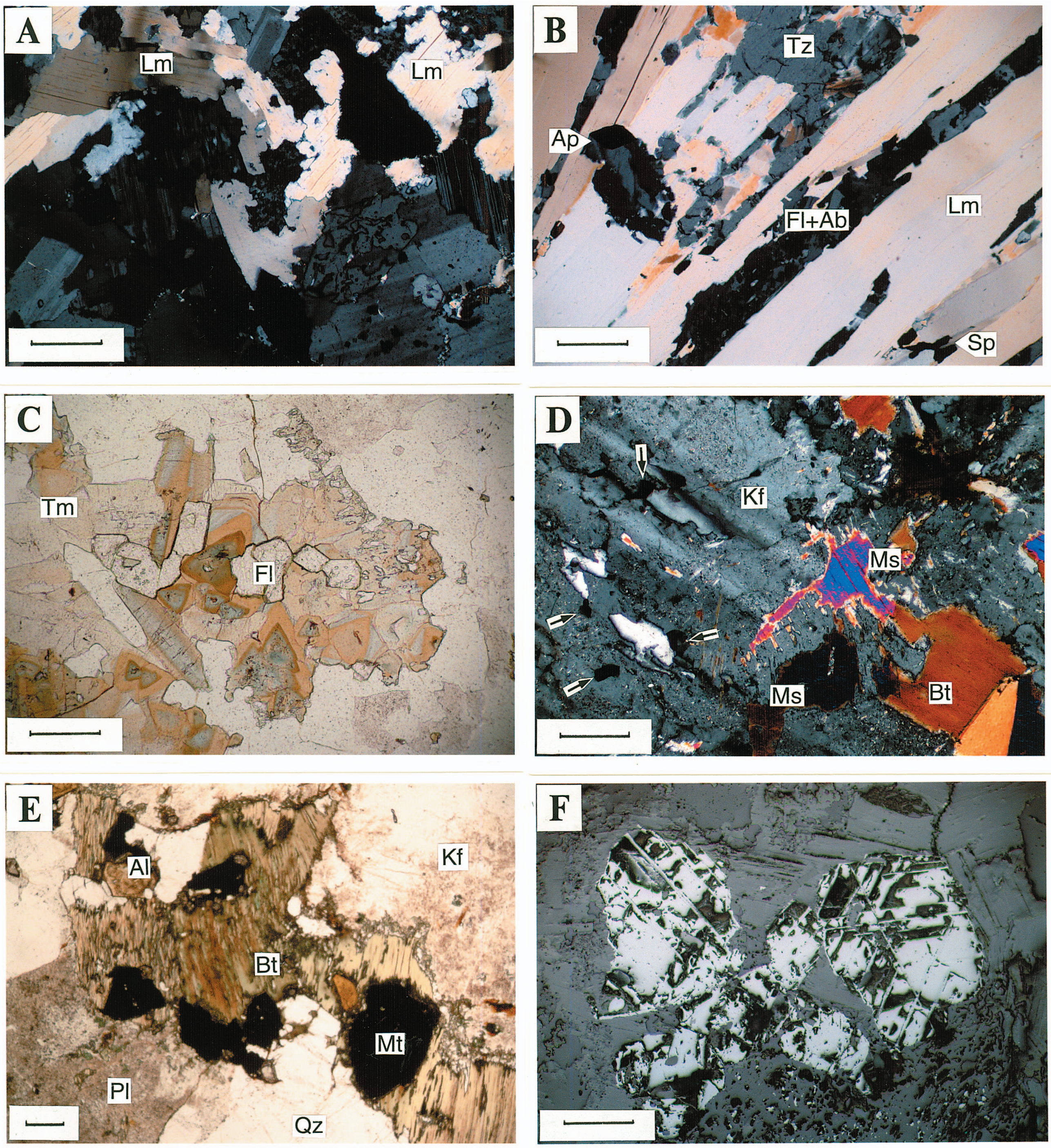

Fig. 5 Microphotographs of studied specimens.

A) Greisenized leucogranite from the Voznesenka stock (94SA19a). Li-mica (light, Lm) coexists with albite, K-feldspar, quartz, fluorite and topaz (dark); B) Fluorite ore rich in Li-mica (Lm) from the Voznesenka deposit (94SA25a); C) Biotite granite with fluorite (Fl)-tourmaline (Tm) veinlets (97SA398), from the same quarry in Yaroslavsky pluton as 97SA403; D) Two-mica granite with abundant accessory fluorite (arrow) from Pervomaisky pluton (97SA475); E) Biotite granite from Grodekovo batholith (97SA480); F) Magnetite grains with ilmenite lamellae in 97SA480, partly replaced by chlorite. A, B and D were taken by transmitted light with crossed polars, while C and E with polarizer only. F was taken by reflected light. Scale bar is 0.2 mm. Mineral abbreviations: Ab, albite; Al, allanite; Ap, arsenopyrite; Bt, biotite; Fl, fluorite; Kf, K-feldspar; Lm, Li-mica; Ms, muscovite; Mt, magnetite; Pl, plagioclase; Qz, quartz; Sp, sphalerite; Tm, tourmaline; Tz, topaz.

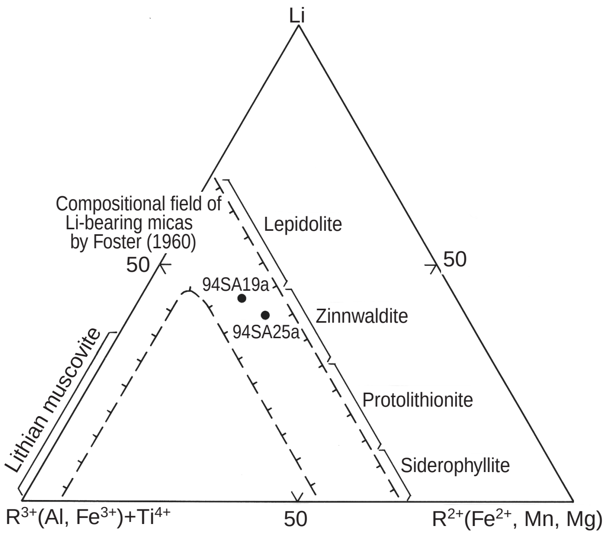

Fig. 6 Relation between Li, R^{2+}(Fe^{2+}, Mn, Mg) and octahedral R^{3+} (Al, Fe^{3+}) +Ti^{4+} for dated Li-micas from the Voznesenka fluorite deposit, Primorie. Compositional field and nomenclatures of Li-bearing micas are after Foster (1960). Protolithionite is an old term corresponding to ferroan zinnwaldite and lithian siderophyllite (Stone et al., 1988; Rieder et al., 1998).

was made at the Teledyne Isotope Labs, New Jersey, U.S.A. Constants for age calculation are $\lambda_\beta = 4.962 \times 10^{-10}$/y, $\lambda_e = 0.58110^{-10}$/y, $^{40}K/K = 0.01167$ atomic % (Steiger and Jäger, 1977). Errors are presented conservatively as 2.5 %.

3.1.2. Results: Results of K-Ar dating for the Li-micas are shown in Table 3. The two samples, greisenized granite and fluorite ore, gave practically identical ages of about 450 Ma, indicating a clear genetic link between the two. It is concluded, in contrast to the previous opinions of Devonian mineralization, that the Voznesenka deposit was formed in Ordovician time. As described below, this age is concordant with the CHIME age of major biotite granite plutons in this district, suggesting a genetic link between the granite activity and fluorite mineralization.

3.2. CHIME age dating

3.2.1. Sample and method: Representative and least weathered samples were selected for five granitoid plutons (Fig. 2). Ages of the four granitic plutons were determined, but a specimen from the Moskalenovsky monzodioritic pluton did not give any reliable age because of the paucity of lead. Followings are brief descriptions of the dated specimens.

97SA403: Coarse-grained biotite granite from the Yaroslavsky pluton. This is one of the least weathered samples collected in an old quarry near the top of Kamennaya Hill, where tourmaline in association with

Table 2 Chemical composition of dated Li-micas.

No.	94SA19a	94SA25a
SiO_2	49.00	49.19
TiO_2	0.08	0.03
Al_2O_3	20.00	19.97
Fe_2O_3	1.99	1.29
FeO	8.13	6.78
MnO	0.79	0.79
MgO	0.04	2.59
CaO	0.01	0.01
Na_2O	0.14	0.15
K_2O	10.04	9.86
Li_2O	4.48	4.13
Rb_2O	0.951	1.039
Cs_2O	0.025	0.025
F	4.94	4.79
Cl	0.00	0.00
Total	100.61	100.65
-O=F	2.08	2.02
Total	98.53	98.63
Formulas on the basis of 22 oxygen atoms		
Si	6.775	6.743
Al^{IV}	1.225	1.257
Al^{VI}	2.034	1.970
Ti	0.008	0.003
Fe^{3+}	0.207	0.133
Fe^{2+}	0.940	0.777
Mn	0.093	0.092
Mg	0.008	0.529
Li	2.489	2.279
Ca	0.001	0.001
Na	0.038	0.040
K	1.771	1.724
Rb	0.085	0.092
Cs	0.001	0.001
F	2.160	2.077
L atomic%	43.07	39.40
A atomic%	38.92	36.42
M atomic%	18.01	24.18

L = Li; A = R^{3+}(Al, Fe^{3+})+Ti^{4+}; M = Fe^{2+}+Mn+Mg
Analytical method: Electron microprobe for Si, Ti, Al, total Fe, Mn, Mg, Ca, Na, K, F. The results are averaged analyses on six and four spots of 94SA19a and 94SA25a, respectively. Other elements were analyzed by wet chemical methods; titrimetry for FeO, atomic absorption spectrometry for Li and Rb, and flame emission spectrometry for Cs.

Table 3 K-Ar age data for Li-micas from the Voznesenka fluorite deposit.

Sample No.	Rock	K (%)	Rad.^{40}Ar (scc/g×10^{-5})	Atm.^{40}Ar (%)	Age (Ma)
94SA19a	Leuco-	7.99	15.9	2.9	451±11
	granite	7.96	15.8	2.9	449±11
					450±11(av.)
94SA25a	Fluorite	8.20	16.4	3.9	453±11
	ore	8.20	16.4	3.9	453±11
					453±11(av.)

λ_β=4.962×10^{-10}/y, λ_e=0.58110^{-10}/y, ^{40}K/K=0.01167 atomic%

fluorite commonly occur as veinlets or pegmatites (Fig. 5C). This sample contains accessory fluorite but tourmaline is not seen under the microscope. About half of biotite is altered to chlorite, and plagioclase especially its core is replaced by sericite. Zircon (<100 µm) is a minor accessory mineral. Ilmenite (<50 µm) rarely occurs in biotite, but magnetite was not observed.

97SA475: Medium-grained muscovite-bearing biotite granite from the Pervomaisky pluton. The area of this pluton is a flat grassland without bedrock exposure, and the samples were collected from boulders. The specimen has a porphyritic texture due to K-feldspar phenocryst of up to 3 cm. Biotite and plagioclase are relatively fresh. Accessory fluorite up to 100 µm occurs in plagioclase and K-feldspar and at grain boundaries of major constituent minerals (Fig. 5D). Tourmaline is not observed though common in other samples from the same pluton. Ilmenite (<100 µm) rarely occurs in biotite, but magnetite was not identified. Zircon and monazite occur as minor accessory minerals (<100 µm).

97SA480: The specimen was collected at a road cut about 5 km north of Grigoryevka Village, where coarse-grained biotite granite of the southeastern margin of the Grodekovo batholith is exposed (Fig. 2). In contrast to the other plutons which show very low magnetic susceptibility values less than 0.3×10^{-3} SI, this outcrops and surrounding boulders sometimes show weakly magnetic values up to 4.0×10^{-3} SI, though weathered parts of reddish brown color show very low values ($0.1–1.0 \times 10^{-3}$ SI). Tourmaline was not seen in the sample site. The dated specimen is the least weathered biotite granite showing the highest magnetic susceptibility value. It is characterized by pinkish K-feldspar, and contains minor amounts of hornblende. Opaque oxides occur in association with biotite (Fig. 5E). They are mostly magnetite (<500 µm) with ilmenite lamellae and often replaced by chlorite (Fig. 5F), suggesting initially high magnetic susceptibility before alteration and weathering. Biotite is strongly altered, being replaced by chlorite with lesser amount of epidote, sphene and clay minerals. Zircon (<100 µm) and allanite (up to 500 µm) are common accessory minerals. Double zoning is occasionally seen in zircon grains even under the microscope.

97SA481: Medium-grained biotite granite of the Grigoryevka pluton was collected from a quarry about 3 km southeast of Grigoryevka Village, where outcrops and boulders generally show reddish brown color due to alteration and weathering. Abundant fractures and faults are conspicuous, and they appear to be related with alteration. The dated specimen is the least weathered gray color rock showing magnetic susceptibility values of about 1.0×10^{-3} SI, slightly higher than the reddish brown rocks ($<0.2 \times 10^{-3}$ SI). Biotite is almost completely altered to chlorite and dusty opaque material. Accessory fluorite up to 500 µm is common, though tourmaline is not observed. Ilmenite (<150 µm) rarely occurs in biotite, but magnetite was not visible under the microscope.

Polished thin sections were prepared for electron microprobe analysis (EPMA) of zircon, monazite, xenotime and thorite. The analysis was carried out at Nagoya University using a JEOL JXA-733 microprobe analyzer equipped with four wavelength-dispersive spectrometers. Operating conditions were accelerating voltage of 15 kV, electron beam current of 0.3 µA and beam diameter of 5 µm. The detection limit of ThO_2, UO_2 and PbO at a 2σ confidence level are 0.015, 0.02 and 0.005 wt%, respectively. The relative errors in the ThO_2 and UO_2 determinations are 20, 10, 5, 3 and 1 % at 0.1, 0.3, 4 and >8 wt% levels, respectively. The relative errors in the PbO determination are 30, 10, 5 and 3 % at 0.02, 0.1, 0.2 and 0.4 wt% levels, respectively. Details of sample preparation and analytical procedures have been described in Suzuki and Adachi (1991, 1998) and in Suzuki et al. (1999).

3.2.2. Results: Results of CHIME age dating are summarized in Figure 7. In consideration of microscopic texture, chemical and chronological homogeneity, individual analyses are classified into three groups; compositions of inherited core, primary magmatic compositions and compositions of secondary growth or recrystallization. The isochron ages for the primary magmatic compositions of zircon, monazite and xenotime in the examined four plutons are clearly divided into two groups; (1) Late Ordovician to Early Silurian (ca. 451–432 Ma) and (2) Late Permian to Early Triassic (ca. 250 Ma). The ages do not show any clear correlation with mineral assemblages of major constituents nor degree of secondary alteration, but the above two groups appear to be correlated with the characteristics of accessory minerals (Table 1). That is, the older group plutons, Yaroslavsky, Pervomaisky and Grigoryevka, are characterized by the common occurrence of fluorite and tourmaline in contrast to the younger Grodekovo granite. The Grodekovo sample contains hornblende, magnetite and allanite, which are practically free from the older samples.

As far as the analytical errors are concerned, the age difference between the Yaroslavsky, Pervomaisky and Grigoryevka plutons may be insignificant. It is rather likely that these three plutons of similar petrochemistry were emplaced as a result of a single tectonic event, although more detailed study is required in the future. Another and more important result is the similarity of age between the Voznesenka fluorite deposit and the older granite plutons characterized by F-rich chemistry, indicating a clear genetic link between the two. As seen in the diagrams of Figure 7, secondary phenomena are also important. Followings are detailed descriptions of the CHIME results

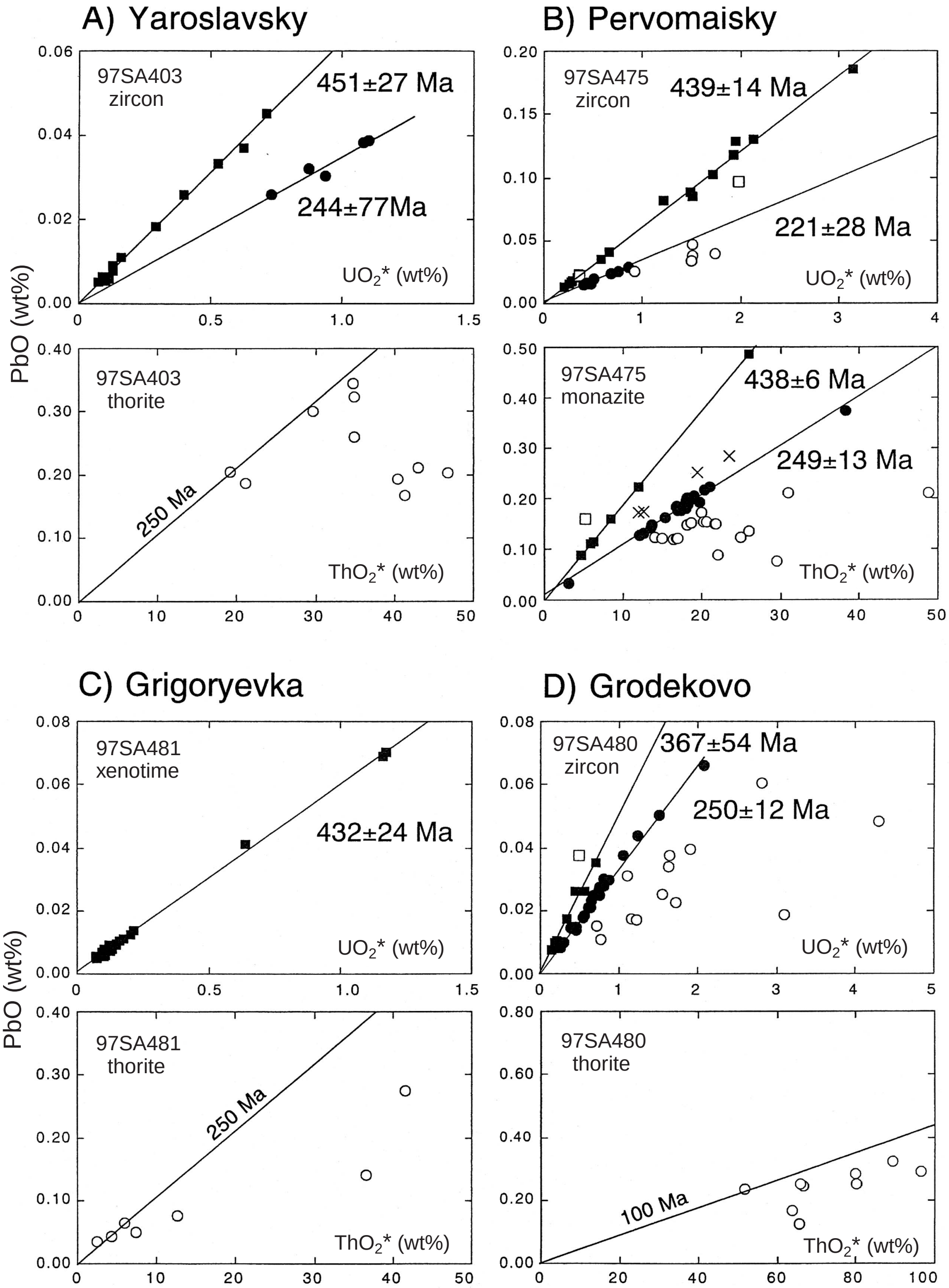

Fig. 7 Plots of PbO vs. UO_2* of zircon and xenotime and PbO vs. ThO_2* of monazite and thorite from four major granite plutons in the Voznesenka district: A) Yaroslavsky, B) Pervomaisky, C) Grigorievka, and D) Grodekovo. UO_2* represents measured UO_2 plus UO_2 equivalent of the measured ThO_2, and ThO_2* represents measured ThO_2 plus ThO_2 equivalent of the measured UO_2 (e.g., Suzuki and Adachi, 1991, 1998). Solid symbols are data points for age calculation. Permian to Triassic ages for 97SA403 (A), 97SA475 (B) were obtained from the analyses along cracks and margins (solid circles), suggesting secondary thermal events. Solid square and circle in D indicate inherited zircon core and magmatic overgrowth, respectively. Open square in B indicates data for the portions that show metamictization or presence of sulfur. Open square in D represents a spot of unusually old apparent age (536Ma) within a zircon core. Cross and open circle represent data for partially recrystallized or heterogeneous portions. Data for thorite are widely scattered, without any significant isochron, probably due to low retentivity of lead in this mineral. Lines of 250 Ma and 100 Ma are reference isochron. See the text for details.

for individual specimens of the two groups.

97SA403: Two zircon and one thorite grains were analyzed. Zircons contain 0.03–0.43 wt% ThO_2 and 0.08–1.01 wt% UO_2. A total of nineteen analyses on zircons are clearly divided into two groups as shown in Figure 7A; fourteen analyses of relatively low UO_2 contents (<0.60 wt%) show an apparent age of ca. 450 Ma and the rest of higher UO_2 content (>0.69 wt%) show an apparent age of ca. 250 Ma. Regression analysis of the two data sets yielded an isochron of 451±27 Ma (MSWD=0.2) with an intercept value of 0.0001±0.0007 for the low-U group, and an isochron of 244±77 Ma (MSWD=0.2) with an intercept value of 0.0004±0.0099 for high-U group. The latter group data near the 250 Ma reference isochron were obtained along margins and cracks of the zircon grains, suggesting secondary thermal event in the latest Permian. Data for thorite are widely scattered below the 250 Ma reference isochron, probably due to much lower retentivity of Pb in this mineral than in zircon.

97SA475: Thirty spots on four zircon grains were analyzed. Three grains show euhedral prismatic shape with concentric growth zoning, suggesting to be of magmatic origin. Most spots (16 of 19) on these grains yielded apparent ages from 480 to 410 Ma, and only three spots on margins yielded 280–230 Ma apparent ages. Regression analysis of the sixteen data gave 439±14 Ma (MSWD=0.3) with an intercept value of 0.0004±0.0017 (Fig. 7B). Another zircon grain also shows euhedral prismatic shape, but does not have any distinct internal structure except for a blunt growth zoning in its central portion. This grain is chemically and chronologically heterogeneous; the UO_2 contents range from 1.97 to 0.37 wt% and the apparent ages from 426 to 164 Ma with a cluster around 250 Ma. Data points with apparent ages of 280–240 Ma gave an age of 221±28 Ma (MSWD=0.1) with an intercept value of 0.0030±0.0026.

Fifty-four spots on nine monazite grains were analyzed (Fig. 7B). Apparent ages show a wide variation; they are mostly younger than 480 Ma, but three dates are unusually old: 2700, 1500 and 720 Ma. The three spots contain substantial amount of S, suggesting the existence of PbS. Therefore, these Precambrian ages may have no geological significance. Among the other fifty-one analyses, six data points with apparent ages older than 400 Ma (solid squares) were obtained on two relatively large grains and they gave an isochron of 438±6 Ma (MSWD=0.1) with an intercept value of 0.0008±0.0026. The remaining forty-five analyses show apparently irregular distribution on the PbO-ThO_2* diagram (Fig. 7B), but twenty-four data points (solid circles) clustered around the 250 Ma apparent age (263–230 Ma) define an isochron of 249±13 Ma (MSWD=1.5) with an intercept value of 0.0013±0.0087. These isochron ages correspond to the ages of 439±14 Ma for major parts of magmatic zircon and 221±28 Ma for their recrystallized margins, respectively. The age clusters around 250 Ma recognized both in zircon and monazite imply a thermal event in latest Permian to early Triassic time.

97SA480: Two grains among six analyzed zircon grains exhibit distinct core-mantle structure under the optical microscope. These grains yielded 536–337 Ma apparent ages for the core and 270–240 Ma apparent ages for the mantle with exceptionally young ages of 208, 143 and 120 Ma for U-rich (UO_2 = 1.1–3.1 wt%) spots on the mantle. Eight data points on the cores give an isochron of 404±98 Ma (MSWD=1.7) with an intercept value of –0.0007±0.0048. If we discard the 536 Ma data point (Fig. 7D, open square), we can obtain 367±54 Ma (MSWD=0.5) isochron with an intercept value of 0.0002±0.0026. A total of fifteen data points with 270–240 Ma apparent ages (solid circles) on the mantles together with nine data points on the other euhedral zircons are regressed with an isochron of 250±12 Ma (MSWD=0.2) with an intercept value of 0.0003±0.0010. This age is considered to be the time of solidification of granitoid magmas, because the data for the mantle are consistent with those for euhedral grains without core, both of which show concentric growth zoning. On the other hand, the cores yielding Devonian age may be inherited zircons. Data for thorite did not give any isochron again (Fig. 7D), suggesting low retentivity of Pb in this mineral. The CHIME data for zircons indicate that the Grodekovo batholith was emplaced in Late Permian time; this conclusion does not support the current opinion of Silurian intrusion (e.g., Ryazantseva, 1998).

97SA481: Only xenotime and thorite were identified. Twenty-two analyses for two xenotime grains yielded ThO_2 contents from 0.076 to 1.45 wt%, UO_2 contents from 0.041 to 0.72 wt%, and PbO contents from 0.0057 to 0.07 wt%. All data points, giving apparent ages from 590 to 410 Ma, are arranged linearly on the PbO-UO_2* diagram and are regressed with an single isochron of 432±24 Ma (MSWD=0.2) with an intercept value of 0.0007±0.0005 (Fig. 7C). A thorite grain in this sample, containing 2.2–36.9 wt% ThO_2 and 0.10–1.44 wt% UO_2, gives highly fractionated apparent ages of 330–90 Ma without any significant isochron, as in the case of 97SA403 and 97SA480.

4. Discussion

4.1. Age of fluorite mineralization at Voznesenka

The two K-Ar Li-mica ages for the Voznesenka fluorite deposit, 450 Ma for the greisenized granite and 453 Ma for the fluorite ore (Table 3), are identical within the analytical error. This concordance in age corroborates a genetic link between the fluorite mineralization and granite magmatism. It demonstrates, in other words, that the greisenization and fluorite mineralization are two aspects resulted from a single magma-hydrothermal activity. These age data also clearly indicate that the Voznesenka deposit formed in Late Ordovician, in contrast to the current view of Devonian mineralization (e.g., Khanchuk et al., 1996; Ryazantseva, 1998; Belyatsky et al., 1999). The Devonian mineralization was suggested from a Rb-Sr whole-rock isochron age of 384 Ma for the greisenized leucogranite collected from drill cores in the Pogranichny deposit (Ryazantseva et al., 1995). Rub and Rub (1994) also reported a Rb-Sr whole-rock age of 399 Ma using a sample set from both the Voznesenka and Pogranichny stocks. In addition Ryazantseva et al. (1995) reported a Rb-Sr age of 441 Ma for leucogranite in the Voznesenka deposit and proposed a long-lasted magmatism and mineralization of more than 50 m.y. from Ordovician to Devonian time. When examined closely, however, their Rb-Sr isotope data show a significant scatter as illustrated in Figure 8, resulting in very large errors both in age and initial strontium ratio. The large scatter of the Rb-Sr isotope data may be due to heterogeneities of the leucogranite stocks formed during magmatic and subsequent alteration stages. Rub and Rub (1994) described highly heterogeneous textures and chemistry of the stocks and indicated strong alteration including greisenization and albitization in shallow levels; virtually no unaltered rocks in the stock exposed in the Voznesenka pit. Their sample sets for age dating include the altered rocks. For example, all the samples for the isochron of 384 Ma by Ryazantseva et al. (1995) are greisenized Li-mica granites from the Pogranichny stock, and resulted in an unusually high values of initial strontium ratio (0.736) compared with the Voznesenka leucogranite (0.707) although they are apophyses from a single pluton (Fig. 3). The sample sets for the previous age dating do not seem to represent an isotopically closed system, because the samples were derived from heterogeneous intrusions modified by significant subsolidus alteration. The whole-rock Rb-Sr isochron method may not yield reliable age of such a complex system like the Pogranichny and Voznesenka stocks.

Belyatsky et al. (1999) suggested Devonian mineralization based on a Rb-Sr whole-rock age of 405 Ma obtained only from two samples of basaltic dikes, for which they defined as "intra-mineral" dikes, although they reported Sm-Nd whole-rocks ages of 452–467 Ma for leucogranite from the Pogranichny and Voznesenka stocks. They also proposed a long-lasted magmatism and related mineralization for more than 50 m.y. As described before, however, our observation indicates that the basaltic dikes are of post-ore, although reliable age data for the dikes have not been reported. We consider, in contrast to the current views, that the fluorite mineralization in the Voznesenka district was a relatively short-lived activity in association with the intrusion of leucogranite and subsequent greisenization at about 450 Ma in Late Ordovician time, rather than unusually long-lasted magma-hydrothermal system for more than 50 m.y. Actual duration of the granite magmatism and related fluorite mineralization is not known, although it is an interesting subject. The duration could possibly be within the error of age dating of Early Paleozoic samples, and it may be difficult to determine by radiometric methods. It is of interest to note, however, that wide spread occurrences of coarse-grained Li-mica and fine-grained muscovite (sericite) in the fluorite ores and greisenized intrusion in the Voznesenka deposit appear to reflect a significant change of the ore-forming environment, probably from pneumatolytic to hydrothermal condition, during the mineralization. Understanding of the ore-forming system and its evolution in the Voznesenka deposit requires more detailed mineralogical and geochemical investigations.

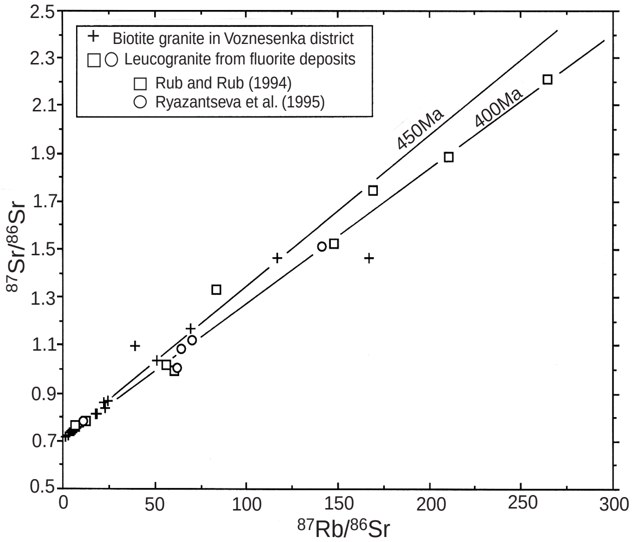

Fig. 8 Rb-Sr isotope data for isochron ages of leucogranite stocks in the Voznesenka and Pogranichny fluorite deposits and Rb-Sr isotope data for biotite granites in the Voznesenka district (Rub and Rub, 1994; Ryazantseva et al., 1995). The specimens for age dating include Li-mica granite and its greisenized or albitized varieties and a plagioclase separate. Reference isochrons of 450 Ma and 400 Ma with initial strontium ratio of 0.710 are shown for comparison. Note that the data for leucogranites show a wide scatter without unique isochron, although isochron ages of 399 Ma and 384 Ma were reported by Rub and Rub (1994) and Ryazantseva et al. (1995), respectively.

4.2. Age and character of granite magmatism in Voznesenka district

Results of CHIME dating for representative granite plutons in the Voznesenka district are summarized in

Figure 9 together with the results of K-Ar dating for the Voznesenka fluorite deposit. It is remarkable that the Yaroslavsky, Pervomaisky and Grigoryevka plutons characterized by the common occurrence of accessory fluorite and the lack of accessory magnetite show similar ages to the fluorite deposit (ca. 450 Ma), suggesting a strong genetic link to the mineralization. On the other hand, the granite sample from the southeastern margin of the Grodekovo batholith shows much younger age at about 250 Ma, boundary between the Late Permian and Triassic. This result is inconsistent with the current view of Silurian age and its relevant tectonic problems will be discussed later in 4.5. It is noted here that secondary ages of recrystallization from the Permian to Triassic were recognized along grain margins or cracks of analyzed zircon and monazite in the older plutons. It is likely that the secondary thermal overprint was caused by the Grodekovo batholith. Schematic cross section in the lower part of Figure 9 was depicted in consideration of these petrographical and chronological observations on the granite plutons in the Voznesenka district.

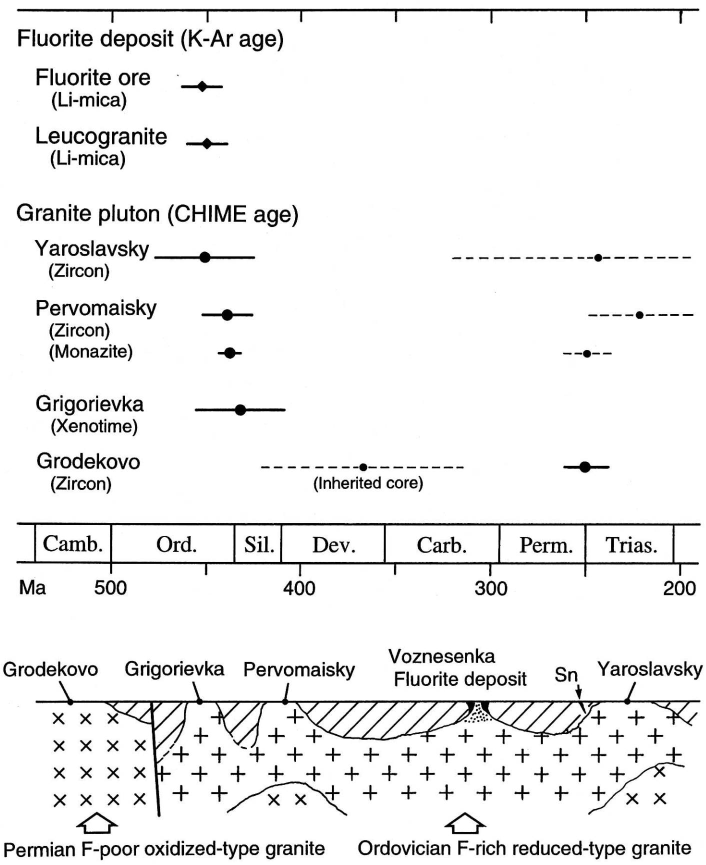

Fig. 9 Summary of age dating for fluorite ore and granitic rocks in the Voznesenka district. Diamond and circle indicate K-Ar and CHIME ages, respectively. Large circle represents ages of granite emplacement without significant influence from secondary crystallization or inherited core represented by small circle. Sketch in the lower part is a schematic cross section of the Voznesenka district showing a geologic relation between ore deposits and granite plutons; Sn denotes cassiterite-bearing veins such as Yaroslavsky deposit (Table 1). Li-F-rich leucogranite in the Voznesenka deposit (dotted) is thought to be a product of differentiation from a large F-rich batholith. Late Permian Grodekovo batholith may have thermally influenced, to some extent, the Ordovician granite batholith, resulting in recrystallization along cracks or rims of some zircon and monazite grains.

The F-rich chemistry and reduced condition of the older plutons, as suggested by the occurrence of accessory fluorite and the lack of accessory magnetite (Table1), are in contrast with the younger granites from the Grodekovo batholith. Rub and Rub (1994) and Ryazantseva et al. (1995) reported F-contents of 0.06–0.31 wt% (n=6; average=0.17 wt%) for the older plutons, while 0.02 wt% for the Grodekovo sample. Based on the magnetic susceptibility corroborated with microscopic observations, the older plutons are classified as the ilmenite-series or the reduced-type, while the younger granites as the magnetite-series or the oxidized-type (Ishihara, 1977; Sato et al., 1992). The redox state of the granites appears to be one of the essential factors for the fluorite mineralization (Sato, 1980), as discussed below in 4.3. It is also of interest to note that the change of granitoid types with time, from the reduced to oxidized, is consistent with the general trends in the Circum-Pacific orogenic belts, where younger granitoid activity tends to form the oxidized-type (Sato, 2000; Sato et al., 2000b).

4.3. Genetic link between fluorite deposit and granite plutons

The Voznesenka deposit has been revealed to have formed in Late Ordovician time at about 450 Ma. It is remarkable that this age is nearly identical with the intrusive ages for the Yaroslavky, Pervomaisky and Grigoryevka plutons (Fig. 9) which were emplaced around the Voznesenka deposits (Fig. 2) and are composed of biotite granite of the reduced-type. It is important to note that reduced condition may be more favorable for the concentration of fluorine in residual melts during the fractionation of granitoid magmas than oxidized condition, because partition of fluorine is strongly dependent on the Fe/Mg ratio of mafic silicates, major F-bearing phases, and the ratio is controlled by oxygen fugacity (Sato, 1980).

The fluorite mineralization is evidently related to the

Table 4 Comparison of Li-mica granite at Voznesenka with representative high Li-F felsic rocks

No.	Vozn-3	PRG/1-6	TG2273	1-0	1700/1-4	HH2	HH3	JV1
Rock (n)	Li-mica granite (6)	Topaz granite (6)	Topaz granite (12)	Ongonite (1)	Ongonite (4)	Topaz rhyolite vitrophyre (whole rock 1)	Topaz rhyolite vitrophyre (glass 1)	Macusani glass (1)
Locality	Voznesenka, Primorie, Russia	Pleasant Ridge, Canadian Appalachians	St. Austell, Cornwall, UK	Ongon Khairkhan, Mongolia	Arybulak, Transbaikal, Russia	Honeycomb Hill, Utah	Honeycomb Hill, Utah	Macusani, SE Peru
Age	Ordovician	Devonian	Permian	Mesozoic	Late Meso.	Pliocene	Pliocene	Pliocene
SiO_2	74.74	75.30	73.5	75.49	71.42	73.3	70.9	72.26
TiO_2	0.17	0.01	0.04	0.00		0.01	<0.01	0.04
Al_2O_3	14.06	13.53	13.3	13.95	17.17	14.0	16.6	15.83
Fe_2O_3	0.01	0.79*	0.83*	0.02	0.58*	0.28	0.05	0.04
FeO	1.12			0.42		0.55	0.52	0.57
MnO	0.02	0.08	0.07	0.12	0.02	0.07	0.12	0.06
MgO	0.12	0.09	0.09	0.00	0.05	<0.01	<0.01	0.02
CaO	0.17	0.29	0.54	0.20	0.67	0.42	0.34	0.22
Na_2O	4.49	4.36	3.73	5.24	4.13	4.59	5.05	4.14
K_2O	4.22	4.28	4.49	3.31	4.42	4.44	4.60	3.66
Li_2O	0.06	0.21	0.362	0.10	0.06	0.074		0.74
Rb_2O	0.12	0.18	0.168	0.13	0.19	0.150	0.191	
Cs_2O	0.002	0.005	0.009	0.003		0.004	0.0065	
P_2O_5	0.02	0.01	0.48	0.02	0.17	<0.01	<0.01	0.53
H_2O^+	0.66	0.18#^{1}	1.03#^{2}	0.34	1.15#^{1}	0.80		0.46#^{1}
H_2O^-	0.09			0.03		0.24		
F	0.45	0.79	1.04	0.48	0.82	0.61	2.36	1.33
Total	100.05	100.16	99.46	99.85	100.85	99.4	100.9	99.90
O=F	0.18	0.33	0.44	0.20	0.34	0.28	1.0	0.56
Total	99.87	99.83	99.02	99.65	100.51	99.1	99.9	99.34
ASI	1.15	1.10	1.11	1.11	1.34	1.07	1.19	1.42
Source	Rub & Rub (1994)	Taylor (1992)	Manning & Hill (1990)	Stemprok (1991)	Kovalenko et al.(1975)	Congdon & Nash (1988)	Congdon & Nash (1988)	Pichavant et al.(1987)

n: Number of analyses for average; Vozn-3: Average of 6 analyses for Li-mica granites from lower levels of deep drill hole at the Pogranichny deposit;
*: Total Fe as Fe_2O_3 ; #^{1}: $(H_2O^+)+(H_2O^-)$; #^{2}: Ignition Loss;
ASI: Aluminum Saturation Index = $Al_2O_3/(Na_2O+K_2O+CaO)$ in mole (Zen, 1986)

intrusion of leucogranite observed in the ore deposits (Fig. 3), but geological relation between the leucogranite stocks and biotite granite plutons is unknown in the field. The F-rich and reduced-type plutons are accompanied by tin mineralization in association with the deposition of fluorite and tourmaline as seen in the Pervomaisky and Yaroslavsky deposits (Fig. 2). On the other hand, minor cassiterite and tourmaline also occur in the Voznesenka deposit, suggesting another linkage. We infer, from the chronological, geochemical and mineralogical features mentioned above, that the leucogranite is a highly fractionated part of granite magmas that formed the biotite granite plutons as illustrated in Figure 9.

4.4. *Comparison of Li-mica granite at Voznesenka with high Li-F felsic rocks and source of fluorine*

As an idea for explaining the formation of huge fluorite deposit, we once assumed an unusually high-F magma such as ongonite or topaz-rhyolite (e.g., Kovalenko et al., 1971; Burt et al., 1982), but no such igneous body was encountered during our field work. Although ongonite nor topaz rhyolite has not been identified near Voznesenka, Li-mica granite itself could possibly be a corresponding igneous body. Table 4 and Figure 10 are comparisons of the chemical composition of Li-mica granite at Voznesenka with those of representative high Li-F felsic rocks including ongonite and topaz rhyolite. It is remarkable that the Li-mica granite is similar in composition to the representative high Li-F rocks from various localities in the world (Fig. 10). It is also noticed that there is no significant difference between granitic rocks and rhyolitic rocks (ongonite or topaz rhyolite), although volcanic glass sometimes shows very high F concentrations (Table 4). Congdon and Nash (1988) suggested that the Honycomb Hills rhyolite dome in western Utah represents an eruptive pegmatite magma rich in fluorine and other rare-elements. They reported 2–3 wt% F for matrix glass and melt inclusions in quartz phenocrysts, with variably lower F contents for pumice glass and whole rocks probably due to selective leaching of fluorine after eruption. The occurrences of high-F glass suggest high solubility of fluorine in felsic melt, being consis-

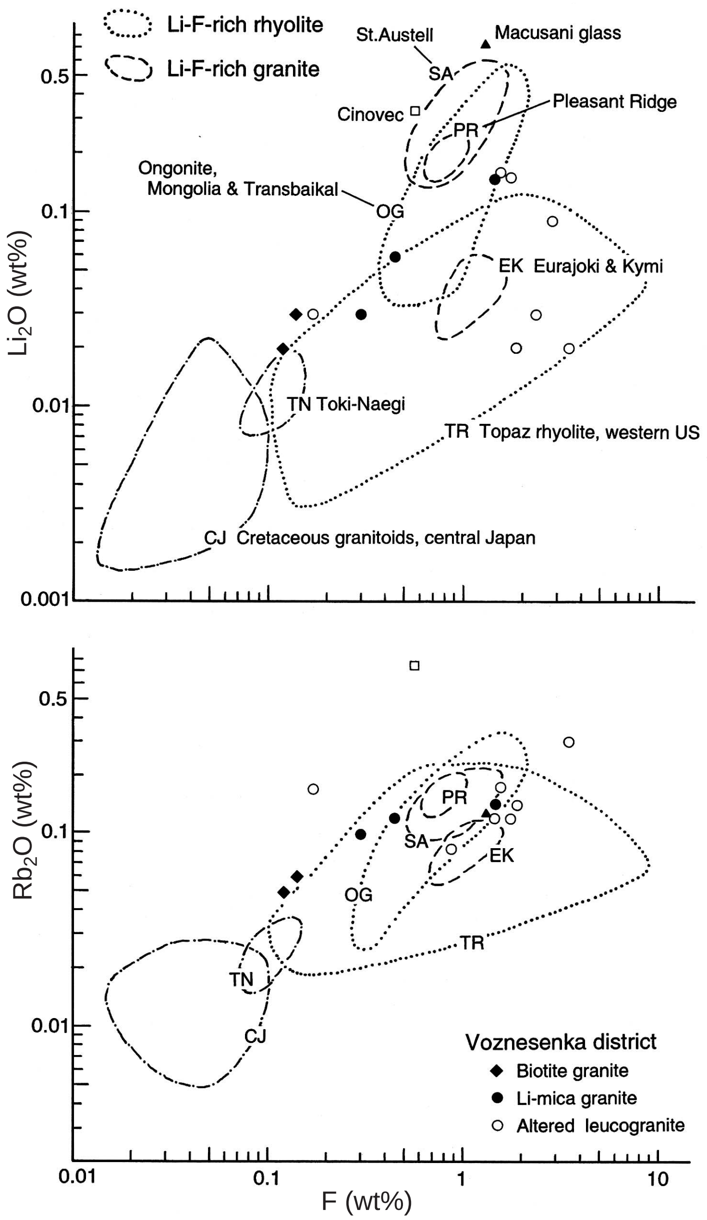

Fig. 10 Li-Rb-F concentrations in Li-F-rich leucogranites and biotite granites from the Voznesenka district in Primorie, Russia (Rub and Rub, 1994). Li-mica granite samples, least altered leucogranites, were obtained from lower levels of deep drill hole (~1200m) at the Pogranichny fluorite deposit. Also shown for comparison are fields for Li-F-rich felsic rocks: (1) Li-F-rich granite from Pleasant Ridge in Canadian Appalachians (Devonian, Taylor, 1992), St. Austell in Cornwall (Permian, Manning and Hill, 1990), Eurajoki and Kymi in southern Finland (Proterozoic, Haapala, 1988) and Cinovec in Erzgebirge (Carboniferous, Stemprok and Sulsek, 1969), (2) Ongonite from Mongolia and Transbaikal (Mesozoic; Stemprok, 1991; Kovalenko et al., 1975), (3) topaz rhyolite from western Unites States (Cenozoic; Christiansen et al., 1986; Congdon and Nash, 1988), Macusani glass from southeast Peru (Pliocene, Pichavant et al., 1987), and (4) Cretaceous normal granitoids and F-rich Toki-Naegi granites from central Japan (Ishihara and Terashima, 1977).

tent with the results of experimental work (Manning, 1981).

Unfortunately, original fluorine content of magmas that formed the Li-mica granite at Voznesenka is not known. If the fluorine content was as high as that of the Honeycomb Hills glass and its significant part emerged from the magma system to form fluorite deposits, original volume of magmas for the formation of Voznesenka fluorite ores needs not to be very large (Sato et al., 2002). For example, a cubic magma body with a side of 500 m and 2 wt% F can provide about 13 million tons of CaF_2, which is approximately 28 times of average annual production from USSR and 2.7 times of average annual world production in 1980's, according to the production statistics listed in the Minerals Year Book (e.g., Pelham, 1985; Miller, 1990). Unusually large size of the Voznesenka deposit compared with the small leucogranite stock attracted attention of many Russian economic geologists. This led some of them to the ideas of two stage model, in which primary stratiform deposits or enriched zone in Cambrian sediments or Precambrian basement were remobilized and concentrated to the present position by the Devonian granite magmatism (Androsov and Ratkin, 1990; Khanchuk et al., 1996; Ryazantseva, 1998). As indicated already the age of Devonian mineralization is a misunderstanding. The assumption of primary stratiform deposits is not necessary, because actual volume of Li-mica granite is large enough for the mass balance estimates mentioned above (Fig. 3).

Based on chemical similarities between the Li-mica granite at Voznesenka and other high Li-F granites and rhyolites (Table 4 and Fig. 10), we consider that these high Li-F rocks are products from a unique group of fractionated magmas. Thus, the Li-mica granite at Voznesenka as well as topaz granites from Canadian Appalachians and Cornwall could be intrusive equivalents of ongonite and topaz rhyolite. Although genesis of the high Li-F magmas is not well understood, examples of close association of topaz granite with biotite granite in the St. Austell pluton in Cornwall, England (Manning and Hill, 1990) and the Davis Lake pluton in Nova Scotia, Canada (Dostal and Chatterjee, 1995) suggest a close genetic relation between the two. Dostal and Chatterjee (1995) proposed an idea of fractional crystallization accompanied by fluid fractionation involving fluorine complexing. Similar process might have occurred in the Voznesenka district, although no direct connection between the Li-mica granite and biotite granite is observed in the field (Fig. 9).

4.5. Problem of Grodekovo batholith: Silurian? or Permian?

Among the granitoid plutons examined in this study, only Grodekovo granite (97SA480) showed a primary magmatic age of Late Paleozoic to Early Mesozoic; the rest are Early Paleozoic in age as described above (Table 1 and Fig. 9). The CHIME data indicate that this granite intruded at about 250 Ma, the boundary between Late Permian and Early Triassic time. This is an unexpected result, because our sample was collected from a southeastern margin of the large Grodekovo batholith which has been thought to be Silurian (Ryazantseva, 1998) or Silurian to Devonian (USSR Ministry of Geology, 1986; Khetchikov et al., 1996). This significant discrepancy may cause a serious problem in the tectonic history of the Khanka massif, because the Grodekovo batholith is one of the largest Paleozoic batholiths in Primorie (USSR Ministry of Geology, 1986) and it is considered to be a representative “collision-related” batholith generated in the Late Silurian-Early Devonian amalgamation of sub-terranes to form the Khanka massif (Khanchuk et al., 1996, Khetchikov et al., 1996).

The Grodekovo batholith is widely exposed to the west of the Voznesenka district up to the area near China border; its exposure is about 60 km EW and 30 km NS. If the batholith to the west of Lake Khanka is included, the total exposure will be much larger. This batholith intrudes Cambrian and Silurian sequences and is overlain by Cretaceous or younger sediments (USSR Ministry of Geology, 1986). Khanchuk et al. (1996) indicated that the Grodekovo and Shmakovka batholiths are Silurian in age and are overlain by Devonian sequences. The reported petrographic features are consistent with those of our sample (97SA480). The Late Silurian Rb-Sr whole-rock age of 411 Ma was obtained for a set of four granite samples collected near our sample site in the Voznesenka district (Ryazantseva et al. 1995), though no petrographic data, nor detailed localities of the samples were presented. Cause of the large difference in age between the CHIME and Rb-Sr methods is unknown, and age of the Grodekovo batholith is to be examined for more samples. The Grodekovo batholith is characterized by the dominance of biotite granite and abundant wall-rock xenoliths (Ryazantseva et al., 1995; Khetchikov et al., 1996; Khanchuk et al., 1996). The Silurian Rb-Sr age could possibly be an errorchron due to local heterogeneity of granitic magmas caused by incomplete mixing or mingling of isotopically various source materials.

We believe that the Grodekovo batholith, at least its southeastern margin where we collected the sample 97SA480, is the latest Permian in age. In this connection, it is of interest to note that Late Permian to Triassic ages of recrystallization were recognized in the Ordovician biotite granites from the Yaroslavsky (97SA403) and Pervomaisky (97SA475) plutons by our CHIME dating (Figs. 7 and 9), although such evidence has not been found in the Grigoryevska sample (97SA481). These secondary ages could possibly reflect intrusion of the latest Permian granitoids and/or related thermal event.

Permian granitoids are known to occur in many areas in the Khanka massif (Khanchuk et al., 1996; Sato et al., 2000a); they are generally magnetite-bearing as in 97SA480. It may be also possible to assume that the Grodekovo batholith is a composite batholith including Permian plutons. Reliable chronological data covering the whole exposures are required for more understanding of the Grodekovo batholith and related tectonic history of the Khanka massif.

5. Concluding Remarks with Relevance to Future Mineral Prospecting

It has been concluded that the Voznesenka fluorite deposit was formed in relation to the F-rich leucogranite at about 450 Ma in Late Ordovician. If the sub-terranes of the Khanka massif amalgamated in Silurian time and the fluorite deposit was formed in Devonian time (Khanchuk et al., 1996; Ryazantseva, 1998), we may expect a similar mineralization in other sub-terranes than the Voznesenka terrane. However, such expectation has lost its base because the mineralization occurred before the “Silurian amalgamation” of sub-terranes which had essentially different geodynamic histories.

Paleozoic mineralization of economic significance is scarce in the Khanka massif. The paucity may be partly due to deep erosion level (Sato et al., 1999, 2000a) and partly due to wide cover of Mesozoic and Cenozoic sedimentary and volcanic sequences. The Voznesenka sub-terrane dominated by carbonate rocks (Khanchuk et al., 1996) seems to be more promising than the others because carbonate sequences often provide favorable site of ore deposition. In the Voznesenka fluorite deposit indeed, the ores replace limestone near the leucogranite plutons. Such highly evolved intrusions emplaced in limestone will be future targets when mineral prospecting will be extended to the regions covered by young strata.

Our CHIME data indicate that the Grodekovo batholith (97SA480), a representative Silurian batholith according to the current view, is the latest Permian which is one of the most common age peaks of granitoid magmatism in the Khanka massif. If this is the case for all areas of the batholith, the scenario of “Silurian amalgamation” is to be revised and the potential area of fluorite mineralization similar to the Voznesenka deposit could basically be extended to the whole region of the Khanka massif. Paleozoic granitoid areas are generally poor in good exposures due to strong weathering. Collection of reliable age data resistant to alteration and weathering is required for more understandings of the tectonic history and mineralization in the Khanka massif.

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