# New Data on the Stratigraphy, Volcanism, and Zeolite Mineralization of the Cenozoic Vanchinskaya Depression in Primorye

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Received December 29, 2009

Abstract—This paper presents the results of studying the Cenozoic volcanogenic-sedimentary cover of the Vanchinskaya depression of Sikhote Alin. It was established that, in terms of the taxonomic composition of the fossil plants, the basal part of the Cenozoic section is attributed to the Paleocene, while the overlaying coal-bearing sequence, to the Early Eocene. The geochronological (K–Ar) dating showed that the volcanic rocks intruding and overlaying the coal-bearing deposits are Middle Eocene in age: rhyolites—44.7  $\pm$  1.0; trachyandesites—43.7  $\pm$  1.4 Ma. The petrographic and geochemical characteristics of the volcanic and volcanogenic-sedimentary rocks and related zeolitites are described. The zeolitized rocks containing plant detritus differ in their extremely high contents of Y and HREE. The zeolitization of the volcanic glass in tuffs, tuffites, and perlites was caused by hydrothermal solutions that ascended along NW fault zones from the subsurface magmatic chamber.

*Key words*: Cenozoic, stratigraphy, volcanism, geochemistry, zeolitites, Sikhote Alin. **DOI:** 10.1134/S1819714010040044

# INTRODUCTION

The Cenozoic Vanchinskaya depression is situated in the axial part of the Sikhote Alin Range in the upper reaches of the Milogradovka River (the old name of the Vanchin River). Its central part is drained by the Vanchin–Ugol'nyi Creek (Chernokamenskii), while the marginal parts, by the Bezymyannyi and Tigrovyi creeks (Fig. 1). The depression is small in size  $(3-5 \times 15 \text{ km})$  and filled with Cenozoic coal-bearing volcanogenic-sedimentary deposits.

The Cenozoic cover of the Vanchinskaya depression has been studied for more than 100 years. Tertiary coal-bearing deposits were described in this area for the first time by Ya. S. Edel'shten as early as in 1900 (see Ispolinov, 1963). During the geological survey on a scale of 1 : 200000 at the beginning of the 1930s, Mikhnovich collected plant remains from the coalbearing sequence, which were ascribed by Shtempel to the Oligocene (Ispolinov, 1963). In 1936, G.P. Vol-

arovich carried out the first specialized study of this structure. The prospecting for brown coal carried out by E.G. Stromberg in 1950–1955 revealed the limited (a few hundred thousand tones) resources of this structure. During the subsequent geological surveys, V.A. Ispolinov and V.G. Babich (1961–1963), and Yu.P. Bidyuk (1965–1968) compiled geological maps of the depression and its framing on a scale of 1 :50 000 and provided the stratigraphic framework for the Cenozoic deposits [1].

In the early 1970s, I.N. Tomson and V.S. Kravtsov discovered the Soyuznoe gold—silver deposit in the southeastern flank of the depression. This deposit was later explored by a group of geologists under the leadership of Matyushonok [24]. The mid 1970s were marked by the discovery of zeolite mineralization in the volcanogenic and volcanogenic-sedimentary deposits of the depression [8]. The prospecting works carried out under the direction of F.I. Rostovskii in



**Fig. 1.** Schematic geological map and section of the Vanchinskaya depression (complied using the materials of V.A. Ispolinov, Yu. P. Bidyuk, B. F Kozhinov, Yu.A. Gorobets, N.A. Matyushonok, and F.I. Rostovskii).

(1) Quaternary deposits; (2–5) Eocene: (2) conglomerates and sandstones, (3) trachyandesites and tuffaceous conglomerates, (4) lavas and tuffs of rhyolites, volcanic glasses, (5) often tuffaceous sandstones, mudstones, and siltstones; tuffstones; rhyolite tuffs; and brown coal; (6) Paleocene conglomerates, tuffstones, tuffites, and tuffs; (7) Late Cretaceous–Paleocene volcanics and extrusions of felsic and intermediate composition; (8) Pre-Cretaceous terrigenous deposits; (9) dip and strike of the rocks; (10) faults: proved (a), inferred (b), and hidden beneath Quaternary deposits (c); (11) Milogradovskii Fault zone; (12) inferred eruption centers of felsic magmas (extrusions, tuffisite bodies, and concentric structures deciphered from satellite images); (S) Soyuznenskii volcanic center; (13) points: collections of plant remains (a), sampling localities for the palynological analysis (b); (14) geochronological sampling localities (K–Ar method); (15) boreholes; (16) zeolitite occurrences (1—Gribok, 2—Rus-lovoe, 3—Nizhnee, 4—Ugol'noe, 5—Berezovoe, and 6—Dorozhnoe); (17) Soyuznoe deposit; (18) outlines of a magmatic chamber distinguished from the geophysical data.

1988–1994 spanned the area including the Vanchinskaya depression. At the end of the 1980s, coal beds with high concentrations of rare-earth elements [19] and tin—porphyry mineralization in the rhyolite extrusion [22] were found here.

This paper reports the results of studying the Cenozoic volcanogenic-sedimentary rocks of the Vanchinskaya depression, which require revision of the existing concepts on the time of the manifestation and evolution of the magmatism and sedimentation in this structure. The paper is underlain by factual material obtained by the authors in 1987–2007 during the geological–geochemical study of the Vanchinskaya depression, as well as by materials of previous works.

#### GEOLOGICAL–GEOMORPHOLOGICAL CHARACTERISTICS

Tectonically, the Vanchinskaya depression represents a NW-trending asymmetrical graben that is well expressed in the modern relief. It has a steep southwestern side manifested in the relief by the scarp along the Milogradovskii fault and a gentler northeastern side. Transverse northeastern faults split the depression into a series of small blocks (Fig. 1).

The basement of the depression is made up of the Jurassic and Lower Cretaceous terrigenous deposits of the Taukhe and Zhuravlevka terrane, as well as Late Cretaceous and Paleocene volcanics of the East Sikhote Alin volcanic belt (Fig. 1). Data on the geological structure and composition of the volcanic complexes that constitute Eastern Sikhote Alin are reported in [1, 24]. They compose the base of the Vanchinskaya depression and its eastern framing. In this work, these rocks are not considered. The depression is filled with sedimentary and volcanogenic rocks up to a few hundred meters thick. The rocks dip monoclinally at 15–25° toward the steep southwestern side of the depression. Along the longitudinal and transverse faults, the structure of the cover is significantly complicated, the Cenozoic rocks here often have a steeper dip  $(30-60^\circ)$ , and the orientation of the bedding is different from the general northwestern strike.

The maximal thickness (up to 100–200 m) of the Cenozoic cover is fixed in the northwestern part of the depression (boreholes 108 and 111), while the lowest thickness (a few tens of meters) is observed in its southeastern sector in the area of the Soyuznoe deposit. The rocks are characterized by the substantial facies variability and nonpersistent strikes. In the southeastern part of the depression, the volcanogenic–sedimentary rocks are replaced by volcanic rocks (tuffs, lavas, explosive breccias, and extrusive bodies of rhyolites and dacites). The section is crowned by the alluvial–proluvial deposits (fanglomerates), whose thickness near the Milogradovskii fault reaches a few hundred meters.

The central part of the graben is marked by an intense gravity maximum. The fact that this part of the graben contains late rhyolite flows and extrusions overlaying and cutting across the coal-bearing sequences, as well as intense hydrothermal alteration of the volcanogenic-sedimentary cover, makes it possible to link this anomaly with a subsurface magmatic chamber [19].

# STRATIGRAPHY OF THE VOLCANOGENIC-SEDIMENTARY DEPOSITS

According to the previously accepted scheme [1], the coal-bearing volcanogenic-sedimentary deposits that fill the Vanchinskaya depression are subdivided into the Eocene-Oligocene Uglovskaya Formation and the conformably overlaying Oligocene Nadezhdinskaya Formation. They are unconformably overlain by the "liparites, their tuffs, and tuffolavas" of the Oligocene Brusilovskaya Formation. Upward, these rocks are replaced by the basaltic andesites, and dacites arbitrarily ascribed to the Early Miocene Sandugan Formation. The section is crowned by a thick sequence of bouldery-pebbly deposits, which are correlated with the Pliocene Suifun Formation in Western Primorye.

The coal-bearing deposits previously ascribed to the *Uglovskaya Formation* rest on the heterogeneous basement rocks of the depression with an erosion and angular unconformity. They are subdivided into two sequences: the basal and the coal-bearing. The basal sequence is made up of poorly sorted conglomerates, which consist of variably rounded fragments of Jurassic and Cretaceous rocks embedded in ash and a sandy-clayey matrix. Upsection, they grade into a unit of alternating vitric-crystal rhyolite tuffs, tuffstones, and tuffites. The thickness of the basal sequence varies from 20 to 50 m.

The coal-bearing sequence is made up of tuffstones, mudstones, and tuffaceous siltstones with horizons of gravelstones and conglomerates and thin (from 0.3 to 1.7 m) beds and lenses of brown coal (Fig. 2). The large fragments and pebbles in the coarse-clastic deposits of the coal-bearing unit are mainly represented by hydrothermally altered rhyolites. The thickness of the coal-bearing sequence varies from 50 to 100 m.

Tuffaceous-sedimentary rocks of the basal and coal-bearing sequences are exposed along both sides of the Vanchin–Ugol'nyi Creek and are recovered by prospecting boreholes (Fig. 1, boreholes 108 and 113).

At the beginning of the study of the Vanchinskaya depression, the plant remains from the deposits of the Uglovskaya Formation were dated to the Oligocene (Ispolinov, 1963). The study of the macrophytofossils collected by E.G. Stromberg and V.A. Ispolinov later led Nevolina to the conclusion that the host deposits have a late Eocene–Early Oligocene age. The taxo-

nomic composition of the fossil plants is shown in [1]. We collected plant remains from tuffites and tuffstones from the basal sequence and from tuffaceous siltstones of the coal-bearing sequence. The collection from the tuffstones and tuffites was preliminarily viewed by S.I. Nevolina, who concluded that the taxonomic composition of the flora is close to that of the Early Paleocene (Danian) Tadushin flora, which is known in the Zerkal'nenskaya depression. A detailed study of the collection allowed B.I. Pavlyutkin to determine typical Paleocene plants in its composition (Fig. 3).

The following plants were identified there: Osmunda sachalinensis Krysht., Woodwardia bureiensis Fed., (?) Sequoia sp. (carpellate cone), Taxites olrikii Heer, Trochodendroides cryshtofovichii (Iljinskaja) Iljinskaja, T. speciosa (Ward) Berry, T. evelinae Iljinskaja, *Tiliaephyllum tsagajanicum* (Krysht. et Baik) Krass., Protophyllum sp., Fagus sp., Betula sp., *Vitis protoamurensis* Kamaeva, and *Dicotylophyllum* sp. Unambiguous Danian remains were not found in the poor phytocomplex derived from the tuffaceous siltstones in the overlaying coal-bearing sequence. B.I. Pavlyutkin determined there Osmunda sachalinensis Krysht., Metasequoia occidentalis (Newb.) Chaney, Glyptostrobus europaeus (Brongn.) Heer, Tetracentron sp. (?), Hamamelites cf. kinkilensis Budants., "Acer" arcticum Heer, Fraxinus chunchunensis Wang, Li et Ablaev, Planatus sp., and Cercidiphyllum richardsonii (Heer) Sew. et W. Edw. (Fig. 3). The aforementioned taxa are known from the Eocene and Paleocene floras of Primorye and the adjacent regions.

Simultaneously, the tuffaceous siltstones and sandstones from the coal-bearing sequences were sampled for palynological studies. In the opinion of T.I. Petrenko, the set of microfossils in the spore-andpollen assemblage somewhat differs from the other Eocene palynofloras of Primorye. The prevailing taxa are gymnosperms, mainly Taxodiaceae. Angiosperms contain single pollens of specific Fagaceae-Quercus glacilis Boitz., Q. graciliformis Boitz., Q. conferta Boitz., and Quercites sparsus (Mart.) em. Samoil., as well as higher contents of Castanea (up to 4.6%) and Castanopsis (up to 3.3%). Noteworthy is the almost complete absence of Fagus pollen. The thermophile components of the palinoflora are represented by poor spectra: Trochodendron, Fothergilla, Hamamelis, Liquidambar, Altingia, and Engelhardtia. Pollens of formal genera occur as single representatives: Triporopollenites sp., Triatriopollenites plicoides Zakl., Plicatopollis plicatus R. Pot., Tricolpollenites liblarensis (Th. et Pfl) subsp. fallax R. Pot., Tricoloporopollenites sp., and Parviprojectus dolium Samoil.

In general, the spectra are vague and reflect, according to T.I. Petrenko, a definite stage in the evolution of the Eocene flora, possibly of the "preoptimal" Early Eocene.

According to [1], the *Nadezhdinskaya Formation* overlaying the coal-bearing sequence includes tuffs-





**Fig. 2.** Detailed lithological columns of the coal-bearing sequence: (a) Ugol'noe occurrence; (b) 1st right (from bottom) tributary of the Vanchin–Ugol'nyi Creek. (1) tuffaceous conglomerates; (2) tuffstones and tuffites; (3) tuffaceous siltstones and mudstones; (4) coaly tuffstones and mudstones; (5) coals; (6) zones of layer silicification of coals; (7) coal inclusion. The numbers to the right of the column are the sample numbers (see Tables 3 and 5).

tones, tuffaceous mudstones and siltstones with thin intercalations of brown coals and conglomerates, horizons of tuffites, and vitric and ash rhyolite tuffs [1]. The section is crowned by dark gray mudstones and siltstones with an insignificant admixture of volcaniclastic material. The most complete section of this formation 65 m thick was recovered by borehole 108 (Fig. 1). The age of the distinguished stratotone was taken to be Oligocene [1].

Mudstones ascribed by A.Yu. Bidyuk to the Nadezhdinskaya Formation were sampled by us for palynological studies. It was established that the palynological spectra are similar to the above described spectra identified in the coal-bearing sequence (conclusion of T.I. Petrenko). The obtained data suggest that the rocks that overlay the coal-bearing sequences were also formed in the Eocene. The conformable deposition on the coal-bearing sequence, the similarity of the palynological spectra, and the insignificant thickness do not allow us to distinguish these rocks as an individual lithostratotone. We included these deposits into the coal-bearing sequence.

The rhyolite tuffs and lavas in the interfluve of the Vanchin–Ugol'nyi and Bezymyannyi creeks were previously recognized as the Oligocene *Brusilovskaya Formation*. In this area, volcanic rocks 100–150 m

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**Fig. 3.** Fossil remains from the Vanchinskaya depression: the basal sequence—the Paleocene (1-3, 5-7); the coal-bearing sequence—the Lower Eocene (4, 8-10) The determinations are by B.I. Pavlyutkin of the Far East Geological Institute of the Far East Division of the Russian Academy of Sciences.

(1) Vitis protoamurensis Kamaeva, 9190/15; (2) (?) Protophyllum sp., 9190/1; (3) Trochodendroides speciosa (Ward) Berry, 9190/16; (4) Osmunda sachalinensis Krysht., 9185/17; (5) T. kryshtofovichii (Iljinskaja) Iljinskaja, 9190/7; (6) Tiliaephyllum isagajanicum (Krysht et Baik.) Krass., 9190/10; (7) T. evelinae Iljinskaja, 9190/13; (8) Fraxinus chunchunensis Wang, Li et Ablaev, 9185/9; (9) Hamamelites cf. kinkilensis Budants, 9185/6; (10) "Acer" arcticum Heer, 9185/15

Table 1. Results of K-Ar age determinations of rhyolites of the Vanch	hinskaya depression
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Ordinal no.	Sample	Rock	Coord	linates	Potassium,	<sup>40</sup> Ar <sub>rad.</sub> ,	Age, Ma ±2σ
	Sample		Lat.	Long.	wt % ±2σ	$(ng/g) \pm 2\sigma$	
1	P-504/5	Rhyolite, WR	43°30′50′′	134°15′20″	$4.70\pm0.05$	$14.72\pm0.03$	$44.7\pm1.0$

Note: The determinations were made at the Laboratory of Isotope Geochemistry and Geochronology of the IGEM RAS. The contents of radiogenic argon were determined using an MI-1201 IG mass spectrometer using isotope dilution and <sup>38</sup>Ar as the tracer; the K was determined by flame photometry. The ages were calculated using the following constants:  $\lambda_k = 0.581 \times 10^{-10} \text{ yr}^{-1}$ ,  $\lambda_{\beta-} = 4.962 \times 10^{-10} \text{ yr}^{-1}$ , and <sup>40</sup>K = 0.01167 (at %). The analyst was V.A. Lebedev.

Table 2. Results of the K–Ar age determinations of the trachyandesites of the Vanchinskaya depression

Ordinal no.	Sample	Rock	Coor	dinates	Potassium,	$^{40}\text{Ar}_{r.} \times 10-5,$	Air Ar %	Age, Ma ±2σ
	Sample	NOCK	Lat.	Long.	wt %	nmm <sup>3</sup> /yr	All Al, 70	
1	P-514/5	Trachyandesite, WR	43°31′55″	134°14′55″	3.337	475.58	85.6	$43.7\pm1.4$

Note: The determinations were conducted at the Laboratory of Isotopy and Geochronology of the Earth's Crust Institute of the Siberian Branch of the Russian Academy of Sciences using technique [16]. The age was calculated using the following constants:  $\lambda_{\alpha} = 0.581 \times 10^{-10} \text{ yr}^{-1}$ ;  $\lambda_{\beta} = 4.962 \times 10^{-10} \text{ yr}^{-1}$ ; <sup>40</sup>K = 0.01167 at % K. The potassium contents are the averages of three flame photometric measurements; \* average radiogenic argon of two aliquots.

thick overlay the coal-bearing rocks of the Uglovskaya Formation [1] and compose tuff and lava sequences of rhyolites and volcanic glasses, as well as cross-cutting bodies of trachyrhyolites, explosive breccias, and intrusive pyroclastites (tuffisites) of felsic composition. The latter are developed in the Bezymyannyi Creek basin. The tuffisites have discordant steep contacts and consist of large fragments and blocks of rhyolite tuffs, tuffaceous stones, coaly mudstones, and coal embedded into decomposed volcanic glass.

Downstream from the Bezymvannyi mouth, numerous exposures of rhyolitic explosive breccias are observed in the steep rocky walls of the Milogradovka River. They have cross-cutting relations  $(65-70^\circ)$  with host vitric-crystal rhyolite tuffs. The explosive bodies are made up of angular rhyolitic fragments embedded into an argillically altered matrix. The brecciated bodies are highly disintegrated and cut by a dense network of veinlets of chalcedony-like quartz. The near-mouth part of the Vetvistyi Greek contains individual flows of volcanic glasses of characteristic black color. We studied the extended rhyolite flow that crops out in the lower reaches and near-mouth part of the Vanchin– Ugol'nyi Creek and in the Milogradovka River basin (up- and downstream of the Vanchin–Ugol'nyi Creek). The feeder of the rhyolite flow (neck) was recovered by erosion 800 km downstream of the Bezymyannyi Creek mouth. The visible footwall contact of the neck with tuffs is gentle with dip angles no of more than  $8-10^{\circ}$ . The rhyolite flow lies horizontally. The lava flow is emphasized by its fluidal texture. The thickness of the near-contact neck zone with the host rhyolite tuffs is 1–1.5 m. It is made up of volcanic glass with quartz and sanidine phenocrysts. The rhyolites also contain a significant amount (about 30%) of quartz and sanidine phenocrysts embedded in the felsitic groundmass. The K–Ar date of the rhyolite neck (44.7  $\pm$  1.0 Ma) indicates their Middle Eocene age (Table 1). Similar age values of 44.85  $\pm$  0.1 Ma and 44.95  $\pm$  3 Ma (with correction for the constants accepted in 1985) were previously obtained for the same body by dating of sanidine and whole-rock samples (unpublished data of I.N. Tomson and O.P. Polyakova and of M.G. Rub, respectively, of the IGEM RAS).

According to Yu.P. Bidyuk, the Sandugan Formation includes concordant and discordant bodies of basaltic andesites, andesites, and dacites 80-100 m thick. These rocks are exposed on the left and right sides of the Vanchin–Ugol'nyi Creek, as well as on the right side of the Bezymyannyi Creek. 1600 m upstream the Vanchin-Ugol'nvi Creek, the base of the andesite flow is built up of tuffaceous conglomerates consisting of rounded fragments (up to 5-15 m across) of oxidized, chlorizited, and bleached andesites and basaltic andesites, and occasional rhyolites embedded into the groundmass of the palagonized volcanic glass. The tuffaceous conglomerates are overlain by the flows of glassy andesite lavas. Extrusions and dikes of the same composition were found in the Bezymvannyi Creek's basin. The age of the rocks of the Sandugan Formation was determined as Miocene, because the andesite lavas rest on the rhyolite of the Brusilovskava Formation and are overlain by the Pliocene deposits [1]. The K-Ar datings of glassy trachyandesites in the Vanchin–Ugol'nyi Creek basin (Table 2) suggest the Middle Eocene age of the volcanic rocks of this sequence [14].

According to Yu.P. Bidyuk, the *Suifun Formation* consists of boulders, pebbles, and semirounded frag-

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**Fig. 4.** Stratigraphic sequence of the deposits of the Vanchinskaya depression.

(1) stratigraphic boundaries: proved (a), inferred (b); (2) unconformities: (a) proved, (b) inferred; (3) facies boundaries; (4) stratigraphic gaps; (5) formation time of the Soyuznoe deposit; (6) inferred formation time of the zeolite mineralization.

ments of the Mesozoic and Paleozoic rocks weakly cemented by sandy-clayey material with rare intercalations of brown inequigranular sandstones, gravelstones, conglomerates, and clays. The poor sorting of the material indicates its mainly proluvial nature. Near the southwestern wall of the depression, these deposits were partly recovered by borehole 111 to a depth of 170 m (Fig. 1). According to the data of E.G. Stromberg (1955) and V.A. Ispolinova (1963), the thickness of similar deposits in the adjacent Berezovskaya depression based on drilling data is estimated to be 600 m. The age of the formation was supposedly taken as Pliocene [1]. According to B.I. Pavlyutkin (oral communication), the list of plant remains from the Suifun Formation reported in [1] corresponds to the Eocene-Miocene and cannot be determined more accurately. The proluvial-alluvial deposits were accumulated in the near-fault part of the depression. The formation of similar thick complexes of fanglomerates near the steep near-fault sides is typical of many Cenozoic depressions of Primorye (Ivanovskaya, Shmakovskaya, Artemo-Tavrichanskaya, and others), where their Eocene age was proved. The fanglomerates of the Vanchinskaya depression, by analogy with the sections of similar depressions, were conditionally ascribed by us to the Eocene.

Thus, the obtained results of the palynological and isotope–geochemical studies made it possible to revise the age of the volcanogenic–sedimentary and volcanic rocks of the Vanchinskaya depression. A new scheme of the sequential formation of the Cenozoic deposits filling the depression was proposed in Fig. 4.

### PETROGRAPHIC CHARACTERISTICS OF THE ROCKS

The volcanogenic–sedimentary rocks of the basal and coal-bearing sequences are represented by conglomerates of tuffstones and tuffaceous siltstones, tuffites, mudstones, brown coal, and vitric–crystal tuffs of dacite–rhyolite composition.

The psammitic, psephitic, and coarse-grained tuffstones of the basal sequence consist of angular grains of quartz, feldspars, and rare fragments of the basement rocks. The matrix is made up of pelite-size fragments and contains numerous particles of decomposed volcanic glass. The rocks are unevenly lithified and locally strongly ferruginated. The ash gray tuffaceous siltstones with silt-size fragments have a similar petrographic composition. Due to the secondary alteration, the volcanic glass is replaced by zeolites, micaceous minerals, and opal. Separate zeolitized beds of tuffstones and tuffaceous siltstones contain plant slime of ash brown color, while some interbeds contain coalified fragments of plants.

Ash-gray and greenish gray tuffites are made up of fine ash particles of felsic volcanic glass, individual coarser (up to 5 mm) pumice fragments, and scarce fine grains of quartz, feldspar, and coal. The matrix consists of clay minerals. Secondary alterations are expressed in the zeolitization and opalization of the rocks.

Vitric—crystal tuffs of rhyolites and dacites have a light greenish gray color and well pronounced bedding. The rocks consist of flattened and more rarely different-size angular fragments of decomposed light green volcanic glass. The groundmass comprises psammite-size glass particles and fragments of quartz,

sericitized K-feldspar, and opacitized biotite flakes. There are also clay minerals formed by the decomposition of the volcanic glass.

The coals are mainly made up of vitrinite group macerals ( $\beta$  and  $\Delta$ -vitrinite,  $\beta$ -parenhinite, fellinite, and desmite-vitrinite) and contain a sufficiently large amount of lipoid trace components (cutinite and microsporinite). The fusinitic microcomponents are of subordinate significance and represented by small lenses of  $\beta$  fusinite and micrinite. The vitrinite reflectance varies in a narrow range ( $\mathbb{R}^\circ = 0.36-0.37$ ) and corresponds to the O<sub>2</sub> stage of coal rank.

The coal seams often contain an admixture of tuffaceous material constituting thin (a few mm to 2 cm) kaolinite tonsteins. In the Bezymyannyi Creek mouth, the coal seam contains macroscopically discernible lapilli completely replaced by kaolinite—smectite aggregates.

Silicification zones were noted in the coal seams in several exposures along the Vanchin–Ugol'nyi Creek valley and its tributaries. They are subdivided into two morphologically different types, which were presumably formed at different stages of the transformation of the organic matter.

The first type is represented by massive and fluidal zones with traces of the flow of siliceous and organic masses and layered silicification of coal seams (Fig. 2). They were presumably formed during peat accumulation and the early diagenesis of the organic matter owing to the discharge of highly siliceous solutions into the permeable organic matter. The second type is expressed by quartz microstockworks cross-cutting coal seams. Such epigenetic silicification of coal seams has evidently already occurred after the coalification of organic matter [19].

The tuffaceous siltstones of the coal unit are brown-gray stratified rocks of silty-pelitic and pelitic texture. The silt grains are represented by quartz, feldspars, and muscovite. Some grains are replaced by chlorite and sericite. The pelitic groundmass was also subjected to intense sericitization and chloritization and contains a small amount of zeolitized felsic pyroclastics.

The rhyolites that compose the escarpment of the basement terrace of the Milogradovka River sides down- and upstream of the Vanchin–Ugol'nyi Creek and its walls in the near-mouth part have a light gray color. The rhyolite flows are fluidal banded, porphyritic, and with phenocrysts of quartz, sanidine, rare acid plagioclase, and biotite. The accessory minerals are represented by ore minerals, zircon, and apatite. The groundmass is glassy, microfelsitic, and, locally, up to granophyric. The marginal facies of the neck are made up of volcanic glass with numerous (15–20 vol %) large phenocrysts (5–7 mm across) of quartz and sanidine. In the interfluve of the Vanchin–Ugol'nyi and Bezymyannyi creeks, the rhyolites are characterized by the presence of small (1–2 mm) and scarce porphy-

ric phenocrysts of quartz, K-feldspar, and biotite embedded in the felsitic groundmass. A significant part of the rocks in this area was subjected to superimposed silicic metasomatism, which resulted in the silicification and sericitization of the phenocrysts and groundmass.

The volcanic glasses developed in the basins of the Vanchin–Ugol'nyi, Bezymyannyi, and Vetvistyi creeks have a black or dark gray color and contain insignificant amounts of phenocrysts of quartz, pla-gioclase, scarce biotite, and ore minerals. In the groundmass, the glass is colorless with a prominent fluidal–banded structure. Secondary alterations in the zones of hydrothermal reworking are expressed in the zeolitization and formation of hydromicaceous minerals.

Tuffisite bodies consist of different-size (from a few centimeters to a few meters across) fragments of coalified mudstones, siltstones, tuffstones, and mudstones, as well as volcanic glasses. They are cut by fissures impregnated by the groundmass material. Coalified wood fragments occasionally occur. The light gray cement consists of decomposed felsic volcanic glass and is saturated with small coal particles.

The tuffaceous conglomerates of the andesite sequence were formed at the initial explosive stage of the andesite volcanism and consist mainly of boulders of massive and amygdaloidal variably oxidized, chloritized, and bleached andesites. The variegated color of these rocks is caused by the secondary alterations. Fragments of rhyolites and their tuffs are fairly rare. The volcanic clastic material varying in size from 5 to 20 cm accounts for from 60% to 80–90 vol %. The matrix is represented by palagonized and chloritized ash matter of yellowish green color. The rocks show coarse bedding with the alternation of "beds" with variable contents and sizes of rounded fragments. Similar rocks related to the Eocene andesite explosive volcanism were previously studied by us in the Kraskinskaya depression [13].

The trachyandesites that compose extrusions, dikes, and lava flows have a dark gray color and a glassy aphyric or fine-grained groundmass. The rocks have a porphyritic texture with scarce phenocrysts of olivine, plagioclase, and clinopyroxene, and fragments of xenogenic quartz. Microscopically, the groundmass of the glassy rocks is represented by pure transparent glass of light brown composition. The texture is hyalopilitic in the marginal facies of the flows and intersertal in the central parts. Secondary alterations are expressed in the partial chloritization of the olivine and clinopyroxene.

# ZEOLITE MINERALIZATION OF THE VANCHINSKAYA DEPRESSION

Zeolitites (rocks with a zeolite content of more than 50%) are typical of the volcanogenic deposits of

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Fig. 5. Zeolites from the Vanchinskaya depression.

(a) clinoptilolite crystals filling pores (vitro-crystal tuff, sample P-503, polished thin section, parallel nicols); (b) replacement of volcanic glass particles by zeolite–smectite aggregates (tuffstone, sample R-7-1, secondary electron images made using a ZEISS EVO 50 XVP scanning electron microscope, Far East Geological Institute, Far East Division, Russian Academy of Sciences).

the Vanchinskaya depression. Zeolite-smectite aggregates replace felsic volcanic glass, which constitutes both ash particles in tuffites, tuffaceous siltstones, tuffstones, and tuffaceous conglomerates, and large fragments in the vitric tuffs. These rocks are mainly exposed in the edge of the distinctly expressed in relief linear scarp tracing the normal fault in the central part of the depression (Fig. 1). Zeolitites were found among the tuffstones, tuffites, and vitric-crystal tuffs of the basal Paleocene horizon as chains of occurrences along the Vanchin-Ugol'noe Creek (the Nizhnee, Berezovoe, and Dorozhnoe); among the tuffaceous siltstones of the Lower Eocene carbon-bearing horizon (the Ugol'noe occurrence); and in the vitric-crystal tuffs of the Eocene volcanic complex (the Ruslovoe and Gribok occurrences in the Milogradovka River's bed) (Fig. 1). The visible thickness of the zeolitized rocks varies from 1.5 m (the Ugol'noe occurrence) to 20 m (the Berezovoe occurrence).

The zeolite mineralization has a stratiform morphology. The exposures of zeolitites on the right bank of the Vanchin-Ugol'nyi Creek, including the Nizhnee and Berezovoe occurrences studied by us in detail, are similar. They are composed of tuffstones and tuffites of the subcoal bed with a significant admixture of coalified plant detritus. The Dorozhnoe occurrence, which is also confined to the northwestern fault, is represented by zeolitized vitric-crystal tuffs of rhyodacite composition. The thickness of the zeolitic bed reaches 15 m here. The Ugol'noe occurrence is represented by a thin exposure of zeolitized tuffaceous siltstones beneath the bed of brown coal at the head of the right tributary of the Vanchin-Ugol'nyi Creek. The Ruslovoe occurrence is situated in the Milogradovka River bed upstream of the emptying of the Vanchin-Ugol'nyi Creek into it. In this area, the zeolitization is

developed after felsic vitric tuffs, which compose a bed 5 m thick. The Gribok occurrence is located in the bifurcation area of the upper tributaries of the Milogradovka River (the Vetvistyi, Dlinnyi, and Bezymyannyi creeks). It is also confined to the vitric tuffs located at the base of the perlite flow. The visible thickness of the zeolites is 5 m.

According to the X-ray data, the mineral composition of the zeolitites is approximately similar in all the occurrences and consists of 50–70% zeolites of the heulandite–clinoptilolite group, as well as quartz, feldspar, cristobalite, and clay minerals of the smectite group (Fig. 5). The predicted reserves of zeolitites with a clinoptilolite content of 70% in the Vanchinskaya depression are estimated at 30 million tones [8].

In general, the zeolitites of the Vanchinskii graben are ascribed to the subfacies of highly siliceous K–Na zeolites of the zeolite–smectite facies of argillically altered rocks known in the development areas of the dacite-andesite volcanism [5]. The zeolite mineralization of the Vanchinskaya depression is developed after tuffaceous–sedimentary rocks enriched in the vitric component, being controlled by the longitudinal NWtrending faults, which served as channels for the circulation of hydrothermal solutions presumably produced by a deep-seated magmatic chamber. Judging from the mineral composition of the metasomatites, these solutions had a temperature of  $130-150^{\circ}$ C and lower and represented a weakly alkaline (pH 7–1) environment.

# GEOCHEMICAL CHARACTERISTICS OF THE VOCLANIC AND VOCLANOGENIC– SEDIMENTARY ROCKS

Most of the rocks that fill the Vanchinskaya depression experienced strong alteration. Volcanogenic-

Sample no	Rock	Locality	Analytical method	Reference
P-504/5	Porphyritic rhyolite	Vetvistyi Creek	KHIM, ICP-MS	This work
631/74	Extrusion of quartz—feldspathic porphyries	Soyuznoe deposit	KHIM	[18]
113/73	Rhyolite	Soyuznoe deposit	KHIM	[18]
1928	Rhyolite	Vetvistyi Creek	KHIM	[1]
P-504/2	Aphyric perlite	Vetvistyi Creek	KHIM, ICP-MS	This work
P-504/3	Perlite	Bezymyannyi Creek	KHIM, ICP-MS	the same
P-504/6	Perlite	Vanchin–Ugol'nyi Creek	KHIM, ICP-MS	"
84a	Perlite	Vanchin–Ugol'nyi Creek	KHIM	[1]
P-504/8	Trachyandesite	Vanchin–Ugol'nyi Creek	KHIM, ICP-MS	This work
049-18	Trachyandesite	Vanchin–Ugol'nyi Creek	KHIM, ICP-MS	the same
P-514/5	Vitric trachyandesite	Bezymyannyi Creek	KHIM, ICP-MS	"
V-1/88	Trachyandesite extrusion	Vetvistyi Creek	KHIM, INAA	"
V-600/87	Trachyandesite dike	Bezymyannyi Creek	KHIM, INAA	"
P-503	Zeolitized vitric-crystal rhyolitic tuff	Vanchin–Ugol'nyi Creek, Dorozhnoe occur- rence	KHIM, ICP-MS	"
2-3g	Zeolitized vitric-crystal rhyolitic tuff	Milogradovka River, Rechnoe occurrence	KHIM, ICP-MS	"
3-5g	Zeolitized tuffite	Vanchin–Ugol'nyi creek, Nizhnee occur- rence	KHIM, ICP-MS	"
R-7-1	Zeolitized tuffstone	Vanchin–Ugol'nyi Creek, Berezovoe occur- rence	KHIM, ICP-MS	"
R-7-2	Zeolitized tuffstone	the same	KHIM, ICP-MS	"
R-7-3	Zeolitized tuffstone	the same	KHIM, ICP-MS	"
2-43	Zeolitized tuffaceous siltstone	Vanchin–Ugol'nyi Creek, Ugol'noe occur- rence	KHIM, ICP-MS	"
V-1/03	Zeolitized tuffaceous siltstone	the same	XRF, INAA	"
V-1/03u	Coal inclusion	the same	ICP-MS	"

**Table 3.** List of studied samples used in this work

Note: Analytical methods: CHIM—chemical; XRF—X-ray fluorescence analysis, INAA—instrumental neutron activation analysis, ICP MS inductively coupled plasma mass spectrometry. Samples 113/73, 631/74, V-600/87, V-1/88, V-1/03, and V-1/03u were analyzed at the laboratories of the IGEM RAS. The other analyses: the chemical analysis—at the Far East Geological Institute of the Far East Branch of the Russian Academy of Sciences using the wet chemistry method; the ICP MS was conducted at the Vinogradov Institute of Geochemistry and Analytical Chemistry of the Siberian Branch of the Russian Academy of Sciences.

sedimentary rocks, lavas, and tuffs of rhyolites were subjected to the maximal hydrothermal reworking, which caused significant transformations in their chemical composition, while the trachyandesites experienced the least alterations. Information on the locality of the studied samples and the methods of their study is given in Table 3. The chemical and trace element composition of the least altered volcanic rocks is shown in Table 4, while that of zeolitites, in Table 5.

In the  $SiO_2-K_2O + Na_2O$  classification diagrams, the data points of the felsic rocks are plotted in the fields of dacites, rhyodacites, and rhyolites (Fig. 6a). In terms of the Al<sub>2</sub>O<sub>3</sub> and alkali contents, the rocks are ascribed to the plumasite type. The rhyolites and volcanic glasses belong to the high-K series (Fig. 6b). In the rhyolites, K significantly predominates over Na. In the zeolitized rocks, the total alkali content is lower relative to that in the unaltered rhyolites and volcanic glasses. In the perlites, the  $K_2O/Na_2O$  ratio is close to 1. This ratio is preserved in the other zeolitized rocks: vitric tuffs (the Dorozhnoe occurrence) and tuffites (the Berezovoe and Nizhnee occurrences). The zeolitized vitric tuffs, tuffites, and tuffstones from different parts of the volcanogenic-sedimentary sequence have similar chemical compositions.

In the SiO<sub>2</sub>- $K_2O$  + Na<sub>2</sub>O diagram, the data points of the lava flows and extrusive bodies of andesites from the Vanchin–Ugol'nyi and Bezymyannyi creeks are plotted at the andesite–trachyandesite–trachydacite boundary (Fig. 6a). In terms of the Na<sub>2</sub>O/K<sub>2</sub>O ratio (0.82–1.06), the rocks are ascribed to the K–Na series. In terms of the aluminum index, the trachyandesites are classified as highly aluminous and

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Table 4. Chemical composition of the unaltered and weakly altered volcanic rocks of the Vanchinskaya depression

Sam	Rocks												
ple		Rhyo	lites		Perlites				Trachyandesites				
no.	P-504/5	631/74	113/73	1928	P-504/2	P-504/3	P-504/6	84a	P-504/8	049-18	P-514/5	V-600/87	V-1/88
SiO <sub>2</sub>	79.60	74.52	74.64	75.86	72.65	71.77	70.51	69.40	62.96	62.56	62.96	62.32	64.00
TiO <sub>2</sub>	0.13	0.08	0.20	0.12	0.14	0.12	0.16	0.09	0.85	0.85	0.88	0.91	0.88
$A1_2O_3$	8.00	12.13	12.87	12.61	12.04	11.93	11.94	13.63	14.04	15.75	15.38	15.50	14.73
$Fe_2O_3$	1.87	1.94	1.47	1.81	0.89	1.16	1.99	2.27	4.65	3.89	2.40	3.40	3.49
FeO	1.17	0.34	1.24	1.07	1.60	0.85	0.59	0.84	3.96	2.57	4.31	2.45	1.72
MnO	0.01	0.05	0.04	0.04	0.06	0.05	0.08	0.05	0.14	0.28	0.20	0.15	0.12
MgO	0.24	0.06	0.17	0.02	0.33	0.05	0.18	0.28	1.05	0.81	1.29	0.91	0.25
CaO	0.33	0.45	0.28	0.38	0.33	1.05	1.08	1.44	2.45	3.09	2.45	3.57	3.68
Na <sub>2</sub> O	2.75	3.56	2.24	3.88	3.80	4.25	3.98	3.78	3.88	3.39	4.14	3.26	3.52
K <sub>2</sub> O	5.27	4.38	5.08	4.45	3.62	3.01	3.60	3.71	3.65	3.55	3.75	3.94	3.32
$P_2O_5$	0.05	<	0.06	0.02	0.02	0.03	0.07	0.05	0.33	0.36	0.41	0.67	0.97
L.O.I.	0.78	1.10	0.70	0.21	4.67	5.55	5.32	4.44	1.69	2.41	1.36	1.95	2.81
Total	99.95	98.61	98.99	100.47	100.15	100.16	99.50	99.98	99.65	99.51	99.53	99.03	99.49
Sc	2.0	_	_	_	3.0	3.0	7.0	_	_	14.9	18.0	20.0	20.9
V	5.0	_	_	_	4.0	4.0	7.0	—	_	69.9	120.0	_	—
Ga	18.0	_	_	_	18.0	19.0	17.0	_	_	19.5	22.0	_	_
Ge		_	_	_	1.8	1.4	1.3	_	_	1.4	1.7	_	—
Rb	217.0	—	—	—	455.0	478.0	174.0	—	_	92.8	112.0	_	—
Sr	56.0	—	—	_	103.0	75.0	97.0	—	_	249.4	366.0	—	—
Y	39.0	—	—	—	51.0	39.0	30.0	—	_	30.7	42.0	_	—
Zr	98.0	—	—	_	232.0	216.0	199.0	—	_	273.7	314.0	—	—
Nb	26.0	—	—	_	21.0	45.0	14.0	—	_	19.4	24.0	—	—
Sn	5.0	—	—	-	6.0	3.0	4.0	_	_	1.9	4.0	_	—
Cs	4.5	—	—	_	74.9	209.7	10.7	—	_	7.0	17.7	21.0	8.2
Ba	153.0	—	—	-	453.0	436.0	494.0	_	_	631.3	805.0	_	—
La	41.3	—	—	_	56.6	44.8	32.6	—	_	41.6	45.7	46.5	46.5
Ce	100.6	—	—	_	116.3	98.5	71.8	—	_	72.7	97.0	94.0	98.0
Pr	10.2	—	—	-	13.1	11.6	8.2	—	_	9.4	11.1	_	—
Nd	34.8	—	—	—	50.8	37.5	29.3	—	—	37.1	43.5	50.7	52.2
Sm	7.4	—	—	-	11.0	8.4	6.0	—	_	7.3	8.9	10.5	11.3
Eu	0.3	—	—	—	1.1	0.8	0.7	—	—	1.9	2.2	2.6	2.6
Gd	8.1	—	—	-	11.0	7.7	5.6	-	_	6.8	9.7	8.3	8.3
Tb	1.1	—	—	—	1.5	1.2	1.0	—	—	0.8	1.3	1.2	1.2
Dy	6.3	—	—	-	8.3	6.7	5.2	-	_	5.4	6.7	—	—
Но	1.3	—	—	—	1.6	1.4	1.1	—	_	1.1	1.3	_	—
Er	3.8	—	—	-	4.9	3.6	3.1	—	_	3.0	3.8	—	—
Yb	4.0	—	—	—	4.8	3.6	3.1	—	_	2.9	3.3	3.5	3.6
Lu	0.6	—	—	-	0.7	0.5	0.4	—	_	0.4	0.5	0.5	0.5
Hf	4.1	_	_	-	6.6	7.5	6.4	—	—	7.7	7.3	7.9	8.6
Ta	3.0	—	—	-	2.0	4.0	1.0	—	—	1.2	2.0	1.2	1.3
Pb	49.0	—	—	-	32.0	24.0	20.0	-	—	14.4	31.0	—	_
Th	17.9	—	—	-	18.5	20.7	16.0	-	—	12.3	11.7	9.6	9.8
U	4.2	—	—	—	4.5	4.1	3.8	—	—	2.4	2.6	2.0	2.8

Note: For the characteristics of the samples, see Table 3; "-" the contents were not determined; < denotes contents below the detection limit.

	Rocks									
	Tu	ıffs	Tuffites		Tuffstones		Tuffaceou	Tuffaceous siltstones		
Sample no.	P-503	2-3g	3-5g	<b>R-7-1</b>	R-7-2	R-7-3	2-43	V-1/03	V-1/03u	
SiO <sub>2</sub>	75.69	69.31	71.87	66.93	68.04	68.03	70.58	67.30	_	
TiO <sub>3</sub>	0.18	0.2	0.2	0.24	0.22	0.2	0.2	0.24	-	
$A1_2O_3$	9.71	14.5	12.44	12.63	12.36	11.95	16.55	14.50	-	
Fe <sub>2</sub> O <sub>3</sub>	1.21	1.86	2.37	2.60	2.57	2.31	1.02	3.85	_	
FeO	1.08	0.13	0.29	_	_	_	0.35	_	_	
MnO	0.01	0.03	0.03	0.03	0.04	0.02	0.02	0.03	_	
MgO	0.22	0.99	0.16	0.18	0.17	0.16	0.13	0.54	_	
CaO	0.24	1.78	1.79	0.68	0.69	0.7	0.92	1.71	_	
Na <sub>2</sub> O	2.68	1.58	1.92	2.85	2.52	2.85	1.81	0.41	_	
K <sub>2</sub> O	3.71	6.79	2.87	3.42	3.25	3.23	3.48	0.45	_	
$P_2O_5$	0.05	0.05	0.03	0.02	0.02	0.02	0.04	0.02	_	
L.O.I.	5.06	2.67	5.6	10.74	10.37	10.74	4.73	10.20	-	
Total	99.84	99.89	99.57	100.32	100.25	100.21	99.83	99.25	-	
Sc	7.0	8.0	8.0	10.0	7.0	7.0	1.2	7.4	0.8	
V	7.0	_	10.0	12.0	9.0	8.0	6.0	4.0	4.0	
Ga	20.0	20.0	24.0	37.0	28.0	26.0	21.3	45.0	22.8	
Ge	0.9	1.7	1.0	-	_	_	0.7	2.0	188.1	
Rb	182.0	234.0	168.0	210.0	154.0	148.0	106.9	35.0	2.0	
Sr	197.0	92.0	207.0	94.0	63.0	62.0	7.8	107.0	102.6	
Y	68.0	49.0	72.0	69.0	41.0	43.0	21.3	63.0	171.0	
Zr	494.0	203.0	507.0	595.0	470.0	445.0	250.2	849.0	233.7	
Nb	28.0	22.0	37.0	39.0	32.0	28.0	34.4	36.0	262.2	
Sn	5.0	5.0	4.0	5.5	4.6	3.9	4.9	7.0	<	
Cs	9.8	13.5	25.4	17.2	13.2	13.2	10.8	5.9	0.3	
Ba	424.0	483.0	373.0	131.0	91.0	91.0	48.4	212.0	5.1	
La	45.1	41.6	63.4	61.9	37.6	35.6	10.7	38.7	14.9	
Ce	91.6	85.0	138.4	114.9	74.0	68.9	4.9	81.2	31.8	
Pr	10.0	9.1	15.6	12.0	7.1	7.2	3.0	9.0	4.1	
Nd	36.1	33.1	57.9	47.0	28.9	28.3	10.2	31.6	23.6	
Sm	7.4	7.2	11.7	8.9	6.0	5.8	2.3	7.3	10.0	
Eu	0.65	0.80	0.94	0.86	0.53	0.63	0.12	0.46	0.52	
Gd	8.5	8.1	12.9	9.3	6.0	6.1	2.4	9.0	21.2	
Tb	1.3	1.1	1.9	1.5	1.0	1.0	0.4	1.4	3.4	
Dy	7.8	6.4	10.5	9.1	5.6	6.1	3.3	6.5	20.3	
Но	1.9	1.4	2.3	1.9	1.2	1.2	0.7	1.2	4.7	
Er	6.4	4.5	6.8	5.5	3.7	3.9	2.1	3.5	15.1	
Yb	7.5	4.8	7.1	6.1	4.6	4.6	2.8	4.0	17.8	
Lu	1.2	0.8	1.1	1.0	0.7	0.7	0.4	0.7	2.6	
Hf	11.8	5.9	11.7	12.0	9.9	9.8	8.9	17.3	0.5	
Та	2.0	2.0	3.0	-	—	—	2.3	2.8	0.3	
Pb	44.0	30.0	50.0	19.0	17.0	34.0	27.6	70.0	4.0	
Th	19.7	22.0	19.7	16.0	14.0	15.0	5.4	27.1	6.4	
U	4.5	3.3	3.1	3.0	2.5	2.9	3.0	5.9	10.8	

 $\label{eq:table 5. Chemical composition of the zeolitized volcanic and volcanogenic-sedimentary rocks and the coalified organic matter (OM) buried in them$ 

Note: For the characteristics of the samples, see Table 3; "-" the contents were not determined; < denotes contents below the detection limit.



Fig. 6. Petrochemical diagrams according to [28] for volcanogenic rocks of the Vanchinskaya depression ((a)  $SiO_2 - K_2O + Na_2O$ ; (b)  $SiO_2 - K_2O$ ).

(1) rhyolites; (2) perlites; (3) trachyandesites; (4) vitric-crystal tuffs

aluminous rocks (al' = 1.45-2.7). In the K<sub>2</sub>O-SiO<sub>2</sub> diagram, the data points of the trachyandesites fall in the field of the high-K volcanic series (Fig. 6b). The rocks show high contents of large ion lithophile elements (LILE) and high-field strength elements (HFSE). In the spidergrams, the trachyandesites display negative Sr, Nb, and Ti anomalies. The upper crust-normalized REE patterns [23] show depletion in LREE and enrichment in HREE at a positive Eu anomaly. It should be noted that, geochemically, the trachyandesites of the Vanchinskaya depression are close to the Oligocene–Early Miocene trachybasalts of the Sineutesovskaya depression and the trachyandesites of the Poimenskaya depression in southwestern Primorye [14].

The weakly altered felsic volcanics and zeolitized volcanogenic and volcanogenic—terrigenous rocks are fairly close in terms of their trace element abundance and have similar trace- and rare-earth element-normalized plots (Tables 4, 5. Figs. 7, 8), except for the subcoal zeolitized tuffaceous siltstones (sample 2-43) depleted in many trace elements. The latter were subjected to intense acid leaching during the filtration of solutions enriched in organic acids supplied from the overlaying coal seam during the diagenesis of the organic matter of the coals. A similar process, which is typical of coal-bearing deposits and known as "subcoal weathering," led to the kaolinitization of zeolites and the removal of many trace elements, including REE.

The zeolitites are enriched in Y and HREE as compared to the weakly altered rocks. This is well expressed in the positive Y anomalies and the asymmetric REE patterns of the zeolitites as compared to the REE patterns of the weakly altered felsic volcanics.

The enrichment of the solutions that caused the zeolitization of the tuffs and tuffaceous-sedimentary rocks in these elements is supported by the abundant accumulation of Y and HREE in the coalified organic matter (OM) (sample B-1/03u, ash content of 5.7%) buried in the zeolitized tuffaceous siltstones (sample V-1/03) overlaying the coal seam (the Ugol'noe occurrence). In addition to the HREE and Y, this natural sorbent is enriched in some other elements (Ge, Nb, and Zr), which indicates their high contents in the hydrothermal solutions circulating throughout the volcanogenic-sedimentary cover of the Vanchinskaya depression.

The elevated REE contents in the zeolitites enriched in plant detritus are presumably related to the elevated OM sorption capacity, which was noted previously [27]. However, the REE sorption by organic matter was best expressed in the high contents of these elements in the near-contact zone of the coal seams located among the zeolitized rocks [19]. The substantially organic mode of the REE occurrence in the coals of the Vanchinskii graben extremely enriched in these elements was confirmed experimentally [20].

### **INTERPRETATION**

The formation of the Vanchinskaya riftogenic depression, as other similar negative NW-striking and sublatitudinal structures of Eastern Sikhote Alin (the



**Fig. 7.** The upper-crust normalized [23] trace element distribution pattern for the unaltered and weakly altered felsic (a, c) and intermediate (b, d) volcanic rocks of the Vanchinskaya depression.

Zerkal'nenskaya, Verkhnebikinskaya, Maksimovskaya, Kedrovskaya, and others), marks the Early Cenozoic stage of the tectonic activation of the Asian continental margin in response to a change in the movement of the oceanic and continental lithospheric plates with the formation of transform faults between the Pacific plate and the Asian continent [10, 26]. This stage is characterized by the subsequent development of the sinistral [25] and dextral [4, 21, 31] strike-slip faults and the formation of pull-apart basins with inherent volcanism and sedimentation.

In the continental margin of the Sea of Japan basin, the pull-apart basins were united into the Hasan– Amur area of riftogenic depressions [15], which extended from the Kiljoo–Menchon depression and the Kenson depression (North Korea) to the Bukhtyanskaya and Maslovskaya depressions in the nearmouth part of the Amur. It includes riftogenic volcanic depressions imposed onto the accreted pre-Cenozoic basement rocks and the suprasubduction Late Cretaceous volcanics of the Eastern Sikhote Alin volcanic belt.

As was shown in [7], the volcanism of the Cenozoic riftogenic depressions of the Eastern Sikhote Alin (within the Taukhe and Zhuravlevka terranes) in terms

of the age and geochemical features of the rocks is close to the volcanism of the Cenozoic riftogenic depressions of the Laoelin-Grodekovo terrane (southwestern Primorye). However, the new K-Ar dates obtained by us for the rhyolites (44.7  $\pm$  1.0 Ma) and trachyandesites  $(43 \pm 4 \text{ Ma})$  of the Vanchinskaya depression and the U/Pb zircon age for the trachydacites from the Kedrovskaya caldera in northern Primorye (43.2  $\pm$  1.3 Ma, unpublished original data), together with the K/Ar data on the basalts from the Zerkal'nensyaya depression (47.3  $\pm$  1.2 Ma [29] and  $45.8 \pm 1.1$  Ma [30]), indicate that the areal basaltrhyolite volcanism in Eastern Sikhote Alin occurred in the Early-Middle Eocene. In the riftogenic depressions of the Laoelin-Grodekovo terrane, bimodal volcanism occurred later: 48.1-34.4 (basalts and andesites) and 33.5 (rhyolites and dacites) Ma ago [17]. The exception is the extrusive dacite of Mt. Shkol'naya (the southwestern flank of the Ambinskaya depression) located near the tectonic suture separating the Arsen'evskaya zone from the Laoelin-Grodekovo terrane. It has an Rb–Sr isochron age of  $46.2 \pm 0.5$  Ma [17]. According to [17], the revealed trend in the spatiotemporal migration of the volcanism is regarded to be related with the sign-variable rotation of the Pacific

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**Fig. 8.** The upper crust-normalized [23] trace element distribution pattern for the zeolitized volcanic and volcanogenic-sedimentary rocks (a, c) and the organic matter buried in them (b, d).

plate, which caused alternating compression and extension of the continental margin in the Arsen'evskaya zone and the Laoelin–Grodekovo terrane.

The Vanchinskaya and the adjacent west Berezovskaya depressions represent pull-apart basins along the Central Sikhote Alin (sublongitudinal) and Furmanovskii (northeastern) faults, which were responsible for repeated sinistral strike-slip movements with up to 100-km amplitudes of the horizontal displacements (along the Central fault) in the Mesozoic–Cenozoic [6].

The pull-apart nature of the Cenozoic depressions of Eastern Sikhote Alin, which are similar to the Vanchinskaya and Berezovskaya depressions, was shown previously in the works of Utkin [3, 25, and others].

The Paleocene age determined by S.V. Nevolina and B. I. Pavlyutkina for the fossil plants from the lower part of the coal-bearing sequences of the Vanchinskaya depression indicates that this structure was initiated at the initial stage of the eruptions of the Soyuznenskii volcano located in its southeastern flank. The quartz–adularia stringers with gold–silver mineralization at the Soyuznoe deposit were formed within 45–49 Ma [18, 24], i.e., simultaneously with the cessation of the long-term evolution of the felsic volcanism in the Soyuznenskii volcanic center and with the beginning of the bimodal volcanism in the central part of the graben.

The Vanchinskaya depression represented a closed half-graben with a large lacustrine basin, which was the main accumulator for terrigenous and volcaniclastic sediments. The Paleocene-Early Eocene subsidence of the depression was compensated for by the accumulation of conglomerates and finer volcanogenic-sedimentary rocks. The significant admixture of volcanic ashes in them and the change of the tuffstones, tuffaceous siltstones, and tuffites to vitric rhyodacite tuffs in the southeastern direction indicate simultaneous sedimentation and volcanism. The variable grain-size and mineral composition of the sedimentary rocks, the ubiquitous admixture of pyroclastic material, the insignificant thickness and discontinuity of the coal seams, the inconsequent alternation of sedimentary and volcaniclastic rocks, the disturbance of the bedding, and the traces of stirring up and sliding of the bed indicate an unstable sedimentation setting typical of the depressional structures of active volcanic areas [2].

In terms of lithological composition and floral assemblage, the basement rocks of the depression well correlate with the volcanogenic—sedimentary rocks of

the Tadushin Formation from the base of the Zerkal'nenskaya depression, which also contains horizons of zeolitized rocks. As was shown for the Zerkal'nenskaya depression [12], the volcaniclastic material occupying a significant part of its deposits was supplied by explosive rhyolite eruption of the Bogopol Complex, which occurred within the range of 59.68  $\pm$  1.59 to 52.92  $\pm$  1.0 Ma ago. It is conceivable that the influx of volcaniclastic material in the Vanchinskaya depression occurred in a similar manner at the initial stage of its evolution. Its sources were presumably the products of explosive eruptions of the Soyuznenskii paleovolcano.

The rhyolites of the Vanchinskaya depression in terms of age and chemical composition are correlable with the rhyolites and trachydacites of the Kedrovskii complex distinguished in the upper reaches of the Kuznetsovaya River (Kedrovyi Creek) in northern Primorye. The felsic volcanic glasses and ashes of the Kedrovskii Complex in the eponymous caldera also contain manifestations of zeolitites [9, 11]. The final volcanic stage of the depression evolution was completed by the eruptions of trachyandesidacites, which formed a small volcanic edifice. Its fragments were found in the central part of the depression in the form of explosive tuffaceous conglomerates, lava flows, and extrusive bodies of aphyric and glassy trachyandesites. The unusual HFSE and REE distribution in the trachyandesites could have been caused by the interaction of basaltic melts with felsic crustal material with the subsequent selective contamination of the magmas. Such a mechanism was considered previously during studying potassic trachybasalts and trachyandesites in the calc-alkaline series [14]. The final phase of the trachyandesite volcanism was presumably responsible for the formation of the zeolite mineralization in the Vanchinskaya depression.

The subsequent evolution of the Vanchinskii graben was amagmatic and consisted mainly in vertical tectonic movements and the accumulation of a thick fanglomerate sequence near its steep fault-related side.

#### CONCLUSIONS

The Vanchinskaya depression is filled with a Paleocene–Early Eocene coal-bearing volcanogenic–sedimentary sequence and a Middle Eocene lava-pyroclastic sequence of rhyolites and trachyandesites. This is confirmed by the paleobotanical data and the results of the K–Ar dating of the volcanic rocks.

The Middle Eocene rhyolites and trachyandesites of the Vanchinskaya depression in terms of age (43–45 Ma) are comparable with similar rocks from the riftogenic depressions of Eastern Sikhote Alin. The formation of geochemically close andesites and rhyolites in the riftogenic depression of the Laoelin–Grodekovo terrane (Southwestern Primorye) occurred substantially later—38–33 Ma ago.

The volcanic rocks are ascribed to the high-K series and characterized by significant variations in their large ion lithophile, high-field strength, and rareearth element abundances with a negative Eu anomaly in the rhyolites and a positive one in the trachyandesites.

The zeolitized rocks (perlites, vitric tuffs, and tuffstones) from different parts of the volcanogenic-sedimentary deposits of the depression have a similar chemical composition, and most of them are extremely enriched in Y and HREE. The formation of the zeolitites is related to the hydrothermal alteration of felsic volcanic and volcanogenic-sedimentary rocks at the final stage of the volcanic activity in the Vanchinskii graben.

#### ACKNOWLEDGMENTS

We are grateful to B.I. Pavlyutkina and T.I. Petrenko for paleobotanical determinations and useful advice.

This work was supported by the Far East Division of the Russian Academy of Sciences (project nos. 09-III-B-08-462 and 09-III-A-08-407), the Russian Foundation for Basic Research (project no. 08-05-90300-Viet\_a), and the Presidium of the Russian Academy of Sciences (program 1.1.2., project no. 14).

#### REFERENCES

- Yu. P. Bidyuk, Explanatory Notes to Geological Map on a Scale 1 : 200000 Sikhite Alin Series, Sheet K-53-III (Moscow, 1983) [in Russian].
- 2. A. V. Van and Yu. P. Kazanskii, *Volcaniclastic Material in Sediments and Sedimentary Rocks* (Nauka, Novosibirsk, 1985) [in Russian].
- 3. *East Asian Volcanic Belts* (Nauka, Moscow, 1984), p. 504 [in Russian].
- V. V. Golozubov, S. V. Miklovda, Dong Woo Lee, et al., "Dynamics of the Formation of the Cenozoic Uglovsky Basin (Southern Primorye)," 26 (4), 22–33 [Russ. J. Pac. Geol. 1 (4), 324–334 (2007)]
- V. A. Zharikov, V. L. Rusinov, and A. A. Marakushev, *Metasomatism and Metasomatic Rocks* (Nauch. mir, Moscow, 1998) [in Russian].
- 6. B. A. Ivanov, "Central Sikhote Alin Fault (Strike-Slip)," Dokl. Akad. Nauk SSSR **138** (4), 900–903 (1961).
- Yu. A. Martynov, S. V. Kovalenko, S. V. Rasskazov, and E. V. Saranina, "Geochemistry and Metallogenic Problems of Postsubduction Calc-Alkaline Volcanics of the Southwestern Primorye," in *Ore Deposits of Continental Margins* (Dal'nauka, Vladivostok, 2001), No. 2, pp. 5– 20 [in Russian].
- A. S. Mikhailov, A. I. Burov, and P. O. Ablyamitov, *Economic Zeolite Potential of Siberian and Far East* (VIEMS, Moscow, 1980) [in Russian].

2010

- 9. A. M. Panichev, *Animal Solonetz of Sikhote Alin (Biological–Geological Aspect)* (DVNTS Akad. Nauk SSSR, Vladivostok, 1987) [in Russian].
- L. M. Parfenov, N. A. Berzin, A. I. Khanchuk, et al., "Model" of the Formation of Orogenic Belts in the Central and Northeastern Asia," Tikhookean. Geol. 22 (6), 4–41 (2003).
- V. K. Popov, Petrology of the Paleogene-Neogene Complexes of the East Sikhote Alin (Vladivostok, 1986) [in Russian].
- V. K. Popov and A. V. Grebennikov, "New Age Data of the Voclanic Rocks of the Bogopol Formation, Primorye," Tikhookean. Geol. 20 (3), 47–54 (2001).
- V. K. Popov, "Features of Occurrence and Composition of Intrusive Pyroclastites in the Cenozoic Depressions of the Southwestern Primorye," in *Proceedings of IInd All-Russian Symposium on Volcanology and Paleovolcanology on Volcanism and Geodynamics, Yekaterinburg, Russia, 2003* (Inst. Geol. Geokhim. UrO RAN, Yekaterinburg, 2003), pp. 704–709 [in Russian].
- V. K. Popov, S. V. Rasskazov, I. Yu. Chekryzhov, et al., K-Ar Datings and Geochemical Characteristics of the Cenozoic Trachybasalts and Trachyandesites of Primorye in *Annual Seminar on the Geochemistry of Magmatic Rocks*. Proceedings of scientific School "Alkaline Magmatism of teh Earth, Moscow, Russia, 2005," (Moscow, 2005), pp. 133–135 [in Russian].
- V. K. Popov and A. V. Grebennikov, "Khasan–Amur Area (Paleocene–Miocene). Felsic Volcanism," in *Geodynamics, Magmatism. And Metallogeny of Russian East*, Ed. by A. I. Khanchuk (DVO RAN, Vladivostok, 2006) [in Russian].
- 16. S. V. Rasskazov, N. A. Logachev, I. S. Brandt, et al., Geochronology and Geodynamics of the Late Cenozoic (Southern Siberian–South and East Asia (VO Nauka, Novosibirsk) [in Russian].
- S. V. Rasskazov, E. V. Yasnygina, E. V. Saranina, et al., "Cenozoic Magmatism of the Southwestern Primorye: Pulsed Melting of Mantle and Crust," Tikhookean. Geol. 23 (6), 3–31 (2004).
- M. G. Rub and N. A. Ashikhmina, "Silver-bearing Volcanoplutonic Associations of the Southern Primorsk Region: Compositional Features," Dokl. Ross. Akad. Nauk 355 (1), 97–100 (1997) [Dokl. Earth Sci. 355, 769–772 (1997)].
- V. V. Seredin, "On New Type of the Rare-Earth Mineralization of the Cenozoic Coal-Bearing Depressions," Dokl. Akad. Nauk SSSR 320 (6), 1446–1450 (1991).
- V. V. Seredin and M. Yu. Shpirt, "Rare Earth Elements in the Humic Substance of Metalliferous Coal," Litol. Polezn. Iskop., No. 3, 281–286 (1999) [Lithol. Miner. Resour. 34, 244–248 (1999)].
- 21. V. V. Seredin and I. N. Tomson, "The West Primorye Noble-Rare Metal Zone: A New Cenozoic Metallo-

genic Taxon in the Russian Far East," Dokl. Akad. Nauk **420** (6), 799–804 (2008) [Dokl. Earth Sci. **420**, 745–750 (2008)].

- V. V. Seredin and I. Yu. Chekryzhov, New Data on the Cenozoic Volcanism and Hydrothermal Mineralization of the Vanchinskaya Depression, Primorye, in *Proceedings of Scientific Conference on 100th Anniversary of Academician V.F. Chukhrov. Moscow, Russia, 2008* (IGEM RAN, Moscow, 2008), pp. 187–189 [in Russian].
- 23. S. R. Taylor and S. M. McLennan, *The Continental Crust: Its Composition and Evolution* (Blackwell, Oxford, 1985; Mir, Moscow, 1988).
- I. N. Tomson, O. P. Polyakova, A. A. Sidorov, and V. Yu. Alekseev, "The Soyuznoe Gold–Silver Deposit in the Primor'e Region and Its Potential," Geol. Rudn. Mestorozhd. 44 (4), 304–313 (2002) [Geol. Ore Deposits 44, 267–275 (2002)].
- 25. V. P. Utkin, *Strike-slip Dislocations, Magmatism, and Ore Formation* (Nauka, Moscow, 1989) [in Russian].
- 26. A. I. Khanchuk, V. V. Golozubov, Yu. A. Martynov, and V. P. Simanenko, "Early Cretaceous and Paleogene Transform Margins (Californian Type) of Russian Far East," in *Proceedings of 30th Tectonic Conference. Tectonics of Asia, Moscow, 1997* (Moscow, 1997), pp. 240– 243 [in Russian].
- I. Y. Chekrizhov, V. K. Popov, and A. M. Panichev, "Geochemistry and Geodynamic Regimes of Formation of Paleogenic Zeolitebearing Volcaogenic Complexes of Primorye," in *Metallogeny of the Pacific Northwest: Tectonics, Magmatism and Metallogeny of Active Continental Margins. Proceedngs of the Intern. IAGOD Conf., Vladivostok. Russia, 2004*, (Vladivostok, Russia, 2004), pp. 1–20.
- R. W. Le Maitre, P. Bateman, A. Dudek, et al., *A Classification of Igneous Rocks and Glossary of Terms*, Ed. by R. W. Le Maitre (Blackwell, Oxford, 1989).
- 29. S. Okamura, Y. A. Martynov, K. Furuyama, and K. Nagao, "K–Ar Ages of the Basaltic Rocks from Far East Russia: Constraints on the Tectono-Magmatism Associated with the Japan Sea Opening," The Island Arc, No. 7, 271–282 (1998).
- Y. Otofuji, T. Matsuda, T. Itaya, et al., "Late Cretaceous To Early Paleogene Paleomagnetic Results from Sikhote Alin, Far Eastern Russia: Implications for Deformation of East Asia," Earth Planet. Sci. Lett. 130, 95–108 (1995).
- V. V. Seredin and V.V. Golozubov, Metallogeny of Cenozoic Rifting Structures of Primorye Region, in *Proceedinsg of the Leonid Parfenov Memorial Conference. Tectonics and Metallogeny of the Circum-North Pacific and Eastern Asia, Khabarovsk, Russia, 2007*, Ed. by A. I. Khanchuk (ITIG RAS, Khabarovsk, 2007).

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