# Typomorphic features of Cr-spinel and mineralogical prospecting guides for Cr ore mineralization

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[1]  Alpine-type dunite-harzburgite-lherzolite massifs have long attracted much attention of geologists as reference objects for geological and petrological models and as massifs hosting economic deposits of Cr, Ni, and asbestos. Russia's largest deposits of Cr ores, Ni ores in weathering crusts, as well as deposits PGE, asbestos, and some other minerals are hosted by Alpine-type ultrabasic massifs of the Urals. The results of our long-term fieldwork and of the experimental and theoretical research of the mineralogy, petrography, and metallogeny of Uralian Alpine-type ultrabasites and the analysis of literature data on analogous rocks elsewhere led us to the following conclusions. The evolution of the mineral assemblages of the Alpine-type ultrabasites occurred in six major stages: mantle, regional metasomatic, pegmatitic, retrograde and prograde metamorphic, and hypergenesis. The Alpine-type ultrabasites evolved during the metamorphic stage in a closed system and could exchange only energy with the environment. The driving forces of the evolution of the mineral assemblages were variations in the intensive parameters of the mineral-forming medium, namely, a temperature and pressure decrease, variations in the fluid regime and in the pH and Eh. Certain ranges of thermodynamic parameters, and thus, certain types of mineral assemblages, corresponded to the typomorphic rocks of each stage.    *INDEX TERMS:* 1009 Geochemistry: Geochemical modeling; 1020 Geochemistry: Composition of the continental crust; 1090 Geochemistry: Field relationships; 3617 Mineralogy and Petrology: Alteration and weathering processes; *KEYWORDS:* alpine-type massifs, orogenic belts, petrology, Urals.

## Introduction

[2] Alpine-type dunite-harzburgite-lherzolite massifs are components of gabbro-ultramafic belts in mountaineous areas. They have long attracted much attention of geologists as reference objects for geological and petrological models and as massifs hosting economic deposits of Cr, Ni, and asbestos. Russia's largest deposits of Cr ores, Ni ores in weathering crusts, as well as deposits PGE, asbestos, and some other minerals are hosted by Alpine-type ultrabasic massifs of the Urals. Another noteworthy feature of these massifs in Urals, which are sometimes strongly altered and disturbed elsewhere, is a broad spectrum of metamorphic grades of these rocks, from unaltered varieties to eclogites, and their weak tectonic disturbance, which makes it possible to trace all alterations and transformation stages of the

rocks themselves and their mineralogy. This applies, first of all, to the ultrabasic rocks in the Polar Urals (Figures 1–5).

[3] We conducted topomineralogical studies of Alpine-type ultrabasic massifs in the Polar Urals for more than two decades with the aim of collecting materials on the compositions of the rocks and minerals, determining the crystallization successions and thermodynamic conditions of mineral assemblages and related complex ore mineralization. Our conclusions are based on more than 2500 chemical analyses of rocks, Cr-spinels, and rock-forming silicates [*Bryanchaninova,* 2004; *Bryanchaninova et al.,* 2004a, 2004b; *Makeyev,* 1989, 1990, 1992a, 1992b, 1994; *Makeyev and Bryanchaninova,* 1999; *Makeyev and Zaripova,* 1984; *Makeyev et al.,* 1982, 1984, 1985].

[4] In this research we widely utilized microprobe analyses. We also examined the physical properties of minerals, including their magnetic susceptibility, unit cell parameters, dispersion of their reflectance, hardness, and density. Numerous IR spectroscopic determinations were carried out to evaluate the compositions of the accessory
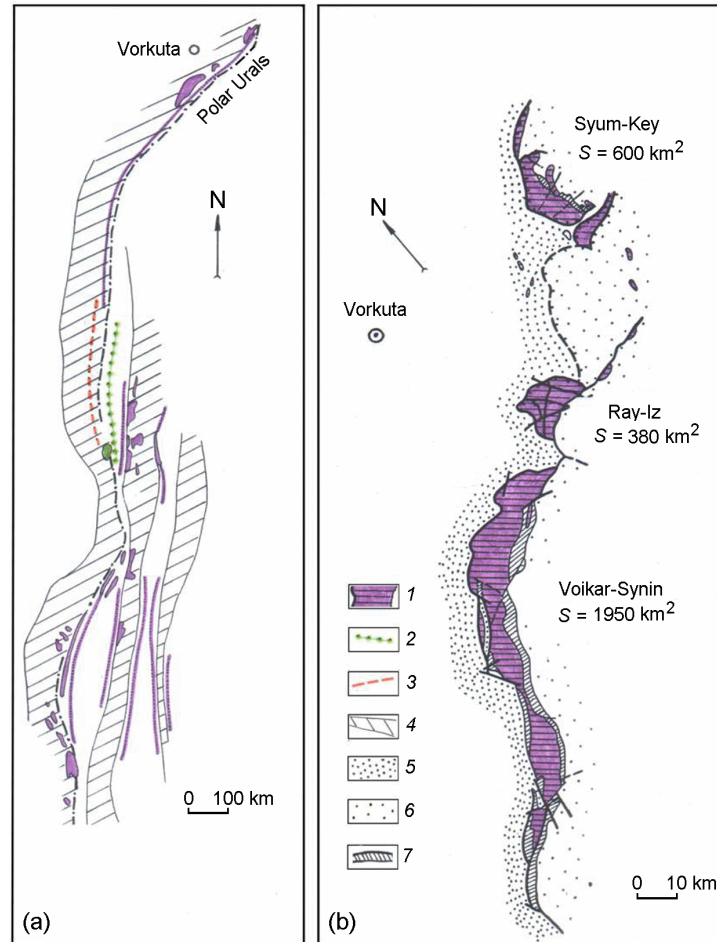
**Figure 1.** (a) Location map of ultrabasite belts in the Polar Urals and (b) schematic map showing ultrabasite massifs in the Polar Urals. 1 – Alpine-type ultrabasites of the dunite–harzburgite association; 2 – ultrabasites of the Pt-bearing association; 3 – layered ultrabasites; 5 – rocks of the western paleoceanic sector; 6 – rocks of the eastern paleoceanic sector; 7 – ultrabasites of the dunite–wehrlite–clinopyroxene complex [*Schteinberg and Zoloev*, 1985].



**Figure 2.** Northern part of the Rai-Iz Massif (as seen from the settlement of Polyarnyi).

**Figure 3.** Southern part of the Rai-Iz Massif (as seen from the Engaiskoe-I occurrence of ore mineralization). Violet rock blocks in the foreground are Cr ore. The resources of Cr ore at the Engaiskoe occurrence are 100,000 tons. The serpentine road seen in the middle distance is used to transport ore from the Tsentraloe deposit. In the background, Mount Chernaya is seen, with a contact of ultrabasites (dvc) and gabbroids.



**Figure 4.** Opencast mine of the Tsentralnoe chromite deposit with active mining operations. July 2005.

**Figure 5.** Tsentralnoe deposit: extraction of chromite ore at the smaller opencast mine (orebody 9). *R* marks Rubinonyi Log, *Z* marks the Zapadnoe chromite deposit (on the other side of the Makar-Ruz River valley).

Cr-spinels. Selected samples were additionally studied by luminescence and absorption spectroscopy within the optical region, electronic microscopy of the ultrabasic rocks and their minerals, electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), nuclear gamma resonance (Mössbauer spectroscopy) of minerals, and the geochemistry of oxygen and carbon isotopes [*Bryanchaninova et al.,* 2004a; *Makeyev,* 1989, 1990, 1992a, 1992b, 1994; *Makeyev and Bryanchaninova,* 1999; *Makeyev and Zaripova,* 1984; *Makeyev et al.,* 1982, 1984, 1985].

## Results and Discussion

[5] The results of our long-term fieldwork and of the experimental and theoretical research of the mineralogy, petrography, and metallogeny of Uralian Alpine-type ultrabasites and the analysis of literature data on analogous rocks elsewhere led us to the following conclusions.

[6] The evolution of the mineral assemblages of the Alpine-type ultrabasites occurred in six major stages: mantle, regional metasomatic, pegmatitic, retrograde and prograde metamorphic, and hypergenesis [*Makeyev,* 1992b; *Makeyev and Bryanchaninova,* 1999].

[7] The Alpine-type ultrabasites evolved during the metamorphic stage in a closed system and could exchange only energy with the environment.

[8] The driving forces of the evolution of the mineral assemblages were variations in the intensive parameters of the mineral-forming medium, namely, a temperature and pressure decrease, variations in the fluid regime and in the pH and Eh. Certain ranges of thermodynamic parameters, and thus, certain types of mineral assemblages, corresponded to the typomorphic rocks of each stage.

[9] The lherzolites, diopside harzburgites, plagioclase lherzolites, bronzitites, and plagioclase-bronzite veins complimentary to the gabbro were produced during the first stage in the mantle. The $P$–$T$ crystallization conditions of minerals and rocks during the first stage were evaluated by the pyroxene geothermometer at $T$=1200±100°C and $P$=20±5 kbar [*Makeyev,* 1992b; *Makeyev and Bryanchaninova,* 1999; *Mercier,* 1980].

[10] The rocks of the dunite–harzburgite complex (dunites, harzburgites, and websterites), the dunite–wehrlite–clinopyroxenite complex, and the high-quality metallurgical Cr ores were produced during the regional

metasomatic stage, which occurred at $T = 900\pm50°$C and $P = 12\pm5$ kbar.

[11] Regional metasomatism resulted in the olivinization of the ultrabasites, with MgO and $SiO_2$ becoming the major mobile components. The origin of large dunite masses was related to the accumulation of MgO and the removal of $SiO_2$. The olivinization of the harzburgites and lherzolites was associated with the synchronous origin of clinopyroxenite and websterite veins in which excess components (CaO, $Al_2O_3$, and $Na_2O$) were accumulated. Regional metasomatism facilitated the development of large economic deposits of Cr, whose ore mineral is chromite. The metasomatic genesis of the chromite follows from the existence of analogous metasomatic zoning (from top to bottom): harzburgite $\longrightarrow$ dunite $\longrightarrow$ chromite; an increase in the contents of ore Cr-spinel from the periphery to the cores of chromite bodies; the symmetric inner structures of the lens-shaped chromite bodies; the aureoles of lower Fe# of olivine around the chromite bodies; and other features.

[12] Under the original $P$–$T$ conditions ($T = 900\pm50°$C, and $P = 12\pm5$ kbar), contact metasomatism proceeded along contacts of ultrabasites and gabbro. This Mg–Ca metasomatism produced the dunite-wehrlite-clinopyroxenite complex. Thus, the clinopyroxenite developed after gabbro and the dunite and wehrlite replaced harzburgite and lherzolite.

[13] We were the first to identify a pegmatite stage in the evolution of the ultrabasite rocks. This stage was responsible for the origin of pegmatoid dunite with early antigorite, whose water is likely of juvenile origin. The Cr-bearing silicates (kemmererite, kochubeite, amesite, uvarovite, and pargasite) crystallized in the Cr ores during this stage in fractures and small cavities. The rare mineral association of corundum with plagioclase should also be attributed to the pegmatite stage. This association with oligoclase, ruby, phlogopite, fishmanite (Sr-bearing mica), pargasite, Fe–Al chromite, and ferroaluminochromite occurs most widely at Rubinovyi Log in the central part of the Rai-Iz Massif. The rocks are ruby-bearing pegmatites (Figure 6). The ruby plagioclasites were dated by the K–Ar method on phlogopite at $320\pm20$ Ma. The typomorphic Cr-spinel of this association is ferrochromite $(Fe_6Mg_2)_8(Cr_{12.5}Al_3Fe_{0.5})_{16}O_{32}$. The occurrence of water-, chlorine- and fluorine-bearing minerals in this mineral assemblage suggests their crystallization in the presence of a pegmatite fluid [*Bryanchaninova et al.,* 2004b; *Makeyev,* 1992b; *Makeyev and Bryanchaninova,* 1999].

[14] X-ray diffraction data demonstrate that the antigorite forms syntactic aggregates with olivine. These syntactic intergrowths suggest that the antigorite and olivine crystallized in equilibrium with each other. This is the highest temperature generation of the antigorite, which likely crystallized at temperatures of no less than $700\pm50°$C. The contents of the primary antigorite in the pegmatoid dunites vary from 1% to 5%, and, hence, the water concentration in the fluid can be evaluated at $0.13\pm0.65\%$. This was most probably juvenile water, which belonged to the ultrabasite system itself. Conversely, the serpentinization of olivine in the ultrabasite rocks proceeded under the effect of seawater [*Bryanchaninova et al.,* 2004a].

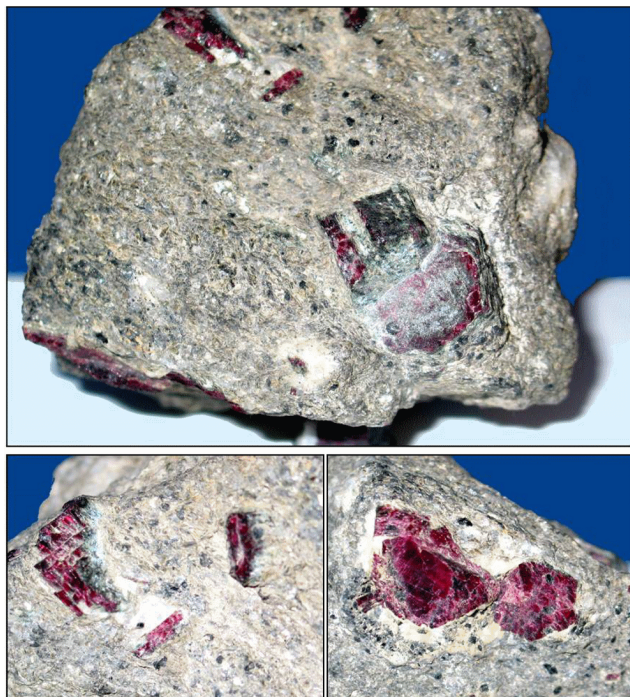[15] The pegmatites were formed after the regional meta-



**Figure 6.** Hand-specimens of plagioclasite from the Rubinonyi Log pegmatites, Rai-Iz Massif. Black inclusions in the specimens are ferrochromite; the rock contains barrel-shaped ruby crystals with rims and external films of newly formed Sr-bearing mica [*Bryanchaninova et al.,* 2004b].

somatic stage, simultaneously with the solid-state (subsolidus) transformations of the rocks, their recrystallization with the participation of a fluid, and the accumulation of Ca, K, Na, Al, and Sr in the reaction products. All minerals of the ultrabasite rocks contain isomorphous Cr and are enriched in Al. We determined that the Rubinovyi Log pegmatites bear a new Sr-bearing mica, which contains 6% SrO [*Bryanchaninova et al.,* 2004b].

[16] The main indicator of the mineral assemblages of Alpine-type ultrabasites is Cr-spinel, a mineral occurring in practically all rock varieties and having a composition and structure typomorphic of each of these varieties. The compositional evolution of the Cr-spinel (Figure 7) proceeded from Cr-picotite to chromite and then to magnetite and was associated with the depletion of Mg, Al, Zn, and Ni and enrichment of Fe (both $Fe^{2+}$ and $Fe^{3+}$), Mn, Ti, and V.

[17] Cr-spinel is one of the most widely spread typomorphic minerals of ultrabasic rocks and is contained in each of them (it is a so-called telescoped mineral). Cr-spinel is also a major mineral of the Cr ores, and its contents vary from 0.1% to 2% in various rocks: dunites, harzburgites, lherzolites, wehrlites, websterites, pyroxenites, troctolites, and metamorphic ultrabasites. The contents of Cr-spinel in dunites often increases to 10%.
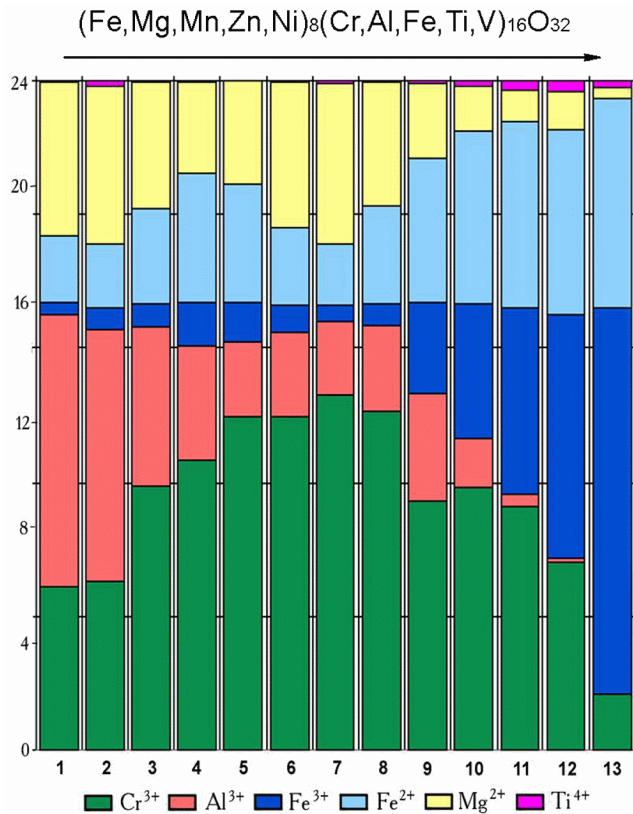
**Figure 7.** Scheme of the compositional evolution of accessory and ore Cr-spinels from high-Al to high-Cr and high-Fe types. The diagram displays the average compositions of Cr-spinel from certain rock complexes. 1 – Cr-picotite (Cpi) from lherzolites of the H complex of ultrabasites at the Kempirsai Massif; 2 – Cr-picotite (Cpi) from lherzolites of the H complex of ultrabasites at the Polar Urals; 3 – accessory and ore aluminochromite (Ach) from harzburgites of the H and DH ultrabasite complexes of the Urals; 4 – subferrialuminochromite (Sfach) from metamorphosed harzburgites and Cr ores; 5 – subferrichromite (Sfch) from metamorphosed dunites and Cr ores in the D and DH complexes of ultrabasite rocks in the Polar Urals; 6 – ore chromite from the Tsentralnoe deposit (ChT); 7 – ore chromite from the Almaz-Zhemchuzhina deposit, Kempirsai Massif, Kazakhstan (ChA); 8 – accessory chromite (Ch) from dunites of the D complex of ultrabasites of the Polar Urals; 9 – accessory subferrosubalumochromite (Fach) from metamorphosed (amphibolite facies) harzburgites of the DH ultrabasite complex of the Polar Urals; 10 – accessory and ore Cr-spinels and subaluminoferrichromite (Sfach) form metamorphosed (amphibolite facies) dunites and Cr ores in these dunites; 11 – accessory ferrochromite (Fch) from metamorphosed (high-grade prograde metamorphism) ultrabasites of the Polar Urals; 12 – chrome-magnetite (Cmt), high-Fe rims around highly metamorphosed accessory and ore Cr-spinel in ultrabasites of the Polar Urals; 13 – magnetite (Mt), an accessory ore mineral from voikarites, sagvandites, brucite–antigorite schists and other high-grade metamorphic (hornfels facies of contact metamorphism) ultrabasites of the Polar Urals.

[18] Cr-spinel grains broadly vary in shape and size: from dust-sized (0.001 mm) inclusions in silicates to large (5–25 mm) grains and their aggregates (Figures 8, 9). Their shapes and color also vary. Anhedral transparent grains of Cr-spinel of color varying from yellowish green to brown were found only in the primary lherzolites and harzburgites. Equant reddish brown transparent grains are typical of the aluminochromite ores. Euhedral Cr-spinel crystals of octahedral habit, opaque (usually black) are contained in the secondary metasomatic rocks: dunites, pyroxenite veins, and high-Cr ores. Anhedral and skeletal crystals, which are sometimes replaced by serpentine and chlorite, are typical of accessory Cr-spinel in the metamorphic ultrabasites. Metamorphic Cr-spinel is usually black and opaque and often contains multiphase inclusions.

[19] The reflectance indices ($R$) of polished Cr-spinel grains and their microprobe analyses indicate that these grains are either homogeneous or zonal, with cores of primary composition and younger ferro-ferri Cr-spinel margins (Figure 10). Such grains are often surrounded by kemmererite rims (rinds) and consist of three zones: (i) cores, (ii) peripheral rims of ferrochromite, ferrichromite, and Cr-magnetite, (iii) and rinds of chlorite with magnetite dust.

[20] The composition of Uralian Cr-spinel varies within fairly broad ranges. We have compiled a database of analyses of Cr-spinel (more than 1000 chemical and microprobe analyses; Figures 11–13). Most of these analyses characterized ultrabasite massifs in the Polar Urals [*Makeyev,* 1992b; *Makeyev and Bryanchaninova,* 1999]. The database also includes approximately 200 analyses of accessory and ore Cr-spinel from the Kempirsai, Sarany, Nizhnii Tagil, and Veresobyi Bor massifs, from the Western Sayan Range, and from some other territories [*Makeyev and Bryanchaninova,* 1999; *Pavlov and Grigorieva-Chuprynina,* 1973]. These analyses were used for comparison.

[21] The composition of the ore Cr-spinel usually varies from Cr-picotite to chromite, and the composition data points plot near the left corner of N. V. Pavlov's triangular diagram [*Pavlov and Grigorieva-Chuprynina,* 1973]. Each of the massifs is characterized by its own variability ranges of the composition and physical properties of its Cr-spinel. We established two isomorphic trends for the ore Cr-spinel: Mg, Al $\longrightarrow$ Fe$^{3+}$ and Mg, Al $\longrightarrow$ Fe$^{2+}$, Fe$^{3+}$. The former and latter trends characterize the primary and metamorphic ores, respectively. The accessory Cr-spinel is even more variable in composition. In Pavlov's triangular plot, the data points of the accessory Cr-spinel scatter not only in the left-hand part (as the ore Cr-spinel points do) but also extend into the right-hand part (Figures 11–13). The most broadly variable composition is characteristic of Cr-spinel from the Syum-Keu, Rai-Iz, and Nizhnii Tagil massifs. Their metamorphic Cr-spinel is ferrochromite, ferrialuminochromite, ferrichromite, Cr-magnetite, and magnetite. The Voikar-Syninskii and Kempirsai massifs contain primary picotite, Cr-picotite, aluminochromite, and chromite. This reflects the intensity of metamorphic transformations of the ultrabasites of these massifs. The compositional variations of the accessory Cr-spinel were traced from picotite to chromite according to the following tendency: Mg, Al, Zn, Ni $\longrightarrow$ Cr, Fe$^{2+}$, Fe$^{3+}$, Mn, Ti, V. The Cr-spinel in the

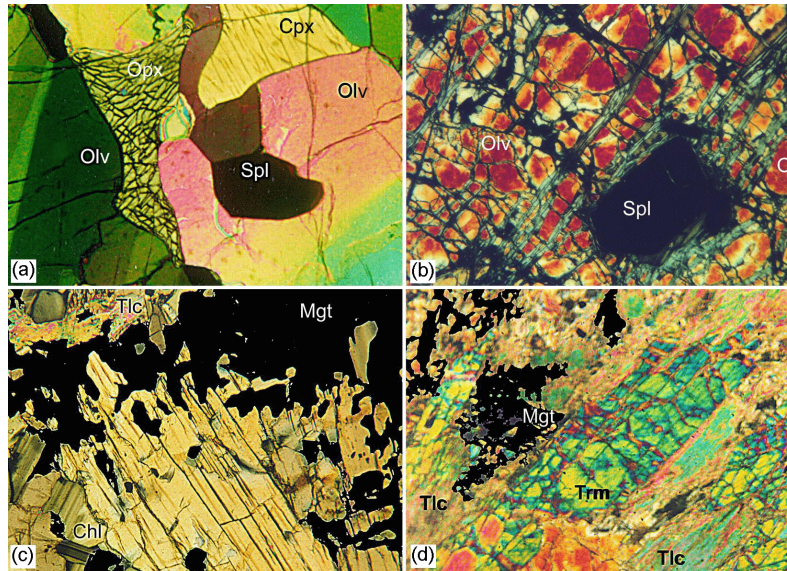**Figure 8.** Morphology of Cr-spinels from various ultrabasite rocks (fragments of thin sections, crossed polarizers, magnification 80×). (a) Unaltered lherzolite, Voikar-Synninskii Massif, Levaya Paiera River. Protogranular texture. The primary mineral assemblage is $Olv + Cpx + Opx + Spl$. Cr-spinel occurs as pale brown anhedral grains of Cr-picotite. (b) Coarse-grained dunite, Rai-Iz Massif, Tsentralnoe deposit. The primary mineral assemblage is $Olv + Spl$; the secondary assemblage is $\alpha - Liz + Brs + Chl$. Cr-spinel occurs as black octahedral crystals of chromite. (c) Sadvandite. Zone of prograde metamorphism in the Rai-Iz Massif. The secondary mineral assemblage is $Olv_2 + Opx_3 + Mgt - Act + Tlc + Chl + Mzt$. Cr-spinel occurs as black anhedral crystals of magnetite. (d) Harzburgite partly replaced by talc and amphibolite, western contact of the Syum-Keu Massif. The secondary assemblage is $Act + Tlc + Chl - \alpha - Liz + Brs + Mzt$. Cr-spinel occurs as black anhedral crystals of magnetite.
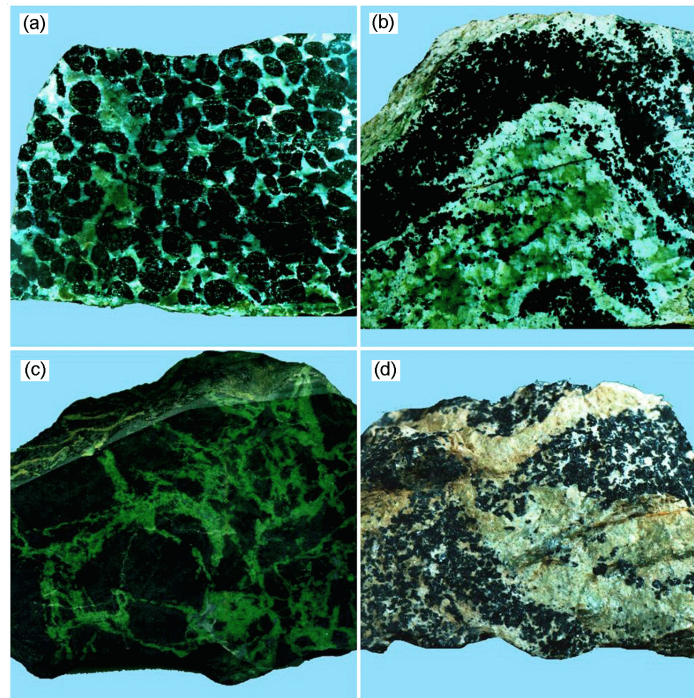


**Figure 9.** Typical Cr ores of the Polar Urals. Polished platelets, scaled 1/2. (a) Nodular rich disseminated chromite ore. Rai-Iz Massif, Enganskoe-II ore occurrence. (b) Medium-grade disseminated chromite ore. Rai-Iz Massif, Tsentralnoe deposit. (c) Brecciated rich disseminated Cr ore with dunite and uvarovite veinlets in DVC dunite. Voikar-Syninskii Massif. (d) Stockwork lean metamorphosed Cr ore with kemmererite. Syum-Keu Massif, Nyaro-Pe block.
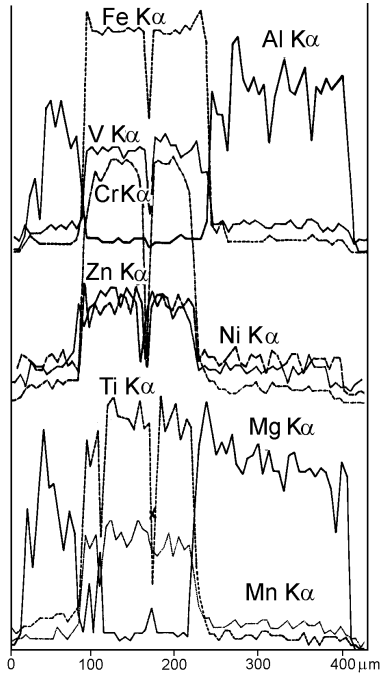
**Figure 10.** Microprobe scanning profiles (Camebax Microbeam microprobe, characteristic radiation) across a zonal Cr-spinel grain. The reversed zoning was caused by the metamorphic transformation of Cr-picotite into Cr-magnetite along a crack intersecting the grain core.

rocks of the mantle stage is picotite, Cr-picotite, and low-Cr aluminochromite; the rocks of the regional metasomatic stage contain high-Cr aluminochromite and chromite; the pegmatite-stage rocks bear ferro-aluminochromite and fer-

rochromite; and the rocks of the contact metamorphic stage contain ferro-feri Cr-spinel (Figure 7).

[22] Microprobe analyses of one grain of accessory Cr-spinel from dunite of the Rai-Iz Massif revealed a zonal structure of this grain: it had a core of aluminochromite $(Mg_{3.5}, Fe_{4.5})_8(Cr_{10.8}Al_{4.8}Fe_{0.4})_{16}O_{32}$ and peripheral portions consisting of chromite $(Mg_{3.2}Fe_{4.8})_8(Cr_{12.0}Al_{3.5}Fe_{0.5})_{16}O_{32}$. This grain clearly illustrates the Mg, Al $\longrightarrow$ Cr, Fe compositional trend of the Cr-spinels and the original high-Al composition of the Cr-spinel with respect to the chromite. Other grains often display evidence of the exsolution of unstable ferrichromite and chrome-magnetite phases into ferrochromite and magnetite. This process can be expressed by the scheme: ferrochromite (Cr, Zn) $\longrightarrow$ ferrichromite, Cr-magnetite (Al, $Fe^{2+}$, Mg – const) $\longrightarrow$ magnetite ($Fe^{3+}$, Mn, V, Ti).

[23] It is now quite obvious that ferrochromite $(Fe_6Mg_2)_8(Cr_{12}Fe_3Al)_{16}O_{32}$, magnetite $(Fe_6Mg_2)_8(Fe_{12-15}Cr_{4-1})_{16}O_{32}$ could crystallize in ultrabasite rocks only during prograde metamorphism, at relatively low temperatures.
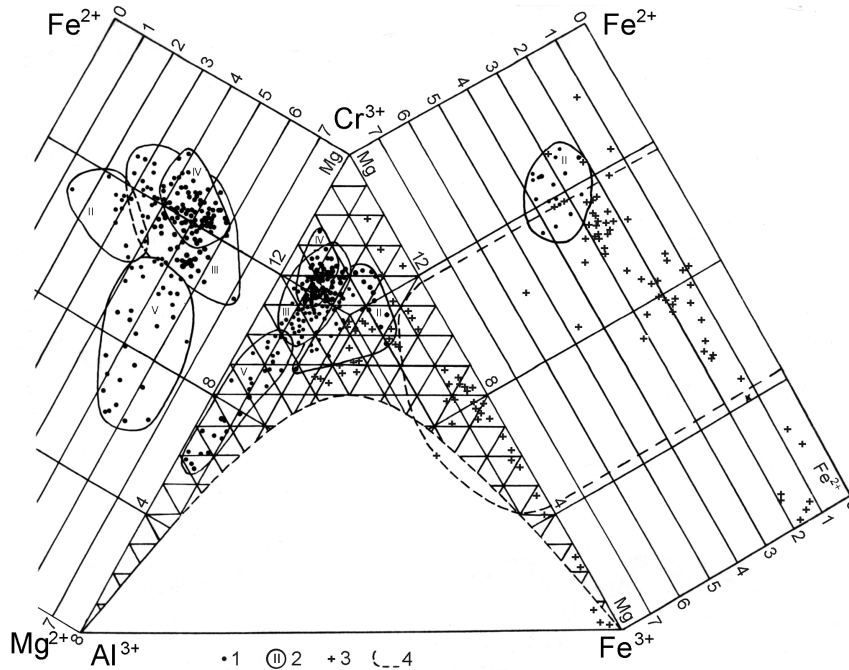


**Figure 11.** Triangular diagram for the composition of ore and metamorphosed accessory Cr-spinel from the Rai-Iz Massif. I – Ore Cr-spinel; 2 – compositional field of Cr-spinel in various ore types: II – lean disseminated metamorphosed Cr ore; III – Cr ore in the rocks of the DH complex; IV – ores of the Tsentralnoe and Zapadnoe deposits; V – high-Al Cr ores in the rocks of the H complex; 3 – accessory Cr-spinel of the chromite–magnetite series (ferro-ferri-chrome spinel); 4 – miscibility gap in the chromite–magnetite series (Mössbauer and IR spectroscopic data).
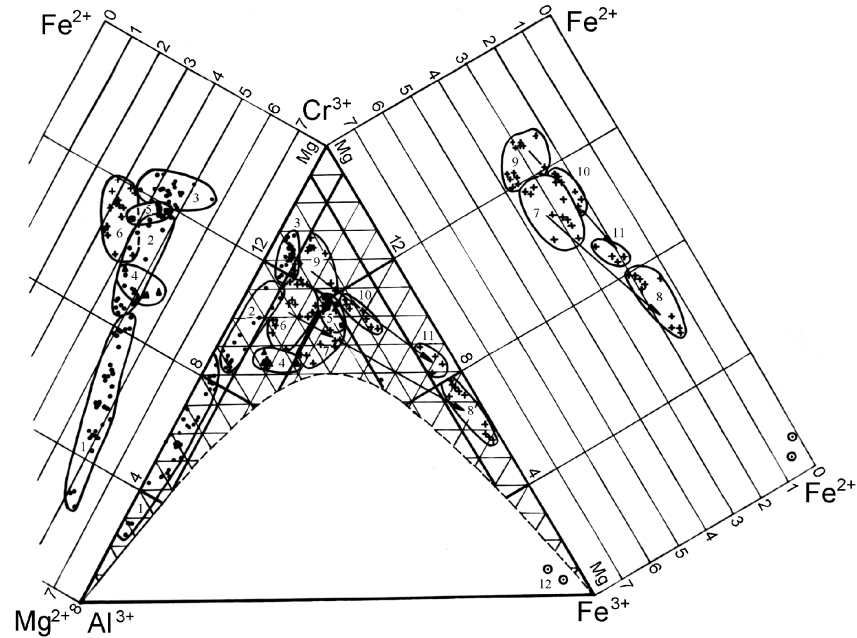
**Figure 12.** Triangular diagram for the composition of accessory Cr-spinel and the compositional fields of spinel from individual massifs and rock complexes. Fields: 1–3 – Kempirsai and Rai-Iz Massifs; 1 – picotite, Cr-picotite, and aluminochromite from lherzolites and harzburgites of the H complex; 2 – aluminochromite from harzburgites and dunites of the DH complex; 3 – chromite from dunites of the D and DH complexes; 4 – Sarany Massif; 5 – Nizhnii Tagil Massif; 6–8 – compositional fields of metamorphosed Cr-spinels from harzburgites of the DH complex, Tsentralnoe deposit (Cr-spinel is metamorphosed from subferri-aluminochromite – ferrialuminochromite –chrome-magnetite); 9–11 – compositional fields of accessory Cr-spinel from dunites of the D complex (subferrichromite – subaluminoferri-chromite – ferrichromite); 12 – Kochkanar Massif magnetites.
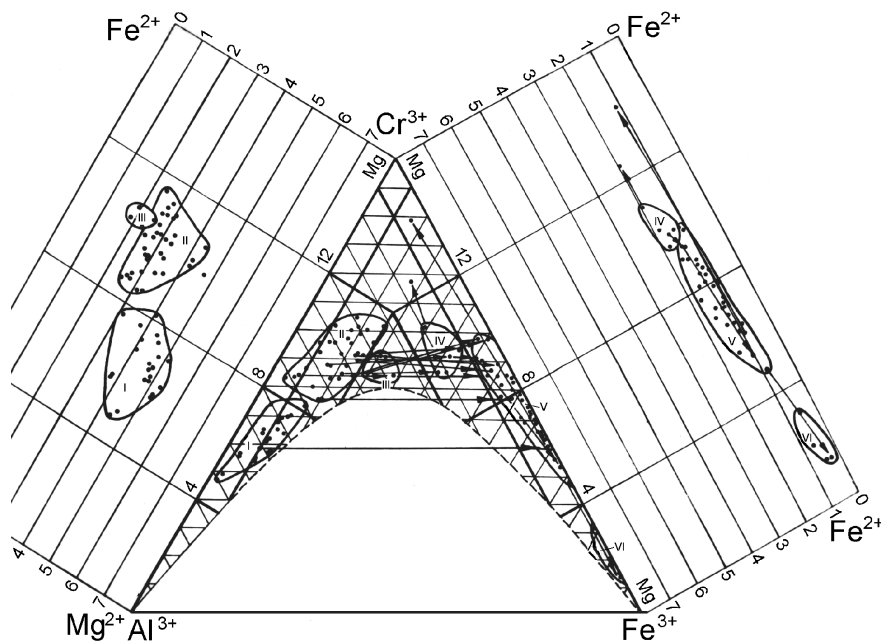


**Figure 13.** Triangular diagram for the composition of accessory Cr-spinel from the Khadatinskii area of the Syum-Key massif. Compositional fields of Cr-spinel: I – Cr-picotite from harzburgites and lherzolites of the H complex, II – aluminochromite and subferrialuminochromite from the rocks of the DH complex, III – ferrialuminochromite; IV – subaluminoferrichromite; V – ferrichromite + chrome-magnetite; VI – magnetite. Arrows indicate the compositional trends of zonal Cr-spinel grains (from cores to margins).

**Table 1.** Composition and properties of chrome spinellides

| no. Samples | Formula coefficient | | | | | $a_0$, Å | IRS $\nu_1$, cm$^{-1}$ | $\chi \cdot 10^{-6}$ Cl | Mgt, % |
|---|---|---|---|---|---|---|---|---|---|
| | $Mg^{2+}$ | $Fe^{2+}$ | $Cr^{3+}$ | $Al^{3+}$ | $Fe^{3+}$ | | | | |
| M-1025 | 5.60 | 2.40 | 7.20 | 8.08 | 0.72 | 8.219 | 650 | 132 | − |
| M-1374 | 5.60 | 2.40 | 10.24 | 2.64 | 3.12 | 8.303 | 636 | 364 | 0.2 |
| M-1491 | 4.48 | 3.52 | 12.56 | 2.64 | 0.80 | 8.300 | 630 | 232 | − |
| M-1652 | 3.20 | 4.80 | 11.60 | 1.52 | 2.78 | 8.361 | 616 | 2204 | 1.0 |
| M-1323 | 1.12 | 6.88 | 8.24 | 0.32 | 7.44 | 8.382 | 608 | 23500 | 11.6 |
| M-1089 | 1.36 | 6.64 | 8.24 | 0.96 | 6.80 | 8.382 | 604 | 24200 | 12.0 |
| M-1254 | 3.12 | 4.88 | 6.00 | 2.40 | 7.60 | 8.379 | 600 | 54200 | 27.0 |
| M-1111 | 1.20 | 6.80 | 4.64 | 0.24 | 11.12 | 8.382 | 591 | 143000 | 70.5 |
| M-1873a | 1.28 | 6.72 | 4.64 | 0.60 | 11.76 | 8.380 | 590 | 157000 | 78.0 |
| M-1243a | 1.12 | 6.88 | 0.32 | 0.48 | 15.20 | 8.384 | 580 | 221000 | 100.0 |

[24] The series of spinel $MgAl_2O_4$ and magnetite $FeFe_2O_4$ is known to have a miscibility gap.

[25] Together with L. D. Zaripova of the Kazan State University [*Makeyev,* 1992a, 1992b; *Makeyev and Zaripova,* 1984], we examined the Mössbauer spectra of approximately 100 samples of natural primary and metamorphosed Cr-spinels from the Rai-Iz Massif. The composition and some other characteristics of some of these samples are listed in Table 1. The ferrichromites and chrome-magnetites were determined to consist of two phases and display a broad compositional miscibility gap in the chromite–magnetite series (Figures 14–16). The dependence of the quadrupole split ($\Delta E$) of iron ions at three sites ($_BFe^{3+}$, $_BFe^{2+}$, and $_AFe^{2+}$) on the Al mole fraction [Al/(Al + Cr)] in the Cr–Al Cr-spinel series (chromite–picotite, where $Fe^{3+} < 1$ f.u.) can be expressed in the form of the following two linear and one quadric regression equations:

$$\Delta E = 1.075 \, [Al/(Al + Cr)] + 0.578 \text{ mm s}^{-1} \quad (_BFe^{3+}),$$

$$\Delta E = 0.345 \, [Al/(Al + Cr)] + 0.469 \text{ mm s}^{-1} \quad (_BFe^{2+}),$$

$$\Delta E = -3.736 \, [Al/(Al + Cr)]^2$$
$$+ 4.047 \, [Al/(Al + Cr)] + 0.572 \text{ mm s}^{-1} \quad (_AFe^{2+}).$$

[26] The exsolution of the Cr-spinel solid solution in the chromite–magnetite series was also confirmed by the data of IR spectroscopy, magnetic susceptibility, and, for some samples, by their microprobe analyses. Occasional finds of ferrichromite and chrome-magnetite, which are identified by chemical analyses, should be attributed to natural
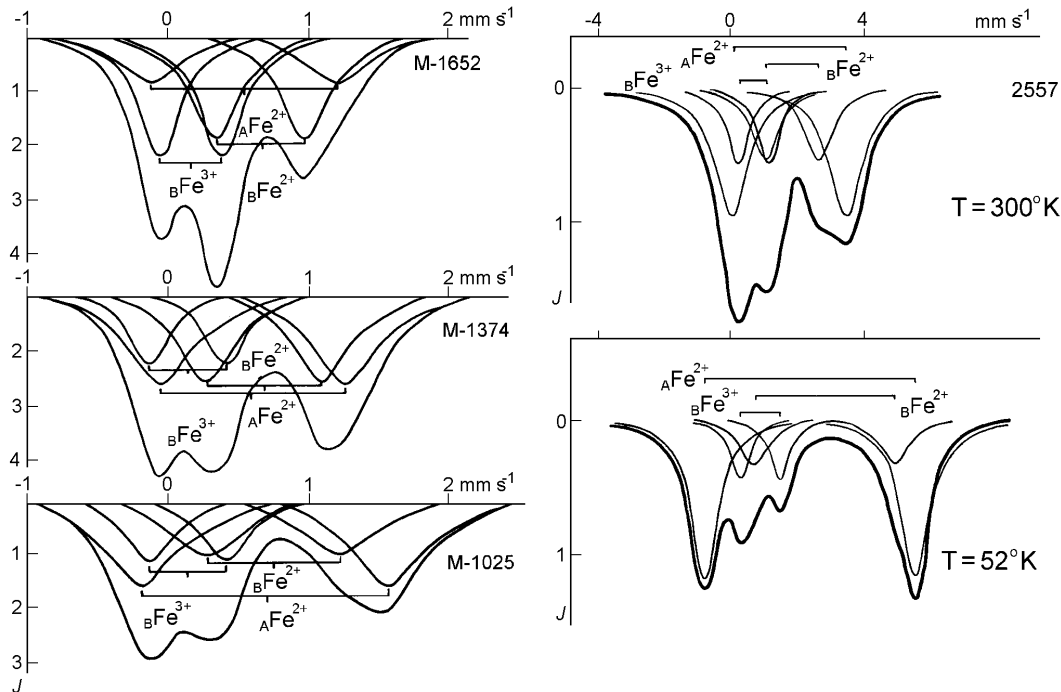


**Figure 14.** Mössbauer spectra of ore Cr-spinels: sample M-1652 – subferrichromite, sample M-1374 – subferrialuminochromite, samples M-1025 and 2557 – chrome-picotite.
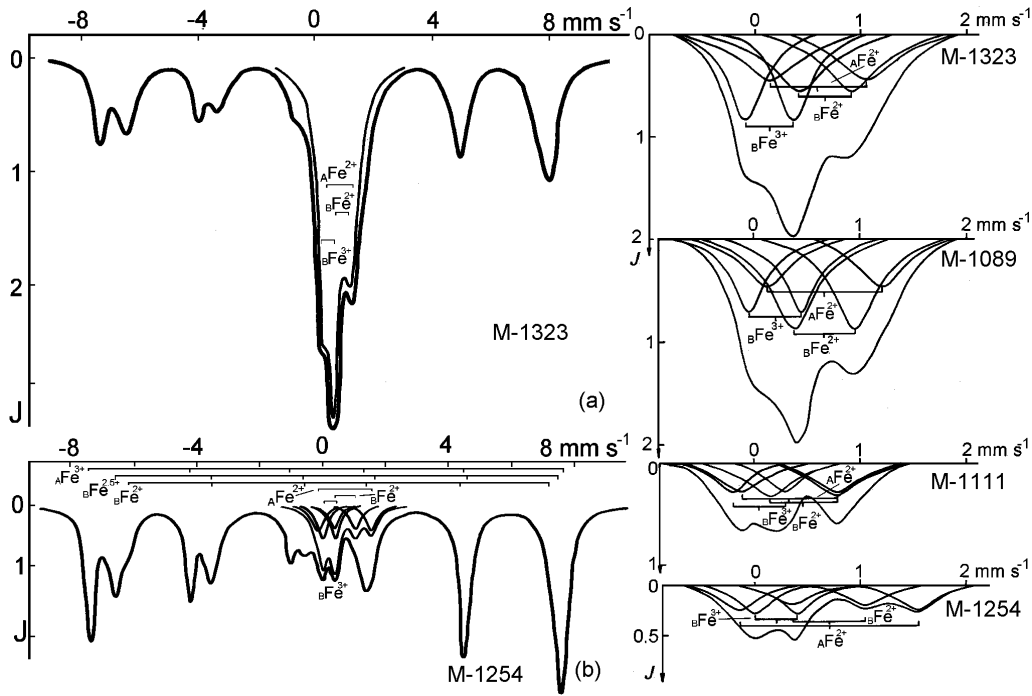
**Figure 15.** Mössbauer spectra of accessory Cr-spinel from the Rai-Iz Massif. The spectra exhibit doublets (paramagnetic region) and sextets (magnetic region, magnetite). Samples: (a) M-1323, (b) M-1254. The doublet region of the Mössbauer spectra of two-phase metamorphic Cr-spinels: samples M-1089 and M-1323 – ferrochromite, sample M-1111 – aluminochromite, sample M-1254 – chrome-picotite.
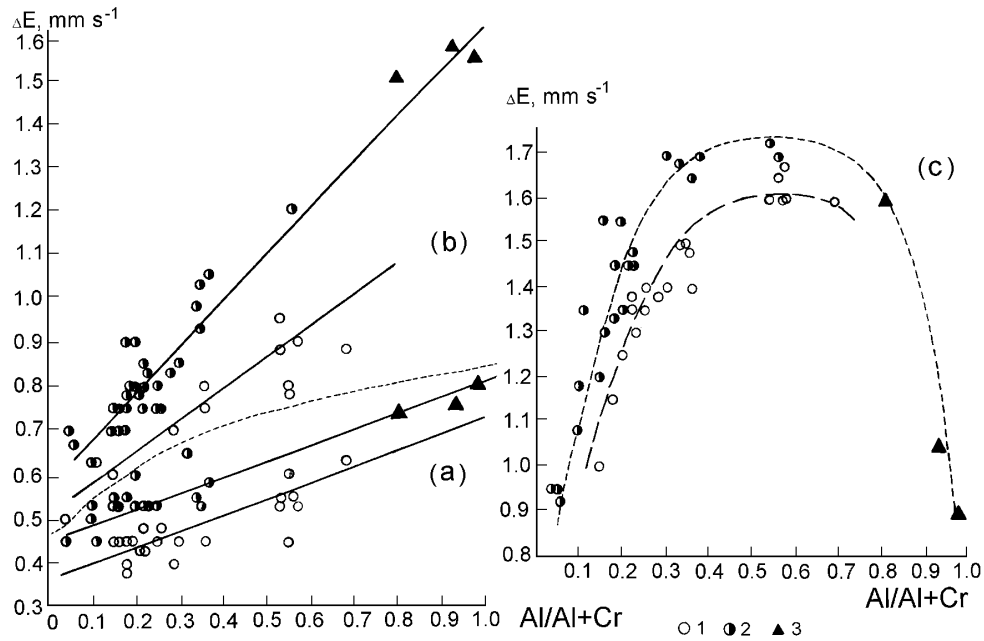


**Figure 16.** Quadrupole splitting of variably coordinated Fe ions ($a - _BFe^{3+}$, $b - _BFe^{2+}$, $c - _AFe^{2+}$) as a function of the Al mole fraction $Al/(Al + Cr)$ of natural Cr-spinels. Cr-spinels: 1 – high-$Fe^{3+}$ ($>1$, FE); 2 – low-$Fe^{3+}$ ($<1$, FE); 3 – picotite with the highest $Al^{3+}$ concentration.
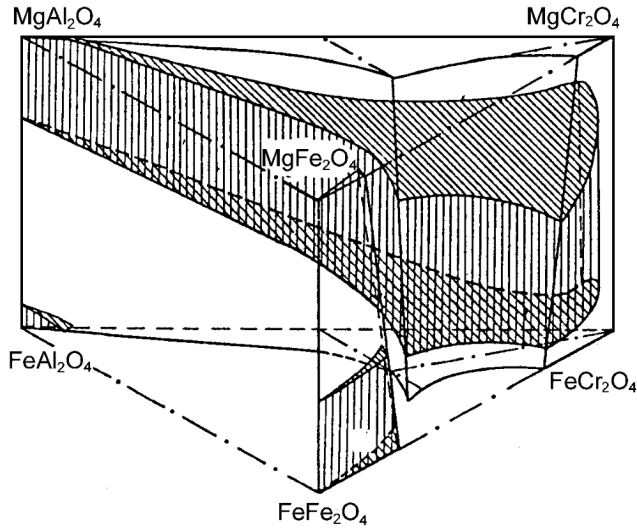
**Figure 17.** $FeCr_2O_4 - MgCr_2O_4 - FeAl_2O_4 - MgAl_2O_4 - FeFe_2O_4 - MgFe_2O_4$ phase diagram based on the probabilistic model of the distribution of chemical analyses of natural Cr-spinels and their Mössbauer and IR spectra.

mixtures with variable proportions of two members of the ferrochromite–feromagnetite series on a microscopical (cluster) scale.

[27] This newly discovered miscibility gap in the chromite–magnetite series is shown in a spinel–hercynite–magnetite–magnesiomagnetite–magnesiochromite–chromite diagram (Figure 17). As can be seen from this Figure, only three of the end members (spinel, hercynite, and magnetite) were found in nature, and none of the other end members is known to occur in natural rocks. Hence, we were the first to constrain the stability region of the limited solid solution of natural Cr-spinels. This region is bounded by a compli-

catedly curved surface within a tetrahedral compositional diagram and includes two miscibility gaps.

[28] We examined the typomorphic features of the composition and properties of natural Cr-spinels (Figures 18–20). The following regression equations can be proposed to relate the composition of this mineral to its unit-cell parameter $a_0$, wavelength of the IR spectrum $\nu_1$, and the reflectance R:

$$a_0(\mathring{A}) = 8.162 - 0.0098 \times Mg^{2+} + 0.0146 \times Cr^{3+} + 0.0139 \times Fe^{3+},$$

$$\nu_1(cm^{-1}) = 671.8 + 0.580 \times Mg^{2+} - 3.268 \times Cr^{3+} - 1.607 \times Fe^{3+},$$

$$R(\%) = 9.872 - 0.406 \times Mg^{2+} + 0.369 \times Cr^{3+} + 0.605 \times Fe^{3+}.$$

[29] Other indicator minerals of Alpine-type ultrabasites are olivine, clinopyroxene, plagioclase, pentlandite, and some others. Their composition and physical characteristics vary during the evolution of the rocks similarly to those of the Cr-spinel. These minerals can also be utilized for the purposes of genetic analysis and petrological reconstructions.

[30] The results of our research allowed us to identify new mineralogical indicators and propose new criteria for the assessment of the occurrences and deposits of Cr ore mineralization related to Alpine-type ultrabasites. The first of them is a correlation between the compositions of the accessory and ore Cr-spinels. This criterion makes it possible to predict the composition of Cr-spinel in concealed and unidentified orebodies. The composition of the ore Cr-spinel is correlated with the composition of the accessory Cr-spinel, a mineral that is contained in practically all of the rocks. The other criterion is the concentration of the fayalite end member of the rock-forming olivine (or the index of refraction Ng of this olivine), which decreases toward orebodies and zones with Cr ore mineralization [*Bryanchaninova and Makeyev, 1988*]. The third criterion is the mineral assemblages of the rocks, the compositions of the typomorphic minerals, and the spatial distribution of ultrabasite complexes, with this
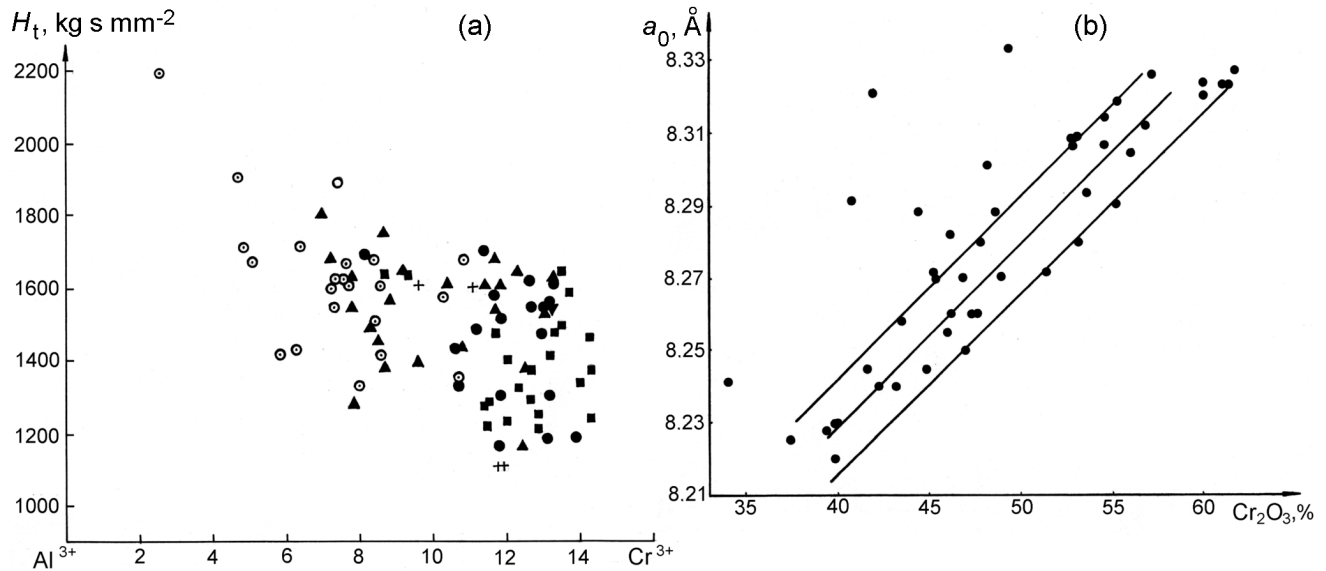


**Figure 18.** Dependences of (a) the hardness $H_t$ and (b) unit-cell parameter $a_0$ of natural Cr-spinels on their Cr concentrations.
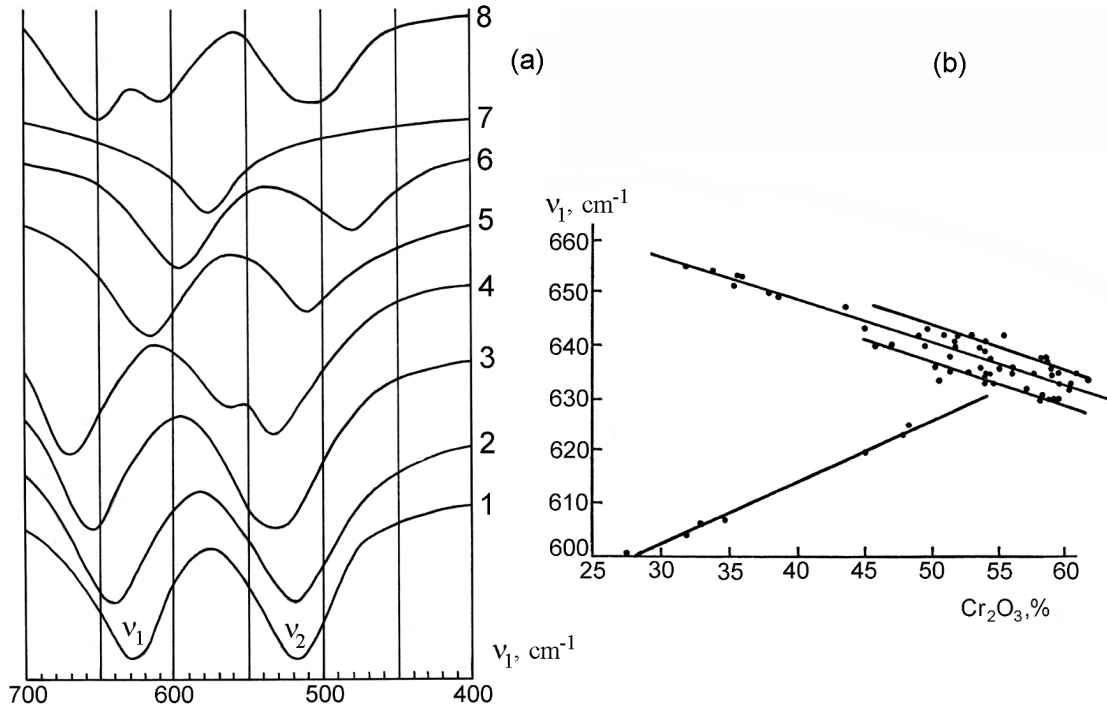
**Figure 19.** (a) IR absorption spectra of Cr-spinels and (b) the dependence of the wavelength of the IR spectra $\nu_1$ on the $Cr_2O_3$ concentration of Cr-spinels. Spectra: 1 – chromite; 2 – aluminochromite; 3 – chrome-picotite; 4 – picotite; 5 – ferrochromite; 6 – chrome-magnetite; 7 – magnetite; 8 – zonal aluminous Cr-spinel with a Fe-rich outer zone.
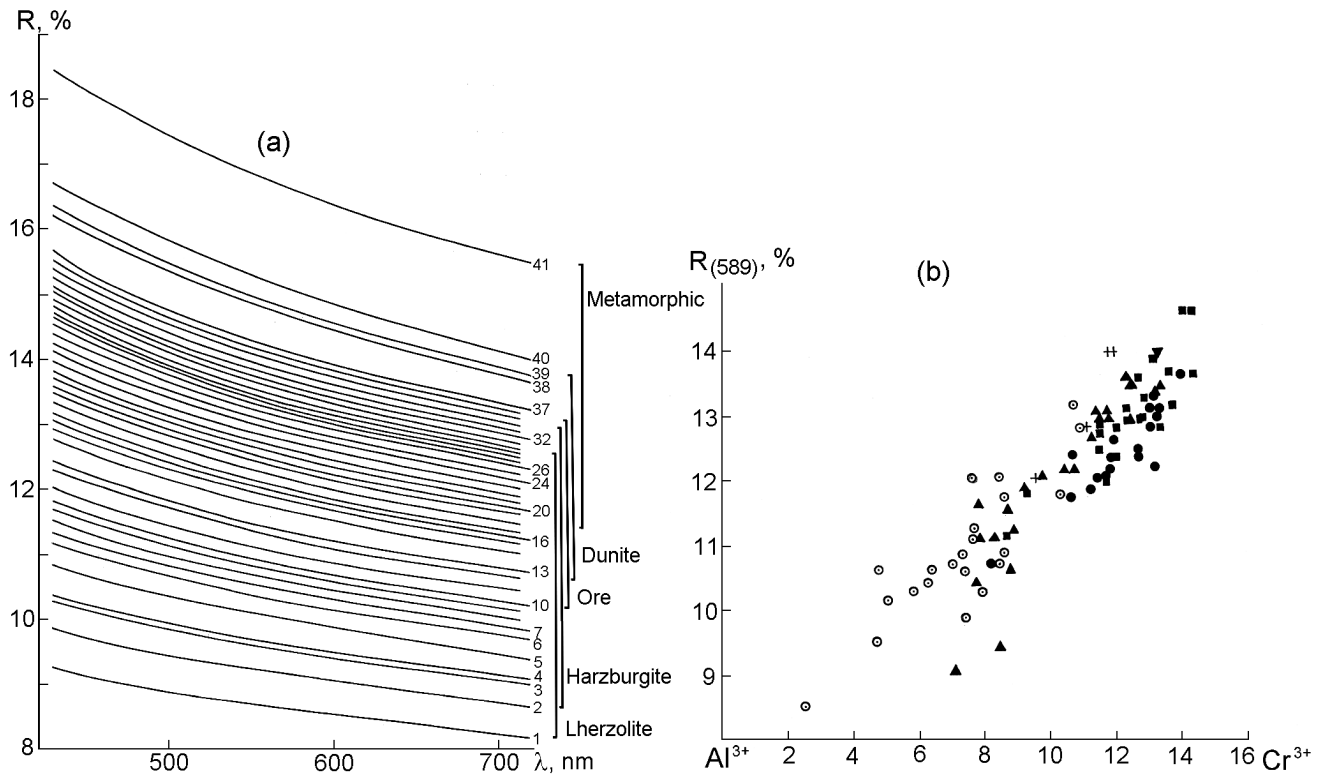
**Figure 20.** (a) Reflection spectra of natural Cr-spinels and (b) the dependence of their reflectance index R (at $\lambda = 589$ nm) on the Cr concentration.
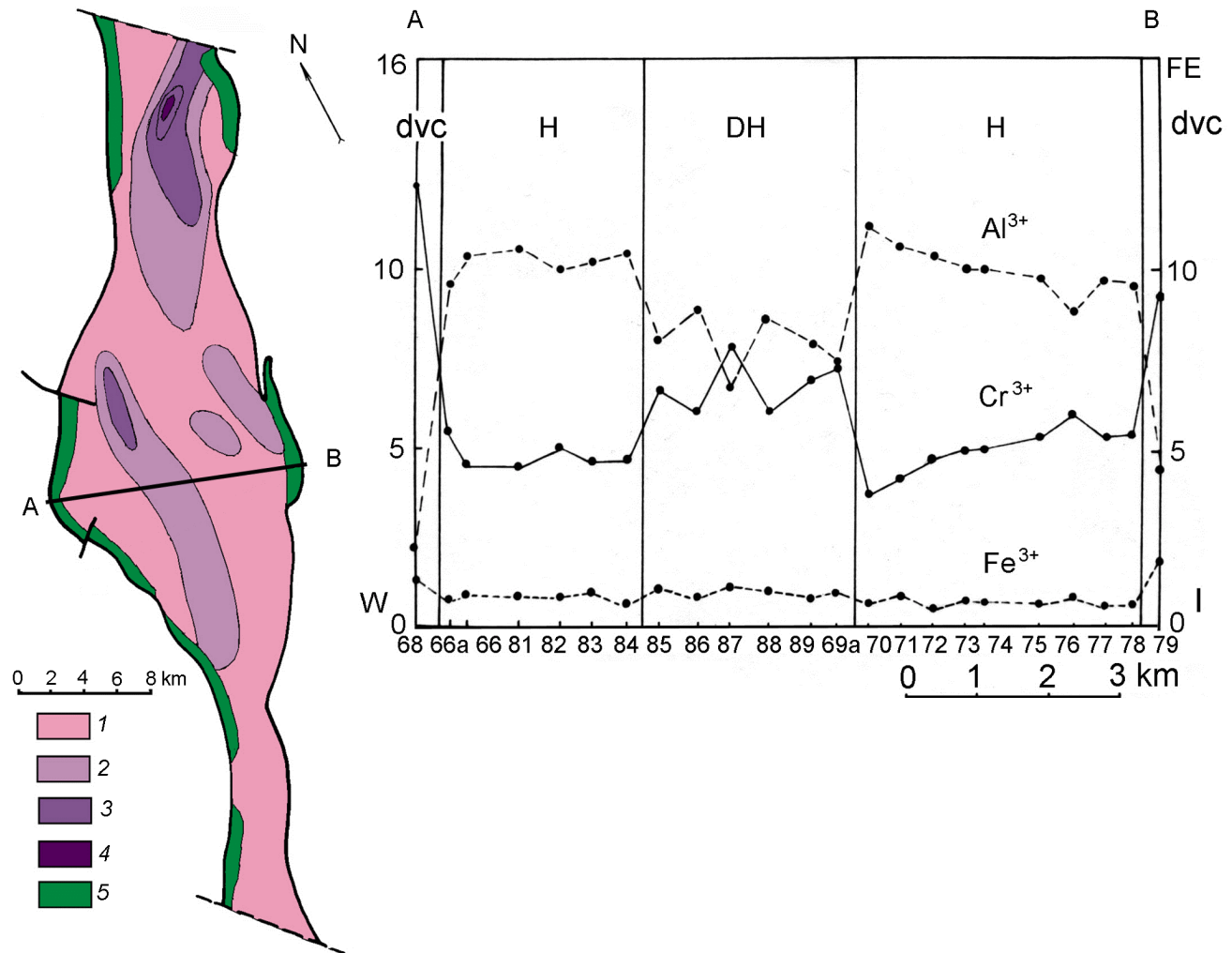
**Figure 21.** Composition of accessory Cr-spinel from ultrabasite rocks sampled along a profile perpendicular to the strikes of structures in the Voikar block of the Voikan-Syninskii Massif (the profile was oriented from west to east and intersected the dvc–H–DH–H–dvc rock complexes). Shown at the button are the numbers of crushed samples. Rock complexes: 1 – harzburgite–lherzolite (H); 2 – dunite–harzburgite (DH) with 10–30% dunites (D); 3 – dunite–harzburgite (DH) with D = 30–70%; 4 – dunite complex (D) D≥70%; 5 – dunite–wehrlite–pyroxenite complex (dvc).

criterion making it possible to assay the possible reserves of the Cr ores.

[31] Our data on accessory and ore Cr-spinel in ultrabasites from the Polar Urals indicate that the composition of this mineral seems to be a sensitive indicator of prograde metamorphism but is almost insusceptible to retrograde metamorphism. The prograde metamorphism of ultrabasites to the amphibolite and greenschist facies transforms and recrystallizes their accessory Cr-spinel and is favorable for its depletion in Cr and Al, the oxidation of its $Fe^{2+}$ to $Fe^{3+}$, and, eventually, in enrichment of the mineral in the magnetite end member. The final metamorphic product of the accessory Cr-spinel is newly formed magnetite and kemmererite, which concentrates some Al and Cr removed from Cr-spinel.

[32] The analysis of our data led us to identify two trends

in the correlations between the compositions of ore and accessory Cr-spinel in chromite-bearing ultrabasites.

## Conclusion

[33] Our materials on the rocks of the lherzolite–harzburgite, dunite–harzburgite, and dunite complexes (which are either not altered at all or were affected only by retrograde metamorphism) suggest a weak correlation between the compositions of their ore and accessory Cr-spinels: dunites contain high-Cr accessory Cr-spinel–chromite, and lherzolites and harzburgites contain, respectively, high-Al aluminochromite and Cr-picotite (Figure 21). A striking example of the aforesaid is offered by the Kempirsai Massif
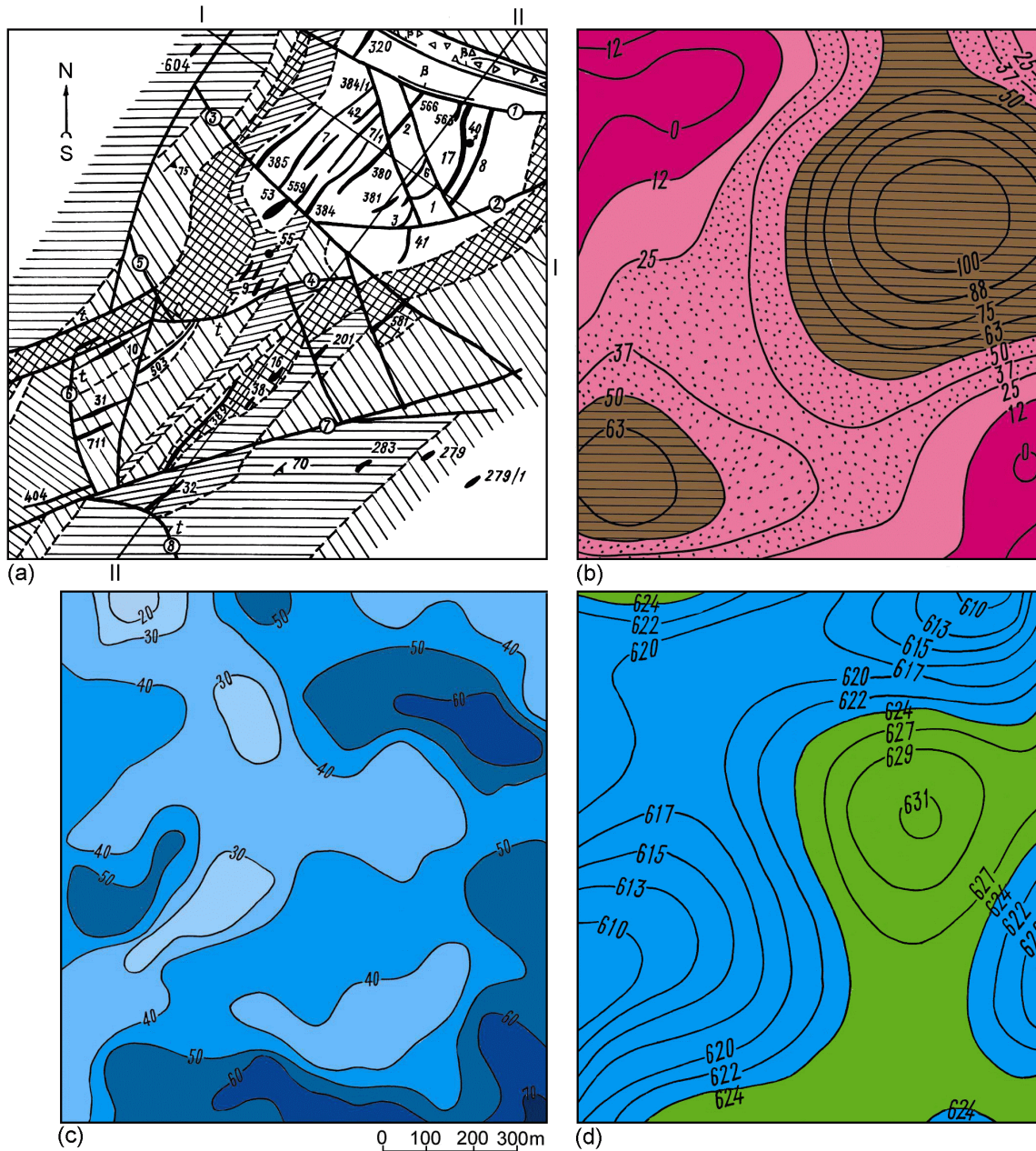
**Figure 22.** Results of mineralogical mapping (sale 1 : 10,000, area 1.3 km$^2$) of an area at the Tsentralnoe deposit, Rai-Iz Massif (data as of 1980, before the development of the deposit was started). Maps: a – schematic geological map of the deposit with indicated chromite orebodies [*Makeyev et al.,* 1985]; b – dunite component; c – degree of serpentinization of the rocks; d – composition of accessory Cr-spinel (IR spectroscopic data).

[*Pavlov and Grigorieva-Chuprynina,* 1973]. Other ultrabasites metamorphosed during the retrograde stages show some inconsistencies between the compositions of their ore and accessory Cr-spinels. This can be illustrated by the examples of the Tsentralnoe and Zapadnoe economic deposits of high-Cr ores of the Rai-Iz Massif, whose orebodies consisting of chromite and subferrialuminochromite are hosted by rocks with metamorphic accessory spinel of high-Fe composition: ferro-ferri Cr-spinel (Figure 22).

[34] An efficient method for the evaluation of the Cr$_2$O$_3$
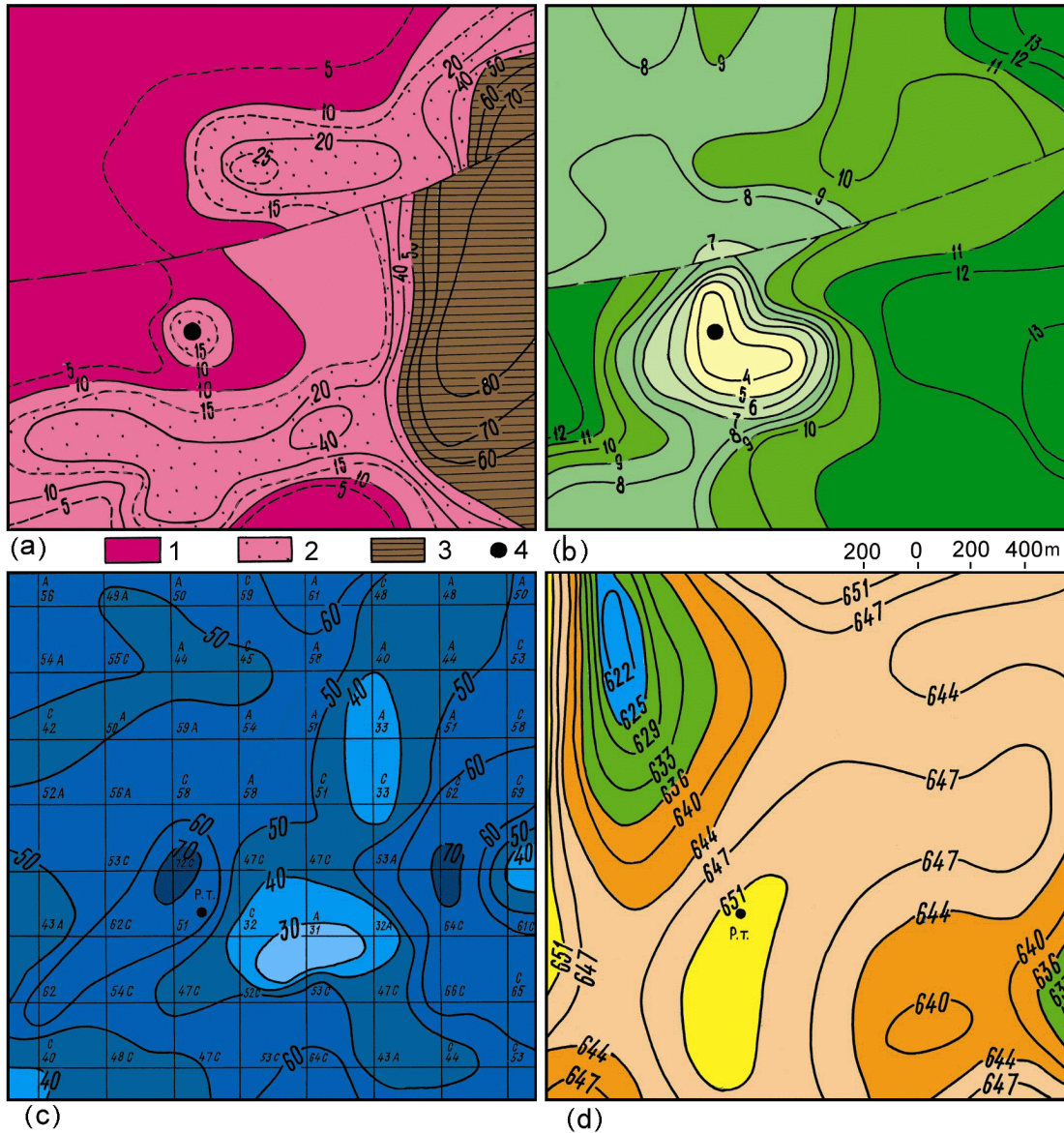
**Figure 23.** Results of mineralogical mapping (sale 1 : 25,000, area 4 km$^2$) of the Kershor area of the Voikar-Syninskii Massif. Maps: a – dunite component; b – Fe# of olivine; c – degree serpentinization of rocks; d – composition of accessory Cr-spinel (IR spectroscopic data). Rocks: 1 – H complex; 2 – DH complex; 3 – dunites of the dvc complex; 4 – position of the Kershor occurrence of massive chrome-picotite ores.

concentration in spinel is infrared spectroscopy. The position of IR absorption bands in the spectra depends on the composition of the Cr-spinel, and this makes it possible to rapidly and accurately enough evaluate the $Cr_2O_3$ concentrations in large collections of samples. In the course of studying the Polar Urals, we have obtained and interpreted more than 10000 IR spectra of Cr-spinels. Maps were prepared (Figures 22, 23) that show the variability of this pa-

rameter over an area of approximately 2000 km$^2$ for all of the three massifs in the Polar Urals [*Makeyev,* 1990, 1992a, 1992b; *Makeyev and Bryanchaninova,* 1999].

[35] We conducted mineralogical mapping at these three ultrabasite massifs in the Polar Urals: Syum-Keu, Rai-Iz, and Voikar-Syninskii. Figures 22–25 demonstrate the potentialities of large-scale mineralogical mapping, as illustrated by the example of application of these techniques at the
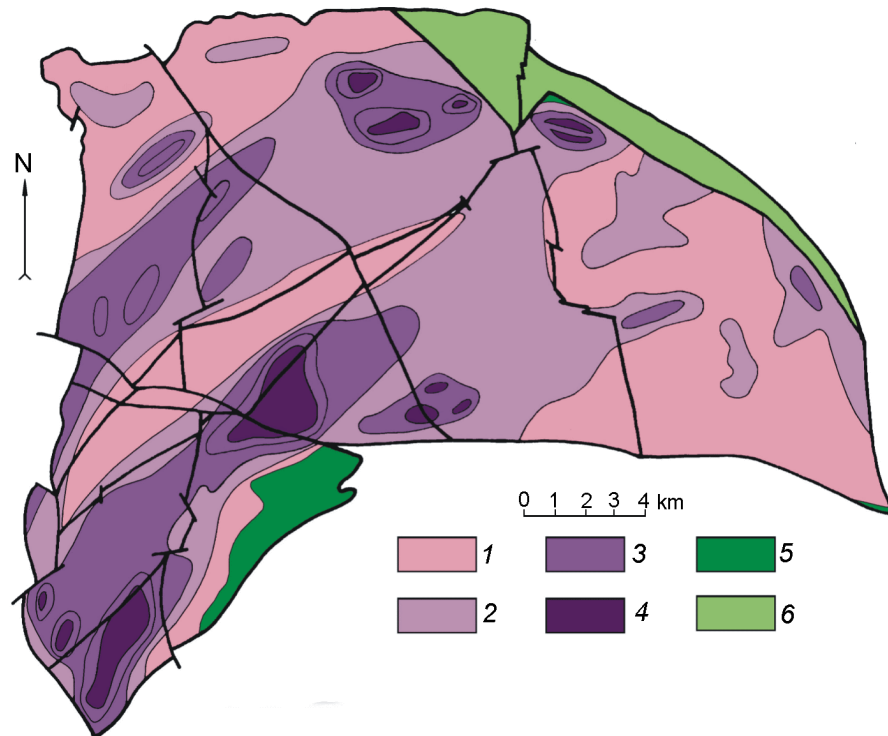
**Figure 24.** Map showing the dunite component of the Rai-Iz Massif. Colors correspond to various dunite contents: 1 – 0–10% (harzburgite-lherzolite complex); 2 – 0–10% (dunite–harzburgite complex); 3 – 30–70% (dunite–harzburgite complex); 4 – >70% (dunite complex); 5 – banded dunite-wehrlite-clinopyroxenite complex; 6 – mélange zone.

Rai-Iz Massif. The reader can find all other mineralogical and prediction maps for the whole Polar Uralian ultrabasite belt in the monograph [*Makeyev and Bryanchaninova, 1999*]. The criteria used for the mapping included the dunite constituent (Figures 22a, 23b, 24) in the rock complexes (this was the basis used to prepare the geological maps of the ultrabasite massifs), the Fe mole fraction (Figures 22b, 25b) of the rock-forming olivine (this parameter was evaluated from the indices of refraction of this mineral or was calculated from its microprobe analyses and makes it possible to reliably localize orebodies), and IR spectroscopic data (Figures 22d, 23d, 25a, 25b) on the accessory and ore Cr-spinel (these data allowed us to assay the composition the quality of the Cr ores). The materials were generalized in the form of a prediction map of the chromite potential of the massif (Figure 25d).

[36] Areas highly promising for exploration for chromite ores are those where the dunite–harzburgite complex with high dunite contents contains accessory Cr-spinel corresponding to chromite or ferrichromite in composition (with the $\nu_1$ parameter of the IR spectra ranging from 620 cm$^{-1}$ to 635 cm$^{-1}$). The Cr concentration in the accessory Cr-spinel of the dunites increases toward chromite orebodies. Conversely, the areas (fields) of the harzburgite and dunite–

harzburgite complexes with low dunite contents and high Al concentrations in the accessory Cr-spinel (with the $\nu_1$ parameter lower than 600 or higher than 640 cm$^{-1}$) are not promising as exploration targets for Cr ore mineralization.

[37] Blocks of ultrabasite rocks most promising for exploration for large deposits are those with large dunite bodies and with adjacent fields of the dunite–harzburgite complex containing much dunite. These areas are characterized by low contents of pyroxene in the harzburgite (10–12%), accessory Cr-spinel high in Cr, and relatively Fe poor olivine from the dunite composing the ore zone.
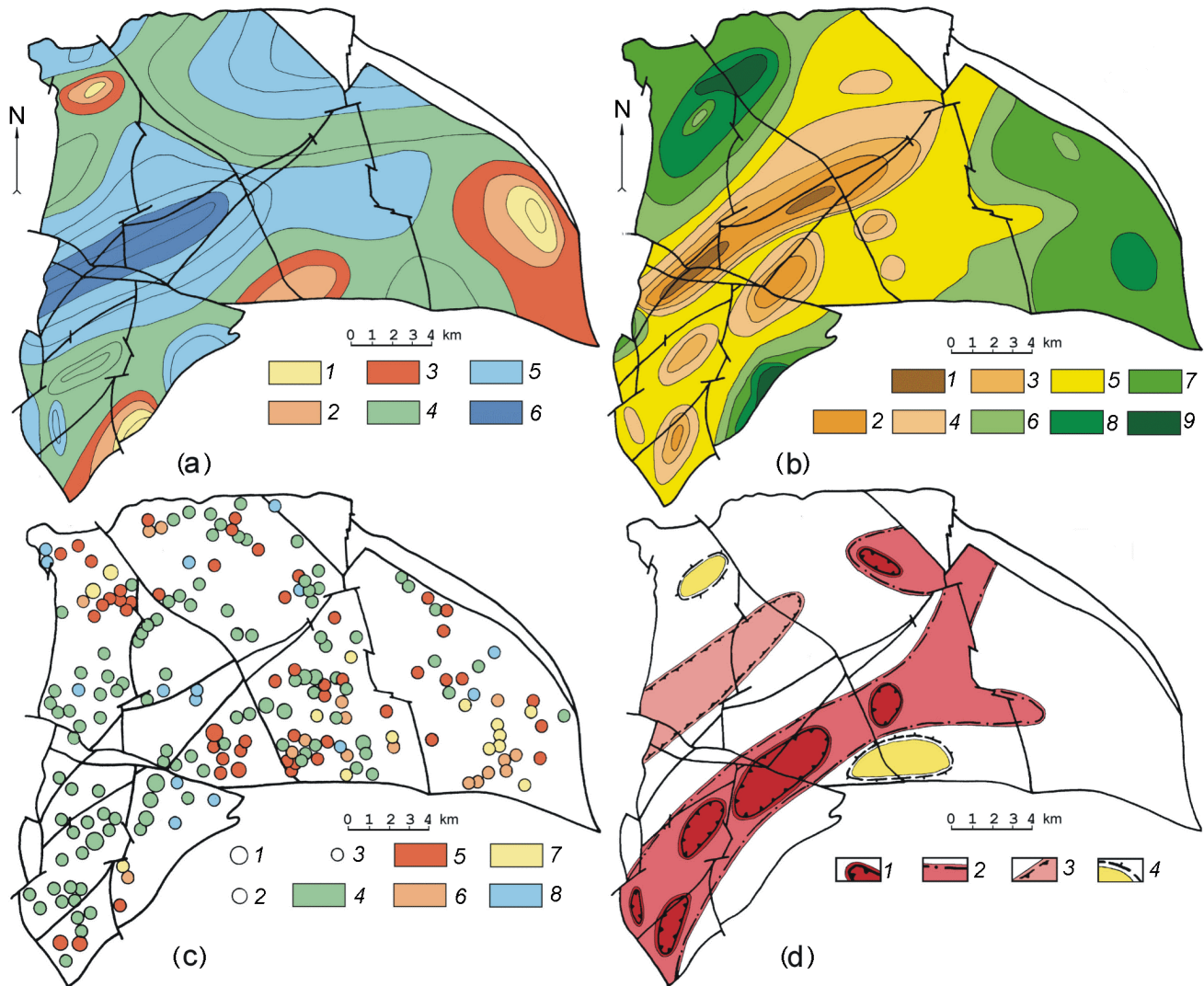
**Figure 25.** Mineralogical prediction map of the Rai-Iz Massif (prepared based on the results of 1 : 50,000-scale mineralogical mapping [*Makeyev and Bryanchaninova,* 1999]). (a) Map showing the composition of accessory Cr-spinel from the Rai-Iz Massif. Colors correspond to variations in the composition of accessory Cr-spinel in the ultrabasite rocks (IR spectroscopic data, isopleth map of the $\nu_1$, cm$^{-1}$, parameter): 1 – >644; 2 – 644–638; 3 – 638–631; 4 – 631–624; 5 – 624–605; 6 – <605. The variations in the $\nu_1$ parameter roughly correspond to the compositional variations from (1) picotite to (2, 3) aluminochromite, (4) chromite, (5) ferrichromite and chrome-magnetite, and (6) magnetite. (b) Map showing the Fe# of the rock-forming olivine from the Rai-Iz Massif. Colors correspond to variations in the index of refraction n$_g$ of olivine: 1 – <1.682; 2 – 1.682–1.684; 3 – 1.684–1.686; 4 – 1.686–1.688; 5 – 1.688–1.690; 6 – 1.690–1.692; 7 – 1.692–1.694; 8 – 1.694–1.697; 9 – >1.697. The variations in the n$_g$ parameter roughly correspond to variations in the olivine composition from 2% to 14% of the fayalite end member. (c) Technological map of the quality of Cr ores at the Rai-Iz Massif. 1 – Mineral deposits; 2 – occurrences of ore mineralization; 3 – occasional grains of Cr ore minerals. Quality of Cr ores: 4 – high-grade metallurgical chromite ores; 5 – low-Cr metallurgical Cr ores (aluminochromite and subferialuminochromite); 6 – low-Cr Cr ores for chemical industry (low-Cr aluminochromite and subferrialuminochromite); 7 – low-Cr Cr ores (Cr-picotite and subferrichromepicotite); 8 – lean disseminated metamorphosed refractory Cr ores (ferroferrichrome-spinel). (d) Prediction map of the Cr ore potential of the Rai-Iz Massif. Areas delineated as promising for exploration: 1 – for large deposits of high-grade metallurgical chromite ores; 2 – for middle-sized deposits; 3 – for small deposits; 4 – for small deposits of high-Al Cr ores for chemical industry.

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