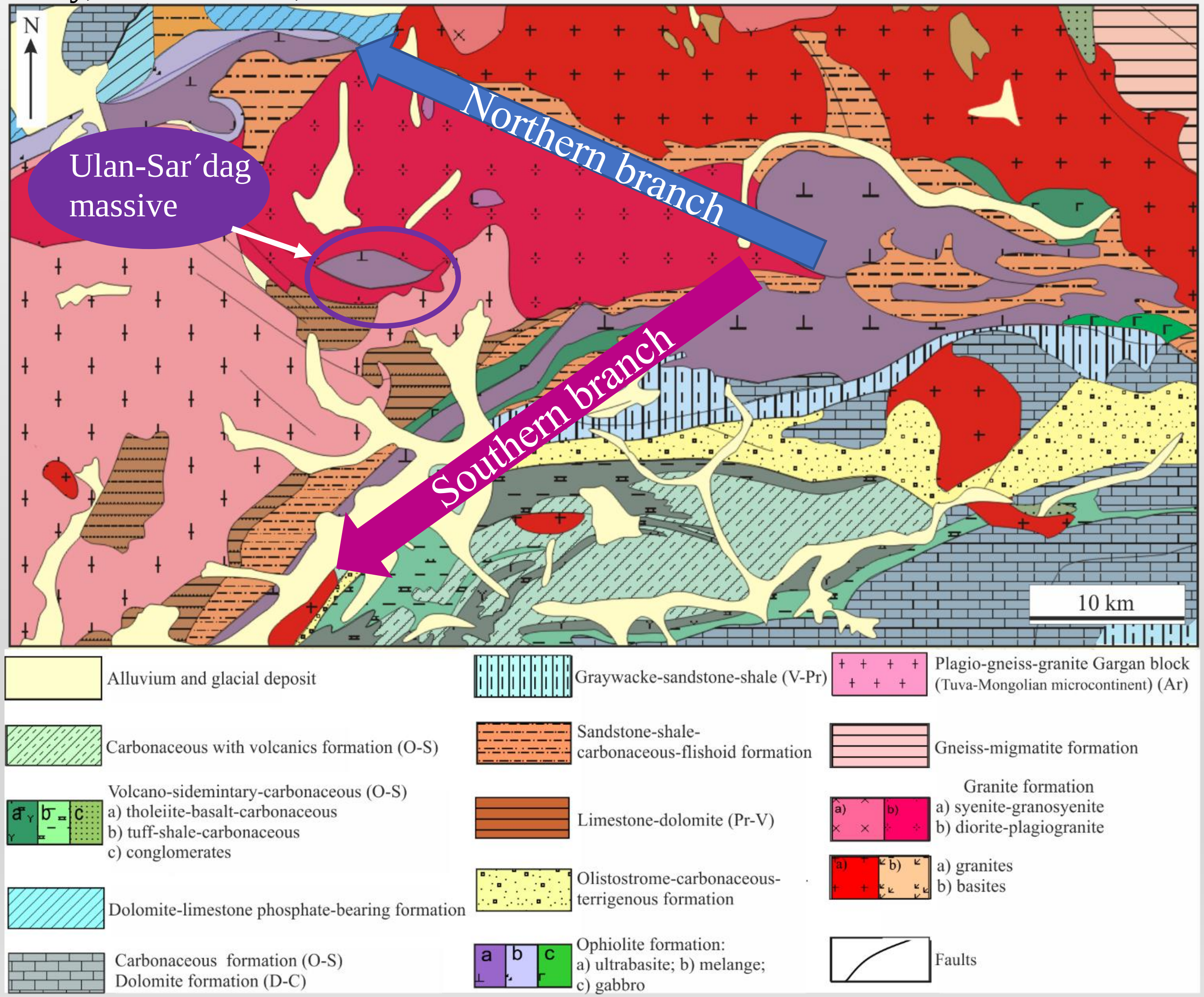
Origin and alteration of platinum group minerals in chromite deposits of the Ulan-Sar′dag ophiolite

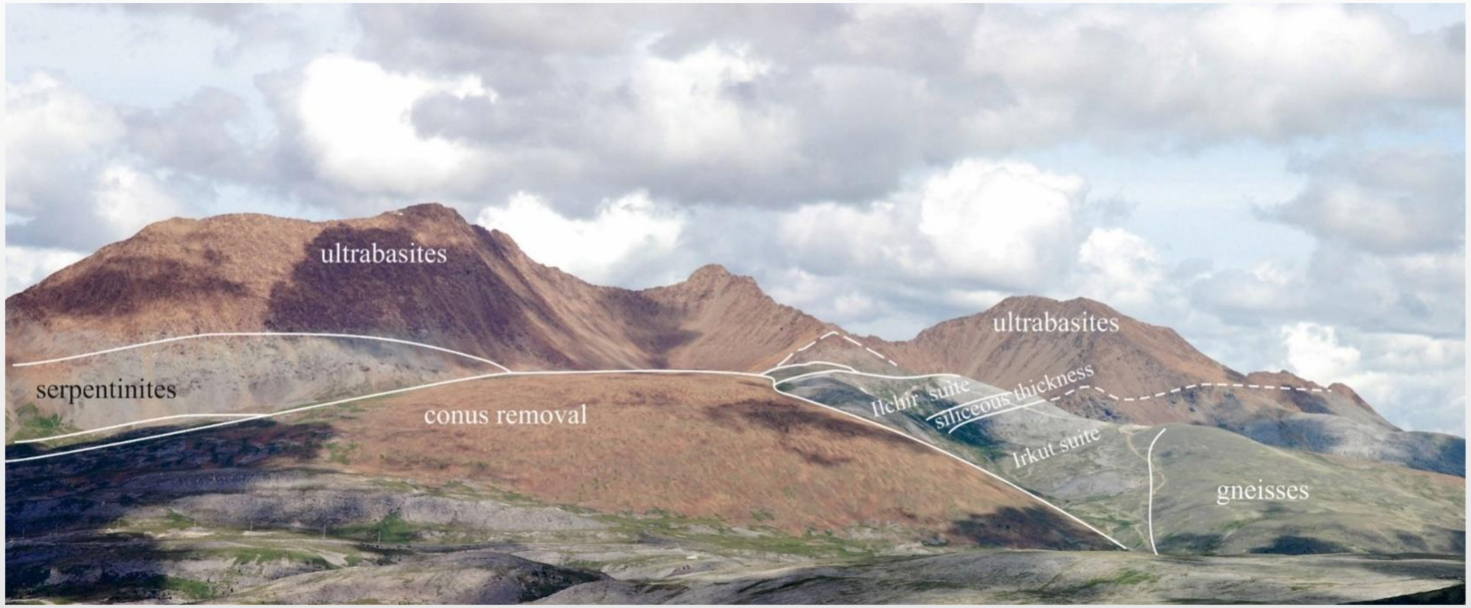
Olga Kiseleva[1], Evgeniya Airiyants[1], Dmitriy Belyanin[1,2], Sergey Zhmodik[1,2]
1 – Sobolev Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russian Federation
2-Novosibirsk State University, Novosibirsk, Russian Federation

The geographical position of the Ulan-Saridag massif

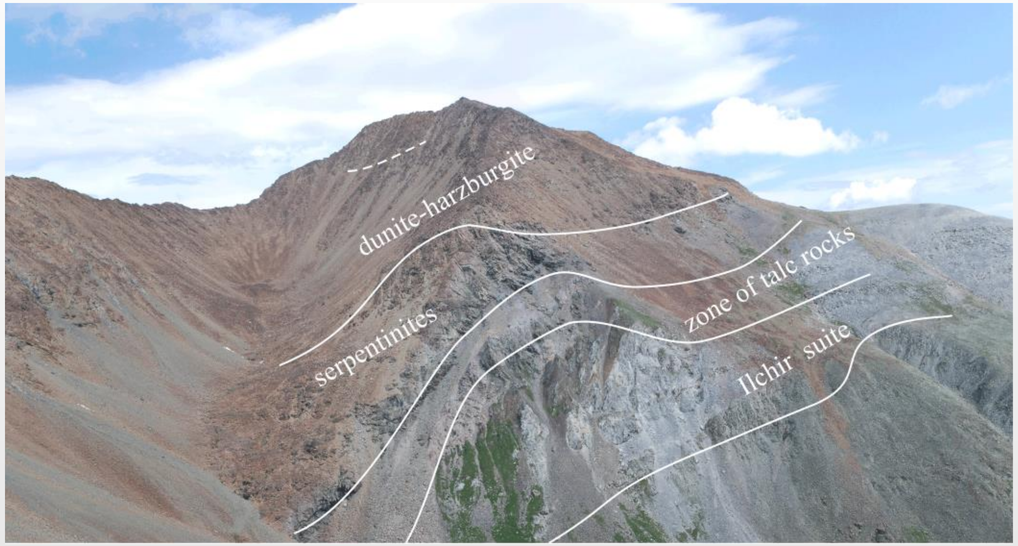
The Ulan-Sar′dag ophiolite massive is tectonic sheet. It is part of ophiolite complexes of Eastern Sayan and fold–thrust region of Central-Asian Fold Belt. The massive is part of the Dunzhugur Island Arc of Paleosian Ocean in Riphean-Vend Age. The ophiolite complex consists of the northern and southern branches, which may have been formed in different geodynamic settings. The Ulan-Sar′dag ophiolite is located between these structural branches. We received some interesting new data chemical composition of chrom-spinelides and platinum mineralization for this massive.



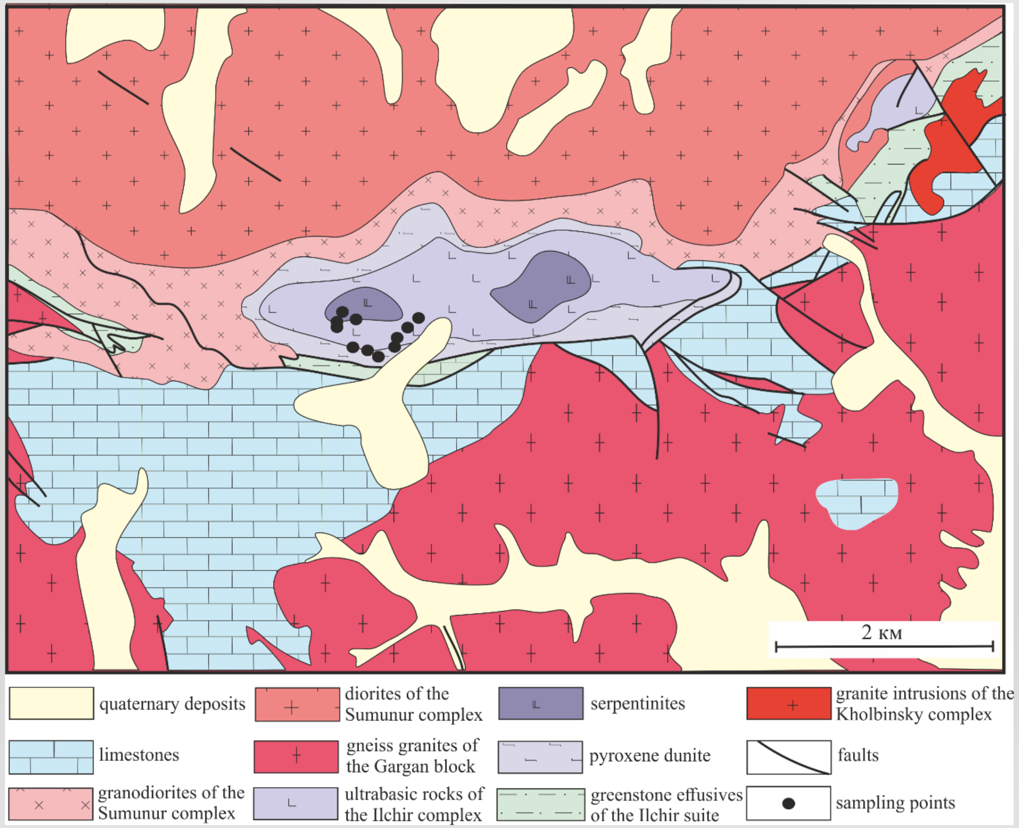
Geological schematic map of the south-eastern part of the Eastern Sayan



Photos Ulan-Sar´dag ophiolite massive.



Scheme of the geological structure of the Ulan-Sar´dag ophiolite massive.



Ophiolite massive Ulan-Sar'dag consist of mantle section (serpentinites, dunites, peridotites - garzburgites, pyroxenites, gabbro). Volcanic-sedimentory formation are presented Ilchir suit. The rocks of ophiolitic complexes are deformed in condition of greensheet to amfibolites facies.

A trench 200 meters long opens the volcanites of the Ilchir suit and their contact with the ultrabasites. Those was volcanogenic thickness with interbedding volcanites and sulfidized black shale.

Rocks of the normal and subalkaline series represent in volcanic association: picrobasalts, basalts, andesibasalt, boninites, andesites, trachyandesites, trachytes, dacites.

Features of volcanic rocks

The distribution of rare-earth elements, HFSE (high field strength elements) and LILE (lithophilic elements) in volcanic rocks are typical of MORB, boninites, island-arc volcanics and OIB basalts.

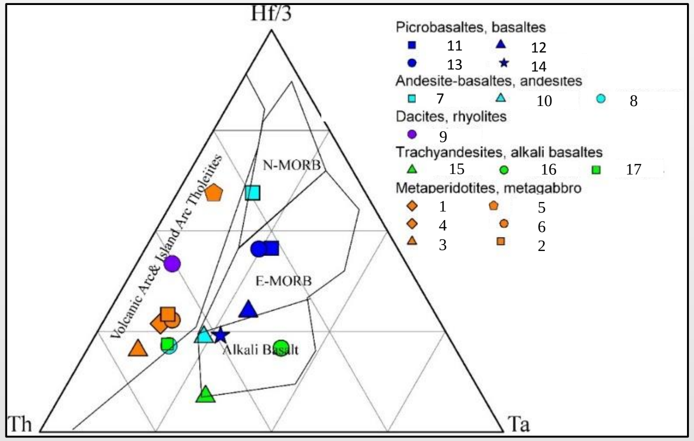
E-MORB
- Picrobasalt

Boninite
- Andesibasalt

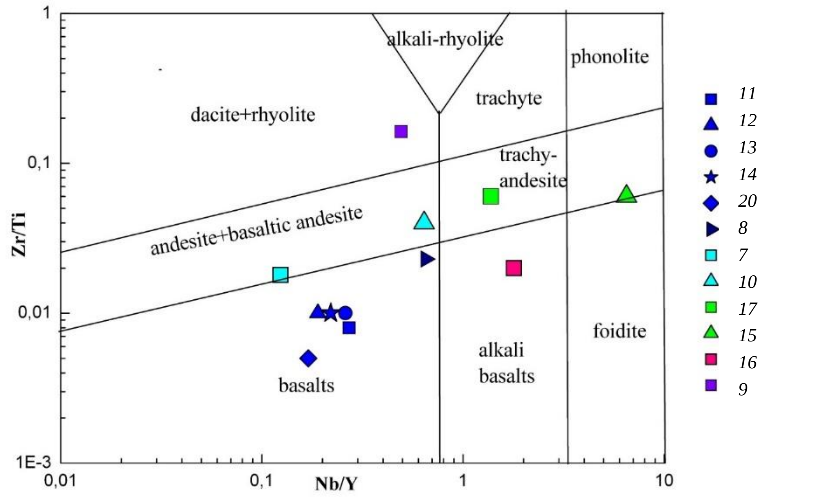
CAB (calc-alkiline basalt)
- Andesites

OIB (alkiline oceanic within-plate basalts)
- Trachyandesite

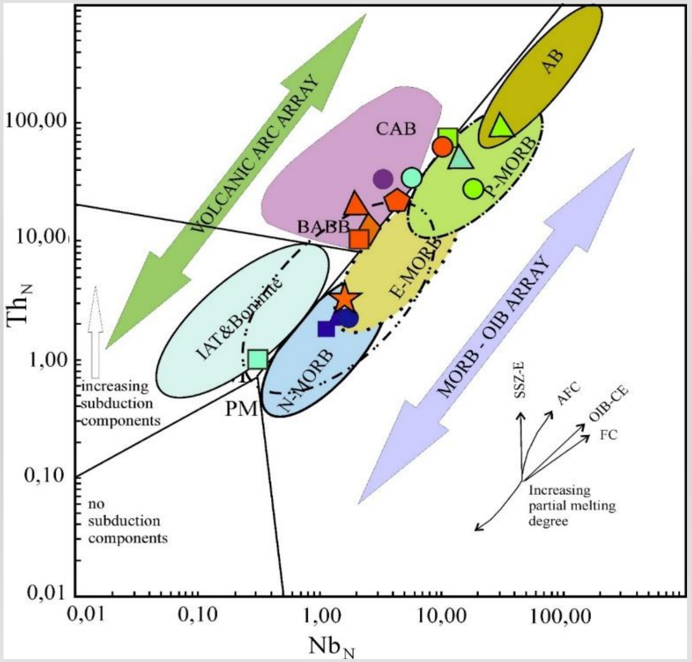
Discrimination diagramm of Th-Hf/3-Ta



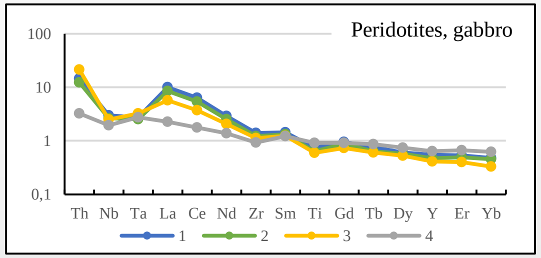
Discrimination diagrams of Nb/Y and Zr/Ti for volcanic rocks and apogabbros of the Ulan-Sar´dag massive

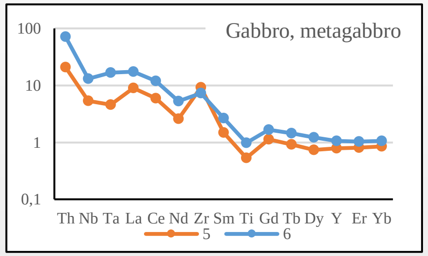


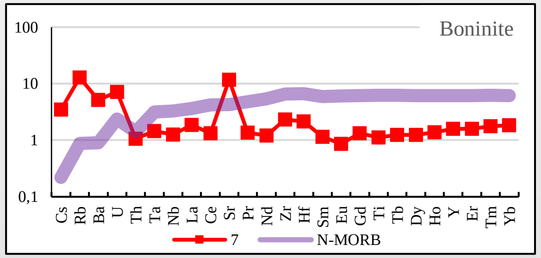
Discrimination diagramm of Th_N-Nb_N

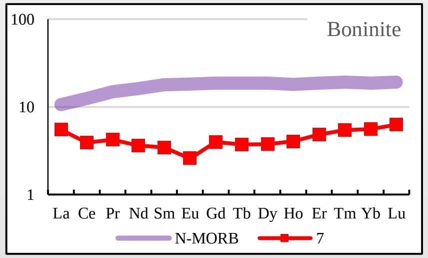


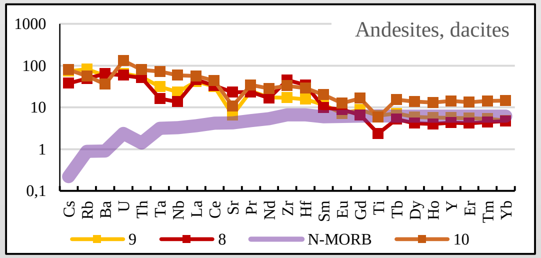
MORB-normalized diagrams distribution of HFSE in vulcanites and peridotites of Ulan-Sar´dag massif

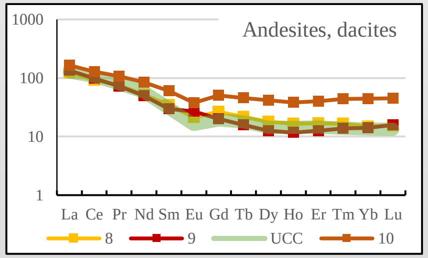


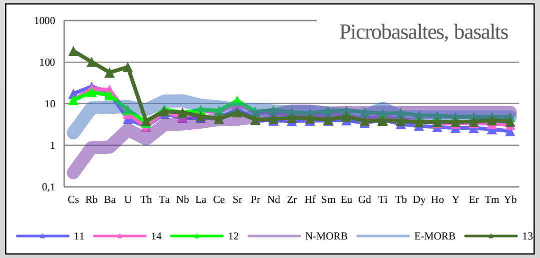


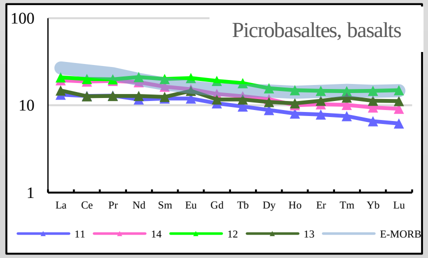


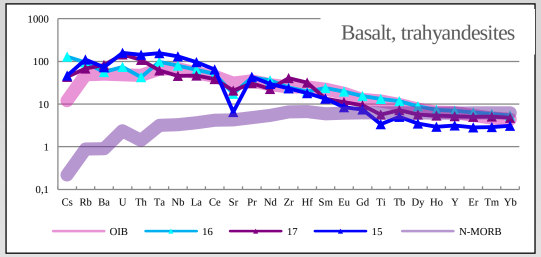


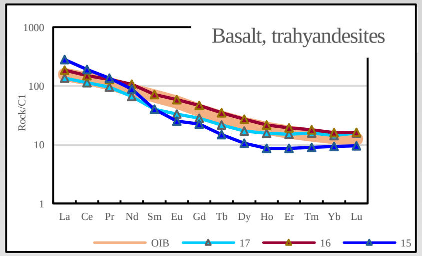








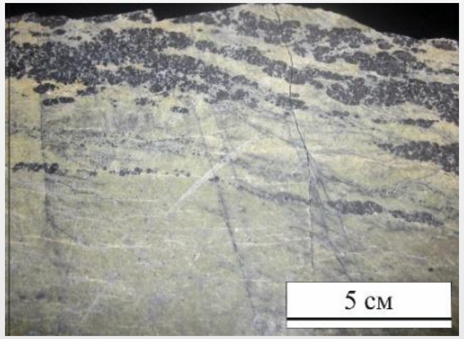




Features of chromitites

Chromitites are located within the mantle section (dunites, garzburgites, serpentenites). Massive chromitites consist of aggregate euhedral to subhedral crystal shape of chromite grains, only separated one from the other by a thin film of chlorite and serpentine or olivine and minor serpentine.

Shlieren, lensoidal pods



Shlieren, lensoidal pods

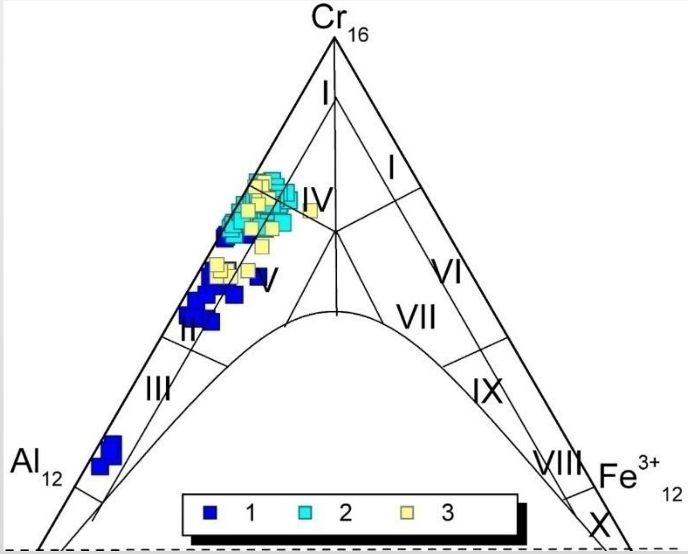
Vein type, deformed pods

Vein type

Structure of "snowball"

Deformed structure

Structural and textural features and stages of deformation are:
1) lenticular (from one to three centimeters in thikness);
2) irregular ore bodies (lenses some centimeters thick, pods, schlieren); some lenses, pods, schlieren pods is grouped forming vein type.
3) schlieren type during the tectonic processes is transformed to structure of tectonic flow, deformation structure up to forming the structure of "snowball" type – massive chromitites;



Ore Chr-spineles consist of chrompicotite, alumochromite, chromite, ferrochromite and Chr-magnetite and magnetite. Chr-spineles have composition (wt.%): Al_2O3 10÷22 и 36÷39, Cr_2O_3 46÷53 и 28÷35; MgO 12÷15 и 19÷20 wt.%.
Studied chromitites show chemical characteristics typical of podiform chromite deposits

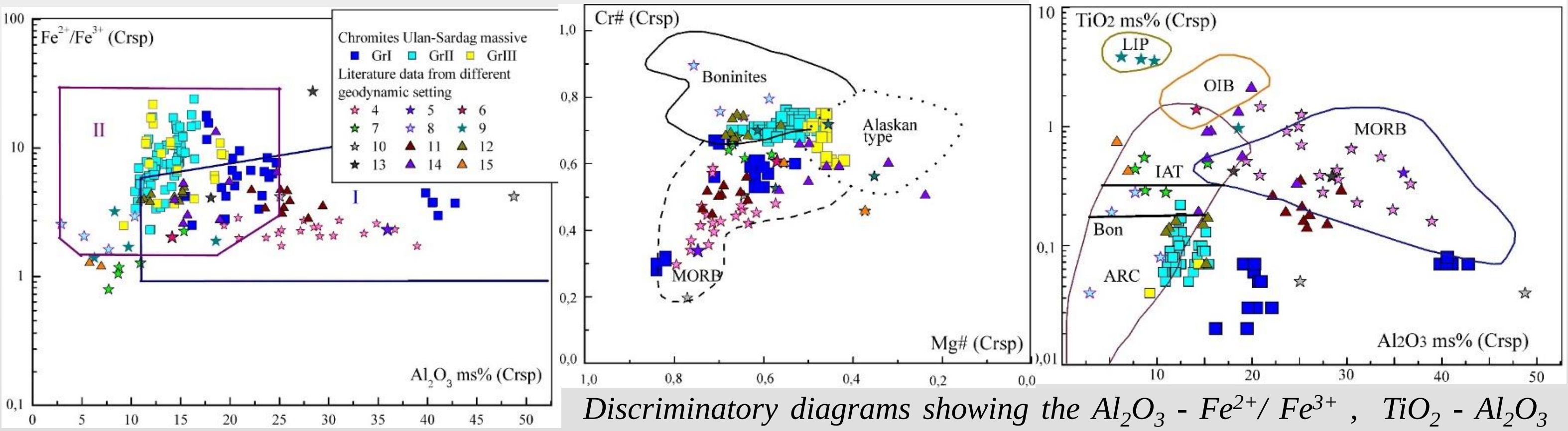
Diagram compositions of Chr-spineles of the Ulag-Sar´dag massive

Table of Chr-spinel parameters

	Al#	Cr#	Mg#
I group	24-60	36 - 74	45 - 74
II group	14 - 23	74 - 81	32 - 48
III group	13 - 27	68 - 81	28 - 35

Features of chromitites

Chromite in the mantle peridotites of the massif. a) thin-banded, b) massive veins, c) schlieren.



Discriminatory diagrams showing the Al_2O_3 - Fe^{2+}/Fe^{3+}, TiO_2 - Al_2O_3 ratios and $Cr^{\#}$-$Mg^{\#}$ in the chromites of their chromites according to literature data and data Ulan-Sar´dag massive.

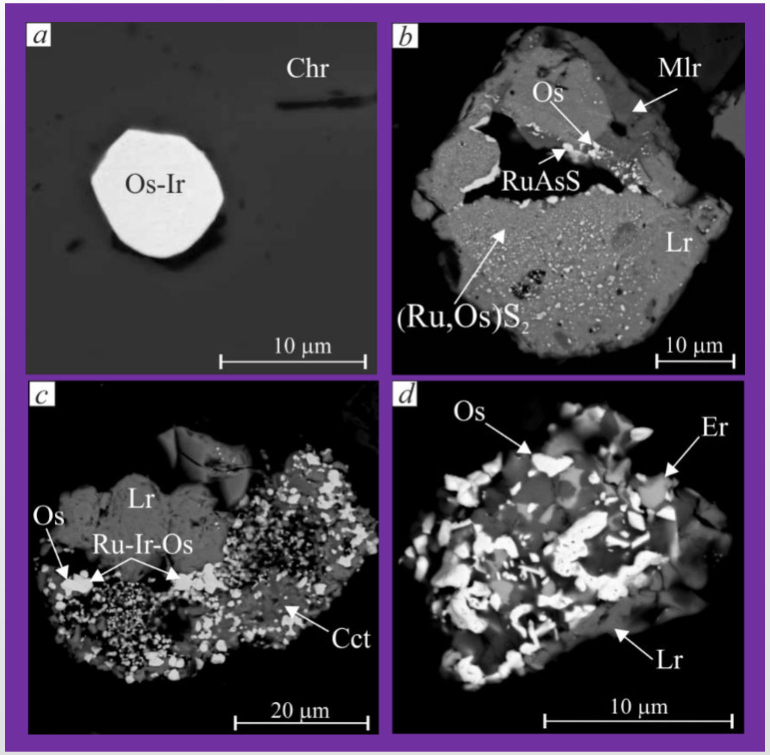
- MORB ES; Al# (21-60), Cr# (36-74), Mg# (59-84)
- Boninite ES; Al# (14-23), Cr# (74-81), Mg# (46-63)
- Alyskyn type ES; Al#13-20), Cr# (67-81), Mg# (42-50)

Literature data

- MORB from Mid oceanic ridge basalt; Cr#<0,7
- Back-arc basalt; Cr#<0,7
- Oceanic-island basalt; Cr<0,7
- Island arc, high K and calc-alcalain basalt; Cr#>0,7
- Iisland arc boninite and tholeite basalt; Cr>0,7
- Large igneous province: Flood Basalt; Cr#>0,7
- Spinel in abissal peridotites
- Chromite in ophiolitic mantle high Al#
- Chromite in ophiolitic mantle high Cr#
- Chromitite in subcontinental mantle
- Chromitite in continental layered intrusion
- Chromitite in Alaskan-type complexes

Chemical parameters of chrom-spinelides and parental melt composition in equilibrium with podiform chromitites are located in three fields: MORB, suprasubduction zones, boninites, Alaskan type.

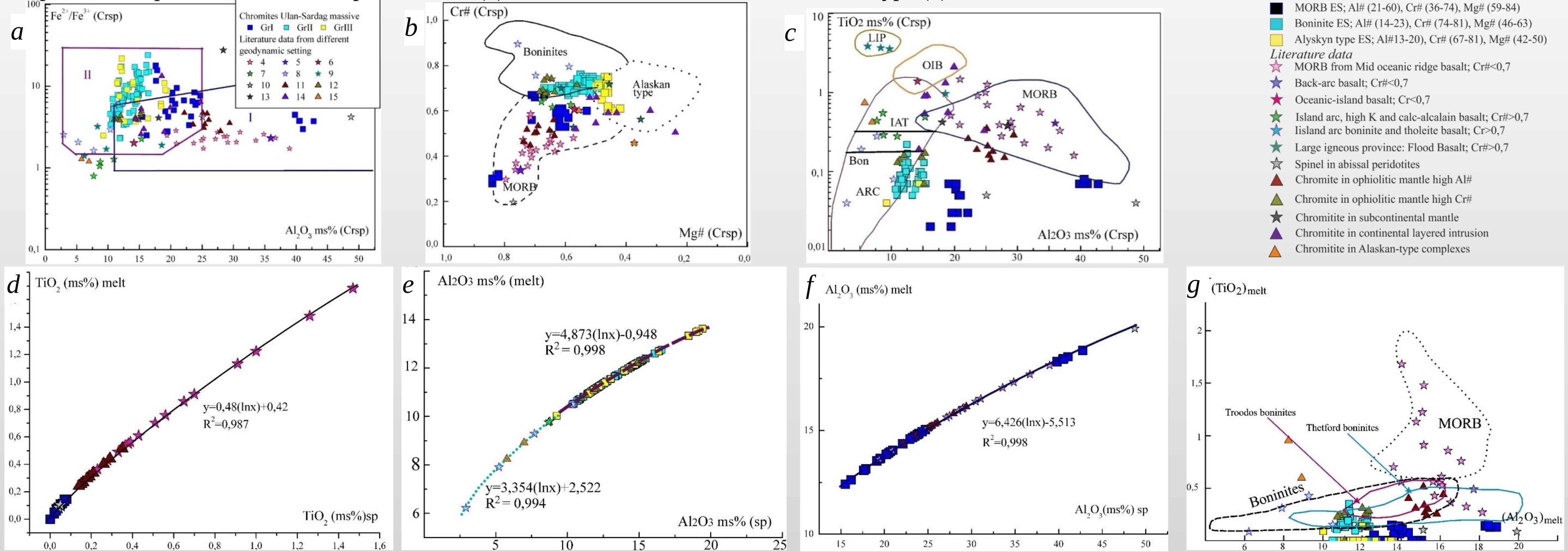
Features of MPG mineralization in chromitites



Minerals of the platinum group in chromites (BSE): a) grain of iridosmin in chrom- spinelide; b) concretion of millerite and zonal grain of laurite (in the center of the phase with erlichmanite minal and inclusions of osmium; c) concretion of laurite and laurit-erlichmanite with multiple inclusions (Os-Ir-Ru); d) interpenetrating concretion of laurite and erlichmanite with nanosized inclusions Os.

Distribution and PGE mineralization are typical for podiform chromitites of world ophiolite complexes. Platinum group mineralization consist of Os-Ir solid solution, two generation of sulfides PGE (magmatic Lr-Er and hydrothermal newly-formed Lr). Native osmium, ruthenium, RhNiAs are in close assotiation with chlorite, serpentine, sulfides of nikel. Metamorphism from green shale to amphibolite facies leads to a change in magmatic platinum group minerals, dissolution, remobilization PGE. The rise in temperature leads to the enlargement and agglomeration of nanoparticles of PGE from nano- to micro-level.

Ore chr-spinels from the podiform chromite on the discriminatory diagrams are divided into three groups and localized in the fields MORB-type (I group), supra-subduction zone (boninites) peridotites (I, II groups), Alaskan type (III group) (a-c). Graphic plots of calculated Al_2O_3 composition of melts in equilibrium with Ulan-Sar´dag chromitites, compared with spinel melt relationship for MORB (*a*) and Arc lavas and chromitites Alaskan type (*b*).



The chr-spinels composition of podiform chromitites, in terms of their FeO, MgO, Al_2O_3, TiO_2 contents, is considered to function of the parental melt composition. We estimated the Al_2O_3, TiO_2 contents and FeO/MgO of the parental melt composition in equilibrium with the podiform chromite (table above). The chr-spineles of group I correspond to trend $(Al_2O_3)_{sp}$ – $(Al_2O_3)_{melt}$ for MORB setting (d). The chr-spineles of group II and III correspond to trend Island arc boninites (8) Alaskan type chromitites (15) (e). The calculated abundance TiO_2 in melt is very low and do not reach (arrive) the field of MORB type. Despite the low TiO_2 content, the trend of $(TiO_2)_{sp}$ – $(TiO_2)_{melt}$ corresponds to this trend for MORB spinel’s. It is remarkable that the ratios of $(TiO_2)_{sp}/(TiO_2)_{melt}$ are similar to this ratio in chr-spinels from abyssal peridotites (f). Based on calculated of abundance TiO_2 and Al_2O_3 in melt chr-spineles of massive Ulan-Sar´dag lie in Boninitic field (g).

PGE distribution and mineralization

Total PGE concentration in 9 chromitites samples ranges from 242 to 992 ppb and is about 2.5 to 5.5 times higher than in serpentinized peridotites. The all chromitites have enrichment Pd (78-903 ppb). It is unusual for chromitites. There is no obvious correlation between PGE abundance and chromite composition. All samples has positive correlation among the pairs Os-Ir (R_2=0.79), Ir-Ru (R_2=0.71), Os-Ru (R_2=0.64). Palladium has no correlation with another elements.

Chondrite-normalised PGE patterns of Ulan-Sar´dag chromitites display average (Os+Ir+Ru)/(Rh+Pt+Pd) ratios typical of Cr-rich chromitites formed in the mantle section of supra-subduction zone ophiolites In most cases, PGE patterns are characterized by a consistent positive anomaly in Ru, and a negative anomaly in Pt.

Literature data:

I - Ahmed Hassan Ahmed, Hesham M. Harbi, Abdelmonem M. Habtoor (2012). Compositional variations and tectonic settings of podiform chromitites and associated ultramafic rocks of the Neoproterozoic ophiolite at Wadi Al Hwanet, northwestern Saudi Arabia. Journal of Asian Earth Sciences 56,118–134.

II - Prichard H. M., Lord R. A., Neary C. R. (1996). A model to explain the occurrence of platinum – and palladium – rich ophiolite complexes. Journal of the Geological Society, 153, 323-328. (Chromitittes from Oman ophiolite, northen Semail)

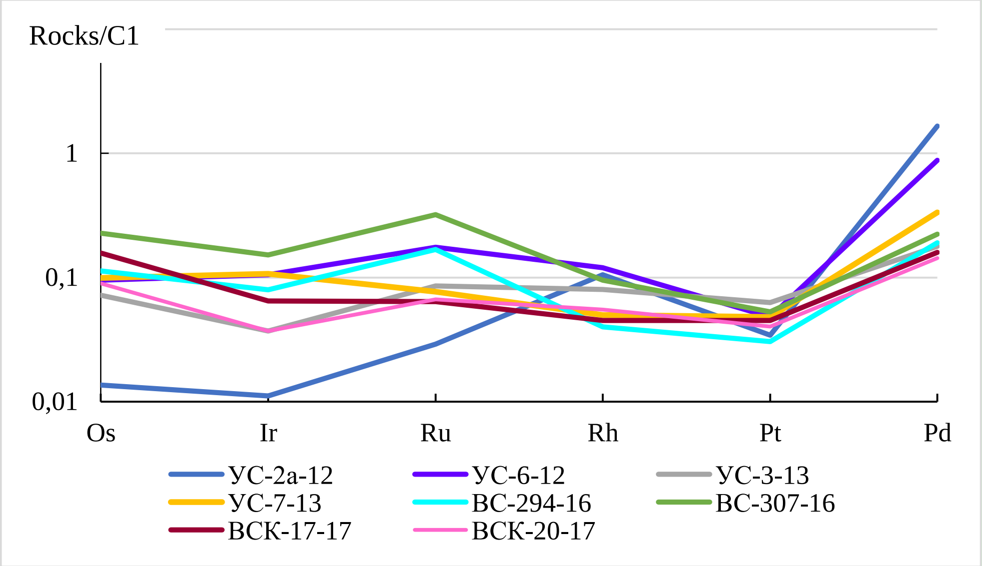
III – Tsoupas G. , Economou-Eliopoulos M. (2008). High PGE contents and extremaly abundant PGE-minerals hosted in chromitites from Veria ophiolite complex, northern Greece. Ore Geology Reviews 33, 3-19.

IV – Gurskaya L.I., Smelova L.V., Kolbancev L.R., Lyahnickiy U.S., Shahova S.N. (2004) Platinum mineralization in chromite-bearing ultrabasic-basic massives of chromitites from Ray-Iz massive Polyar-Ural. Publishing office St-Pet. mapfactories FSBI. 306 p (in Russian).

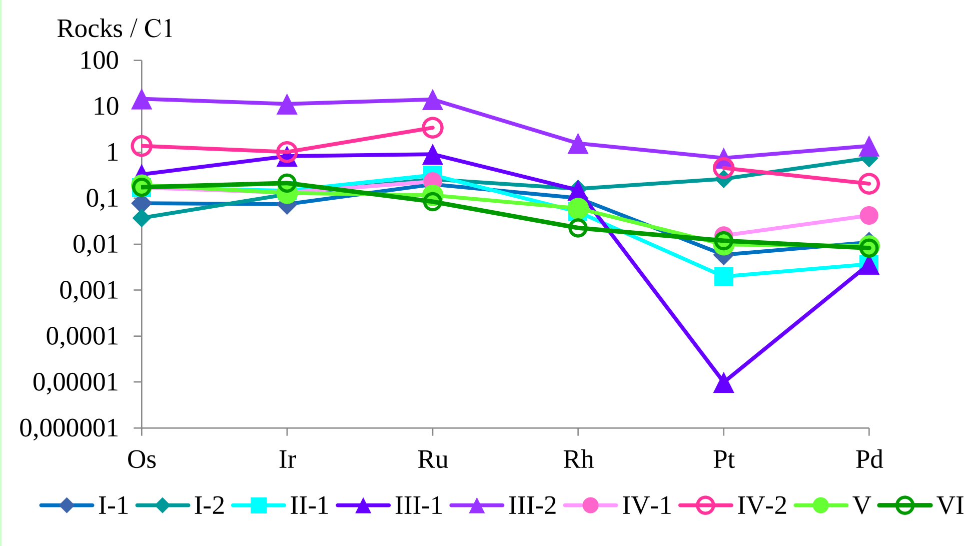
V – Agafonov L.V., Lhamsuran G, Kuguget K.S., Oydup Ch.K. (2005). Platinum-bearing of ultramafic-mafic complexes of Mongolia and Tuva. Ulaan-Batar, 224.

For all publications: 1 - the chromitites are enriched in Os-Ir-Ru, 2 - chromitites enriched in Pt-Pd

Graphs of the distribution of PGE in chromitites of Ulan-Sar´dag ophiolite



Graphs of the distribution of PGE in massif chromitites (literatura data)



PGE mineralization are represented by Os-Ir-(Ru) solid solutions, native Os, Ru, laurite-erlichmanite $(Ru,Os)S_2$, laurite (RuS_2), irarsite (IrAsS), zakarinit (RhNiAs).

- Sulfides of PGE are the predominant phases in the chromitites of the Ulan-Sar´dag ophiolite. They occur as idiomorphic inclusions in chrom-spineles. Solid solutions of Os-Ir-(Ru) were found as idiomorphic inclusions in spinel, and in xenomorphic grains in intergrowths with laurite. Solid-solution laurite-erlichmanite and Os-Ir correspond to early high-temperature magmatic stage.
- The phases (Os, Ir, Ru) of varying composition are common as numerous micro - and nano-size inclusions in laurite-erlichmanite. Native Os (Os> 80 wt.%) and Ru (Ru=93 wt.%) occur in polyphase aggregates, together with chalcocite, laurite, laurite-erlichmanite, heazlewoodite , zakarinite, Os-Ir-Ru solid solutions.
- Laurite and laurite-erlichmanite RuS_2-$(Ru,Os)S_2$ are represented most widely. There are two groups: 1) laurite-erlichmanite $(Ru,Os)S_2$; 2) laurite RuS_2 – phase of variable composition $(Ru,Os)S_2$ occurring in multi-component aggregates of heterogeneous composition and containing a large number of rounded and rectangular micro-inclusions of native Os, (Os-Ir), and Ru. Laurite has homogeneous microstructure and composition consistent with the stoichiometric composition. It forms individual grains in chlorite and serpentine. It is known that (Os-Ir) and solid solutions of laurit-erlichmanite are forming before or nearly simultaneously with the segregation of chrome - spinel in the upper mantle at T=1200°C and P= 5-10 kbar.
- Sulfo-arsenides and arsenides of Ru, Ir, Rh, Ni are formed from the residual fluid phase at post-magmatic stage, together with heazlewoodite. It is possible that in chromitites from Ulan-Sar´dag ophiolite there are two generations of sulphides:
- The first generation – magmatic solid solutions of laurite-erlichmanite.
- The second stage– the newly formed laurite, with primary laurite-erlichmanite or intergrowths with chalcosine, and millerite confined to zones of chloritization.
- The predominance of Os, Ru sulphides over the solid solutions of Os-Ir-Ru indicates a higher sulfur fugacity in the mantle source of Ulan-Sar´dag ophiolite

Diagram of composition Os-Ir-Ru alloys

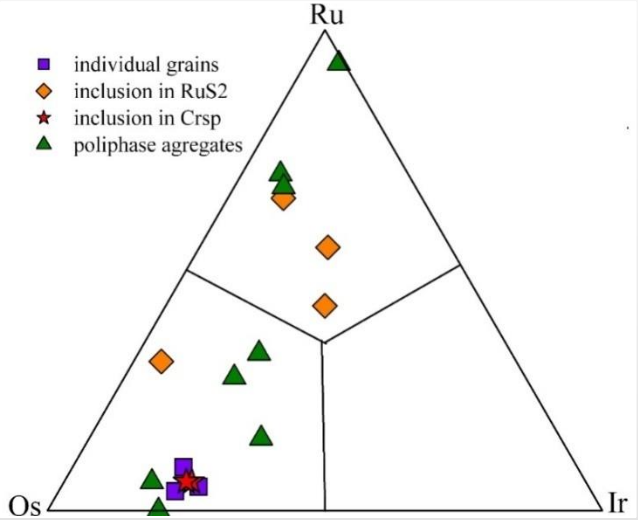
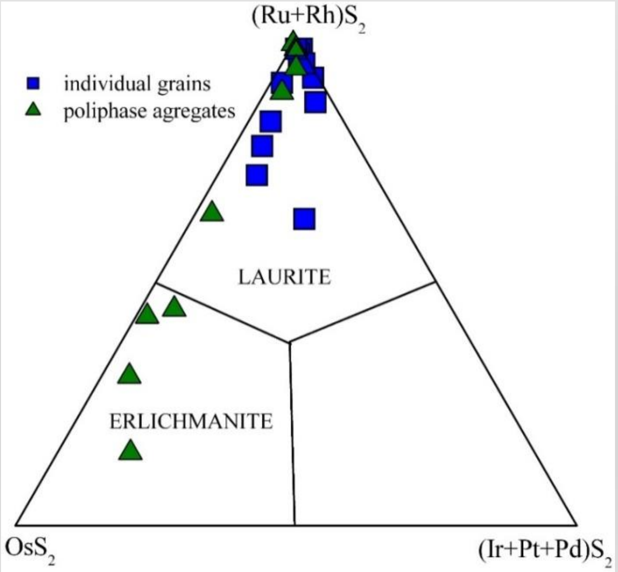
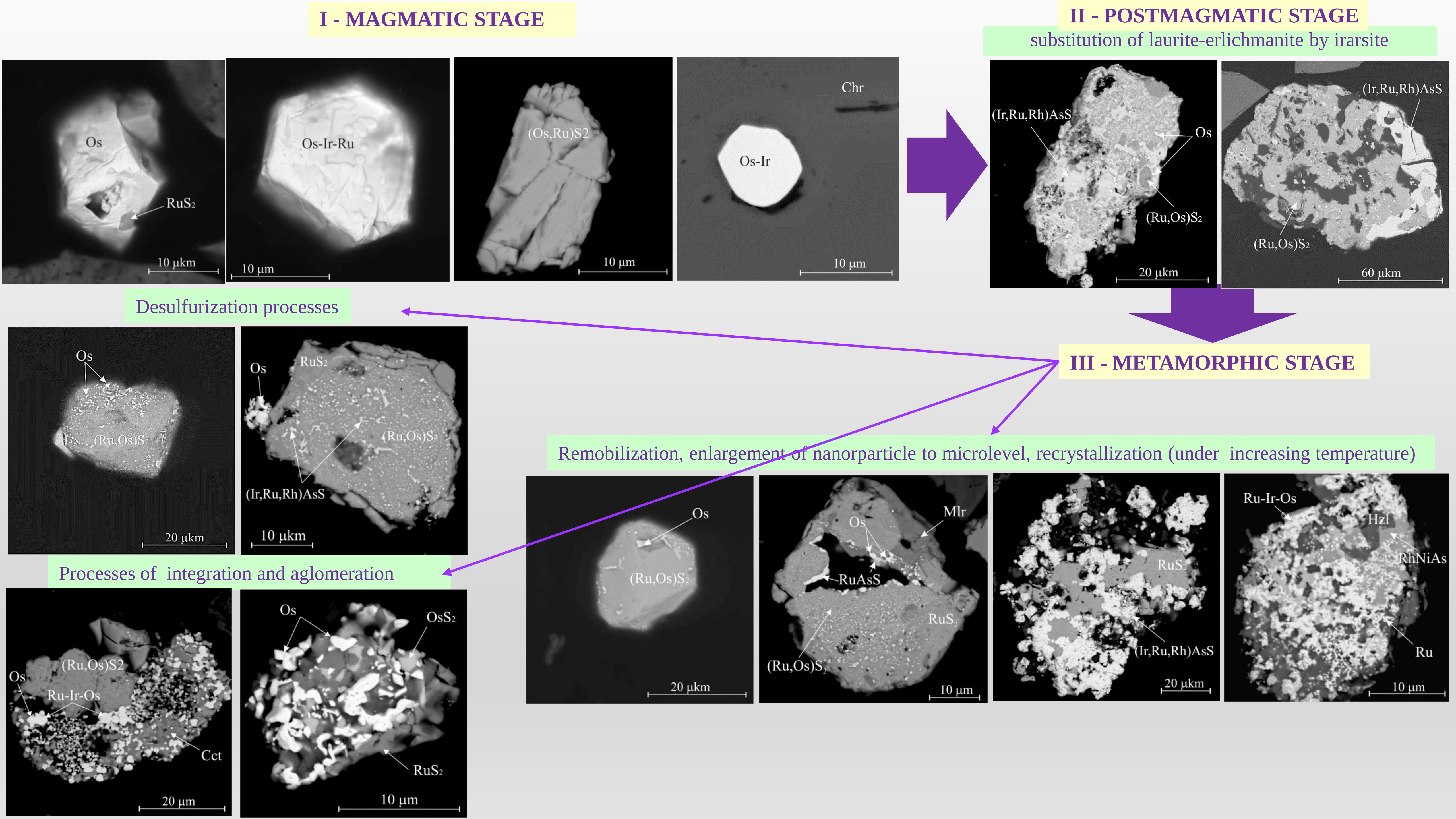


Diagram of composition PGE sulfides




I - MAGMATIC STAGE
Os
RuS_2
10 μkm
Os-Ir-Ru
10 μm
(Os,Ru)S2
10 μm
Chr
Os-Ir
10 μm
II - POSTMAGMATIC STAGE
substitution of laurite-erlichmanite by irarsite
(Ir,Ru,Rh)AsS
Os
$(Ru,Os)S_2$
20 μkm
(Ir,Ru,Rh)AsS
$(Ru,Os)S_2$
60 μkm
Desulfurization processes
Os
$(Ru,Os)S_2$
20 μkm
Os
RuS_2
$(Ru,Os)S_2$
(Ir,Ru,Rh)AsS
10 μkm
III - METAMORPHIC STAGE
Remobilization, enlargement of nanorparticle to microlevel, recrystallization (under increasing temperature)
Os
$(Ru,Os)S_2$
20 μkm
Mlr
Os
RuAsS
RuS_2
$(Ru,Os)S_2$
10 μm
RuS_2
(Ir,Ru,Rh)AsS
20 μkm
Ru-Ir-Os
Hzl
RhNiAs
Ru
10 μm
Processes of integration and aglomeration
$(Ru,Os)S_2$
Os
Ru-Ir-Os
Cct
20 μm
Os
OsS_2
RuS_2
10 μm

CONCLUSION

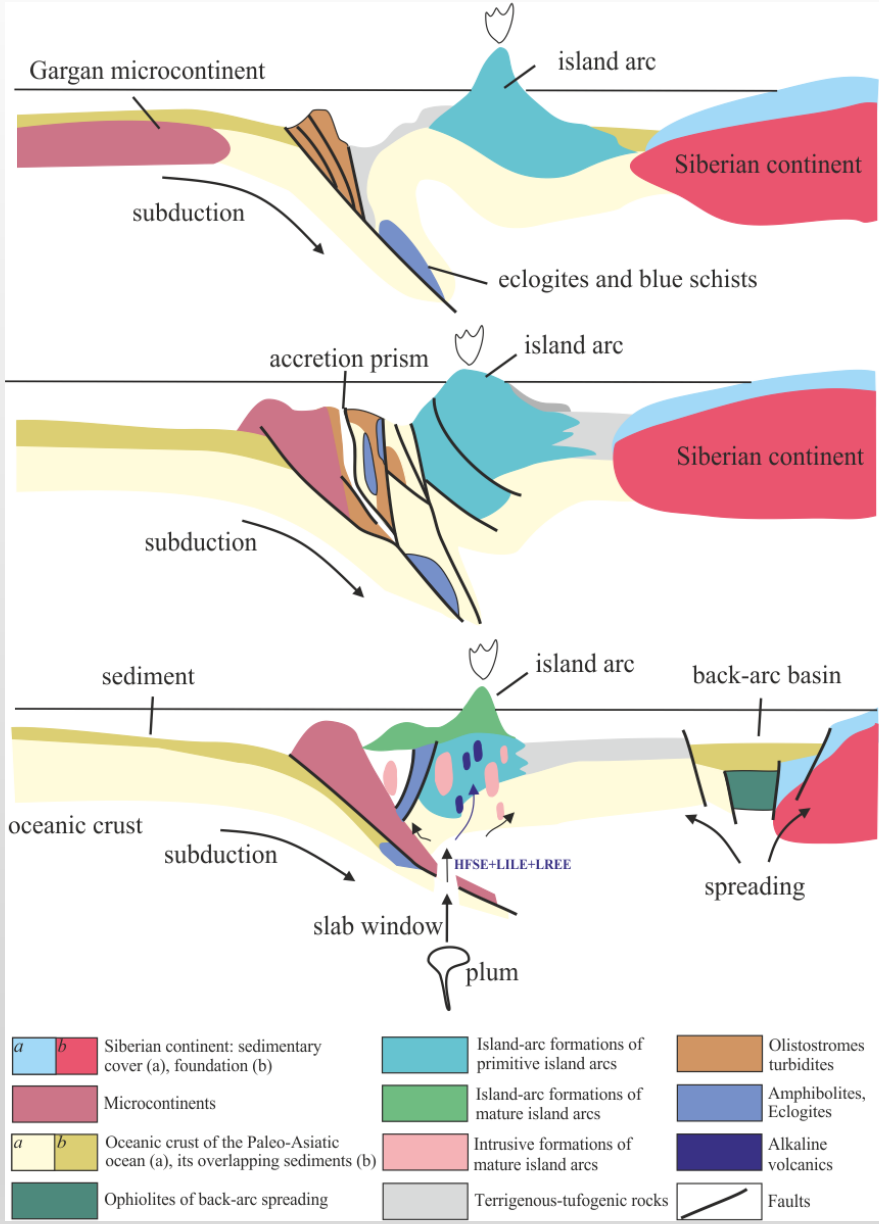
1. The geochemical features of the volcanic and ultramafic rocks are consistent with Supra-Subduction Zone
2. Chr-spinels rarely alteratied and can be used a reliable petrogenetic indicator. The primary chemistry of chr-spinels provides important information about the composition of the parental melt, magmatic processes (partial melting). Chr-spinels formed by participation of magmas of different composition and then changed in suprusubduction setting. Chr-spinels are localized into three fields: MORB, High-Al chromites from MORB-like tholeiitic magmas (in a back-arc setting), during melt/mantle interaction with a subsequent change to a subduction setting. High-Cr spineles are thought to form from boninitic magmas in an island arc environment (subduction setting)
3. Chr-spinels are localized in the fields MORB-type (the first group), Supra-subduction zone (Boninites) peridotites (the second and part of the first group), Alaskan type (the third group). The chromites falling into the field of the Uralo-Alaskan type could be formed during the partial melting of the fluid metasomatized mantle, with the interaction of andesitoid melts with the rocks of the overlying mantle wedge.
4. Chondrite-normalised PGE patterns of Ulan-Sar´dag chromitites display average (Os+Ir+Ru)/(Rh+Pt+Pd) ratios typical of Cr-rich chromitites formed in the mantle section of supra subduction zone ophiolites. The processes leading to extreme fractionation of PGE can be connected fluid-saturated supra-subduction.

It is known that (Os-Ir) and solid solutions of laurite-erlichmanite are forming before or nearly simultaneously with the segregation of chrome - spinel in the upper mantle at T=1200°C and P= 5-10 kbar.

We suppose there are two generation of sulphides in chromitites from Ulan-Sar´dag massive
1- PGM generation – magmatic solid solutions of laurite-erlichmanite.
2 - generation the newly formed laurite, with primary laurite-erlichmanite or intergrowths with chalcosine, and millerite is found in zones of chloritization. It has assotiation with serpentine, chlorite, irarsite, and BSE sulfides (Ni).

The predominance of Os, Ru sulphides over the solid solutions of Os-Ir-Ru indicates a higher sulfur fugacity in the mantle source of Ulan-Sar´dag massive, than other ultrabasic massive of Dunzhugur ophiolites.

Sulfo-arsenides and arsenides of Ru, Ir, Rh, Ni are formed from the residual fluid phase at post-magmatic



The paleoreconstruction of the formation of the Sayano-Baikal-Muya accretionary-collisional belt


Thank you for attention