

Structure of the lecture

Spinel group minerals - cubic oxides of general formula

- AB_2O_4

- crystallochemistry of the spinel group minerals
- mineral formula calculation and graphic presentation
- Cr-spinels
- Al-spinels
- Fe^{3+} -spinels

spinel group minerals

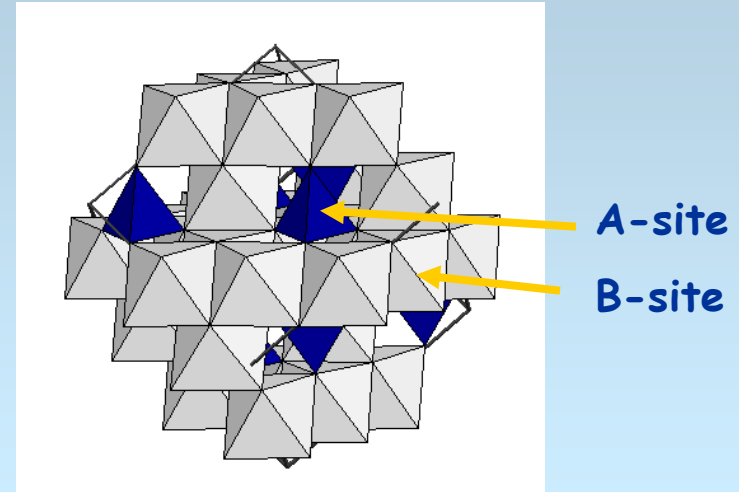
- common accessory minerals in the mantle and crustal rocks
- economically interesting ore deposits (magnetite, chromite)
- transparent, translucent and attractively colored varieties are respected gemstones (from ancient times)
- interesting for petrogenetic interpretations (PT conditions) -geothermometers

Skupina spinelu (spinelidy)

- general formula AB_2O_4
- crystallize in the **cubic** symmetry, space group Fd-3m
- common crystal forms are octahedron (usually twinned); rarely rhombic dodecahedron, tetrahedron, (and their simple or complicated combinations).
- usually fine- to coarse grained aggregates
- It has an imperfect octahedral cleavage and a conchoidal fracture.
- Its hardness is 8,
- its specific gravity is 3.5-4.1
- Spinel group minerals are subdivided into three series - based on dominant trivalent cation in B-site:
 - Spinel series (B = Al)
 - Magnetite series (B = Fe^{3+})
 - Chromite series (B = Cr)

Spinel structure

- general formula AB_2O_4
- A-site: Mg, Fe^{2+} , Zn, Mn, Ni - divalent cations
- B-site: Al, Cr, Fe^{3+} , V, Ti- trivalent cations



- Structure of spinel was solved at 1915 (Bragg W.H., Nishikawa S.)
- Spinel has so-called „normal“ and „inverse“ spinel structure
- Structure - oxygen atoms in spinel have a cubic close-packed structure
 - tetrahedral points are smaller than the octahedral points
 - „normal“ spinel structure (a common example is $MgAl_2O_4$)
 - the cations A^{2+} occupy 1/4 of the tetrahedral sites
 - and cations B^{3+} occupy half of the octahedral sites
 - „inverse“ spinel structure (a common example is $FeFe_2O_4$)
 - If the A^{2+} ions have a strong preference for the octahedral site, they will force their way into it and displace half of the B^{3+} ions from the octahedral sites to the tetrahedral sites.

Spinel group minerals

Spinel series (B = Al)

name	T-site	O-site	structure
Hercynite	Fe ²⁺	Al ₂	Normal
Spinel	Mg	Al ₂	Normal
Gahnite	Zn	Al ₂	Normal
Galaxite	Mn _{0,71} Al _{0,29}	Mn _{0,29} Al _{1,71}	29% Inverse

Chromite series (B = Cr)

name	T-site	O-site	structure
Chromite	Fe ²⁺	Cr ₂	Normal
Magnesiochromite	Mg ²⁺	Cr ₂	Normal

Spinel group minerals

Magnetite series (B = Fe³⁺)

name	T-site	O-site	struktura
Magnetite	Fe ³⁺	Fe ²⁺ Fe ³⁺	Inverse
Magnesioferrite	Mg _{0,1} Fe ³⁺ _{0,9}	Mg _{0,9} Fe ³⁺ _{1,1}	from 90% inverse
Franklinite	Zn	Fe ³⁺ ₂	Normal
Jaccobsite	Mn _{0,85} Fe ³⁺ _{0,15}	Mn _{0,15} Fe ³⁺ _{1,85}	from 15% Inverse
Trevorite	Fe ³⁺	Fe ³⁺ Ni	Inverse

➤ Ti-spinels

Někdy se přiřazují k Fe-spinelům, ale na rozdíl od nich neobsahují Fe³⁺

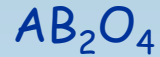
name	T-site	O-site	structure
Ulvöspinel	Fe ²⁺	Fe ²⁺ Ti ⁴⁺	100% inverse
Quandilite	Mg ²⁺	Mg ²⁺ Ti ⁴⁺	100% inverse

Mineral formula calculation and graphic presentation

B-site
Al
Cr
Si
Fe ³⁺
Fe ²⁺
V ³⁺
subsum 2

A-site
Ti ⁴⁺
Mg
Fe ²⁺
Mn ²⁺
Zn ²⁺
Ni ²⁺
Ca
subsum 1

SUM 3
O 4



- mineral formula recalculation on the basis of 3 cations
- All trivalent cations are assigned to the B site (Al, Cr, V). Elevated Si content indicates that alteration takes a place.
- Take a care to the ulvöspinel component $Ti^{4+}Fe^{2+}_2O_4$. Assign the Ti in to the A site and the double amount of Fe^{2+} assign to the B-site.
- The divalent cations (except Fe) should be assigned to the A-site.
- The rest of Fe is split between the A-site (Fe^{2+}) and the B-site (Fe^{3+})
- the FeO/Fe_2O_3 is calculated on the basis of the Fe^{2+}/Fe^{3+} atomic ratio (The EMP measure only FeO or Fe_2O_3)

Graphical presentation

- useful combination of dominant cations in A-site and B-site
 - A-site on X-axis and B-site on Y-axis

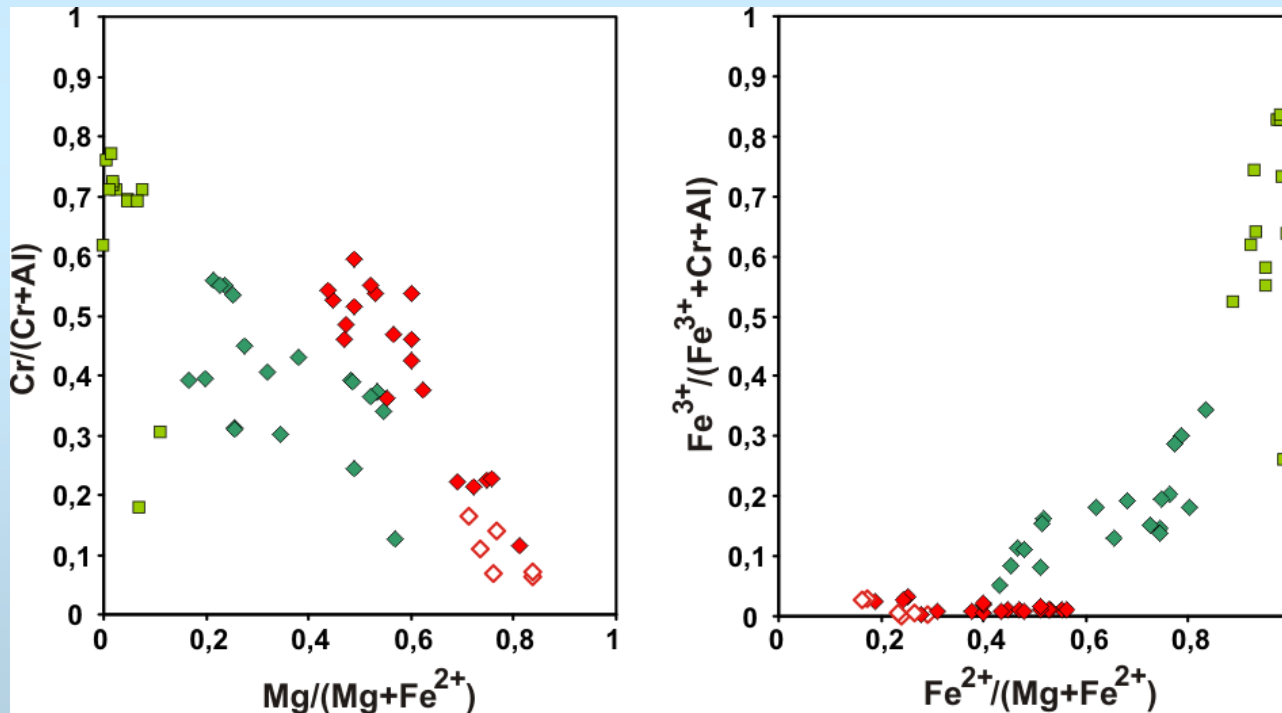
e.g. for Cr-spinels

in plots so-called Cr-number ($Cr\#$) - equals to $Cr/(Cr + Al)$

Mg-number ($Mg\#$) - equals to $Mg/(Mg+Fe^{2+})$

Fe^{3+} -number ($Fe^{3+\#}$) - equals to $Fe^{3+}/(Fe^{3+} + Cr + Al)$

Fe-number ($Fe\#$) - equals to $Fe^{2+}/(Mg+Fe^{2+})$

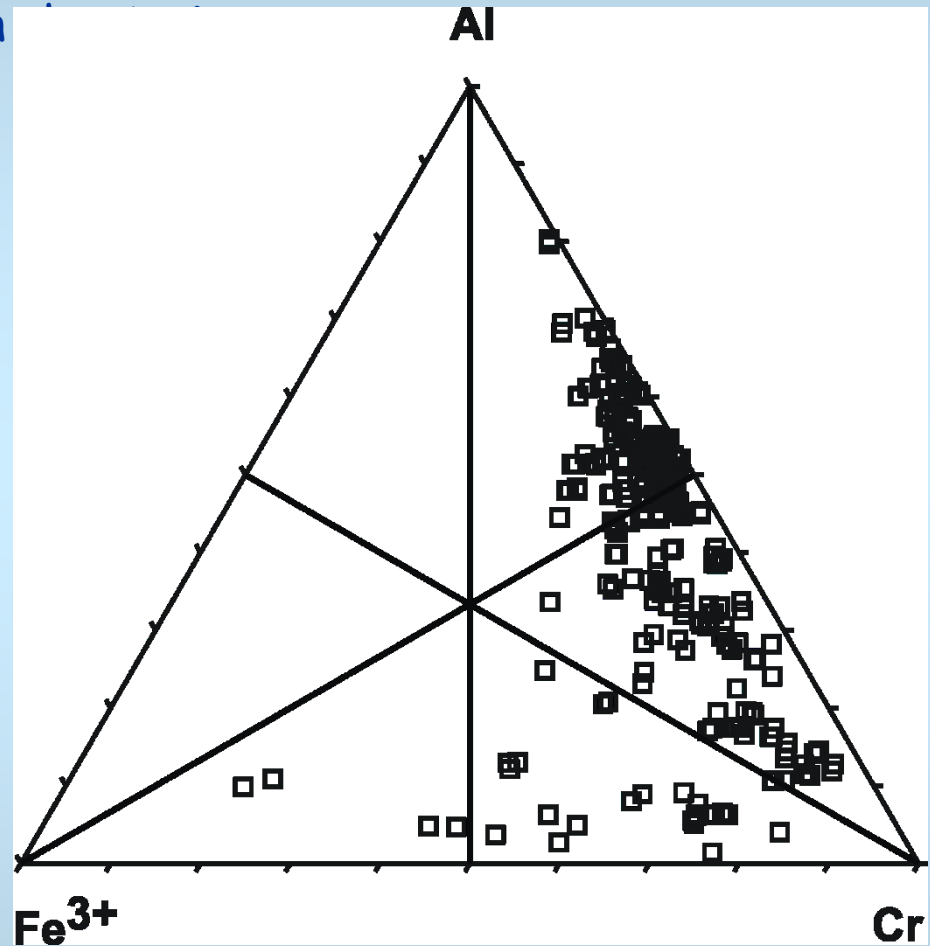


Chemické složení Cr-spinelů z oblasti ranského masivu a kutnohorského krystalinika
(Čopjaková, Štědrá 2007)

Graphical presentation

- ternary plots
- display of 3 major components in or B-site

suitable for variable B-site



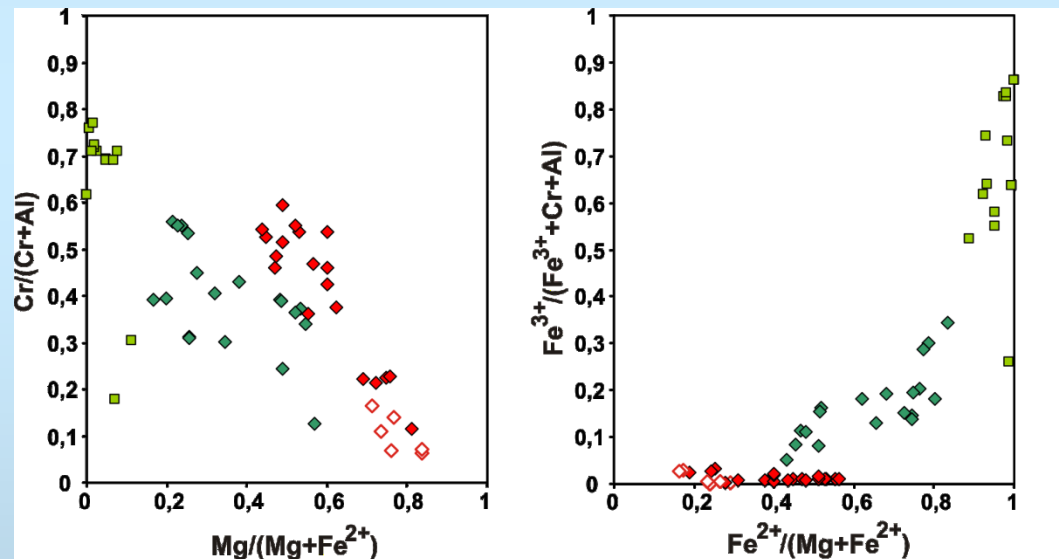
Chemical composition of detrital Cr-rich spinels in the Moravo-Silesian Culm Basin, Drahany Upland (Čopjaková 2007)

Spinelidy

- Very good miscibility among end-members at high temperature, even among Fe, Cr, Al and Ti spinels.
- Spinel often forms solid state solution of many end-members, e.g. spinel-hercynite-chromite-magnetite; chromite-hercynite-magnetite-franklinite

A-site						B-site									
Mg	Fe ²⁺	Mn ²⁺	Zn ²⁺	Ti ⁴⁺	subsum	Al	Cr	Si	Fe ³⁺	Fe ²⁺	V ³⁺	subsum	catsum	ansum	
0,27	0,67	0,03	0,01	0,03	1,00	0,85	0,87	0,01	0,21	0,05	0,01	2,00	3	4	
0,02	0,82	0,05	0,13	0,01	1,00	0,47	1,10	0,02	0,37	0,02	0,01	2,00	3	4	

- Spinel is often strongly chemically heterogeneous - evolution through several different members of the spinel group, even within one rock.



Chemické složení Cr-spinelů z oblasti ranského masivu - troctolity (tmavě zelené kosočtverce - primární Cr-spinely), světle zelené čtverce - sekundární Cr-spinely a z oblasti kutnohorského krystalinika - granátické peridotity (Čopjaková, Štědrá 2007)

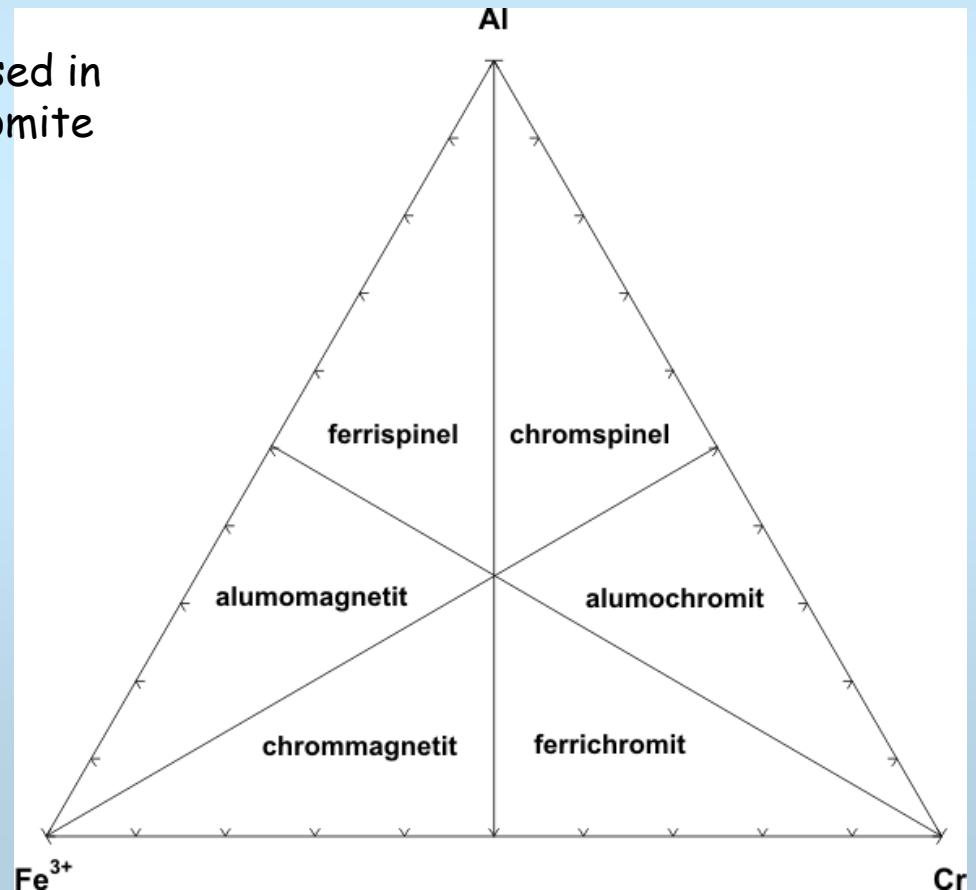
⇒ Difficult terminology - how to name such heterogeneous grains?

Cr-spinels

- Cr-spinels $(\text{Mg}, \text{Fe}^{2+})(\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_4$
- According to the new classification: **chromite** (FeCr_2O_4); **magnesiochromit** (MgCr_2O_4); **nichromite** (NiCr_2O_4); **zincchromite** (ZnCr_2O_4) ...

OLD classification ternary plot Stevens (1944), based on the B-site trivalent ions

Note, the old naming is commonly used in the recent literature, e.g. ferrichromite



Cr-spinels

Cr-rich spinels - solid solution of **chromite-magnesiochromite-spinel-hercynite**

- Cr-rich spinels are ubiquitous accessory minerals in various mafic and ultramafic rocks such as mantle peridotites, gabbros, mafic volcanic rocks (basalts, tholeiites) and their metamorphic equivalents.
- Cr-spinels crystallized typically as an early stage magmatic mineral.
- Continuous spinel crystallization together with other silicate phases (olivine, pyroxenes and plagioclase) over a significant range of temperatures is common. In some cases the crystallization temperature interval for Cr-spinel may exceed 200-250 °C.
- Chemical composition of Cr-spinels is controlled by several factors and as the most important are considered
 - PT conditions,
 - Melt composition,
 - degree of partial melting,
 - fractional crystallization,
 - subsolidus reequilibration with the co-existing silicates
 - oxygen fugacity

(see e.g., Irvine, 1965; Hill and Roeder 1974; Medaris, 1975; Pinsent and Hirst, 1977; Fisk and Bence, 1980; Dick and Bullen, 1984; Kepezhinskas et al., 1993).

Factors governing chemical composition of Cr-spinels

- The ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ is sensitive to variations in $f\text{O}_2$, it increases dramatically in magmas as they ascend (Sato, 1978).
- The effect of pressure on chromian spinel composition is controlled by the partition coefficient for Cr between crystals and melts
 - at high pressure conditions - partition coefficient for Cr is close to 1
 - high partition coefficient are accepted for low pressures of melt segregation (Kurat et al. 1980; Dick and Bullen, 1984).
- Spinel Cr # (Al_2O_3 abundances) depend on the melt composition, which is a function of pressure, temperature, and degree of partial melting
- During fractional crystallization or partial melting - Cr and Mg are strongly partitioned into the solid, and Al and Fe into the melt
- Fractional crystallization (decreasing melt Mg # and temperature) should lead to related change in the Mg # of co-crystallizing olivine and spinel.
- Partitioning of Mg and Fe^{2+} between chromian spinel, silicate melts and minerals is strongly temperature dependent (thermometry)

Factors governing chemical composition of Cr-spinels

- Spinel Mg # should be interpreted with caution, as it is a complex function of a number of factors, the most important of which are
 - (1) Mg # of the parental melt;
 - (2) temperature dependent
 - (3) partitioning of Al and Cr in spinel, and hence Al₂O₃ in the melt;
 - (4) post-entrapment re-equilibration with silicate minerals
- (3) The distribution coefficient $K_d = (Mg/Fe)_{\text{olivine}} / (Mg/Fe^{2+})_{\text{spinel}}$ varies significantly from 2.5 (cr-number 20-30) to 10-12 (cr-number 80-90) => spinel coexisting with olivine becomes more Mg rich with decreasing cr-number.
- (4) => the cooling rate and spinel grain size are important factors. Consideration of the kinetics of olivine-spinel Mg-Fe²⁺ interdiffusion precludes significant subsolidus re-equilibration for rapidly cooled, volcanics - insufficient time for re-equilibration at near-magmatic temperatures. Slowly cooled subaerial thick lava flows and intrusive rocks (cooling rates of 0.1-0.001°C/h) can show extensive re-equilibration.

Cr-spinels from mantle rocks - peridotites

- Cr-rich spinels crystallized typically as an early stage magmatic mineral.
- Cr-rich spinel is common in peridotite in the uppermost Earth's mantle, between approximately 20 - 120 km, possibly to lower depths depending on the chromium content.
 - At significantly shallower depths, calcic plagioclase is the more stable aluminous mineral in peridotite,
 - garnet is the stable phase deeper in the mantle below the spinel stability region.

Cr-spinel from „peridotites “

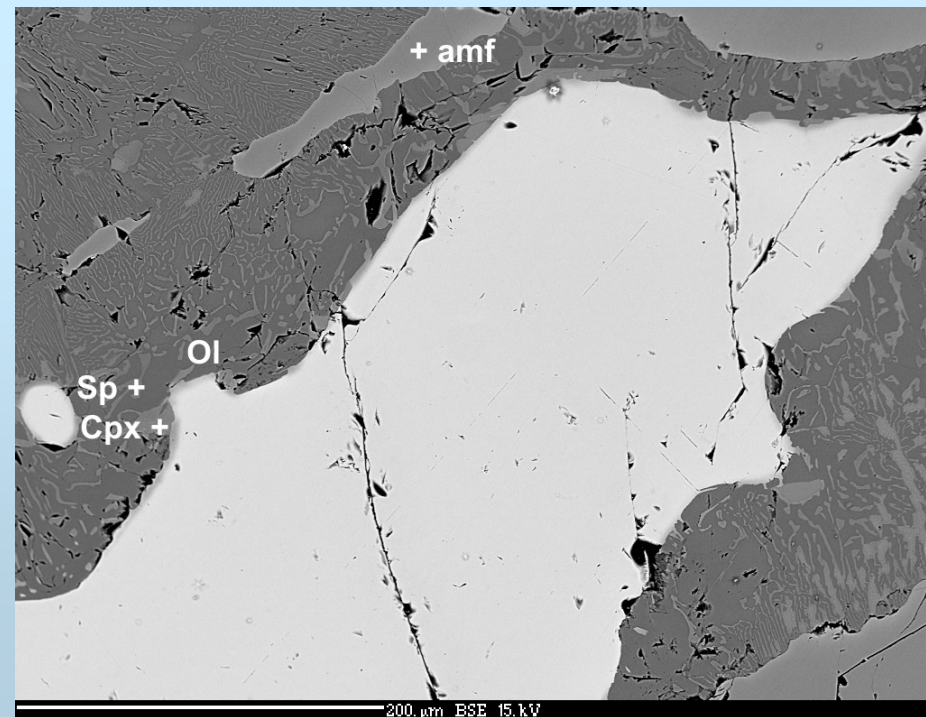
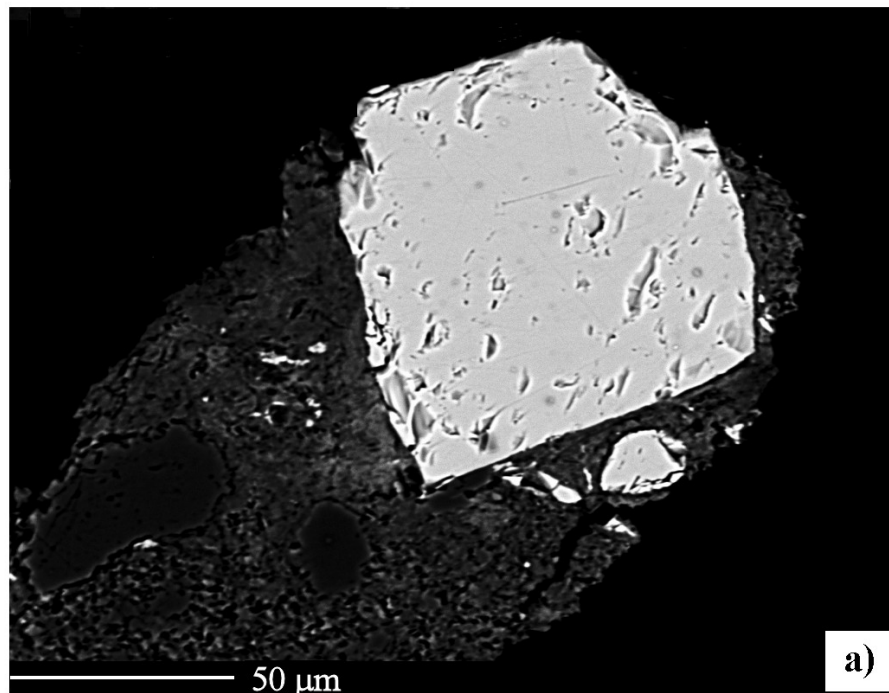
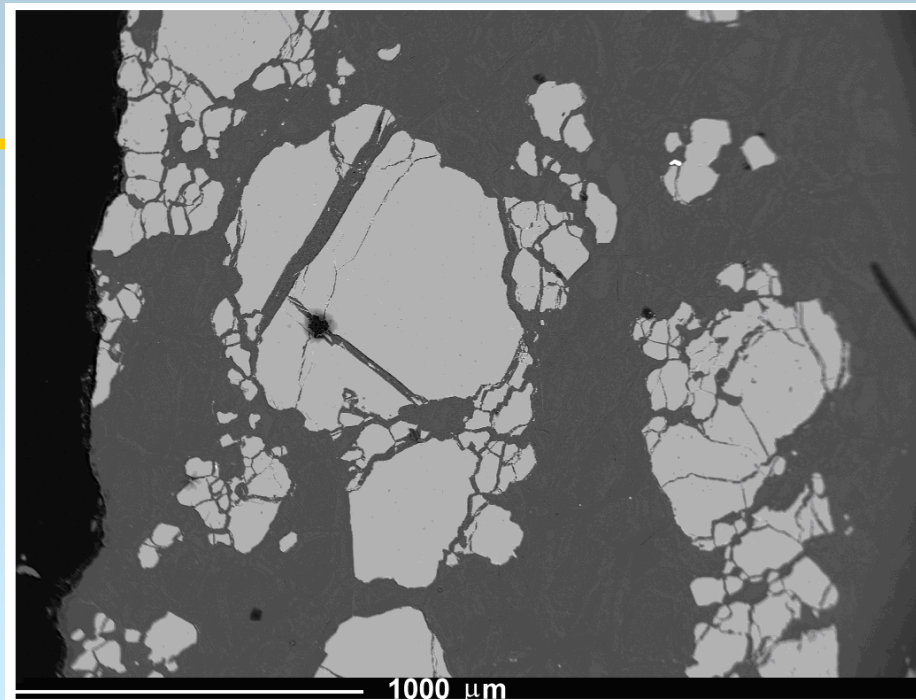
- mantle origin

Cr-spinel in BSE image

Cr-spinels form:

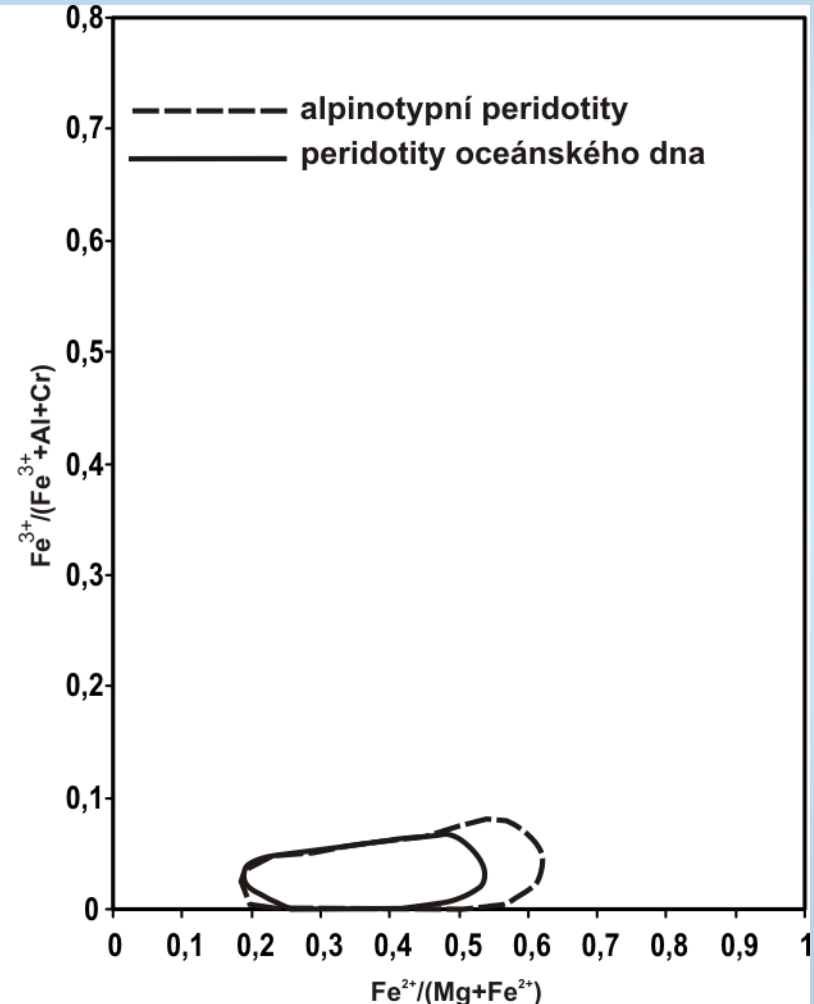
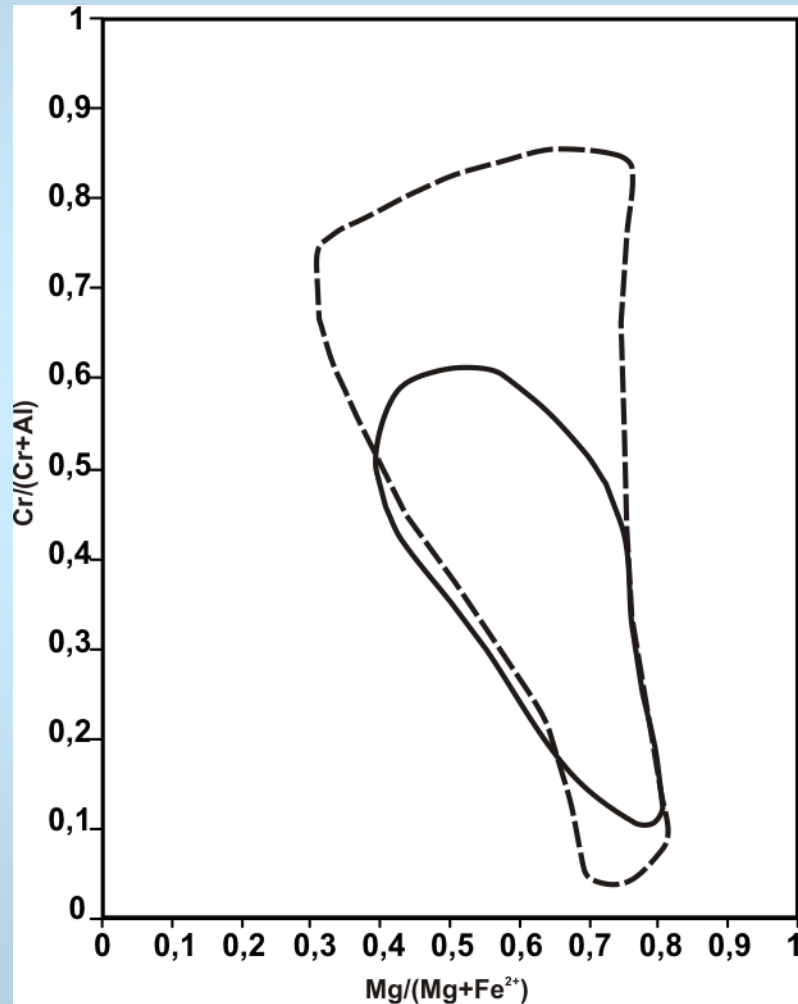
- fine- to coarse-grained aggregates
- massive cumulates
- disseminated anhedral grains
- disseminated euhedral grains (octahedron)

no melt inclusions !



Cr-spinels from mantle peridotites

----- Alpinotype peridotites
————— Ocean floor peridotites



Discriminant fields according to Cr-spinel database from Barnes and Roeder (2001)

Cr-spinel from volcanic rocks vs. Cr-spinel from peridotites

Chemical composition

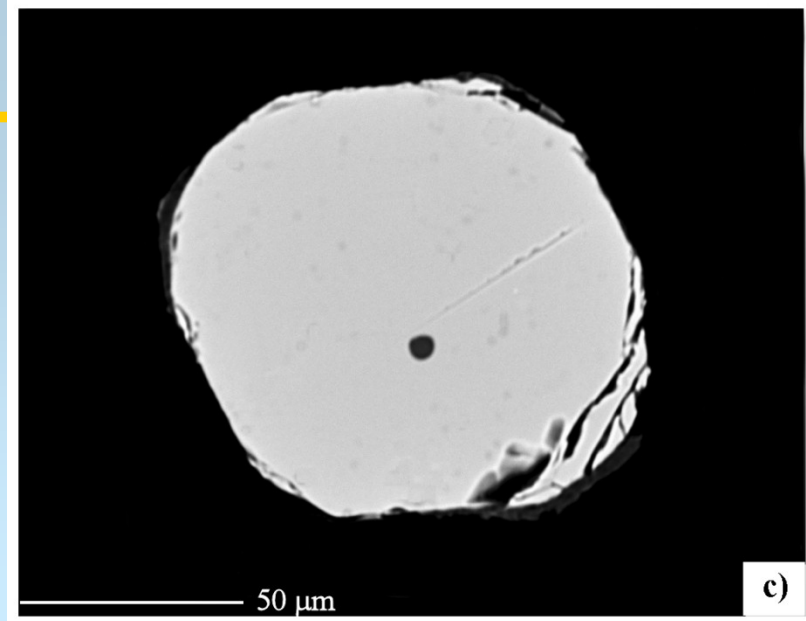
- Plutonic and volcanic complexes representing various geotectonic settings show remarkable differences in composition of chromian spinel (e.g., Dick and Bullen, 1984; Arai, 1992; Kepenzhinskas et al., 1993).
- In order to distinguish between intrusive peridotitic and extrusive volcanic spinels TiO_2 content and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio are used.
- The contents of Ti and Fe^{3+} from mantle rocks (peridotites) are consistently low ($\text{TiO}_2 < 0.25$ wt. % and $\text{Fe}^{3+} < 5$ wt. %) (Dick and Bullen, 1984; Lee, 1999).
- Volcanic spinels with TiO_2 below 0.2 wt. % are uncommon, only sporadically some arc boninites and tholeiites or low-Ti MORB have lower TiO_2 contents (Barnes and Roeder, 2001; Lenaz et al., 2000).
- On the other side, comparing with peridotitic spinels, volcanic spinels have higher Fe^{3+} contents, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio is usually < 4 (Kamenetsky et al., 2001). Cr-spinels from peridotites have $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio usually > 3

Cr-spinels from „volcanic “ rocks

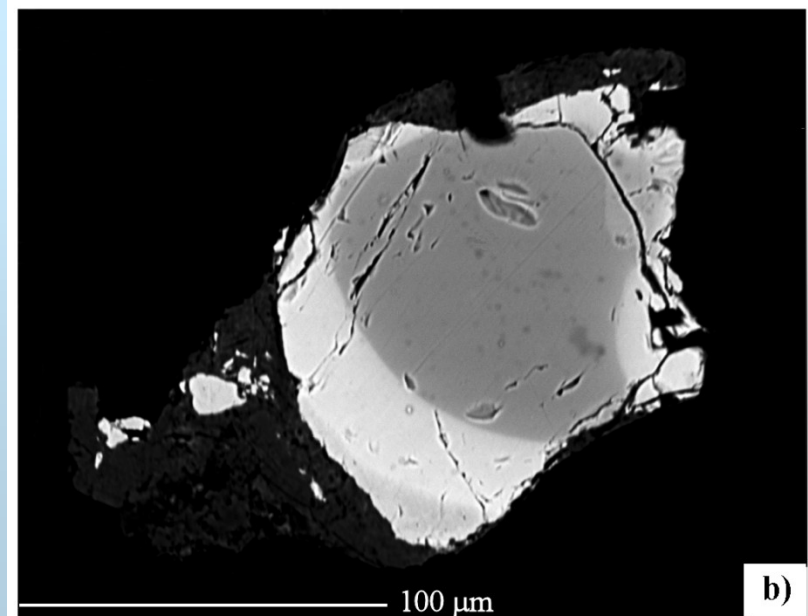
Cr-spinel in BSE image

- never massive
- usually euhedral to subhedral discrete grains
- smaller grains
- commonly form inclusions in other major rock forming minerals (olivine, pyroxene)
- presence of melt inclusions in Cr-spinel
- usually show zonation

Zonal Cr-spinel from volcanic “ rock
- range from Mg-chromite in the core
to aluminous Ti-magnetite in the rim

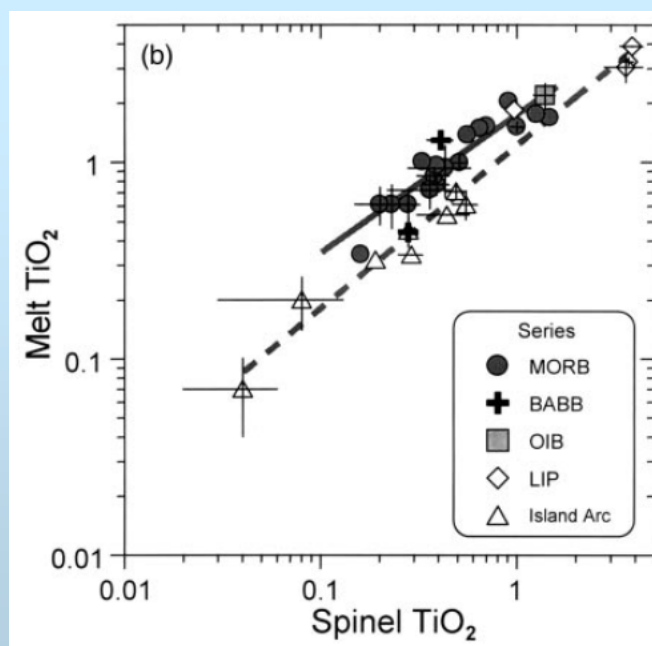
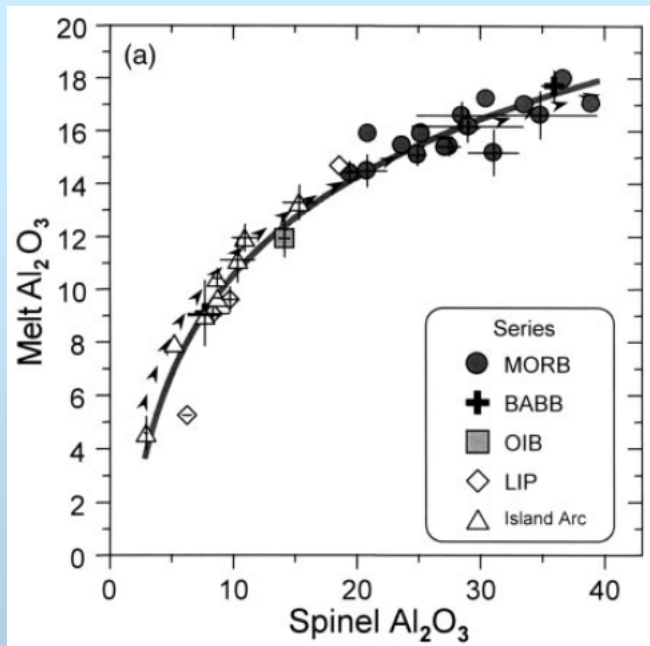


Subhedral Cr-spinel from volcanic “ rock
with melt inclusion



Cr-spinels from „volcanic “ rocks

- Spinel Al_2O_3 vs TiO_2 - a guide to magma chemistry and tectonic provenance
- The compositional pairs of coexisting spinel and glass were studied to examine the effects of melt composition on the abundances of Al_2O_3 and TiO_2 in spinel (Kamenetsky et al. 2001).
- A positive correlation between Al_2O_3 and TiO_2 contents in spinel and coexisting melt is demonstrated over significant intervals of averaged spinel and melt compositions (e.g. 3-39 and 4.6-18 wt % Al_2O_3 , and 0.04-3.9 and 0.07-3.9 wt % TiO_2), sampled from a variety of magmatic types and tectonic environments
- Observed relationships are primarily controlled by magmatic Al_2O_3 and TiO_2 contents.



MORB - middle ocean ridge basalts

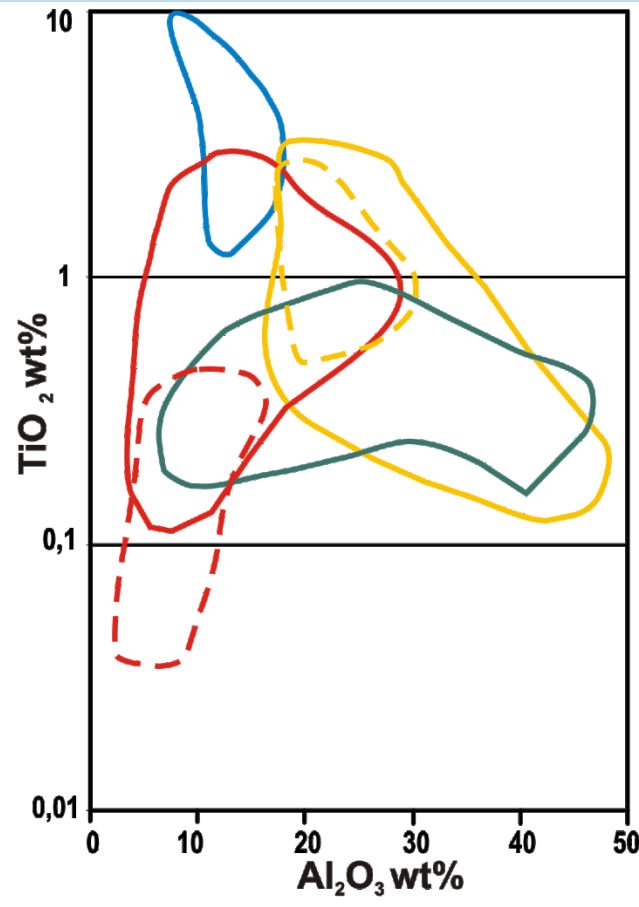
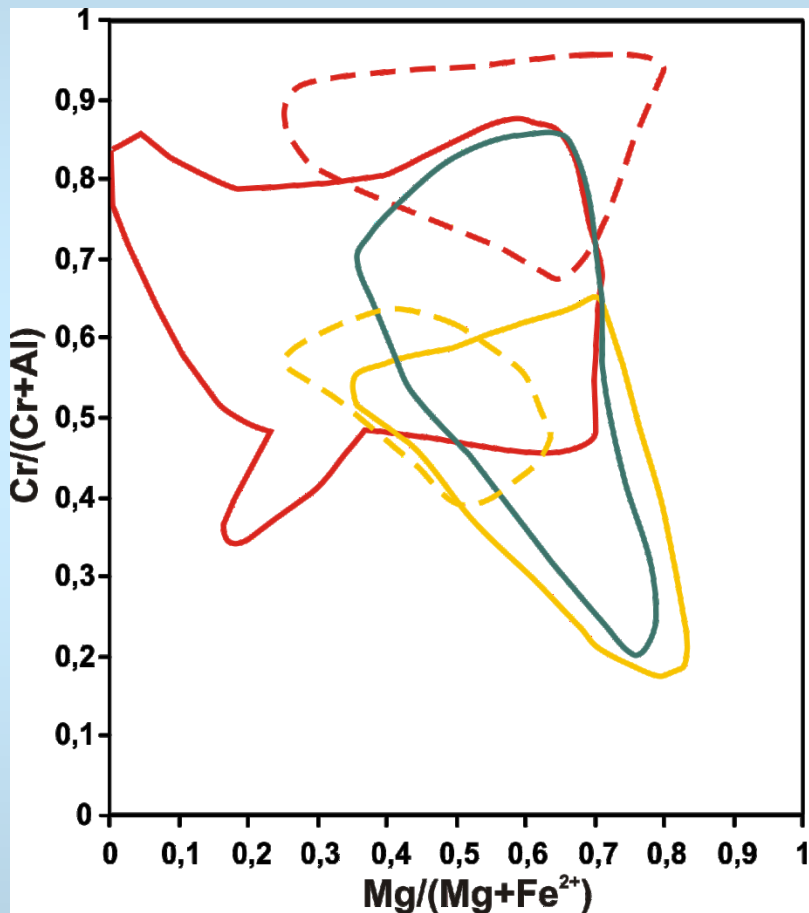
BABB - back arc basin basalts

OIB - ocean island basalts

Island Arc - basalts of volcanic island arcs

Continuous and dashed lines in (b) are for the high-Al and low-Al compositions

Cr-spinels from „volcanic“ rocks



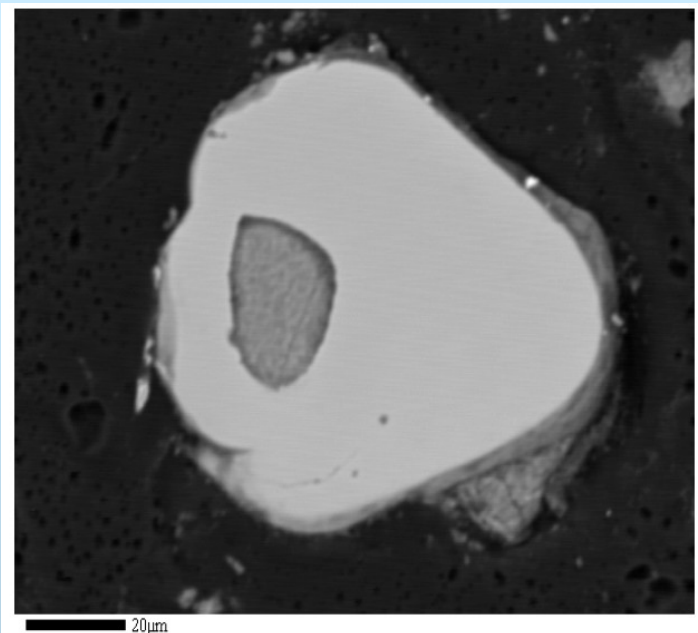
Al₂O₃ vs TiO₂
diagram

to
discriminate
spinel
that
crystallized
from
different
magmas
in
different
geodynamic
settings

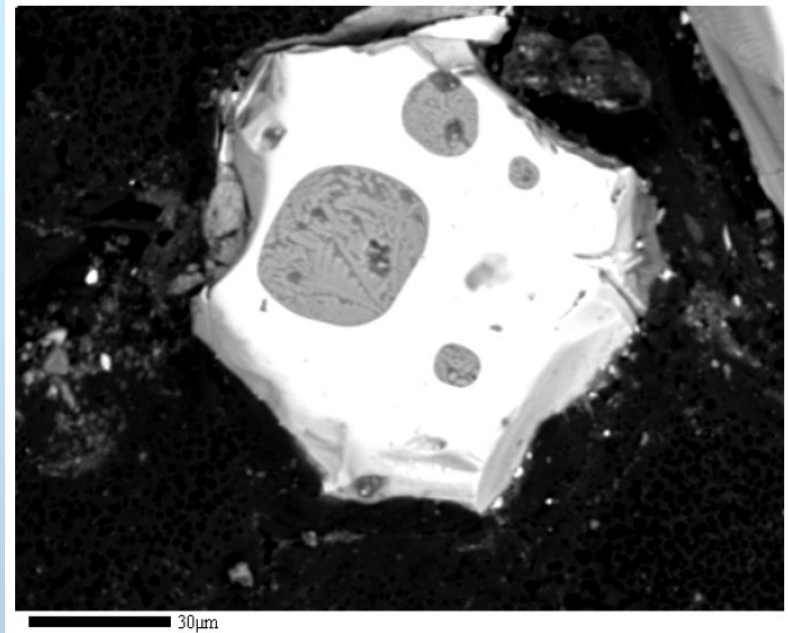
Discriminant fields according to Cr-spinel database from Barnes and Roeder (2001), Kepezhinskis et al. (1993) and Kamenetsky et al. (2001)

Melt inclusions in Cr-spinels

- Melt inclusions found in mineral grains (olivine, pyroxene, Cr-spinel) as tiny droplets trapped during crystal growth offer a unique way of catching instantaneous melt composition as magma cools due to their effective isolation from the influence of later processes, and thus they can reveal the melt evolution that may not be recorded in bulk-rock data (Watson, 1976; Roeder and Poustovetov, 2001).
- Cr-spinel = early-formed mineral => melt inclusion reflect composition of primary melt
- Melt inclusions - offer a unique way for study of melt chemistry
 - glass
 - usually mixture of glass and crystals



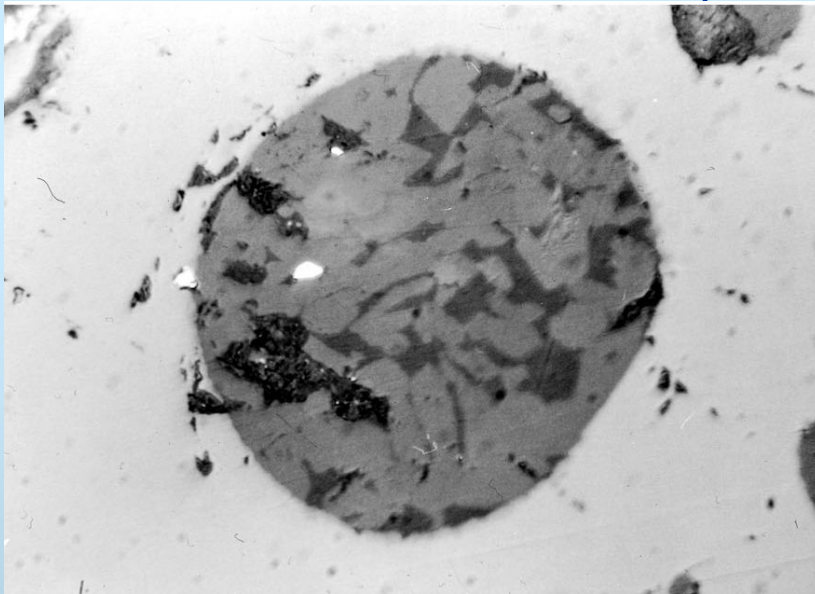
Melt inclusion containing very small partially crystallized minerals. (Zhou et al.)



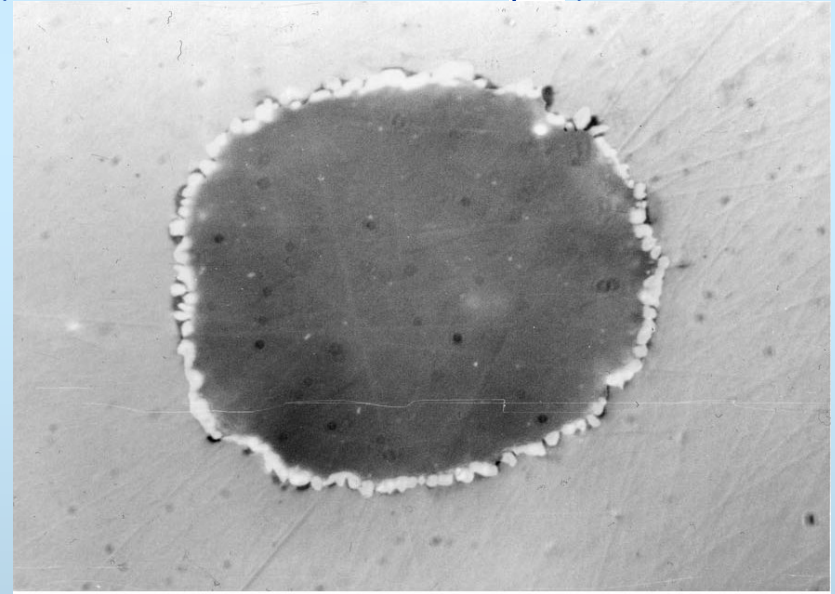
Melt inclusion - clinopyroxene crystals with spinifex-like texture (Zhou et al.)

Melt inclusion in Cr-spinel

- Melt inclusions - offer a unique way for study of melt chemistry
 - glass
 - mixture of glass and crystals
- melt inclusions composed from mixture of glass and crystals - Cr-spinels must be heated (for X0 hours at $T \sim 1200-1400$ °C) and quenched
- Both unheated (glass) or heated (homogenised) melt inclusions are studied with electron microprobe (a beam diameter 5-10 μm).



Unheated melt inclusion in Cr-spinel (diameter 0.04 mm) containing a mixture of glass (dark gray) and pyroxene crystals (light gray - occupy over 70% of the surface).

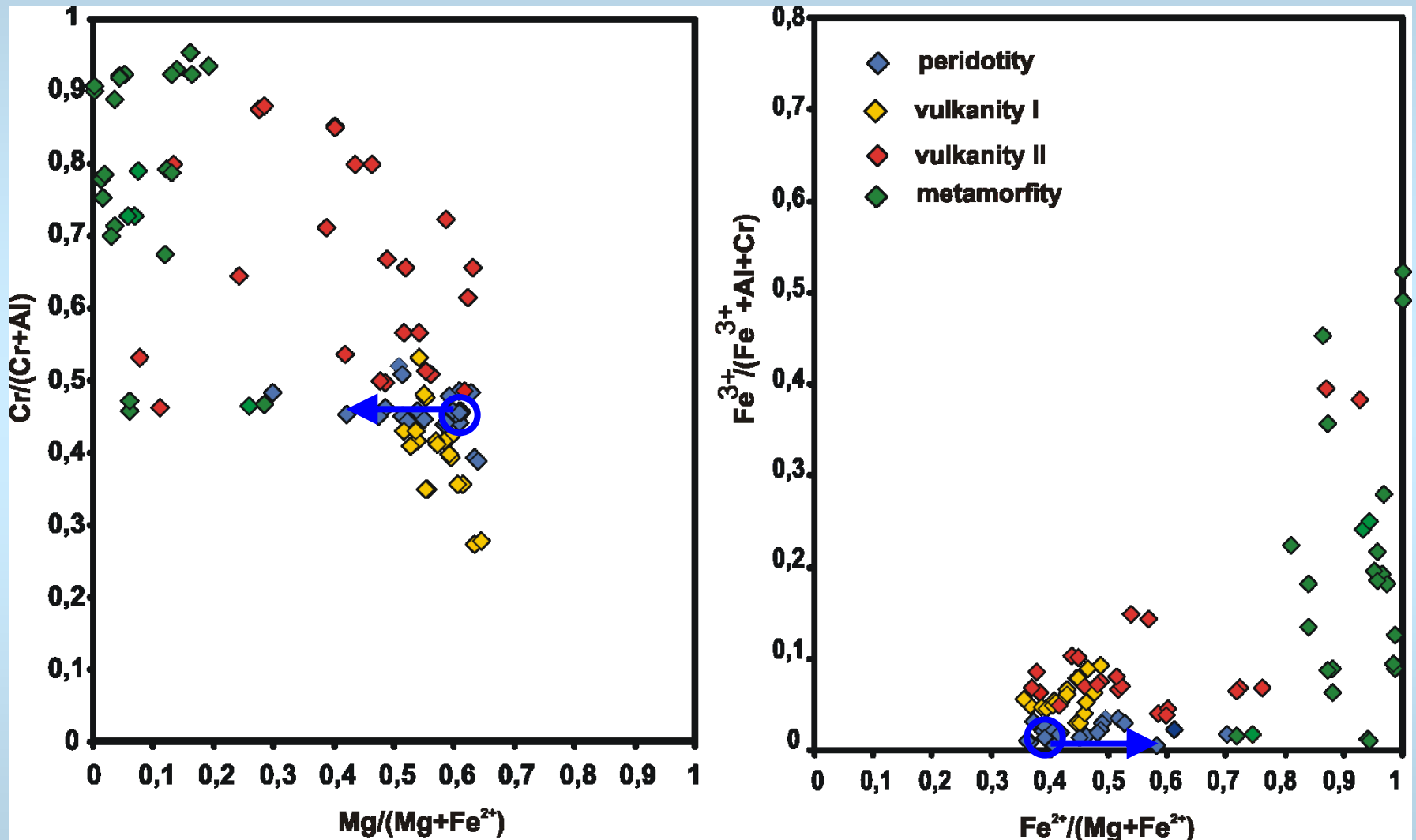


Heated and quenched (from 1360 °C) melt inclusion in Cr-spinel (diameter 0.06 mm) - contain glass with no silicate crystals (Sigurdsson et al. 2000).

Melt inclusions in Cr-spinels

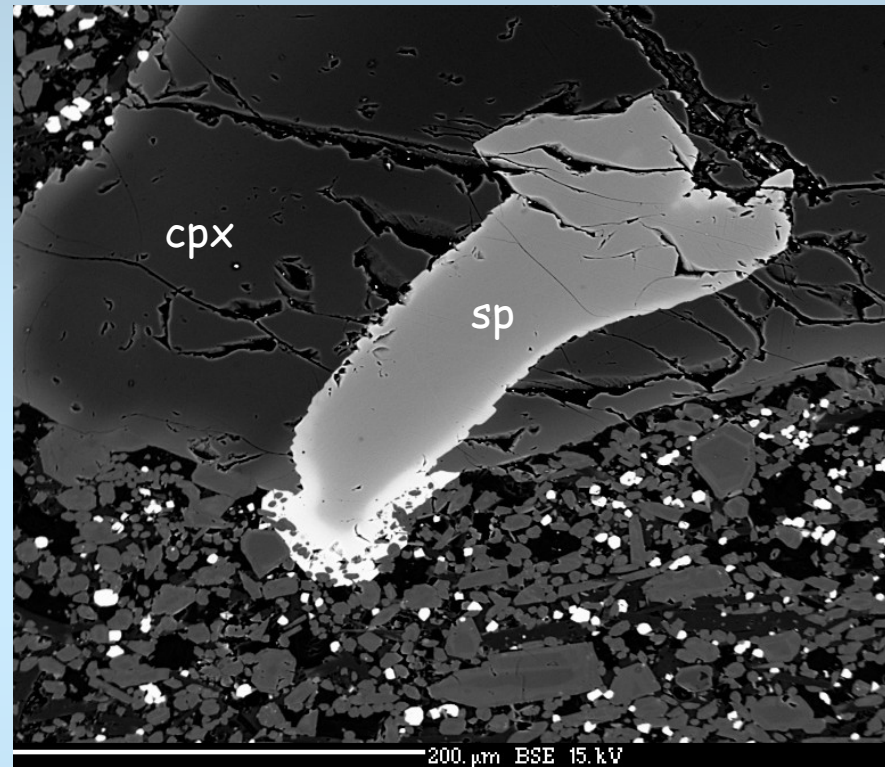
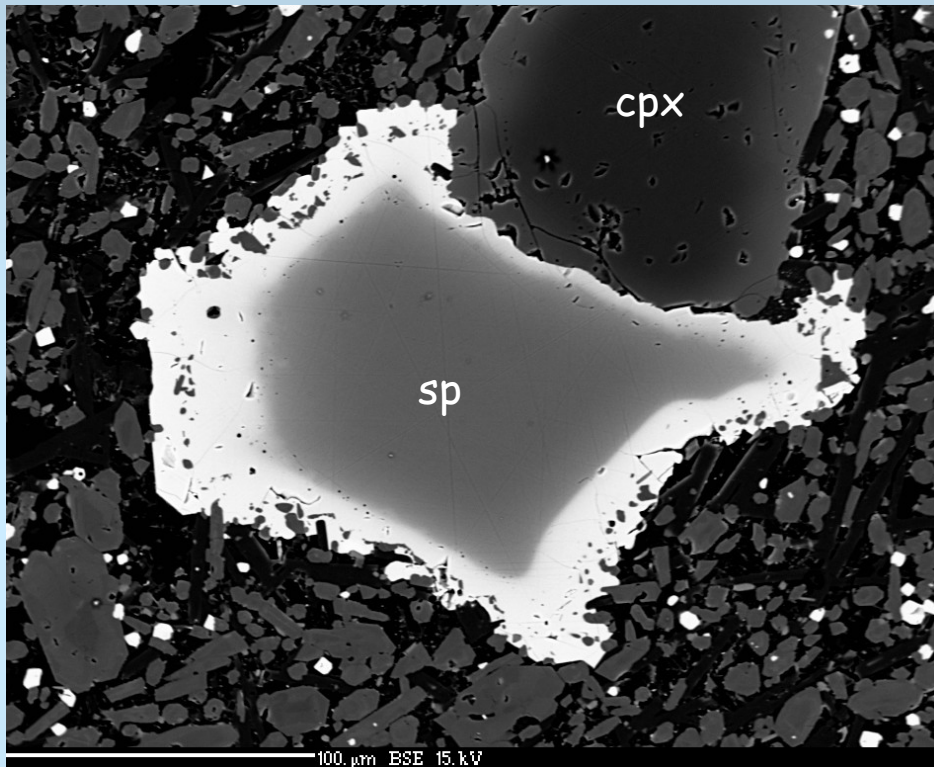
- Sigurdsson et al. (2000) observed two groups of primitive melts as inclusions in Cr-spinels in a picrite.
- These primitive melts were isolated inside the crystals before the two types of magma had an opportunity to mix.
- The inclusions are probably close to being true samples of these two types of primary melt.

Zonality in Cr-spinel - mantle peridotites



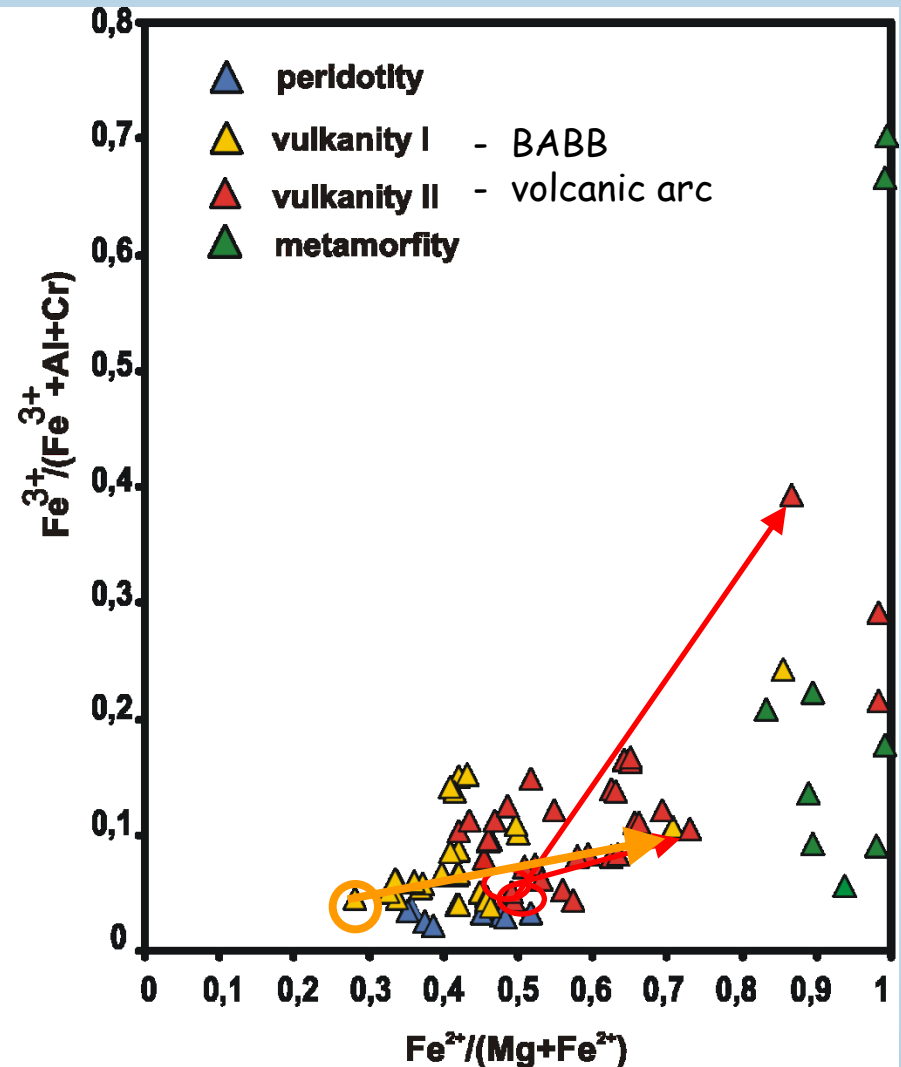
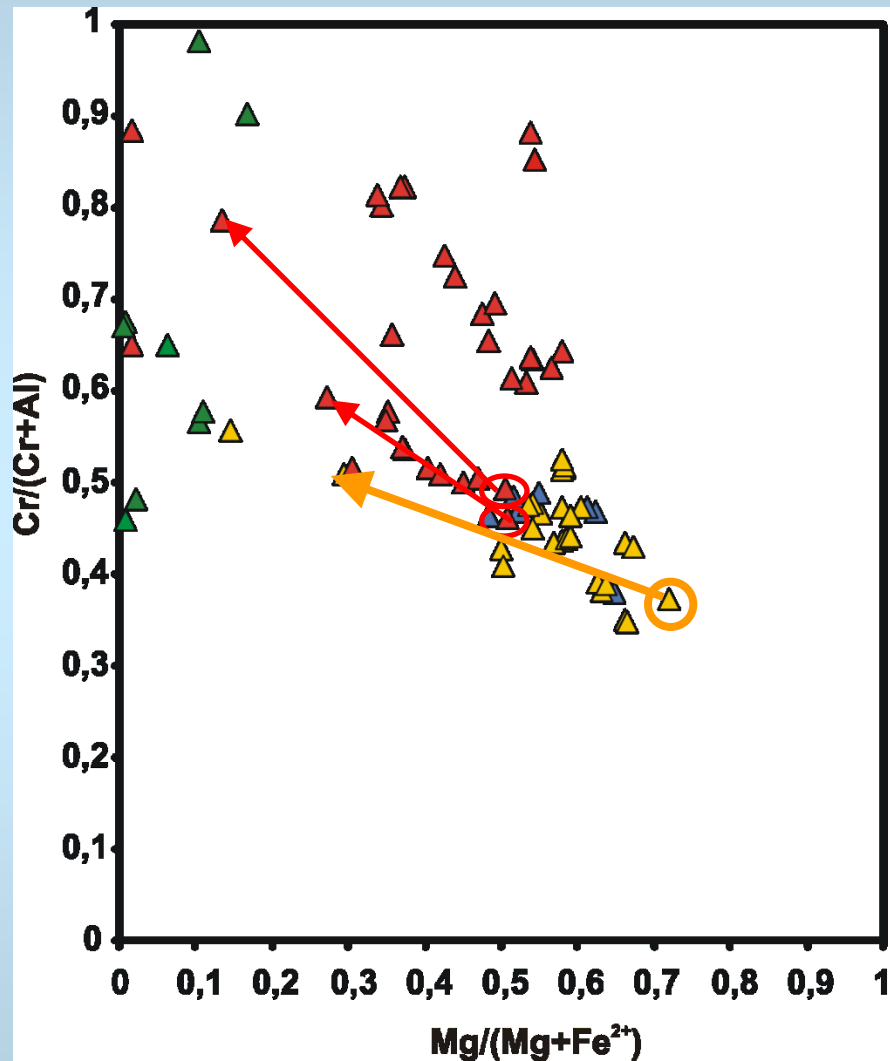
Decreasing Mg # - with decreasing T and/or due to subsolidus re-equilibrations with silicates

Zonality in Cr-spinel - volcanic rocks



- Zonal spinel groups mineral from basaltic rock (Mrázová 2007)
Compositional evolution from - Cr-rich spinel in the core (up to 30 wt. % Cr_2O_3)
to - Ti-magnetite in the rim (up to 18 wt. % TiO_2)
small Ti-magnetites are common in matrix
usually observed in intraplate basalts and lamprophyres

Zonality in Cr-spinel - volcanic rocks



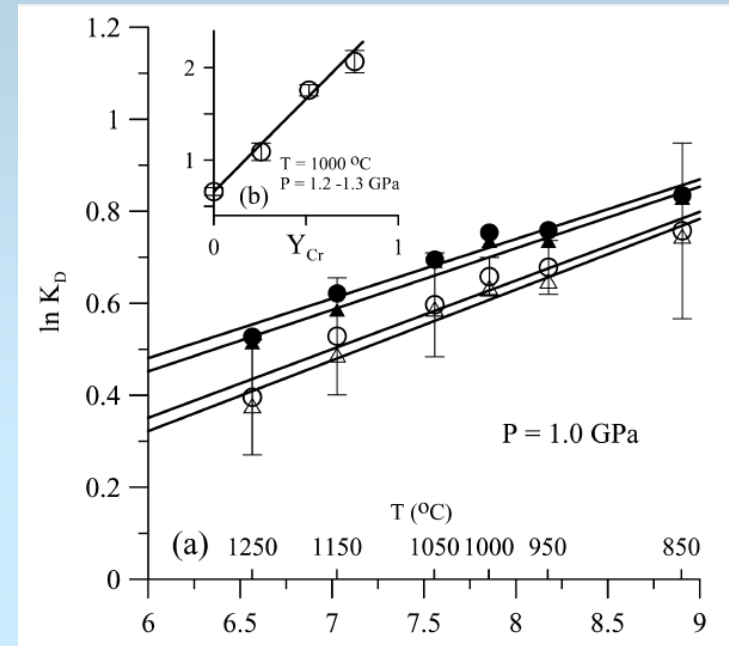
Commonly observed zonality in OFB, BABB and volcanic arc basalts and andesites (low TiO_2)
This zoning pattern reflect decreasing PT conditions (a) and increasing fO_2 (b)

Cr-spinel thermometry

- Olivine-spinel Fe^{2+} -Mg thermometers
 - Roeder et al, 1979
 - O'Neill and Wall (1987), modified by Ballhaus et al. (1991)
 - Sack and Ghiorso, 1991
 - Jianping et al., 1995
- To evaluate the T dependence of olivine-spinel Fe-Mg partitioning in analyzed pairs
- Spinel-olivine empirical and theoretical thermometers are calibrated for mantle rocks (low Fe^{3+} and very low Ti^{4+}), although spinel-olivine pairs are also common in basaltic volcanic rocks and in shallow mafic intrusions
- Olivine-spinel pairs for volcanic rocks (basanite; Fedele and Tracy 2003) appears to underestimate absolute crystallization T, due to significant concentrations of the usp end member in the magmatic spinels.
 - Ti is not taken into account in thermometers of Roeder et al. and Jianping et al.) and apparently is not fully accounted in the model of Sack and Ghiorso.
 - approximately linear relationships was observed between Ti content and T- underestimation for all 3 thermometers

Cr-spinel thermometry

- Orthopyroxene-spinel Fe^{2+} -Mg thermometers
 - Mukherjee and Viswanath 1987; Mukherjee et al. 1990
 - Liermann and Ganguly 2003; 2007
- To evaluate the T dependence of orthopyroxene -spinel Fe^{2+} -Mg partitioning in analyzed pairs
- Effect of Fe^{3+} content in spinel
 - Although a thermodynamic correction was proposed for the effect of Fe^{3+} content of spinel, practical application of this correction is problematic due to inaccurate determination of Fe^{3+} content in spinel.
 - The $\text{Fe}^{3+}/\Sigma\text{Fe}$ in minerals is usually determined from the microprobe data by imposing the condition of electroneutrality. However, this procedure absorbs the error of the analytical data into the estimated Fe^{3+} content.



- $\ln K_D(\text{Fe-Mg})$ between orthopyroxene and spinel versus a temperature (K)
- $Y_{\text{Cr}}(\text{Sp})$, i.e., $\text{Cr}/(\text{Cr}+\text{Al})$ in spinel at 1.2-1.3 GPa, 1,000 C.

The $\ln K_D$ values with correction for the effect of Al substitution in orthopyroxene are shown as closed symbols, whereas those without correction for this effect are shown as open symbols.

The triangles and circles stand for the different estimation of Fe^{3+}

Cr-spinel thermometry

olivine-spinel Fe^{2+} -Mg
thermometer

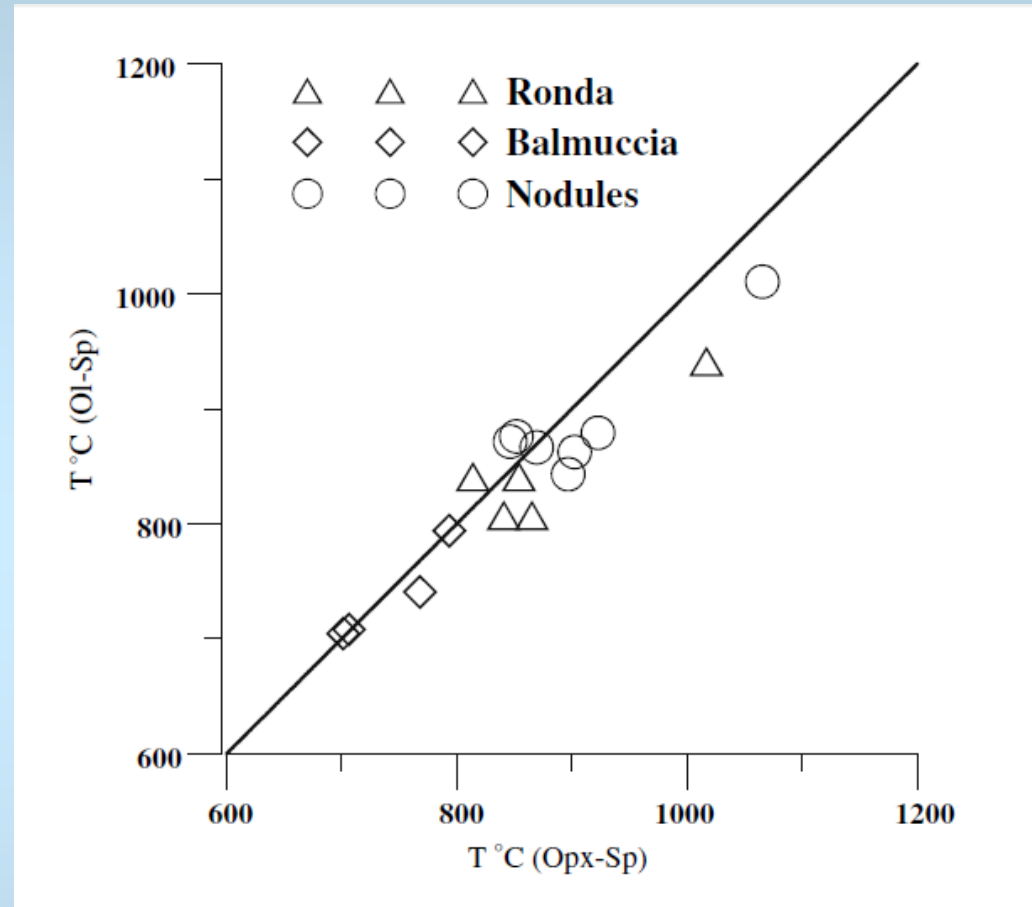
(Ballhaus et al. 1991)

vs.

orthopyroxene-spinel Fe^{2+} -Mg
thermometer

(Liermann and Ganguly 2003; 2007)

There are no significant differences between the temperatures estimates according to olivine-spinel and orthopyroxene-spinel thermometers at $T < 900$ °C. Above 900°C, T °C (Opx-Sp) is 30-75 °C higher than T °C (Ol-Sp) that may be due to the problem of resetting of olivine-spinel thermometer.



Comparison of temperatures of Cr-spinel bearing calculated from the orthopyroxene-spinel thermometer and the olivine-spinel thermometer of O'Neill and Wall (1987), as modified by Ballhaus et al. (1991)

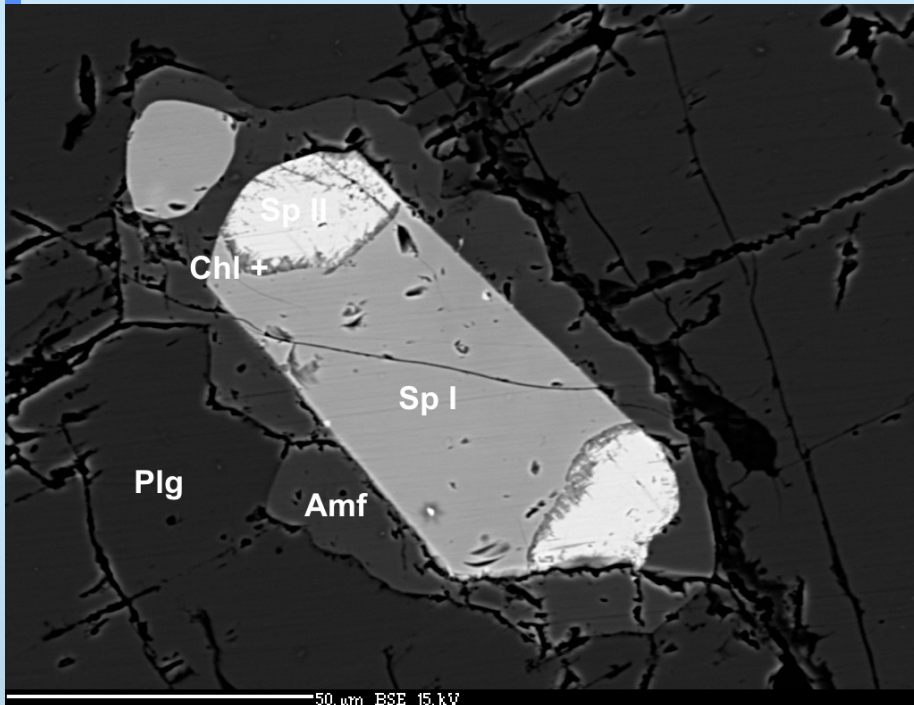
Cr-spinels from metamorphic rocks

- Metamorphic processes do not modify chemical composition of chromian spinels up to lower amphibolite facies conditions.
- Pinsent and Hirst (1977) noticed different behavior of chromian spinels with variable Cr-content.
 - chromian spinels with high Cr# are more stable in metamorphic conditions.
 - For Al-rich chromian spinels with Cr# <0.5 the reaction **spinel + serpentine + brucite = "ferritchromite" + chlorite** proceeded in peridotites.
 - Metamorphism of chromian spinels with Cr# >0.5 shifts their composition to **"ferritchromite" and Cr-enriched magnetite**, and chlorite does not originate.
 -
- Substitution of Mg by Fe²⁺ (or Zn, Ni, Mn) as a result of exchange with associated silicates in subsolidus changes significantly Mg# in highly metamorphosed rocks;
- Substitution of Cr and Al by Fe³⁺ proceeded during oxidation process;
- Consequently, metamorphosed chromian spinels are largely Fe²⁺ -enriched and locally Fe³⁺-enriched relative to their magmatic precursors (e.g., Oberhänsli et al., 1999; Barnes, 2000; Barnes and Roeder, 2001).
- Cr-spinels from metamorphosed rock (≥ amphibolite facies) can be enriched in Zn (up to 7 wt. % ZnO), Mn (up to 3 wt. % MnO), or Ti compared with their magmatic precursor. Higher Si and Ca contents are typical for these metamorphosed ferritchromites and Cr-rich magnetite.

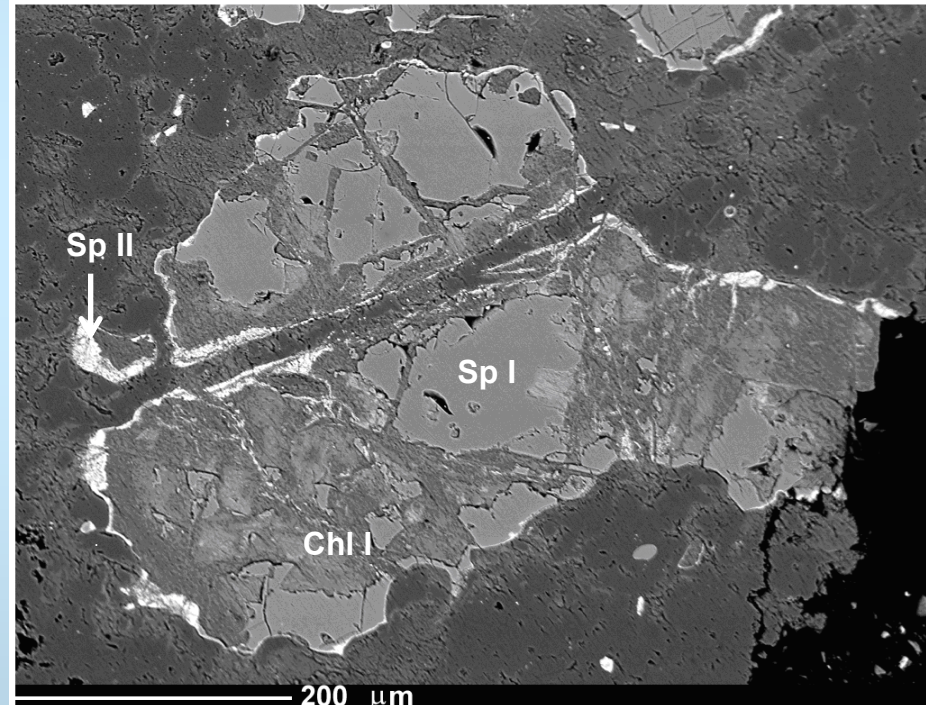
Cr-spinels from metamorphic rocks

Cr-spinels in BSE image

Al-rich chromian spinels with $Cr\# < 0.5$
spinel (Sp I) \longrightarrow "ferrichromite" (Sp II) + chlorite
Cr-rich magnetite



Replacement reaction of magmatic spinel from the Ransko gabbro-peridotite massif



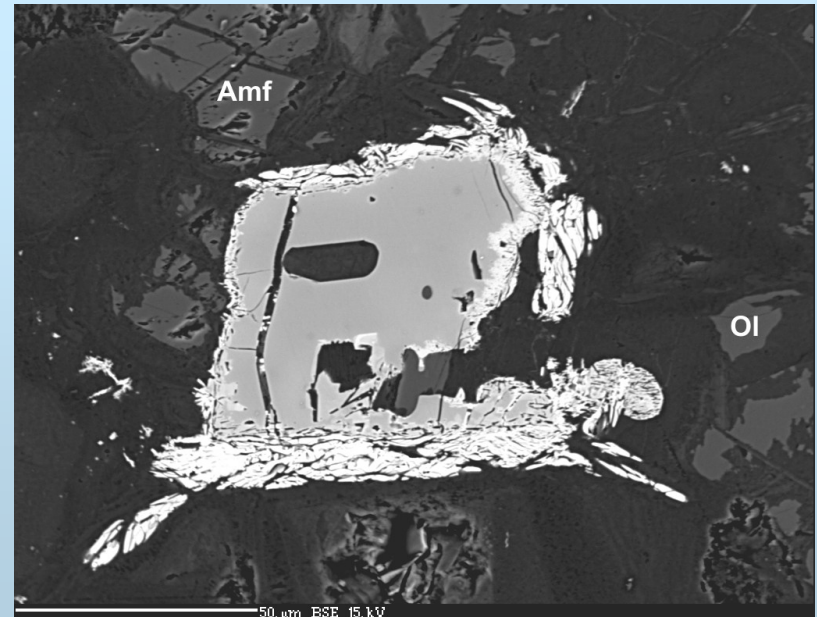
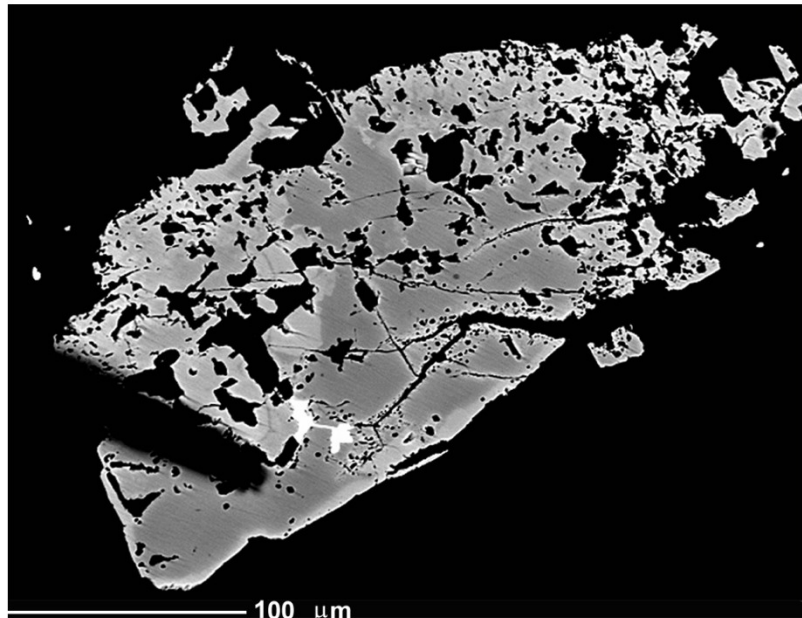
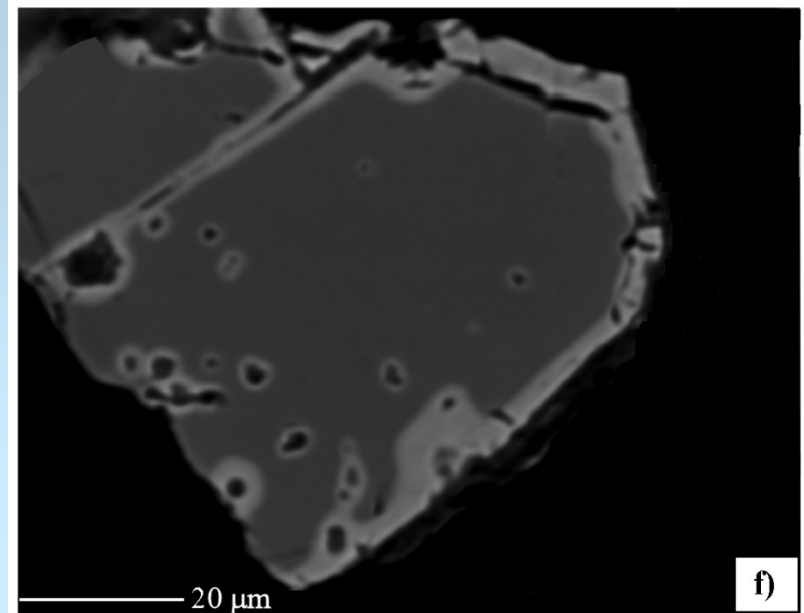
Replacement reaction of magmatic spinel from the Moldanubian spinel peridotite

Cr-spinels from metamorphic rocks

Cr-spinels in BSE image

Metamorphism of chromian spinels with
 $\text{Cr}\# > 0.5$

**Cr-rich spinel \longrightarrow ferrichromit or
Cr-enriched magnetite**



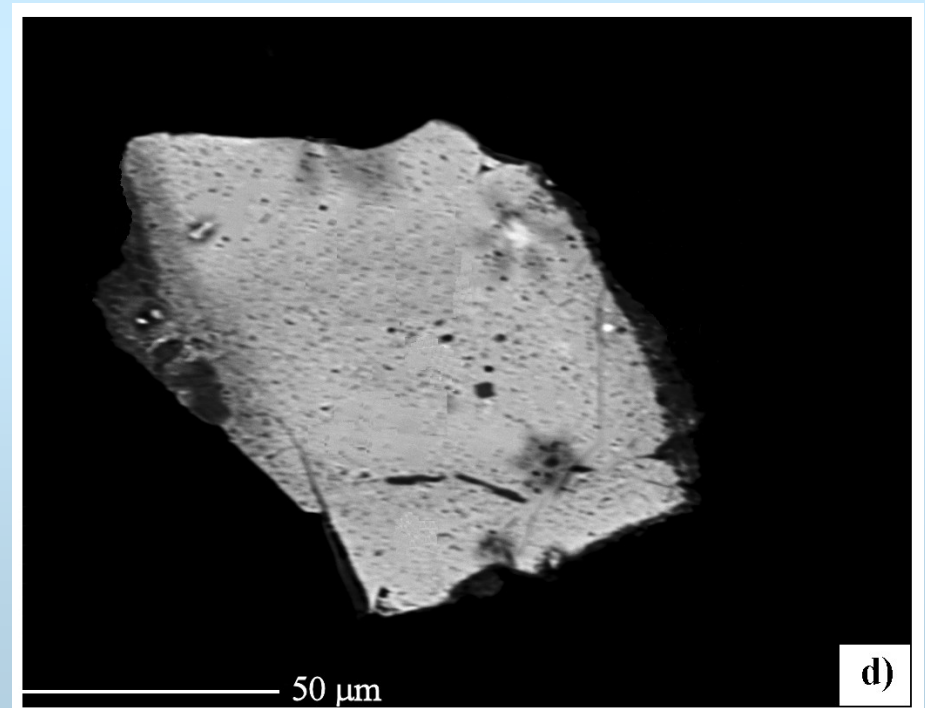
Cr-spinels from metamorphic rocks

Cr-spinels in BSE image

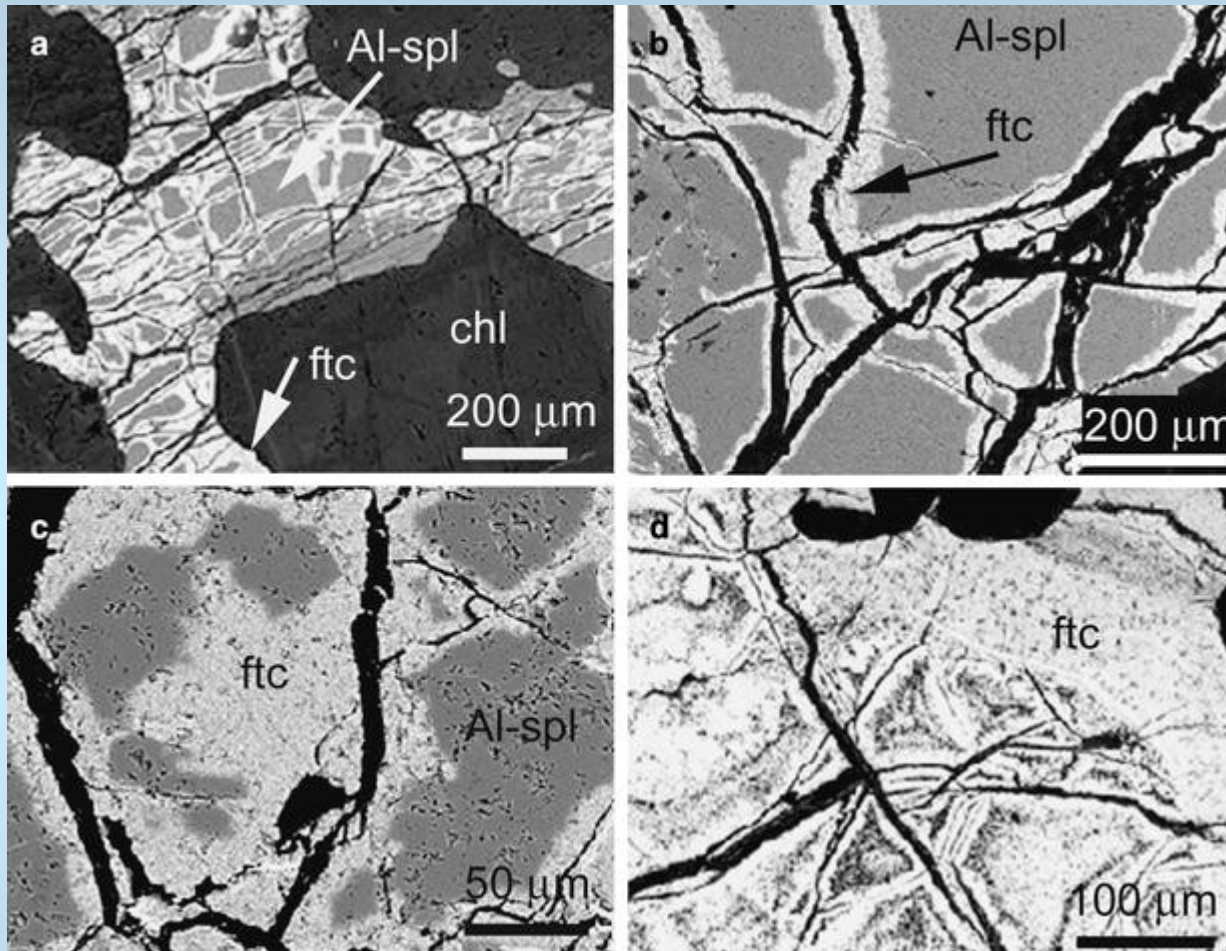
Metamorphism of chromian spinels with $Cr\# > 0.5$

Cr-rich spinel \longrightarrow **ferrichromit or Cr-enriched magnetite**

Primary magmatic Cr-rich spinels
can be fully replaced by secondary
metamorphic Cr-rich magnetite

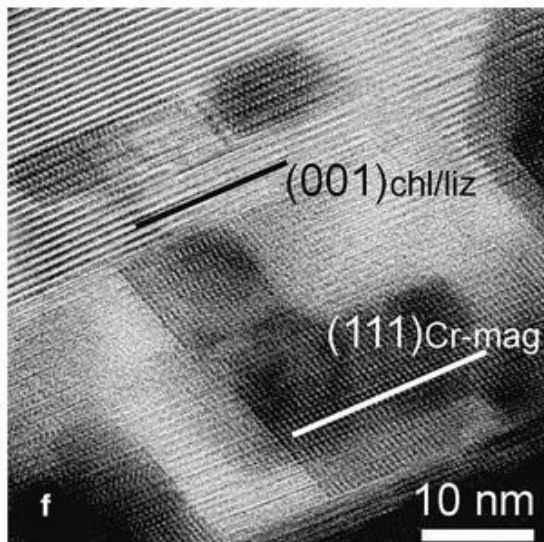
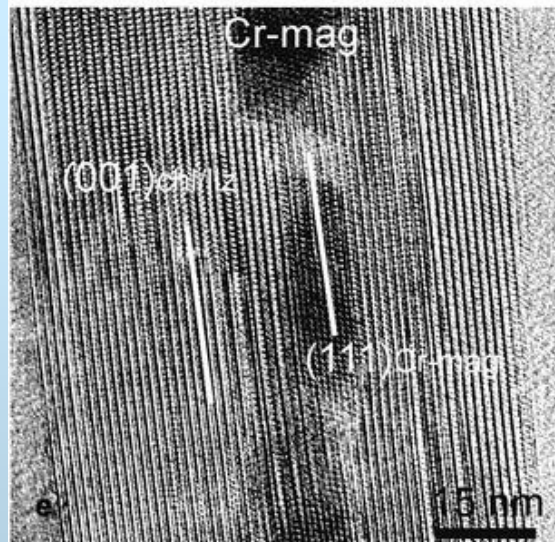
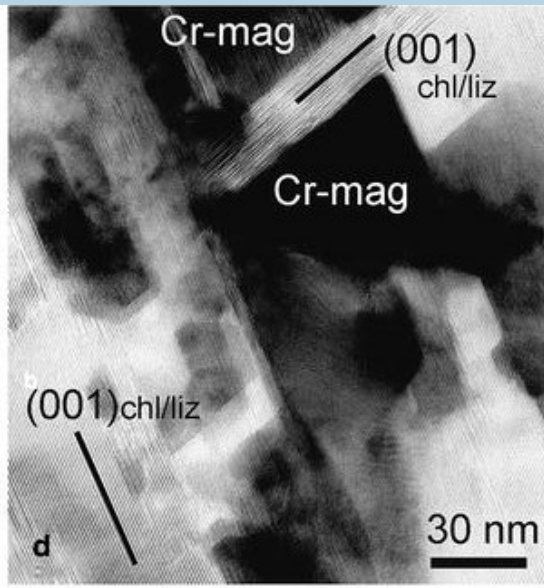
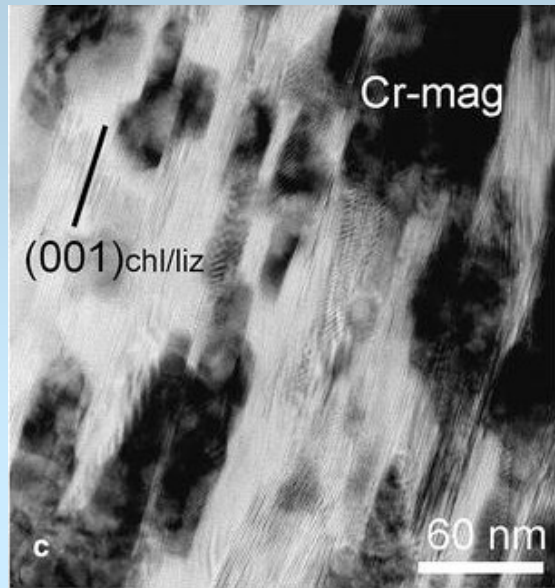


Cr-spinels from metamorphic rocks



Secondary Cr-spinel (so called ferrichromite) in BSE image - porous, enriched in SiO_2 and CaO replacing primary magmatic Cr-spinel in serpentinites observed Mellini et al. (2005).

Cr-spinels from metamorphic rocks



Transmission electron microscopic investigation shows that ferritchromit actually consists of a complex, nanometric association of Cr-rich magnetite

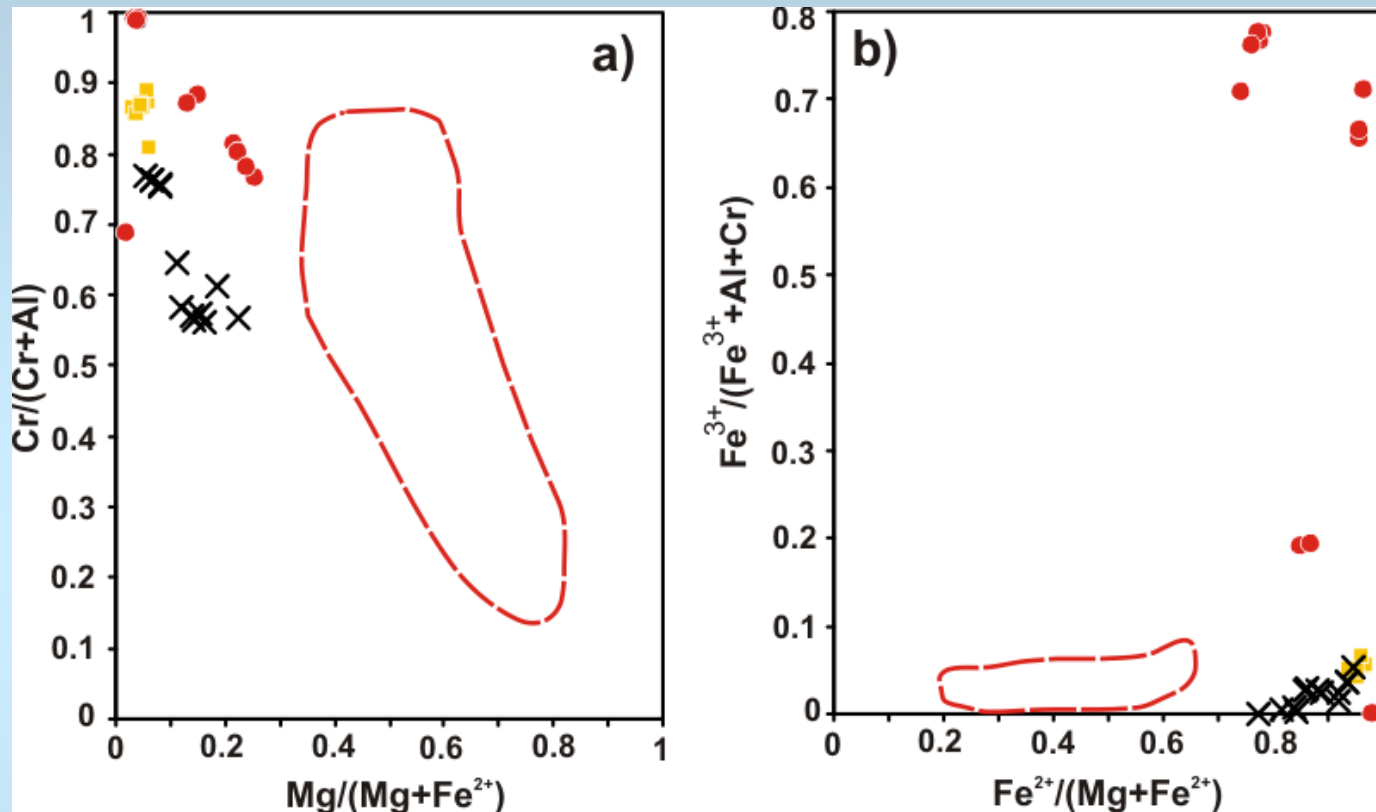
$(\text{Mg}_{0.03}\text{Fe}^{2+}_{0.97}\text{Al}_{0.11}\text{Cr}_{0.89}\text{Fe}^{3+}_{1.00}\text{O}_4)$, chlorite and lizardite, with (001)chl/liz always parallel to (111)Cr-mag.

Bellow the resolution of electron microprobe

Mg and Al, released from the altered Cr-spinel, giving rise to chlorite, lizardite.

TEM images of ferritchromit (Mellini et al. 2005)

Cr-spinels from the Bohemian Massif



➤ a,b) Moldanubian Zone

red field - primary Cr-spinels from spinel and garnet peridotites;

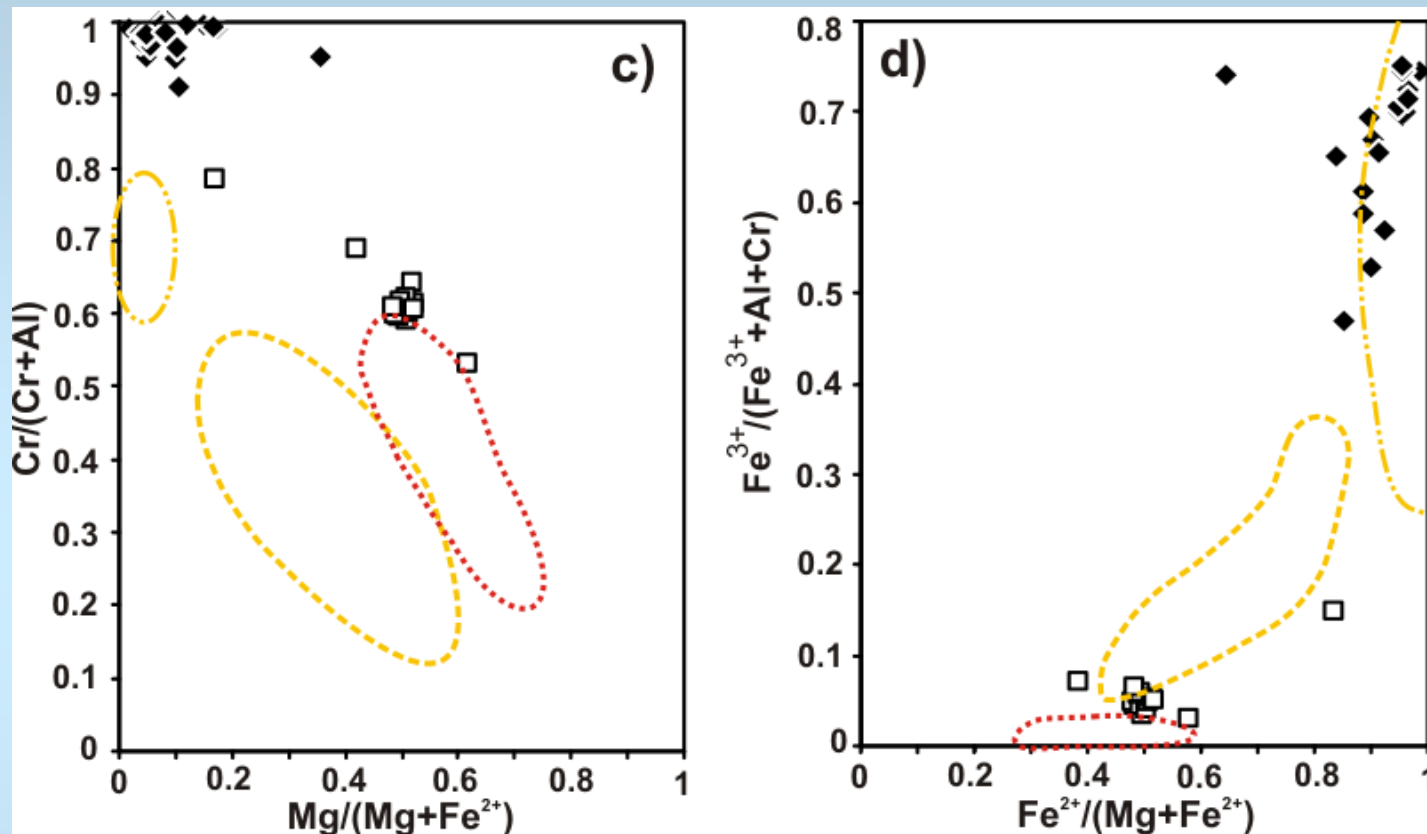
full red circle - secondary Cr-spinels from spinel peridotites;

křížky - tremolite rock (metamorphosed ultrabasic cumulate);

yellow square - durbachites (Třebíč massif)

- Čopjaková et al. (2005b), Medariş et al. (2005), Sulovský (2001), Van der Veen and Maaskant (1995) and unpublished data of Stědrá and Čopjaková

Cr-spinels from the Bohemian Massif



c,d) Letovice-Rehberg ofiolite and Nasavrky massif;

Letovice-Rehberg ofiolite - white square - primary Cr-spinels;

black rhombus - secondary Cr-spinels;

Nasavrky massif - red field - garnet and spinel mantle peridotites;

yellow dashed line field - gabbro and spinel peridotite - Alaskan type;

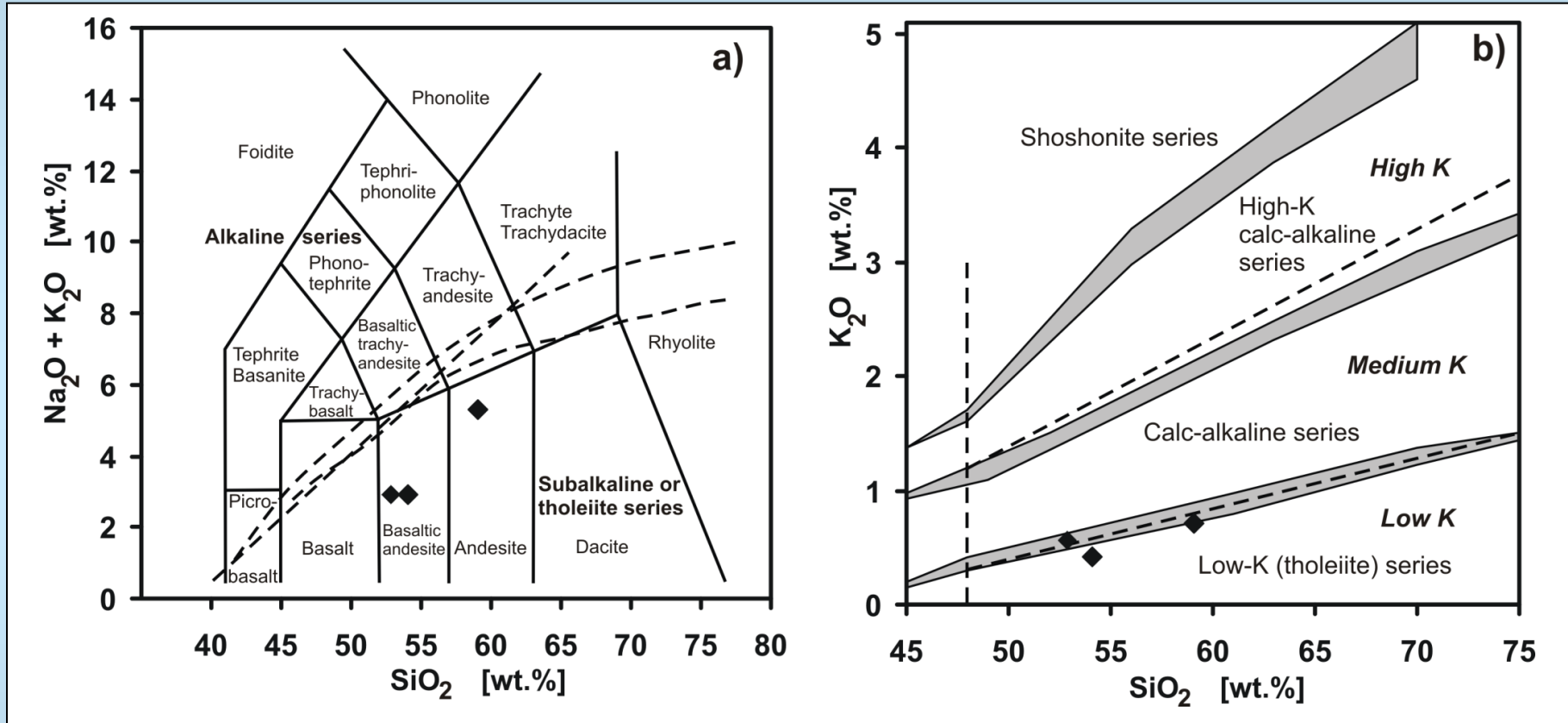
yellow dot-and-dashed line field - secondary Cr-spinel from the Alaskan type gabbro;

Detrital Cr-spinels in siliciclastic sedimentary rocks

- Cr-spinels are important HM in siliciclastic sediments for provenance studies.
- They are stable during diagenesis and quite resistant to late hydrothermal alterations particularly relative to other high temperature minerals of mafic and ultramafic rocks such as olivines and pyroxenes.
-
- They represent a unique provenance indicator for various mafic and ultramafic rocks and subsequently for geotectonic implications.
- Using chemical composition of chromian spinels for provenance and geotectonic implications - e.g., Utter, 1978, Press, 1986, Arai and Okado, 1991, Cookenboo et al., 1997, Oberhänsli et al., 1999
- Chemistry of detrital spinels and melt inclusion compositions in the detrital volcanic spinels from the Claut/Clauzetto and Julian Basins (N Italy and NW Slovenia) is used to constrain petrological and geochemical affinities and tectonic provenance of the source rocks - Lenaz et al. (2000) This is the first study of melt inclusions in detrital spinels.

Detrital Cr-spinels in siliciclastic sedimentary rocks

Melt inclusions in detrital Cr-spinels from volcanic rocks (Drahany Upland) - reflect origin from arc-related volcanic rocks (basaltic andesites and andesites)



a) TAS diagram according to Le Maitre et al. (1989)

b) diagram according to Le Maitre et al. (1989) - and Rickwooda (1989)

Al-spinels

Spinel s.s. $MgAl_2O_4$

- Pure is colorless, often is colorized by chromophorm elements: bluish (Co), greenish chlorospinel (Fe^{3+}), redish (Cr)
- Typical mineral of HT metamorphosed rocks.
 - Common mineral in metamorphosed dolomite marbles - together with diopside and forsterite (e.g. In the Varied Unit, Moldanubian Zone - mineral assemblage Cal+Dol+Fo+Sp+Phl+Ch+Cho - (Čopjaková et al. 2008) - spinel-gahnite; 660-730°C, 3-4 kbar (Novák 1989))

A-site						B-site							
Mg	Fe2+	Mn2+	Zn2+	Ti4+	subtot	Al	Cr	Fe3+	Fe2+	V3+	subtot	catsum	ansum
0,95	0,04	0,00	0,01	0,00	1,00	1,99	0,00	0,01	0,00	0,00	2,00	3	4
0,83	0,03	0,00	0,14	0,00	1,00	1,97	0,00	0,03	0,00	0,00	2,00	3	4

- Mg-rich skarnes
 - granulites (spinel-hercynite) or HT metapelites
 - From mafic and ultramafic rocks (Cr-enriched)
- Magmatic rocks rich in Al_2O_3 - pegmatites, gabros
 - Typical alluvial mineral (high density, mechanical and chemical durability), e.g. in pyrope gravelites in České středohoří (Třebívlice, Měrunice), Jizerska Louka

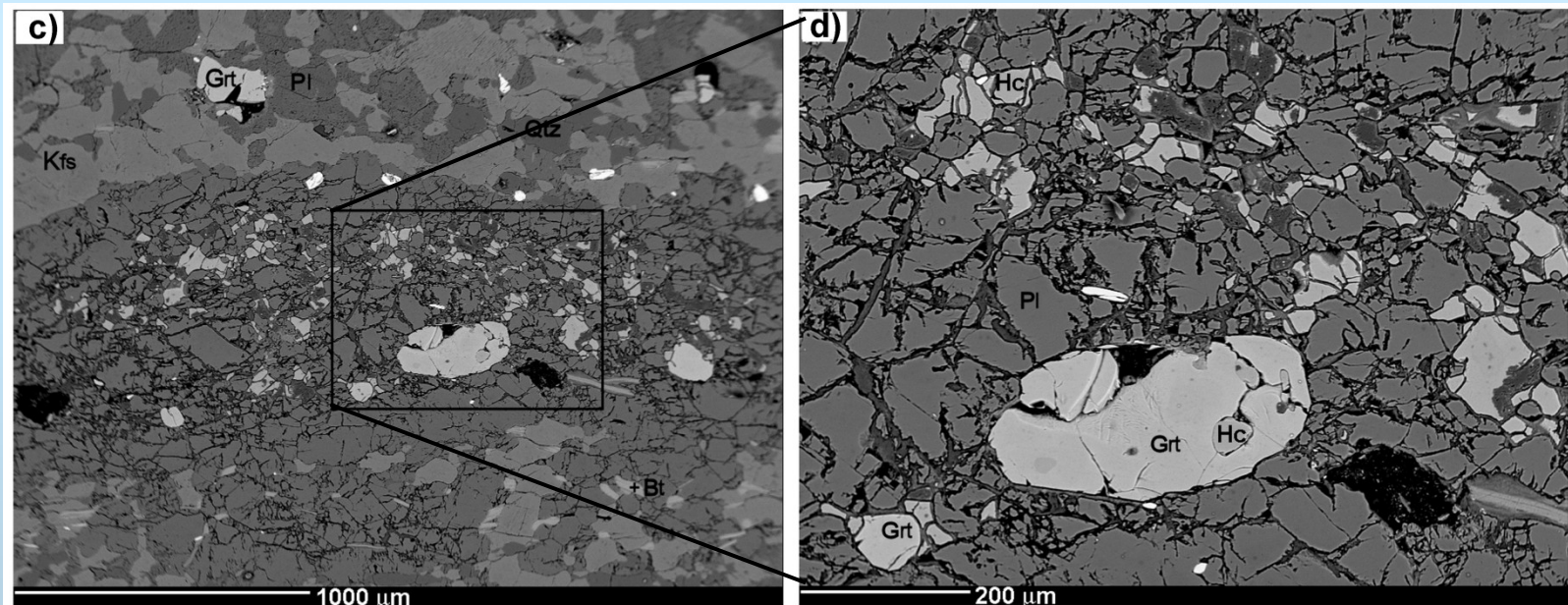
Al-spinels

Hercynite $\text{Fe}^{2+}\text{Al}_2\text{O}_4$

- Usually from metamorphosed (granulite grade) Fe-rich sediments
- Less common from mafic to ultramafic magmatites, pyroxenites and felsic granulites

Tabule - spinels - composition hercynite-spinel from felsic granulites - (Čopjaková 2007)

A-site						B-site							
Mg	Fe ²⁺	Mn ²⁺	Zn ²⁺	Ti ⁴⁺	subsum	Al	Cr	Fe ³⁺	Fe ²⁺	V ³⁺	subsum	catsum	ansum
0,43	0,55	0,00	0,02	0,00	1,00	1,91	0,00	0,09	0,00	0,00	2,00	3	4
0,40	0,58	0,00	0,02	0,00	1,00	1,91	0,00	0,08	0,00	0,00	2,00	3	4



Garnet-hercynite-plagioclase domain in felsic granulite originate by decomposition of kyanite during isothermal decompression - hercynite is partially replaced by AlOOH - diaspore? (Čopjaková 2007)

Al-spinels

Gahnite $ZnAl_2O_4$

- Usually forms solid solution with spinel and hercynite
- Common mineral in metamorphosed contaminated marbles (Al enriched) and skarns enriched in Zn
- gahnite-spinel solid solution in Bohemian Massif
 - marbles in the Polička Crystalline Unit; marbles in the Hraničná Group (Staré Město Crystalline Unit) - mineral assemblage Cal+Dol+Tr+Phl+Di (Novák, Houzar, Srein 1997)
 - marbles in Varied Unit, Moldanubian Zone (min. assemblage Cal+Dol+Fo+Sp+Phl+Ch+Cho) (Čopjaková et al. 2008)

A-site						B-site							
Mg	Fe2+	Mn2+	Zn2+	Ti4+	subtotal	Al	Cr	Fe3+	Fe2+	V3+	subtotal	catsum	anum
0,16	0,00	0,00	0,83	0,00	1,00	1,98	0,01	0,01	0,00	0,00	2,00	3	4
0,19	0,04	0,00	0,77	0,00	1,00	2,00	0,00	0,00	0,00	0,00	2,00	3	4

- granitic pegmatites (Maršíkov, Otov, Přibyslavice)
- gahnite-hercynite solid solution - metapelites - staurolite bearing garnet mica schist - inclusions in staurolite (Svratka Crystalline Unit) - (Buriánek, Čopjaková 2008)

A-site								B-site									
Mg	Fe2+	Mn2+	Zn2+	Ni2+	Ti4+	Ca	subsum	Al	Cr	Si	Fe3+	Fe2+	V3+	subsum	SUM	O	
0,07	0,37	0,00	0,56	0,00	0,00	0,00	1,00	2,00	0,00	0,00	0,00	0,00	0,00	2,00	3	4	

- Metamorphosed ore deposits (Franklin, USA; Broken Hill, Austrálie)

Galaxite $MnAl_2O_4$

- Very rare, described from Mn rich vein deposits.

Fe-spinels

- **Magnetite** - the most common spinel group mineral

Occurs in the wide variety of magmatic and metamorphic rocks-basic to intermediate magmatites (volcanic and plutonic), scarn deposits of economic importance, volcano-sedimentary and sedimentary rocks.

Amphibolites, metamorphic ultrabasic rocks, metapelites, Alpine veins and authigenic

- **Magnesioferrite** - jako koncový člen vzácný (vysokoteplotní - fumaroly, hořící haldy, Mg-mramory a skarny). Obvykle v pevném roztoku s magnetitem (obvykle do několika molárních %)

- **Franklinit** - vzácnější;

- vyskytuje na Zn ložiscích Franklin a Sterling Hill (USA) - metasomatický, vzniklý reakcí hydrotermálních fluid s okolními horninami
- metamorfované bazické a ultrabazické horniny obsahující Cr-bohaté spinely minimálně ve spodní amfibolitové facii - obvyklá minoritní komponenta ve spinelidech (

- **Jaccobsit** - metasomatická ložiska Mn

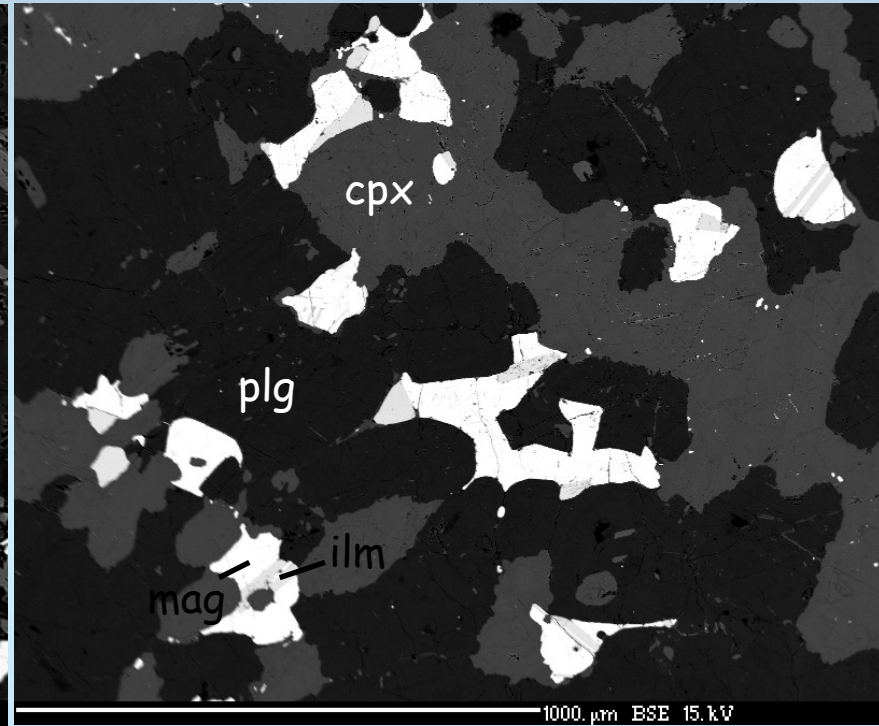
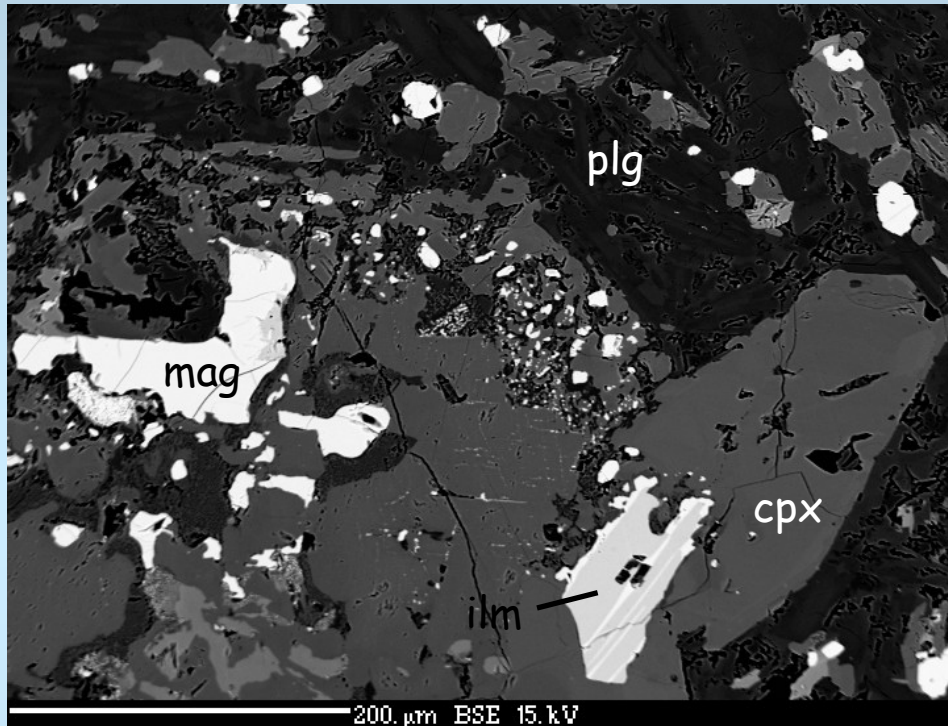
- **Trevorit** - vzácný; známý z mastkových fylitů v Jižní Africe, Ni-bohatý serpentinit

Fe-spinels

Magnetite

- Elevated Usp component signalize elevated temperature. Increase of fO_2 cause the rise in Fe^{3+} content in the system and the magnetite component as well.
- Good miscibility between magnetite and ulvospinel molecule at elevated temperature (Ti-rich magnetite from volcanic rock)
- The slow decrease of temperature usually generate exsolution of ilmenite lamellas (commonly observed in gabros, amphibolites)
- The rock containing both Mt-Usp (magnetite) and Ilm-Hmt(ilmenite)
 - Its chemical composition is unambiguously determined by T and fO_2 at the time of the equilibrium
 - can be used as geothermometers

Magnetite



- Gabbro - Nasavrky massif (Mrázová 2007)
exsolved ilmenite from magnetite; bright in BSE image - magnetite; dark in BSE image - ilmenite

Magnetite as provenance indicator

- Detrital magnetite grains carry textural and chemical features that can be used in provenance research. Petrographic analysis of cca 3000 detrital magnetite grains from Holocene sands was performed by Grigsby (1990)

Chemical composition

- TiO_2 , MgO , V_2O_3 , and Al_2O_3 contents in magnetite best discriminate between detrital magnetite grains from felsic plutonic and volcanic, intermediate volcanic, and mafic plutonic parent rocks.
- However, grains from mafic volcanic and metamorphosed mafic/ultramafic sources were not chemically distinct, emphasizing the importance of integrating petrographic and chemical analyses in provenance research.

Texture

- Sands from mafic volcanic sources are characterized by a 1:1 relationship between polymineralic (grains with trellis- or composite-type magnetite-ilmenite intergrowths) and monomineralic grains.
- Monomineralic (homogeneous) grains are characteristic of sands derived from felsic plutonic and intermediate volcanic sources.

V and Ni in spinels

- V - no V dominant end member
- V - enters into the Cr-spinel (mafic and ultramafic rocks) and Fe-spinel (magnetite - mafic magmatic rocks)
- in Al-spinel - usually close to the detection limit of EMP
 - In Cr-rich spinel peridotites - usually below 0.3 wt. % V_2O_3)
 - In Cr-rich spinel from volcanic arcs - usually below 0.8 wt. % V_2O_3
 - In magnetite and Ti-magnetite from basalts and andesites - usually below 0.6 wt. % V_2O_3
 - V-deposit Abitibi - layered gabbro intrusion, ilmenite and magnetite; V-rich magnetite (up to 1.5 wt.% V_2O_3)
- Ni (nichromite - $NiCr_2O_4$, trevorite $NiFe^{3+}_2O_4$)
 - usually enters Cr-rich spinel from mantle peridotites - up to 0.3 wt.% NiO;
 - and secondary ferrichromite - during metamorphism of primary Cr-spinel in peridotites (amphibolite facie) - > 1 wt. % NiO