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Chemical composition and alteration of Cr-spinels from Meliata and Penninic serpentinized peridotites (Western Carpathians and Eastern Alps)

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Cr-spinel is a relatively widespread accessory mineral in the Mesozoic ophiolites of the Western Carpathians (mainly in the Meliata Unit) and in the Penninic Unit (Rechnitz tectonic window group). Cr-spinel chemical composition in both these occurrences (Meliaticum, Penninicum) shows the lherzolitic character of the original ultrabasites. It was found impossible to distinguish the source rocks (peridotites) of these two oceanic domains on the basis of the chemical composition of the Cr-spinels. Many Cr-spinels from both tectonic units are affected by various levels of alteration (in general, decrease of Al_2O_3, Cr_2O_3, MgO, enrichment in FeO, Fe_2O_3, SiO_2, locally also in MnO and ZnO).

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INTRODUCTION

Cr-spinel is a common accessory mineral in the Mesozoic ultramafites of the Western Carpathians (e.g. Rojkovič *et al*., 1978; Hovorka *et al*., 1985) or in the ultramafic complexes of the Eastern Alps. The chemical composition of Cr-spinels from the Western Carpathian ultramafic rocks was studied by Rojkovič *et al*. (1978), Spišiak *et al*. (2000) and others. Cr-spinels from the Penninic ultramafites were studied by Pober and Faupl (1988).

The chemical composition of Cr-spinels from Mesozoic ultramafic bodies (Meliaticum and Penninicum) was examined because these ultramafic rocks are supposed to be one of the possible sources for detrital spinels often occurring in siliciclastic Cretaceous and Paleogene flysch sedimentary rocks and carbonate pebbles in the Central Western Carpathians (e.g. Mišík *et al*., 1980; Jablonský *et al*., 2001). One of the aims of this study was to find out if it is possible to discriminate ultramafic rocks of the Meliatic tectonic unit from those of the Penninic Unit on the basis of Cr-spinel composition.

Cr-spinel alteration in serpentinized ultramafic rocks has been recognized in various tectonic settings (e.g. Michailidis, 1990; Burkhard, 1993; Mellini *et al*., 2005). As the host rocks of the spinels are altered, the chemical composition of the altered spinel was also studied, because in the absence of detailed mineralogical control, spinel composition should not be interpreted uniquely in terms of igneous processes. The degree of serpentinization of the host rock can have a pronounced effect on the spinel chemistry.

GEOLOGY AND PETROLOGY OF ULTRAMAFIC BODIES

The temporal and spatial distribution of Mesozoic ultramafic bodies in the Western Carpathians and Eastern Alps is related to the closing of two subduction zones, i.e. the Kimmerian of the Meliata ocean in the south (Callovian, Oxfordian) and the Penninic suture of the Penninic ocean in the north (Upper Cretaceous; Plašienka *et al*., 1995). We have studied Cr-spinels from different ultramafic bodies in the Western Carpathians and from ultrabasites from the Penninic unit of the Rechnitz and Bernstein windows (Eastern Alps).

MELIATA UNIT

Ultramafic bodies of the Inner Western Carpathians (Slovakia) are known from several Mesozoic tectonic units.

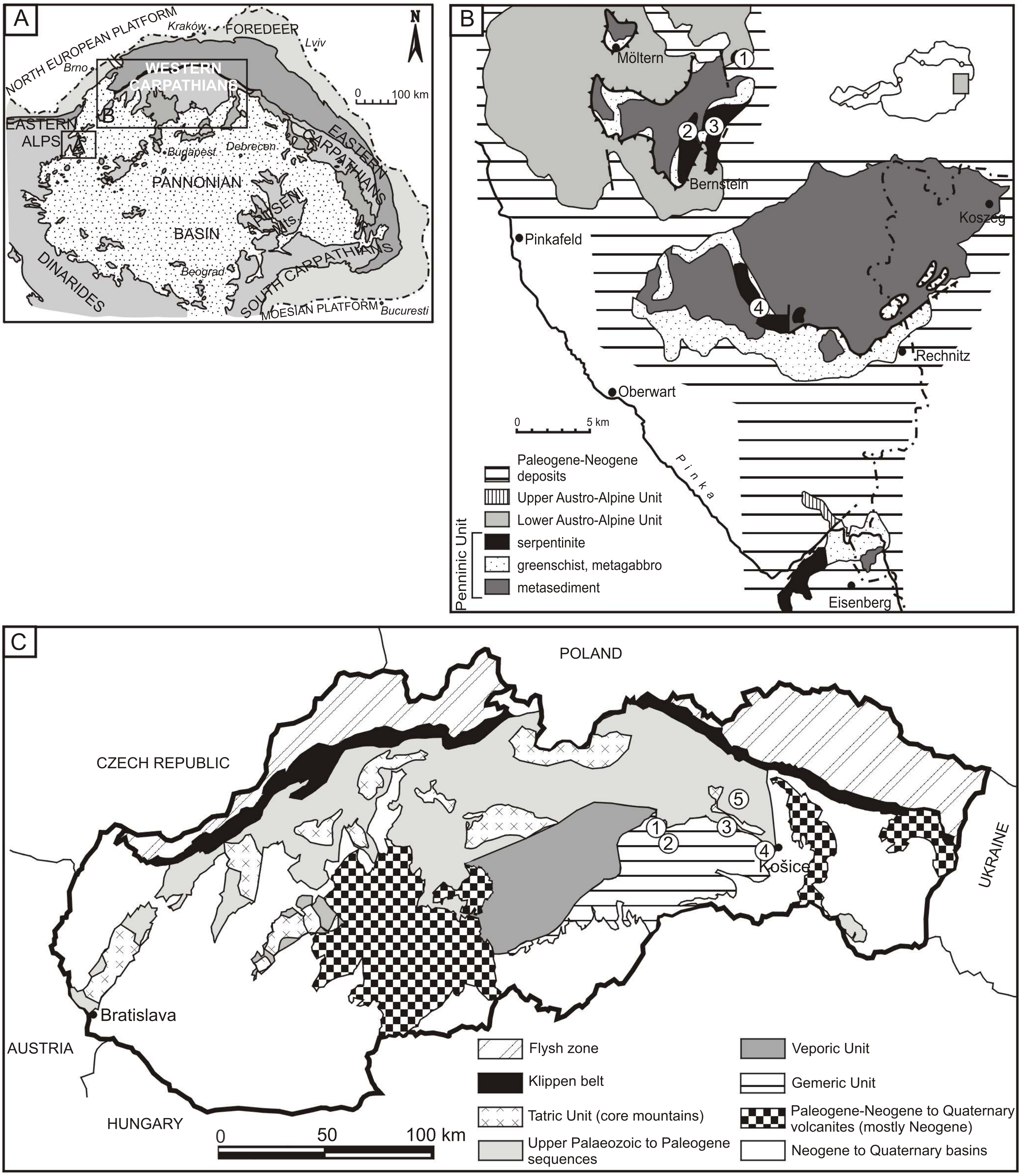

Fig. 1. Location of the samples studied

A — ;**B** — geological map of the Penninic Window at the eastern end of the Alps according to Koller and Pahr (1980), localities studied: 1 — Steinbach, 2 — Kinberg, 3 — Kanitzriegel, 4 — Rumpersdorf; **C** — simplified sketch of the Slovak part of the Western Carpathians according to Biely *et al*. (1996), localities studied: 1 — Dobšinská Ľadová Jaskyňa, 2 — Dobšiná, 3 — Jaklovce, 4 — Hodkovce, 5 — Sedlice

Most of these are widely distributed in the (anchimetamorphosed) Triassic formations of the Meliata unit (Fig.1). The bodies represent incomplete ophiolite formation. They typically occur in the schistose sequence of the Lower Triassic of the north-Gemeride zone and around the boundary between this sequence and the Middle Triassic carbonate rocks. The contacts of the ultramafic bodies with the surrounding rocks are tectonic. The best-known bodies are at Dobšiná and Jaklovce. Peridotite bodies have different shapes (lenticular, platy *etc.*) and sizes (deca- to hectometre dimensions, Hovorka and Zlocha, 1974). The prevailing rock type is spinel peridotite. All known bodies are characterized by their intensive hydratation (serpentinization up to 70–90%). Lizardite, chrysotile, pyroxene relics, chlorites and calcite are the main rock-forming minerals of serpentinites (Hovorka *et al*., 1985).

At Sedlice, there is a peridotite body with an exceptional geological position. The grade of serpentinization is lower (30–70%). This peridotite olistolite (a few-hundreds of metre across) is located within basal Paleocene-Oligocene sedimentary rocks. The geological position of this body has not been determined.

The Hodkovce body is the largest ultramafic body (90–100 km^2) in the entire Carpathian belt and crops out in the western part of the Košice depression. It is covered by Tertiary sedimentary rocks. With its degree of serpentinization and lithological character, this ultramafic body is fully equivalent to bodies in the Meliaticum (Hovorka and Spišiak, 1998).

Cr-spinels from Upper Cretaceous Gosau-type conglomerates from the Dobšinská Ľadová Jaskyňa village (Slovenský Raj Mts.) have also been studied. Ophiolitic rocks are the principal clast type in the lowermost part of the sequence. The conglomerate is poorly sorted with a serpentinite matrix (Hovorka *et al*., 1990). A tectonic mélange in the Meliaticum is thought to be the source of the detrital ultramafic material (e.g. Hovorka *et al*., 1990; Ivan, 2002).

PENNINIC UNIT

Major occurrences of ophiolites and related rocks in the Eastern Alps are restricted to the Penninic windows, that emerge locally from beneath Austro-Alpine units. We have studied Cr-spinels from Mesozoic rocks at the eastern end of the Alps — the Rechnitz window group (Austria). From the north to the south, four small windows can be named: Möltern, Bernstein, Rechnitz and Eisenberg. They contain metasedimentary rocks together with several ophiolites (Koller and Pahr, 1980; Koller, 1985). The Rechnitz window group consists of tectonically fragmented ophiolite, interpreted as a fragment of the south Penninic ocean. The maximum thickness of ultramafic rocks does not exceed 270 m. The metasedimentary rocks are represented by calcareous mica schists (thickness 2000 m), quartz phyllites, and to a lesser extent by graphitic phyllites, marls, conglomerates and rauhwackes. The ultramafic rocks are completely serpentinized harzburgites. Serpentine minerals are represented by chrysotile and lizardite (Koller and Höck, 1992).

The Cr-spinel samples from the Bernstein tectonic window were collected from the serpentinites cropping out in the Kinberg and Kanitzriegel localities (Fig. 1). A relatively less altered ultramafic body is situated in Steinbach and belongs to the Sieggraben unit (Mittelostalpin). The Rumpersdorf sample comes from the Rechnitz tectonic window.

METHODS OF STUDY

Spinel grains (octahedral crystals and fragments) were hand-picked from crushed serpentinized ultramafic rocks (<2 mm fraction), mounted in epoxy resin, polished and coated with carbon. The spinels were analyzed using a wave-dispersion (WDS) electron microprobe and imaged using back-scattered electrons (BSE) at the Department of Mineralogy in the Natural History Museum, London (UK). The microprobe used was a *Cameca SX50* probe. The operating conditions were as follows: 20 kV accelerating voltage, 20 nA beam current, beam diameter 2–5 μm, ZAF corrections, standards (n —natural, sy — synthetic): TiO_2 (sy), $CaTiO_3$ (sy), V (sy), wollastonite (n), Cr_2O_3 (sy), Mn (sy), hematite (sy), Co (sy), Ni (sy), ZnS (sy), Al_2O_3 (sy), diopside (n), MgO_2 (sy). Fe^{2+} and Fe^{3+} in Cr-spinels were calculated assuming an ideal stoichiometry.

RESULTS

SPINEL TEXTURES

Various spinel textures affected by serpentinization are shown in Figures 2 and 3. Stages of alteration were suggested according to the optical and chemical heterogeneity of the Cr-spinel. Spinel chemical heterogeneity resulting from alteration will be described later in the text. Cr-spinels from Dobšiná and Jaklovce are characterized by their cataclastic textures. Euhedral magnetite rims formed during serpentinization are commonly observed (e.g. Fig. 2A, B). The altered spinel textures are inhomogeneous. The connection of the altered zones with cracks or veinlets shows that these played an important role in providing pathways for the fluids involved. Many altered Cr-spinel grains show progressive alteration (Fig. 2A–C). Cr-spinel grains are optically and chemically zoned. Reaction boundaries between zones are irregular.

Primary silicate inclusions (cpx —diopside, hbl — hornblende) trapped in Cr-spinels as bubbles are rare and commonly serpentinized. Some spinel grains from Hodkovce and Sedlice are sheared and fractured with cracks filled with magnetite. The prevailing unaltered grains are microscopically as well as chemically homogeneous. Cr-spinel from Sedlice occurs in association with cpx (diopside), opx (enstatite) and olivine (ol; Fig. 2D). Anhedral grains suggest interstitial crystallization from a residual magma. Most Cr-spinels from Steinbach show post-magmatic subsolidus exsolution (Fig. 2E).

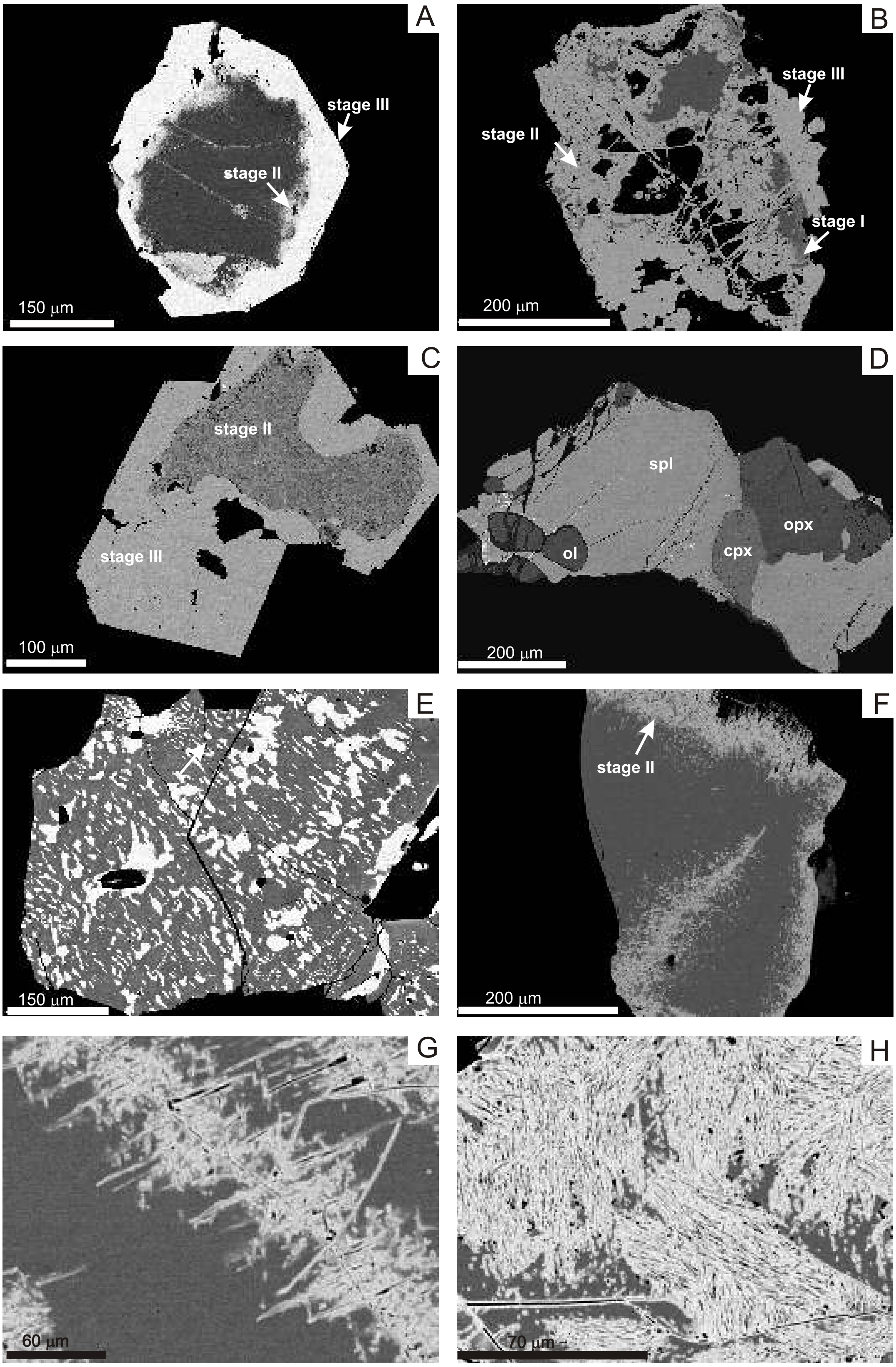

Fig. 2. Various textures of Cr-spinels from Dobšiná (A–C), Sedlice (D), Steinbach (E) and Kanitzriegel (F–H)

A–**C** — various stages of Cr-spinel alteration at Dobšiná; Al-rich (A), almost completely altered core (B) and completely altered spinel core (C) with porous structure overgrown by an euhedral magnetite rim; **D** — association of silicate minerals (ol — olivine, cpx — diopside, opx — enstatite, spl — spinel) occurring with unaltered Cr-spinel from the Sedlice body; **E** — postmagmatic subsolidus exsolutions of Cr-Fe^{3+} phase in Al-rich spinel, Steinbach; **F, G, H** — beginning and progress of alteration at the Kanitzriegel locality; cracks are convenient structures for circulation of alteration fluids; BSE images

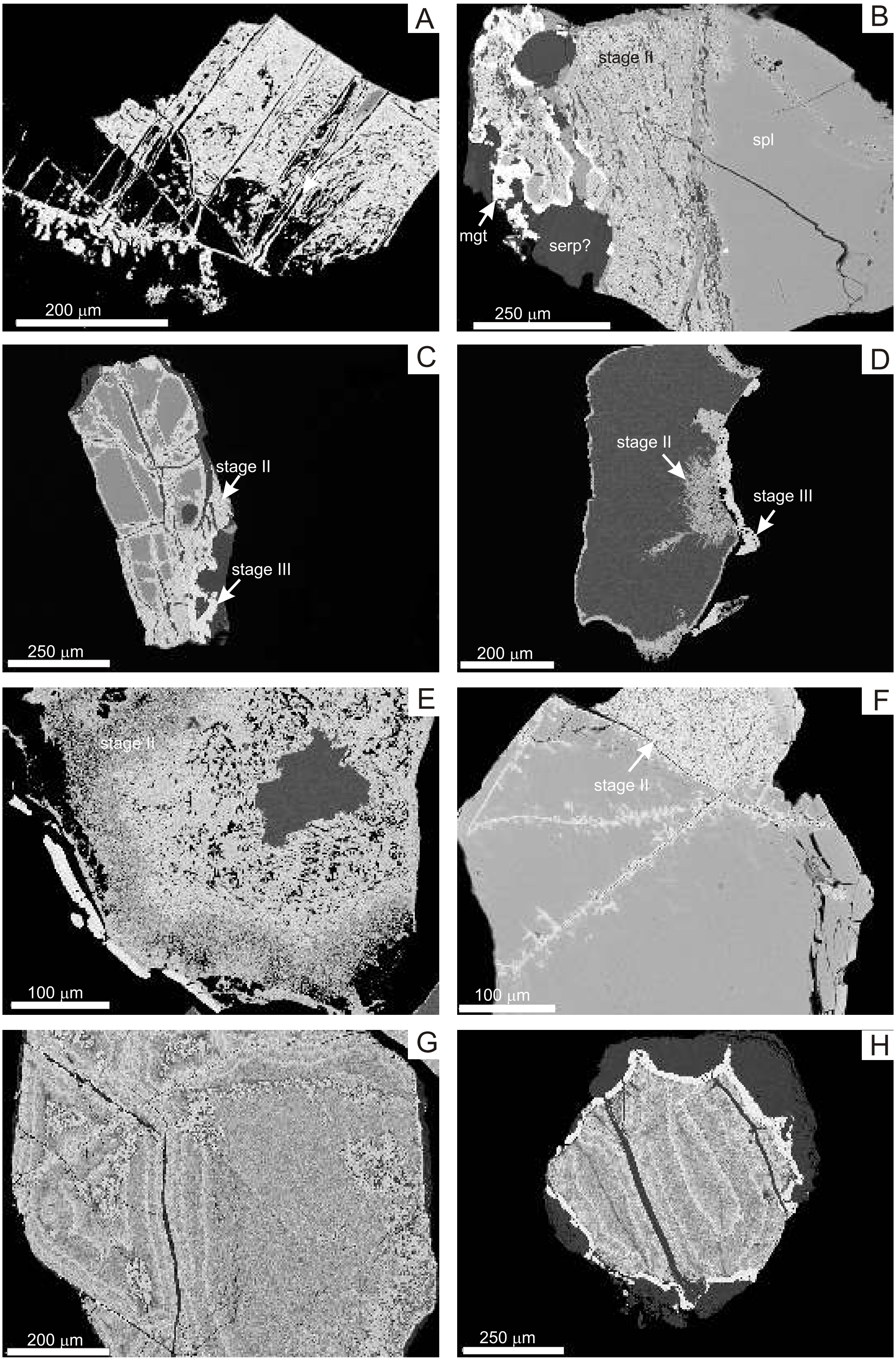

Fig. 3. Various textures of altered Cr-spinels from Kanitzriegel (A, D, E), Jaklovce (B, C) and Kinberg (F, G, H)

A — almost completely altered spinel grain replaced by magnetite; **B, C** — porous texture and alteration progress via cracks, spl — spinel, serp — serpentine, mgt — magnetite; **D** — progress of alteration from the grain margins, dark phase represents an unaltered homogeneous Al-richer phase; **E** — unaltered homogeneous Al-richer spinel core surrounded by a porous heterogeneous spinel phase; **F** — altered phase fills microfractures; **G, H** — porous spinel structure with the highest SiO_2 content; BSE images

Exsolutions (size up to 40 μm) of oval shape (blebs, dots *etc.*) are randomly distributed in the host spinel. The largest exsolutions are near inclusions of silicate minerals (ol, opx, cpx, amph — amphibole).

THE COMPOSITION OF CR-SPINELS FROM ULTRAMAFIC BODIES IN THE MELIATIC UNIT

Spinels from the Mesozoic ultramafic bodies show significant variation in chemistry, mainly in terms of the most important parameters such as Mg# (Mg/Mg + Fe^{2+}), Cr# (Cr/Cr + Al), TiO_2 and Fe^{2+}/Fe^{3+} (Table 1). To distinguish between fresh spinels, the most useful variables are TiO_2 content combined with the Fe^{2+}/Fe^{3+} ratio (Lenaz *et al.*, 2000; Kamenetsky *et al.*, 2001). "Mantle" spinels (from ophiolitic peridotites and mantle xenoliths) have statistically (>95%) lower TiO_2 (<0.2 wt%) and higher Fe^{2+}/Fe^{3+} (>3) over the whole interval in Al_2O_3 (6–56 wt%) than volcanic spinels (Kamenetsky *et al.*, 2001). Volcanic spinels with TiO_2 <0.2 wt% are uncommon (some suites of low-Ti MORB, arc tholeiites and boninites) and those with TiO_2 <0.1 are exceptionally rare (some low-Ca boninites). Lenaz *et al.* (2000) have set a compositional boundary between peridotitic and volcanic spinels at TiO_2 = 0.2 wt%. Volcanic spinels tend to have a Fe^{2+}/Fe^{3+} ratio of usually up to four (Kamenetsky *et al.*, 2001).

Cr-spinels from all the samples from ultramafic bodies (Meliaticum, Penninicum) show TiO_2 contents <0.20 wt% and Fe^{2+}/Fe^{3+} ratios >4; therefore, these spinels are peridotitic spinels (Lenaz *et al.*, 2000).

In order to characterize the diversity of the original tectonic settings of the ophiolites, the Cr-spinel-based classification of peridotites by Dick and Bullen (1984) was used. Representative microprobe analyses are given in Tables 1 and 2. Characteristic spinel textures are shown in Figures 2 and 3. Chemical variations are depicted in Figures 4, 5, 6, 7 and 8.

Cr-spinels from Dobšiná and Jaklovce have very similar chemical compositions. The Al_2O_3 content is 27–35 wt% (Fig. 4) and the Cr_2O_3 content is 32–37 wt%. Cr# values are between 38–54 mol% and Mg# values are between 63–70 mol%.

Cr-spinels from the Hodkovce and Sedlice bodies comprise another group with similar chemical compositions (Table 1). The Al_2O_3 content is 38–44 wt% (Fig. 4) and the content of Cr_2O_3 is 23–29 wt%. Cr# values (24–38 mol%) are lower than in the first group. Mg# (69–75 mol%) is slightly higher.

Cr-spinels from the Dobšinská Ľadová Jaskyňa conglomerates (DLJC) have exceptional chemical compositions among the samples studied. These spinels show the highest Al_2O_3 (51–59 wt%; Fig. 4) content. Therefore, their Cr# values are the lowest (13–50 mol%) and the Mg# values are the highest (63–81 mol%). Only a few spinel grains are of volcanic origin (TiO_2 = 0.49 and Fe^{2+}/Fe^{3+} = 2.1) according to the Kamenetsky *et al.*, (2001) classification. The Al_2O_3 content is 27–32 wt% (Table 1). These compositions are well within the field of spinel from MORB-type back-arc rocks or BABB.

THE COMPOSITION OF CR-SPINELS FROM ULTRAMAFIC BODIES IN THE PENNINIC WINDOWS

In general, Cr-spinels from all the occurrences studied in the Bernstein and Rechnitz tectonic windows show lower Al_2O_3 contents than Cr-spinels from the Western Carpathians ultramafic complexes (Fig. 4). The Al_2O_3 content varies within the range of 26–30 wt% in the Kanitzriegel and Kinberg localities (Table 2). The Cr_2O_3 content is between 36–40 wt%. Cr-spinels from the Kinberg locality show a relatively higher TiO_2 content (0.33 wt%; Fig. 4). Cr# values are 42–52 mol% and Mg# values are 62–67 mol%.

Cr-spinels from the Steinbach locality (Mittelostalpin unit) (Table 2) have the most variable composition which is, at the same time, different from those of the other localities. Homogeneous Cr-spinels show the highest Al_2O_3 content (41–43 wt%). The Cr_2O_3 content is between 16–18 wt% and Cr# and Mg# values are between 20–22, 64–67 respectively. The Al_2O_3 content in these spinels is similar to those of the spinels from Sedlice and Hodkovce (Western Carpathians; Fig. 4). However, all of these samples have higher Cr_2O_3 (23–29 wt%) contents.

Host Cr-spinels and exsolutions are different mainly in their Al_2O_3, MgO and Fe_2O_3 contents. Exsolved spinels (Fe-Cr phase) are rich in Fe_2O_3 (40.44–52.77 wt%), FeO (26.85–28.88 wt%) and have even higher TiO_2 (0.40–0.80 wt%) and V_2O35 (0.39–0.64 wt%) contents.

Almost all Cr-spinels studied from the Western Carpathians show affinity to abyssal peridotites (Dick and Bullen, 1984; Fig. 5). Only several Cr-spinels from the easternmost part of the Eastern Alps show continuous transition from abyssal spinel peridotite to fore-arc spinel harzburgite.

The most important Cr-spinel compositional variations follow the effects of tetrahedral Mg ↔ Fe^{2+} substitution (Fig. 6A) and octahedral Cr ↔ Al substitution (Fig. 6B), whereas $2Fe^{3+} \leftrightarrow Fe^{2+} + Ti^{4+}$ exchange is not so evident, but takes place in altered spinels and magnetites (Fig. 6C). Cr ↔ Al substitution is the dominant mechanism for Cr-spinel chemical variability (Fig. 7). This trend of widely variable Cr/(Cr+Al) at generally low $Fe^{2+}/(Mg+Fe^{2+})$ and at low concentrations of Fe^{3+} and TiO_2 is referred as the Cr-Al trend (Barnes and Roeder, 2001). It is particularly evident in the various mantle and lower-crustal samples (xenoliths, ophiolites and ocean-floor peridotites). This sloping trend corresponds to spinels equilibrating with olivine of constant composition at constant temperature (Irvine, 1967).

CR-SPINEL ALTERATION

Altered Cr-spinels cannot reflect primary igneous crystallization conditions although they may be useful in understanding post-magmatic processes. According to degrees of optical and chemical heterogeneity three stages of Cr-spinel alteration may be suggested:

Table 1

Representative microprobe analyses of Cr-spinels from Western Carpathians localities (mostly Meliata Unit)

Sample	Jaklovce				Dobšiná					Sedlice			Hodkovce				Dobšinská Ľadová Jaskyňa			
Degree of alteration	U	U	II	II	U	U	I	II	III	U	U	U	U	U	I	I	U	U	U	U
Analyse	1	27	2	3	98	117	103	94	93	4	5	17	1	3	2	3	38	49	54	56
SiO_2	0.00	0.14	2.67	4.39	0.04	0.02	0.04	3.38	0.10	0.10	0.05	0.08	0.03	0.05	0.05	0.03	0.05	0.00	0.10	0.10
TiO_2	0.07	0.10	0.08	0.08	0.04	0.09	0.17	0.60	0.19	0.08	0.07	0.05	0.05	0.03	0.11	0.14	0.04	0.02	0.49	0.48
Al_2O_3	35.45	30.13	5.67	2.94	33.12	35.26	13.35	0.55	0.03	43.47	44.39	45.77	42.94	46.73	9.90	9.80	53.96	59.55	27.19	32.49
Cr_2O_3	33.01	38.89	27.28	28.20	34.00	34.12	46.55	20.96	1.25	23.68	22.68	21.44	23.68	21.40	49.95	50.43	13.00	9.05	41.03	34.18
Fe_2O_3*	1.96	1.71	32.67	34.95	3.10	1.72	9.44	44.21	67.76	2.58	2.59	2.44	3.02	2.06	6.39	5.74	2.45	1.75	4.44	4.66
FeO	12.52	13.04	6.50	2.86	14.68	13.58	22.79	21.30	30.91	11.69	11.93	12.43	10.93	10.99	26.65	26.48	9.46	8.93	8.25	10.88
MnO	0.21	0.21	13.00	16.14	0.23	0.16	0.47	3.77	0.19	0.14	0.09	0.15	0.20	0.20	0.96	0.89	0.11	0.11	0.16	0.13
MgO	16.05	15.00	7.04	7.49	14.43	15.64	6.88	3.76	0.07	17.48	17.40	17.22	17.69	18.26	2.61	2.69	19.65	20.86	17.82	16.68
CaO	0.01	0.36	0.06	0.05	0.03	0.02	0.00	0.27	0.02	0.00	0.00	0.03	0.01	0.04	0.02	0.01	0.00	0.01	0.04	0.01
ZnO	0.16	0.07	1.04	1.32	0.20	0.16	0.27	0.36	0.00	0.09	0.21	0.27	0.19	0.25	1.41	1.39	0.19	0.23	0.03	0.08
V_2O_3	0.18	0.23	0.14	0.09	0.19	0.24	0.23	0.07	0.03	0.17	0.17	0.17	n.a.	n.a.	n.a	n.a.	0.10	0.08	0.18	0.19
total	99.61	99.89	96.15	98.50	100.06	101.00	100.18	99.23	100.55	99.48	99.56	100.02	98.74	100.02	98.05	97.58	99.05	100.57	99.78	99.89
Formula based on 3 cations																				
Si	0.000	0.004	0.096	0.155	0.001	0.000	0.001	0.125	0.004	0.003	0.001	0.002	0.001	0.001	0.002	0.001	0.001	0.000	0.003	0.003
Ti	0.002	0.002	0.002	0.002	0.001	0.002	0.004	0.017	0.005	0.002	0.001	0.001	0.001	0.001	0.003	0.004	0.001	0.000	0.011	0.010
Al	1.203	1.047	0.240	0.122	1.141	1.187	0.525	0.024	0.001	1.421	1.446	1.480	1.412	1.496	0.416	0.413	1.680	1.786	0.940	1.108
Cr	0.751	0.906	0.776	0.789	0.786	0.771	1.229	0.610	0.038	0.519	0.496	0.465	0.522	0.460	1.408	1.427	0.271	0.182	0.952	0.782
Fe^{3+}	0.042	0.038	0.884	0.930	0.068	0.037	0.237	1.224	1.951	0.054	0.054	0.050	0.064	0.042	0.171	0.155	0.049	0.033	0.098	0.101
Fe^{2+}	0.301	0.321	0.195	0.085	0.359	0.325	0.636	0.655	0.989	0.271	0.276	0.285	0.255	0.250	0.794	0.793	0.209	0.190	0.202	0.263
Mn	0.005	0.005	0.396	0.484	0.006	0.004	0.013	0.117	0.006	0.003	0.002	0.004	0.005	0.005	0.029	0.027	0.002	0.002	0.004	0.003
Mg	0.689	0.659	0.377	0.395	0.629	0.666	0.342	0.206	0.004	0.723	0.717	0.704	0.736	0.740	0.139	0.143	0.774	0.791	0.779	0.719
Ca	0.000	0.011	0.002	0.002	0.001	0.001	0.000	0.011	0.001	0.000	0.000	0.001	0.000	0.001	0.001	0.000	0.000	0.000	0.001	0.000
Zn	0.003	0.002	0.028	0.035	0.004	0.003	0.007	0.010	0.000	0.002	0.004	0.005	0.004	0.005	0.037	0.037	0.004	0.004	0.001	0.002
V	0.003	0.005	0.003	0.002	0.004	0.005	0.005	0.002	0.001	0.003	0.003	0.003	–	–	–	–	0.002	0.001	0.003	0.004
Cr#	38	46	76	87	41	39	70	96	–	27	26	24	27	24	77	78	14	9	50	41
Mg#	70	67	66	82	64	67	35	24	–	73	72	71	74	75	15	15	79	81	79	73
Fe^{2+}/Fe^{3+}	7.1	8.5	0.2	0.1	5.3	8.8	2.7	0.5	0.5	5.0	5.1	5.7	4.0	5.9	4.6	5.1	4.3	5.7	2.1	2.6

*Fe_2O_3 calculated from stoichiometry; U — unaltered fresh spinel grains; major oxides in [wt%]; Cr#, Mg# in [mol%]

Table 2

Representative microprobe analyses of Cr-spinels from Eastern Alps (Rechnitz and Bernstein window, Penninic Unit)

Degree of alteration	Kanitzriegel					Rumpersdorf				Kinberg					Steinbach					
	U	U	II	II	II	II	II	II	III	U	II	II	II	II	U	U	Host	Host	Ex	Ex
Analyse	48	53	31	56	66	6	19	16	17	47	48	52	36	56	11	15	7	4	20	1
SiO_2	0.08	0.03	5.05	4.28	0.09	1.55	0.04	0.15	0.07	0.01	0.00	0.00	12.27	10.43	0.06	0.08	0.11	0.15	0.07	0.05
TiO_2	0.10	0.14	0.24	0.10	0.21	0.12	0.05	0.07	0.05	0.31	6.62	4.50	0.22	0.18	0.05	0.04	0.21	0.13	0.73	0.41
Al_2O_3	30.39	25.54	0.96	0.74	3.93	0.26	2.67	0.04	0.06	25.77	17.47	20.43	1.10	8.60	41.73	43.54	28.07	25.53	2.06	6.50
Cr_2O_3	36.25	40.90	29.92	28.06	35.99	25.31	36.91	9.36	5.15	40.84	31.70	30.66	32.21	27.96	17.96	16.23	26.87	29.96	11.89	20.98
Fe_2O_3*	4.27	4.45	32.59	38.62	29.00	42.63	28.61	59.49	63.96	3.70	12.86	11.46	27.66	24.23	8.55	8.92	13.54	12.76	52.77	40.44
FeO	13.42	14.73	20.65	12.31	18.69	26.02	27.05	30.07	31.03	14.81	23.35	26.30	10.64	14.25	14.59	13.96	19.17	19.48	28.88	26.85
MnO	0.15	0.23	2.08	8.17	7.74	1.45	2.52	0.55	0.21	0.23	0.45	1.69	2.12	1.93	0.17	0.13	0.29	0.47	0.20	0.42
MgO	15.10	13.65	4.95	6.75	2.28	2.41	0.89	0.31	0.00	13.51	6.73	3.94	12.27	10.87	14.98	15.68	10.66	9.94	1.16	3.15
CaO	0.00	0.00	0.00	0.00	0.02	0.00	0.02	0.00	0.02	0.01	0.00	0.01	0.04	0.00	0.00	0.00	0.02	0.00	0.02	0.00
ZnO	0.09	0.12	1.17	1.30	2.68	0.60	1.17	0.19	0.05	0.14	0.28	1.16	1.32	1.04	0.37	0.45	0.29	0.41	0.02	0.03
V_2O_3	0.23	0.30	0.08	0.02	0.32	0.00	0.21	0.06	0.00	0.26	0.27	0.27	0.10	0.08	0.13	0.06	0.28	0.25	0.62	0.39
Total	100.07	100.1	97.70	100.35	100.97	100.35	100.15	100.28	100.58	99.59	99.74	100.40	99.96	99.57	98.61	99.08	99.50	99.06	98.41	99.21
Formula based on 3 cations																				
Si	0.002	0.001	0.185	0.152	0.003	0.057	0.002	0.006	0.003	0.000	0.000	0.000	0.409	0.342	0.002	0.002	0.003	0.005	0.003	0.002
Ti	0.002	0.003	0.007	0.003	0.006	0.003	0.001	0.002	0.001	0.007	0.165	0.112	0.006	0.004	0.001	0.001	0.005	0.003	0.021	0.011
Al	1.054	0.911	0.042	0.031	0.168	0.011	0.117	0.002	0.002	0.923	0.681	0.797	0.043	0.332	1.406	1.446	1.019	0.944	0.093	0.278
Cr	0.844	0.979	0.867	0.786	1.029	0.741	1.080	0.282	0.156	0.981	0.830	0.802	0.848	0.724	0.406	0.361	0.655	0.743	0.359	0.601
Fe^{3+}	0.095	0.101	0.899	1.029	0.789	1.187	0.797	1.707	1.838	0.085	0.320	0.285	0.693	0.597	0.184	0.189	0.314	0.301	1.515	1.103
Fe^{2+}	0.330	0.373	0.633	0.365	0.565	0.805	0.837	0.959	0.991	0.376	0.646	0.728	0.296	0.390	0.349	0.329	0.494	0.511	0.921	0.813
Mn	0.004	0.006	0.064	0.245	0.237	0.046	0.079	0.018	0.007	0.006	0.013	0.047	0.060	0.053	0.004	0.003	0.008	0.013	0.006	0.013
Mg	0.663	0.616	0.270	0.356	0.123	0.133	0.049	0.017	0.000	0.612	0.332	0.194	0.609	0.531	0.638	0.658	0.489	0.465	0.066	0.170
Ca	0.000	0.000	0.000	0.000	0.001	0.000	0.001	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.000	0.001	0.000
Zn	0.002	0.003	0.032	0.034	0.072	0.016	0.032	0.005	0.001	0.003	0.007	0.028	0.032	0.025	0.008	0.009	0.007	0.009	0.001	0.001
V	0.004	0.006	0.002	0.001	0.008	0.000	0.005	0.001	0.000	0.005	0.006	0.006	0.002	0.002	0.002	0.001	0.006	0.005	0.016	0.009
Cr#	44	52	95	96	86	99	90	99	98	52	55	50	95	69	22	20	39	44	79	68
Mg#	67	62	30	49	18	14	6	2	0	62	34	21	67	58	65	67	50	48	7	17
Fe^{2+}/Fe^{3+}	3.5	3.7	0.7	0.4	0.7	0.7	1.1	0.6	0.5	4.4	2.0	2.5	0.4	0.7	1.9	1.7	1.6	1.7	0.6	0.7

Explanations as in Table 1

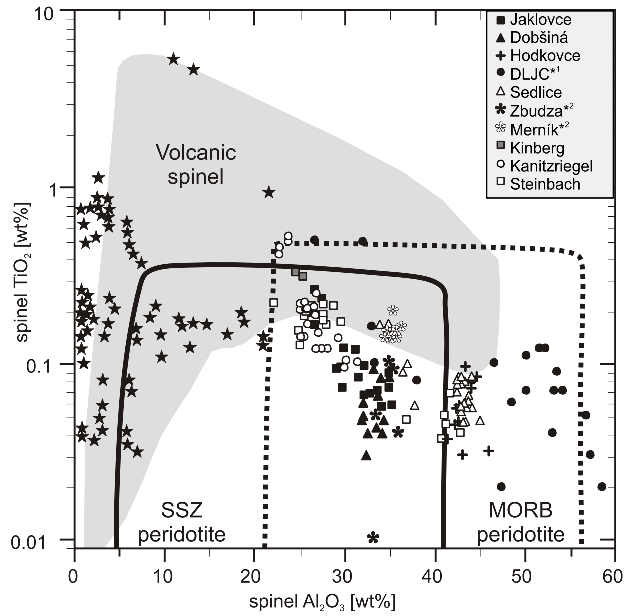

Fig. 4. Al_2O_3 *vs.* TiO_2 compositional relationships in fresh spinels from the Mesozoic ultramafic bodies in the Western Carpathians and Eastern Alps (Penninic Window)

Spinels are compared with compositional fields of spinel from volcanic rocks and mantle peridotites (according to Kamenetsky *et al.*, 2001);*[1]— Dobšinská Ľadová Jaskyňa conglomerates; *[2] — Cr-spinel analyses from Merník and Zbudza published by Soták *et al*. (1990; 1995); black stars represent altered spinels

Stage I: This stage is typical of Cr_2O_3, Fe_2O_3 and FeO enrichment, and a moderate decrease in Al_2O_3 and MgO (e.g. analysis 103, Table 1).

Stage II: During this stage spinel has lost almost all its Al_2O_3 content and is starting to lose Cr_2O_3 (e.g. analysis 94, Table 1). The MgO content is continuously decreasing. Spinel is extremely enriched in Fe_2O_3 while the FeO content is rising only slightly. At this stage, spinels are enriched in ZnO (<1.34 wt%) and the MnO content reaches considerable values (13–16.87 wt% — Jaklovce or 2.76–6.39 wt% — Dobšiná). The SiO_2 content detected in spinel (up to 4.39 wt%) will be discussed in the following text. Cr-spinel texture at this stage is very porous (Fig. 2C).

Stage III: The final product of alteration is a phase with a dominant magnetite component (91–97 mol%).

The trend of Cr-spinel alteration from Hodkovce is similar to those from Dobšiná and Jaklovce. Only stage I was observed (decrease in Al_2O_3 and MgO, enrichment in Cr_2O_3, FeO, slightly in Fe_2O_3). Spinel is enriched in ZnO (1.37–1.41 wt%) during this stage (Table 1).

Similarly, Cr-spinels from the Eastern Alps (Rechnitz and Bernstein tectonic windows) are also altered. There were observed only two stages of alteration which are comparable with stages II and III in the Western Carpathians (e.g. Dobšiná). The entire process can be properly described at the Kanitzriegel locality (Fig. 2F–H). Alteration fluids have attacked spinel grains from their margins or via cracks and microfractures. Completely altered spinel grains are not (Fig. 3A). Enrichment in Cr_2O_3 was not observed.

During stage II spinels are enriched in FeO and show a very high proportion of Fe_2O_3 (29–38 wt%). Alteration fluids enriched spinel in MnO (2.61–8.17 wt%) and ZnO (1.30–2.68 wt%). The SiO_2 content is up to 5.41 wt %. Textures at this stage of alteration are full of pores.

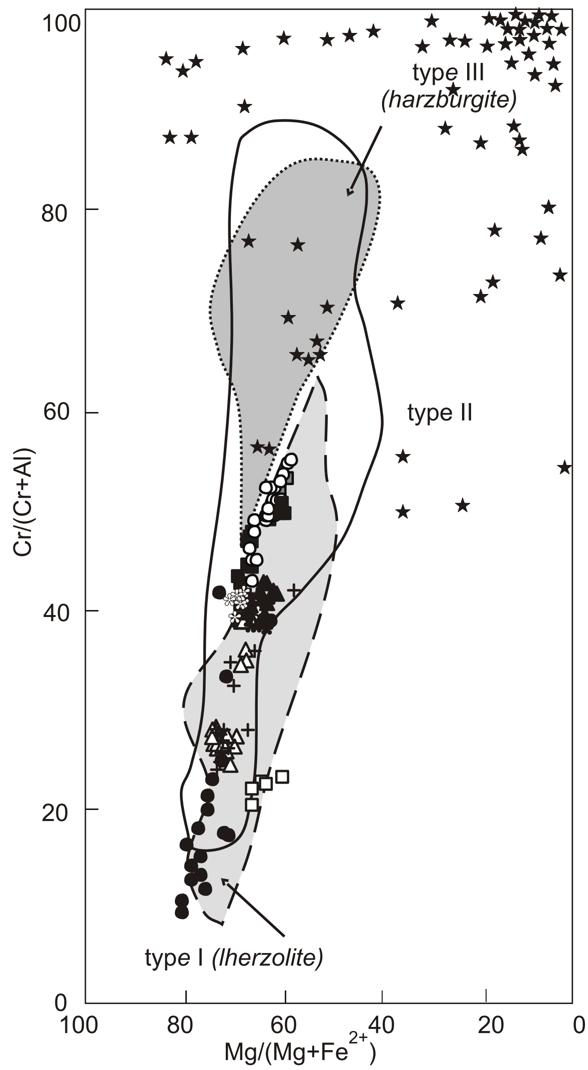

Fig. 5. Relationship between $Mg/(Mg+Fe^{2+})$ *vs.* Cr/(Cr+Al) in the fresh peridotitic spinels studied

Compositional fields are used according to the classification of Dick and Bullen (1984); explanations as in Figure 4

The last stage III is produced a phase which corresponds to magnetite with a Cr_2O_3 content of up to 1.65 wt%. The SiO_2 content is within the range of 0.82–1.02 wt%.

The scenario of alteration at the Kinberg locality, where almost all spinel grains are altered, is similar to that in Kanitzriegel. A small difference was observed at the beginning of stage II, when spinel is enriched in TiO_2 (0.9–6.62 wt%). Euhedral magnetite rims contain up to 15 wt% of Cr_2O_3. Some spinel grains are so strongly serpentinized that their porous structure is full of serpentine minerals (Fig. 3G, H). This is the reason why spinel shows high content of SiO_2 (7–16 wt%) and MgO (7–15 wt%). These two oxides are the main components of serpentine.

In the Rumpersdorf locality, only altered spinels were identified (Fig. 7). Both alteration stages were recognized (Table 2). A typical feature of spinels in stage II is a high content of Fe_2O_3 (40–45 wt%). Cr_2O_3 content ranges between 23–28 wt%.

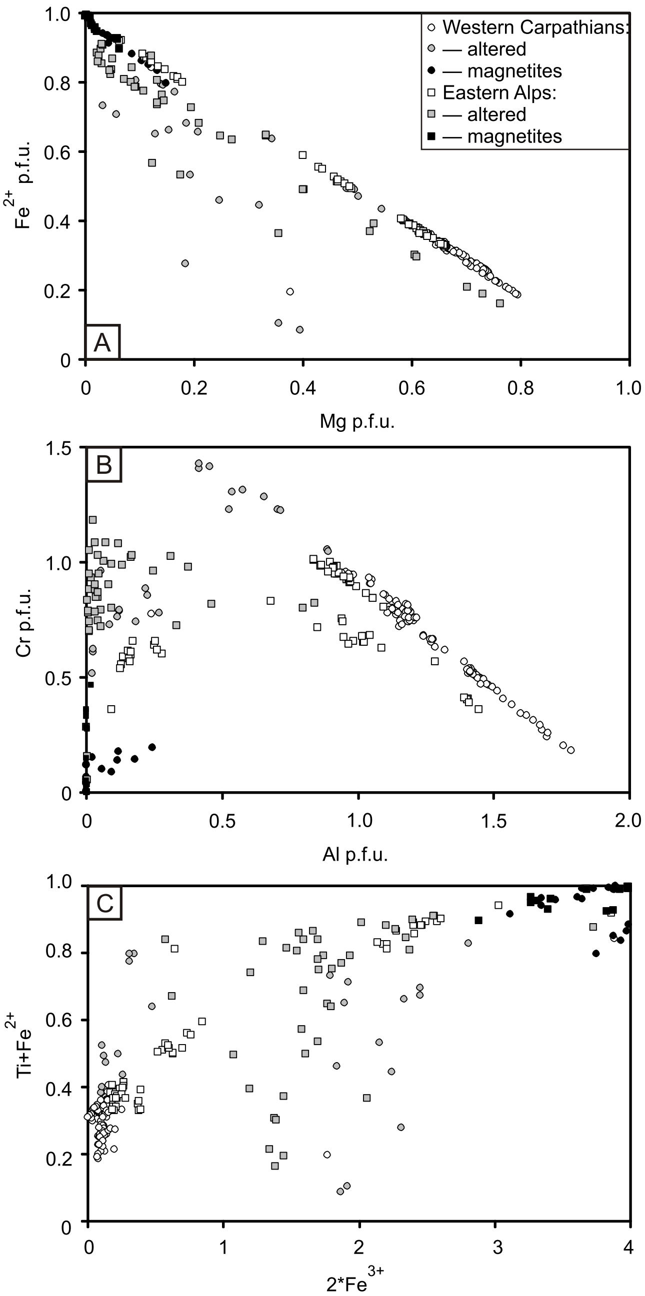

Fig. 6. Correlations of major elements in the peridotitic spinels from the Western Carpathians and Eastern Alps

A — contents of Mg (p.f.u — per formula unit) *versus* Fe^{2+} (p.f.u); **B** — Al (p.f.u) *versus* Cr (p.f.u); **C** — $2*Fe^{3+}$ *versus* $Ti+Fe^{2+}$; note the existence of different substitution mechanisms displayed for unaltered and altered spinels (see the text for explanation)

Magnetites (III stage) have a different Cr_2O_3 content, which is continuously decreases from 12 wt% to pure magnetite.

The alteration process, by which Mg-Al-Cr rich spinel changes to magnetite can be described as a stable decrease in Mg, Al and Cr (except Cr-enrichment during stage I). These cations are substituted by Fe^{2+} and Fe^{3+} ($Mg \Leftrightarrow Fe^{2+}$, Cr^{3+} and $Al^{3+} \Leftrightarrow Fe^{3+}$; Fig. 7).

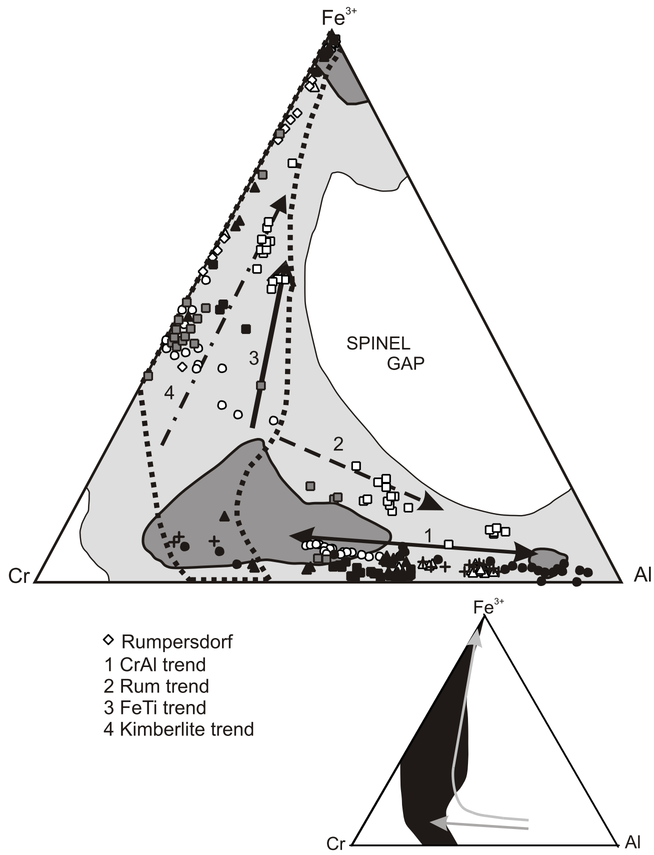

Fig. 7. Changes in content of trivalent cations during alteration

Grey fields represent the most densely packed of the spinel data points (pale grey 50%, dark grey 95%) according to Barnes and Roeder (2001); arrows indicating spinel trends are taken from the same work; spots within the dotted area represent altered spinels; this area is black in the smaller triangle with grey arrows indicating alteration trend: loss of Al and Mg, Cr decrease and enrichment in Fe^{3+}; other explanations as in Figure 4

DISCUSSION

PRIMARY MAGMATIC CR-SPINELS

On the basis of the chemical composition, degree of alteration and textural features of the Cr-spinels from the Mesozoic ultramafic bodies in the Western Carpathians, two slightly different groups can be distinguished (Figs. 4 and 5). The first group of Cr-spinels shows a lower amount of Al_2O_3 (27–35 wt%; e.g. Jaklovce, Dobšiná). According to their composition (Cr# and Mg#), they should be classified as spinels from a mid-ocean ridge setting (MORB) type I peridotite (lherzolitic affinity; Dick and Bullen, 1984). The same chemical composition is shown by Cr-spinels from Zbudza and Merník (Figs. 4 and 5). A large amount of Cr-spinels in this group are strongly altered (serpentinized). A different localities only small differences in the spinel MnO, ZnO contents were observed.

The second group of Cr-spinel shows higher Al_2O_3 (38–44 wt%) contents. The samples from Sedlice and

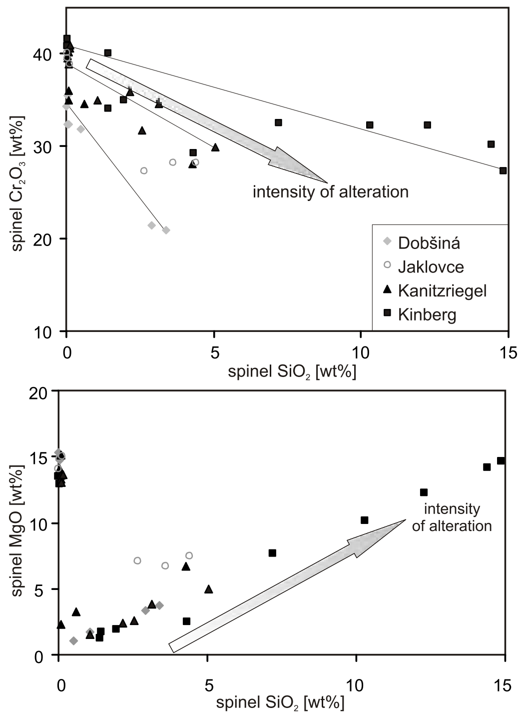

Fig. 8. Correlation between SiO_2 *vs.* Cr_2O_3 and MgO content in altered Cr-spinels

Hodkovce fall into this group. Their composition (Cr# 24–38 mol%, Mg# 69–75 mol%) corresponds best to that of spinels from a mid-ocean ridge setting (MORB type I peridotite) according to Dick and Bullen, (1984) classification. Cr-spinels from this group are rarely altered, which is a distinguishing feature among the localities studied. Non-altered spinels were found only at the Sedlice locality from all the localities studied. This observation is consistent with the lowest observed degree of serpentinization of the host ultramafic body.

The highest content of Al_2O_3 (51–59 wt%) from all the samples studied is shown by MORB-type peridotite Cr-spinels from the Dobšinská Ľadová Jaskyňa conglomerates (DLJC). Such a high Al_2O_3 spinel content in the Western Carpathians was observed in MORB-type peridotitic spinels (in part of mantle xenolith origin) from Mesozoic (Cretaceous) alkali basalts (hyaloclastites) at the Podmanín locality (Mikuš *et al.*, 2006). Cr-spinels of volcanic type from DLJC which correspond to spinel from a BABB setting are consistent with geochemical data from Meliatic basalts obtained by Ivan (2002).

Cr-spinels from the Penninic ultramafic complexes (Rechnitz and Bernstein windows) have similar chemical compositions to the Cr-spinels of the first group (Dobšiná, Jaklovce) from the Meliaticum (Western Carpathians). Many have, also, the same composition as Cr-spinels from Jaklovce. They are characteristic in having the lowest contents of Al_2O_3 (25–30 wt%) among all the samples studied. Spinel compositions from Kanitzriegel and Kinberg correspond to spinels from transitional type II peridotite or to those from a mid-ocean ridge setting (MORB type I peridotite), according to Dick and Bullen, (1984; Fig. 5). Similar Cr-spinel compositions as in the Rechnitz and Bernstein windows were observed in the Tauern Penninic Window (Pober and Faupl, 1988) and also in the Penninic ophiolite of the Val Malenco and Arosa-platta nappe in the Central Alps (Burkhard, 1993).

However, the intensity of alteration is stronger in the Bernstein and Rechnitz windows than in the first Cr-spinel group in the Meliaticum (Dobšiná, Jaklovce). A high degree of Cr-spinel alteration in the easternmost end of the Eastern Alps (Bernstein, Rechnitz windows) can be directly linked with the strong deformation and metamorphism of the ophiolite complexes (Koller and Hock, 1992).

TESTING THE VALIDITY OF ALTERED CR-SPINELS AS A PETROGENETIC INDICATOR

Problems may occur when altered spinels are plotted on discrimination diagrams (Figs. 4 and 5) of Kamenetsky *et al.* (2001) and Dick and Bullen, (1984). As shown, a number of analyses plot well within the fields of SSZ peridotites or into the harzburgite (type III peridotite) field (Figs. 4 and 5). However, most of the fresh spinels correspond to MORB peridotites or mostly to lherzolite (type I peridotite). If serpentinization has a significant effect on the chemistry of the *in situ* Cr-spinels, this will inevitably impact upon the detrital spinel chemistry, especially as provenance studies usually rely on the ~125 micron size fraction (i.e. especially where the entire grain is altered or only an altered fragment is preserved) where the context of the grain is lost. In this case, the resalts of provenance studies would be misleading.

The ophiolite discrimination fields are valid for *in situ* Cr-spinel within unserpentinized ophiolilic rocks. However, Cr-spinels undergo subsolidus reequilibration as a result of solid-solid and solid-liquid reaction during cooling, hydrothermal activity and serpentinization of the host rock. It is important to consider these factors in order to determine the extent of chemical change of the Cr-spinel (Power *et al.*, 2000). Therefore, the use of these fields in provenance and petrogenetic studies of dismembered and deformed ultramafic complexes, where some or all of these factors cannot be assessed, is not recommended (Power *et al.*, 2000).

CR-SPINEL ALTERATION

Cr-spinel is commonly regarded to be resistant to low-grade alteration. It is different with intensively serpentinized ultramafic bodies that show strongly altered Cr-spinels. In general, three optically and chemically heterogeneous spinel phases were recognized, which correspond to proposed alteration stages: (1) unaltered Al-rich spinel cores, (2) the low-alumina chromite formed during stages I and II which is often termed "ferritechromite" and (3) Cr-magnetite or pure magnetite rims or grains. This represents a gradual transformation of Al-rich spinel to ferritechromite and finally to Cr-bearing magnetite. The criteria for alteration are the same as those suggested by Burkhard (1993): (1) optical and chemical inhomogenity; (2) textural changes (zonation with decrease in Mg, Al, Cr towards the margins, porous textures, magnetite rims, *etc.*); (3) detection of SiO_2, ZnO and MnO in Cr-spinels. Cr_2O_3 enrichment during Cr-spinel alteration was observed only at the Dobšiná and Hodkovce localities. The observed Cr-enrichment is interpreted as a reprecipitation caused by locally oxidizing conditions, because serpentinizing fluid contains CO_2 and has oxidizing potential (Burkhard, 1993).

The Cr/(Cr+Al) of primary igneous magnetite is distinct from that of magnetite modified by metamorphism. This ratio is low for primary igneous magnetite: because magnetite appears on the liquidus of mafic magmas there is little Cr (<100 ppm) but still a significant amount of Al present in the melt. Thus primary igneous magnetite plots along the Al-Fe^{3+} join of Cr-Al-Fe^{3+} (Barnes and Roeder, 2001). Magnetite tends to lose Al during metamorphism and the resulting spinel plots along the Cr-Fe^{3+} join of Cr-Al-Fe^{3+} (Fig.7).

A comparable alteration trend of Cr-spinels inherited in laterites from weathered ultramafic rocks from Northern Greece (Edessa area) was referred to by Michailidis (1990). Three main zones in chromites were distinguished (an inner chromite zone, an intermediate ferritechromite zone and a magnetite rim). The major oxides MgO and Al_2O_3 decrease from the chromite core to the "ferritechromite" zone, while FeO increases and Cr_2O_3 either increases or decreases. A characteristic chemical feature of the "ferritechromite" zone is the very high Mn-content (up to 20 wt% MnO) and this zone is also enriched in Si and impoverished in Mg and Al. The zoning and high Mn-content of chromite is considered as a result of serpentinization in the presence of Mn-rich fluids. Such a high Mn content was found also at the Jaklovce locality (MnO is up to 17 wt%). The alteration process is a metasomatic phenomenon, though in reality a "solid state diffusion" in which Mg and Al diffuse out as Fe and Mn ions diffuse in.

Another similar alteration trend was described in serpentinized harzburgites from southern Italy (Mellini *et al*., 2005). Three different kinds of spinel were found: (a) relic, magmatic Al-spinels, (b) hydrothermally altered spinels occurring as "ferritechromite" rims, (c) syn- and post-serpentinization magnetites. As was also found our study, replacement of Al-spinel by ferritechromite rims starts along fractures and progressively affects the Al-spinel sub-grains.

The intensity of alteration (serpentinization) is to a considerable degree reflected by the SiO_2 content in the spinel (Fig. 8). Since we do not expect a high Si content in Cr-spinel, the detection of SiO_2 in Cr-spinel suggests the presence of a sub-microscopic silicate phase (serpentine-group minerals). Direct correlation between the amounts of MgO and SiO_2 (increase of MgO with increase of SiO_2; Fig. 8) points to the presence of submicroscopic serpentine ($Mg_6[(OH)_8 \times Si_4O_{10}]$). A larger portion of the detected MgO should belong to serpentine, because, during serpentinization, spinel loses MgO. TEM observations show, that ferritechromite actually consists of a complex, nanometric association of Cr-magnetite, chlorite and lizardite. Mg and Al, released during the Al-spinel $\rightarrow$ ferritechromite replacement, interact with mesh-textured serpentinite, giving rise to chloritic aureoles (Mellini *et al*., 2005).

Stable spinel in antigorite-serpentinites is Al-poor magnetite, Cr-magnetite or ferritechromite, depending on the local Cr/Fe^{3+} ratio in the rock (Evans and Frost, 1975). With increasing metamorphic grade up to middle amphibolite facies conditions, more chromiferous spinels are encountered, containing modest amounts of Al, due to the fact that chromite is the only phase where Cr could be accommodated. Whether a primary chromite alters during serpentinization to magnetite or ferritechromite is not so much a function of temperature as of the abundance and availability of Cr at the site of alteration (Evans and Frost, 1975).

Overall observations indicate that Al-spinel undergoes dissolution, giving rise to the ferritechromite rim; the new spinel retains Cr and Fe (Cr-magnetite), whereas Al and Mg are fixed in the coexisting layer silicates (chlorite/lizardite). The chemical change reflects hydrothermal metamorphic reactions between magmatic spinels and surrounding post-serpentinization silicate matrix.

CONCLUSIONS

1. The chemical composition of unaltered Cr-spinels from ultramafic bodies from the Western Carpathians and Eastern Alps (Meliatic and Penninic units) suggests a lherzolitic character for the original rocks.

2. Harzburgite parental rocks of the Meliaticum or Penninicum have not been confirmed by analysis of Cr-spinel chemical composition.

3. It is not possible to distinguish ultramafic rocks of the Penninic and Meliatic units on the basis of detailed study of accessory Cr-spinel chemical composition. Consequently, it is not possible to constrain the tectonic setting of the Sedlice body (Meliatic or Penninic?).

4. It was found that a large number of Cr-spinels are altered. Alteration trends of Cr-spinel from ultramafic bodies in the Western Carpathians and the easternmost end of the Eastern Alps are comparable with those from the Central Alps (Burkhard, 1993), Northern Greece (Michailidis, 1990), and southern Italy (Mellini *et al*., 2005). Alteration of Cr-spinel is interpreted here as a gradual transformation of Al-rich spinel to "ferritechromite" and finally to Cr-bearing magnetite. In altered spinels from individual localities, small differences were observed only in MnO, ZnO or SiO_2 contents.

5. The use of detrital spinel chemistry in provenance studies must be carefully treated in cases where spinels are optically and chemically heterogeneous or have higher Mn, Zn, Si contents, especially if the entire grain is altered or only altered fragments are preserved where the textural context of the grains is lost.

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