

THE CRYSTAL CHEMISTRY OF DETRITAL CHROMIAN SPINEL FROM THE SOUTHEASTERN ALPS AND OUTER DINARIDES: THE DISCRIMINATION OF SUPPLIES FROM AREAS OF SIMILAR TECTONIC SETTING?

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ABSTRACT

Chromian spinel is a common heavy mineral in the flysch basins of the southeastern Alps and Outer Dinarides. Various tectonic settings have been found for the suites of chromian spinel studied herein, related to suprasubduction for both Internal and Outer Dinarides, and ocean-floor-spreading zones for the Outer Dinarides. Because the composition of the chromian spinel cannot discriminate between the two areas, we performed crystallochemical studies in order to find some differences. These studies show that it is possible to discriminate between the suprasubduction zones of the Outer and Inner Dinarides by means of the positional parameter u of the oxygen atom, which is close to 0.2625 for spinel grains from Outer Dinarides and greater than 0.2626 for spinel grains from Inner Dinarides. Intracrystalline temperatures ranging from 790 to 1050°C have been calculated for spinels with u close to 0.2625, and 730 to 750°C for those with u higher than 0.2626. These temperatures are consistent with those calculated for Outer and Inner Dinarides, respectively.

Keywords: chromian spinel, flysch, southeastern Alps, Dinarides, positional parameter of oxygen.

SOMMAIRE

Le spinelle chromifère est répandu comme minéral lourd dans les bassins de flysch du secteur sud-est des Alpes et des Dinarides externes. Divers milieux tectoniques ont été attribués aux suites de spinelle chromifère dans notre collection, allant d'un milieu de suprasubduction pour les Dinarides internes et externes, à un milieu de ride océanique pour les Dinarides externes. On ne peut pas faire la discrimination entre les deux endroits en utilisant la seule composition du spinelle. Nous nous sommes donc fiés aux aspects cristallochimiques pour les distinguer. Nous montrons qu'il est possible de discriminer entre le milieu de suprasubduction des Dinarides internes et externes en utilisant le paramètre u décrivant la position de l'atome d'oxygène, près de 0.2625 pour les grains de spinelle des Dinarides externes et supérieure à 0.2626 pour les grains de spinelle des Dinarides internes. Nous avons calculé des températures intracrystallines allant de 790 à 1050°C pour les échantillons de spinelle ayant u près de 0.2625, et allant de 730 à 750°C pour les échantillons où le paramètre u dépasse 0.2626. Ces températures concordent avec celles qui ont été calculées pour les Dinarides externes et internes, respectivement.

(Traduit par la Rédaction)

Mots-clés: spinelle chromifère, flysch, secteur sud-est des Alpes, Dinarides, paramètre de position de l'oxygène.

INTRODUCTION

Chromian spinel is a common mineral in mafic and ultramafic rocks, and its chemical composition is known to be influenced by the geodynamic environments of formation (Irvine 1967, Evans & Frost 1975, Dick & Bullen 1984, Sack & Ghiorsio 1991, Barnes & Roeder 2001). Chromian spinel also occurs as an accessory mineral in detrital rocks, in which it preserves its compositional signature after burial in sedimentary strata, has mechanical stability, and is easy to recognize in both transmitted and reflected light (Cookenboo *et al.*

1997). For these reasons, it has been used in provenance study by several authors (Utter 1978, Press 1986, Pober & Faupl 1988, Arai & Okada 1991, Cookenboo *et al.* 1997, Sciunnach & Garzanti 1997, Lenaz *et al.* 2000, 2001, 2003).

On the basis of the composition of spinel-group minerals from the Claut, Julian, Brkini and Istrian flysch basins, in the southeastern Alps and Outer Dinarides, in Italy, Slovenia and Croatia (Fig. 1), and of the silicate inclusions enclosed in them, Lenaz *et al.* (2000, 2001, 2003) found a clear relationship with various source-rocks. In particular, it became evident, on the basis

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of the possible source-rocks occurring in the nearby areas, that there were continuous supplies of material from the Inner Dinarides from the beginning (Maas-trichtian) until the end of deposition (Upper Eocene). These source areas are characterized by the presence of spinel compositions derived from a suprasubduction zone (SSZ) environment, with harzburgite, island-arc- and back-arc-related suites. Also present were supplies of material from an ocean-floor spreading zone (MORB and Iherzolite-related spinels). The latter materials, of Upper Paleocene to Upper Eocene in age, were identified on the basis of the presence of the Iherzolite-related chromian spinel from the Outer Dinarides.

With the composition of spinel-group minerals, we successfully discriminated between different tectonic settings, but this approach was not very useful in discriminating between two different source-areas developed in the same tectonic setting (*i.e.*, SSZ of the Inner and Outer Dinarides). Our aim here is to document the crystal chemistry of spinel-group minerals from different flysch basins of the southeastern Alps

and Outer Dinarides area, and to test whether crystal chemistry can help distinguish their area of provenance despite the similarity in tectonic setting.

GEOLOGICAL SETTING

In the Western Tethys, the Jurassic period was characterized by seafloor spreading to the west and north of the Adria plate, causing the subduction of Tethys along the eastern border of the Adriatic promontory (Channell & Horvath 1976, Robertson & Karamata 1994). The Apulian plate fractured successively, and small troughs formed within it. By the end of the Jurassic, a Periadriatic (Vardar) ocean formed (Channell & Kozur 1997). In Early and Middle Cretaceous, plate motion involved further seafloor spreading, so that island arcs and part of the eastern microplate collided, resulting in two suture zones, from which the Dinarides originated, separated by the Drina-Ivanjica microcontinent (Robertson & Karamata 1994, Lawrence *et al.* 1995). In the Late Cretaceous, the subduction of oceanic

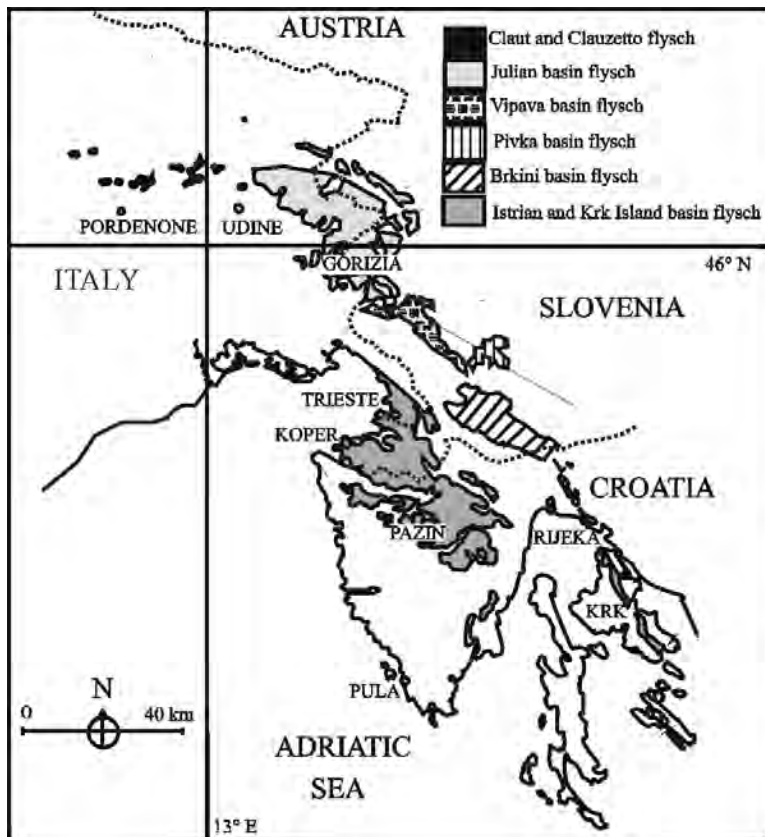


FIG. 1. Flysch deposits of the southeastern Alps and Outer Dinarides (Lenaz *et al.* 2003).

crust occurred to the north of the Adria plate, which was followed by collision and formation of ophiolite complexes (*e.g.*, first emplacement of ophiolite accompanied by high-pressure metamorphism, Pamić *et al.* 1998). Closure culminated in continental collision along Alpine orogenic belts in the Late Cretaceous to Early Tertiary (Lawrence *et al.* 1995, Channell & Kozur 1997). The progressive contraction of oceanic crust caused the uplift of previously rifted continental margin and platforms, and the formation of foredeep basins of flysch sediments.

In northeastern Italy, western Slovenia, the Istria Peninsula (Croatia) and the Kvarner Islands (Croatia), several of these flysch basins are exposed (Fig. 1). They are: the Claut and Clauzetto basins (CL hereafter), spanning from the Upper Paleocene to the Eocene (Sarti 1979); the Julian Basin (JB), spanning from the Maastrichtian to the Middle Eocene (Tunis & Venturini 1989), the Vipava Basin (VI), spanning from Paleocene to Early Eocene (Engel 1974), the Pivka Basin (PK), spanning from Lower to Middle Eocene (Pavlovec *et al.* 1991), the Brkini Basin (BK), spanning from the Early Eocene to the Middle Eocene (Tunis & Venturini 1996), and the Istrian Basin and Krk Island (IB), spanning from the Middle Eocene to the Late Eocene (Marincic *et al.* 1996). The important details were provided by Lenaz *et al.* (2000, 2001, 2003).

All of these basins contain sandstones carrying heavy minerals (*e.g.*, chromian spinel, garnet, tourmaline, rutile, zircon, staurolite, chloritoid, pyroxene, amphibole). Chromian spinel occurs in all sandstones in a significant amount (Magdalenic 1972, Lenaz & Princivalle 1996, Lenaz *et al.* 2000, 2001, 2003).

EXPERIMENTAL

About 150 samples of sandstone were crushed, and the spinel grains (octahedral crystals and fragments) were magnetically separated and sought in the 63–177 μm fraction. More than 700 grains were chemically analyzed, and the results are presented in Lenaz *et al.* (2000, 2001, 2003).

Single-crystal X-ray-diffraction spectra of 26 crystals of spinel were recorded on an automated KUMA–KM4 (K-geometry) diffractometer, using $\text{MoK}\alpha$ radiation, monochromatized with a flat crystal of graphite at the University of Trieste. The cell parameter a was obtained with the same standard program of the diffractometer, centering in a very careful way 24 equivalent reflections of (12 8 4) at about 90° of 2θ . The selected crystals are from CL (two crystals), JB (11 crystals), VI (one crystal), PK (one crystal), BK (four crystals) and IB basins (seven crystals). Each crystal represents a different sandstone horizon in the whole stratigraphic column of the basins. VI and PK are represented by only one crystal owing to the very low proportion of siliciclastic material.

Data collection was made up to a 2θ of 110° with $\omega - 2\theta$ continuous scan mode, and counting time from 20 to 40 s, depending on standard deviation of the peaks. Up to six equivalents were measured, so that after correction for Lorentz and polarization effects and secondary isotropic extinction, a set of about 211 observed structural factors F_{0hkl} was obtained from each experiment. Correction for absorption was performed according to North *et al.* (1968).

Structural refinement using the SHELX–93 program (Sheldrick 1993) was carried out using $F_o^2_{hkl}$ in the space group $Fd\bar{3}m$ (with origin at m), because no evidence of a different symmetry was found. Refined parameters were scale factor, coordinate of the oxygen atom, occupancies of the tetrahedral and octahedral sites, and displacement parameter (U). Site occupancies can vary with the ionization level of the oxygen scattering curve and, to a lesser extent, on the ionization level of the cations. The best results were obtained using scattering curves for fully ionized species, Mg *versus* Fe and Cr *versus* Al at the T and M sites, respectively, and a ionization level of 70% for oxygen. The constraints of full site-occupancy and equal displacement parameters were adopted without chemical constraints.

After X-ray data collection, the same crystals used for X-ray analyses were mounted on glass slides, polished and carbon-coated for electron-microprobe analysis. Chemical analyses were performed on 15 refined crystals (the other crystals were unfortunately lost during preparation owing to their very small dimension). Ten to fifteen spot-analyses were made on the same crystals as used for X-ray data collection using a CAMECA CAMEBAX electron microprobe operating at 15 kV and 15 nA and 20 s counting time for both peak and total background. Synthetic oxide standards (MgO, FeO, MnO, ZnO, NiO, Al_2O_3 , Cr_2O_3 , TiO_2 and SiO_2) were used. The raw data were reduced with a PAP-type correction software provided by CAMECA.

Results are considered accurate to $\pm 2\text{--}3\%$ for major elements and 10% for minor elements. Structural and chemical data are listed in Table 1 and 2, respectively. Cation partitioning (Table 2) was calculated on the basis of average chemical and crystallographic data, according to the procedure described in Carbonin *et al.* (1996).

RESULTS

Structural data

In spinel-group minerals, the anions form a nearly cubic close-packed array, and the cations fill part of the tetrahedral (T) and octahedral (M) interstices available in the framework. Each oxygen atom is linked to three octahedrally and one tetrahedrally coordinated cations, lying respectively on opposite sides of the layer of oxygen atoms. Hafner (1960) highlighted the role played by the oxygen parameter u on the deformation

TABLE 1. STRUCTURAL DATA FOR THE SPINEL GRAINS ANALYZED

Sample	CL 1	BG 17	BG 17A	BG 17B	BG 23	BG 24	BG 26	VI _{DOL}
<i>a</i> Å	8.2837(1)	8.2905(1)	8.2339(2)	8.2367(5)	8.3232(2)	8.1947(1)	8.2892(1)	8.2134(2)
<i>u</i>	0.26291(7)	0.26271(5)	0.26254(6)	0.26308(4)	0.26244(8)	0.26245(6)	0.26249(6)	0.26268(8)
m.a.n. <i>M</i>	19.92(14)	20.18(12)	18.35(4)	18.19(4)	21.16(19)	16.83(8)	20.41(18)	17.34(24)
m.a.n. <i>T</i>	20.57(14)	19.45(11)	17.28(3)	17.74(4)	20.48(16)	15.82(6)	18.41(15)	17.61(16)
<i>T</i> - <i>O</i>	1.979(1)	1.977(1)	1.961(1)	1.957(1)	1.981(1)	1.951(1)	1.974(1)	1.959(1)
<i>M</i> - <i>O</i>	1.970(1)	1.972(1)	1.961(1)	1.970(1)	1.983(1)	1.952(1)	1.974(1)	1.955(1)
Ueq _{<i>M</i>}	0.0037(1)	0.0047(1)	0.0060(1)	0.0040(1)	0.0052(1)	0.0051(1)	0.0047(1)	0.0041(1)
Ueq _{<i>T</i>}	0.0063(1)	0.0070(1)	0.0083(1)	0.0063(1)	0.0078(1)	0.0069(1)	0.0065(1)	0.0065(1)
Ueq _{<i>O</i>}	0.0060(2)	0.0071(1)	0.0089(1)	0.0063(1)	0.0077(2)	0.0083(2)	0.0069(1)	0.0076(2)
N _{ref}	185	184	185	175	192	171	198	167
R1	1.89	1.97	2.55	2.05	1.80	1.78	2.09	2.18
wR2	4.20	3.31	5.11	3.82	4.58	3.50	4.56	3.75
Goof	1.375	1.196	1.278	1.165	1.304	1.286	1.274	1.098

Sample	BK 30	BK 35	BK36	IB _{PIC01}	IB _{PIC02}	IB _{KRKV3A}	IB _{KRKV3B}
<i>a</i> Å	8.2453(2)	8.2701(2)	8.1904(3)	8.1256(1)	8.1513(3)	8.2977(1)	8.2416(1)
<i>u</i>	0.26246(7)	0.26248(7)	0.26235(6)	0.26374(10)	0.26349(9)	0.26251(8)	0.26283(7)
m.a.n. <i>M</i>	18.59(11)	19.93(26)	17.45(12)	14.19(18)	14.49(18)	20.80(17)	18.68(13)
m.a.n. <i>T</i>	17.31(10)	17.82(16)	16.438(11)	15.41(17)	15.29(15)	19.82(14)	17.67(10)
<i>T</i> - <i>O</i>	1.963(1)	1.969(1)	1.948(1)	1.953(1)	1.955(1)	1.976(1)	1.968(1)
<i>M</i> - <i>O</i>	1.964(1)	1.970(1)	1.952(1)	1.926(1)	1.934(1)	1.976(1)	1.960(1)
Ueq _{<i>M</i>}	0.0047(1)	0.0044(1)	0.0046(1)	0.0047(2)	0.0026(2)	0.0043(1)	0.0037(1)
Ueq _{<i>T</i>}	0.0071(1)	0.0069(1)	0.0067(2)	0.0066(3)	0.0051(2)	0.0071(1)	0.0060(1)
Ueq _{<i>O</i>}	0.0080(2)	0.0069(2)	0.0079(2)	0.0070(3)	0.0059(3)	0.0065(2)	0.0064(2)
N _{ref}	168	180	180	150	154	177	169
R1	1.67	1.83	1.61	2.86	2.59	1.76	1.77
wR2	3.41	3.58	4.39	5.56	5.64	3.72	3.89
Goof	1.206	1.336	1.352	1.141	1.224	1.245	1.247

a: cell edge (Å); *u*: oxygen positional parameter; m.a.n.: mean atomic number; *T*-*O* and *M*-*O*: bond distances (Å); Ueq_{*O*}, Ueq_{*M*}, Ueq_{*T*}: equivalent thermal factors for O, *M* site and *T* site (Å²). N_{ref}: unique reflections from set of observed ones [$I > 3\sigma(I)$]; R1, wR2, Goof as defined in Sheldrick (1993). Estimated standard deviations in brackets.

of the octahedral site along the direction of the 3-fold axis. Only the position of the oxygen atom and the value of the cell dimension may vary within the structure, whereas the *T* and *M* cations are fixed in special positions. The oxygen coordinate *u* depends only on the ratio (*M*-*O*)/(*T*-*O*). For *u* < 0.2625, (*M*-*O*) is greater than (*T*-*O*), and *vice versa* for *u* > 0.2625. The oxygen positional parameter *u* is one of the most important considered in this study. Princivalle *et al.* (1989) demonstrated that within a single suite of ultramafic rocks, the ratio of the *M*-*O* to *T*-*O* bond lengths, and consequently *u*, are constant, despite important changes in composition. Conversely, *u* may differ in suites with similar bulk-composition but different degrees of Mg-Al order between *T* and *M* sites. This pattern is related to the physical environment; for example, it depends on the cooling history undergone by the rocks.

In the samples studied, *u* shows a relatively large variability, between 0.2624 and 0.2637. In the CL suite of samples, the *u* value of the oldest sample is about 0.2629, whereas in the youngest one is about 0.2625. In the JB suite of samples, *u* ranges from 0.2624 to 0.2631.

The only analyzed sample from the VI suite shows *u* equal to 0.2627. In the PK and BK suites, *u* is invariably lower than 0.2625. In the IB suite, *u* ranges from 0.2625 to 0.2637. Previous studies on three samples of spinel from IB (Lenaz & Princivalle 1996) showed *u* equal to 0.2626.

Chemical composition

Lenaz *et al.* (2000, 2001, 2003) studied the same flysch basins considered here; on the basis of the composition of the spinel and of the silicate-melt inclusions present in some of them, they showed that there are spinel samples that can be related to rocks with peridotitic or mantle-derived volcanic rocks. By analogy with spinel from similar rocks worldwide, low Ti content and high Fe²⁺/Fe³⁺ value are considered typical of a spinel derived from a mantle peridotite. The peridotitic group of spinel grains contain less than 0.2 wt% TiO₂ and have a FeO/Fe₂O₃ value greater than 3, whereas the volcanic group show greater than 0.2 wt% TiO₂ and a FeO/Fe₂O₃ value less than 4.

Regarding spinel samples derived from peridotitic rocks, according to the diagram $Mg\#$ [*i.e.*, $100 Mg/(Mg + Fe^{2+})$] versus $Cr\#$ [*i.e.*, $100 Cr/(Cr + Al)$] proposed by Dick & Bullen (1984), they seem to be related mostly to type-II peridotite rocks ($Cr\# > 40$), although spinel from type-I peridotite rocks is present also. The spinels from the JB and IB basins considered herein may be related to both type-II and type-I peridotites (Fig. 2). Peridotites are classified as type I if the $Cr/(Cr + Al)$ value of the spinel does not exceed 60. This limit coincides with the upper $Cr/(Cr + Al)$ limit of abyssal peridotites. According to Dick & Bullen (1984), peridotites in ophiolitic suites with $Cr/(Cr + Al)$ values similar to those of the abyssal peridotites seem to have evolved in a mid-ocean ridge setting. This classification is comparable to that used for the subdivision of ophiolites based on the Ti content of basaltic members and gabbroic intrusive bodies by Beccaluva *et al.* (1980, 1983). High Ti contents are typical of mid-ocean-ridge magmatism, the residua typically exhibiting a lherzolitic character. Peridotites containing spinel with $Cr/(Cr + Al)$ values essentially above 60 are classified as type III. The formation of type-III peridotites is related to early stages of arc formation in environments of oceanic crust. Type-III peridotites correspond to the harzburgitic and dunitic residua of the low-Ti and very low-Ti ophiolites related to the island arc and backarc system (Beccaluva *et al.* 1980, 1983). The spinels of type-II peridotites span the greatest range of $Cr/(Cr + Al)$ and may represent a transitional classification comprising type-I and type-III peridotites.

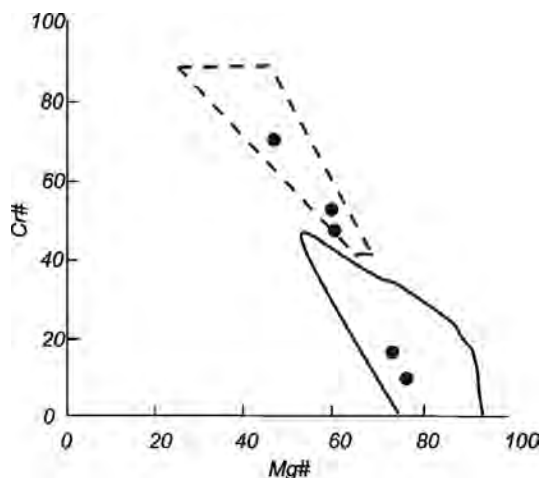


FIG. 2. Relationships between $Mg\#$ [$100 Mg/(Mg + Fe^{2+})$] versus $Cr\#$ [$100 Cr/(Cr + Al)$] in spinel from peridotitic rocks ($TiO_2 < 0.2$ wt%) from flysch and ophiolites from the Dinarides (Maksimović & Jovanović 1984). Dotted line: Inner Dinarides; solid line: Outer Dinarides.

Regarding spinel grains derived from magmatic rocks, according to the Al_2O_3 versus TiO_2 diagram proposed by Lenaz *et al.* (2000) and Kamenetsky *et al.* (2001) and in analogy with spinel compositions found in the same flysch basins (where the composition of silicate inclusions was studied as well), they seem to be related to a subduction-related back-arc environment ($0.2-1$ wt% TiO_2 , $15-25$ wt% Al_2O_3), intraplate ($TiO_2 > 1$ wt%, $10-15$ wt% Al_2O_3) and MORB-type back-arc basalts ($TiO_2 > 0.2$ wt%, $Al_2O_3 > 20$ wt%). Spinel compositions from the CL basin point to subduction-related back-arc affinity. Those from the JB basin are attributed to subduction-related back-arc, MORB-type back-arc, and intraplate basalts. Spinel compositions from the VI basin are related to MORB-type back-arc, and those from BK and IB seem related both to subduction-related and MORB-type back-arc basalts (Fig. 3).

DISCUSSION

The positional parameter u of the oxygen atom may be related to the thermal history of the source rock, and its increase (*i.e.*, increased order) may be related to a drop of the intracrystalline closure temperature. The closure temperature depends on the cooling rate of the host rock so that, for rapid cooling, the closure of intracrystalline exchange between T and M sites occurs at a higher temperature. Thus the samples with

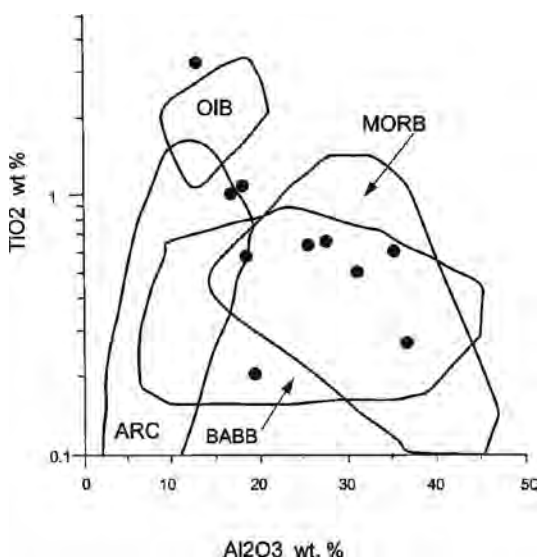


FIG. 3. Al_2O_3 versus TiO_2 (wt%) relationship in spinel from volcanic ($TiO_2 > 0.2$ wt%) rocks from flysch. ARC: island arc basalts, OIB: ocean island basalts, BABB: back-arc basin basalts, MORB: mid-ocean ridge basalts. ARC, OIB, MORB fields are from Kamenetsky *et al.* (2001), and the BABB field from Lenaz *et al.* (2000).

TABLE 2. CHEMICAL COMPOSITION AND CATION DISTRIBUTIONS OF SPINEL GRAINS STUDIED

Sample	CL 1	BG 17	BG 17A	BG 17B	BG 23	BG 24	BG 26	V_{Dol}
Al ₂ O ₃ wt.%	19.19(57)	18.33(25)	28.41(64)	27.24(88)	12.68(35)	37.80(71)	16.96(22)	32.44(58)
Cr ₂ O ₃	44.65(29)	43.36(39)	35.58(31)	40.81(53)	43.56(32)	28.91(43)	45.79(87)	32.59(47)
MgO	9.37(25)	10.82(15)	15.58(25)	13.01(19)	10.19(94)	17.84(18)	11.48(27)	15.16(50)
MnO	n.d.	n.d.	0.19(4)	0.24(4)	n.d.	n.d.	n.d.	n.d.
FeO _{tot}	25.82(49)	25.63(39)	18.84(34)	17.61(33)	28.43(70)	14.72(25)	24.26(48)	17.95(56)
TiO ₂	0.58(4)	1.15(3)	0.67(2)	0.11(2)	3.30(13)	0.27(4)	0.98(3)	0.53(2)
ZnO	0.23(10)	0.19(11)	n.d.	0.26(9)	0.20(9)	0.05(4)	0.16(9)	0.05(8)
NiO	0.07(5)	0.12(7)	0.14(2)	0.06(4)	0.25(6)	0.14(5)	0.13(3)	0.24(7)
SiO ₂	n.d.	0.04(5)	0.12(2)	0.05(1)	0.03(5)	0.10(2)	0.05(3)	0.13(3)
Sum	100.45	100.36	100.17	99.58	99.50	100.23	100.50	99.51
T site								
Al <i>apfu</i>	0.001	0.005	0.051	0.034	0.001	0.089	0.018	0.045
Fe ²⁺	0.516	0.497	0.312	0.390	0.517	0.228	0.433	0.312
Fe ³⁺	0.065	0.027	0.055	0.030	0.057	0.032	0.024	0.082
Mg	0.413	0.464	0.574	0.533	0.419	0.647	0.520	0.556
Mn	-	-	0.005	0.006	-	-	-	-
Si	-	0.002	0.003	0.001	0.001	0.003	0.001	0.004
Zn	0.005	0.005	0.000	0.006	0.005	0.001	0.004	0.001
M site								
Al <i>apfu</i>	0.722	0.678	0.937	0.939	0.491	1.165	0.610	1.101
Fe ²⁺	0.046	0.014	0.013	0.012	0.053	0.031	0.045	0.018
Fe ³⁺	0.060	0.143	0.089	0.017	0.153	0.056	0.147	0.012
Mg	0.031	0.047	0.110	0.055	0.080	0.099	0.023	0.121
Cr	1.125	1.087	0.833	0.973	1.133	0.641	1.149	0.731
Ni	0.002	0.003	0.003	0.001	0.007	0.003	0.003	0.006
Ti	0.014	0.028	0.015	0.003	0.082	0.005	0.023	0.011

Up to 15 spot analyses were performed on each crystal. Numbers within parentheses are the estimated standard deviations and refer to last digits.

u less than or close to 0.2625 cooled more quickly than those with u higher than 0.2625. Moreover, our samples with u higher than 0.2625 have a major variability in u , which indicates the presence of different and lower rates of cooling compared to those samples with u less than 0.2625. In Figure 4, T -O versus M -O bond distances of all the spinel samples studied by means of X-ray diffraction are compared. There are three different groups; the first group comprises spinel samples with u values ranging from about 0.2626 to 0.2629, which correspond to samples found in flysch basins older than 56 Ma (full circle). The second group comprises spinel grains with u values very close to 0.2625, which correspond to spinel found in flysch basins younger than 56 Ma (open circles); the third group comprises spinel grains with u values ranging from about 0.2625 to 0.2637 and corresponds to grains found in the IB suite (open triangles). Therefore, different cooling histories can be inferred for these samples.

Considering their chemical composition, one can see that spinel grains from peridotites show different values of u depending on their affinity to type-I or

type-II peridotites. Those belonging type-II peridotite as well as one spinel grain studied by Lenaz & Princivalle (1996) show a value of u ranging from 0.2625 to 0.2631 (Fig. 5a), whereas those belonging type-I peridotites show a value of u ranging from 0.2635 to 0.2637. There is a linear correlation between Al content and u value. Grains of chromian spinel from various suites of ultramafic rocks commonly show u values ranging from 0.2625 to 0.2631 (Della Giusta *et al.* 1986, Princivalle *et al.* 1989, Carraro 2003), similar to those found here. In our experience, it is quite difficult to find in peridotitic rocks spinel with a value of u between 0.2635 and 0.2637. In the literature, such values were found only in spinel grains from the Balmuccia complex, which were formed by incongruent melting of the clinopyroxene present in the original peridotite and by subsequent crystallization during the differentiation processes of the ascending melts (Basso *et al.* 1984, Princivalle *et al.* 1989), and in those from metamorphosed pyroxenites of the Dinarides (Lenaz *et al.* 2002). As there is no correspondence between their composition and literature data on structural parameter, at the moment,

TABLE 2 (cont'd). CHEMICAL COMPOSITION AND CATION DISTRIBUTIONS OF SPINEL GRAINS STUDIED

Sample	BK 30	BK 35	BK 36	IB _{PIC01}	IB _{PIC02}	IB _{KRRV3A}	IB _{KRRV3B}
Al ₂ O ₃ wt.%	26.59(42)	19.40(45)	37.31(80)	58.97(35)	49.95(56)	14.44(38)	26.05(68)
Cr ₂ O ₃	38.73(61)	48.73(70)	28.71(80)	8.78(24)	18.01(54)	55.10(50)	42.61(91)
MgO	14.46(38)	12.21(20)	16.83(81)	20.19(28)	18.84(30)	9.38(17)	13.18(42)
MnO	n.d.	n.d.	n.d.	0.11(5)	0.15(7)	n.d.	n.d.
FeO _{tot}	19.34(81)	19.38(49)	15.42(20)	11.04(23)	11.93(37)	20.46(14)	17.80(25)
TiO ₂	0.65(4)	0.21(2)	0.52(6)	0.07(2)	0.04(2)	0.18(4)	0.05(2)
ZnO	0.11(7)	0.14(7)	0.02(7)	0.15(7)	0.18(6)	0.30(7)	0.18(8)
NiO	0.10(6)	0.11(4)	0.21(8)	0.36(7)	0.24(9)	0.07(12)	0.10(2)
SiO ₂	n.d.	n.d.	n.d.	0.03(2)	0.04(3)	0.06(1)	0.04(3)
Sum	100.5	100.5	99.50	99.83	99.54	100.05	100.22
T site							
<i>Al apfu</i>	0.056	0.041	0.131	0.103	0.093	0.043	0.023
Fe ²⁺	0.359	0.415	0.271	0.213	0.233	0.387	0.531
Fe ³⁺	0.017	0.001	0.018	0.017	0.007	0.014	0.016
Mg	0.565	0.540	0.580	0.661	0.659	0.551	0.421
Mn	-	-	-	0.002	0.003	-	-
Si	-	-	-	0.001	0.001	0.001	0.002
Zn	0.003	0.003	0.000	0.003	0.004	0.004	0.007
M site							
<i>Al apfu</i>	0.888	0.674	1.133	1.688	1.494	0.885	0.523
Fe ²⁺	0.001	0.014	0.008	0.000	0.000	0.013	0.014
Fe ³⁺	0.095	0.074	0.049	0.008	0.023	0.034	0.001
Mg	0.082	0.028	0.142	0.114	0.096	0.046	0.036
Cr	0.916	1.202	0.652	0.180	0.381	1.019	1.422
Ni	0.003	0.003	0.005	0.008	0.005	0.002	0.002
Ti	0.015	0.005	0.011	0.002	0.001	0.001	0.004

Up to 15 spot analyses were performed on each crystal. Numbers within parentheses are the estimated standard deviations and refer to last digits.

it is difficult to relate structural data and tectonic setting for spinel grains derived from peridotites.

Considering spinels in mantle-derived volcanic rocks, the u values range from 0.2624 to 0.2630, but a u value lower than or close to 0.2625 is present only in the spinel grains from rocks younger than 56 Ma (Fig. 5b). Note that in this case, no correlation between Al content and u value exists. On the basis of their Al content, the spinel compositions here studied may be assigned to a single tectonic setting, but differences in the oxygen parameter u seem to indicate that they underwent a different cooling history.

Lenaz *et al.* (2000, 2001, 2003) suggested that supplies of spinel grains enclosed in the sandstones of the various flysch basins here considered are related to the Dinarides, where rocks with spinel compositions similar to those established here are known to occur. According to the interpretation of the tectonic evolution of the Mesozoic Tethys in Serbia given by Robertson & Karamata (1994), and its relationships with the surrounding Cretaceous – Tertiary flysch basins (Lenaz *et al.* 2003), the main spinel-bearing detritus from the

suprasubduction zone of the Vardar Ocean (spinel from peridotite with harzburgitic affinity and spinel of volcanic origin from subduction-related back-arc, island arc and intraplate extrusive rocks) was supplied in the Julian Basin during the beginning of deposition in the Maastrichtian. These supplies probably continued until the end of deposition in the Middle Eocene flysch of the Istrian basin. From the Upper Paleocene onward (56 Ma), new supplies from MORB-type tectonic settings were added to the previously encountered supplies. These supplies are probably related to the Pindos Ocean. From the Middle Eocene onward, Iherzolite- and SSZ-related supplies from the Pindos Ocean filled the Brkini and Istrian basins, but there is also evidence of reworked material from the Vardar Ocean.

In a study of the thermal evolution of the Dinarides, Maksimović & Jovanović (1984) concluded that the values of temperature for the olivine–spinel association in the Internal Zone are in the range 560–790°C, whereas those for the Outer Dinarides are 800–1220°C. In the peridotites of the Outer Dinarides, they considered cation exchange between olivine and spinel only

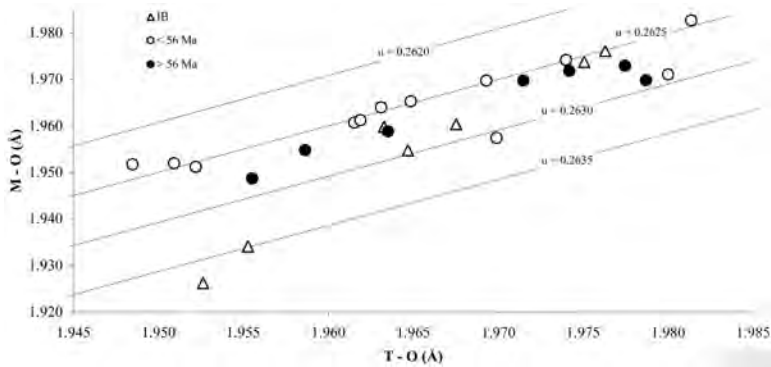


FIG. 4. T-O versus M-O bond distances. Full circle: spinel from sandstones older than 56 Ma; open circle: spinel from sandstones younger than 56 Ma; open triangle: spinel from sandstones from the Istrian basin.

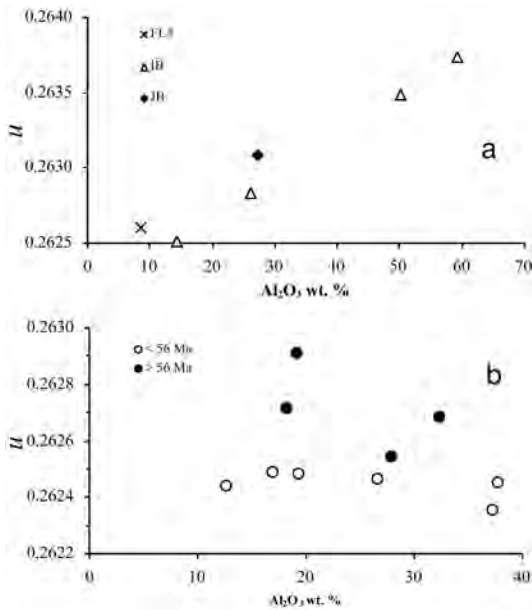


FIG. 5. Al_2O_3 wt% versus the oxygen positional parameter u . a) spinel from peridotitic rocks. Full diamond: spinel from the Julian Basin; Open triangle: spinel from the Istrian basin, cross: FL3 (Lenaz & Princivalle 1996). b) Magmatic spinel. Full circle: spinel from sandstones older than 56 Ma; open circle: spinel from sandstones younger than 56 Ma.

occurred over a longer period and persisted to lower temperatures, which produced greater homogeneity in the minerals and smaller variations in the limiting temperatures for the individual ultrabasic intrusive complexes.

In the flysch samples older than 56 Ma, it is possible to find spinel samples with u values spanning from 0.2626 to 0.2630. In the flysch samples younger than 56 Ma, it is possible to find spinel samples with a value of u spanning from 0.2624 to about 0.2625, with a few of them pointing to higher values. It seems possible that spinel samples with a value of u lower than 0.2625 could be related to the Pindos Ocean and is missing in older samples. Those samples with a higher value of u than 0.2625 could be derived from the Vardar Ocean for older samples and recycled Vardar Ocean in younger samples.

Using the thermometer proposed by Princivalle *et al.* (1999), temperatures ranging from 790 to 1050°C are calculated for spinel samples from mantle-derived volcanic rocks with a value of u close to 0.2625, and 730 to 750°C for those with u higher than 0.2625 (Fig. 6). This finding may indicate that the spinel grains enclosed in sandstones of different age (*e.g.*, older or younger than 56 Ma) are related to different sources, and that the source rocks may have been subjected to a different thermal regime, in agreement with geological reconstructions by Robertson & Karamata (1994) and Lenaz *et al.* (2003) and the geothermometric estimates of Maksimović & Jovanović (1984).

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during the high-temperature stage of subsolidus cooling, and it then halted because of a sharp increase in the cooling rate. In the Internal Dinarides, ion exchange

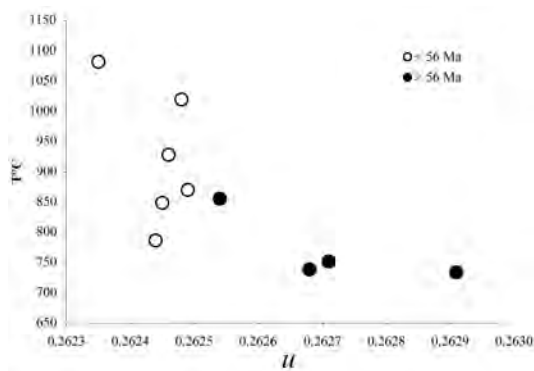


FIG. 6. Intracrystalline temperature versus the oxygen positional parameter u . Full circle: spinel from sandstones older than 56 Ma; open circle: spinel from sandstones younger than 56 Ma.

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REFERENCES

- ARAI, S. & OKADA, H. (1991): Petrology of serpentine sandstone as a key to a tectonic development of serpentine belts. *Tectonophysics* **195**, 65-81.
- BARNES, S.J. & ROEDER, P.L. (2001): The range of spinel compositions in terrestrial mafic and ultramafic rocks. *J. Petrol.* **42**, 2279-2302.
- BASSO, R., COMIN-CHIARAMONTI, P., DELLA GIUSTA, A. & FLORA, O. (1984): Crystal chemistry of four Mg-Fe-Al-Cr spinels from the Balmuccia peridotite (Western Italian Alps). *Neues Jahrb. Mineral., Abh.* **150**, 1-10.
- BECCALUVA, L., GIROLAMO, D., MACCIOTTA, G. & MORRA, V. (1983): Magma affinities and fractionation trends in ophiolites. *Ophioliti* **8**, 307-324.
- _____, PICCARDO, G.B. & SERRI, G. (1980): Petrology of Northern Apennine ophiolites and comparison with other Tethyan ophiolites. In *Proc. Int. Ophiolite Symp.* (A. Panayotou, ed.). *Geological Survey of Cyprus*, 314-331.
- CARBONIN, S., RUSSO, U. & DELLA GIUSTA, A. (1996): Cation distribution in some natural spinels from X-ray diffraction and Mössbauer spectroscopy. *Mineral. Mag.* **60**, 355-368.
- CARRARO, A. (2003): Crystal chemistry of Cr-spinels from a suite of spinel peridotite mantle xenoliths from the Predazzo area (Dolomites, northern Italy). *Eur. J. Mineral.* **15**, 681-688.
- CHANNELL, J.E.T. & HORVATH, F. (1976): The African / Adriatic promontory as a palaeogeographic premise for alpine orogeny and plate movements in the Carpatho-Balkan region. *Tectonophysics* **35**, 71-101.
- _____, & KOZUR, H.W. (1997): How many oceans? Meliata, Vardar, and Pindos oceans in Mesozoic Alpine paleogeography. *Geology* **25**, 183-186.
- COOKENBOO, H.O., BUSTIN, R.M. & WILKS, K.R. (1997): Detrital chromian spinel compositions used to reconstruct the tectonic setting of provenance: implications for orogeny in the Canadian Cordillera. *J. Sed. Res.* **67**, 116-123.
- DELLA GIUSTA, A., PRINCIVALLE, F. & CARBONIN, S. (1986): Crystal chemistry of a suite of natural Cr-bearing spinels with $0.15 < Cr < 1.07$. *Neues Jahrb. Mineral., Abh.* **155**, 319-330.
- DICK, H.J.B. & BULLEN, T. (1984): Chromian spinel as a petrogenetic indicator in abyssal and alpine-type peridotites and spatially associated lavas. *Contrib. Mineral. Petrol.* **86**, 54-76.
- ENGEL, W. (1974): Sedimentologische untersuchungen im Flysch des Beckens von Ajdovščina (Slowenien). *Göttinger Arb. Geol. Paläont.* **16**, 71 p.
- EVANS, B.W. & FROST, B.R. (1975): Chrome spinels in progressive metamorphism – a preliminary analysis. *Geochim. Cosmochim. Acta* **39**, 959-972.
- HAFNER, S. (1960): Metalloide mit Spinellstruktur. *Schweiz. Mineral. Petrogr. Mitt.* **40**, 208-242.
- IRVINE, T.N. (1967): Chromian spinel as a petrogenetic indicator. II. Petrological applications. *Can. J. Earth Sci.* **4**, 71-103.
- KAMENETSKY, V., CRAWFORD, A.J. & MEFFRE, S. (2001): Factors controlling chemistry of magmatic spinel: an empirical study of associated olivine, Cr-spinel and melt inclusions from primitive rocks. *J. Petrol.* **42**, 655-671.
- LAWRENCE, S.R., TARI-KOVACIC, V. & GJUKIC, B. (1995): Geological evolution model of the Dinarides. *Nafta* **46**, 103-113.
- LENAZ, D., ALBERTI, A., TUNIS, G. & PRINCIVALLE, F. (2001): A heavy mineral association and its paleogeographical implications in the Eocene Brkini flysch basin (Slovenia). *Geol. Carpathica* **52**, 239-245.
- _____, GOZZI, E., CVETKOVIC, V., RESIMIC SARIC, K. & PRINCIVALLE, F. (2002): Crystal-chemistry of clinopyroxenes and Cr-spinels from two Serbian pyroxenites: equilibration conditions. *Plinius* **28**, 186-187 (abstr.).
- _____, KAMENETSKY, V.S., CRAWFORD, A.J. & PRINCIVALLE, F. (2000): Melt inclusions in detrital spinel from SE Alps (Italy-Slovenia): a new approach to provenance studies of sedimentary basins. *Contrib. Mineral. Petrol.* **139**, 748-758.

- _____, _____ & PRINCIVALLE, F. (2003): Cr-spinel supply in Brkini, Istrian and Krk Island flysch basins (Slovenia, Italy and Croatia). *Geol. Mag.* **140**, 335-342.
- _____, _____ & PRINCIVALLE, F. (1996): Crystal-chemistry of detrital chromites in sandstones from Trieste (NE Italy). *Neues Jahrb. Mineral., Monatsch.*, 429-434.
- MAGDALENIC, Z. (1972): Sedimentologija Fliških naslaga srednje Istre (Sedimentology of central Istra flysch deposits). *Acta Geologica Zagreb* **7**(2), 71-100.
- MAKSIMOVIĆ, Z. & JOVANOVIĆ, L. (1984): The thermal evaluation of the ultrabasites in the Central and Internal Dinarides (Yugoslavia). *Geochem. Int.* **21**(2), 59-70.
- MARINCIC, S., ŠPARICA, M., TUNIS, G. & UCHMAN, A. (1996): The Eocene flysch deposits of the Istrian peninsula in Croatia and Slovenia: regional, stratigraphic, sedimentological and ichnological analyses. *Annales – Annals for Istrian and Mediterranean Studies* **9**, 139-156.
- NORTH, A.C.T., PHILLIPS, D.C. & SCOTT-MATHEWS, F. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.
- PAMIĆ, J., GUČIĆ, I. & JELASKA, V. (1998): Geodynamic evolution of the Central Dinarides. *Tectonophysics* **297**, 251-268.
- PAVLOVEC, R., KNEZ, M., DROBNE, K. & PAVŠIĆ, J. (1991): Profiles: Košana, Sv. Trojica and Leskovec; the disintegration of the carbonate platform. In Field Trip Guidebook. IGCP Project 286 – Early Paleogene Benthos, Second Meeting (Postojna). Univ. of Ljubljana, Ljubljana (69-72).
- POBER, E. & FAUPL, P. (1988): The chemistry of detrital spinels and its implications for the geodynamic evolution of the Eastern Alps. *Geol. Rundsch.* **77**, 641-670.
- PRESS, S. (1986): Detrital spinels from alpinotype source rocks in the Middle Devonian sediments of the Rhenisch Massif. *Geol. Rundsch.* **75**, 333-340.
- PRINCIVALLE, F., DELLA GIUSTA, A. & CARBONIN, S. (1989): Comparative crystal chemistry of spinels from some suites of ultramafic rocks. *Mineral. Petrol.* **40**, 117-126.
- _____, _____, DE MIN, A. & PICCIRILLO, E.M. (1999): Crystal chemistry and significance of cation ordering in Mg–Al rich spinels from high grade hornfels (Predazzo–Monzoni, NE Italy). *Mineral. Mag.* **63**, 257-262.
- ROBERTSON, A.H.F. & KARAMATA, S. (1994): The role of subduction–accretion processes in the tectonic evolution of the Mesozoic Tethys in Serbia. *Tectonophysics* **234**, 73-94.
- SACK, R.O. & GHIORSO, M.S. (1991): Chromian spinels as petrogenetic indicators: thermodynamics and petrological applications. *Am. Mineral.* **76**, 827-847.
- SARTI, M. (1979): Il Paleogene della Val Tremugna (Prealpi Carniche). *Boll. Soc. Geol. It.* **98**, 87-108.
- SCIUNNACH, D. & GARZANTI, E. (1997): Detrital chromian spinels record tectono-magmatic evolution from Carboniferous rifting to Permian spreading in Neotethys (India, Nepal and Tibet). *Ofioliti* **22**, 101-110.
- SHELDRIK, G.M. (1993): SHELX–93. Program for crystal structure refinement. University of Göttingen, Göttingen, Germany.
- TUNIS, G. & VENTURINI, S. (1989): Geologia dei Colli di Scriò, Dolegna e Ruttars (Friuli orientale): precisazioni sulla stratigrafia e sul significato paleoambientale del Flysch di Cormons. *Gortania* **11**, 5-24.
- _____, _____ & _____ (1996): L'Eocene delle Prealpi Carniche, dell'altipiano di Brkini e dell'Istria: precisazioni biostratigrafiche e paleoambientali. *Natura Nascosta* **13**, 40-49.
- UTTER, T. (1978): The origin of detrital chromites in the Klerksdorp Goldfield, Witwatersand, South Africa. *Neues Jahrb. Mineral., Abh.* **133**, 191-209.

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