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

DAVIDE LENAZ§ AND FRANCESCO PRINCIVALLE

Dipartimento di Scienze della Terra, Università di Trieste, Via Weiss 8, I–34127 Trieste, Italy

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 intracristallines 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


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

§ E-mail address: lenaz@univ.trieste.it
of the possible source-rocks occurring in the nearby areas, that there were continuous supplies of material from the Inner Dinarides from the beginning (Maastrichtian) 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 lherzolite-related spinels). The latter materials, of Upper Paleocene to Upper Eocene in age, were identified on the basis of the presence of the lherzolite-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 ophiolitic 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 Pirëka 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 (Marinic 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).

RESULTS

Data collection was made up to a 2θ of 110° with ω – 20 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 Fe(hkl) 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 Fe(hkl) in the space group Fd3m (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, Al2O3, Cr2O3, TiO2 and SiO2) were used. The raw data were reduced with a PAP-type correction software provided by CAMECA.

Results are considered accurate to ±2–3% 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).

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 MoKα 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.
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 Fe$^{2+}$/Fe$^{3+}$ value are considered typical of a spinel derived from a mantle peridotite. The peridotitic group of spinel grains contain less than 0.2 wt% TiO$_2$ and have a FeO/Fe$_2$O$_3$ value greater than 3, whereas the volcanic group show greater than 0.2 wt% TiO$_2$ and a FeO/Fe$_2$O$_3$ value less than 4.
Regarding spinel samples derived from peridotitic rocks, according to the diagram Mg# \([100 \text{Mg}/(\text{Mg} + \text{Fe}^{2+})]\) versus Cr# \([100 \text{Cr}/(\text{Cr} + \text{Al})]\) 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.

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 \((i.e., \text{increased order})\) 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. 2.** Relationships between Mg# \([100 \text{Mg}/(\text{Mg} + \text{Fe}^{2+})]\) versus Cr# \([100 \text{Cr}/(\text{Cr} + \text{Al})]\) in spinel from peridotitic rocks \((\text{TiO}_2 < 0.2 \text{ wt}%)\) from flysch and ophiolites from the Dinarides (Maksimović & Jovanović 1984). Dotted line: Inner Dinarides; solid line: Outer Dinarides.

**Fig. 3.** Al_2O_3 versus TiO_2 (wt%) relationship in spinel from volcanic \((\text{TiO}_2 > 0.2 \text{ wt}%)\) 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).
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, \( T-\Omega \) versus \( M-\Omega \) 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 felsch 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 felsch 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,
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, lherzolite- 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

### Table 2 (cont’d). Chemical composition and cation distributions of spinel grains studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>BK 30</th>
<th>BK 35</th>
<th>BK 36</th>
<th>IBROX</th>
<th>IBROX</th>
<th>IBKROX</th>
<th>IBKROX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$, wt.%</td>
<td>26.59(42)</td>
<td>19.40(45)</td>
<td>37.31(80)</td>
<td>58.97(35)</td>
<td>49.95(56)</td>
<td>14.44(38)</td>
<td>26.05(68)</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>38.73(61)</td>
<td>48.73(70)</td>
<td>28.71(80)</td>
<td>8.78(24)</td>
<td>18.01(54)</td>
<td>55.10(50)</td>
<td>42.61(91)</td>
</tr>
<tr>
<td>MgO</td>
<td>4.46(38)</td>
<td>12.21(20)</td>
<td>16.82(11)</td>
<td>20.19(28)</td>
<td>18.84(30)</td>
<td>9.38(17)</td>
<td>13.18(42)</td>
</tr>
<tr>
<td>MnO</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.11(5)</td>
<td>0.15(7)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>FeO</td>
<td>19.34(81)</td>
<td>19.38(49)</td>
<td>15.42(20)</td>
<td>11.04(23)</td>
<td>11.93(37)</td>
<td>20.46(14)</td>
<td>17.80(25)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.65(4)</td>
<td>0.21(2)</td>
<td>0.52(6)</td>
<td>0.07(2)</td>
<td>0.04(2)</td>
<td>0.18(4)</td>
<td>0.05(2)</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.11(7)</td>
<td>0.14(7)</td>
<td>0.02(7)</td>
<td>0.15(7)</td>
<td>0.18(6)</td>
<td>0.30(7)</td>
<td>0.18(8)</td>
</tr>
<tr>
<td>NiO</td>
<td>0.10(6)</td>
<td>0.11(4)</td>
<td>0.21(8)</td>
<td>0.36(7)</td>
<td>0.24(9)</td>
<td>0.07(2)</td>
<td>0.10(2)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>0.03(2)</td>
<td>0.04(3)</td>
<td>0.06(1)</td>
<td>0.04(3)</td>
</tr>
<tr>
<td>Sum</td>
<td>100.5</td>
<td>100.5</td>
<td>99.50</td>
<td>99.83</td>
<td>99.54</td>
<td>100.05</td>
<td>100.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>T site</th>
<th>M site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_{alp}$</td>
<td>0.056</td>
<td>0.041</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.359</td>
<td>0.415</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.017</td>
<td>0.001</td>
</tr>
<tr>
<td>Mg</td>
<td>0.565</td>
<td>0.540</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Al$_{alp}$</td>
<td>0.888</td>
<td>0.674</td>
</tr>
<tr>
<td>Fe$_{3+}$</td>
<td>0.001</td>
<td>0.014</td>
</tr>
<tr>
<td>Fe$_{2+}$</td>
<td>0.095</td>
<td>0.074</td>
</tr>
<tr>
<td>Mg</td>
<td>0.082</td>
<td>0.028</td>
</tr>
<tr>
<td>Cr</td>
<td>0.916</td>
<td>1.202</td>
</tr>
<tr>
<td>Ni</td>
<td>0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>Ti</td>
<td>0.015</td>
<td>0.005</td>
</tr>
</tbody>
</table>

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

ACKNOWLEDGEMENTS

We thank A. Della Giusta, G. Garuti and F. Zaccarini for their constructive comments on a preliminary draft of this paper, and H.O. Cookenboo and R.F. Martin for very helpful reviews. The Italian C.N.R. financed the
installation and maintenance of the electron-microprobe laboratory at the University of Padova. The authors also gratefully acknowledge financial support from MURST and Trieste University grants (Cristallochimica e reazioni di scambio cationico in spinelli, olivine e pirosseni; COFIN 2001; F. Princivalle). R. Carampin kindly assisted with the micro-analyses.

REFERENCES


