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https://doi.org/10.12681/bgsg.16750

To cite this article:

Ananiadis, G., Vakalas, I., Zelilidis, A., & Tsikouras, B. (2004). PROVENANCE OF PINDOS FLYSCH DEPOSITS IN METSOVO AND FOURNA AREAS USING SCANNING ELECTRON MICROSCOPY AND MICROANALYSIS. Bulletin of the Geological Society of Greece, 36(1), 534-541. doi: https://doi.org/10.12681/bgsg.16750
PROVENANCE OF PINDOS FLYSCH DEPOSITS IN METSOVO AND FOURNA AREAS USING SCANNING ELECTRON MICROSCOPY AND MICROANALYSIS

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ABSTRACT

Petrographic observation of sandstones that contain detrital grains and lithic fragments along with microanalytical data from certain minerals suggest that detrital material in Pindos flysch deposits, in Metsovo and Fournas areas, may have been sourced in the Pindos ophiolite and the Pelagonian metamorphic rocks; additionally some material from Fournas has probably been derived from the Koziakas ophiolite outcrop. The Loumnitsa Unit (Pindos ophiolite), has probably supplied the Pindos foreland with material from the erosion of amphibolites while the Dramala Unit was the most probable source of spinels and ultramafic material. Fragments of acid plutonic rocks have been observed, too, owing their origin from the plutonite of Varnounta-Kastoria (Pelagonian Zone). The area of Fournas has been also fed by the Koziakas ophiolites, as evidenced from the composition of chlorites and epidotes.

1 INTRODUCTION

The early Tertiary renewed crustal compression initiated eastward subduction of the remnant Pindos Ocean Basin, where submarine fans accumulated during Paleogene giving rise to the flysch of Pindos zone. Pelagonian zone and ophiolites from the East were thrust over Pindos flysch deposits during Tertiary. Metsovo and Fournas areas are situated on the Northern and central part of Pindos zone respectively, and they consist of inner and middle fan deposits that filled the Pindos basin coming from the North (Fig. 1).

2 ANALYTICAL METHODS

Samples were collected from the cross-sections A-A’ (road from Votonosi to Metsovo) situated in Metsovo area and cross-section B-B’ (road from Fournas to Loutra) in NE Karpenisi area. The sandstone samples had an average thickness of 15 cm and characterized by the presence of the subdivision Ta of Bouma sequence. Polished thin sections were prepared for petrographic investigation and microanalytical work on certain minerals. Spot microanalyses were performed in polished-thin sections, using a Jeol JSM-6300 SEM equipped with EDS and WDS, with accelerating
voltage of 20kV and a beam current of 3nA, in the Laboratory of Electron Microscopy and Micro-
analysis, University of Patras.

3 PETROGRAPHY

The collected sandstone samples from both the Metsovo and Fournas areas contain mainly
quartz, alkali feldspars, plagioclase and minor muscovite. Detrital grains are often in both areas.
Samples from Metsovo contain less than 15% lithic fragments while those from Fournas are rela-
tively richer in lithic fragments (up to about 50%). The observed detrital grains include spinel, ti-
tanite, clinopyroxene, garnet, apatite, zircon, plagioclase, K-feldspar (including microcline), epidote,
chlorite and rarely tourmaline; in the Fournas area amphibole grains (both magnesiohornblende
and tremolite) occur, too. The lithic fragments comprise serpentinites, basaltic rocks (usually dis-
playing typical oceanic alteration), polycrystalline quartz, cherts, granitic rocks (sometimes with
perthitic crystals and/o. granophyric textures), dolomites and low-grade metapelitic rocks. The
grains are cemented usually with micritic calcite while local sparite occurs, too.

4 MINERAL CHEMISTRY

4.1 Feldspars

Representative plagioclase and alkali feldspar analyses are listed in Table 1. The analysed plagioclases from Metsovo are mostly albites except one crystal that is andesine (Fig. 2a). Plagioclase grains from Fournas area have variable compositions. The majority of the analysed crystals are albites while a second group clusters at oligoclase and andesine fields (Fig. 2b). Andesines typically occur in intermediate and basic igneous rocks while the occurrence of albites is not conclusive since this mineral is hosted in a wide variety of rocks. Distinctly one analysed crystal from Fournas is anorthite (Fig. 2b). Such plagioclases can be fractionated only by a hydrous magma of primitive arc-tholeiitic composition (e.g. Wilson, 1989) and are commonly present in gabbroic and ultramafic rocks that are related to SSZ regime such as the Pindos ophiolite.

Alkali feldspars from both areas are similar being mostly K-feldspars with K2O contents ranging from 15.94 to 16.87%, and compositions from Or95 to Or80. One crystal from each area differs in containing significant Ab content and plots in the area of high-temperature alkali feldspars thus advocating for an origin from acid-intermediate volcanic rocks (Figs. 2a, b).

4.2 Chlorites

Representative chlorite analyses from Metsovo and Fournas sandstones are listed in Table 2. According to the classification of Hey (1954) the analysed crystals from Metsovo fall into two dis-
tinct groups, thus suggesting probably two different rock sources. The first group includes chlorites of ripidolite to pycnoclymorite composition, while the second includes diavantites (Fig. 3a). The chlorites from Fournas suggest a different source clustering at the fields of pycnoclymorite to diabantine, while one crystal plots as brunsvigite (Fig. 3b). The analysed chlorite crystals from Fournas are comparable to chlorites from mafic rocks of the Koziakas ophiolite (Fig. 3b).
Table 1. Representative feldspar microanalyses from Metsovo (Mets) and Fournas (F) areas (\textendash: below detection limit)

|         | Mets6 | Mets6 | Mets6 | F1 | F12 | F16 | Mets1 | Mets10 | F1 | F12 |
|---------|-------|-------|-------|----|-----|-----|-------|--------|----|-----|
|         | k5(E) | k5(E6) | K2(H) | k5(66) | K2(9) | K7(3) | k1(4) | k1(16) | k4(11) | k1(12) |
| SiO2    | 99.09 | 68.00 | 57.61 | 68.96 | 69.11 | 58.09 | 65.82 | 53.10 | 65.76 | 64.39 |
| TiO2    | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  |
| Al2O3   | 19.57 | 19.33 | 25.96 | 20.28 | 19.87 | 26.86 | 18.34 | 31.09 | 18.42 | 20.93 |
| Fe2O3t  | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| MgO     | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| MnO     | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| CaO     | 11.02 | 9.66  | 7.06  | 9.92  | 10.17 | 4.90  | 4.43  | 0.57  | 0.44  | 0.80  |
| Na2O    | 1.46  | 1.46  | 1.46  | 1.46  | 1.46  | 1.46  | 1.46  | 1.46  | 1.46  | 1.46  |
| K2O     | 0.18  | 0.17  | 0.17  | 0.17  | 0.17  | 0.17  | 0.17  | 0.17  | 0.17  | 0.17  |
| P2O5    | 0.76  | 0.76  | 0.76  | 0.76  | 0.76  | 0.76  | 0.76  | 0.76  | 0.76  | 0.76  |
| Total   | 99.68 | 98.77 | 99.24 | 100.00 | 99.86 | 99.09 | 99.97 | 99.43 | 101.17 | 100.58 |

Structural formulae on the basis of 8 O

| Si     | 3.013 | 3.099 | 2.601 | 2.993 | 3.005 | 2.606 | 2.998 | 2.467 | 3.005 | 2.930 |
|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| AlV    | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  | 0.09  |
| Ti     | 1.005 | 1.007 | 0.981 | 1.030 | 1.041 | 1.025 | 0.982 | 1.137 | 0.991 | 1.052 |
| Cr     | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| FeTi   | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| Mg     | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| Mn     | -     | -     | -     | -     | -     | -     | -     | -     | -     | -     |
| P      | -     | -     | -     | -     | -     | -     | -     | -     | 0.039 | 0.071 |
| Ca     | 0.627 | 0.627 | 0.627 | 0.627 | 0.627 | 0.627 | 0.627 | 0.627 | 0.627 | 0.627 |
| Na     | 0.326 | 0.326 | 0.326 | 0.326 | 0.326 | 0.326 | 0.326 | 0.326 | 0.326 | 0.326 |
| K      | 1.937 | 1.937 | 1.937 | 1.937 | 1.937 | 1.937 | 1.937 | 1.937 | 1.937 | 1.937 |
| Ab     | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| An     | 93.44 | 93.44 | 93.44 | 93.44 | 93.44 | 93.44 | 93.44 | 93.44 | 93.44 | 93.44 |
| Or     | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  | 0.00  |

4.3 Muscovites

Representative detrital muscovite grain analyses from Metsovo and Fournas areas are given in Table 3. The Si/AlV ratio of the studied muscovites is greater than 3, and Si lies between 3.2 and 3.6 (atoms p.f.u., on the basis of 11 oxygens) indicating increased phengitic component (Massone and Shreyer, 1986). Consequently, their original formation is related to relatively high pressure conditions (Guidotti & Sassi, 1976, Massone & Shreyer, 1986). Analogous muscovite crystals are widespread in metapelitic rocks from the Pelagonian Zone.

4.4 Garnets

Representative garnet analyses are listed in Table 4. The garnet grains from both Metsovo and Fournas areas have two distinct compositions: a grossular-rich and an almandine-rich, revealing two different supply sources. Grossular garnets are commonly found in both ultramafic and metamorphic (amphibolite sole) rocks in ophiolites, while almandine-rich garnets are usually related to metasedimentary rocks of greenschist, amphibolite or and eclogitic metamorphic facies similar to those occurring in the Pelagonian Zone.
Table 3 (right). Representative detrital muscovite microanalyses from Metsovo (Mets) and Fourna (F) areas. (-: below detection limit)

Table 2. Representative chlorite microanalyses from Metsovo (Mets) and Fourna (F) areas. (-: below detection limit)

|        | Mets10 | Mets10 | Mets10 | F1      | F12     |
|--------|--------|--------|--------|---------|---------|
| SiO₂   | 25.28  | 26.02  | 25.71  | 35.52   | 25.57   |
| TiO₂   | -      | -      | -      | -       | -       |
| Al₂O₃  | 20.77  | 21.11  | 22.91  | 15.22   | 17.99   |
| CrO₃   | -      | -      | -      | -       | -       |
| FeO₂   | 24.43  | 26.06  | 27.11  | 19.14   | 34.28   |
| MgO    | 13.03  | 12.50  | 9.72   | 15.32   | 6.02    |
| MnO    | -      | 0.43   | 0.46   | 1.03    |         |
| CaO    | 1.24   | 0.21   | 0.40   | 0.38    |         |
| NaO    | 1.31   | 0.23   | -      | 0.43    |         |
| K₂O    | -      | -      | -      | -       |         |
| Total  | 86.06  | 85.12  | 83.65  | 85.60   | 85.70   |

Structural formulae on the basis of 28 O

|        | Si     | AlIV   | AlVI   | Ti      | Cr      | Fe²⁺   | Mg     | Mn     | Ca     | Na     | K      |
|--------|--------|--------|--------|---------|---------|--------|--------|--------|--------|--------|--------|
| Mets10 | 5.456  | 5.597  | 5.540  | 7.248   | 5.855   | -      | -      | -      | -      | -      |
| Mets10 | 5.454  | 2.403  | 2.460  | 0.752   | 2.145   | -      | -      | -      | -      | -      |
| Mets10 | 8.000  | 8.000  | 8.000  | 8.000   | 8.000   | -      | -      | -      | -      | -      |
| F1     | 5.456  | 5.597  | 5.540  | 7.248   | 5.855   | -      | -      | -      | -      | -      |
| F12    | 5.454  | 2.403  | 2.460  | 0.752   | 2.145   | -      | -      | -      | -      | -      |

Figure 3. Plot of the analysed chlorite grains from Metsovo (a) and Fournas (b) on the classification diagram of Hey (1954); for comparison fields of chlorites from the ophiolitic complex of Koziakas are also shown (data from Pomonis, 2003).
4.5 Epidotes

Representative epidote microanalyses are listed in Table 5. $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios calculated according to stoichiometric considerations. The pistacite component ($\text{Ps}=100 \times \text{Fe}^{3+}/\text{Fe}^{3+} + \text{Al}^{VI}$) in the epidotes from Metsovo ranges between 24.4 and 46.0. The epidote grains from Fournas are clearly poorer in Fe$^3$ relative to the epidotes from Metsovo area, pointing to a different source and resulting in lower Ps contents (between 11.3 and 28.1).

In both places, the pistacitic component in the analysed epidotes show no compositional gap, consistent with relatively HP/HT conditions during metamorphism, probably within amphibolite facies (e.g. Caruso et al. 1988, Freiberger et al. 2001). Significantly, the epidotes from Fournas, on a Fe$^3$ vs. Al$^{VI}$ diagram, form a well defined trend, indicative for provenance from a unique source rock, and are strongly compared to epidotes from the Koziakas ophiolite (Fig. 4).

4.6 Spinels

Spinel microanalyses from Metsovo and Fournas areas are listed in Table 6. In each area, there is one crystal is rich in Cr and one rich in Al. Cr-spinels are typically hosted in depleted rocks while Al-spinels are commonly found in fertile Iherzolites. The low Cr# (<60) spinels are analogous to those occurring in ultramafic rocks of oceanic (including back-arc basin) origin (Dick & Bullen, 1984). Chemical affinity of the detrital spinel grains from Metsovo and Fournas are similar and are compared well to those from Pindos ophiolite (Fig. 5).

Figure 4. Projection of the compositions of the epidotes from Fournas on a Fe$^3$ vs. Al$^{VI}$ diagram. For comparison the field of the epidotes of the subophiolitic metamorphic sole of Koziakas are shown (data from Pomonis 2003).
Table 5. Representative epidote microanalyses from Metsovo (Mets) and Fourna (F) areas. (-: below detection limit)

|      | Mets6 K2(A) | Mets10 K3(7) | F20 K4(3) | F20 K5(2) |
|------|-------------|-------------|-----------|-----------|
| SiO₂ | 38.60       | 40.14       | 38.62     | 39.57     |
| TiO₂ | -           | -           | -         | -         |
| Al₂O₃| 21.43       | 23.88       | 27.36     | 22.14     |
| Cr₂O₃| -           | -           | -         | -         |
| FeO| 15.62       | 12.71       | 9.18      | 13.55     |
| MgO | 0.70        | 0.46        | -         | -         |
| CaO | 22.51       | 22.75       | 24.17     | 23.46     |
| Na₂O| 0.28        | -           | -         | 0.49      |
| K₂O | -           | -           | -         | -         |
| Total| 99.14       | 99.48       | 99.79     | 99.21     |

Structural formulae on the basis of 25 O

- Si⁶⁺ 6.119 & 6.224 & 6.950 & 6.214
- Al³⁺ 4.001 & 4.381 & 4.914 & 4.095
- Ti⁴⁺ 1.860 & 1.48  & 1.063 & 1.600
- Fe³⁺ 5.861 & 5.841 & 5.977 & 5.695
- Fe²⁺ -     & -     & -     & -
- Mg  -       & -     & -     & -
- Mn  0.094   & 0.060 & -     & -
- Ca  3.823   & 3.780 & 3.990 & 3.947
- Na  0.086   & -     & -     & 0.149
- K   4.003   & 3.780 & 4.050 & 4.096
- Ps  31.735  & 25.338 & 17.637 & 28.065

Figure 5. Composition of the analysed spinels from Metsovo (a) and Fournas (b) in comparison to spinels from Pindos, Othris, Vourinos, Koziakas and Rodiani ophiolites (data from Economou et al. 1986, 1995, 1999, Gartzos et al. 1990, Migiros et al. 1991 and Pomonis 2003).
5 SUPPLEMENTARY DATA

5.1 Paleocurrent data

The main palaeocurrent directions of both Metsovo and Fourna areas interpreted from sole marks (flute and groove marks) indicate a south-southwest direction (Fig. 6), which means that the source of the material in both areas is from north-northeast. This fact is consistent with supply from the Pindos ophiolite and Pelagonian Zone for both areas, as well as from the Koziakas ophiolite for Fournas.

![Figure 6. Simplified geological maps of the studied areas showing the main paleocurrent directions.](image)

6 CONCLUSIONS

Microprobe analyses from Metsovo area combined with results from paleocurrent data reveal two different supply sources, the Pindos ophiolite and metamorphic rocks from the Pelagonian Zone. The Loumitsa unit, in the Pindos ophiolite, may represent the source of the metamorphic materials, while spinels may have come from harzburgite of the Dramala complex. The source of acid materials may be the plutonite of Varnounta-Kastoria (Pelagonian mass). A unique tourmaline grain analysed arises a question about its provenance. The composition of the studied tourmaline is analogous to tourmalines from Polidendri-Kolchiko area of the Serbomacedonian massif, the latter comprises the most likely proximal source (Ananiadis 2003). However, absence of published analytical data from tourmalines from the Pelagonian Zone must be considered.

The same consideration for Fourna area (cross-section I-I’) reveals Pindos and Koziakas ophiolites and Pelagonian mass as probable sources of the material. Thus, the studied spinels may have come from Pindos ophiolite, while the provenance of chlorites may be harzburgites, basalts and rodingites from the Koziakas ophiolite complex. The major part of the studied epidotes may have as a source Koziakas ophiolites, while the minor part may have come from amphibolite facies metamorphic rocks of the Pelagonian Zone.

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