MINERALOGY AND PETROGRAPHY
OF TERRIGENOUS FORMATION IN BRARI SECTION, ALBANIA

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Abstract. The Brari section in Tirana Depression is represented by a succession of molasses deposits, Middle to Late Miocene in age, developed in inner-outer and outer neritic zones. These shallow marine deposits comprise several depositional sequences, which were carefully studied using polarized light microscope, SEM-EDS and XRD. Their petrographic and mineralogical composition enables the characterization of each sequence in terms of both nature and provenance of the clastic constituents. In addition, three main facies have been identified. Facies 1 (quartz-lithic) was derived by the erosion of the igneous rocks from the eastern part of Albania and of the low to medium-grade metamorphic rocks (mainly quartzite and slate). Facies 2 (calcareous sandstones) and Facies 3 (quartz-arenite) were produced by the reworking of sedimentary rocks (flysch and carbonate rocks) from Kruja and Krasta Cukali zones. In addition to the sandstones petrography, this provenance is supported by the mineralogy of some interbedded clay. Thus, the clays related to facies 1 and 2 have a more variegated composition (illite-smectite mixed-layer), while the interbedded clays from facies 1 are characterized by the presence of chlorite.

Keywords: Brari, terrigenous formation, facies, provenance.

Rezumat. Mineralogia şi petrografia formaţiunii terigene în secţiunea Brari, Albania. Secţiunea Brari din Depresiunea Tirana este reprezentată de o succesiune de depozite de molasă, de vârstă Miocen mediu-târziu, acumulate în zone neritice intern-externe şi externe. Aceste depozite marine de mică adâncime au fost studiate cu atenţie, utilizând microscopul cu lumină polarizată, SEM-EDS şi XRD. Compoziţia lor petrografică şi mineralogică permite caracterizarea lor în ceea ce priveşte natura constituenţilor clastici şi provenienţa acestora. În plus, au fost identificate trei faciesuri principale. Faciesul 1 (cuarţo-litic) provine din eroziunea rocilor eruptive din partea de est a Albaniei şi a rocilor metamorfice (în principal cuarţ şi ardezie). Faciesul 2 (gresii calcaroase) şi Faciesul 3 (cuarţ-arenitic) provin din remanierea rocilor sedimentare (fliş şi roci carbonatice) din zonele Kruja şi Krasta Cukali. Această provenienţă este susţinută şi de mineralogia intercalaţiilor de argile. Astfel, argilele asociate faciesurilor 1 şi 2 au o compoziţie interstratificată (illit-smectite), în timp ce intercalaţiile de argile din Faciesul 1 se caracterizează prin prezenţa cloritului.

Cuvinte cheie: Brari, formaţiune terigenă, facies, provenienţă.

INTRODUCTION

Brari is located in Tirana Depression being situated in the north-eastern part of the Periadriatic Depression (Albania), which consists of Miocene and Pliocene molasses. It lies discordantly with Ionian and Kruja zone deposits (SHEHU et al., 1981). According to GELATI et al., (1997) Aquitanian, Langhian, Serravallian, Tortonian formations were determined into this section (Fig. 1).

Brari section belongs to inner-outer and outer neritic zones. Marine sediments (60-70m) of Brari section consist of basal sandy conglomerate beds with concretions of yellowish calcareous sandstones, cross bedded conglomerates and very thin layers of silty mudstones, parallel bed gravelites, and massive, coarse sandstone with Echinoidea fossiliferous sandstones with bivalves (Fig. 1). Upward, the section continues with *Lithothamnium* limestones (30m) overlapped by a terrigenous succession (60m) and, again, there are present *Lithothamnium* limestones (50m). At the top of the section, there can be found sandstone interbedded with thin layers of mudstone and limestone with Ostreidae (GJANI et al., 2003).

The purpose of this study is to determine the provenance of this terrigenous material based mainly on mineralogical sandstone composition.

MATERIAL AND METHODS

For this study 11 clay samples were chosen and 20 thin sections were prepared from the most representative samples collected during the field work. The petrographic studies were conducted by using Nikon Eclipse 50iPOL optical microscope. Moreover, the mineralogical studies of the sandstones and shales were conducted using XRD and SEM (Philips XL 30 ESEM) equipped with EDS. The diffractograms were obtained from the samples using X-Ray Diffraction under Co Kα radiation, with a step scanning 3 to 60°2θ in steps of 0.01°2θ with a counting time of 1.00 s per step. First X-ray Diffraction analyses were done from the samples in natural conditions and after these, the two most representative samples were selected for further detailed analysis.

The analyses aimed at documenting the mineralogy and especially clay mineralogy of Brari section. A clay fraction (< 2 μm) was separated from the samples by disaggregating them with different acids according to JACKSON (1958) method and dispersing the sample in distilled water and immediately washing by centrifugation. The fraction of < 2 μm was isolated by centrifugation and suspension was dried on glass slides. The clay samples in oriented mounts were run under three different conditions. The first one was done in air dry state. During the second treatment, the slide

samples were placed in an oven and heated at 330°C and 500°C for 2 hours. After this, they were immediately analyzed right after taking them out of the oven; in this way, we stopped the rehydration of the samples. The ethylene glycol treatment was done by adding 100-200 ml of ethylene glycol in a desiccator with the sample slides being placed on a ceramic plate. The desiccator was left in the oven at 60°C for at least 10 hours. The digital data were interpreted using X-Pert Highscore Plus software, which comprises a search-match routine based on a Powder Diffraction File.

Figure 1. Generalized lithological column of Brari section (modified after GJANI et al., 2003).
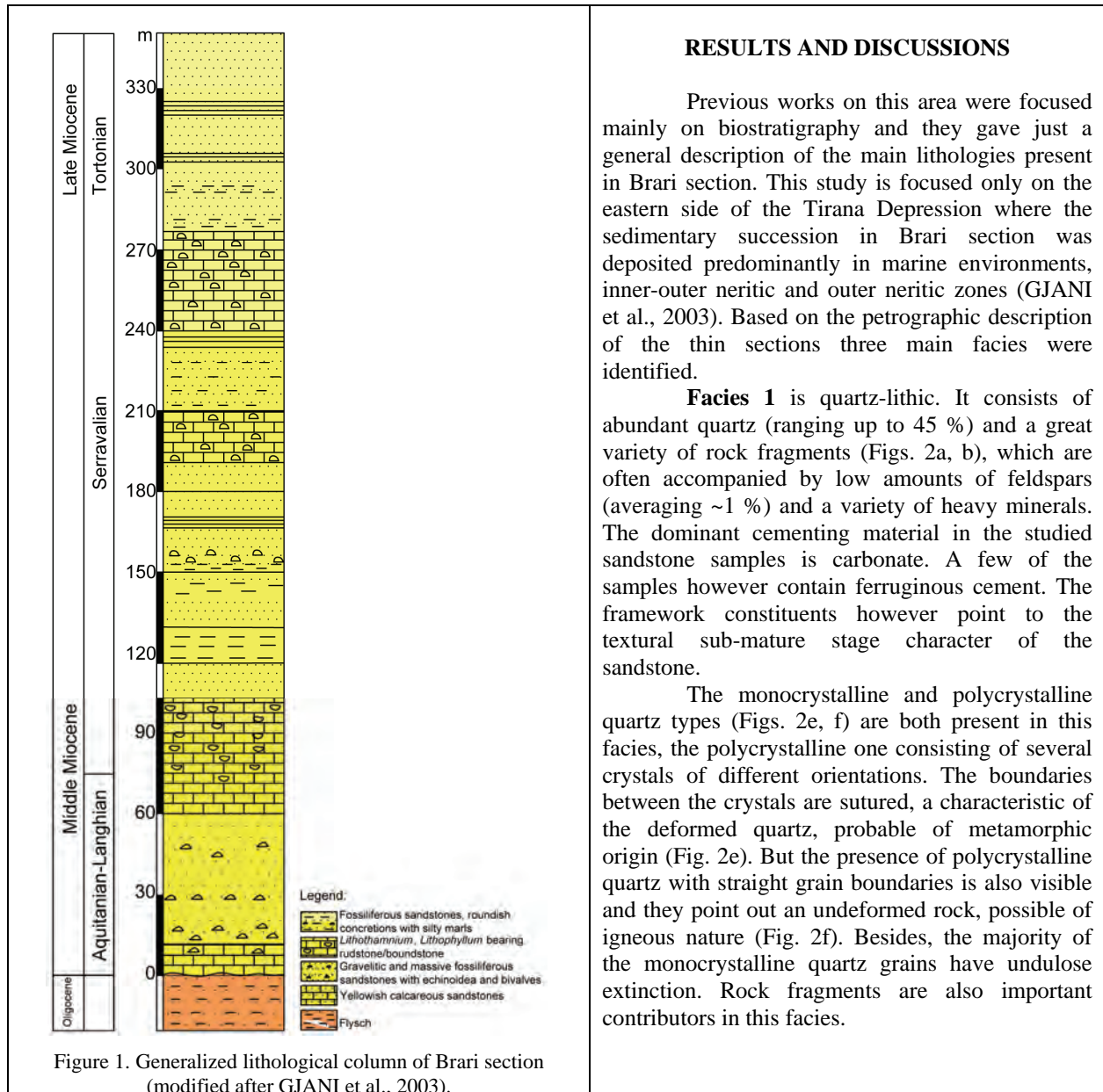
RESULTS AND DISCUSSIONS

Previous works on this area were focused mainly on biostratigraphy and they gave just a general description of the main lithologies present in Brari section. This study is focused only on the eastern side of the Tirana Depression where the sedimentary succession in Brari section was deposited predominantly in marine environments, inner-outer neritic and outer neritic zones (GJANI et al., 2003). Based on the petrographic description of the thin sections three main facies were identified.

Facies 1 is quartz-lithic. It consists of abundant quartz (ranging up to 45 %) and a great variety of rock fragments (Figs. 2a, b), which are often accompanied by low amounts of feldspars (averaging ~1 %) and a variety of heavy minerals. The dominant cementing material in the studied sandstone samples is carbonate. A few of the samples however contain ferruginous cement. The framework constituents however point to the textural sub-mature stage character of the sandstone.

The monocrystalline and polycrystalline quartz types (Figs. 2e, f) are both present in this facies, the polycrystalline one consisting of several crystals of different orientations. The boundaries between the crystals are sutured, a characteristic of the deformed quartz, probable of metamorphic origin (Fig. 2e). But the presence of polycrystalline quartz with straight grain boundaries is also visible and they point out an undeformed rock, possible of igneous nature (Fig. 2f). Besides, the majority of the monocrystalline quartz grains have undulose extinction. Rock fragments are also important contributors in this facies.

The rock fragments occur as different size subangular to subrounded grains and include igneous, sedimentary and metamorphic types. Much fine grained material cannot be resolved even under high magnification. They have a platy shape probably due to the good cleavage of the source rock, containing abundant platy minerals, representing shale or slate (Fig. 2c). Muscovite-bearing quartz rich rocks with micas show preferential orientation forming a schistose texture and these clasts can be classified as quartzites (Fig. 2d). Volcanic rock fragments consisting of plagioclase laths set in altered groundmass of too fine grained are also present (Figs. 2a, b, g).

The most common sedimentary rock type present in this facies is cherts (Fig. 2a). The grains of chert are fine to medium in size and have subangular to rounded boundaries (Fig. 2a). The overall abundance of rock fragments is around 35 %. Trace amounts of muscovite occur as flakes in this facies.

Facies 2 is calcareous sandstone. This facies consists of angular to subangular quartz grains together with angular calcite grains cemented by calcium carbonate. Some fauna fragments, poorly preserved can be found in this facies (Fig. 2a).

Facies 3 represents sandstone, which consists almost entirely of quartz and is thus classified as quartz arenite. This facies is texturally immature according to FOLK (1951), while it is mineralogically mature. Dark black bioclast are present in the sample. Based on the petrographic description of the samples even SEM analyses have revealed to us more or less the same major constituents. The most common mineral identified in thin sections is quartz as the main constituent.
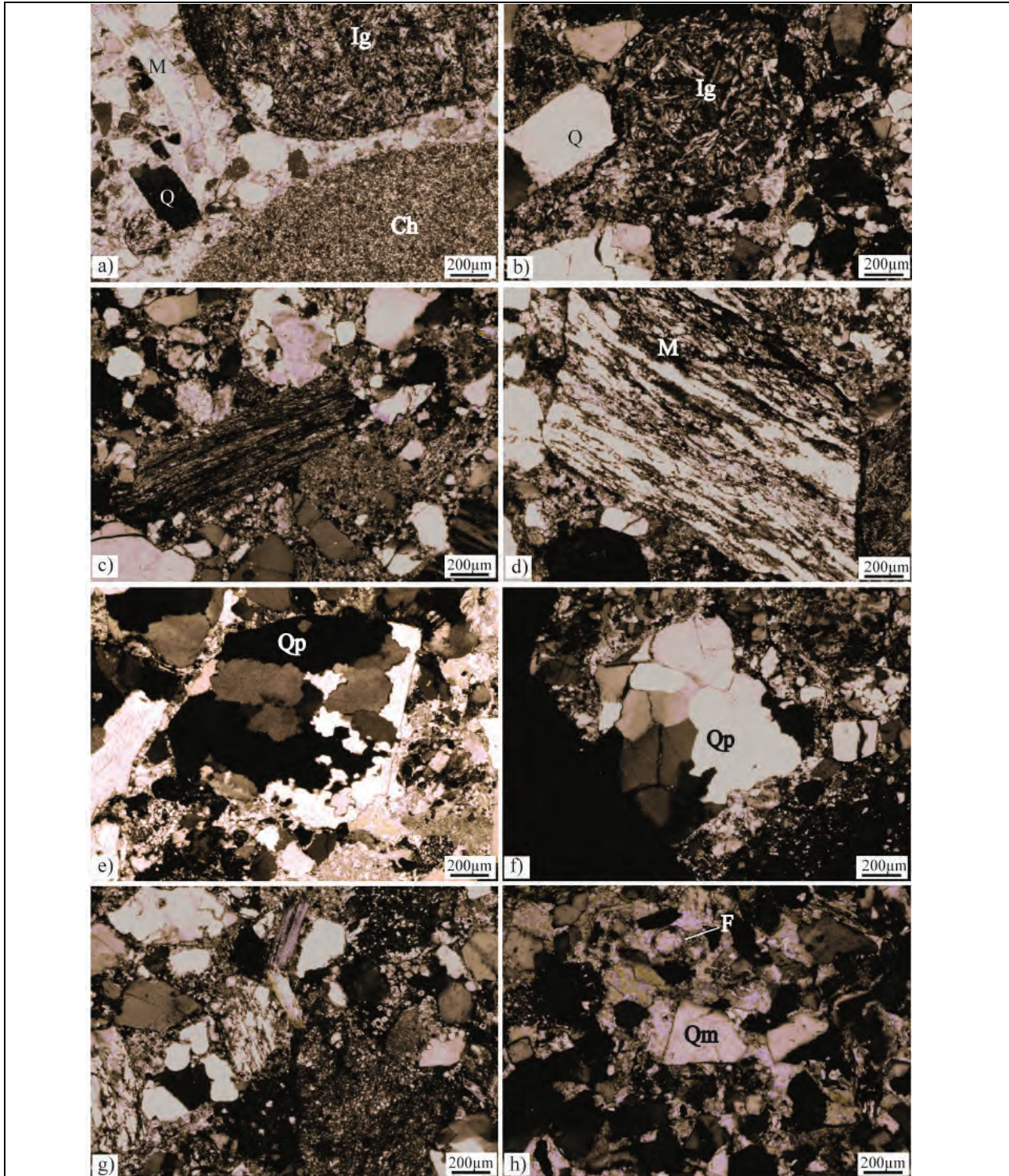

Figure 2. Microphotographs of different sandstones facies taken under crossed polars. a) main constituents of Facies 1 (Q-quartz, M-muscovite, Ig- igneous rock fragment, Ch-chert rock fragment); b) same as previous; c) slate fragment; d) angular schistose quartz, (M-metamorphic rock fragment); e) polycrystalline quartz (Qp), with sutured crystal boundaries; f) polycrystalline quartz (Qp) with straight grain boundaries; g) angular monocrystalline quartz grains; h) Angular monocrystalline quartz grain (Qm) and fauna fragment (F).

Most of the quartz grains are fresh and clean, while some of them have a "dirty surface" and display shades of pale yellow to brown colours due to staining with ferruginous cementing material. Some of the quartz grains also contain inclusions of tourmaline, mica and zircon. They show also fractures filled by cement or opaque material.

SEM equipped with EDS has provided us a better understand for accessory and trace constituents in the three facies.

Facies 1 contains amounts of feldspars often weathered into clay minerals (chlorite). Most of the feldspar grains are of medium size and only a minor proportion occurs as small or large grains that are randomly distributed among the medium-grained feldspars. The grains of feldspar show alteration into clay minerals. These grains are mostly fractured, the fractures being filled with opaque minerals or cement (Fig. 3a). The most abundant type of feldspars is plagioclase and microcline. The plagioclase show characteristic polysynthetic twinning while microcline, less frequently occurs as small grains, most of them showing cross-hatched twinning.

Calcite and dolomite appear mainly as cement (Fig. 3e). Dolomite core often appears dissolved. Trace amounts of muscovite occur as bent flakes in the studied samples. Their composition shows a considerable quantity of Mg and Ca.
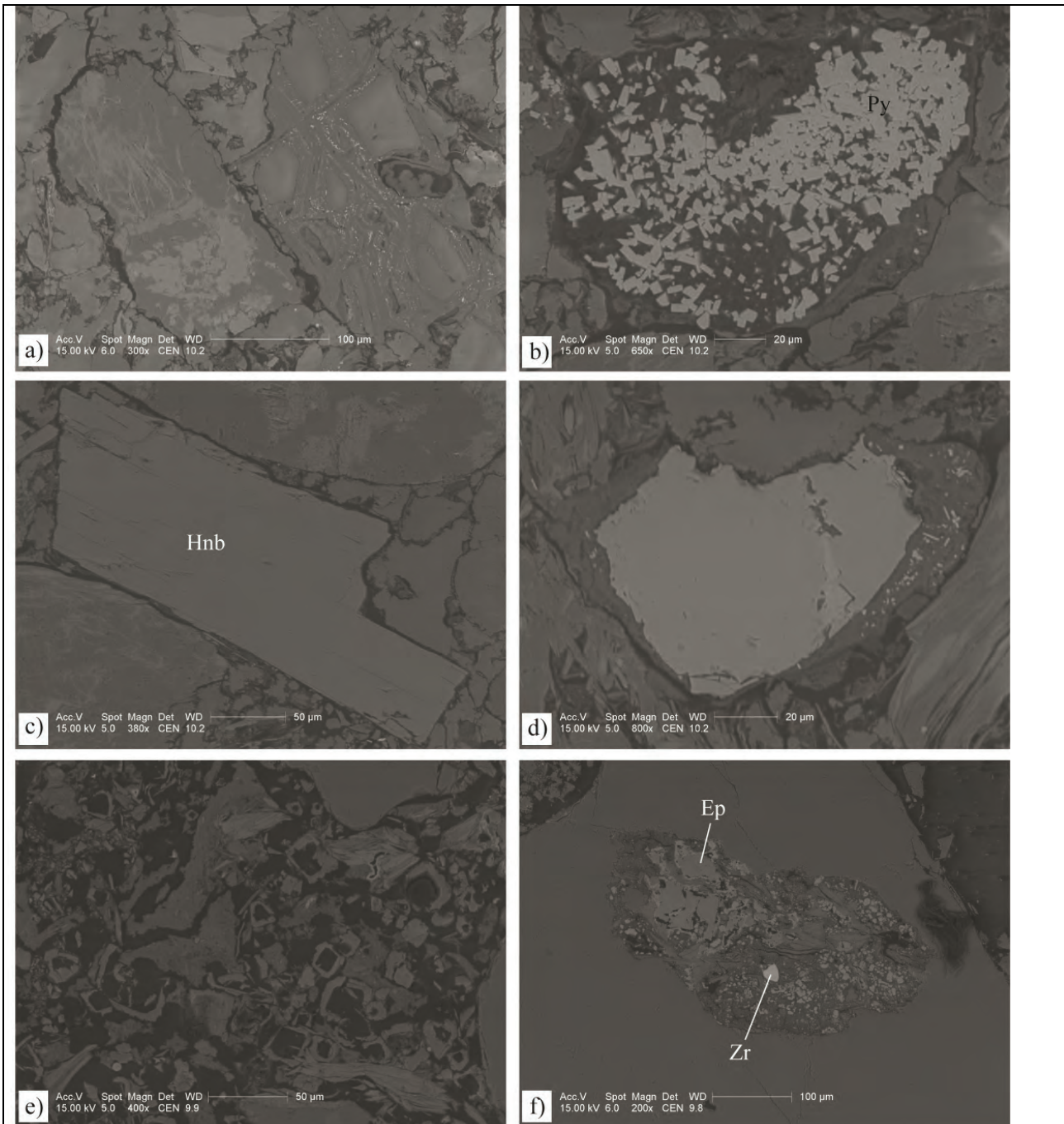

Figure 3. Microphotographs of different constituents in sandstones facies, taken under SEM: a) weathered feldspars (coarse grains); b) pyrite(Py?); c) hornblende (Hnb?); d) magnesium chromite (light gray); e) dolomite cement (rhomb-shaped); f) epidote (Ep?) and zircon (Zr?).

Glauconite grains also occur. The presence of glauconite supports shallow marine conditions for the deposition of the studied sandstone. However, it mostly appears to be authigenic and its abundance increases in the facies 2 and 3. Small isometric pyrite crystals (up to 5 μm in size) and framboids (Figs. 3b, 4l) dispersed within the rock are associated with secondary minerals and Fe oxyhydroxides.

A heavy mineral found in the studied samples is zircon, in very small grains. It is rather rare and mostly occurs as inclusions in quartz (Figs. 3f, 4j).

Monazite is another heavy mineral that occurs in the rocks. The grains of monazite are generally small and have subrounded to rounded outlines (Figs. 4k, n). Hornblende occurs as elongate prismatic crystals up to 0.5 mm in size, located adjacent to quartz (Fig. 3c).
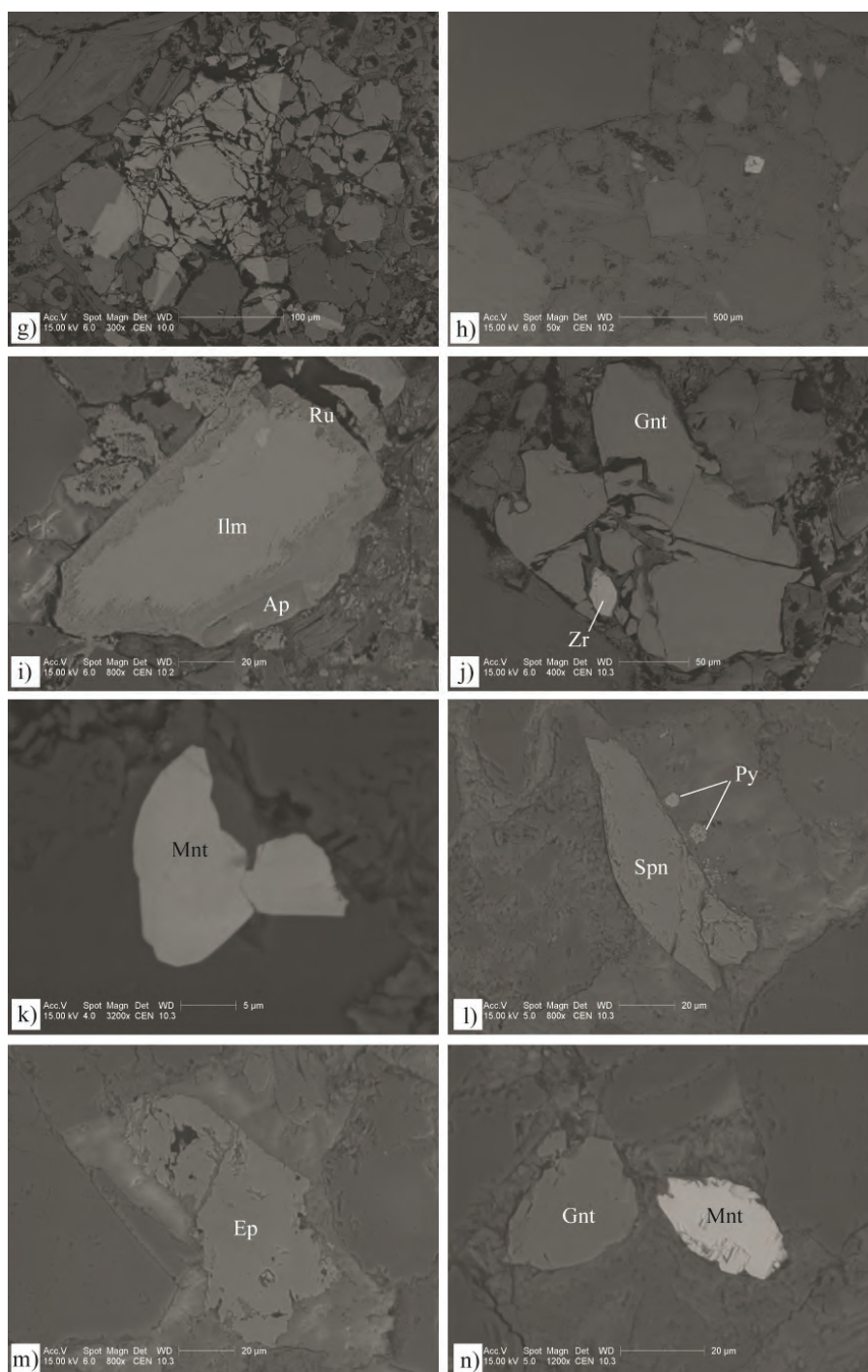

Figure 4. Microphotographs of different constituents in sandstones facies, taken under SEM: g) pure epidote (gray) and epidote rich in REE (light gray); h) angular quartz grain (upper left corner); i) ilmenite (Ilm), rutile (Ru) and apatite (Ap); j) garnet (Gnt) and zircon (Zr); k) monazite (Mnt); l) spinel (Spn) and framboidal pyrite (Py); m) epidote (Ep); n) garnet (Gnt-pyrope-almandine) and monazite (Mnt).

A few of the samples also contain grains of epidote (Figs. 3f, 4m). Epidote sometimes appears to be rich in rare earth elements (REE). This is a common accessory phase in igneous, metamorphic, metasomatic, and sedimentary rocks. Other heavy minerals present in studied samples are ilmenite, rutile, chromite, spinel, apatite, garnets (Figs. 4i, n) (Fig. 5). Chromite is present as magnesio-chromite ($MgCr_2O_3$) (Fig. 3d). Grains of ilmenite-rutile are always zoned and consist of ilmenite cores enveloped by rutile (Fig. 4i).

Clay mineralogy was deciphered based on the diffractograms achieved by XRD analysis. Those indicate that the main minerals present in the clay samples are quartz, calcite, aragonite, albite, gypsum, ankerite, muscovite, glauconite. Chlorites, smectites and a small quantity of serpentine (Fig. 6) were better evidenced after the aforementioned treatments of the samples. For their further description we have grouped the minerals into main groups like non clay minerals and clay minerals. Non clay minerals present in Brari section are quartz, calcite, aragonite, albite, gypsum, ankerite, muscovite, and glauconite.

Quartz is one of the most abundant minerals in most of the samples. It is identified by its distinctive reflections at 4.26 Å and 3.35 Å. The 3.35 Å peak of quartz was more intense than the other peaks and it is present in all of the samples. In some samples, there was a coincidence between quartz with a strong reflection of illite at 3.35 Å, which makes this 3.35 Å peak difficult to use in such cases.

Calcite is identified according to a weak characteristic reflection for the interplanar distances at 3.03 Å and 1.87 Å showing its presence in trace amounts.

Aragonite highest peak reflections are at 3.03 Å, 3.27 Å, 2.69 Å.

Albite is present in most of the samples, but in minor amount. It is identified by distinct reflection in the spacing range of 3.8 Å to 3.2 Å.
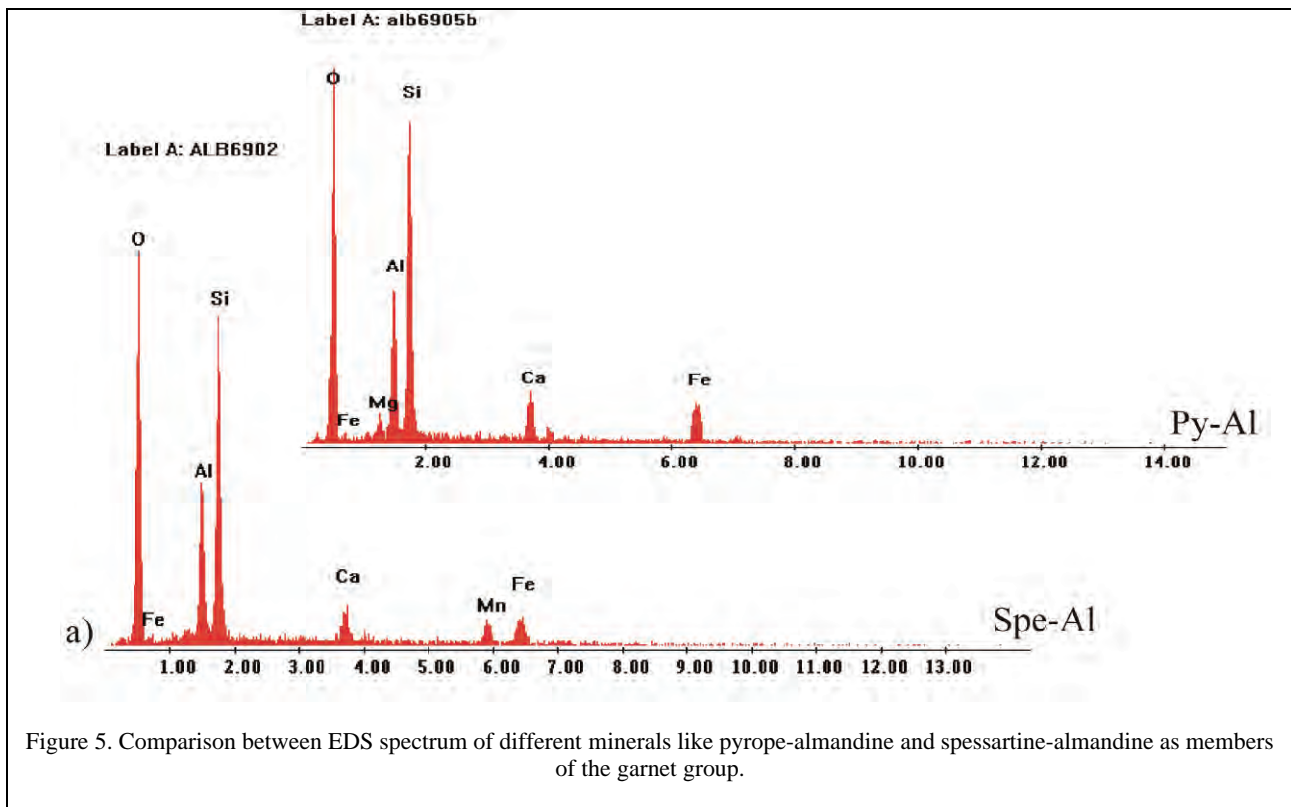

Figure 5. Comparison between EDS spectrum of different minerals like pyrope-almandine and spessartine-almandine as members of the garnet group.

Gypsum has the strongest reflection at 7.6 Å; other peaks correspond to 4.28 Å 3.06 Å 2.86 Å.

Ankerite is identified only by a weak reflection at 2.91 Å, indicating a trace amount of this mineral.

Muscovite is identified by not such a strong reflection at 2.56 Å and 9.9 Å, indicating its presence in our samples.

Glauconite is present in some of the clay samples. When it is present, it shows the highest intensity peak at 2.58 Å, 1.52 Å and 3.31 Å.

Clay minerals present in Brari section are chlorite and smectite.

Chlorite is represented by its basal reflections at 14.25 Å, 7 Å, 4.7 Å and 3.5 Å respectively. The basal reflection at 14.25 Å could not be used directly for the identification of chlorite because of interference with an illite-smectite mixed layer, and 7.14 Å also could not be used for chlorite identification because of the interference and coincidence with kaolinite reflections (NECZKO, 1965).

Smectite was identified using XRD technique. The petrographic and mineralogical studies indicate that smectite is the earliest mineral to form, due to the transformation reactions.
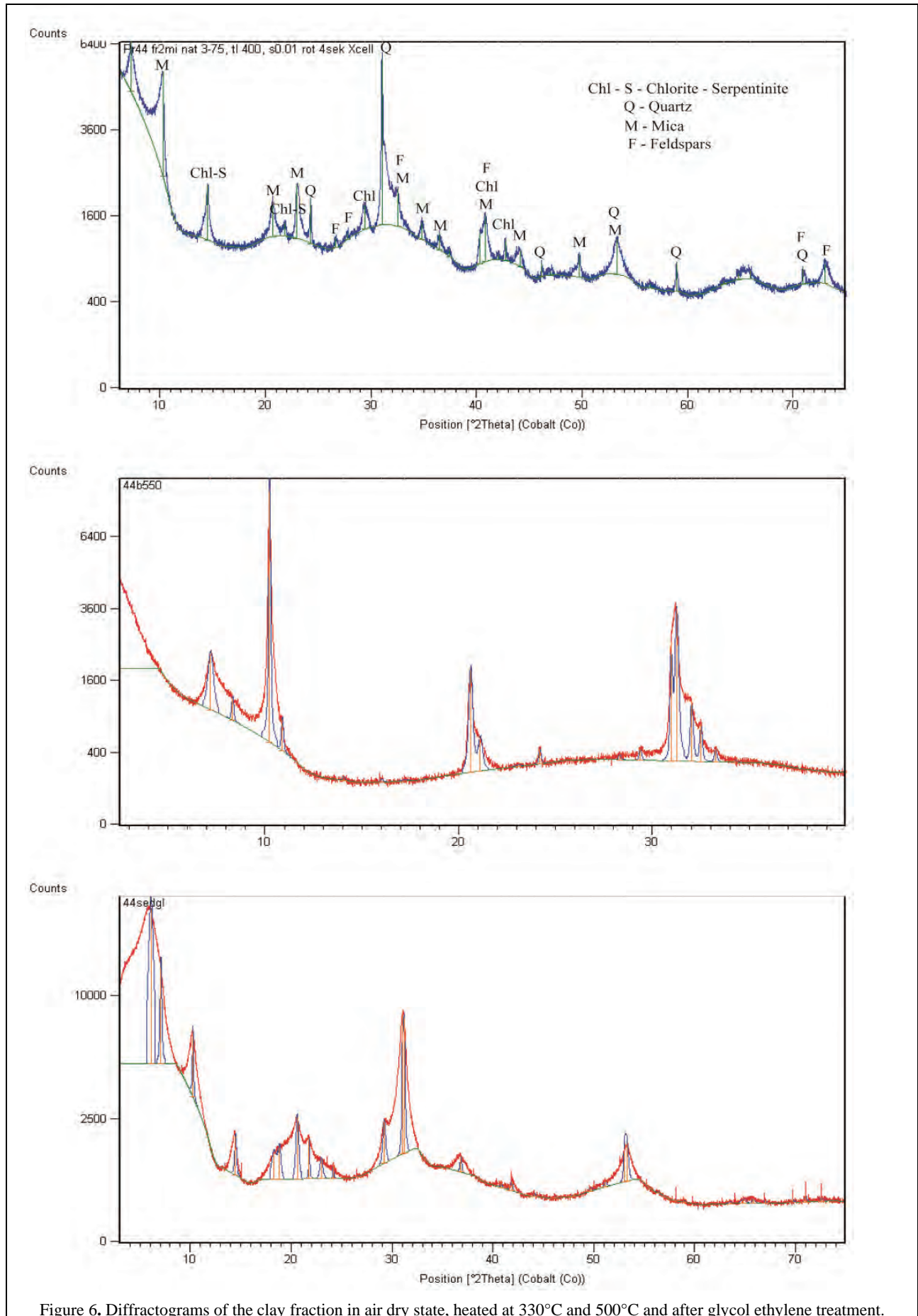
Figure 6**.** Diffractograms of the clay fraction in air dry state, heated at 330°C and 500°C and after glycol ethylene treatment.

CONCLUSIONS

Petrographic identification of detrital minerals and lithic fragments was used to identify the source rock nature (FOLK, 1974; PETTIJOHN, 1975). Because of the heterogenity of the terrigenous formation in Brari section, different aspects of the framework grains composition reveal particular information about their provenance.

A higher proportion of quartz grains with moderate to strong undulose extinction and a higher proportion of poly-crystalline quartz grains with four or more sub-grains characterize a metamorphic source (BASU, 1985). Plutonic rocks tend to produce non-undulose and weakly undulose mono-crystalline quartz grains or poly-crystalline grains with only two or three sub-grains (BASU, 1985). However, according to FOLK (1974) and BASU et al. (1975), poly-crystalline grains containing more than five crystals with straight to slightly curved intercrystalline boundaries also suggest a plutonic source.

Our quartz grains show the aforemantioned characteristic. Moreover, the quartz grains contain some vacuoles, crystal sizes are typically unequal, and the original crystals are typically anhedral. According to KRYNINE (1937, 1940, 1950), these features suggest the same results as that of the above mentioned authors, a plutonic igneous quartz. The presence of quartzites can be related with parent rocks like phyllite or schist. Recycled sedimentary quartz is present in very low quantities, mainly appearing in the quartz-arenitic facies.

Many rock fragments present in the samples have recognizable characteristics of their parent deposits. They are cherts, siliceous siltstone, fine-grained quartzites and mixed quartz-feldspar volcanic rocks. Feldspars make up less than 1% of all the studied samples. According to PETTIJOHN et al. (1987), the scarcity of feldspars suggests that the source area for the sandstone underwent a long period of intensive chemical weathering in a warm humid climate. The feldspar from acidic plutonic rock is believed to be orthoclase or microcline and/or perthitic alkali feldspar (PETTIJOHN, 1975).

Although it rarely appears, alkali feldspars are the dominant type of feldspars in the studied samples. Hence, their source might have been acidic plutonic.The heavy minerals have long been used as indicators of provenance because certain assemblages indicate specific source rocks (BOSWELL, 1933; MILNER, 1926). PETTIJOHN et al., (1987) and reveal that an association of minerals such as apatite, biotite, hornblende, monazite, muscovite, rutile and zircon indicates an acidic igneous source.

The presence of chromite is related to mafic to ultramafic igneous rocks. Garnets and epidotes occur mainly in metamorphic rocks. All of the aforementioned costituents form facies 1 and all data suggest that this facies was derived from the erosion of acidic plutonic rock, mafic to ultramafic igneous rocks and low- to medium-grade metamorphic rocks. These constituents are part of the Albanian ophiolites (together with the metamorphic basement), which were probably the main parent rocks.

Calcareous and quartz-arenitic facies were produced by recycled sedimentary formations. Phosphorous skelethons, echinoid fragments, calcisphere, radiolarian relicts are present in Facies 2. They are very angular and poorly sorted, suggesting close parent rock (probably from Krasta-Cukali and Kruja tectonic zones). Coupled with sandstone petrography, these provenance interpretations were supported by clay mineralogy of some interbedded clays.

Clays related to facies 1 and 2 have a more variegated composition like illite, kaolinite, and randomly interlayered illite-smectite mixed-layer clays compared to the clays that characterizes interbedded clays within Facies 3.

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REFERENCES

BASU A., YOUNG S. W., SUTTNER L. J., JAMES W. C., MACK J. H. 1975. Reevaluation of the use of undulatory extinction and pollycrystallinity in detrital quartz for provenance interpretation. *Journal of Sedimentary Petrology.* Society for Sedimentary Geology. Darlington. **45**: 873-882.

BASU A. 1985. Reading provenance from detrital quartz. In: Zuffa G. G., ed., *Provenance of Arenites.* Reidel, Dordrecht: 231-247.

BOSWELL P. G. H. 1933. *Mineralogy of sedimentary rocks.* London. Murby. 393 pp.

FOLK R. L. 1951. Stages of textural maturity in sedimentary rocks. *Journal of Sedimentary Petrology.* Society for Sedimentary Geology. Darlington. **21**:127-130.

FOLK R. L. 1974. *Petrology of sedimentary rocks. 2nd Ed.* Hemphills Press. Austin. TX. 182 pp.

GELATI R., DIAMANTI F., PRENCE J., CANE H. 1997. The stratigraphic record of Neogene events in Tirana Depression. *Rivista Italiana di Paleontologia e Stratigrafia.* Milano **103** (1): 1-19.

GJANI E., MECO S., STRAUCH F. 2003. Litho-biostratigraphic data on the Tirana Depression (Albania) and their correlation with the Periadriatic Depression. *Neues Jahrbuch fur Geologie und Palaeontologie Monatshefte.* Dezember. **12**: 723-738.

JACKSON M. L. 1958. *Soil Chemical Analysis.* Prentice-Hall. Englewood Cliffs. New Jersey. 272-325.

KRYNINE P. D. 1937. Petrology and genesis of the Siwalik series. *American Journal of Science.* Yale University. New Haven **34**: 422-446.

KRYNINE P. D. 1950. Petrology, stratigraphy and origin of the Triassic sedimentary rocks of Connecticut. *State Geological and Natural History Survey Bulletin.* Hartford. **73**: 293.

KRYNINE P. D. 1940. Petrology and genesis of the third Bradford sand. *Pennsylvania State College Bulletin.* School of Mineral Industries. **34**(43): 13-20.

MILNER H. B. 1926. *Supplement to introduction to sedimentary petrography.* London. Murby. 157-160.

NECZKO E. 1965 *Clay Minerals.* Harper and Row. New York: 329-354.

PETTIJOHN F. J. 1975. *Sedimentary rocks*, 3rd *edition*. Harper and Row. New York: 628-630.

PETTIJOHN F. J., POTTER P. E., SEIVER R. 1987. *Sand and Sandstone.* Springer-Verlag, New York: 25-67.

SHEHU R., ZHACKA P., LLESHI B., SHALLO M., MELO V., KODRA A., YZEIRI D., ZHAFA Z. 1981. La structure des Albanides. *International Symposium on Hellenique Arc and Trench.* Athens: 95-98.

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