Geochemistry of Triassic metasediments from the area of the village of Klokotnitsa, SE Bulgaria

Геохимия на триаски метаседименти от района на с. Клокотница, ЮИ България

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Geological setting

The studied metasediments from the area of the village of Klokotnitsa (SE Bulgaria) belong to the Thracian lithotectonic unit, which comprises a variety of protoliths affected by the Maritsa dextral strike-slip shear zone (Sarov, 2012). Initially assigned to the Triassic (Čatalov, 1961), these carbonate-silicate rocks were not studied in detail later, and not considered with the Triassic from the Sakar-Strandzha region (e.g., Čatalov, 1990). Nevertheless, the metasedimentary succession of this area is usually correlated with the Triassic terrigenous-carbonate association of the Sakar type, but its relations with the carbonate-silicate rocks from the western outcrops of the of the Thracian lithotectonic unit remain yet unclear.

Sample description and analytical procedures

Samples were collected along a section SE of the village of Klokotnitsa and from marbles quarries N-NE of the same village. We present geochemical data of 19 whole-rock samples. Major elements were determined in the Geochemical laboratory of Sofia University by carbonate analyses, followed by wet silicate analyses of the insoluble silicate residue. Whole-rock composition was calculated by combining results of both analyses. Trace elements of 13 whole-rock samples were determined by LA-ICP-MS in the Geological institute, BAS, using whole rocks' SiO_2 and CaO contents as internal standards and NIST 610 as external standard.

The major minerals are calcite, dolomite, quartz, and white mica in variable proportions. Minor constituents are chlorite, feldspars, rarely biotite and accessory opaque minerals, rutile and zircon. The structures are heteroblastic, from granoblastic to lepidoblastic, depending on phyllosilicates proportions. The rocks are medium to very fine grained. Most of the samples show well-defined foliation, traced out by subparallel orientation of phyllosilicates, elongate quartz or quartz-feldspar aggregates and rarely carbonate grains. Quartz grains in the aggregates have triple junction grain boundaries, indicating extensive static recrystallization (annealing). The latter overprint obscured preceding metamorphic structures (e.g., foliation, recrystallization, folding, micro-shearing). Some rarely preserved features, such as calcite grains embayed and replaced by calcite, dissolution zones, possibly have a diagenetic origin. For some larger feldspar and quartz grains we suppose a terrigenous source. Summarized petrographic observations suggest a low-grade metamorphic change in the range of the greenschist facies conditions.

Geochemistry

Carbonate analyses show strong variation of both insoluble silicate residue (from 0.7 to 97.4 wt%) and total carbonate proportion (<3 to 99 wt%), thus supporting the petrographic observations of common carbonate-silicate mineral composition of the rocks. The samples correspond to pure marbles (>95% carbonate minerals); impure marbles (50–95%); carbonate-silicate rocks (5–50%); and carbonate-bearing silicate rocks (<5%) according to the recommendations by the IUGS Subcommission on the systematics of metamorphic rocks (Rosen et al., 2007). The variation of CaO and MgO contents in carbonate phases is in agreement with the petrographic observation of widespread calcite or joint presence of dolomite and calcite in the majority of the rocks (respectively CaO/(CaO+MgO) ≤1 and 0.7–1), while dominant dolomite proportion (ratio close to 0.6) is relatively rare.

Distinguishing features of non-carbonate ingredients, considered further siliciclastic components, are high silica (SiO_2 mainly 62–85%), K_2O>Na_2O, and

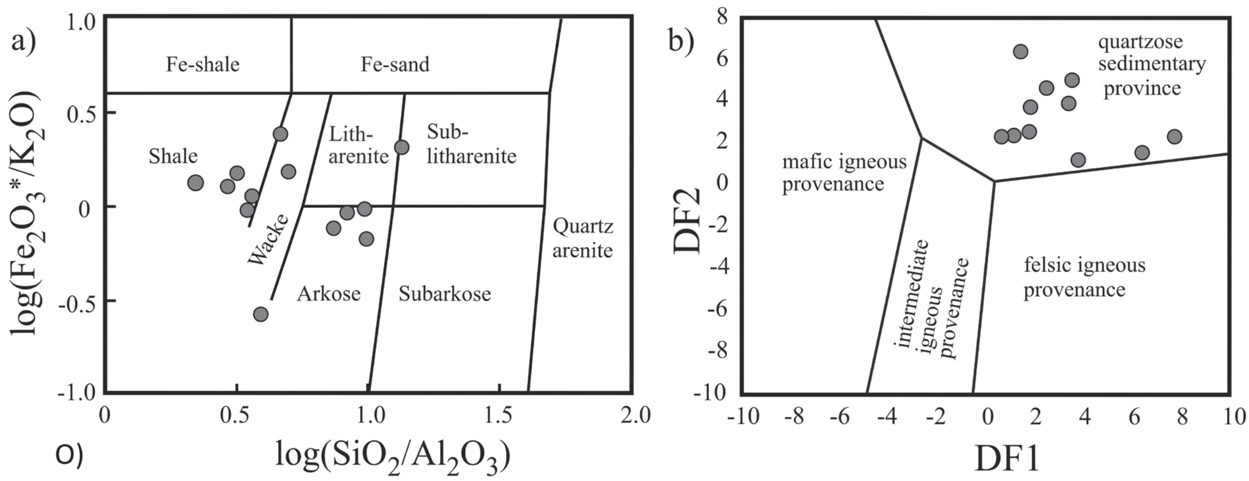

Fig. 1. Major elements in siliciclastic component of the metasedimentary rocks studied: *a*, classification diagram after Herron (1988); *b*, discriminant function diagram after Roser and Korsch (1988)

Fe_2O_3>>FeO. Strong positive correlations between major oxides support a principal association of Al, Fe, Mg, Ti and K controlled by muscovite and chlorite, if present. Low ratio values of $\log(SiO_2/Al_2O_3) < 1$ and $\log(Fe_2O_3/K_2O) < 0.5$ plot the siliciclastic component on the fields of shale, wacke and arkose (Fig. 1a) on the classification diagram of Herron (1988). Discrimination functions (DF) after Roser and Korsch (1988) based on the contents of major oxides suggest quartzose sedimentary provenance for the siliciclastic component (Fig. 1b).

The majority of trace elements (Sc, V, Co, Ni, Zn, W, Ga, Rb, Cs, Ba, Y, Zr, Hf, Nb, Ta, REE, Th, U) correlate positively with the proportion of siliciclastic component indicating incorporation in silicate minerals. Strong positive correlation of Sr and soluble Ca testifies to pronounced preference for calcite. Dolomite or Mg-bearing calcite contains probably Mn, As, Tl and Pb according to the rough positive correlations with soluble Mg. Chondrite-normalized REE patterns correspond to continental crust with negative Eu-anomaly (0.5–0.8) and La_N/Lu_N ratio values in the range mainly of 7 to 13. Immobile elements (La, Th, Sc, Zr, Ti) used for discrimination of tectonic regimes (Bhatia, Crook, 1986) suggest continental island arc setting for the siliciclastic component origin.

Conclusions

We present the first geochemical data on the metasediments from the area of Klokotnitsa village. The rocks originated from shallow marine terrigenous-carbonate sediments, metamorphosed to greenschist facies conditions and intensive deformation. Major elements and immobile trace elements suggest a provenance area of typical upper continental crustal composition. The new data allow comparative studies with other Triassic rock from the Thracian lithotectonic unit. The geochemical data could be used for further detail paleoenvironmental issues like source area characteristics, erosional and transport processes, deposition, etc.

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