The dehydration-rehydration processes of three Zn-hydroxy sulfate minerals with interrupted decorated hydroxide sheets – osakaite, gordaite and Ca-gordaite were investigated. The obtained products and processes were characterized by DTA-TG-MS, in situ and ex situ PXRD and FTIR.

In osakaite structure the two different positions of water molecules cause different ways of dehydration. The derivation of each interlayer molecule results in the formation of discrete phases, with 4, 3 and 1 H2O, without any evidence for dihydrate formation. The process was conducted by both heating and adsorption. The dehydration of these metaphases proceeds reciprocally to the dehydration with relatively high rate at middle and high RH values. The derivation of water molecules from the Zn tetrahedron occurs only on heating. The derivation of only half of the apical molecules was observed. The rehydration of formed hemihydrate metaphase proceeds very slowly even at high RH values. The fully dehydrated phase thus proved to be impossible to form. Structural schemes of monohydrate and hemihydrate phases were proposed. In osakaite structure type all changes occur on the surface of the hydroxide layer, preserving its electrically neutral character, with further possible implications for facilitating intercalation of polar molecules. The negatively charged surface of gordaite hydroxide layer, caused by the occupation of apical position of Zn tetrahedra by Cl− determine dehydration behavior, similar to that of montmorillonite and vermiculite structures. On heating, gordaite and Ca-gordaite form 3 and 2 pillared structures with different sizes of interlayer space and different amount of water molecules for each phase. The rate of dehydration and/or rehydration and particular quantity of derived water molecules is controlled by the interlayer cations. In accordance with the high ionic potential of Ca, the dehydration of Ca-gordaite occurs only on heating and the rehydration proceeds at very low RH conditions. To the contrary, the much lower ionic potential of Na causes the formation of dehydrated gordaite phases by both heating and by adsorption. Similarly to the montmorillonite and vermiculite – these two gordaite minerals can be expected to be used for both cation exchange for interlayer cations and anionic exchange of apical Cl− anion.

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Palaeozoic deposits in the Moesian platform (Northern Bulgaria) are known only from deep wells drilled for oil and gas prospecting. Sixteen microfacies (MFT 1–16) have been distinguished and described in the Givetian to Frasnian carbonate and evaporite sequences, represented in 13 wells from the eastern parts of the platform. They are respectively interpreted as arid peritidal deposits, formed in a variety of carbonate/evaporite environments (from shallow subtidal zones, adjacent to tidal flat, to supratidal sabkha). The shallow subtidal zone is characterised by wave-dominated (possible carbonate sand shoals, MFT 1–3) and protected lagoon (MFT 4–8) settings. The intertidal zone is distinguished by the development of microbial mats with typical lamination (MFT 9 and MFT 10) and “bird’s eyes” type fenestrae (MFT 11). Unfossiliferous laminated mudstones (MFT 12), lag deposits rich in intraclasts (MFT 13), brackish ponds with charophytes (MFT 14), unfossiliferous homogeneous mudstones/dolomudstones (MFT 15) and sabkha evaporites (MFT 16) were formed within the range of the upper intertidal and supratidal zones. These deposits presumably reflect the transition of the platform from carbonate ramp to rimmed shelf. Most of the studied Givetian–Frasnian microfacies are comparable with Wilson’s Standard Microfacies Types and/or with other microfacies described from shallow-marine Middle–Upper Devonian carbonate and evaporite successions in Europe. It seems likely that during the Givetian–Frasnian time the Moesian carbonate platform was located in the arid climate zone on the northern shallow shelf of the Gondwana.


The core complexes of the North Aegean result from the gravity spreading of a thrust wedge, driven by the Hellenic slab rollback, since middle Eocene. The development of the Southern Rhodope Core Complex occurred in two stages: (i) core complex exhumation accommodated by the Kerdylion detachment and (ii) steep normal faulting controlling the deposition of Neogene sedimentary basins that segmented the core complex. Both stages have been controlled by a clockwise rotation of the detachment hanging wall. The bulk amount of extension along the Aegean coastline in Northern Greece reached 120 km. The transition between the two stages occurred in middle Miocene due to an increase in extensional displacement by a factor 5. This transition between two different modes of extension, from localized detachment (i.e., core complex mode) to distributed steep normal faulting (i.e., wide rift mode), occurred at Aegean scale as a result of an acceleration of slab rollback. The Neogene basins emplaced close to the detachment, where brittle upper crust was thin (around 7 km) but containing weak marble layers allowing the formation of ramp-flat extensional systems with rollover-type basin fill. Since Pliocene, the stretching direction
changed, from NE-SW to N-S, due to the propagation of the North Anatolian Fault in the North Aegean domain.


The Early to Late Triassic development of a carbonate ramp system in the subtropical belt of the NW Tethys was controlled by the interplay of several global and regional factors: geotectonic setting (slow continuous subsidence on a passive continental margin), antecedent topography (low-gradient relief inherited from preceding depositional regime), climate and oceanography (warm and dry climatic conditions, storm influence), relative sea-level changes (Olenekian to Anisian eustatic rise, middle Anisian to early Carnian sea-level fall), lack of frame-builders (favouring the maintenance of ramp morphology), and carbonate production (abundant formation of lime mud, non-skeletal grains and marine cements, development of diverse biota controlled by biological evolution and environmental conditions). Elevated palaeo-relief affected the ramp initialization on a local scale, while autogenic processes largely controlled the formation of peritidal cyclicity during the early stage of ramp retrogradation. Probably fault-driven differential subsidence caused a local distal steepening of the ramp profile in middle–late Anisian time. The generally favourable conditions promoted long-term maintenance of homoclinal ramp morphology and accumulation of carbonate sediments having great maximum thickness (~500 m). Shutdown of the carbonate factory and demise of the ramp system in the early Carnian resulted from relative sea-level fall and subsequent emergence. After a period of subaerial exposure with minor karstification, the deposition of continental quartz arenites began. The proximity may be explained by south-directed rollback of the subduction zone, although also post-69 Ma tectonic displacements have to be considered. Together with published age data from other parts of the Rhodopes, the new data confirm that multiple subduction events took place between ~200 Ma and ~40 Ma along this section of the southern European plate boundary.


The Rhodopes in Bulgaria and Greece represent a nappe stack of high-grade units with poly metamorphic history. Constraining the time of metamorphism in individual subunits is essential for unraveling the controversial framework of subduction, exhumation and nappe stacking. Here we present new evidence for Late Cretaceous high-pressure metamorphism in the Eastern Rhodopes. In eclogite from the Byala Reka-Kechros Dome (Kazak eclogite), garnet growth is dated at 81.6±3.5 Ma by Lu-Hf chronometry, indicating that prograde eclogite-facies metamorphism occurred during the Late Cretaceous. Petrological data and modeling suggest peak pressure conditions of 1.2–1.6 GPa, 570–620 °C. We propose that metamorphism took place in a subduction zone dipping towards north under the Sredna Gora section of the Apuseni-Banat-Timok-Sredna Gora continental magmatic arc. Eclogite-facies metamorphism coincides with the main phase of granitoid intrusions in the Sredna Gora Zone. The site of magmatic activity in this area shifted southward during the Late Cretaceous and arrived in the Eastern Rhodopes at ~69 Ma, as shown by granite intrusions of that age only 4 km north of the locality of the dated eclogite sample. This proximity may be explained by south-directed rollback of the subduction zone, although also post-69 Ma tectonic displacements have to be considered. Together with published age data from other parts of the Rhodopes, the new data confirm that multiple subduction events took place between ~200 Ma and ~40 Ma along this section of the southern European plate boundary.


Calcareous nanofossil, calpionellid and ammonite occurrences have been directly constrained across the Jurassic–Cretaceous boundary interval in the section of Kopanitsa, SW Bulgaria. This section reveals a continuous and expanded sedimentary
Depwater hydrocarbon exploration drilling only began in the Black Sea less than 20 years ago, primarily because of the economical/technological challenges associated with mobilizing suitable rigs through the Bosphorus. However, to date (end 2017), c. 20 deepwater wells have now been drilled, targeting a large variety of plays in this underexplored basin. The deepwater wells drilled to date are categorized by their main play objectives, within either the sag/post-riift or syn-riift basin fill of the Black Sea. The sag/post-riift play types have proven to be more successful, finding either biogenic gas in Miocene to Pliocene reservoirs associated with the Paleo-Danube and Paleo-Dnieper/Dniester or oil in Oligocene siliciclastic systems. Syn-riift or early postrift plays, in contrast, assumed mostly shallow water carbonate reservoir targets. Only one well targeted pre-riift stratigraphy. Most of the exploration failures to date are directly related to the lack of reservoir at the targeted stratigraphic levels. However, the recent discoveries have underlined the presence of at least two active and effec- tive petroleum systems that cover large parts of the deepwater Black Sea Basin.


Establishment of geochemical background and threshold values for 8 potential toxic elements is essential for soil management activities. Available topsoil data collected in the Bulgarian soil quality monitoring network are explored for the concentrations of the potentially toxic elements (PTEs) of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn. The ‘median +2MAD’ and TIF methods for obtaining geochemical threshold values, which differentiate sampling sites with background from those with unusually high element concentrations, are presented. Comparison of the derived national geochemical threshold values with those obtained in European studies outlines the specificity of the Bulgarian PTE background concentrations among the other southern European countries. The threshold values for Cd, Cu, Ni, Pb, and Zn are more similar to those derived from the northern European countries since the As and Cr ones are more close to the values derived for southern Europe. The geochemical threshold of Hg is almost one order of magnitude as high as the southern
European derived value. The usage of geochemical threshold values for soil risk assessment is suggested by comparison with soil quality guideline values adopted in other countries. The combination of threshold values based on 90th percentile with geochemical mapping identifies the priority areas for further assessment. Regions with more than 2 PTEs (2.26% of the Bulgarian territory) are suggested for detailed (eco)toxicological assessment.