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The origin of black shale-hosted Mn deposits in Paratethyan basins: Constraints from geological events at the Eocene/Oligocene boundary

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Abstract. The giant, Phanerozoic largest Mn deposits of southern Ukraine and Georgia and the Mn-rich strata of Mangyshlak, northeastern Bulgaria, northwestern Turkey, Hungary, and Slovakia were laid down synchronously at the base of the Early Oligocene interval. Their formation was controlled by an optimum combination of major geological events. The collision of Eurasia and the Indian subcontinent in terminal Eocene time boosted the generation of new sea floor at the crests of the global system of mid-ocean ridges with ensuing global transgression and a huge input of hydrothermal components (Mn, Fe, SiO_2, Ca, CO_2, etc.). Meanwhile in the Paratethys, Early Oligocene was a time of inception of and/or rapid subsidence in the marginal inland basins that stored black shales and vast amounts of dissolved Mn^{2+}. Shelf settings provided the milieu for extensive Mn deposition due to transgressive incursions of dense oceanic waters that displaced the Mn-rich anoxic ones.

Introduction

The Early Oligocene Mn deposits of southern Ukraine and Georgia (largest in Phanerozoic history), Mn concentrations in Mangyshlak, northeastern Bulgaria, and northwestern Turkey, and minor deposits in Hungary and southern Slovakia, all are composed of coeval Mn-rich sediments occurring at the base of the Lower Oligocene (the Rupelian stage in Europe or the Pshekhsky regional stage in the CIS) throughout a vast territory from Central Europe to Central Asia. These deposits have in common tectonic settings (mobile margins of the southern Eurasian craton or slopes of median masses in the Alpine belt), environments of occurrence (tectonically rigid cratonic basement), facies relationships and depositional milieus (the shelves of inland, marginal, and backarc basins), and lithologic, mineral, and chemical compositions of the mineralized beds and their host sequences. The deposits in point account for more than 30% of the world's Phanerozoic Mn resource and over 70% of the Cenozoic one [*Varentsov,* 1996].

Following the discovery of these deposits, broadly differing views on their genesis have been expressed, and the discussion is going on. In addressing Mn deposition in the wide regional context of the Early Oligocene Eastern Paratethyan basin, many researchers over a century ago (see historical reviews in: [*Obruchev,* 1934; *Vernadsky,* 1954a, 1954b] noted the fact that the Mn deposits in southern Ukraine (Nikopol, etc.), Georgia (Chiaturi, etc.), Trans-Caspian region (Mangyshlak Penisula), and Asia Minor, all occur in a very narrow stratigraphic range. To emphasize the fulcrum of the issue, *Obruchev* [1934, p. 436] wrote, "It is also hard to explain the fact that the latter (Mn mineralization-authors' note) is restricted exceptionally to a certain age level and is absent from the overlying and underlying beds, deposited in the same sea, which became abundant in manganese compounds for a brief time interval." *Vernadsky* [1954b, p. 521] pointed out the wide scale of Mn deposition: "The present-day Chiaturi deposits indicate that these are a remnant of a much more extensive past concentration of manganese that encompassed a vast space in the oozes of the Oligocene sea in Eurasia ca. 40 million years ago. Most part of the manganese thus stored was to pass again into a migrant form

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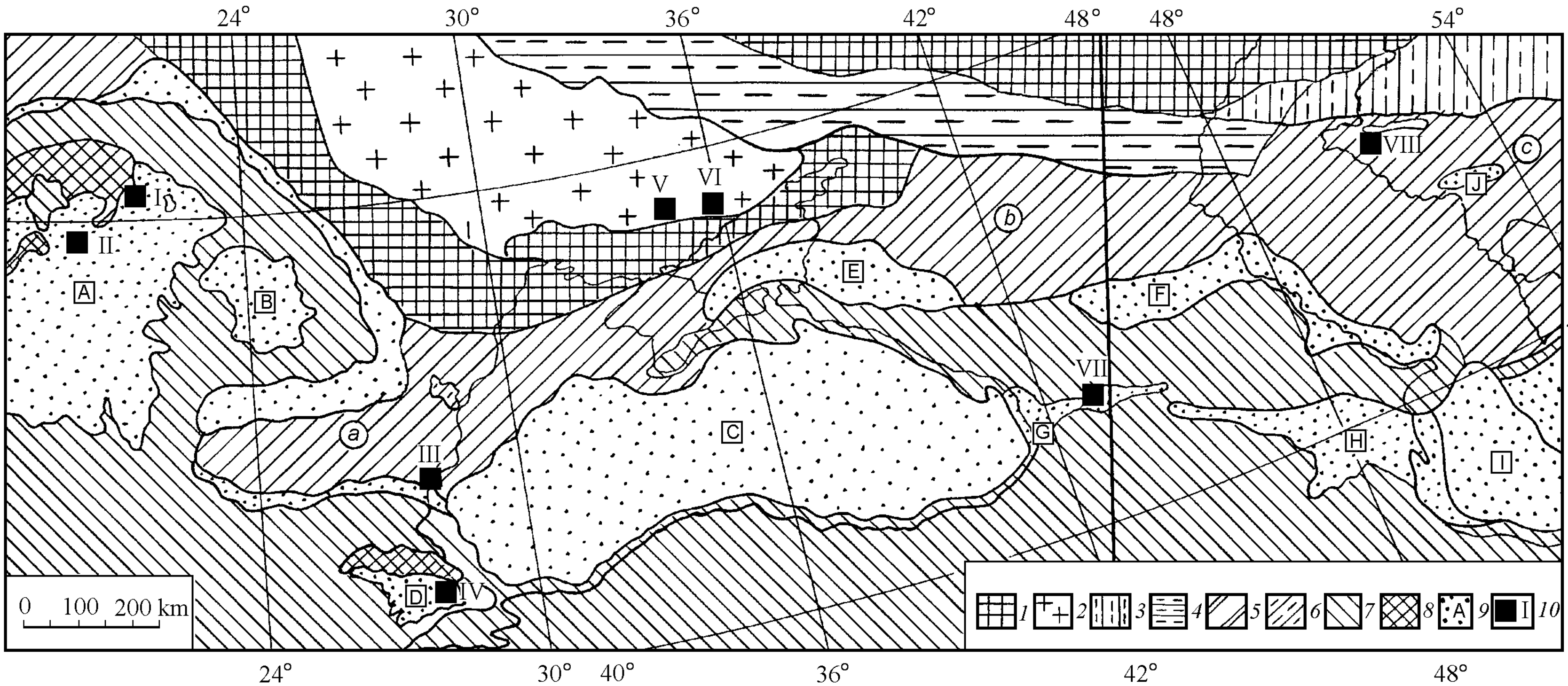

Figure 1. Tectonic setting of Early Oligocene Mn deposits of the Central-Eastern Paratethys (modified from *International...*, 1998). 1 – Precambrian eastern European craton; 2 – Ukrainian shield; 3 – north Ustyurt (Hercynian) block; 4 – Dnieper-Donets basin, Donbass, and Karpinsky Swell; 5 – post-Paleozoic craton (plates: (a) Moesian, (b) Scythian, and (c) Turan); 6 – individual highs of Paleozoic and Early Mesozoic basement of post-Paleozoic craton; 7 – Alpine orogenic area; 8 – individual highs of basement assemblages of various ages in the Alpine orogenic area; 9 – troughs and basins that subsided rapidly in Cenozoic time, filled in with undeformed deposits (A, Pannonian; B, Transylvanian; C, Black Sea; D, Thrace; E, Indol-Kuban; F, Terek-Caspian; G, Rioni; H, Kura; I, South Caspian; J, South Mangyshlak); 10 – Mn deposits (not to scale): I = Kisovce-Svabovce, II = Eger-Demjén, III = Varna group, IV = Thrace group, V = Nikopol, VI = Bolshoi Tokmak, VII = Chiaturi, etc., VIII = Mangyshlak (Sartagan).

and disperse, the remnants being preserved in the Dnieper region, at the Laba River, in Ciscaucasia, Northern Urals, Georgia, and Asia Minor."

The majority of researchers adopted the notion of a sedimentary/diagenetic origin for the Early Oligocene Mn deposits with individual variations as for the nature of the sources of mineralization [*Betekhtin,* 1964a, 1964b; *Shnyukov et al.,* 1993; *Strakhov et al.,* 1967; *Varentsov,* 1963]. A number of studies focused much on the role of basins with elevated hydrogen sulfide concentrations as likely sources of mineralization components [*Kholodov,* 1984; *Kholodov and Nedumov,* 1991; *Sapozhnikov,* 1967a, 1967b; *Stolyarov,* 1958]. However, articles were also published attributing the origin of mineralization to deep seated hypogene processes [*Aleksiev,* 1959; *Chukhrov,* 1974; *Knyazev and Shevchenko,* 1986; *Mstislavsky,* 1985].

Our work is intended to propose, based on our own studies and analysis of the available data, the following issues to be discussed: (a) a genetic model to describe consistently the information at hand, (b) a viable correlation of massive Mn deposition and geological events that occurred at the Eocene/Oligocene boundary, and (c) relationships between the Mn mineralization processes and phenomena of regional and/or global extent. This work is a follow-up on our previous studies on these issues [*Varentsov,* 2002; *Varentsov and Muzyliov,* 2000, 2001].

Stratigraphy. Correlation

Eocene/Oligocene Transition. Correlating the Eocene/Oligocene Boundary and Mn Mineralization with the Nannoplankton Zonal Scheme

In virtually all of the Paratethyan manganiferous basins, the Mn-rich strata are distinctly transgressive relative to their underlying rocks. However, the change in depositional regime at the Oligocene/Eocene boundary was comparatively rapid albeit not catastrophic. Thus, in many Ciscaucasian sections (at the Kuban, Kheu, and Rubas-chai rivers) this transition is gradational, the boundaries between the Beloglinskaya Formation (Upper Eocene) and Maikop Group (Oligocene-Lower Miocene) being not sharp: there is everywhere a transitional ("buffer") zone of a relatively small thickness. Similar relationships are characteristic of many regions in Central Europe-in particular, in the Great Hungarian Basin of Paleogene age, in which the Buda marls of Priabonian age grade into the Tard clay of Rupelian age (early Kissel sequence) with a high (2–7%) TOC [*Báldi,* 1986].

In the Paratethyan basins, the Eocene/Oligocene boundary was featured by an essential change in depositional and hydrochemical environments, expressed in a progressively increasing anoxia. Throughout the vast area encompassing the Rhine graben, the regions of marginal Alpine basins (Helvetides, Switzerland; Austria, Bavaria, French Savoy), the Polish and Ukrainian Carpathians (Sub-Menilitic and Menilitic sequences), Slovakia (Socka beds), Hungary (Early Kissell sequences, Tard clays), Transylvania (Bitusa and Ileanda Formations), and the Eurasian craton margins (Crimea-Caucasus province and Trans-Caspian region: Maikop Group and its correlatives), deposited were sediments considerably enriched in organic matter (up to 5–7% TOC) of sapropelic nature, not infrequently with terrestrial plant remains, pyrite, and associated mineralization [*Rögl,* 1999] (Figure 1). A singular role in the Oligocene Paratethyan sedimentation was played by the deposition of tremendous black shale masses of Maikop sediments in the Black Sea Basin and its surrounding troughs (Guri, Sorokin, Kerch-Taman, Indol-Kuban, Tuapse, Sinop, Burgas, Lower Kamcha, Karkinit, Krylov, etc.). These strata are rather uniform in structure and composition, differing but little from their age correlatives in Transcaucasia, the North Caucasus, and Trans-Caspian region. The gradually increasing anoxia affected the lower layers of the water column in the comparatively deep basins. Initially, this told only slightly on the presence of various benthic organisms, yet eventually this was to result in an increased proportion of planktonic forms. Within the shelf and littoral zones, anoxic impact was very slight.

The studies of *Krasheninnikov and Muzyliov* [1975] show the base of the Maikop Group to coincide with the Eocene/Oligocene boundary – i.e., with the base of the Globigerina tapuriensis planktonic foraminifer Zone and the base of Helicosphaera reticulata nannoplankton Zone CP16. These conclusions were further supported by nannoplankton studies [*Muzyliov and Tabachnikova,* 1987]. However, there exist somewhat different options for placing the Eocene/Oligocene boundary; thus, according to [*Báldi,* 1980, 1986; *Báldi et al.,* 1999], it is positioned somewhat below the base of the Maikop Group. An important datum level to constrain the stratigraphic position of the Mn-mineralized interval is provided by the ostracod (Polbinsky) layer. It is customarily referred to as "the ostracod layer," although its principal rock-forming constituent is nannoplankton, the role of ostracods being minor. Based on nannoplankton studies, *Muzyliov and Tabachnikova* [1987] ascribe the ostracod layer to the narrow transitional interval between Helicosphaera reticulata Zone CP16 and Sphenolitus predistentus Zone CP17. This layer, as evidenced clearly by the available data, occurs above the Mn-rich sediments, which are confined to within Zone CP16.

Paleontological Characteristics of the Mn-Rich Strata.

The majority of previous paleontological studies on the Mn-rich Lower Oligocene strata in the Eastern Paratethys (Figure 1) were chiefly focused on data acquisition. These studies were mostly limited to listing taxa with occasional attempts to interpret them ecologically, bathymetrically, and climatically. As a result, important groups such as calcareous nannoplankton and dinoflagellates from Mn-rich sediments remained unstudied. The below results from the studies performed to date should be regarded as a tentative systematization that allows certain general conclusions to be made.

The Nikopol and other deposits of the South Ukrainian basin. The mineralized bed has yielded selachian teeth that belong, as determined by O. Iekel, to Carcharodon turgidus Ag., Carcharias sp., Notidanus primigenius Ag., and Miliobatis sp. The palinologic assemblage, as determined by I. M. Pokrovskaya, consists of: 1.3%. Pinus (Diploxilon); 0.4% P. (Haploxilon); 35.6% P. (P.) cristata Pokr.; 20.3% Taxodiaceae; 4.4% Taxodium sp.; 6.6% Gliptostrobus sp.; 0.4% Palmae; 0.4% Salix; 2.2% Myrica santaloides Pokr.; 0.4% Carya sp.; 1.7% Juglans sp.; 1.3% Alnus sp.; 11.5% Quercus sp.; 2.2% Fagus sp.; 0.4% Ulmaceae; 0.4% Rutaceae; 1.7% Rhus sp.; 1.7% Oleaceae; and 5.5% Tricolporites sp.

As established by N. K. Bykova, E. Ya. Kraeva, V. G. Morozova, Yu. P. Nikitina, and M. V. Yartseva, the mineralized layer and its underlying one contain virtually identical foraminifer and mollusk assemblages.

The foraminifer assemblage includes: Haplophragmoides deformabilis Subb., Ammobaculites foleaceus Brady, Textularia mauerisma Orb., Triloculina akneriana (Orb.), M. circularis Born., Spiroloculina limbata Born, Nonion umbilicatulum (Montf.), N. nonionoides Andreae, N. praevius Subb., Lagena isabella Orb., L. perlucida (Montf.), L substriata Will., L. tenuis Born., L. sulcata (Walk. et Jacob.), L. clavata Orb., Dentalina approximata Reuss, Nodosaria soluta Reuss, Marginulina alsatica Andreae, Oolina marginata (Walk. et Bous.), Caucasina schischkinskajae (Saml.), Uvigerinella majcopica Kraeva, U. californica Cush., Angulogerina oligocenica Andreae, A. tenuistriata Reuss, A. rogalii Majtl., Bolivina beyrichi Reuss, B. mississippiensis Cush., B. aenariensis Costa, B. cf. antiqua Orb., Gyroidina memoranda Subb., Cibicides oligocenicus (Saml.), C. amphisyliensis (Andreae), C. pseudoungerianus Cush., C. stavropolensis Bogd., Globigerina officinalis Subb., etc.

The macrofaunal assemblage includes: Nucula comta Goldf., Lucina batalpaschinica Korob., Thyasira unicarinata Nyst., Tellina praepostera Koen., Cardium cf. charcovense Slod., C. chadumicum Sel., Laevicardium cingulatum (Goldf.), Crassatella cf. pseudotumida Ben., Astarte kickxi Nyst., Cardita (Vernericardita) tuberculata Munst., C. (V.) borisphaenica Nossov., Miocardiopsis sp., Circe edwardsi Koen., Cyprina perovalis Koen., Isocardia cyprinoides quadrata Koen., Arca sp., Barbatia decussata Nyst., Polymesoda convexa (Brongn.), Pitar splendida (Merian), P. sulcataria (Desh.), Cardiopsis incrassata (Sow.), Pectunculus obovatus Lamk., Pecten arcuatus manganensis Slod., Chlamis composita (Sandb.), Ch. bifida (Munst.), Ch. picta (Goldf.), Ch. permista (Beyr.), Ch. decussata (Munst.), Pseudamussium corneum (Sow.), Modiola micans Braun, Thracia arcuata Koen., Pholadomya weissi Phil., Panopaea haberti Bosq., Aporrhais pescarbonis Brongn., Conus cf. symmetricus Desh., Calyptraea laevigata Speyer, C. striatella Nyst., Tornatella simulata Spl., Pleurotomaria sismondai Goldg., Natica sp., Terebratula grandis Blum., Coeloma vigil M. Edw., Balanus cf. crenatus Darv., and Schizaster sp.

The hiaturi and other deposits of the western Georgian basin. The manganiferous and their host strata of the Chiaturi deposit contain no faunal remains.

Palinologic data. Correlatives of the Mn-mineralized layer from the neighboring regions have yielded similar palinologic spectra constituting a single assemblage dominated by Gymnospermae pollen (up to 77%): the family Pinaceae (genera Pinus, Cedrus, Picea, Tsuga) and sporadic Taxodiacea. The Angiospermae are represented by pollen of the genera Betula, Alnus (the family Betalaceae), Carya, Pterocarya, Engelhardia (the family Juglandaceae). Broadleaved plant remains (Fugas, Quercus, Tilia, Ulmus) were encountered sporadically. Herbaceous plants are represented by Leguminosae-type pollen. The Pteridophyta are classed with the genera Polypodium and Lygodium.

A closely identical palinologic assemblage was established from the strata in question intersected by Hole 11 in the region of Cherat-Khevi Gorge, near the southeastern exposures of the Dzirula massif (Georgian block). Along with palinologic remains, however, these sediments yielded foraminifers: Quinqueloculina sp., Nonion sp., Elphidium aff. anerosum Bogd., Bolivina aff. mississippiensis Cusm., Bolivina sp., Angulogerina aff. anghulosa (Will.), Rotalia canui Cush., Discorbis sp., Cibicides aff. amphisiliensis (Andr.), C. lobatulus (Walk. et Jac.), Globigerina officinalis Subb., Globigerina sp., Pseudohastigerina micra (Cole), Planorotalites sp., Acarinina (?) sp., Chiloguembelina aff. gracillima (Andr.).

Mn deposits of Mangyshlak Penisula. In Mangyshlak Peninsula, basal Maikop Group strata are composed of the Uzunbas Formation (Cristellaria hermanni Zone). In the southern regions, it is represented by clays whose individual intercalations are calcareous or bear Mn-carbonate concretions, totaling a thickness of 10–12 m; the northern regions are dominated by clay, siltstone, and sandstone with oxidized Mn nodules (the Mangyshlak deposit). Foraminifers have been encountered in clays from the southern regions and siltstones from the northern ones, and they include: Cristellaria hermanni Andreae, Quinqueloculina impressa Bornemann, Guttulina sp., Pyrulina sp., Baggina iphigenia (Samoil.), Alabamina aff. admaensis (Samoil.), Caucasina schischkinskayae (Samil.), Bolivina sp., Nonion umbficatulus Montagu, Cibicides oligocenicus (Samoil.), C. aff. pseudoungerianus Cush., Planorotalites sp., Globigerina officinalis Subb., Guembelina sp., and Chilostomellidae. Mollusk assemblages have been recorded from intercalations with Mn-carbonate concretions, and they consist nearly exceptionally of gastropods: Apporrhais cornutus Alex., Polinices dilatata (Phil.), Cassidaria aff. echinata Koen., Cymatium multigranum (Koen.), Typhis schlotheimi Beyr., Euthriofusus suberraticus (Bajar.), Fusinus crassisculptus karagiensis Merklin, Turris (Hemipleurotomata) laticlavia (Gieb.), T. (H.) nodigera (Koen.), T. (H.) cathedralis (Koen.), T. (H.) difficilis (Koen.), T. (H.) konincki stolarovi Merklin, T. (H.) lunulifera (Koen.), T. (H.) flexicostata (Gieb.), Turris (Turris) plana (Gieb.), T. (T.) explanata (Koen.), Surcula ilyinae Merklin, S. beyrichi Phil., Drillia (Cymatosyrinx) nassoides Sol., Vexillum (Sassia) sokolovi (Bajar.), Dentalium (Fustiaria) acutum Hel.

Paleoecological interpretation. The above paleontological data imply that the Mn mineralization was formed in Early Oligocene time in a warm climate, and that of the

Chiaturi and other western Georgian deposits, in a subtropical climate. The Mn mineralization of the southern Ukrainian basin (Nikopol, etc., deposits) and western Georgian basin (Chiaturi, etc., deposits) was deposited in a shallow water nearshore zone, and that of Mangyshlak Peninsula, in comparatively more deep-water parts of the neritic zone at environments with a normal sea-water salinity.

Transgressive-Regressive Cyclicity of Oligocene Strata of the Paratethys

Oligocene strata of the Paratethys include two transgressive-regressive cycles, Rupelian and Chattian [*Muzyliov et al.,* 1992]. Above the ostracod layer in Ciscaucasia, noted are essentially shallow-water sediments containing no nannoplanktonic remains and corresponding to the range of the Batalopasha Formation and, possibly, to the upper part of the Morozkina Balka Formation. Further upsection, the strata take on a more deep-water aspect (marking the beginning of a new transgression); a rather abundant, although not diversified, assemblage of Sphenolitus ciperoensis nannoplankton Zone CP19 appears in the sediments. Therefore, the boundary between the Rupelian and Chattian stages passes between Sphenolitus distentus Zones CP18 and CP19.

Salinity drop in the Atlantic and its correlative event in Paratethyan basins. The deposition of the two symmetrical belts of sediments containing planktonics of a clearly low-salinity aspect is among the most singular events in the Oligocene history of the Atlantic Ocean. This phenomenon was discussed in detail in [*Dercourt et al.,* 1986]. It is shown that in the Southern Hemisphere the belt of sediments composed of a poorly diversified coccolith assemblage of the genus Braarudosphaera was drilled during the numerous cruises of the Glomar Challenger under the DSDP. Its symmetrical belt in the Northern Hemisphere is less conspicuous, possibly due to the smaller number of the holes drilled there. The braarudosphaerid sediments are most widespread in the range of Zones CP17 and CP18, although they are also encountered in the upper part of Zone CP16 and the lower part of Zone CP19. What gave rise to the low salinity belts is largely unclear still. *Muzyliov et al.* [1992] attribute this Oligocene low-salinity event (whose counterparts are unknown in the Phanerozoic) to the lack or poor development of the Circum-Antarctic current with the result that the melting of Antarctic ice sheets took place while heat exchange between this continent and the global oceanic circulation system was limited little, if at all. This must have caused a sharp atmospheric and oceanographic instability, although the specific mechanism to account for these phenomena remains as yet unclear. Note that the modern system of global oceanic circulation was mainly formed at the Oligocene/Miocene boundary due to the opening of Drake Passage [*Ciesielski and Wise,* 1977; *Lisitsyn,* 1980; *Muzyliov et al.,* 1992; *Parker et al.,* 1985; *Varentsov,* 1983]. In the Eastern Paratethys, the counterpart of the sediments in point is the ostracod (Polbinsky) bed [*Muzyliov and Tabachnikova,* 1987]. As a rule, its thickness in the most deep-water parts of the paleobasins is no larger than 1.5–2 m, and along their periphery it may reach 10–20 m. The nannoplankton assemblage is virtually monotypic, consisting of Reticulofenestra ornata and/or R. clathata to the extent of more than 90%. Further studies showed the Polbinsky beds to merely record the peak of this event. Earlier, in the course of the 1960s-late 1970s discussion concerning the number of ostracod beds in the Oligocene section of the former southern USSR, the best grounded opinion to be expressed [*Veselov and Sheremeta,* 1964] had it that there might be several ostracod beds, one of these being the most important. Subsequent studies provided support to this conclusion. In Hungary, established were several such beds, the principal one containing the Reticulofenestra ornata [*Nagymarosu,* 1983].

A similar conclusion was drawn for the Carpathians [*Haczewski,* 1989; *Krhovsky et al.,* 1992]. From the Lower Volgaland, N. G. Muzyliov and V. A. Musatov reported thin intercalations with a monotypic nannoplankton assemblage that remains as yet unstudied. The low salinity episode in the Early Oligocene is marked by the appearance of brackish-water mollusk and ostracod assemblages in the Kendzhalinskaya Formation (Solenovsky Beds) of Mangyshlak Peninsula [*Popkov,* 2000; *Voronina and Popov,* 1984]. Evidently, the appearance of intercalations with low salinity nannofloras in the Oligocene of the Paratethys reflects the low salinity episode in the Atlantic, because the stratigraphic range spanned by it (upper part of Zone CP16-lower part of Zone CP17) is in the ocean confined to the braarudosphaerid ooze member.

Therefore, the deposition of low salinity intercalations in Oligocene time in the Paratethys was due likely to either atmospheric instability with periodically increasing rain precipitation and river input or a resumed communication with the world ocean, where this episode correlates with a warming interval accompanied by glacier melting [*Lipman,* 1981].

Eruptive Activity in the Early Rupelian

Sediments of the lower and middle parts of nannoplankton Zone CP16, deposited during the formation of Mn-rich strata, record evidence of an increased eruptive activity, most distinct in the Maikop and Menilitic basins of the Lesser Caucasus and Carpathians, respectively. It is worth noting that intense volcanism in the Lesser Caucasus had ceased by the beginning of the Priabonian, to be resumed in the middle Rupelian, when the bentonitic clay intercalations were formed [*Kacharava and Khuchua,* 1991]. During this time in the Carpathians the thick tuffaceous sequences of the lower Menilitic sub-formation were deposited [*Gavura and Danysh,* 1988]. The above peaks in endogenous activity are clearly correlative to depositional maxima of basaltic and andesite-rhyolite ash in the world ocean [*Levitan and Lisitsyn,* 1978a, 1978b; *Lisitsyn,* 1980]. The combination of such forms of eruptive activity points to a link between the processes occurring along the axial zones of the ocean (where the proportion of pyroclastics does not normally exceed 3–5% of the total amount of volcanics) and in the active

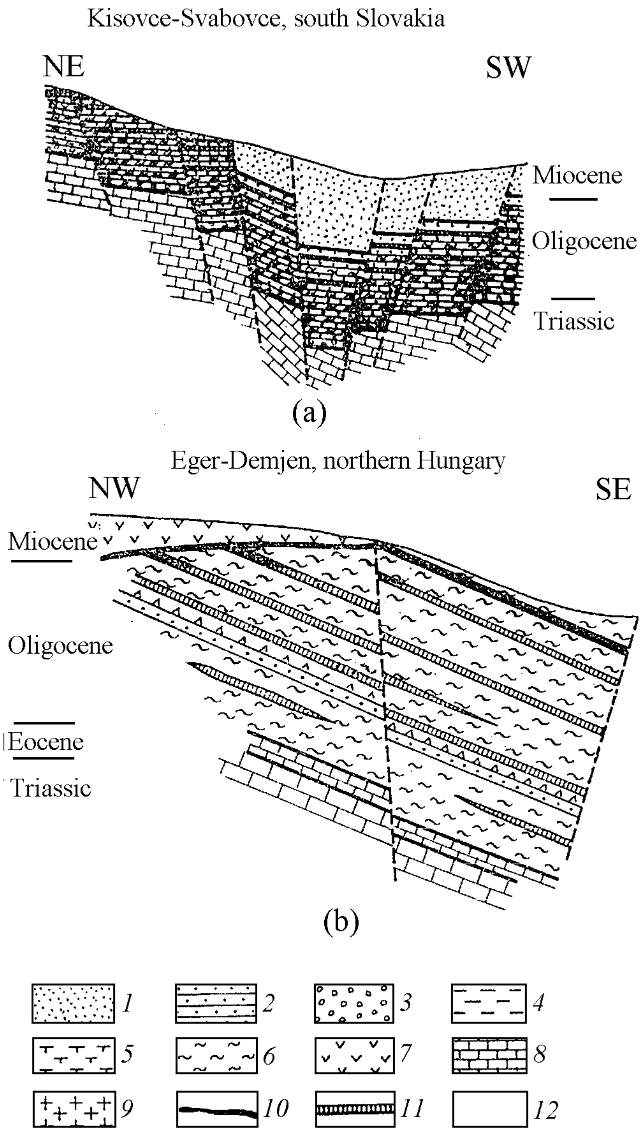

Figure 2. Geological/lithological profiles through Early Oligocene Mn deposits of central Europe: (A) Kišovce-Švabovce, south Slovakia; (B) Eger-Demjén, northern Hungary [modified after *Molnar and Morvai,* 1961] 1 – sand; 2 – sandstone; 3 – conglomerate; 4 – clay; 5 – multicolored clay; 6 – marl; 7 – tuff; 8 – limestone; 9 – granite, gneiss, quartz porphyry; 10 – Mn oxyhydroxide mineralization; 11 – Mn carbonate mineralization; 12 – Pleistocene strata.

continental margins and island arcs (where explosive products of andesite-rhyolite volcanism are dominant).

A certain relationship can be sensed between the peak in global endogenous activity at the Eocene/Oligocene boundary both in the world ocean and at continental margins and island arcs on the one hand and the bloom of siliceous microorganisms (radiolarians, diatoms, sponges, etc.) on the other. In the terminal Eocene-Oligocene time, the strong global cooling [*Savin,* 1977] and a relative increase in the surface water density gave rise to the systems of vertical circulation and bottom currents that operate to this day. The bottom currents, when their velocity increased, transported very appreciable masses of nutrients (of initially hydrothermal, halmyrogenic nature), to result in Early Oligocene time in high biological productivity accompanied by massive siliceous and organic-rich deposition [*Laliev,* 1964; *Lisitsyn,* 1980; *Van Andel,* 1976; *Varentsov et al.,* 1981]. Broad development of such siliceous deposits is typical of sedimentation in the Early Oligocene basin of Georgia. A feature distinguishing the Khadum beds from the middle part of the Maikop Group (upper-Lower to Upper Oligocene) lies in that these beds are markedly dominated by silicites: gaize, diatomite, spongolitic sandstone, and chalcedony masses [*Dzotsenidze,* 1965, 1980; *Khamkhadze,* 1981; *Laliev,* 1964; *Makharadze,* 1979]. In the Carpathians, siliceous sequences are referred to as the “Lower Hornfels Horizon” of the lower Menelitic Sub-formation. The numerous diatomite intercalations of the region are attributed to the same level [*Khamkhadze,* 1981; *Krhovsky et al.,* 1992; *Tkachenko,* 1963]. Early Oligocene sediments of the Bakhchisaray section (the Crimea) have been reported to contain an intercalation abundant in recrystallized radiolarians (A. S. Alekseyev, I. E. Khokhlova, and N. G. Muzyliov, unpublished data). It is highly likely that it is the same intercalation that has been reported [*Levitan and Lisitsyn,* 1978b] from the northern slope of the Peri-Black Sea basin.

The broad development of a variety of silicites (radiolarites, diatomites, spongolites, gaizes) in the sediments in point indicates a massive inflow of hydrothermally derived silica into the depositional basin. In light of the above, the high content of associated zeolites (clinoptilolite-laumontite) in the ore from the southern Ukrainian and western Georgian Mn deposits and the sediments coeval to the lower part of the Maikop Group of the Paratethys [*Butuzova,* 1964; *Dzotsenidze,* 1965, 1980; *Makharadze,* 1979] can be interpreted to result from diagenetic binding of free forms of SiO_2 and Al_2O_3 through the synthesis of these minerals. The events in point are related to the effects of the late phases of the global Pyrenean orogenic episode, timed to the terminal Late Eocene-Early Oligocene [*Schwan,* 1985].

Tectonic Setting of the Early Oligocene Mn Deposits of the Paratethys

The Mn deposits under study are spread across a vast territory of southern Europe (Figure 1). These are located in marginal areas of the lithospheric plates, within peripheral parts of black shale basins. The Nikopol and Bolshoi Tokmak deposits of the south Ukrainian basin occur at the southern margin of the Eurasian plate, near the north slope of the Black Sea basin. The Chiaturi, Kvirila, etc., deposits of the western Georgian basin are located on rigid post-Paleozoic (post-Precambrian) basement of the slopes of the Dzirula massif in the eastern part of the Rioni trough (the southeastern re-entrant of the Black Sea basin). The Obrochishte and other deposits of northeastern Bulgaria rest

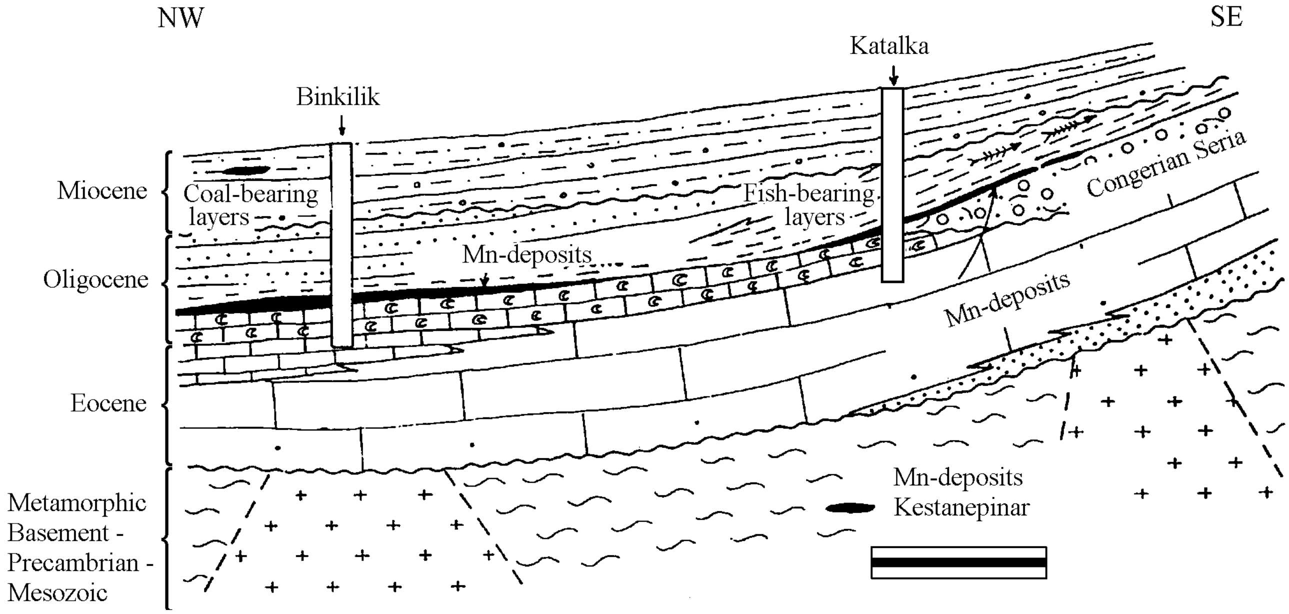

Figure 3. Schematic geological/lithological profile through the north margin of the Thrace basin, NE Turkey. Shown are stratigraphic relationships and position of the Mn deposits. Note the Kastanepinar Mn deposit, occurring in basement rocks (terrane). Scale bar, 10 km [*Oztürk and Frakes,* 1995].

on the slopes of local uplifts of the Moesian plate; these belong to the enclosed Varna basin, linked via the Lower Kamcha trough to the Black Sea basin. The Mn deposits of northwestern Turkey (Binkilis, etc.) occur on rigid Paleozoic crystalline basement of the Thrace basin making part of the periphery of the Black Sea basin. The Mangyshlak deposit is located on the slope of the Hercynian Karatau uplift of the Scythian plate; in Early Oligocene time, this uplift was a nearshore marginal zone of a relatively deep-water black shale basin (southern Mangyshlak basin), which adjoined the Middle Caspian one. The Eger-Demjen (Hungary) and Kisovce-Svabovce deposit (Slovakia) rest on Hercynian basement of the marginal shallow water parts of the Central European (Great Hungarian) Oligocene basin [*Nikolaev,* 1986].

The Mn deposits of northeastern Hungary (Eger-Demjen) and southeastern Slovakia (Kisovce-Svabovce) are located within the Pannonian basin [*Báldi,* 1986; *Konta,* 1951; *Molnar and Morvai,* 1961; *Panto and Molnar,* 1953; *Vadas,* 1964]. The Eger-Demjen deposit (Figures 1, 2) is confined to the northern margin of the Debrecen trough, filled in with deformed flysch-like sequences of Upper Cretaceous-Paleogene age. These strata are up to a few kilometers in thickness, and in the trough's marginal parts they are reduced to 200–400 m. The Mn deposits occur in direct proximity to pre-Mesozoic basement highs (Hungarian Srednegorje and Igal-Bukk) and/or within the steep slopes of basement highs and uplifts of the flysch basin.

The Kisovce-Svabovce deposit is located at the NW terminus of the eastern Slovak basin (Figures 1, 2). Oligocene strata filling in this structure belong to the sedimentary cover assemblage. It is noteworthy that they increase in thickness appreciably toward the basin interiors, where they become over 1.5 km thick. Just west of the deposit, there occur basement highs (Veporides and Zemplinsky Ostrov) composed of deformed Upper Paleozoic rocks.

In the vicinity of the deposits, the deep seated Balaton-Darno fault and the regionally extensive Hernau and Transcarpathian faults occur. Rupelian strata, dominated within most part of the Central European (Great Hungarian) Oligocene basin by black shale sediments (Tard clay, early Kissel sequence), not infrequently contain discontinuous layers of andesitic tuff [*Báldi,* 1986; *Vadas,* 1964].

The Mn deposits of the Varna group (Obrochishte, Rudnik, etc.) are located along the western limit of the Black Sea basin in a belt stretching for ca. 60 km along it and being ca. 20 km in width (Figure 1). The region of the Varna basin belongs to the post-Paleozoic Moesian plate. The Paleozoic-Mesozoic sedimentary cover is ca. 5.0–5.5 km thick. The thickness of Cenozoic strata ranges from a few hundred meters in the vicinity of Varna to 1.5 km in the south part of the Lower Kamcha trough, which opens toward the Black Sea basin. The Varna basin is surrounded by uplifts: the Krapec-Kardamsky swell on the north, the north Bulgarian arch on the west, and the fold piles of the Stara Planina meganticlinorium on the south. The Lower Kamcha trough was incepted in Late Eocene time, and it was a relatively deep water sediment-starved basin [*Tugolesov et al.,* 1985]. The basin is separated from the area encompassed by the Early Oligocene Mn-rich deposits by a flexure that stretches eastward and then swings southeastward and northward, to pass into the continental slope of the Black Sea basin.

The Mn deposits of northeastern Turkey (Binkilis, etc.) [*Oztürk and Frakes,* 1995] are confined to the northeastern slope of the Thrace basin, classed with intermontane troughs and integral to the Alpine orogen (Figures 1, 3). On the north, the basin is bounded by the Istrandja anticlino-

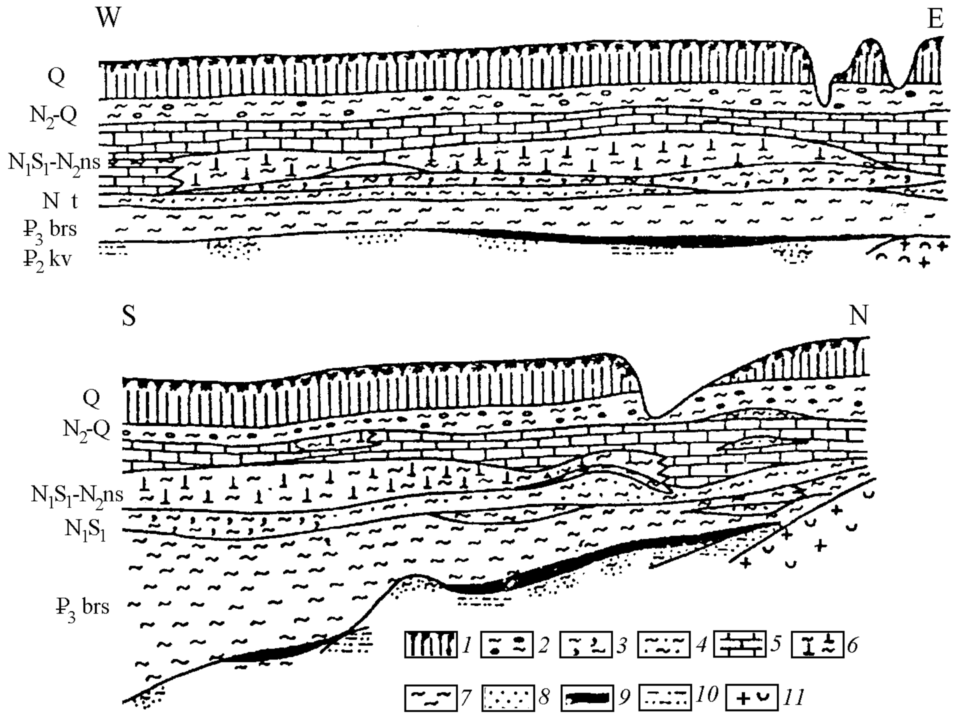

Figure 4. Schematic geological sections through the Novovorontsovsky segment of the western part of the Nikopol (Zelenodolskoe) deposit of the southern Ukrainian manganiferous basin [*Shnyukov et al.,* 1993]. 1 – soil/vegetation layer and loam (Pleistocene-Holocene); 2 – clay with carbonate concretions (Pliocene-Pleistocene); 3 – clay with faunal remains (Lower Miocene); 4 – sandy clay (Lower Miocene); 5 – limestone (Miocene); 6 – marly clay (Miocene); 7 – clay (Oligocene); 8 – sand (Lower Oligocene); 9 – Mn mineralization (Lower Oligocene); 10 – silt (Lower Oligocene); 11 – weathering mantle on Precambrian crystalline rocks.

rium whose axial part exhibits highly deformed and metamorphosed Paleozoic rocks. The same rocks are assumed to occur beneath the Cenozoic cover of the Thrace basin. In the central part of this basin in the terminal Eocene-Oligocene, there apparently existed an uncompensated comparatively deep-water marine basin a few hundreds of meters deep. This is indirectly evidenced by the fact that Upper Oligocene-Miocene sediments increase sharply in thickness from 100–150 m on basin slopes to 500–600 m in basin interior. The basin stratigraphy is known to contain calc-alkaline felsic and intermediate volcanics of Late Eocene-Oligocene age [*Khain,* 1984].

The southern Ukrainian group of Mn deposits occur in a wide (20–25 km) belt stretching for 250 km along the south slope of the Ukrainian shield, composed of highly metamorphosed, often granitized rocks of Archean-Proterozoic age. The Early Oligocene strata hosting Mn deposits (Figures 1, 4) onlap transgressively on the underlying sequences, including basement rocks; as these strata plunge southward, they onlap on various horizons of sedimentary cover of the eastern European craton [*Betekhtin,* 1964a; *Shnyukov et al.,* 1993; *Strakhov et al.,* 1967, 1968; *Varentsov,* 1963; *Varentsov et al.,* 1997]. Structurally, the region of the deposits is a gentle homocline modified by low-amplitude depressions and uplifts. The south slope of the Ukrainian shield displays a system of major, roughly N–S trending basement faults. At the same time, smaller scale roughly E–W trending ancient faults are present. With one of these faults, a flexure is associated that involves young strata of the sedimentary cover and stretches along the line Melitopol-Kakhovka-Nikolaev [*Selin,* 1960]. Note that the Nikopol and other deposits of this group belong to shelf parts of the vast Black Sea basin of Oligocene age. These are sufficiently distal from the central, comparatively deep-water and rapidly subsiding domains. Thus, the axial part of the Indol-Kuban basin is ca. 150 km away (the Maikop Group being as thick as 5 km) [*Tugolesov et al.,* 1985], and the continental slope of the Black Sea Basin proper is approximately 250–300 km away (Figures 1, 5, 6). Early Oligocene Mn mineralization has been reported from the Alma basin occurring near the continental slope of the Black Sea Basin at the western coast of the Crimea [*Viginsky,* 1997].

In western Georgia, the largest Mn deposits occur within the Rioni though ca. 300 km in length. The basin narrows to the east, and on the west it opens toward the Black Sea Basin (Figure 1). In terms of its structure and history, this feature resembles the Lower Kamcha trough located on the western (Bulgarian) slope of the Black Sea Basin. Oligocene strata are the thickest (5–6 km) in the western Rioni though, to become as thin as a few hundreds of meters to the east.

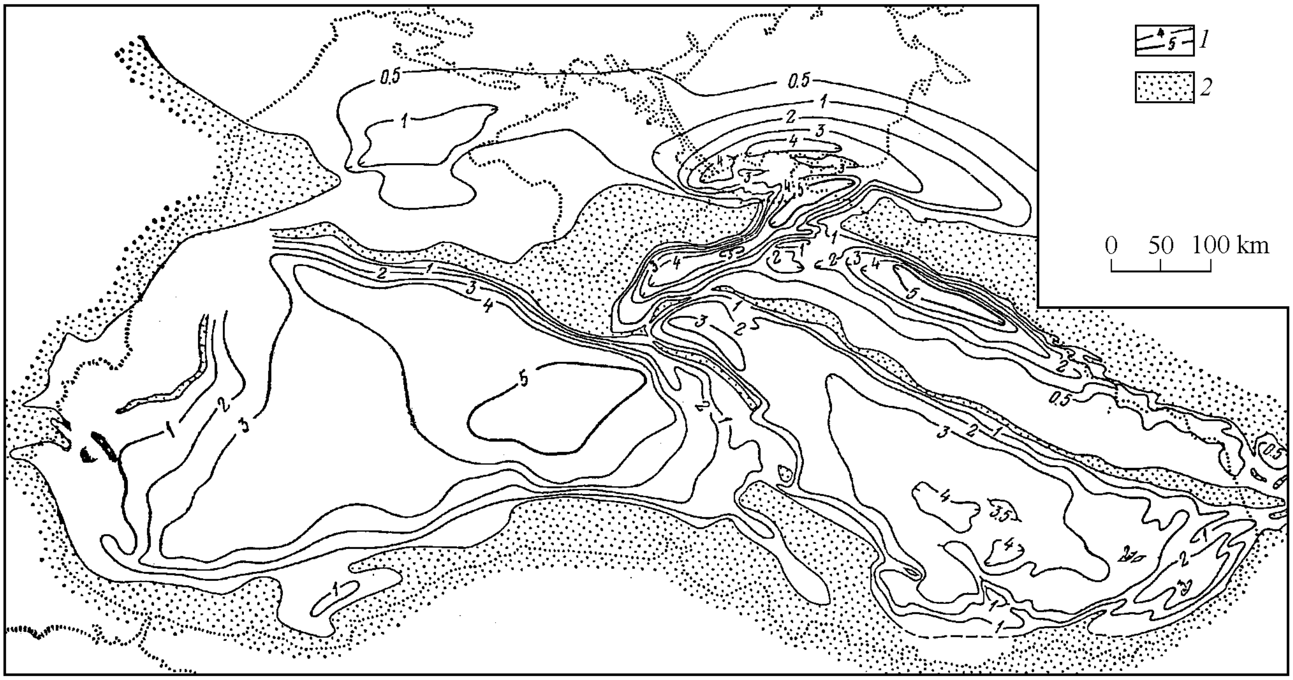

Figure 5. Isopach map of Maikop strata (Lower Oligocene-Lower Miocene) of the Black Sea [*Tugolesov et al.,* 1985].

These strata pinch out in the vicinity of the Dzirula massif, which is a Paleozoic basement high. The Chiaturi and other Mn deposits of western Georgia (Figure 1) occur in the pinch-out zone on the plunging slope of the Dzirula massif. Assumedly, in Early Oligocene time the western part of the Rioni trough was a relatively deep-water feature linked to the Black Sea basin [*Basentsian et al.,* 1981].

The manganiferous strata of southern Mangyshlak Peninsula (the Sartagan deposit) occur on the south slope of the Karatau uplift composed of deformed Permo-Triassic rocks (Figure 1). The Permo-Triassic assemblage plunges gradually southward toward the axial part of the southern Mangyshlak basin. This assemblage is overlain by flatly lying strata of Jurassic-Quaternary age. In the vicinity of the Chakyrgan megasyncline, where the Sartagan deposit proper is located, Oligocene strata rest unconformably and with a break at the base on Permo-Triassic basement rocks. Further south, in the axial part of the southern Mangyshlak basin (Karabarakhta megasyncline), an uncompensated basin of Oligocene age has been identified [*Popkov,* 2000; *Stolyarov and Shlezinger,* 1962]. The latter is filled in with Maikop Group strata whose measured thickness is at least 800 m, its upper part having been eroded away. Seismic surveying has resolved sedimentary clinoforms passing laterally (in relatively deep-water parts) into flatly layered sediments [*Popkov,* 2000]. This is indirect evidence for the existence of a rather deep water basin. Analysis of sediment distribution, Maikop Group thicknesses, and mollusk remains suggests that in the terminal Oligocene the basin was ca. 400–500 m deep [*Stolyarov and Shlezinger,* 1962].

The manganiferous occurrences known from the upper parts of the Maikop Group on the southern slope of the Indol-Kuban basin (Laba and Kerch) are unrelated to the Early Oligocene Paratethyan basin and have a different origin [*Burdzhanidze,* 1995; *Kalinenko,* 1964; *Shnyukov,* 1965, 1981; *Strakhov et al.,* 1967, 1968]. Importantly, the Mn deposits in point are not linked directly to any magmatic and/or hydrothermal activity.

Issues of the Formation and Sedimentation of Mn-Hosting Black Shale Basins of the Paratethys at the Eocene/Oligocene Boundary

We view the formation of the basins in point as a regular event in the context of Pangean breakup, episodes of the opening and closure of the ocean-like Tethys basin, and the inception and development of the system of basins of the Paratethys and Peri-Tethys in the framework of collisional geodynamics that exerted a strong impact on plate arrangement.

The general tectonic upheaval in certain Paratethyan regions in Oligocene time resulted in the development or inception of a number of basins and/or formation of inland and continental-margin basins and tectonism in marginal domains that had been rather passive tectonically. During this time, the Black Sea basin experienced the maximum subsidence since its inception, the thickness of the Maikop Group within its Western basin reaching 4.5–5.0 km and in its Eastern basin, ca. 4 km. [*Gorshkov et al.,* 1989, 1993; *Kazmin et al.,* 2000; *Tugolesov et al.,* 1985; *Viginsky,* 1997].

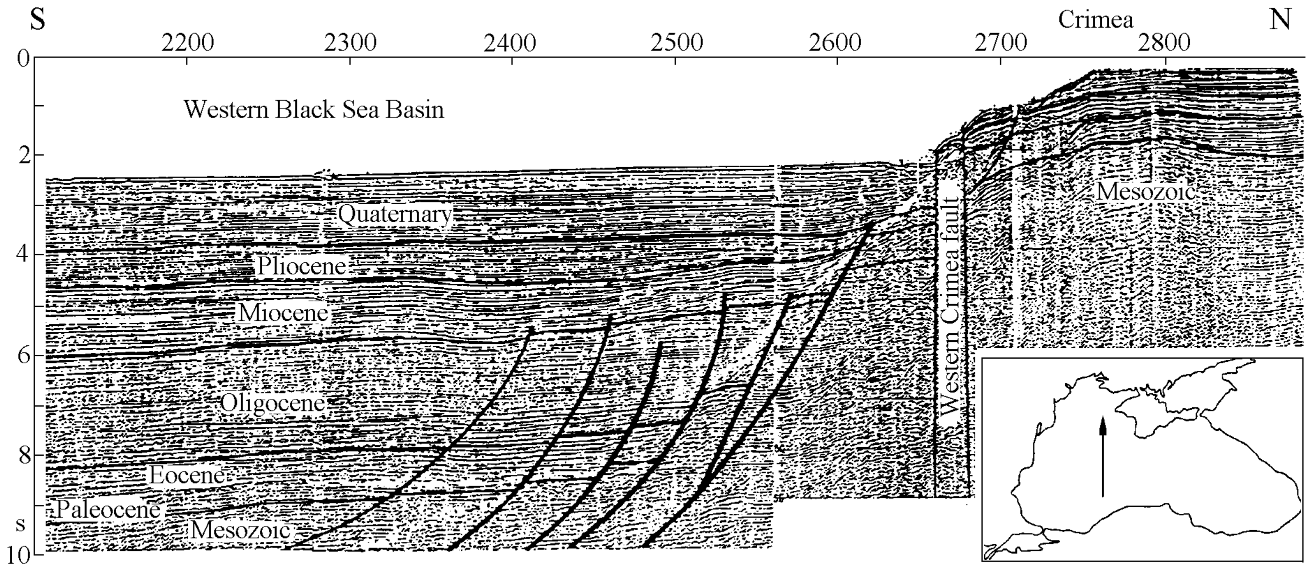

Figure 6. Seismic profile at the north margin of the Western Black Sea Basin. One can see the normal faults active in Oligocene-Early Miocene time [*Zonenshain and Savostin,* 1980].

At the NW margins of the Azov-Black Sea basin, including shelf zones of Bulgaria, Romania, northern Crimean Peninsula, Sea of Azov, and Kuban region, where the domains of the Precambrian (Russian) and Hercynian (Scythian and Moesian) plates are located, Oligocene was a time of formation of orogenic basins and troughs. In particular, along the north periphery of the Black Sea, the Sorokin and Tuapse basins took shape, and the North Caucasus basin subsided at a high rate to accumulate the thick sequences of the Maikop Group. Maikop sediments of similar thickness and lithologic composition, high in bituminous organic matter, were laid down in the South Caspian basin. Within the Tethys proper and its margins, there formed the West Mediterranean basin [*Le Pichon et al.,* 1971] and its coeval rift grabens in adjacent continental plates (the Rhine and Rhone grabens) [*Ricou et al.,* 1986]. From the earliest Oligocene on the dominant shelf sea environment has provided the stage for vigorously subsiding basins with restricted circulation, elevated biologic productivity in the photic zone, and clear evidence of stagnation and anoxia, chiefly in nearbottom water layers.

Black Sea Basin

The Black Sea Basin is among Cenozoic largest and deepest ones. It is rimmed by second order basins and troughs, swells and their slopes, and other tectonic features (Figure 5). This vast feature is subdivided into the West Black Sea Basin (over 600 km long, 150–300 km wide, and with Cenozoic sediments 13–14 km thick) and East Black Sea Basin (over 600 km long, 100–150 km wide, and with Cenozoic strata 10–11 km thick). The basins are divided by the Andrusov Swell, up to 200 km long and with an arch 20–70 km wide [*Gorshkov et al.,* 1989, 1993; *Tugolesov et al.,* 1985].

The hallmark of both Black Sea basins and their surrounding troughs and smaller basins is the development of thick sediments of the Maikop Group (Oligocene-Early Miocene, 34.0–16.3 Ma, [*Chumakov,* 1993; *Golovin and Krasheninnikov,* 1998] accounting for ca. one-third of the volume of Cenozoic sediments. Remarkably, while in the basins and/or troughs the Maikop sediments are as thick as several kilometers (Figure 5), at the crests of the Andrusov and Shatsky swells their thickness is negligibly small. However, post-Maikop strata (Middle Eocene to Quaternary) rest on the tops of the swells without showing any perceptible reduction in thickness. These data suggest a singular tectonic regime for the subsidence of the Black Sea Basin region in post-Eocene and post-Early Miocene times.

Direct evidence for the nature of pre-Cenozoic basement in the inner regions of the West- and East Black Sea basins are extremely sparse and scanty to make any definite conclusions. Nonetheless, interpretation of deep seismic sounding data [*Beloussov and Volvovsky,* 1992; *Volvovsky et al.,* 1989], heat flow measurements, CMP seismics [*Golmshtok et al.,* 1992], and geodynamic reconstructions for Tethyan history enable us to adopt, with certain reservations, the following model. In the central deep water part of the Black Sea the column of sedimentary rocks is immediately underlain by solid crust composed of either "basaltic" layer alone (West Black Sea Basin) or both "basaltic" and "granite" layers (East Black Sea Basin and Central Black Sea Rise). Calculations of the distribution of heat flow from the cooling oceanic lithosphere [*Glasby et al.,* 1997] with due account for experimentally tested thermo-physical parameters that change with time as the sediments keep on piling up and getting denser, show that the West Black Sea Basin is 130–

95 m.y. in age (Valanginian-Cenomanian), and the East Black Sea Basin is ca. 110 m.y. (Aptian). These values are consistent with the concept that the Black Sea basins are remnants of a Late Mesozoic spreading basin that was formed in the backarc of the Lesser Caucasus-Pontides island arc.

Relationships of the Mesozoic basaltic substrate and its overlying Paleocene-Eocene strata in the Black Sea basins are rather intricate and not clear enough. The available data are indicative of a syntectonic (angular) stratigraphic unconformity [*Gorshkov et al.,* 1993; *Robinson et al.,* 1996; *Tugolesov et al.,* 1985]. The results from the subsequent research place significant constraints on the distribution of sediments in question: over most of the West and East basins, Paleocene-Eocene strata vary but little in thickness, which equals some 2–3 km. It is emphasized, however [*Finetti et al.,* 1988; *Kazmin et al.,* 2000], that greatest thicknesses (up to 5–6 km or more) are recorded in those localities corresponding to deep depressions in pre-Cenozoic basement.

The data on the distribution of Oligocene-Early Miocene sediments (Maikop Group) acquired by the PO Yuzhmorgeologiya team [*Tugolesov et al.,* 1985; etc.] and the results of the joint Russian and Italian studies are closely similar (Figures 5, 6). It is pointed out that the rate of subsidence of the Black Sea basins was considerably higher in Oligocene-Early Miocene time than during the preceding stages of geological history. The marked subsidence trend in the regional evolution was also expressed in Maikop time in that the newly formed basins of the Crimea-Caucasus province (Sorokin, Kerch-Taman, Indol-Kuban, Tuapse) took on a distinct shape. Note the clear syntectonic pattern in the distribution of Maikop sediments: within swells and shelf uplifts occurring above the slopes of major basins, these strata are comparatively thin, whereas in the basins they are ca. 4–5 km thick (Figure 5). This being so, the underlying Paleocene-Eocene sequence remained virtually unaffected by folding, while the Maikop strata show heavy folding and evidence of diapirism and mud volcanism.

The Russian-Italian studies [*Finetti et al.,* 1988; etc.] (Figure 6) have located a group of normal faults that operated during the deposition of the Maikop strata. However, the nature of these faults is poorly understood. It is not clear whether they resulted from the compression phase in the terminal Eocene [*Konta,* 1951] or whether they were formed in Oligocene time at an extensional environment involving the subsidence and increasing depth of the Black Sea basin, as opined by [*Kazmin et al.,* 2000].

Based on kinematic and dynamic modeling of subsidence processes in the Black Sea Basin, *Nikishin et al.* [2003] argue the high-rate subsidence of the basin floor to be due mainly to compressional deformations (accompanied by a general lithospheric attenuation) that have operated since Late Eocene time.

Similar conclusions were drawn by [*Cloetingh et al.,* 2003; *Spadini et al.,* 1996] based on thermo-mechanical modeling of the impact from pre-rifting rheology of the Black Sea region lithosphere on the formation of the Black Sea basins. These studies demonstrate the significance of variations in the structure of the lithosphere as a whole and in its mechanical parameters at the different levels of transition of rheological characteristics of the Western and Eastern basins. Gravimetric data further constrain the character of the flexural boundaries of the basin, attesting to considerable lateral variations in the pre-rifting strength parameters of the lithosphere. It is emphasized that these parameters largely predetermined the development of the Black Sea Basin in Mesozoic and Cenozoic time. The contrasts in lithospheric strength characteristics during the post-rifting phase bear on how stresses are transmitted from marginal portions of the basin toward its interior. Such post-rifting compressional stresses are pivotal to the differential movements forced by both rifting and the load of piled sedimentary sequences.

A rather comprehensive model for the subsidence history of continental-margin basins in Maikop time is discussed by the Russian-French team [*Ershov et al.,* 2003] using a case study in the eastern, central, and western parts of the North Caucasus basin based on drilling and seismic profiling data. The results of heat flow modeling imply that the Jurassic-Eocene subsidence of the basin was chiefly controlled by intrusive heating in Late Triassic-Early Jurassic time. This heating resulted in elevated heat flow values within the basin followed by an exponential drop in subsidence rates controlled by lithospheric cooling. In Oligocene-Early Miocene time, the eastern and central basins experienced a high-rate subsidence. The geodynamic cause of this subsidence, according to these workers, is most likely related to the mode of mantle flow after the cessation of Tethyan subduction, as the subducted slab sank to equilibrium. Such a concept invoking deep seated mechanisms to explain the formation of the Paratethyan (Peri-Tethyan) marginal basins that subsided vigorously in Maikop time affords a largely consistent scenario for the origin of Oligocene-Early Miocene basins-the continental margin troughs of the study region. At the same time, this situation can be regarded as a regional-scale expression of a larger scale event: the collision of Eurasia and the Indian subcontinent, which took place in the mid- and terminal Eocene (ca. 45 Ma and ca. 37 Ma, respectively) to entail a general rearrangement in the global system of lithospheric plates [*Lisitsyn,* 1980; *Rögl,* 1999; *Schwan,* 1985; *Tapponnier et al.,* 1986; *Varentsov,* 1996; *Varentsov and Muzyliov,* 2001; *Worral et al.,* 1996; *Zonenshain and Savostin,* 1980].

The latest studies provide exhaustive evidence that the effects of mantle flow and convection bear decisively on the geological processes occurring in the earth's crust [*Bercovoci,* 2003; *Collins,* 2003; etc.]. Noteworthy is the similarity of lithologic features and the relatively deep water nature of the environment of deposition of the Oligocene-Early Miocene strata. These strata are represented by comparatively uniform, mostly dark-colored clayey hemypelagic sediments with a variable proportion of silt/sand admixture. Typical is the presence of dispersed organic matter (1.20–9.17% TOC, averaging 3.76% from 12 samples; [*Ivanov and Limonov,* 1996], represented by altered sapropel-like material with a humic admixture and occasional fragments of terrestrial plants. The localities of massive deposition of organic rich Maikop sediments in the Black Sea basins (in water depths over 2 km) and their adjacent troughs exhibit the generation of hydrocarbons (methane and higher, up to C_7 homologues) accompanied by anomalously high pressures and fluid breakthrough to seafloor surface. Carbon isotope studies reveal the presence of surface (microbacterial) and catagenetic (epigenetic) products in the samples. Such localities display well-developed mud volcanic edifices with typical mud-volcanic breccia [*Volvovsky et al.,* 1989]. A paramount feature of Maikop sediments of the Black Sea is the relatively low content of bituminoids (aromatic/naphthenic compounds) at a considerable organic matter content.

Sedimentologically and lithologically, the Maikop Group has received a rather sporadic coverage. Many workers regard it as a relatively uniform clay sequence deposited in closed basins at well-developed stagnant environments. It has been stressed that in the Sorokin and Tuapse basins, where these sediments are comparatively thicker (Figure 5), the lower parts of the Maikop Group have somewhat elevated organic matter contents and are distinguished by a conspicuous mud volcanism and generation of hydrocarbons and bituminoids.

As noted above, the Maikop Group spans in age interval from Early Oligocene (34.0 Ma) [*Golovin and Krasheninnikov,* 1998] to the terminal Early Miocene (16.3 Ma) [*Chumakov,* 1993; *Harland et al.,* 1989]. The Early/Late Oligocene boundary is dated at 29.0 Ma; the Oligocene/Miocene boundary, at 24.6 Ma; and the Early/ Middle Miocene one, at 16.3 Ma [*Chumakov,* 1993; *Harland et al.,* 1989].

Assuming relatively limited variations in sedimentation rate for the Maikop Group, it can be estimated that, given the total thickness of this Group in the West Black Sea Basin is 5 km, the thickness of sediments piled in the Early Oligocene was 1.4 km; in the Late Oligocene, 1.2 km; and in the Early Miocene, 2.4 km. These values are not inconsistent with the results from their comparison with their counterparts in fossil basins (troughs and depressions) with due regard for the lithotectonic parameters of deposition [*Krasheninnikov and Akhmetyev,* 1996, 1998].

Although in the modern Black Sea the formation of Mn–Fe mineralization is developed very locally and to a minor extent, geochemical characteristics of this water body allow a better understanding of Mn deposition in the Early Oligocene Paratethyan basins. The present-day Black Sea displays a sharp water stratification by density (salinity) due to river input (346 km^3/yr, 0.016 $^o/_{oo}$ Cl) and the inflow of relatively high salinity waters from the Sea of Marmara via Bosporus (340 km^3/yr, 995$^o/_{oo}$ Cl). The density stratification restricting rather radically the vertical circulation of Black Sea waters results in high concentrations of hydrogen sulfide below ca. 200 m BSL with the ensuing complete extinction of phytoplankton, zooplankton, and anaerobic bacteria. The bulk of H_2S in the water column is formed through sulfate reduction in sea water and only a minor proportion, through the decay of sulfur-containing organic compounds.

The distribution of redox-determining parameters (H_2S, O_2, and Eh) controls the vertical distribution of Mn through the water column. Minimum manganese contents are recorded in the surface zone (0–50 m BSL; 25 mcg/l (ppb) $Mn_{tot.}$), where Mn occurs in a suspended, oxyhydroxide form [*Mokievskaya,* 1961; *Skopintsev and Popova,* 1963; *Spencer and Brewer,* 1971]. In the hydrogen sulfide zone, the total Mn content exceeds 250–300 mcg/l (ppb), the dissolved form (Mn^{2+}) being considerably prevalent. According to the calculations of [*Skopintsev and Popova,* 1963], the total Mn amount in the anaerobic zone of the Black Sea is approximately 0.1 billion tons. For the modern geological setting the average Mn residence time in the Black Sea can be deduced by dividing the total Mn amount in the water of the basin by its annual supply, which gives ca. 1,700 years [*Skopintsev,* 1979]. In other words, nearly every 1,000–2,000 years the Mn stored in the Black Sea water is completely replaced. The removal of these masses of Mn may occur through their displacement by pulsatory incursions of higher density sea waters. Such displacement and subsequent transfer of Mn-rich anoxic waters into shallow water, well-ventilated shelf areas to give rise to oxyhydroxide, carbonate deposits, is modeled by the anoxic basins and Mn reworking in the Baltic Sea. The bulk of the associated Fe at such settings was stored in a hydrosilicate form: as Fe-smectite, Fe-illite (glauconite) and less frequently as an oxyhydroxide, carbonate admixture or sulfides.

However, the uniqueness of the Early Oligocene paleogeography of the Central and Eastern Paratethys lies in that, alongside the largest Black Sea anoxic basin, this system incorporated other euxinic basins and depressions (southern Slovak, Hungarian, Rioni, Kvirila, Central Caspian) whose margins provided the setting for comparatively large Mn deposits and rare-metal concentrations coeval to those of the Black Sea region (southern Ukraine, northeastern Bulgaria, and northwestern Turkey). The above data are clearly indicative that the broad region-wide development of Mn- and rare-metal mineralization and massive deposition of siliceous, zeolite-bearing, and organic rich strata were controlled by the early Rupelian sub-global transgression of the world ocean. The incursing oceanic waters were enriched in Mn and associated metals and nutrients whose origin was related to a peak in global endogenous activity in the world ocean-in particular, a considerable increase in hydrothermal activity across the Eocene/Oligocene boundary.

Genesis: Development of Early Oligocene Black Shale Basins Along Paratethyan Margins and the Formation of Giant Mn Deposits in Light of the Events at the Eocene/Oligocene Boundary

The formation of the Early Oligocene Mn giants was controlled by an optimum combination of the principal geological events at the Eocene/Oligocene boundary.

The crucial geodynamic event at the Eocene/Oligocene boundary was the collision of India and Eurasia (38 m.y. ago), which brought about significant changes in the dynamics of plate motions worldwide [*Tapponnier et al.,* 1986; *Lisitsyn,* 1980; *Worrall et al.,* 1996; *Zonenshain and Savostin,* 1980]. This collision resulted in the narrowing and, in some regions, complete closure of the gateway that separated Eurasia and the Gondwanan continents. The collision of Eurasia and the Indian subcontinent and the resultant rearrangement in the global system of lithospheric plates were accompanied by maximum spreading rates and associated hydrothermal activity along the axial zones of the global system of mid-ocean ridges. At continental plate margins, this was attended by a culmination in subsidence rates in the central parts of marginal basins and massive deposition of black shale sediments.

A study of variations in the rate of oceanic crust generation over the last 150 m.y. [*Zonenshain and Khain,* 1989] shows that in Eocene time this rate was 1.5 times the modern rate of basalt generation in the world ocean, the average Eocene rate of crust generation in the Pacific being Cenozoic highest (Figure 7). Estimated rates of the accumulation of metalliferous sediments in Eocene time were an order of magnitude higher than in Oligocene and Holocene-Pleistocene times [*Gurvich,* 1998].

In the terminal Eocene, the global increase in spreading rates and generation of new lithosphere at mid-ocean ridge crests caused a considerable sea-level rise worldwide and an ensuing transgression. This involved a tremendous input of mostly hydrothermal components and a very considerable growth of biogenic productivity and sedimentation due to nutrient inflow. These components (Ca, organic carbon, CO_2, Si, P, as well as Mn, Fe, and other transition metals), although they experienced repeated recycling and biochemical transformations, were initially of an endogenous nature [*German and Angel,* 1995; *German et al.,* 1991].

In the Paratethys, geological rearrangements and consequent changes in oceanological settings at the Eocene/Oligocene boundary were expressed in both a relative change in the configuration of basins and in the hydrologic and hydrochemical regimes. These events were to result, in the terminal Eocene, in the fragmentation and closure of a number of basins of the Western Paratethys and the onset of an active phase in the history of the inland seas as essentially reorganized marine basins. The Mediterranean throughout Oligocene and most part of Miocene time, retained communication with the world ocean. In a number of inland seas in Early Oligocene time recorded is a short episode of a somewhat decreased salinity and anoxic seafloor environments with deposition of relatively thick sequences of organic-rich sediments and extensive development of endemic organisms. Later on, a more open-sea environment was established, at which terrigenous sedimentation prevailed. In the terminal-Early Miocene (Burdigalian time), the collision of the African and Arabian plates with Eurasia resulted in that the Mediterranean lost communication with the Indian Ocean [*Rögl,* 1999].

Mn-rich sediments were deposited in the shelf/littoral environments of such basins due to the input of deep waters enriched in Mn^{2+} and DOC (dissolved organic carbon) from these basins [*Dyrssen and Kremling,* 1990; *Eaton,* 1979; *Franck et al.,* 1987; *Glasby et al.,* 1997; *Sapozhnikov et al.,* 2000].

The role of anoxic basins as reservoirs of Mn, Fe, organic carbon, transition metals, and REE, which occur in open-sea waters in dispersed forms, is to transfer and concentrate these components. In the water of such stagnant basins giant amounts of dissolved Mn^{2+} are as a rule stored, and in many cases, REE also are [*Brewer and Spenser,* 1974; *Eaton,* 1979; *Leventhal et al.,* 1983]. The separation of Mn and Fe in these basins occurs through Fe^{2+} binding in sulfide phases and their deposition in sediments. In open-sea sediments, Mn^{2+} is usually oxidized to Mn^{3+} and then to Mn^{4+}, these compounds are buried in sediment and reduced diagenetically to Mn^{2+}, to diffuse into bottom waters and then be transferred into shelf and littoral areas, where it is ultimately deposited [*Burdige,* 1993; *Thamdrup et al.,* 1994].

Therefore, anoxic basins of the Paratethys in Early Oligocene time operated as reservoirs into which, by the above mechanism, tremendous amounts of Mn, Fe, and other components (supplied into the Eastern Paratethys as a result of the multiple-stage Rupelian transgression) were transported. As noted above, such basins accommodated the transition metals, the rare earth elements, and other components occurring in a dispersed form in the water of this shelf sea. Evidently, the metallogenic role of anoxic basins had likely been maintained until the exhaustion of the resource of the relatively elevated contents of the suspended and dissolved forms of these components (in particular, Mn and Fe) in the open shelf basin. In the Paratethys, the comparatively short episode of Mn deposition is attributed to the earliest Rupelian, the peak time of global transgression.

Conclusions

The Early Oligocene Mn deposits of southern Ukraine (Nikopol, etc.) and Georgia (Chiaturi, etc.), largest in Phanerozoic history, the Mn accumulations in Mangyshlak, northeastern Bulgaria, and northwestern Turkey, and the deposits in Hungary and southern Slovakia, all are composed of geochronologically coeval Mn-rich sediments occurring at the base of the Lower Oligocene (the Rupelian stage in Europe or the Pshekha regional stage in the CIS) throughout a vast territory from Central Europe to Central Asia. These strata have in common tectonic settings (active margins of the southern Eurasian craton or slopes of median masses in the Alpine belt), environments of occurrence (tectonically rigid cratonic basement), facies relationships and depositional milieus (the shelves of inland, marginal, and backarc basins), and lithologic, mineralogical, and chemical compositions of ore minerals and their host strata. These Mn deposits account for more than 30% of the world's Phanerozoic Mn resource or over 70% of the Cenozoic one.

In the Paratethyan basins, the Eocene/Oligocene boundary was featured by an essential change in depositional and hydrochemical environments, expressed in a progressively increasing anoxia. The general tectonic activation of a number of Paratethyan regions in Oligocene time resulted in the development or inception of a number of basins and/or formation of inland and continental-margin basins and activation of marginal domains, previously rather passive tectonically.

During this time, the Black Sea Basin experienced the maximum subsidence since its inception, the thickness of the Maikop Group within its western basin reaching 4.5–5.0 km and in its eastern basin, ca. 4 km. The distribution of redox-determining parameters (H_2S, O_2, and Eh) controls

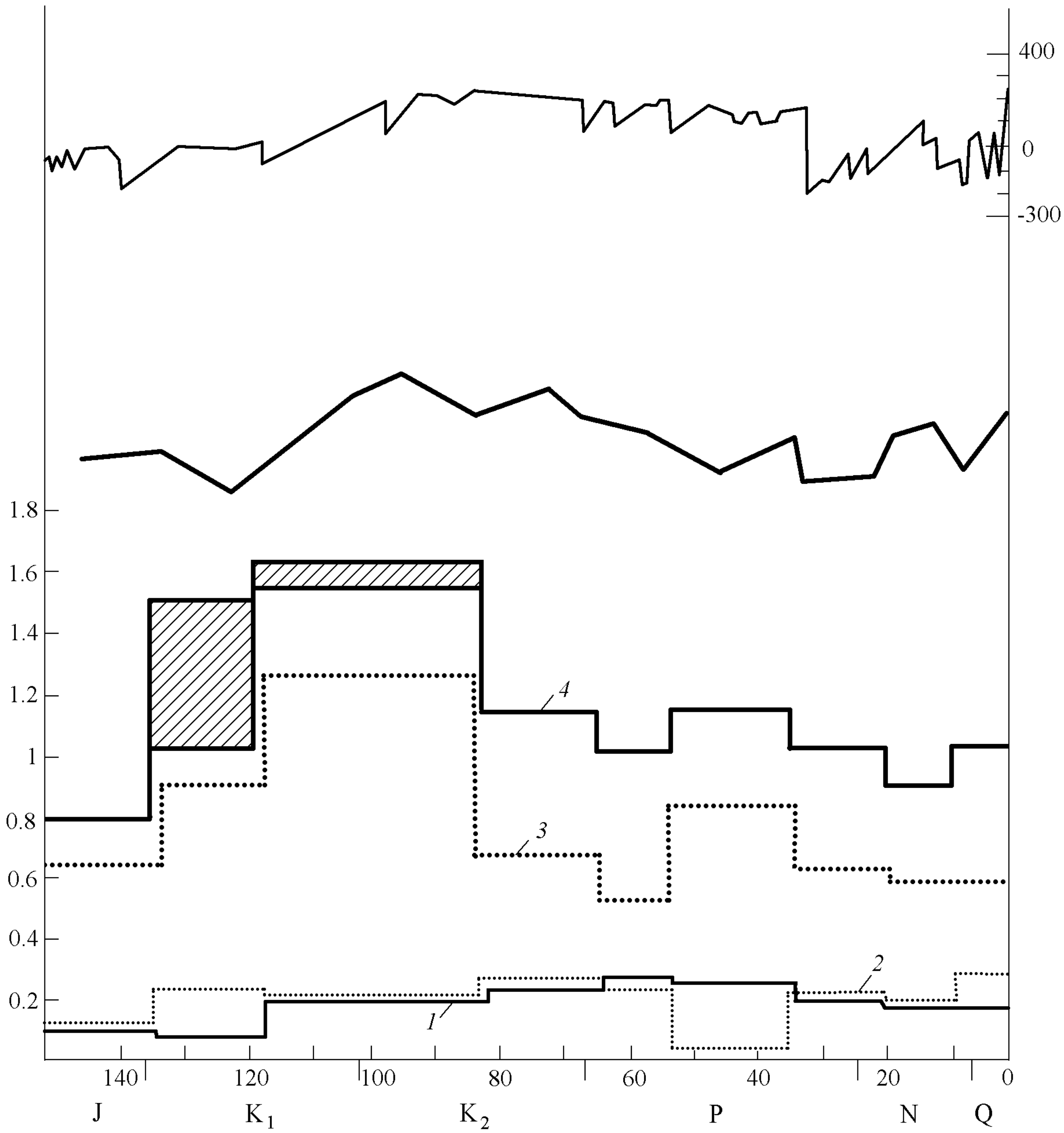

Figure 7. Diagram showing the earth's tectonic activity during the last 155 m.y. Shown are changes in the rate of generation of new oceanic crust (km^2) for the Atlantic (1), Indian (2), and Pacific oceans (3) and a cumulative diagram for the entire world ocean (4). (A) Subduction rate variations [*Lomize,* 1986], (B) global transgression/regression curve [*Zonenshain and Khain,* 1989].

the vertical distribution of Mn through the water column. Minimum manganese contents are recorded in the surface zone (0–50 m BSL; 25 mcg/l (ppb) $Mn_{tot.}$), where Mn occurs in a suspended, oxyhydroxide form. In the hydrogen sulfide zone, the content of Mn_{tot} exceeds 250–300 mcg/l (ppb), the dissolved form (Mn^{2+}) being considerably prevalent. According to calculations, the total Mn amount in the anaerobic zone of the Black Sea is approximately 0.1 billion tons. The removal of these manganese masses was likely to occur through their displacement by pulsatory incursions of denser sea waters. A model for such displacement and subsequent transfer of Mn-rich anoxic waters into shallow-water, well-ventilated shelf environments to lay down oxyhydroxide, carbonate deposits may be provided by the anoxic basins and manganese reworking in the Baltic Sea. Assuming that under these conditions the Early Oligocene episode of Mn deposition spanned a geologically significant time interval (ca. 0.3–0.5 m.y.), such a paleo-Black Sea basin was likely to serve as a periodically replenished Mn reservoir (with 17.6–9.4 billion tons of Mn) generating the deposits occurring on its shelf margins. However, the uniqueness of the Early Oligocene paleogeography of the Central and Eastern Paratethys lies in that, alongside the largest Black Sea anoxic basin, this system displayed other euxinic basins and depressions (southern Slovak, Hungarian, Rioni, Kvirila, Central Caspian) whose margins provided the stage for comparatively large Mn deposits (Kisovce-Svabovce, Eger-Demjen, Chiaturi, Kvirila, Mangyshlak, etc.), coeval to those adjacent to the Black Sea (in south Ukraine, northeastern Bulgaria, and northwestern Turkey).

The above data indicate plainly that the broad, regionwide development of Mn- and rare-metal mineralization and massive deposition of siliceous, zeolite-bearing, and organic rich strata were controlled by the early Rupelian sub-global transgression of the world ocean. The incursing ocean waters were enriched in Mn and associated metals and nutrients whose origin was related to a peak in global endogenous activity in the world ocean-in particular, to the considerably increased hydrothermal activity across the Eocene/Oligocene boundary.

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