Arizona Geological Society Digest 22
2008

Paleo-Tethys, Permian extinction, and stratabound copper-sulfide deposits of the Cimmerides[1]

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ABSTRACT

In late medial to late Permian time, the Paleo-Tethys became an ocean isolated from the Panthalassa by nearly complete closure of the Cathaysian bridge formed from the Chinese and Southeast Asian continental blocks. Because the Paleo-Tethys had a position straddling the Permian equator and it received most of the drainage of the mountain-rimmed Permian Pangaea, it developed both a thermocline and a halocline and its internal circulation came to a standstill, creating a giant anoxic basin. In places this anoxia started even in the latest Carboniferous in abyssal depths and began climbing onto the lower shelves by the end of the Guadalupian. By the end of the Permian, most of the Paleo-Tethys had turned anoxic. The presence of a wide band of fossil fungal spikes around it, local submarine erosion interpreted to be associated with gas escape, and catastrophically increased chemical weathering onland lead us to conclude that the Paleo-Tethys may have erupted enormous amounts of CO_2, H_2S and CH_4 that killed most of the terrestial biota around it. Indeed, the Permian extiction is seen not to have been universal but was concentrated in and around the Paleo-Tethys and affected mostly benthic organisms. The extinction seems to have developed from the deep sea to the shallower regions and finally into the atmosphere. The large amount of black shale in Paleo-Tethyan deposits naturally raises the question as to why many large copper sulfide deposits have not been found within them. The usual answer to this question has been the lack of copper source rocks such as redbeds or rift volcanics plus the lack of exploration in the high mountainous areas of south-central Asia where the Paleo-Tethyan black shales are exposed. However, associated Paleo-Tethyan shales and ophirags of volcanic provenance may have been sites of copper mobilization and movement into sediments later incorporated into Paleo-Tethyan subduction-accretion prisms. The Paleo-Tethyan black shale deposits may yet reveal large copper deposits with sufficient exploration.

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[1]The non-metallogenic parts of this paper are only a summary of a book to be published under the authorship of Şengör and Atayman as a Geological Society of America Special Paper. That is why we have kept the references to a minimum in this summary.

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Şengör, A.M.C., Atayman, Saniye, and Presnell, Ricardo, 2008, Paleo-Tethys, Permian extinction, and stratabound copper-sulfide deposits of the Cimmerides, *in* Spencer, J.E., and Titley, S.R., eds., Ores and orogenesis: Circum-Pacific tectonics, geologic evolution, and ore deposits: Arizona Geological Society Digest 22, p. 19-30.

INTRODUCTION

The Panthalassa, the global ocean that surrounded the assembled late Paleozoic supercontinent of Pangaea, is the ancestor of the modern Pacific Ocean. Breakup of Pangaea and dispersal of its fragments produced the new Indian and Atlantic Oceans, while the Pacific descendent of the Panthalassa continues to shrink. Fragment dispersal within the Tethys Sea, which was a large embayment of the Pangaean supercontinent, had severe hydrological, geochemical, and biological consequences that are briefly outlined and discussed in this paper.

This paper explores the culpability of the Paleo-Tethys in the so-called 'end-Permian' extinction, believed to be the greatest in the Phanerozoic Eon. What led us to this investigation were the following observations: (1) The 'end-Permian' extinction was not an abrupt event (although it included abrupt extinctions of some taxa) confined to the end of the period, but one that developed gradually from the medial Permian to culminate in a final act in the late Permian. Two distinct pulses, one each in the late Guadalupian and late Lopingian (Fig. 1), characterised the temporal pattern of the extinction, with smaller peaks between them (e.g., Stanley and Yang, 1994). (2) Geographically, the Permian extinction was not global. It only appeared so because it struck at the richest biological niches then present, which were in and around the Paleo-Tethys. Large parts of the Panthalassa and the higher latitudes were untouched, except south Africa which was dangerously close to a large Paleo-Tethyan inlet, the Gulf of Malagasy (Benton, 2003). (3) The Permian extinction appears to have broadly followed a significant decrease in atmospheric oxygen, yet it did not exactly follow the pattern of that decrease (Ward, 2006; Berner et al., 2007). (4) Finally, the Permian extinction affected all oxygen-breathing organisms including the airborne insects, which suffered the only significant mass extinction in their history in the Permian (Benton, 2003; Erwin, 2006).

These observations make it clear that the extinction was related to oxygen respiration and that whatever caused it was somehow localized in and around the Paleo-Tethys. That is why we searched for a possible peculiarity in the medial to late Permian geology of the Paleo-Tethys. What we found was a remarkable episode of widespread anoxia that may have affected both the Paleo-Tethyan ocean (but *not* the entire Panthalassa) and, by means of gas eruptions, the atmosphere as well. This discovery not only improved understanding of possible causes of the Permian extinction, but also raised the possibility of metallogenic implications.

Figure 1. Geologic time scale for Permian stages mentioned in the text.

Permian	Lopingian	Changhsingian
		Wuchiapingian
	Guadalupian	Capitanian
		Wordian
		Roadian
	Cisuralian	Kungurian
		Artinskian
		Sakmarian
		Asselian

THE TETHYAN REALM

The term 'Tethyan realm' signifies that portion of the late Paleozoic to early Cenozoic world that includes the two main Tethyan oceans, their continental margins, and the Cimmerian continent that separated them (blue area in Fig. 2). The Paleo-Tethys was the ocean that came into existence not by separation of its conjugate margins following rifting, but by bringing those margins to their Paleo-Tethys-bounding positions during the assembly of Pangaea in latest Carboniferous time. The Hercynian/Appalachian collisions finally welded the Laurasian and Gondwanian parts of Pangaea together and the Paleo-Tethys appeared as a giant, east-facing gulf of the

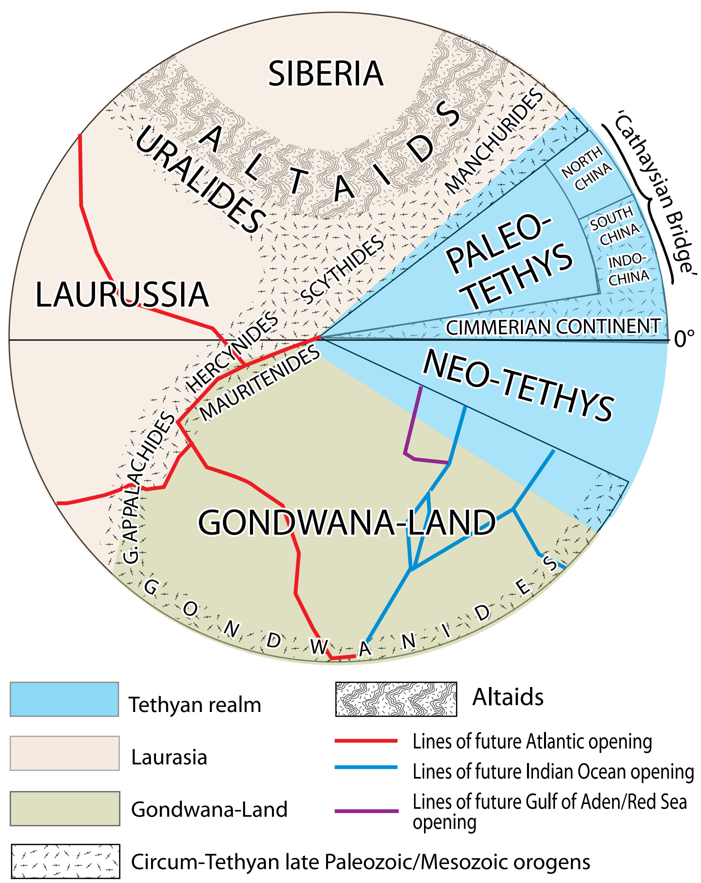

Figure 2. A sketch map of the principal paleotectonic elements of the world in late Permian time showing the terminology employed in this paper.

assembled supercontinent. Simultaneously with that assembly, a strip of continental crust began rifting from the northern margin of Gondwana-Land. This rifting progressed from east to west, reaching the western end of the Tethyan realm in the Triassic. The piece of continent thus rifted is named the Cimmerian Continent (Şengör, 1979). Throughout the late Carboniferous to the Jurassic, it rotated anti-clockwise around a pole in the western end of the Tethyan realm (somewhere near present-day Bulgaria; see Şengör et al., 1984). In the process it closed the Paleo-Tethys and created the Cimmeride orogenic system, and opened behind it the Neo-Tethys (Şengör, 1979; Şengör and Natal'in, 1996).

At its eastern end, the Cimmerian Continent was a string of continental blocks consisting of North China, Yangtze, Huanan, and Annamia. These continental blocks formed an isthmus that sealed the eastern end of the Paleo-Tethys, save for one or possibly two narrow straits in present-day northern Thailand (Fig. 3). This bridge, named the Cathaysian Bridge by Şengör and Atayman (in press), came into being sometime during the late Permian.

The Paleo-Tethys was thus an almost completely isolated inland sea of Pangaea. Şengör and Atayman (in press) called the state of the terrestrial geography containing one or more completely isolated oceans a 'Ptolemaic Earth' in allu-

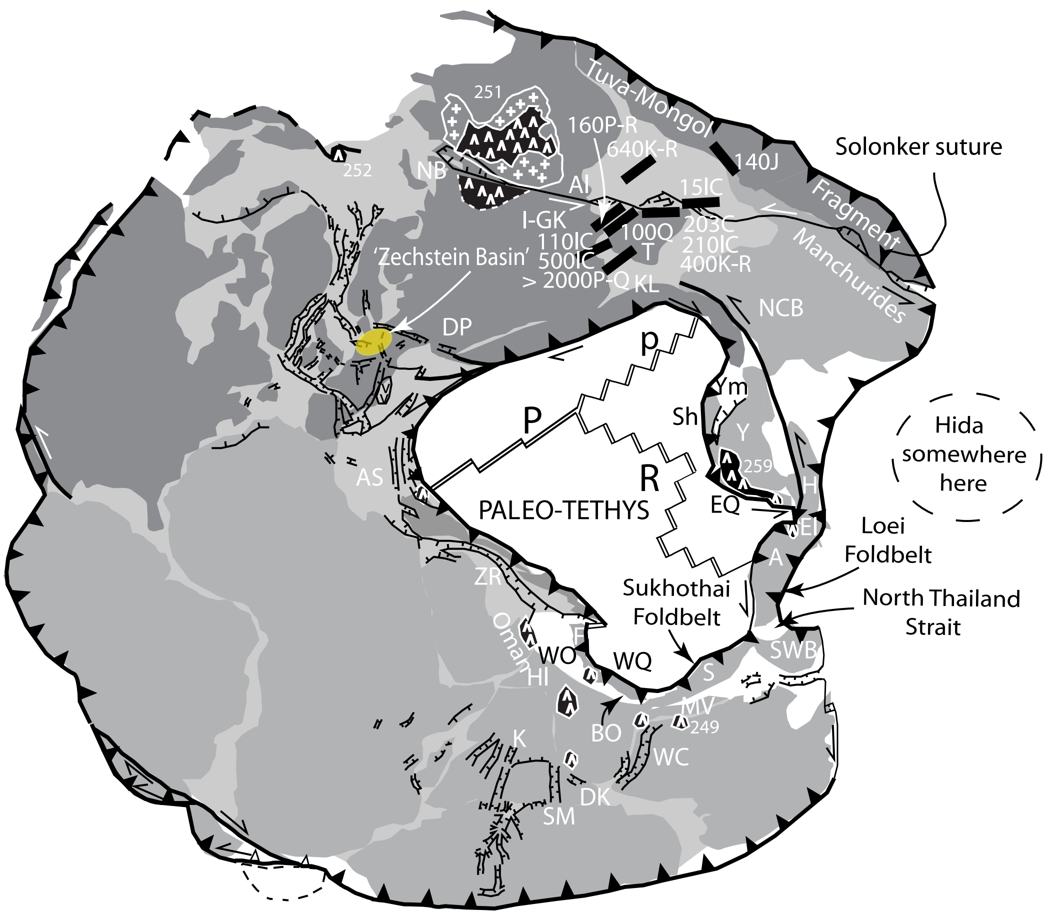

Figure 3. Late Permian tectonics of Pangaea and the Paleo-Tethys. Key to lettering: A: Annamia; Al: Altay Mountains; AS: Apulian shelf; BO: Banggong Co-Nu Jiang Ocean; DK: Damodar-Koel Valley rift; DP: Porte of Dobrudja; El: Emei Shan basalts on Annamia; EQ: eastern Qangtang; F: Farah Block; H: Huanan block; Hl: Helmand Block; I-GK: Irtysh-Gornostaev keirogen; K: Kurduvadi rift; KL: Kuen-Lun; MV: Mount Victoria Land block; NB: Narym Basin; NCB: North China block; S: Sibumasu; Sh: Shaluli Shan ensimatic island arc; SM: Son-Mahanadi rift; SWB: south-west Borneo; T: Tarim block; WC: Western Coastlands taphrogen; WQ: western Qangtang; Y: Yangtze block; Ym Yajiang marginal basin; ZR: future Zagros Mountains. Lone figures are isotopic ages (in Ma) of extensional and/or plume-related igneous rocks, mostly traps. The figures with letters after them represent observed amounts (in km) and times of crustal shortening across the bars associated with them: >2000P-Q: Permian to Quaternary; 160P-R: Permian to Recent; 140J: Jurassic; 640K-R: Cretaceous to Recent; 400K-R: Cretaceous to Recent; 203C: Cenozoic; 203C: Cenozoic; 500lC: late Cenozoic; 110lC: late Cenozoic; 15lC: late Cenozoic; 210lC: late Cenozoic; 100Q: late Quaternary (For sources, see Şengör and Atayman, in press).

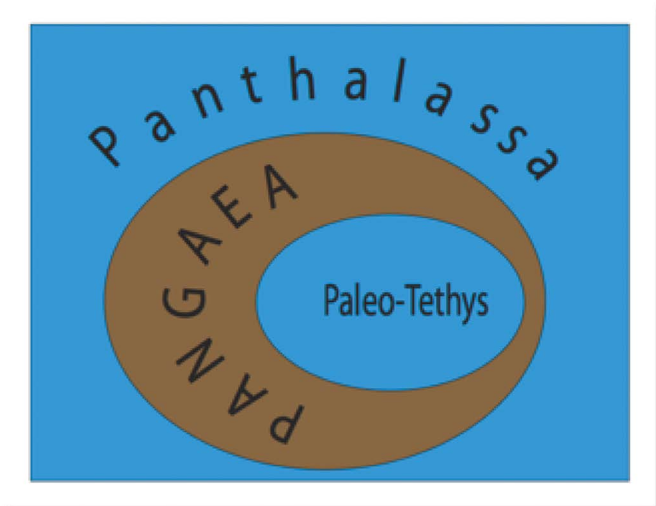

Figure 4. A conceptual map of the Ptolemaic condition on the example of the late Permian Pangaea, the Paleo-Tethys and the Panthalassa. Notice the total isolation of the Paleo-Tethys within a continent similar to the isolation of the Indian Ocean in Ptolemy's world map. This is what we call the 'complete Ptolemaic condition.' A 'partial Ptolemaic condition' occurs when only few narrow and bathyal to neritic passages, of insufficient size to allow significant outflow of heavy waters, connect the enclosed ocean with the outer ocean.

sion to Ptolemy's geography (second century AD) in which he showed the Atlantic and the Indian Oceans as two entirely isolated 'lakes' in a geocratic Earth (Fig. 4). A complete Ptolemaic condition would be one in which no communication between two oceans exists (e.g., the Caspian Sea today). An incomplete Ptolemaic condition is one in which only a very limited exchange of the waters of the oceans may take place (e.g., the Mediterranean today).

Figure 5 is a physical geographical map of the late Permian which shows the almost complete Ptolemaic condition of the Earth at that time. No submarine features are shown within the Panthalassa except the inferred circum-Panthalassan trench which, in fact, may not have existed as a topographic feature everywhere. The white-ruled field represents the 'killing fields of the Paleo-Tethys:' Global fungal-remain localities indicating the areas of maximum amounts of organic debris resulting from dead bodies perished during the killing event at the end of the Permian. The white points are actual observation spots reported by Steiner et al. (2003) and Visscher et al. (1996). We interpret the mass deaths as a consequence of gas eruptions from the Paleo-Tethys (H_2S and CH_4) as all the reported localities form a halo around it and along its deep gulfs (Malagasy gulf) and its spillways (Norwegian-Greenland rift system and north Thailand Strait{s}). The width of the circum-Tethyan belt of fungal remains indicates the extent of areas severely affected by toxic-gas emissions from the Paleo-Tethyan ocean (see Şengör and Atayman, in press).

ANOXIA IN THE PALEO-TETHYS IN THE PERMIAN

Anoxia signifies absence of free oxygen, prohibiting aerobic life to exist. Hypoxia (=low oxygen), suboxia (=under-oxygenated) and/or dysoxia (=badly oxygenated) are used commonly to denote degrees of oxygen deficiency above total anoxia. Both anoxia and dysoxia can happen in the atmosphere as well as in various water bodies making up the hydrosphere including lakes and oceans, but not in flowing rivers.

Under anoxic conditions, decomposition of proteins (animal or plant tissue) releases H_2S following the reaction of carbonic acid with alkaline or alkali-earth sulfides. H_2S becomes oxidized in surface waters and then dissolves and reacts with $CaCO_3$, producing $CaSO_4$. The reduction of $CaSO_4$ in the presence of organic carbon (dead organisms) generates CaS and CO_2, which, when it reacts with water, makes carbonic acid (soda water). The carbonic acid then reacts with $CaSO_4$ and generates $CaCO_3$ and H_2S. If we bring more C and S into the system than can be oxidised, the reactions will go on producing CO_2 and H_2S.

CH_4 is also generated as a result of the degradation of organic matter under anoxic conditions by Fe, Mn and S (Schubert et al., 2006). Formation of CH_4, H_2O, or CO_2 occurs through a complex series of chemical reactions. The major methane contribution to sea water comes from seeps and mud volcanoes.

If all three gases accumulate in very large quantities in the water column over millions of years, such conditions as increasing the temperature of the water or stirring it up vertically will lead to bubble formation and may eventually trigger gas eruptions. Ryskin (2003) further pointed out that such ocean eruptions may have caused the end-Permian extinction, a thesis we support. Examination of widely spaced stratigraphic sections recording Paleo-Tethyan and Panthalassan anoxia reveals progressive and diachronous Permian and local Carboniferous anoxia development (Fig. 6; Şengör and Atayman, in press).

THE PERMIAN EXTINCTION AND THE PALEO-TETHYS

The 'end-Permian' extinction has long been considered to be the greatest extinction during the Phanerozoic eon. The *rate of biodiversity dimunition* during the Permian extinction was, however, much less than that during the end-Cretaceous extinction, probably indicating that the two extinctions had different causes (Şengör et al., 2008). Which processes reduced biodiversity during the Permian then? The answer to that question requires a knowledge of both the temporal and the spatial characteristics of the Permian extinction and of the *common biology* of both the victims *and* the survivors.

Stanley (1987, p. 97) stated that great changes in the biosphere had taken place on land and at sea during the Permian, and these changes were not confined to the very end of the

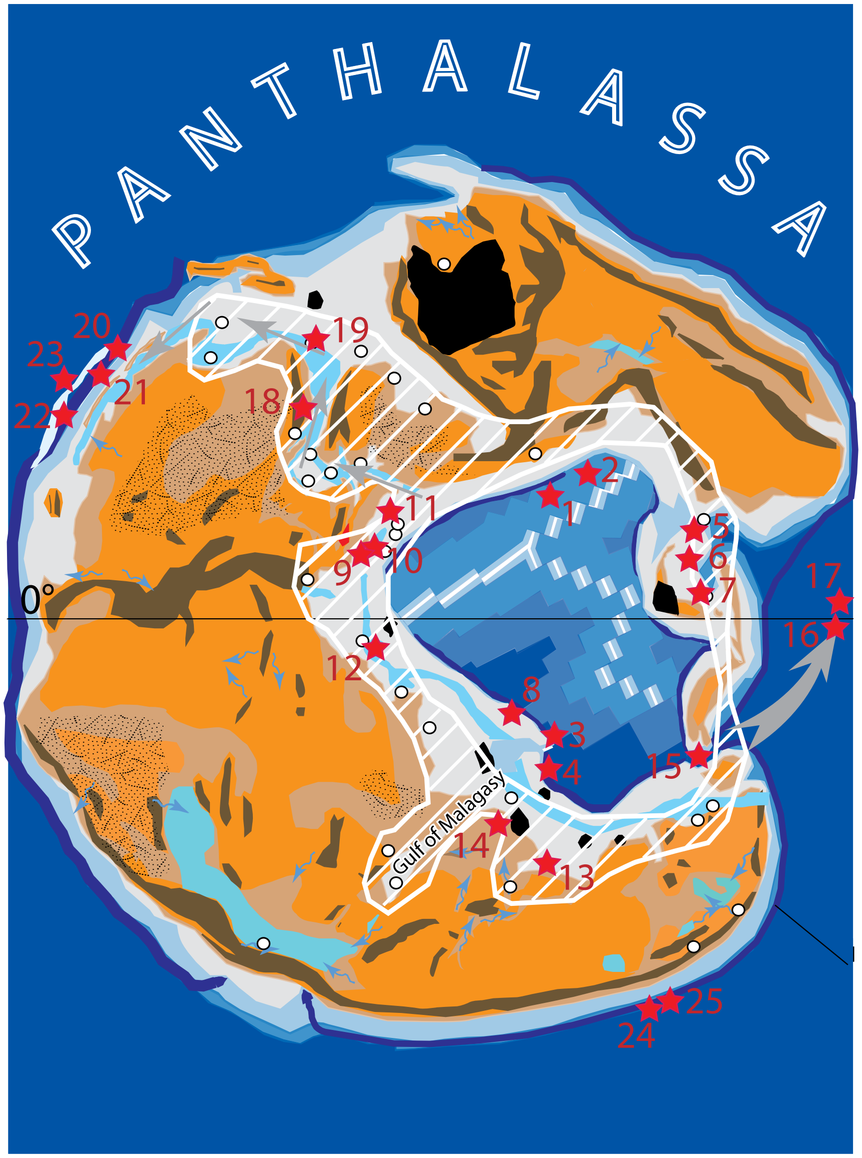

Figure 5. The geomorphology of the Permian world including the floor of the Paleo-Tethys. No morphological elements are shown within Panthalassa except the inferred circum-Panthalassan trench which, in fact, may not have existed everywhere as a bathymetric feature. The red stars represent the locations of the stratigraphic sections in the late Permian world for which redox conditions are summarized in Figure 6. The white ruled area encircling the Paleo-Tethys corresponds to its 'killing fields', recognized by the global fungal-remain localities, which indicate the areas of maximum amounts of organic debris resulting from the remains of organisms that perished during the killing event at the end of the Permian. Data are from Steiner et al. (2003) and Visscher et al. (1996).

Permian, but spread over at least 10 million years. After two decades of detailed paleontological and stratigraphic research on Permian rocks, Stanley's statement remains correct. Furthermore, the time interval for extinctions increases as more research results accumulate, effectively disproving rapid extinction hypotheses involving events such as meteorite impact and catastrophic volcanism.

Later studies showed that indeed there was not a single maximum, but instead two maxima of extinction in the marine realm: one at the end of the Guadalupian, and the other at the end of the Changhsingian (Kozur, 1977, 1980; Stanley and Yang, 1994; Yin et al., 1994) with 58% of all marine genera dying out at the end of the Guadalupian (Stanley and Yang, 1994) and between 83% (Sepkoski, 1989, 1990) and 96% (Raup, 1991) becoming extinct at the end of the Changhsingian.

The groups that suffered during the Guadalupian extinction were dominantly benthic organisms including rugose corals, bryozoans, fusulinid foraminifera and articulate brachiopods plus the necto-benthonic ammonoids. '[T]he extinctions happened especially in Tethyan, mid-latitude regions; there is very little evidence for the event in northern waters' (Benton, 2003, p. 256). Powers and Bottjer (2007) recently pointed out that extinctions not only started in the Capitanian, but began in the deep sea and progressively attacked shallower seas, leading them to suggest that they were a result of 'environmental stress result[ing] from the gradual encroachement of some deep-water phenomenon onto the shelves' (*ibid.* p. 995). In areas affected only irregularly, or not at all, by Paleo-Tethyan anoxia, bryozoans survived, as in the upthrown rift blocks in Greenland and Spitzbergen (Nakrem, 1994).

But this is exactly how anoxia developed at the same time and in the same place, i.e., in the vast, closed equatorial ocean, the Paleo-Tethys, during the Permian, but it reached different marine realms such as the abyssal plains, the bathyal slopes, the lower shelves and the higher shelves at different

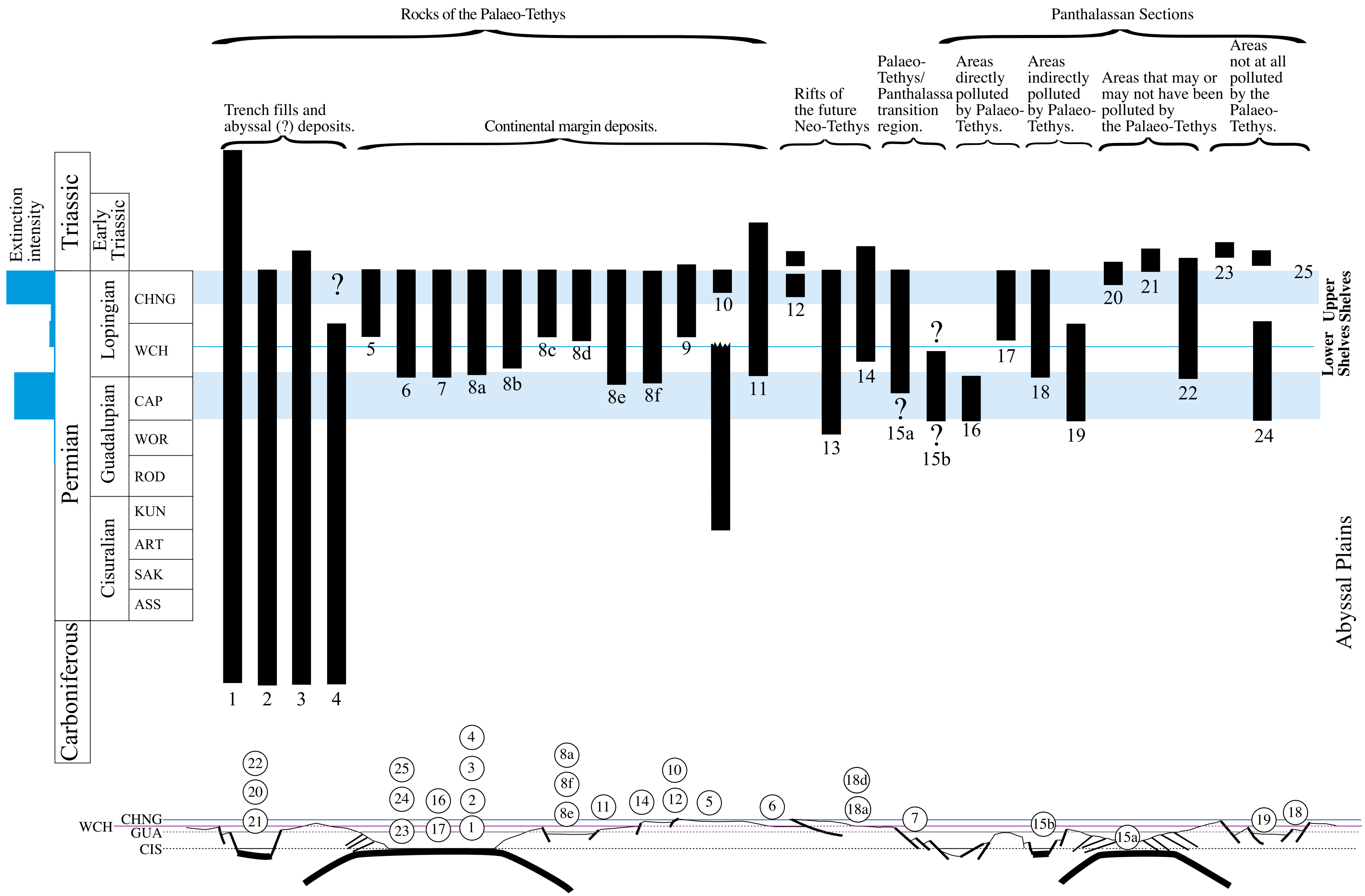

Figure 6. Summary diagram of the development of anoxia (black) in the sections studied by Şengör and Atayman (in press) and its correlation with the Permian extinctions. In these sections, anoxia does not everywhere begin abruptly, but evolves gradually with initial dysoxic onset. Dysoxia leading to anoxia is not distinguished in these summary sections, and both are represented by black. However, most of what is colored black consists of anoxic sedimentary rocks. The blue histogram to the left, taken from Figure 5 in Stanley and Young (1994), shows the relative ratio of last to first appearances of brachiopods for the upper half of the Permian in China. This diagram portrays a faithful picture of the entire Permian extinction pattern on land and at sea. We feel that with accumulation of more data, the Permian extinction peaks will most likely lose their sharpness and reflect more faithfully the progress of anoxia. The long cross-section at the bottom of the figure exhibits a variety of tectonic environments (with no regard to any actual geography) at times when they became invaded by anoxic waters. The numbers in circles correspond to those of the sections above to show which section was deposited in what kind of a morpho-tectonic environment.

times, as the data summarised in this paper document and as Wu et al. (2006) recently also found (see Fig. 6). When Kozur (1977) considered the entire Permo-Triassic extinction picture he was struck by the fact that mostly the warm water benthos had died out, whereas the colder water fauna did not. Wu (2006) made the same general observation that the taxa that died out were warm water, stenobiotic organisms, whereas those few that survived were eurytropic and eurthermal organisms living in cold water environments. Also about 50% of the genera that had disappeared from the record reappeared in the Olenekian to Ladinian interval (early to medial Triassic), forming Lazarus taxa. The most likely asylum from the poisonous Paleo-Tethys was the Panthalassa, which could be reached not only through the North Thailand strait but also through some of the shallower marine connections across the Cathaysian Bridge. Hallam and Wignal (1997, p. 116) were surprised to see that nectonic/necto-benthonic creatures had escaped the extinction. For instance, fish groups were affected very slightly, if at all (Schaeffer, 1973; Patterson and Smith, 1987), probably because they could escape to the immense Panthalassan ocean. The only benthonic groups that could withstand the crisis *in situ* were dysaerobic organisms (Hallam and Wignall, 1997, p. 116).

Many families of foraminifera and the Suborder Fusulina had vanished shortly *before* the end of the Permian (Kozur, 1998). At the end of the Guadalupian, some 45 genera went extinct. Following this extinction, many foraminiferal lineages radiated in the Lopingian until the more severe extinction at the latest Changhsingian (Pasini, 1985; Noé, 1988; Tong, 1993) and it mostly affected the tropical, more complex forms (Brasier, 1988). Dysaerobic groups also survived this event.

Available paleontological observations show that marine extinctions on the deep ocean floor started in the Paleo-Tethys in the medial Permian. With the passage of time, those living in higher and higher places were affected. Those who could swim or had wide distribution to the Panthalassan realm largely survived. By contrast, outside the Paleo-Tethys, not much seems to have happened; but then, there were not many niches outside the Paleo-Tethys except the vast abyssal plains, and the endless expanses of the Panthalassan ocean surface, neither then nor now much popular among organisms as abodes except for the radiolaria (whose record, in the form of deep sea cherts, often gets annihilated by subductive removal). As the outer margins of Pangaea were almost without exception subduction margins, shelf space, the main seat of marine life, along the Panthalassan outer margins was limited and constructed mostly on tectonically and sedimentologically unstable forearc areas (Dickinson and Seeley, 1979). All this indicates that it was most likely the poisonous gases in the Paleo-Tethyan anoxic waters that killed the inhabitants. The geographical confinement to the Paleo-Tethys disproves those hypotheses favoring truly 'global' causes, such as alleged superanoxia events poisoning the entire world ocean. Moreover, if a flood basalt province close to the Arctic (in late Permian time), as the Tunguska Province was, leaves little record of killing in its vicinity, but somehow concentrates most of its killing power in an isolated ocean far away, its contribution to the Permian extinction events would be suspect.

There were close terrestrial parallels with the Permian marine extinction events. For example, the paleophytic flora disappeared by the end of the Guadalupian and the mesophytic flora appeared in the late Permian. The latter mostly characterised dry and/or high regions mainly beyond 30° north and south (late Permian) latitudes, i.e., away from the venue of the most intense extinctions. However, large trees only appeared in the late Triassic. The low-oxygen environment in the late Permian and early Triassic was characterized by sparse forests with small trees, in contrast to larger, more abundant trees of both the Carboniferous and the late Trassic.

Vertebrate life also shows important changes at this time. The dominant reptiles changed from the Pelycosaurs with roots in such late Carboniferous forms as *Ianthosaurus* sp. to the more agile Therapsids that managed to survive into the late Triassic (McLaughlin, 1980; Carroll, 1988, ch. 17), although the Pelycosaur/Therapsid transition happened across what Lucas and Heckert (2001) called 'Olson's gap' spanning an interval from uppermost Kungurian to bottom Kazanian (Upper Cisuralian to uppermost Roadian) in which we have no record of Permian tetrapods anywhere (Lucas, 2004).

The beginning of the Capitanian or even the end of the Wordian witnessed the end of the Dinocephalians (Spencer G. Lucas, written communication, 2007), the largest tetrapods of the Paleozoic world. They were replaced by the smaller and very mammalian-like Gorgonopsians (Battail, 2000; Gebauer, 2007) and Dicynodonts (King, 1988; Battail, 2000). This transition to a more mammalian-like body was the decisive change in the tetrapod world and should perhaps be placed into the end of the Carboniferous, into the dawn of the amniote world (Gregory, 1955). At the end of the Lopingian, the Gorgonopsians also disappeared and only two or three Dicynodont species plus some small diapsids such as the *Proterosuchidae* (Benton, 2004) survived the Permo-Triassic transition. The survivors were small (Price-Lloyd and Twitchett, 2002), lowland, partly aquatic tetrapods (Shishkin, 1997) that, judging from their distribution, could not traverse even moderately high areas such as the lowest parts of the Appalachians and the post-Hercynian Basin-and-Range-like environment of Europe. They were adapted to live in the low-oxygen world of the end-Permian and for that reason seem to have preferred the relatively lower and less harsh eastern Pangaea as opposed to the desert- and mountain-dominated western Pangaea. The *Lystrosaurus*, for example, originated very near the Gulf of Malagasy of Gondwana-Land, in east Africa (King and Jenkins, 1997), and went east (and southwest) and most likely migrated north across the Cathaysian Bridge, in the footsteps of its *Dicynodon* relatives (Battail, 1997), to reach the extensional lacustrine basins of the post-Altaid world in central Asia. From there it reached to the lowlands of the Moscow basin in the early Triassic. Amphibian fossils record a similar story (Steyer et al., 2006)

The overall story from the land biosphere is that the Guadalupian saw a first wave of extinction and the end of the Lopingian another one, leaving the early Triassic world with very few genera. Both extinctions worked to eliminate large animals requiring agility. Almost no carnivores were left by the end of the Permian, despite the fact that many *Lystrosauri* were still wandering about. The progressively more mammal- and avian-like bodies required more oxygen than other tetrapods; thus any reduction in oxygen would first kill off those that are most mammal- or bird-like and, among them, the larger ones that require the most energy. However, the great advantages of the mammalian and avian ability to remain energetic for hours must have outweighed any other advantage, for after every extinction, the surviving lineages created more and more mammal-and avian-like organisms in the amniote world.

Labandeira (2005) pointed out that the only mass extinction insects suffered came at the end of the Permian. There are twenty-two orders in the insect Class (out of 37 total) known from the Permian and eight of them vanished with another five losing many families by the end of the period. Only one or two insect orders have vanished since that time.

What life-supporting mechanism is common to plants, tetrapods, and insects living on land? It is the air they breathe. If that air becomes poisonous they will die. This is something they had in common with their contemporaries living in the Paleo-Tethys. But how can the internal dynamics of an ocean kill not only organisms in it, but also on lands surrounding it? The only process capable of bringing about such a catastrophe is gas eruption. If the gases resulting from anoxia in the ocean erupt, they would create a field of devastation around the ocean proportional to the volume of gas erupted. We have no means of judging how much gas Paleo-Tethys released, if any, but we have a good idea of its lethality on land.

Visscher et al. (1996) pointed out that sedimentary organic matter preserved in end-Permian successions worldwide contain unparalleled abundances of fungal remains irrespective of depositional environment, be it marine, lacustrine, or fluvial, and irrespective of floral province or climatic zone. Their interpretation is that the fungal abundance reflects a widespread dying of arboreous vegetation that led to faunal collapse as well. When one plots their 'worldwide' observations on our reconstruction (Fig. 5), it is apparent that they form a halo of 'killing fields' around the Paleo-Tethys and its channel of communication with the Panthalassa between the Porte of Dobrudja and the Greenland/Norway rift system.

In summary, the land animals became extinct because something happened to the air they were breathing, and whatever it was, it occurred at least twice in the Permian. This is also the record preserved in marine sedimentary rocks.

This double-phased extinction originated in a geographically well-defined area making single-shot global explanations impossible to entertain. Such explanations include bolide impact, eruption of the Tunguskan traps, global warming, and global changes in sea level. Paleo-Tethyan anoxia has a temporal and spatial evolution that best explains the paleontological and paleo-environmental data at hand, especially in a world that was becoming poorer in oxygen (Berner, 2004; Ward, 2006).

But why the double peaks? What could have led Paleo-Tethys to erupt twice (if it really did so)? We know so little now that this would appear a premature question to most prudent minds. We are not even sure how sharp the double peaks really were.

SOME METALLOGENIC IMPLICATIONS

The abundance of black shales of oceanic origin within the remnants of the Paleo-Tethys has led us also to look for associated sediment-hosted copper-sulfide deposits. Sediment-hosted Cu-sulfide deposits typically occur in basins that contain saline marine or lacustrine shales that overlie redbeds, and in isolated non-redbed units within continental redbed unit sequences (Hitzman et al., 2005). Many studies have shown that the redbeds are the copper source (Brown, 2006). Although generally not as large as the redbed-associated deposits, sediment-hosted Cu-sulfide deposits can also occur in shales above basaltic units where the basalts are the source of the copper. It is this second type of Cu-sulfide deposit that may be more widespread within Cimmeride accretionary prisms containing large amounts of ophirags[3] and black shales.

In many sediment-hosted Cu-sulfide deposits, termed *Kupferschiefer* ('copper-shale') -type, sulfides are hosted by carbonaceous black shales. Geologic and geochemical studies show that chemical reduction in the presence of sulfur is the primary means of sulfide precipitation in sediment-hosted Cu-sulfide deposits (Hitzman et al., 2005). The deposits are associated with a redox boundary formed between the reduced shales and underlying oxidized redbeds (the *Rotliegende*, i.e., 'the red underlyer'). In most *Kupferschiefer*-type deposits, the reductant is degraded organic matter or in-situ-generated hydrocarbons within the shales themselves (Hitzman et al., 2005). The *Kupferschiefer* Cu-sulfide deposits of the Zechstein basin of Poland and Germany are hosted by shales and sandstones of medial to late Permian age and are the largest known accumulation of sediment-hosted Cu-sulfides deposits in the world. Although not directly linked to the anoxic Paleo-Tethys of the Permian, the Zechstein basin is a steer-head (in cross section) type basin which began forming in the early Permian in east-central Pangaea along a major channel of communication between the Paleo-Tethys and Panthalassa, and was episodically flooded by the anoxic Paleo-Tethyan waters as shown in Figure 7.

[3]Ophirag is a term introduced by Şengör and Natal'in (2004) to denote mafic and ultramafic rock associations inferred to be parts of previous oceanic crust but do not display the complete ophiolite sequence as in the 'Penrose definition.'

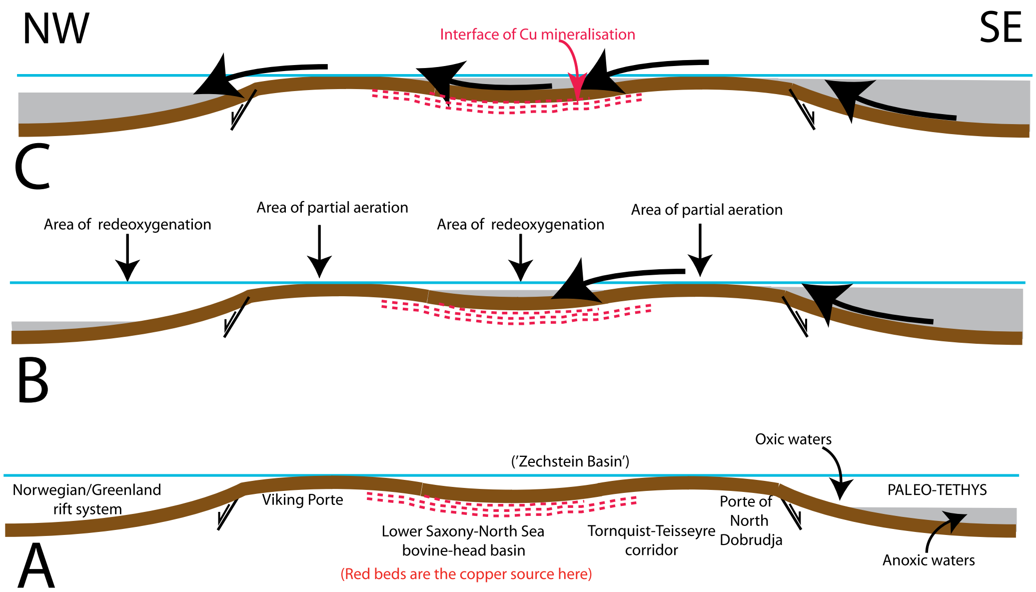

Figure 7. A schematic cross section from the Dobrudja Porte (DP in Fig. 3) to the Norwegian-Greenland Sea rift system across the Zechstein Basin, showing the gradual rise of the top surface of anoxic waters in the Paleo-Tethys and their spilling into the European/future North Atlantic regions. In the Zechstein basin, the invading anoxic waters were underlain by the redbeds, the *Rotliegende* (=the red underlier), of the Lower to Middle Permian. Cu-sulfide deposits formed at the interface of the *Rotliegende* and the invading anoxic waters (and the S-rich evaporites).

However, the Permian black shales of the Paleo-Tethys are not generally associated with rift environments except in such limited areas as the Central and Southern Pamirs, in environments created by the rifting of the Cimmerian Continent. In such basins the shales are in contact with arc and marginal basin volcanics (Gaetani, 1997; Gaetani et al., 2004; see Fig. 3). Thus, the greatest potential for sediment-hosted Cu-sulfide deposits in the Tethyan realm are Permian anoxic shales laid down under euxinic conditions in the most likely presence of H_2S associated with basic volcanic copper-source rocks.

Here are a few examples: The environment of the Paleo-Tethyan black shales, especially in northern Turkey, Transcaucasia, the Pamirs, and northern and western Tibet, indicate that they were deposited in a deep-sea environment above oceanic crust and then stacked in internally highly deformed thrust sheets as large subduction-accretion complexes (for summary and references, see Şengör and Natal'in, 1996, and Şengör and Atayman, in press). In all the places mentioned, they are associated both with depositional and tectonic contacts with submarine mafic, commonly pillowed and locally brecciated, volcanic rocks. After being stacked into accretionary complexes, many became basement to subsequent continental-margin arcs of both the Cimmerides and the Alpides. Some metals have been remobilised in these accretionary complexes, as may have been the case in the eastern Pontides of northern Turkey (Kekelia et al., 2004). All these conditions represent favorable environments for generation of Cu-sulfide deposits.

In northern Turkey, in the Küre Cu-sulfide deposit for example, this expectation is fulfilled (Fig. 8, locality "k"). Here the sulfide ores consist of pyrite, chalcopyrite, bonite, covellite, sphalerite, digenite, marcasite, tennanite and carrolite (Güner, 1979-1980). Both Güner (1979-1980) and Çağatay et al. (1979-1980) pointed out that in this mineral-rich locality, known and exploited since antiquity, the massive sulfide deposits commonly appear at the contact between abyssal tholeiitic basalts (parts of ophirags here) and black shales plus some greywackes. This rock assemblage belongs to the upper Carboniferous(?) to Liassic (lower Jurassic) Akgöl mélange constituting part of a Paleo-Tethyan subduction-accretion complex (Şengör et al., 1984). The pyritic copper deposits are found as stockwork-disseminated ores at the upper levels of the basalts and as massive lenses between the basalts and the black shales. Güner (1979-1980) emphasised that mineralization in Küre is actually both massive and disseminated and most occurrences are related to faults near the basalt/black shale contact, although he has shown that much of the main mineralization was a seafloor hydrothermal event predating the faulting associated with the building of the subduction-accretion complex. If that is so, the H_2S required for sulfide deposition would have been abundantly available in ambient sea water above the abyssal plain of the Paleo-Tethys, as we have argued above.

Along the eastern part of the southern slope of the Greater Caucasus, the younger, Alpide Filizchai (=bud stream) deposit of Pliensbachian age (Eppelbaum and Khessin, 1988), containing pyrite, chalcopyrite, galena, pyrrhotite and sphalerite, plus the associated deposits of Katsdag, Katekh, Mazymchai and Sagator, and the Kyzyl Dara (=red river; see Rundquist,1984), formed under similar conditions in association with shales deposited in oceanic basins of limited circulation (see Fig. 8, locality "ak").

In Iran, stratabound Cu deposits in Permian phyllitic shales and black limestones are associated with the Mashhad ophiolite (Fig. 8, locality "m"; see Wauschkuhn et al., 1984; ages revised in Eftekharnezhad and Behroozi, 1991), suggesting an environment possibly not very different from the Küre occurrences.

In Afghanistan, in the Paropamisus, we see precisely the same situation (Fig. 8, locality "p"), where copper occurrences are associated with ophiolites and abyssal clastic sedi-

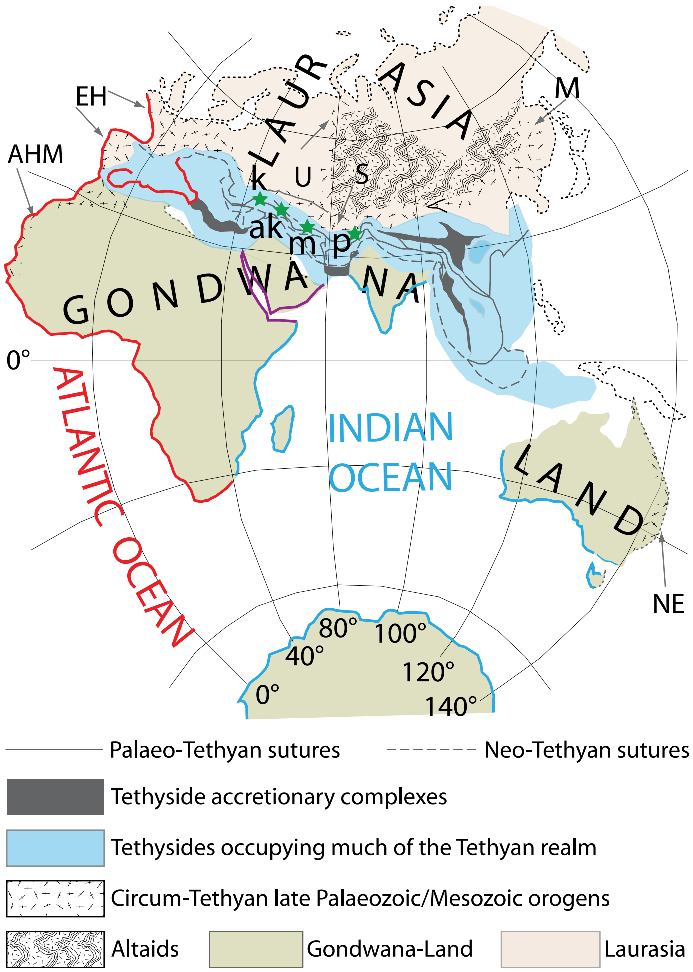

Figure 8. The late Paleozoic to the present tectonic classification of the Old World showing the position of the Tethysides in it. The rifted continental margins of the two different oceans disrupting the Old World are shown in the colors corresponding to the colors in which their names are written (except the Red Sea and the Gulf of Aden, whose names could not be written because of the exigencies of the available space). The colors and patterns in this figure correspond to those in Fig. 2. The green stars are the locations of the historically well-known copper sufide deposits in Paleo-Tethyan accretionary complexes within the Cimmeride edifice. Key to lettering: AHM: African Hercynides and Mauritenides, EH: European Hercynides; M: Manchurides; S: Scythides; U: Uralides; k: the Küre copper sulfide deposit; ak: Filizchai and Kyzyl Dara copper sulfide deposits; m: Mashhad ophirags copper sulfide deposits; p Paropamisus copper sulfide deposits.

ments. Such examples as the Surkhab Complex also have a high Au content (Wolfart and Wittekindt, 1980).

It is not the place here to list all known sulfide occurrences of Permian age in Paleo-Tethyan subduction-accretion complexes, but it is clear that their importance decreases eastward as mountains in which the subduction-accretion complexes of the Paleo-Tethys occur become higher and less accessible. We contend that inaccessibility is the main cause of the small number of known important Permian stratabound sulfide deposits east of the Pamirs and not their primary absence. Many of the necessary conditions for the formation of stratabound sulfide deposits of Permian age (or younger, remobilized) exist in the Paleo-Tethyan subduction-accretion complexes:

1) Their clastic sediments were accumulated in an anoxic ocean basin atop oceanic crust that may have had not only active spreading centers, but also off-axis volcanicity.

2) The abyssal clastics were later stacked into large subduction-accretion complexes in which there must have been significant fluid flow, if the persent-day subduction accretion complexes can be used as a model (e.g., Le Pichon et al., 1991).

3) Most Paleo-Tethyan accretionary complexes later formed arc massifs to both Cimmeride and Alpide continental-margin magmatic arcs, the magmatic systems of which could have remobilized and redeposited any primary ore wealth.

It is clear that more exploration effort must be spent on the high mountains of the Pamirs, the Kuen-Lun, the Anyemaqen Shan and the Hoh Xil Shan to test the hypothesis here advanced.

CONCLUSIONS

From the end of the medial Permian (at the latest) until the Triassic, the Paleo-Tethys had become an inner-Pangaean ocean with very limited communication with the Panthalassa through the north Thailand strait(s) that at most had bathyal depths. This setting, plus its equatorial location and the centripetal endorheic drainage of Pangaea, led to thermal and chemical layering of the Paleo-Tethyan water body that eventually stopped its internal circulation and turned it anoxic. Paleo-Tethyan anoxia may well have started already in the latest Carboniferous in certain restricted areas and invaded the abyssal environments of the Paleo-Tethys by the end of the medial Permian. In Wuchiapingian time the lower shelves had been invaded by toxic waters. By the end of the Chanhsingian all Paleo-Tethys had turned anoxic and extingished most, if not all, of its benthic multicellular life. Evidence from submarine erosive disconformities and increased chemical weathering suggests that the Paleo-Tethys may have erupted gases lethal to oxygen breathing organisms which, combined with a rapid plunge of atmospheric oxygen content since the medial Permian, also created a surrounding halo of extermination. Gas eruptions due to Paleo-Tethyan anoxia account for much if not all of the medial to late Permian extinction events that seem geographically confined to the Paleo-Tethys, to areas it could pollute by water connections, and to its terrestrial surroundings.

The anoxia in the Paleo-Tethys affected a large amount of sedimentary rock, the largest volumes of which are now found in the high mountains of central Asia along the peri-Arabian and the Chinese Cimmerides, i.e., from northern Turkey to the eastern Kuen-Lun (cf. Şengör, 1984). Historically famous

Permian copper sulfide deposits are known from Turkey and the Greater Caucasus, but the known occurrences farther east are not commensurate with the expectations from the geological evolution which, we believe, might reflect inadequate exploration. The Cimmeride chains of central Asia may yet prove to host world class sulfide deposits of Permian age.

ACKNOWLEDGMENTS

This paper, except the metallogenic part, represents a summary of a book by the first two authors now in press as a Geological Society of America Special Paper. The text of that book was originally submitted to the Dickinson (Ores and Orogenesis) Symposium as a contribution, but could not be accepted on account of its size. Jon Spencer advised Şengör and Atayman to submit their large text as a book elsewhere and prepare a summary for the present symposium possibly with an addition on the metallogenic aspects. This appeared very welcome, because Şengör and Presnell were already thinking of publishing a note to draw the attention of the mining companies to the possible copper sulfide potential of the Cimmeride mountain ranges. Thus the authors of this note agreed to pool their resources to generate the summary plus the metallogenic discussion as requested by Jon Spencer. Jon is thus really responsible for our decision to submit our original paper to the Geological Society of America Special Paper (Şengör and Atayman, in press) and this enlarged summary to the AGS Dickinson volume (this volume), and we are accordingly grateful to him. We are also most grateful to all organizers of the Dickinson Symposium for the great honor of contributing a paper to the celebration of one of the greatest geologists of our times.

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