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Did Paleo-Tethyan anoxia kill arc magma fertility for porphyry copper formation?

Jeremy P. Richards[1]* and A.M. Celâl Şengör[2]*
[1]Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada
[2]Maden Fakültesi, Jeoloji Bölümü, and Avrasya Yerbilimleri Enstitüsü, İstanbul Teknik Üniversitesi, Ayazağa 34469 Istanbul, Turkey

ABSTRACT

The Tethyan orogen is host to numerous porphyry Cu ± Mo ± Au deposits, but the majority formed during subduction of the Neo-Tethyan ocean basin in the late Mesozoic–Cenozoic; very few deposits have been found associated with Paleo-Tethyan subduction. We propose that this sparsity is due to widespread anoxia in the Paleo-Tethyan ocean basin, leading to the generation of relatively reduced arc magmas that were infertile for porphyry Cu formation. A compilation of published geochemical data indicates that Neo-Tethyan arc rocks have higher average Cu contents and V/Sc and Sr/Y ratios compared to Paleo-Tethyan rocks, indicating higher magmatic oxidation states and greater fertility for ore formation during Neo-Tethyan subduction. Subduction of relatively reduced oceanic lithosphere, or reduction of normal moderately oxidized arc magmas by interaction with reduced lithosphere, can therefore destroy the ore-forming potential of arc magmatic suites.

INTRODUCTION

Phanerozoic arc magmas are generally hydrous and moderately oxidized, reflecting their derivation from partial melting of metasomatized suprasubduction zone asthenospheric mantle wedge material (Kelley and Cottrell, 2009; Zellmer et al., 2015). These magmas are fertile for the formation of porphyry Cu ± Mo ± Au deposits because chalcophile metals behave as incompatible elements in moderately oxidized magmas [ΔFMQ+1 to +2, where ΔFMQ (fayalite-magnetite-quartz) is the log f_{O_2} (oxygen fugacity) deviation from the FMQ buffer; Richards, 2015a]. Metals can thus be transported to upper crustal levels in magmas prior to partitioning into exsolving hydrothermal fluids, with reprecipitation in economic concentrations under favorable ore-forming conditions (Sillitoe, 2010).

The moderate oxidation state of Phanerozoic arc magmas is a critical metallogenic factor, because sulfur dissolved in the magma is mainly present as sulfate. In contrast, under more reducing conditions (ΔFMQ ≤ 0) the sulfur is predominantly present as sulfide, and early saturation in sulfide melts or solids will rapidly deplete the magma in chalcophile and siderophile elements (i.e., they will behave as compatible elements; Richards, 2015a), rendering the magma infertile for later magmatic-hydrothermal ore formation. It has been suggested that more reducing conditions may have characterized Precambrian subduction zones and arc magmas, thus explaining the rarity of Precambrian porphyry Cu deposits (Evans and Tomkins, 2011; Richards and Mumin, 2013). It is also possible that periods of deep ocean anoxia during the Phanerozoic Eon could have resulted in more reduced subduction zone conditions, similarly limiting magma fertility (Richards and Mumin, 2013).

An example of such a condition occurred in the Paleo-Tethyan ocean basin during the Permian Period, when almost complete isolation of the basin from global ocean circulation resulted in anoxic conditions and the deposition of thick sequences of organic-rich black shale (Figs. 1 and 2; Şengör and Atayman, 2009). Subduction of such sediments and

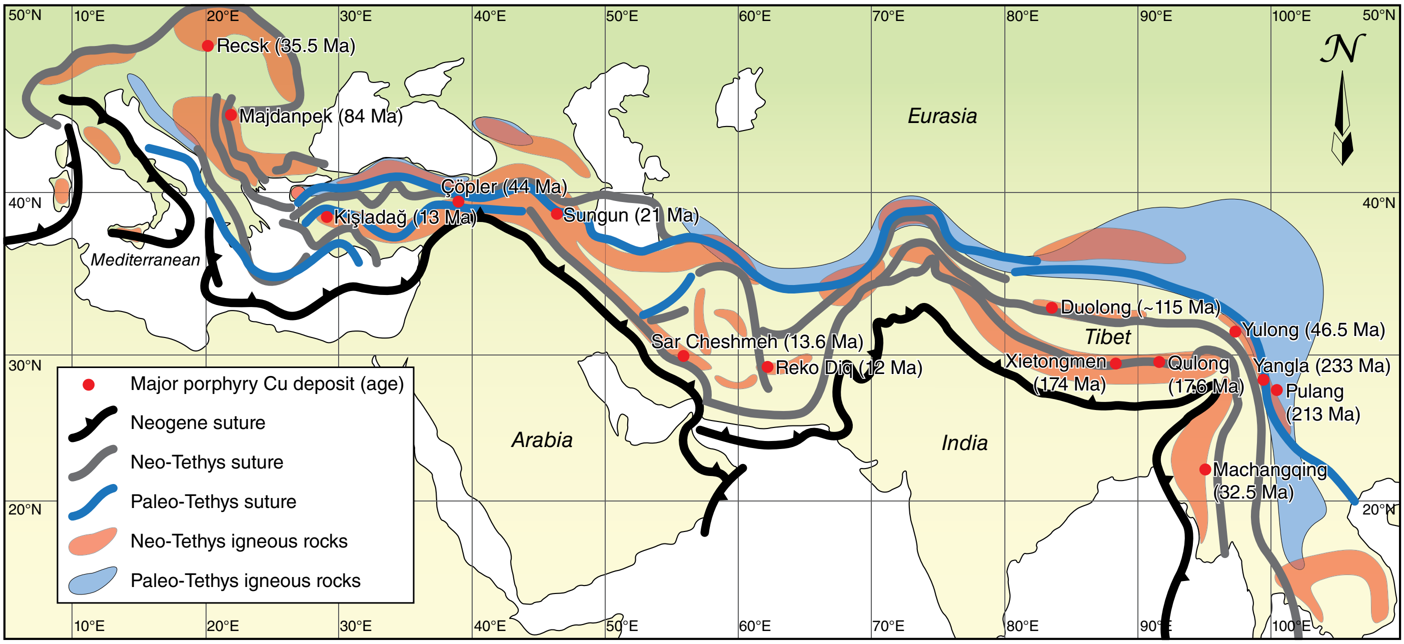

Figure 1. Distribution of igneous rocks associated with Paleo-Tethyan (Permian to Jurassic) and Neo-Tethyan (Cretaceous–Cenozoic) subduction and collisional closure (based on maps of Şengör et al., 1993; Richards, 2015b).

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*E-mails: Jeremy.Richards@ualberta.ca; sengor@itu.edu.tr

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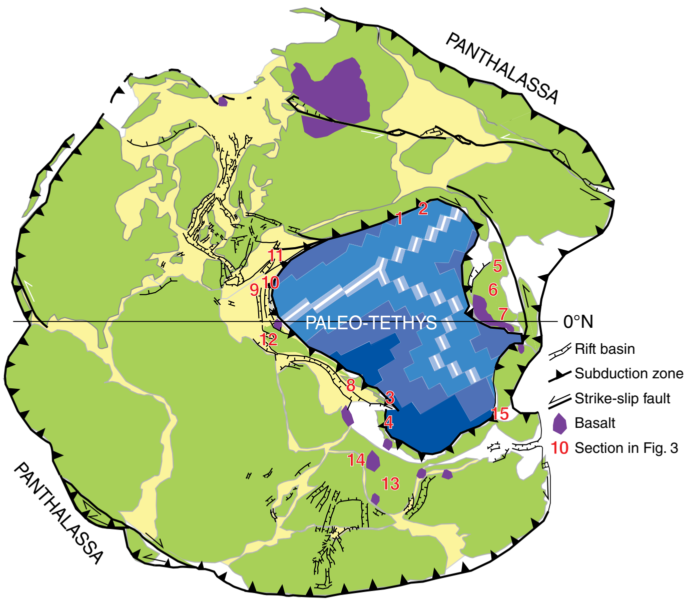

Figure 2. Paleogeographic reconstruction of the Paleo-Tethyan ocean basin during the Late Permian (modified from Şengör and Atayman, 2009). Isolation from global oceanic circulation led to anoxia and the deposition of thick sequences of reduced seafloor sediments.

hydrothermally altered but unoxidized oceanic lithosphere would have generated unoxidized arc magmas (ΔFMQ ~ 0) with low potential for porphyry ore formation. The lack of economic porphyry Cu deposits associated with Paleo-Tethyan arc magmatic systems could be explained by poor preservation of rocks of this age in the Tethyan orogen, and erosional loss of shallow porphyry deposits (generally formed <5 km below surface) (Wilkinson and Kesler, 2007). Alternatively (or additionally), they may simply not have formed due to the reduced nature of the subducting oceanic lithosphere.

Few reliable data exist for the oxidation state of Paleo-Tethyan arc rocks, many of which have undergone some degree of alteration or metamorphism. However, we present a compilation of published data for least-altered Tethyan arc rocks that suggest that Paleo-Tethyan magmas were Cu poor compared with Neo-Tethyan magmas, possibly due to early sulfide saturation under more reducing conditions, rendering them less fertile for porphyry ore formation. These results support system-scale metallogenic models that require the optimal, efficient, and sequential operation of multiple processes for the eventual concentration of metals to form ore deposits (Richards, 2013). Inefficient or suboptimal functioning of any step can limit or destroy ore-forming potential, and reducing conditions in the subduction zone or deep lithosphere may be an early step that will render arc magmas infertile.

TETHYAN PORPHYRY Cu DEPOSITS

The Tethyan orogen is highly prospective for porphyry Cu ± Mo ± Au and associated epithermal Au ± Cu deposits (Fig. 1), but the majority of known deposits are Cretaceous to Cenozoic in age, and are related to subduction and closure of the Neo-Tethyan ocean basin (Aghazadeh et al., 2015; Richards, 2015b). Examples include the Majdanpek porphyry Cu-Mo-Au deposit in Serbia (ca. 84 Ma), the Sar Cheshmeh porphyry Cu-Mo deposit in central Iran (ca. 14 Ma), and the Qulong porphyry Cu-Mo deposit in Tibet (ca. 16 Ma). The oldest known deposits occur in Tibet and the Indosinian porphyry belt of southwestern China, and include Yangla (ca. 233 Ma), Pulang (ca. 213 Ma), and Xietongmen (ca. 174 Ma). These Triassic–Jurassic systems are thought to be related to subduction and closure of various well-aerated Tethyan subbasins (Richards, 2015b). In contrast, there are no economic porphyry deposits known to be associated with subduction of normal Paleo-Tethyan oceanic lithosphere. This rarity of older deposits undoubtedly partly reflects their susceptibility to erosional loss, but some late Paleozoic–early Mesozoic upper crustal plutonic and volcanic rocks are preserved along the orogen (Fig. 1), suggesting that this cannot be the only explanation.

PERMIAN ANOXIA IN THE PALEO-TETHYS

Anoxia in the Paleo-Tethys ocean basin developed as a result of its equatorial location and restricted circulation from the late Carboniferous to Triassic (Fig. 2). The first evidence of reduced deep ocean conditions is found in late Carboniferous black shale sequences from Georgia (Dizi Series), northern and central Pamir (Kwahan, Bazardar suite), and northeastern Tibet (Horpa Tso) (Fig. 3, columns 1–4; Şengör and Atayman, 2009).

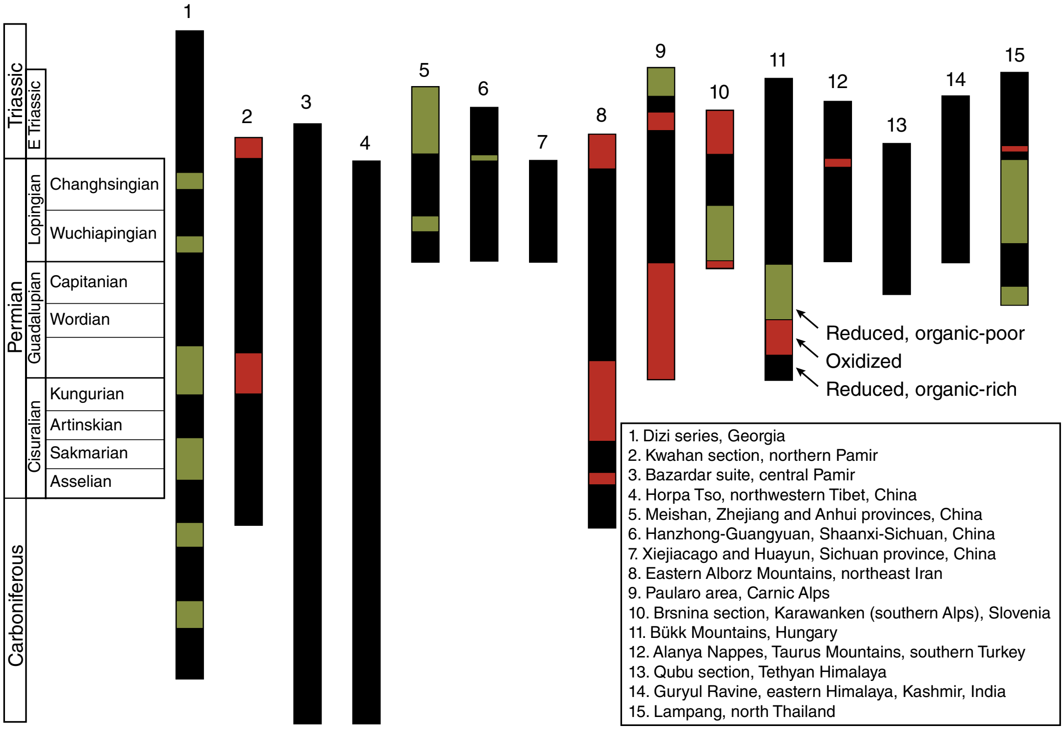

Figure 3. Representative stratigraphic columns from the Paleo-Tethyan ocean basin during the Permian (modified from Şengör and Atayman, 2009). Isolation from global oceanic circulation led to anoxia and the deposition of thick sequences of reduced seafloor sediments.

Anoxia eventually extended into shallow waters, causing bryozoan extinction on continental shelves starting in the Capitanian (Fig. 3, columns 5–15; Powers and Bottjer, 2007). In contrast, there is little evidence for anoxic conditions in the wider Panthalassa Ocean (Şengör and Atayman, 2009).

Northward subduction of the Paleo-Tethyan oceanic lithosphere below the Eurasian continental margin, and opening of the Neo-Tethyan ocean to the south by northward migration of the Cimmerian continental fragments (present-day central Turkey, Iran, and Tibet) effectively destroyed this anoxic ocean basin by the Early Triassic (Fig. 3; Şengör and Natal'in, 1996), limiting its lifespan to ~75 m.y.

TETHYAN ARC MAGMAS

The GEOROC database (Geochemistry of Rocks of the Oceans and Continents; http://georoc.mpch-mainz.gwdg.de) contains a large compilation of geochemical analyses of igneous rocks from the Tethyside orogenic belt. The vast majority of these analyses are of Cretaceous–Cenozoic Neo-Tethyan rocks from the Anatolian-Iranian section of the orogen. We have compiled separately data from early Mesozoic igneous rocks related to subduction and collisional closure of the Paleo-Tethyan ocean, reported from the Pontides, Greater Caucasus, central Iran, Turkmenistan, and Tibet. The data were filtered for lack of noted alteration and loss on ignition <2.0 wt%. (The data sets used are provided in Tables DR1 and DR2, with summary statistics in Table DR3, in the GSA Data Repository[1].)

The simplest assessment of magma fertility is the concentration of ore metals in fresh igneous rocks. Copper is routinely analyzed in geochemical packages, and a plot of Cu versus MgO as a measure of fractionation shows that the Paleo-Tethyan suite is consistently lower in Cu relative to Neo-Tethyan rocks (Fig. 4), suggesting a lower potential for ore formation.

Magmatic oxidation state is an important control on chalcophile element behavior, but this parameter is difficult to measure directly, and is commonly not reported. Instead, it has been suggested that trace element ratios such as V/Sc can be used as proxies for oxidation state (Li and Lee, 2004; Loucks, 2013). Li and Lee (2004) reported that depleted mantle–derived mid-oceanic ridge basalts (MORBs) with oxidation states close to ΔFMQ ~ 0 have V/Sc ratios of 6.74 ± 1.11, whereas Loucks (2013, 2014) suggested that oxidized igneous rocks associated with porphyry Cu deposit have V/Sc > 10 (at 58–70 wt% SiO_2). Selecting samples within this silica range, the Paleo-Tethyan suite has V/Sc ratios of 6.1 ± 2.2 (median = 5.6; n = 54), similar to MORB, whereas the Neo-Tethyan suite has elevated values of 9.1 ± 7.3 (median = 8.4; n = 447), closer to the range of fertile oxidized magmas proposed by Loucks (2013, 2014).

Loucks (2013, 2014) also proposed that fertile arc magmas have Sr/Y > 35, and $(Eu_n/Eu^*)/Yb_n > 2$ at 58–70 wt% SiO_2 [where $Eu^* = \sqrt{(Sm_n \times Gd_n)}$]. Higher values for these ratios reflect higher magmatic water content, which promotes early amphibole crystallization (preferentially removing Y and Yb from the melt relative to light rare earth elements) and suppresses plagioclase crystallization (delaying removal of Sr from the melt) (Richards and Kerrich, 2007), and may also correlate with arc oxidation state (Kelley and Cottrell, 2009). High magmatic water contents are obviously favorable for the formation of magmatic-hydrothermal ore deposits (Burnham, 1979). The Neo-Tethyan suite averages Sr/Y = 29.3 ± 23.0 (median = 26.0; n = 633) compared to lower values of 24.6 ± 18.9 (median = 18.1; n = 121) in the Paleo-Tethyan suite, whereas $(Eu_n/Eu^*)/Yb_n$ ratios are similar or marginally lower (Neo-Tethyan suite average = 1.57 ± 1.31, median = 1.27; n = 323; Paleo-Tethyan suite average = 1.42 ± 0.77, median = 1.35, n = 102) (see Supplementary Tables DR1–DR3).

Thus, the higher average Cu contents and V/Sc and Sr/Y ratios of the Neo-Tethyan suite indicate higher magmatic oxidation states and water contents, and suggest greater fertility for the formation of porphyry Cu deposits compared with the Paleo-Tethyan suite.

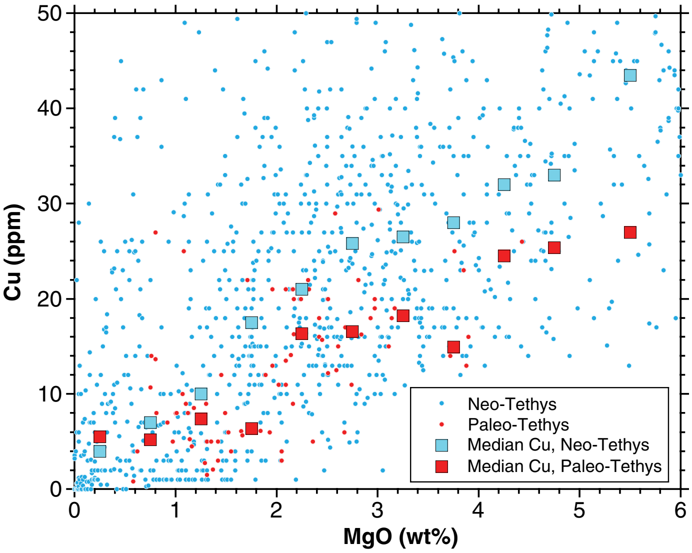

Figure 4. Cu versus MgO in Paleo-Tethyan and Neo-Tethyan igneous rocks; median values are used to highlight the data trends [sources of data: GEOROC database (Geochemistry of Rocks of the Oceans and Continents; http://georoc.mpch-mainz.gwdg.de); Hess et al., 1995; Lemaire et al., 1997; Roger et al., 2003; Zhang et al., 2006a, 2006b, 2007; Cai et al., 2009, 2010; Dokuz et al., 2010; Karimpour et al., 2010; Yang et al., 2011, 2014; Mirnejad et al., 2013; de Sigoyer et al., 2014; Zhang et al., 2014; Xia et al., 2015; Zhang et al., 2016; Dai et al., 2017].

DISCUSSION AND CONCLUSIONS

Because porphyry Cu deposits require relatively oxidized, hydrous magmas to form, it has been proposed that their almost exclusive global restriction to Phanerozoic arc rocks reflects the delay of deep ocean oxidation, and therefore oxidative seafloor alteration and subduction zone metasomatism, until after the Neoproterozoic oxygenation event (Evans and Tomkins, 2011; Richards and Mumin, 2013). However, extensive periods of deep ocean anoxia have occurred during the Phanerozoic; one of the best documented cases is the Paleo-Tethyan ocean basin. Published data for igneous rocks formed in response to Paleo-Tethyan subduction suggest more reduced arc magmatic conditions and lower fertility for porphyry Cu formation, compared to the more typical, moderately oxidized conditions attending subduction of the Neo-Tethyan ocean basin, which resulted in widespread ore formation. Thus, the prospectivity of arc systems may reflect, as a primary control, the oxidation state of the subducted oceanic lithosphere: regions where reduced seafloor materials were subducted for extensive periods of time are unlikely to generate fertile arc magmatic systems. Elsewhere, secondary reduction of otherwise oxidized arc magmas may occur during ascent through crust containing reduced lithologies, resulting in early voluminous sulfide saturation and deep crustal loss of chalcophile metals, rendering the magmas infertile for later porphyry Cu formation (Tomkins et al., 2012; Hou et al., 2015).

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[1] GSA Data Repository item 2017195, Tables DR1–DR3 (supplemental data and summary statistics), is available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.

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