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

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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 [AFMQ+1 to +2, where A FMQ (fayalite-magnetite-quartz) is the log fO2 (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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The deposition of thick sequences of reduced seafloor sediments 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 magmas, and the lack of economic porphyry Cu deposits associated with Neo-Tethyan 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.

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Anoxia eventually extended into shallow waters, causing bryozoan extinction on continental shelves starting in the Capitanian (Fig. 3, columns 5–15; Powers and Botterj, 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 (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 Repository1.)

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.

Magramatic 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% SiO2). 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/Eu*)/Yb > 2 at 58–70 wt% SiO₂ [where Eu* = (Smn × Gd)/[(Smn × Gd)]. 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/Eu*)/Yb 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.

**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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1GSA 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.
