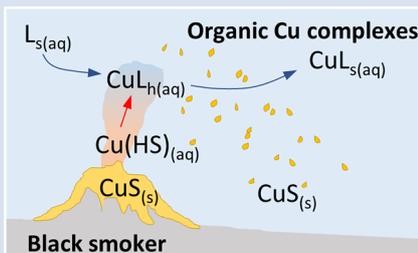


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Abstract



probably close to the modern range, even if the residence time of Cu in seawater was shorter than today. Biological Cu limitation was thus probably lifted in the Proterozoic, but the origin of Cu toxicity for cyanobacteria likely emerged in the Archean. The results provide a new interpretive framework for geochemical records.

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Introduction

Transition metals have long been recognised as essential for numerous cellular functions and metabolic pathways. The course of biological evolution from the Archean to the modern may therefore in part have been driven by the bioavailability of these elements in the early ocean. Earlier theoretical work (Saito *et al.*, 2003) suggested extremely low concentrations of Cu and Zn in the Archean and Proterozoic ocean, which triggered several hypotheses about metal-limited biogeochemical cycles. For example, Zn scarcity has been invoked to explain the late rise of eukaryotes, which have a high Zn demand (Dupont *et al.*, 2006), while Cu limitation has been proposed as a mechanism to build up high levels of N_2O in the Proterozoic atmosphere (Buick, 2007). However, recent studies of marine sedimentary rocks do not support Zn- and Cu-depleted oceans in the Precambrian (Scott *et al.*, 2012; Large *et al.*, 2014; Chi Fru *et al.*, 2016; Robbins *et al.*, 2016). To explain this discrepancy, some workers have suggested a stronger hydrothermal metal influx into the ocean (Scott *et al.*, 2012; Robbins *et al.*, 2013). This hypothesis would be consistent with independent evidence that hydrothermal activity was elevated in the early Precambrian compared to today (Viehmann *et al.*, 2015). Indeed, modern hydrothermal vents can disperse metals widely into the open ocean and enhance biological productivity in surface waters (*e.g.*, Fitzsimmons *et al.*, 2014). However, whether this hydrothermal metal flux could have persisted in the Precambrian remains elusive.

To address this knowledge gap, this study explores the role of organic ligands in stabilising hydrothermally sourced Cu in Precambrian seawater. Copper is chosen as a focus, because thermodynamic data are available to model Cu speciation in hydrothermal fluids. Using those data, Sander and Koschinsky (2011) showed that modern hydrothermal vents contribute 5–14 % of the ocean's Cu budget in the form of organic complexes. Here the thermodynamic model is adapted to Precambrian seawater conditions, and subsequently paired with a box model that combines the hydrothermal Cu flux with the riverine flux and the residence of Cu in seawater to derive a global average Cu concentration through time (see Supplementary Information for methods). In brief, the thermodynamic model simulates mixing between a Cu-rich hydrothermal fluid at 300 °C and Cu-depleted seawater at 4 °C up to a ratio of 1:1000 and allows Cu minerals to precipitate. Organic ligands are included in the hydrothermal fluid (L_{h^+}) and in seawater (L_{s^+}) with empirically-determined stability constants of 10^{-14} for Cu ligand complexes in both fluids (Sander and Koschinsky, 2011). These constants are assumed to be applicable for the Precambrian models as well. The Cu concentration remaining in solution after precipitation has ceased is then entered into the box model as an input parameter for the hydrothermal Cu source to the ocean. The riverine source is taken from the literature. Both Archean and Proterozoic seawater are modelled as ferruginous (anoxic with 100 μM of free Fe^{2+}) (Holland, 1984), but the Archean is defined by having very low concentrations of SO_4^{2-} (20 μM) and minor amounts of dissolved H_2 (Claire *et al.*, 2006) while the Proterozoic is modelled with 3 mM of SO_4^{2-} in

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the absence of H₂ gas. Sensitivity tests on these parameters are described in the [Supplementary Information](#).

Results

For the modern ocean, the model produced marine Cu concentrations of 2.7–3.4 nM (Fig. 1a), in good agreement with observations of 1–3 nM in the Pacific Ocean (Whitby *et al.*, 2018). Hydrothermal fluids contributed 2–20 % of the total Cu (for L_h of 1–10 μM), similar to the 5–14 % found by Sander and Koschinsky (2011). At the 1000:1 mixing ratio, the concentration of ligand-bound Cu (CuL_h⁺ and CuL_s⁺) was of the order of a few nM, while that of free Cu²⁺ was 10⁻¹³ to 10⁻¹⁵ M (Fig. 2), which agrees with measurements from modern seawater (Vraspir and Butler, 2009). The concentration of Cu bound to the seawater ligand (CuL_s⁺) increased from 0.2 nM to 7 nM at the 1000:1 mixing ratio as the concentration of the hydrothermal ligand L_h⁺ was raised from 0 to 10 μM (Fig. 2), although L_s⁺ in seawater stayed constant at 10 nM. This result implies that the hydrothermal ligand prevents some hydrothermally-sourced Cu from precipitating and later passes that Cu on to the seawater ligand as the latter becomes more abundant and thus thermodynamically favourable. Hydrothermal ligands are thus important for

transporting Cu into the ocean. Major precipitates in the modern ocean scenario included chalcocite and ferrite-Cu (Fig. S-2).

In the Archean ocean scenario, even the highest amounts of modern observed ligand concentrations had very little effect on raising total marine Cu concentrations at high mixing ratios with seawater (Cu_T; Fig. 1e). Most Cu was lost by the precipitation of Cu sulfides proximal to the vent. The modelled Cu_T concentration was thus always several orders of magnitude below 1 nM. Values closer to the modern range could be obtained if the temperature of seawater was raised to around 50 °C (Fig. 1f), or if the concentration of L_s⁺ was increased drastically to 1000 μM and the residence time of Cu_T in the ocean was extended to >100,000 yr (Fig. S-7). Increasing L_h⁺ did not have nearly the same effect as increasing L_s⁺ (not shown). In any case, the riverine Cu contribution was less than a few percent (Fig. 1e).

In the Proterozoic, modelled Cu_T levels with the maximum modern ligand load (10 μM L_h⁺ and 10 nM L_s⁺) were still lower than in the modern, but several orders of magnitude above the Archean. The riverine contribution far outweighed the hydrothermal input (Fig. 1c). Similar to the Archean, high concentrations of L_s⁺ were needed to establish high marine Cu_T levels similar to the modern. Importantly, lowering the residence time of Cu_T in seawater, as predicted by the expansion of euxinic

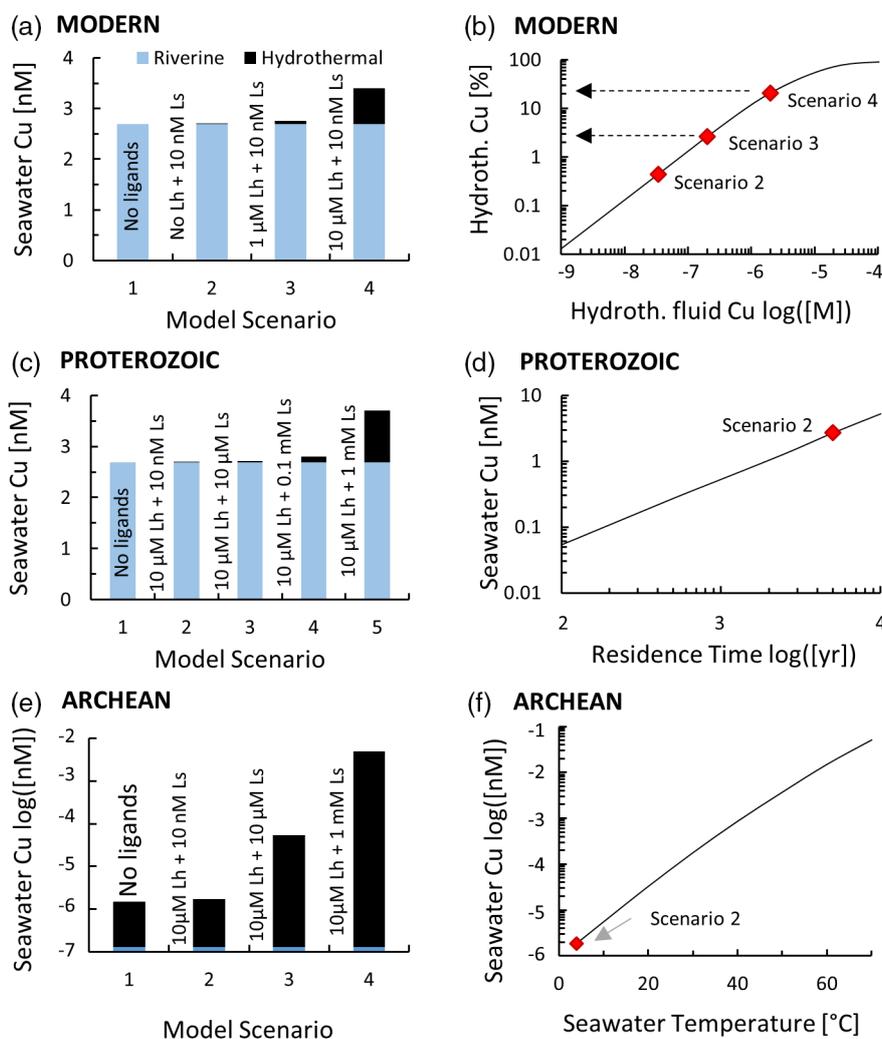


Figure 1 Total Cu concentration in seawater for different model scenarios. (a) Modern ocean. (b) Fraction of hydrothermal Cu contribution to total marine Cu budget in the modern ocean. Scenarios 3 and 4 are deemed the most realistic according to previous work (Sander and Koschinsky, 2011). (c) Proterozoic ocean. (d) Effect of the seawater residence time on Cu_T for scenario 2 in the Proterozoic (panel c). (e) Archean ocean. (f) Effect of seawater temperature on Cu_T for scenario 2 in the Archean (panel e).



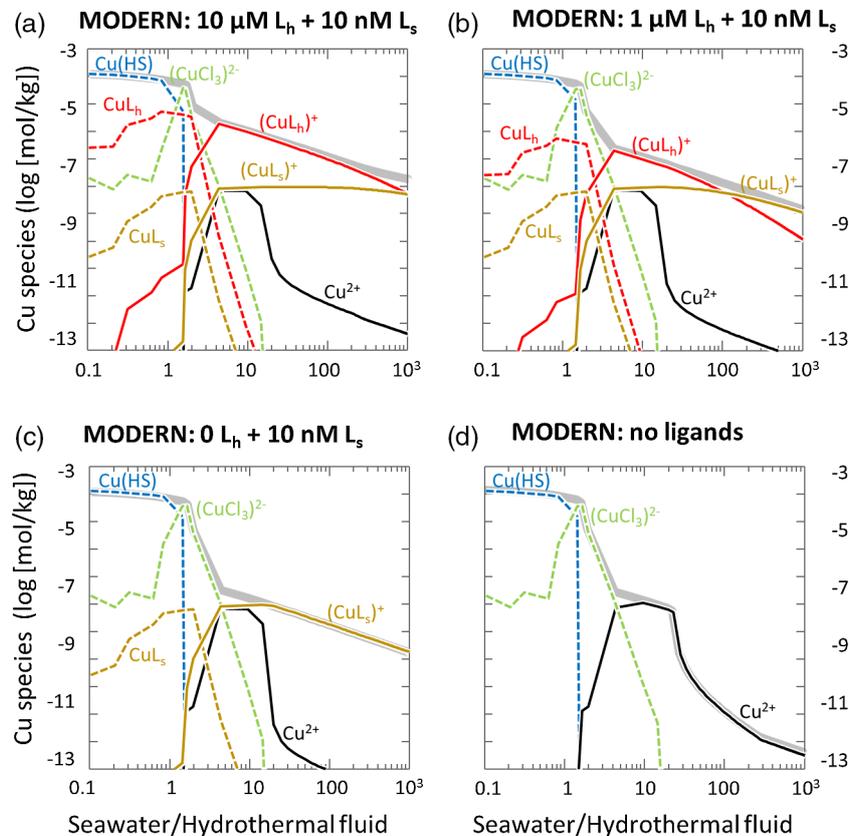


Figure 2 Dissolved copper speciation during mixing between hydrothermal fluid and seawater in the modern ocean under four different model scenarios (see Fig. 1). Note that seawater has an initial Cu_T concentration of zero; the seawater concentration shown in Figure 1 is calculated after combining the hydrothermal mixing model with the ocean box model (Fig. S-1). Solid lines = Cu^{2+} species, dashed lines = Cu^+ species. The x axis shows the mixing ratio of seawater to hydrothermal fluid. Thick solid grey line = Cu_T .

waters along Proterozoic ocean margins (Lyons *et al.*, 2014), did not push Cu_T levels far out of the modern range (Fig. 1d). Sensitivity tests of differing Fe or SO_4^{2-} concentrations within plausible bounds made no significant difference to the overall conclusions (Tables S-2, S-3).

Discussion

In the Archean, only high seawater temperatures (Fig. 1f) or unusually high concentrations of organic ligands in seawater paired with a much longer seawater residence time of Cu_T may have been able to push Cu_T concentrations closer to modern values. It is conceivable that the amount of suspended organic matter in seawater was indeed higher in the Precambrian, prior to the rise of filter feeding metazoans and complex algae (Lenton *et al.*, 2014). For example, a microbially-dominated anoxic lake in Antarctica, which lacks significant input of eukaryotic biomass, reaches DOC levels up to 2000 μM (McKnight *et al.*, 1991). If a high proportion of the organic matter was Cu-binding, it may thus have increased the residence time and concentration of Cu_T in seawater, which may explain the nearly constant Cu levels in sedimentary rocks through time (Large *et al.*, 2014; Chi Fru *et al.*, 2016). Alternatively, the unexpectedly high Archean Cu enrichments in rocks may reflect higher seawater temperatures (Tartèse *et al.*, 2017), which would have raised the solubility of Cu sulfide minerals.

Throughout the Archean, hydrothermal vents were the major source of Cu to the ocean, because the riverine flux was low in the absence of oxidative weathering (Hao *et al.*, 2017). Interestingly, previous workers have pointed out that several

prebiotic reactions may have occurred in hydrothermal settings because of the abundance of catalytic metals (Martin *et al.*, 2008). The results from this study suggest that Cu_T concentrations were closest to modern values proximal to hydrothermal vents where the mixing ratio of seawater to vent fluid was lower (Fig. 3). Hence the model supports the view that the origin of metalloenzymes occurred proximal to hydrothermal environments. At the same time, the dispersal of ligand-bound Cu into the global ocean from hydrothermal point sources may be consistent with the idea that prebiotic hydrothermal products may have undergone further modification and evolution in other environmental niches (Stüeken *et al.*, 2013).

With the onset of oxidative sulfide weathering in the Proterozoic (the most probable Cu source to rivers), Cu_T levels were probably within 1–2 orders of magnitude of modern concentrations (Fig. 1d). Throughout the Proterozoic (Fig. 3c,d) and the modern (Fig. 2), and possibly earlier (Fig. 3b), Cu_T was largely organic-bound, which would explain the difference between these new results and earlier predictions (Saito *et al.*, 2003). Unlike in the Archean, rivers largely controlled the marine Cu_T budget of the Proterozoic, but it is important to note that riverine Cu would also have needed to be ligand-bound to be stable in the Proterozoic ocean, as suggested by the seawater end member composition of the thermodynamic model (Fig. 3) and consistent with observations from modern rivers where Cu is overwhelmingly organic-bound (Hoffmann *et al.*, 2007). Ligand-bound Cu can be bioavailable (Zhao *et al.*, 2016), making it unlikely that Cu was bio-limiting in the Proterozoic and that Cu limitation caused large scale production of N_2O gas (Buick, 2007). On the other hand, Cu toxicity to cyanobacteria may

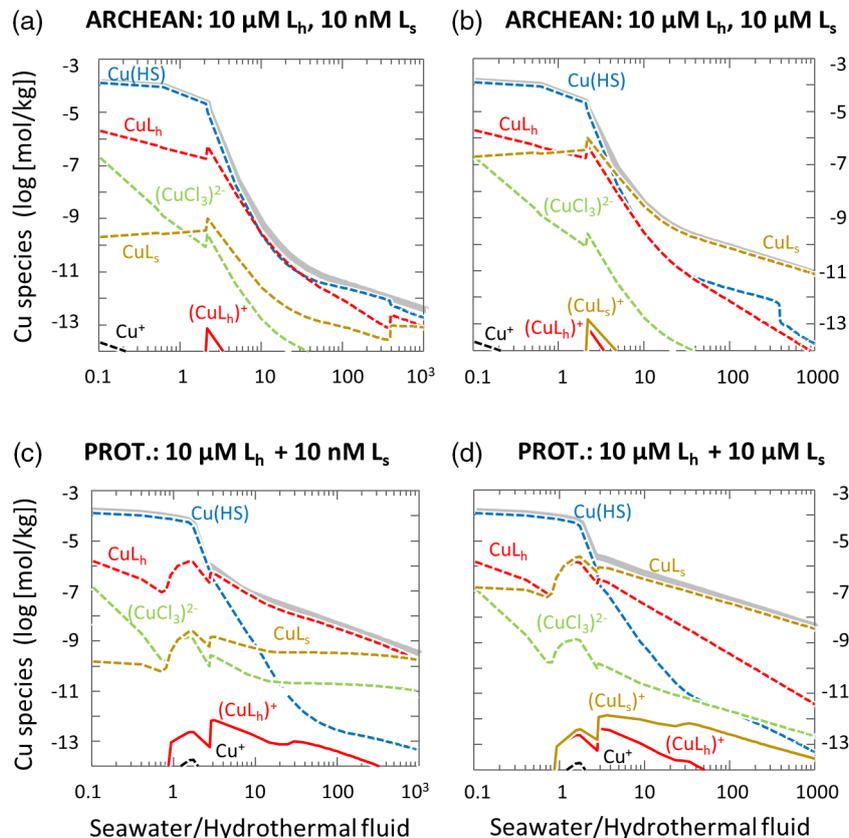


Figure 3 Dissolved copper speciation in the Archean (a, b) and Proterozoic (c, d) during mixing between hydrothermal fluid and seawater, showing two different model scenarios for each time bin. As for Figure 2, seawater Cu_T is set to zero in these simulations and then calculated with the ocean box model in a separate step (Fig. S-1). Colour code and symbols as in Figure 2. In the absence of ligands, aqueous $Cu(HS)$ is the dominant species in both the Archean and Proterozoic ocean (not plotted). Thick solid grey line = Cu_T .

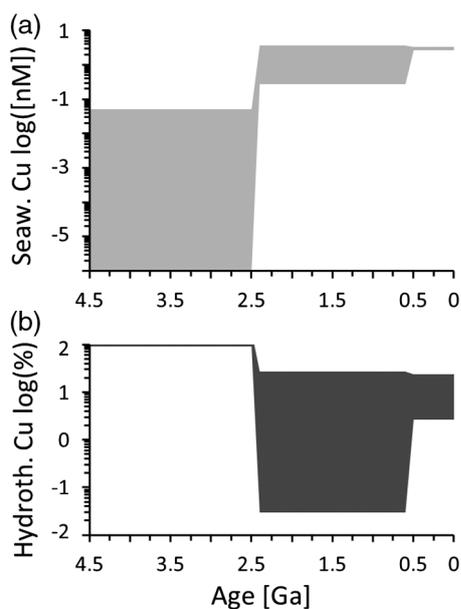


Figure 4 Compilation of (a) the total marine Cu concentration and (b) the hydrothermal contribution to the marine Cu budget through time. For the Archean, the lower bound is scenario 2 in Figure 1e; the upper bound corresponds to scenario 4 in Figure 1e with a 10-fold longer residence time (Fig. S-7). For the Proterozoic, the lower bound is scenario 2 in Figure 1c with a 10-fold shorter residence time (Fig. 1d) while the upper bound corresponds to scenario 5 in Figure 1c with a modern residence time.

have arisen earlier than previously thought. It has been shown that free Cu^{2+} concentrations around 10^{-11} M can negatively impact both CO_2 and N_2 fixation (Rueter and Petersen, 1987). This Cu sensitivity may be an artifact of a relatively Cu-free setting during the origin of cyanobacteria. If so, then the model of this study would support the idea that cyanobacteria originated in the Archean (Lyons et al., 2014), prior to the expansion of the marine Cu_T budget.

Conclusion

Our understanding of Precambrian ocean chemistry has evolved since the original study by Saito et al. (2003) that predicted severe Cu limitation in the Archean and Proterozoic due to rapid scavenging of Cu by free H_2S . It is now evident that such H_2S -rich conditions were spatially limited in the early oceans (Lyons et al., 2014), warranting a new model of Cu_T solubility. The results presented here support the inference that Archean Cu_T levels were probably lower than today (Fig. 4a), unless seawater was warmer or the abundance of organic ligands was markedly higher. Near modern levels of Cu_T were likely reached in the Proterozoic with the onset of oxidative weathering, despite a potentially shorter residence time in the ocean. In the Archean, hydrothermal vents constituted the major source of Cu (Fig. 4b), which provides additional credence to the idea that key prebiotic processes involving the origin of metalloenzymes occurred in hydrothermal settings. From the Proterozoic onwards, and perhaps earlier, the vast majority of Cu_T in seawater has been stabilised by organic ligands, which thus probably lifted Cu limitations for the evolving biosphere. While the model presented in this study



focused on Cu only, it is predicted that similar mechanisms would apply for Zn and perhaps other base metals.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2037>.



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