Tracking the Mesoproterozoic Ocean anoxia: Inferences from Mo isotopic study of black shales from Cuddapah Basin, India

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Introduction

- The boring-billion (~1.8 to 0.8 Ga) is known to be a period of biological stasis in Earth's history. Limited diversification of early life-forms (eukaryotes) during this period have been attributed to both adaptability and unfavorable environmental conditions.
- Available isotopic (Cr, Mo, U and S) studies of sedimentary records from this period indicate a well-stratified oceanic condition with widespread surface oxic layers, deep anoxic-ferruginous layers and the mid-depth euxinic layers in continental margins.
- **The objective of this study is to reconstruct the Mesoproterozoic oceanic redox state and its areal extent using geochemical and Mo isotopic compositions of black shales from the Cumbum Formation, Cuddapah Basin, India.**
- This work is part of our ongoing study to understand Proterozoic environments and the cause-effect linkage between oceanic oxygenation and development of life.

Sampling Details

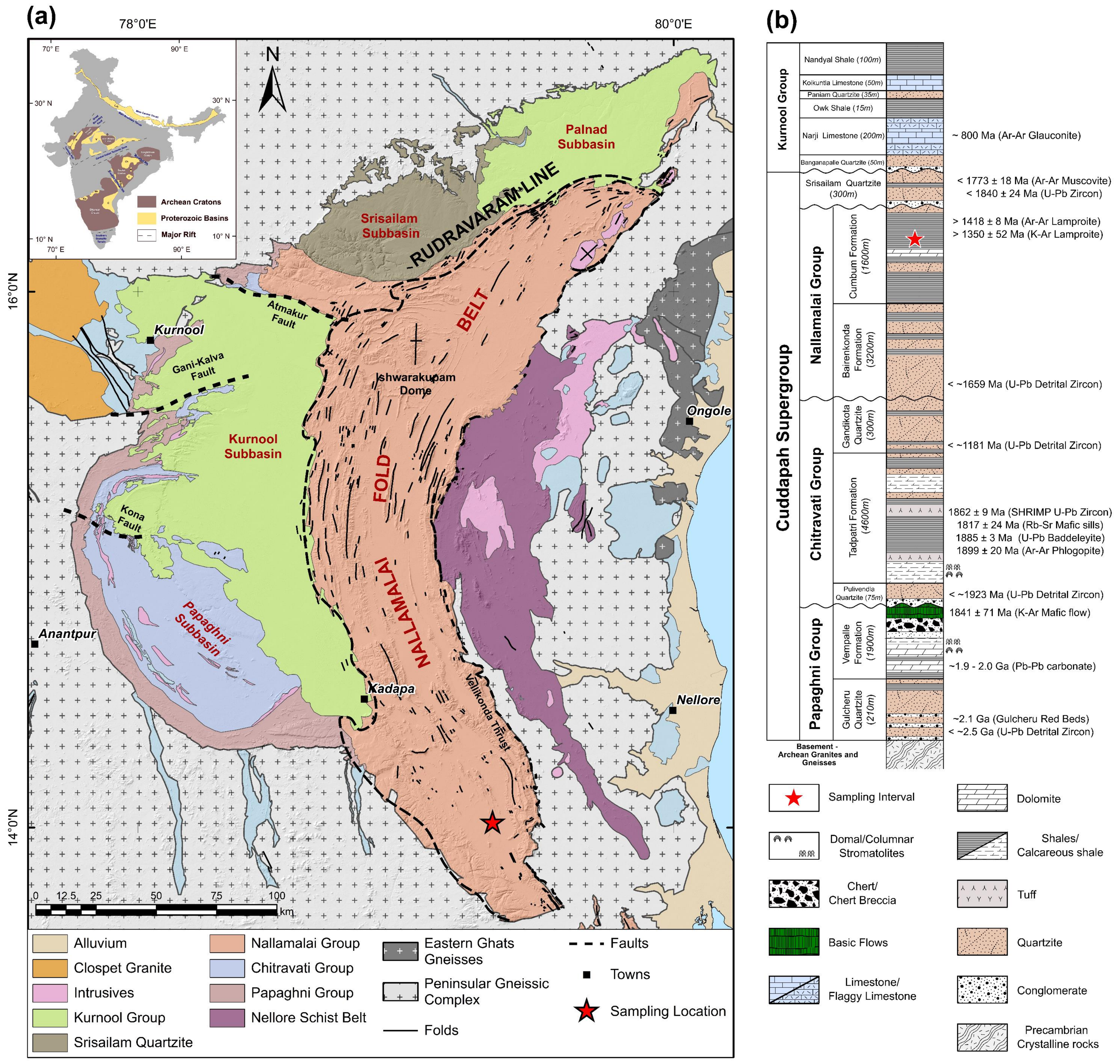

Fig. 1. (a) Geological map and (b) generalized stratigraphic succession of the Cuddapah Basin showing the sampling location (Ref. [3]; [4]; Geochronological data has been taken from multiple sources).

- Fresh black shale samples were collected from an ongoing mine section at Mangampeta, Andhra Pradesh, India (Fig. 1).
- These samples belong to the Cumbum Formation, Nallamalai Group of the Cuddapah Supergroup which is expected to have a depositional age of ~1.5 Ga [1].
- The shale sequence is interpreted to have deposited in a subtidal to peritidal environment within a marginal restricted cratonic basin connected to the open ocean [2].

Analytical Methods

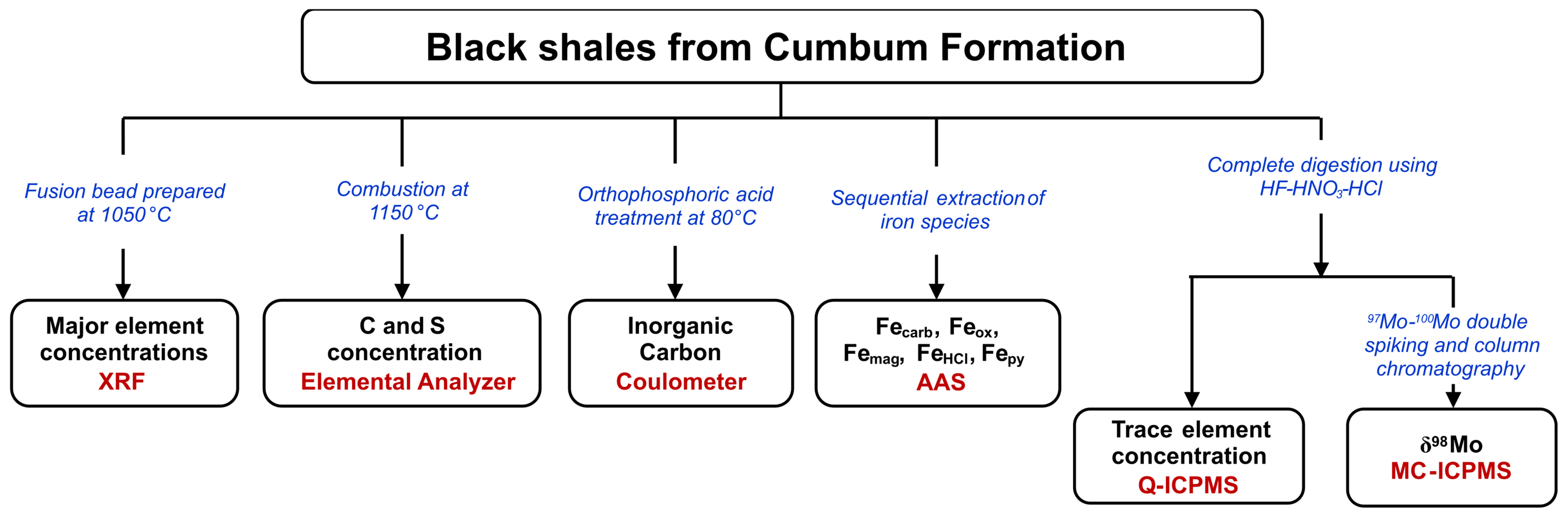

Fig. 2. Schematic diagram showing the analytical methodology followed.

Results

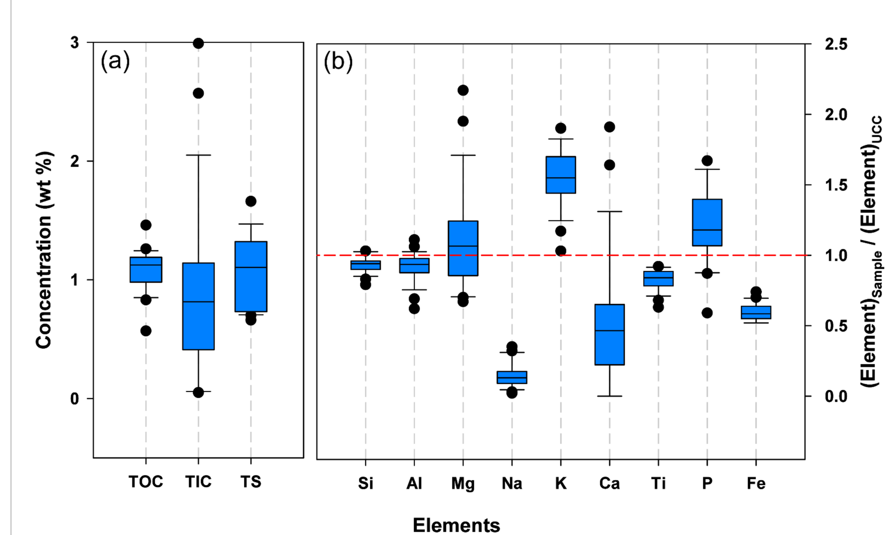

Fig. 3. Box plot showing (a) concentrations and (b) UCC-normalized elemental ratios of major elements.

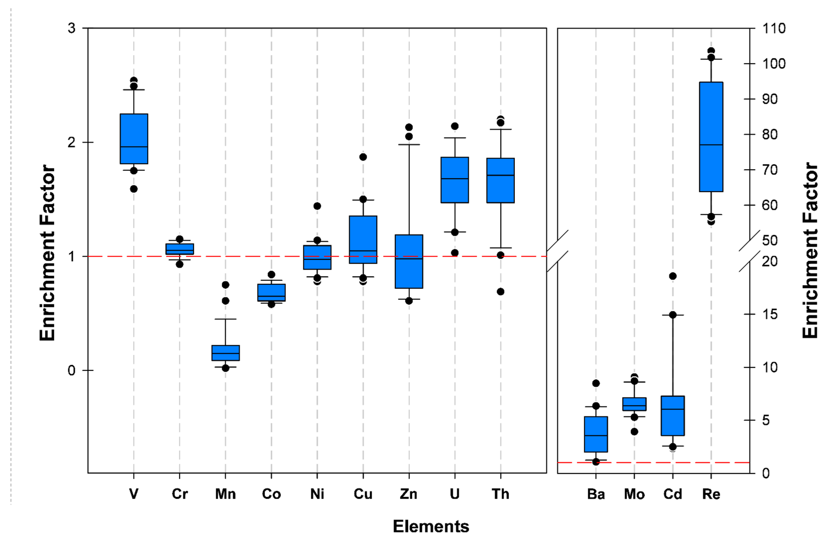

Fig. 4. Enrichment factors of selected trace elements.

Local redox settings and basin hydrography

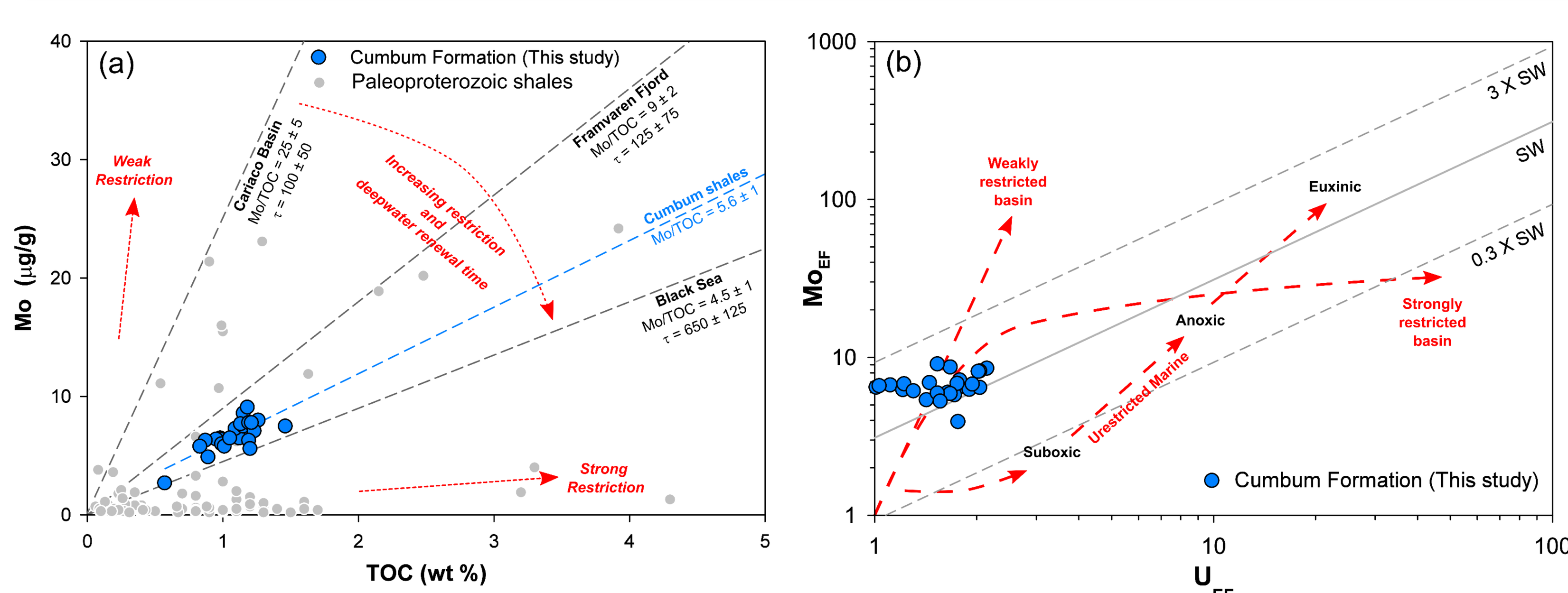

Fig. 5. Co-variation between (a) Mo and TOC (b) Mo_{EF} and U_{EF} . Sediment [Mo]/[TOC] ($\times 10^{-4}$) and deep water renewal time (in years) of modern silled basins are shown [5].

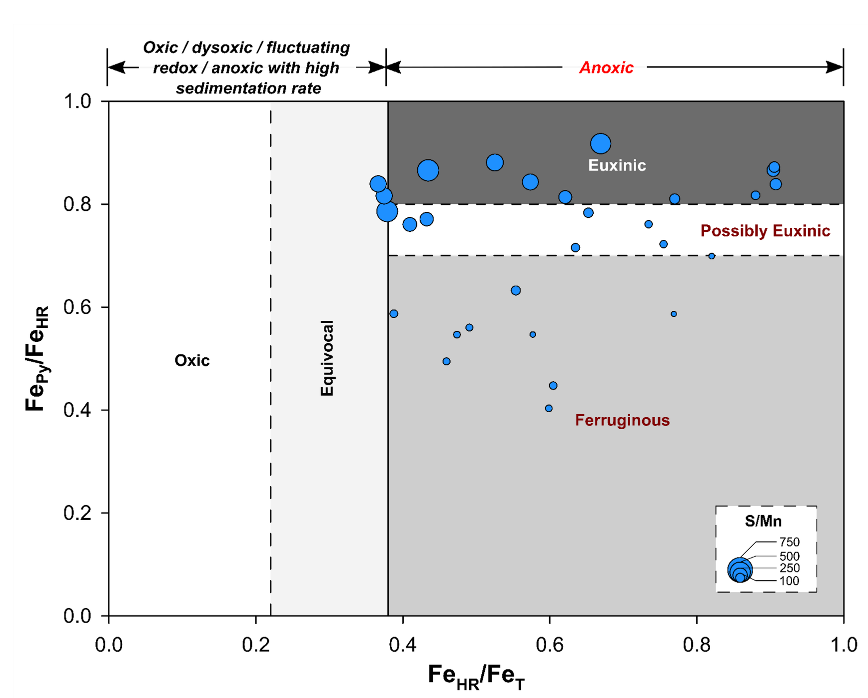

Fig. 6. Constraining redox state using iron speciation parameters [6].

- Similarities between the average Mo/TOC values (~5.6) and Mo/U ratio (~4.6) of these samples with modern restricted basins suggest limited Mo inventory and open ocean connectivity of the basin (Fig. 5a and b).
- The Iron speciation (Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR}) data indicate that these shales were deposited in an anoxic basin where deep water conditions fluctuated between ferruginous and euxinic conditions (Fig. 6).

Quantifying global euxinia at ~1.5 Ga using Mo isotopes

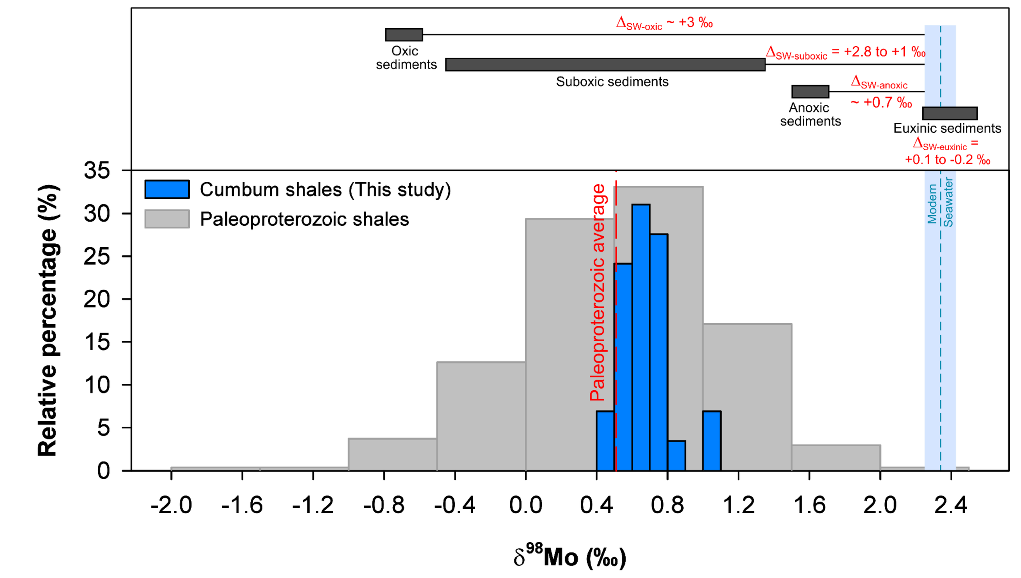

Fig. 7. Frequency distribution of $\delta^{98}Mo$ values of Cumbum shales and other global sections [7]. Expected Mo isotopic fractionation factors in modern sedimentary systems are also depicted [8].

- Molybdenum isotopic signatures from euxinic sedimentary successions have been successfully used to provide constrains on past global redox state and their areal extents [9].
- Our previous effort provides evidence for enhanced Mo removal and sulfidic areal extent (~4 times modern values) during the Pc-C transition [10].
- For the Cumbum shales, a three-sink Mo isotopic mass balance modelling shows that euxinic pathways comprised ~61% of the oceanic Mo sink during this time.
- Areal extent calculations suggest that ~12% of global seafloor were overlain by euxinic waters, which is two orders of magnitude higher than the modern-day sulfidic area.

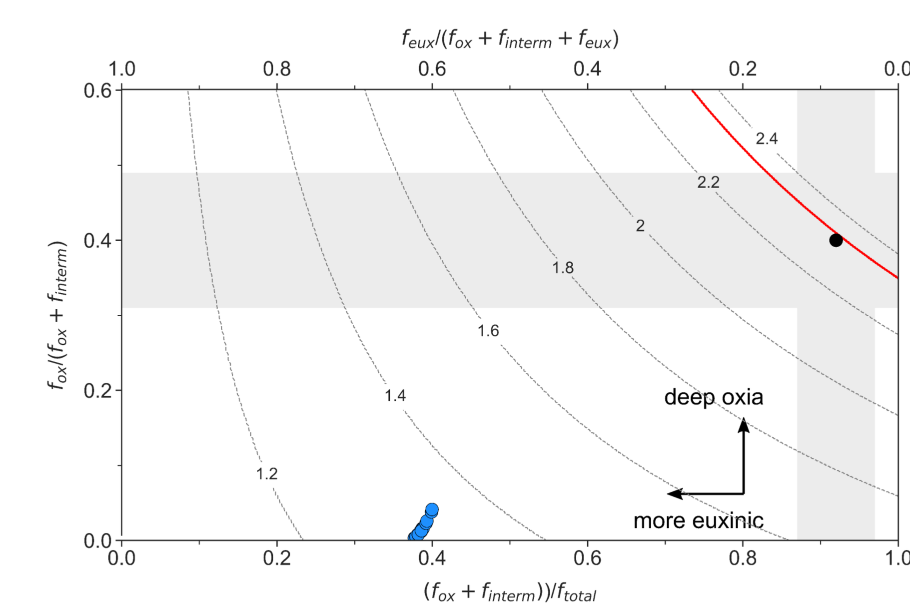

Fig. 8. Model results showing relative Mo flux to oxic, intermediate, and euxinic sinks assuming a steady state condition. Contour lines in the diagram represent theoretical values for different seawater $\delta^{98}Mo$ values.

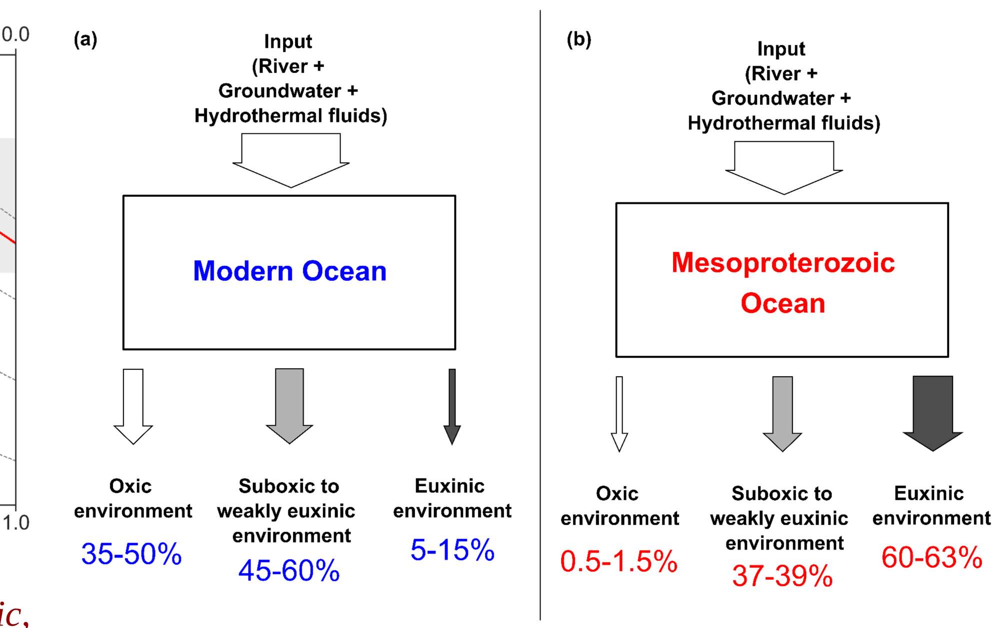

Fig. 9. Schematic diagram of the (a) modern [9] and (b) Mesoproterozoic Mo cycle [This study]

Conclusions

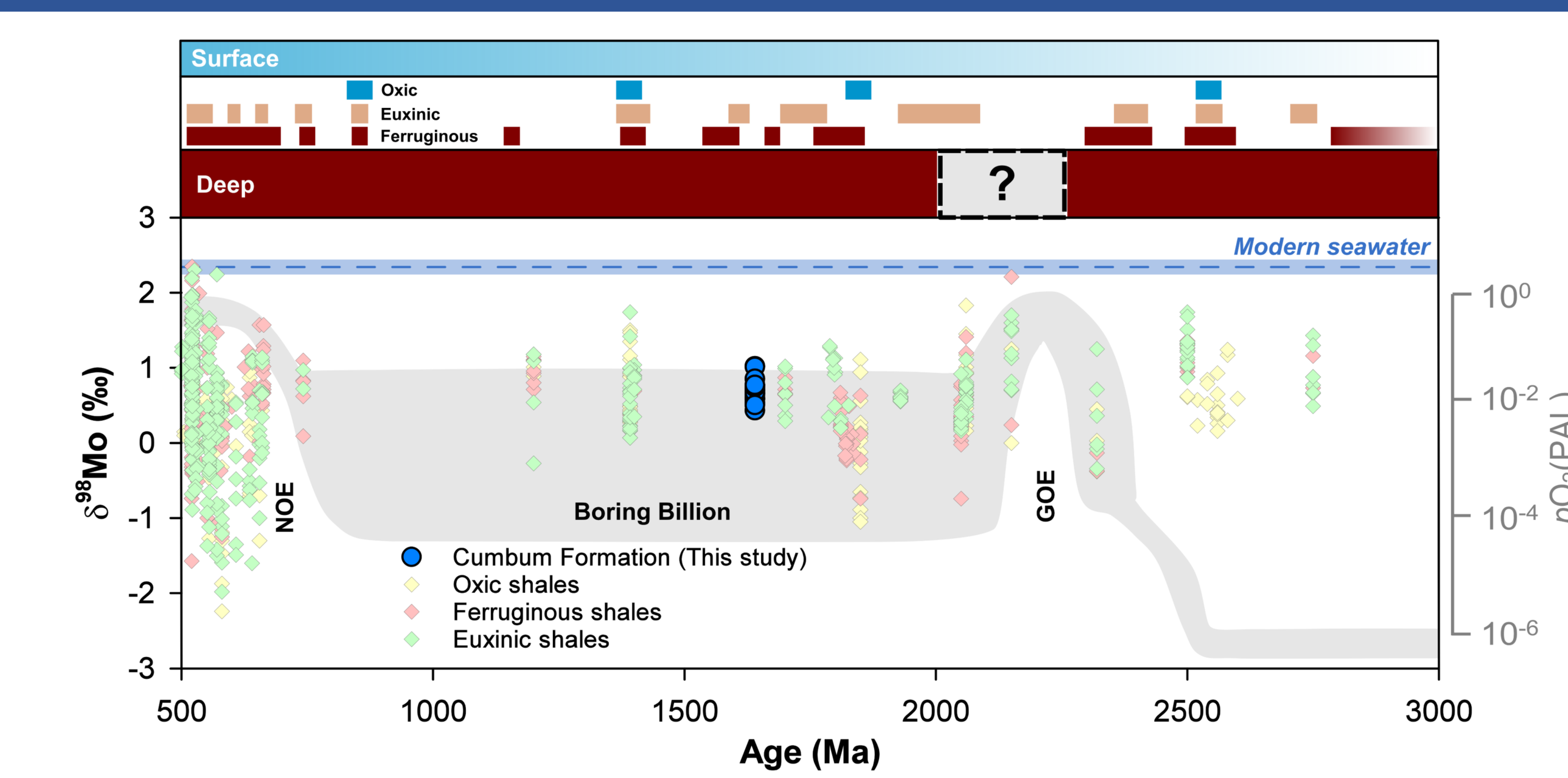

Fig.10. Temporal trends in $\delta^{98}Mo$ composition across geological time. Current understanding of the atmospheric oxygenation trend [11] and global ocean redox [12] are also shown.

- Trace element and Fe-speciation data suggest that the Cumbum shale deposition occurred within an anoxic (ferruginous to euxinic) basin.
- Mo isotopic balance modelling supports expansive euxinia in the global oceans, which would have reduced the availability of bio-essential elements and affected the primary productivity during the Mesoproterozoic Era.
- Further studies encompassing shallow to deep depositional environments from other sedimentary successions can provide more insights into Mesoproterozoic environments and their control on eukaryotic evolution.

Sharing not permitted

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Homepage

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