

# Sedimentary molybdenum and uranium sequestration in a non-euxinic coastal setting: role of the sulfate-methane transition zone

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## 1. INTRODUCTION

- Long-term paleo-redox records vital for mitigating global expansion of coastal hypoxia
- Molybdenum (Mo) and uranium (U) commonly used in sediment-based redox reconstructions (Algeo and Tribouillard, 2009; Bröske et al 2020)
  - Conservative behavior under oxic conditions
  - Uniform concentrations in the ocean due to long residence times (>0.5 Ma)
  - Conversion to particle-reactive species in specific redox zones (Fig. 1)

### RESEARCH QUESTIONS:

- Is this conceptual model (Fig. 1) applicable in eutrophic coastal settings?
- Are Mo and U viable paleo-redox proxies in such settings?

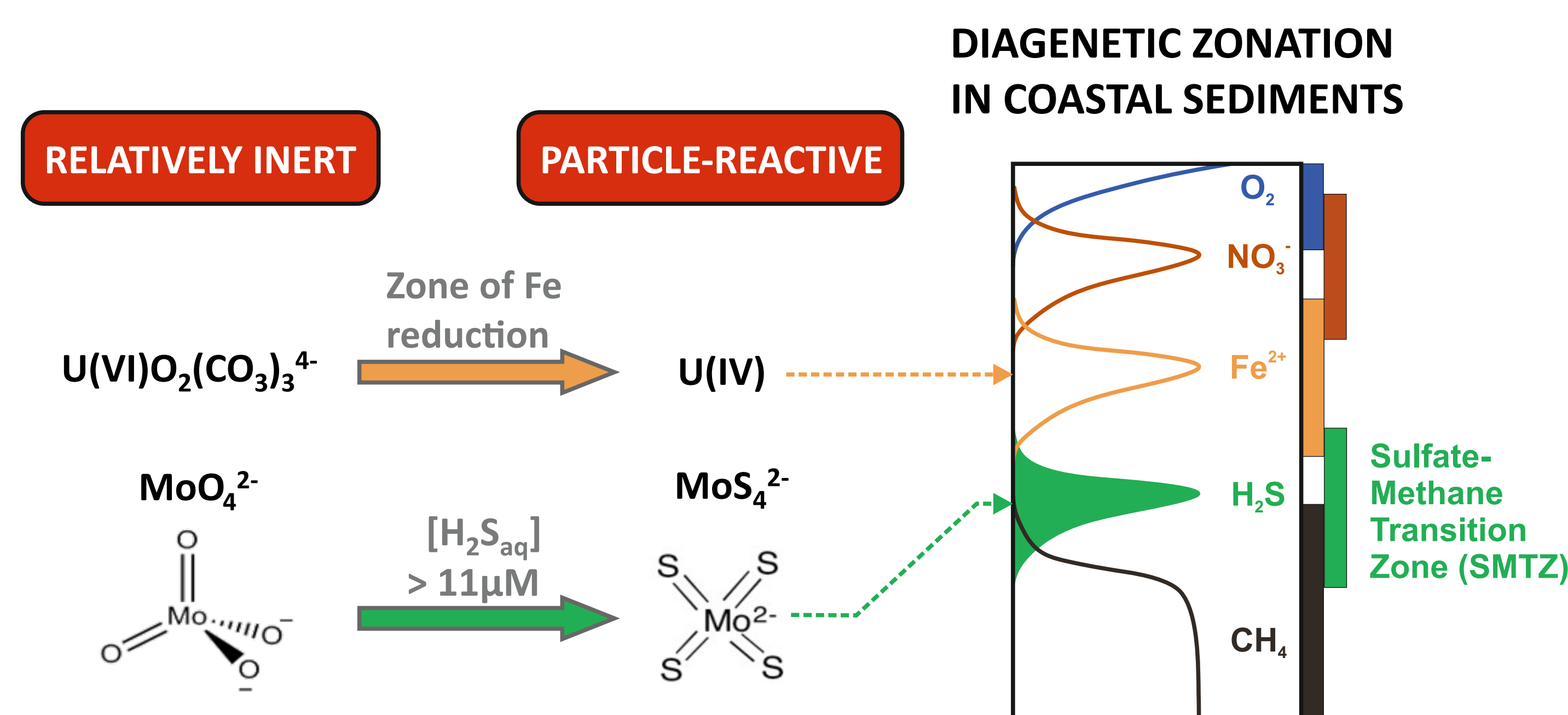


Fig. 1. Conversion of dissolved U and Mo to particle reactive forms during diagenesis in coastal sediments.

## 2. STUDY AREA

- Setting:** Eutrophied coastal area in the Gulf of Finland (Baltic Sea)
- Rationale:** Eutrophication has led to formation of a shallow SMTZ
  - Analogous to many other coastal areas on the trajectory towards hypoxia

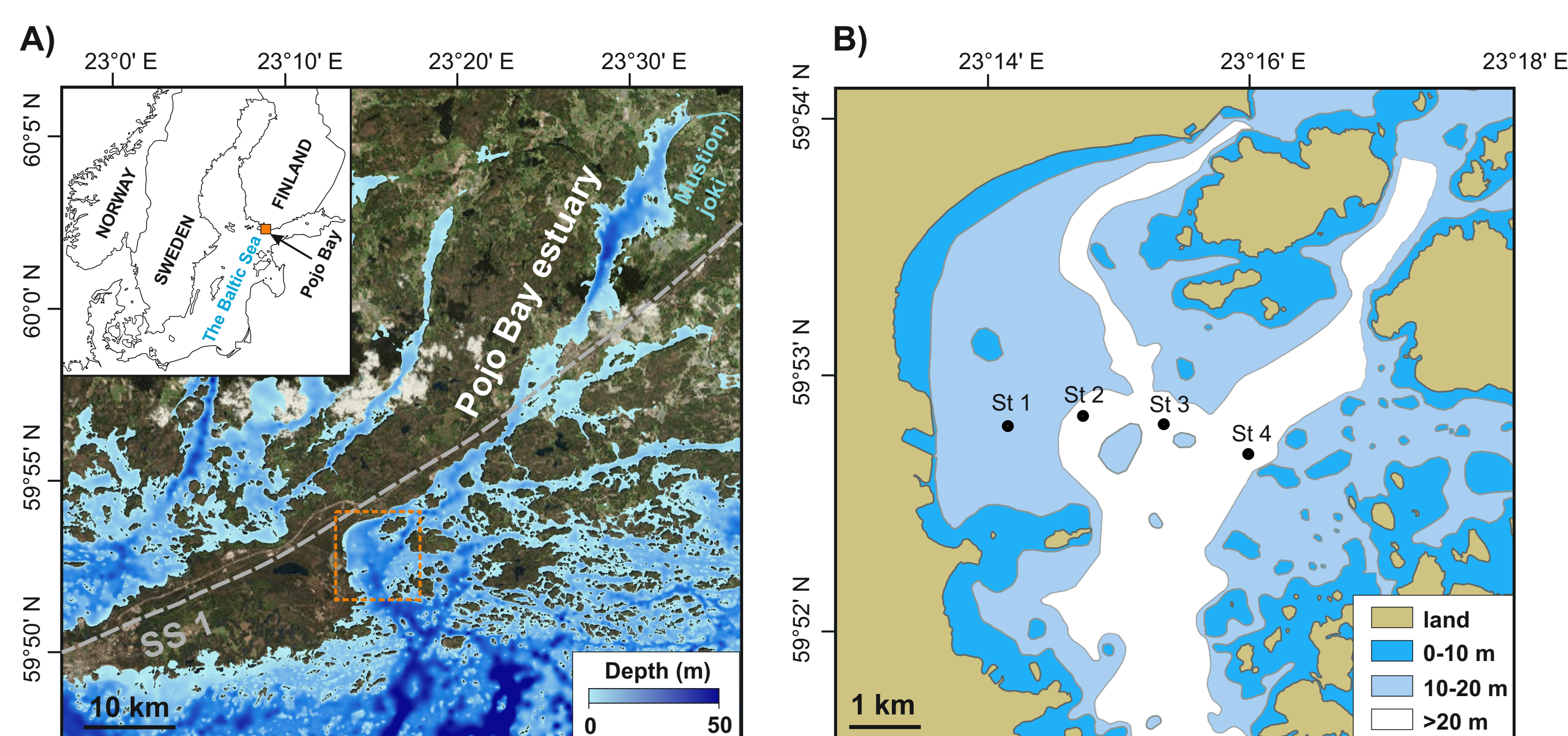


Fig. 2. (A) Bathymetric map of the coastal area adjacent to the Pojo Bay estuarine system. Orange rectangle indicates the study area (Storjärden). (B) Detailed bathymetric map of Storjärden with coring sites indicated.

## 3. MATERIALS AND METHODS

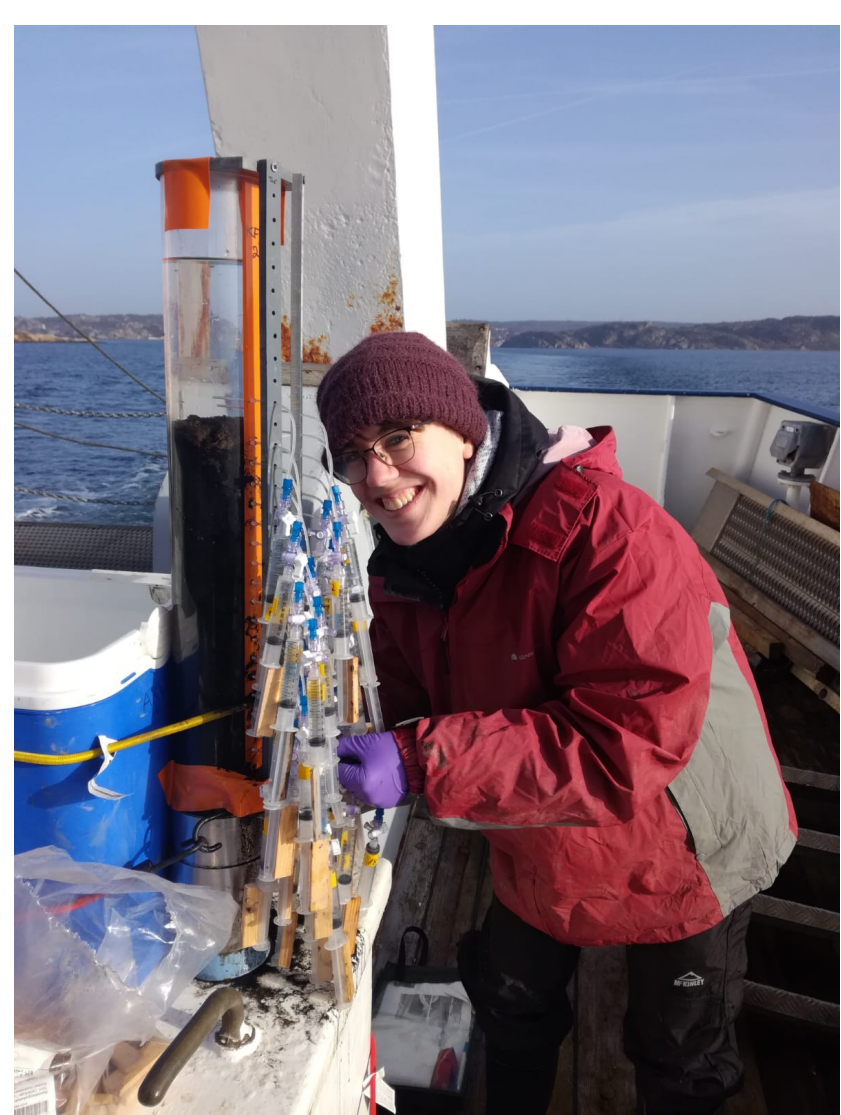


Fig. 3. Pore water sampling.

- Sediment cores from four stations**
  - Solid-phase + pore water samples
- Solid-phase analyses:**
  - Total contents of Mo and U + major constituents
  - Speciation of Mo and U (Sequential extraction)
- Pore water analyses**
  - Concentrations of Mo and U + major constituents
- Calculation**
  - Authigenic Mo and U ( $Me_{XS}$ ), Diffusive fluxes ( $F$ )

$$Me_{XS} = Me_{sample} - \frac{Me_{BG}}{Al_{BG}} \times Al_{sample} \quad F = -\phi D_{sed} \frac{dC}{dx}$$

## 4. RESULTS AND DISCUSSION

- Key feature:** Simultaneous sequestration of both Mo and U within the SMTZ at two specific fronts coupled to increases in pore water  $H_2S$  concentration (Fig. 4)
- Diffusive fluxes of Mo and U = Mass accumulation rates of authigenic Mo and U
  - Quasi-steady state
- Depletion of pore water Mo and U within the SMTZ
  - Sequestration limited by the diffusive flux to the SMTZ

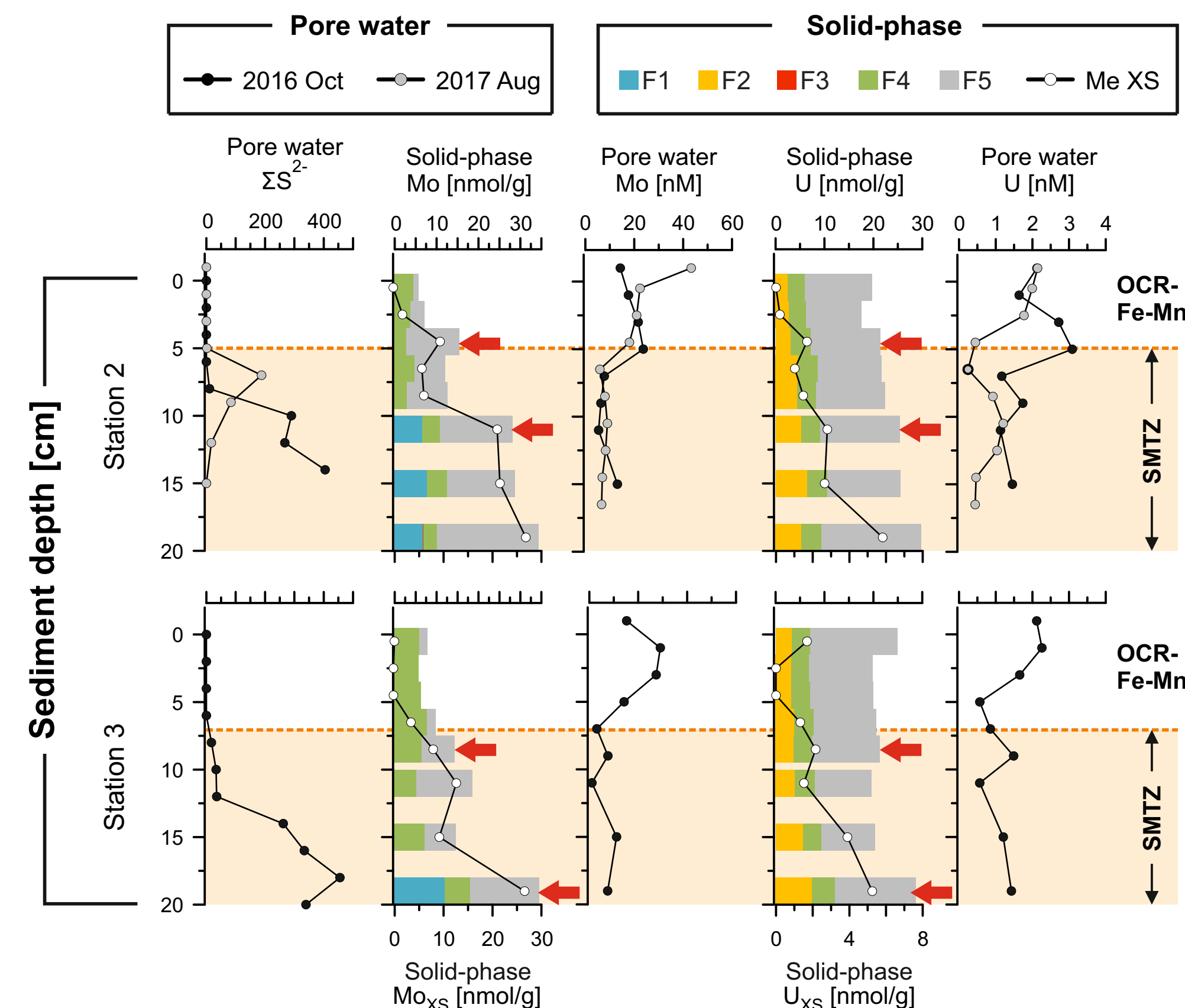


Fig. 2. Pore water and solid-phase profiles of Mo and U plotted alongside total dissolved sulfide ( $\Sigma S^{2-}$ ). Red arrows indicate zones of enhanced authigenic Mo and U sequestration.

### Authigenic Mo and U is largely hosted in stable phases:

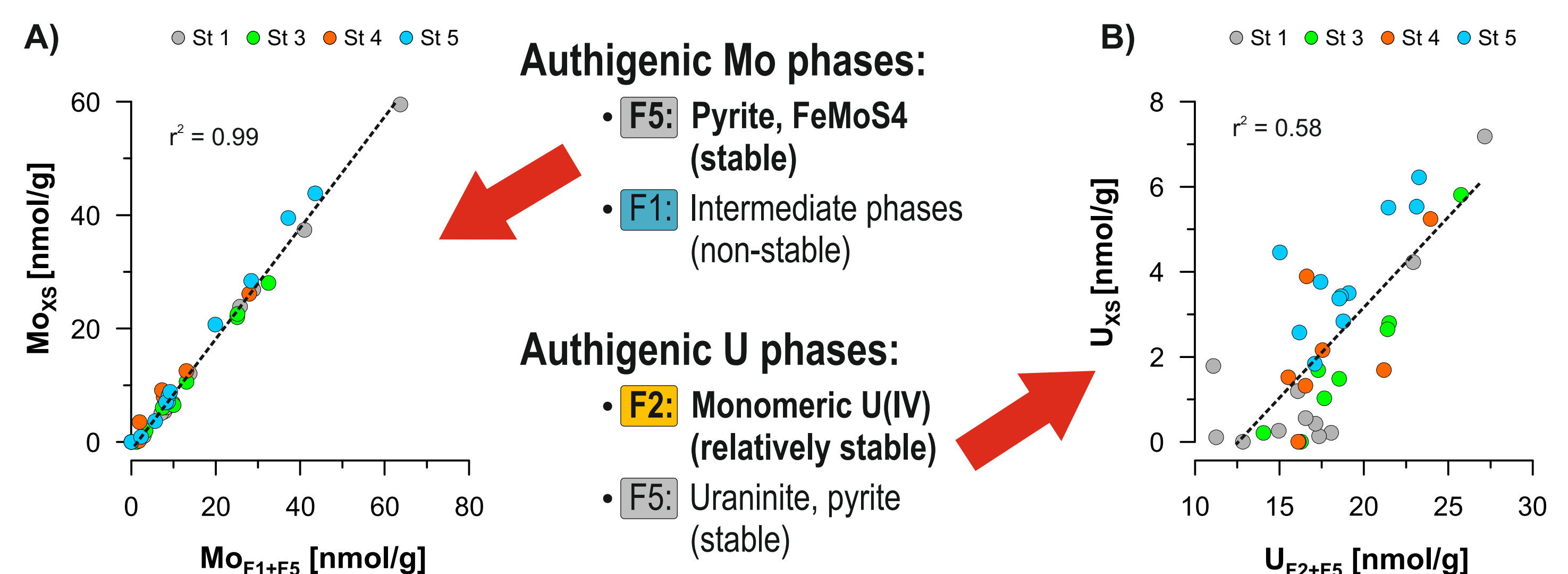


Fig. 5. (A) Cross-plot of authigenic Mo versus the sum of Mo in fractions F1 and F5. (B) Cross-plot of authigenic U versus the sum of U in fractions F2 and F5.

## 5. CONCLUSIONS

- Contrary to the existing theory, simultaneous uptake of Mo and U driven by  $H_2S$  levels
- Depth and intensity of the SMTZ control authigenic sequestration of both Mo and U
- Indirect link between bottom water oxygenation and Mo/U uptake + stable phases dominate the authigenic pools
  - Viable paleo-redox proxies (Mo more robust)
- Caveat:** Limited temporal resolution due to the superimposed character of the signal

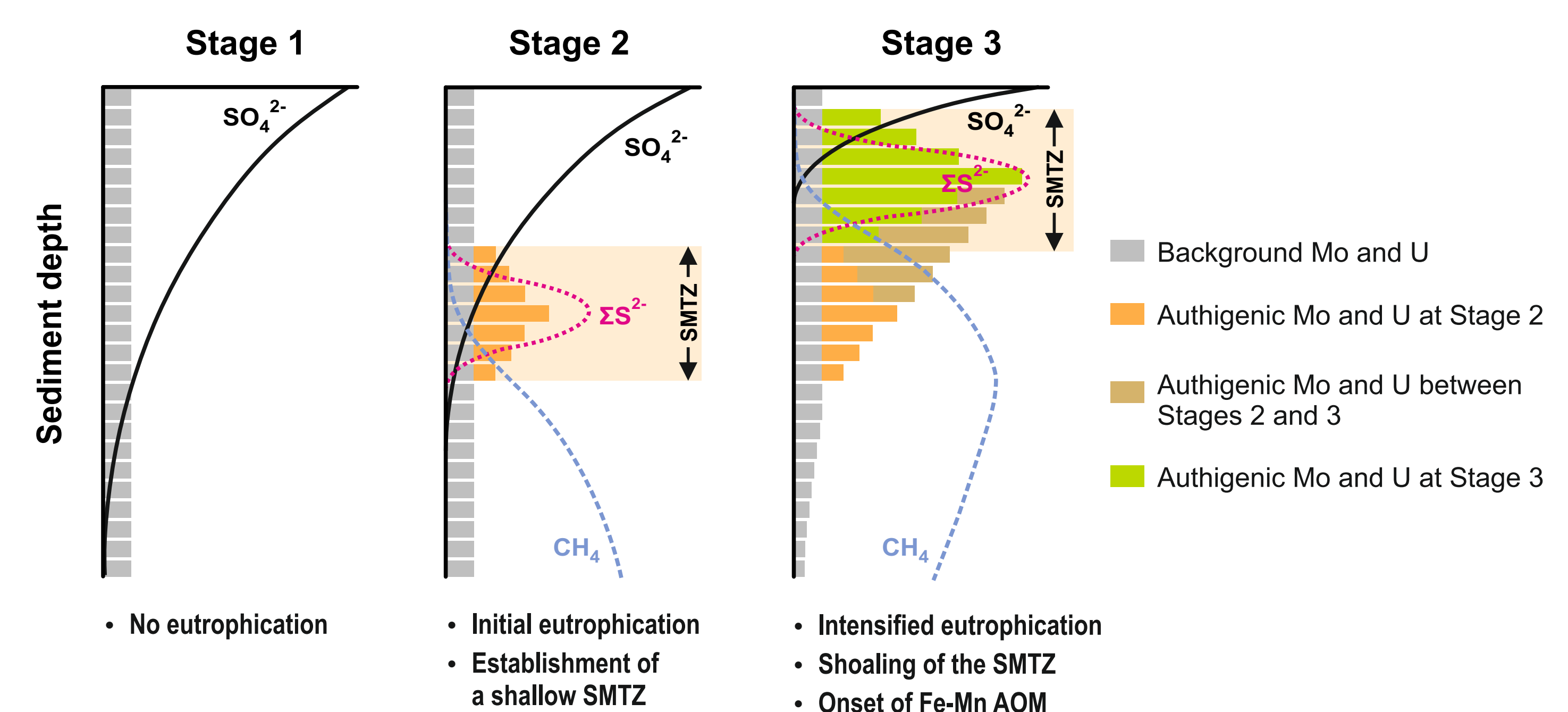


Fig. 6. Conceptual model for authigenic Mo and U sequestration in eutrophied coastal settings that are on the trajectory towards progressive deoxygenation and shoaling of the SMTZ.

## REFERENCES

- Algeo, T.J., Tribouillard, N., 2009. Environmental analysis of paleoceanographic systems based on molybdenum-uranium covariation. *Chemical Geology* 268, 211-225.
- Bröske, A., et al., 2020. Correlated molybdenum and uranium isotope signatures in modern anoxic sediments: Implications for their use as paleo-redox proxy. *Geochimica et Cosmochimica Acta* 270, 449-474.

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