Sedimentary molybdenum and uranium sequestration in silled fjords on the Swedish West coast: implications for trace-metal based paleo redox proxies

Background information for talk (STUDY 1 - submitted)

EGU General Assembly 2022

Mareike Paul (mareike.paul@helsinki.fi)[1], Martijn Hermans[1], Sami A. Jokinen[2], Inda Brinkmann[3], Helena L. Filipsson[3], and Tom Jilbert[1]

[1]University of Helsinki, Helsinki, Finland (mareike.paul@helsinki.fi); [2]Geological Survey of Finland, Espoo, Finland; [43]und University, Lund, Sweden

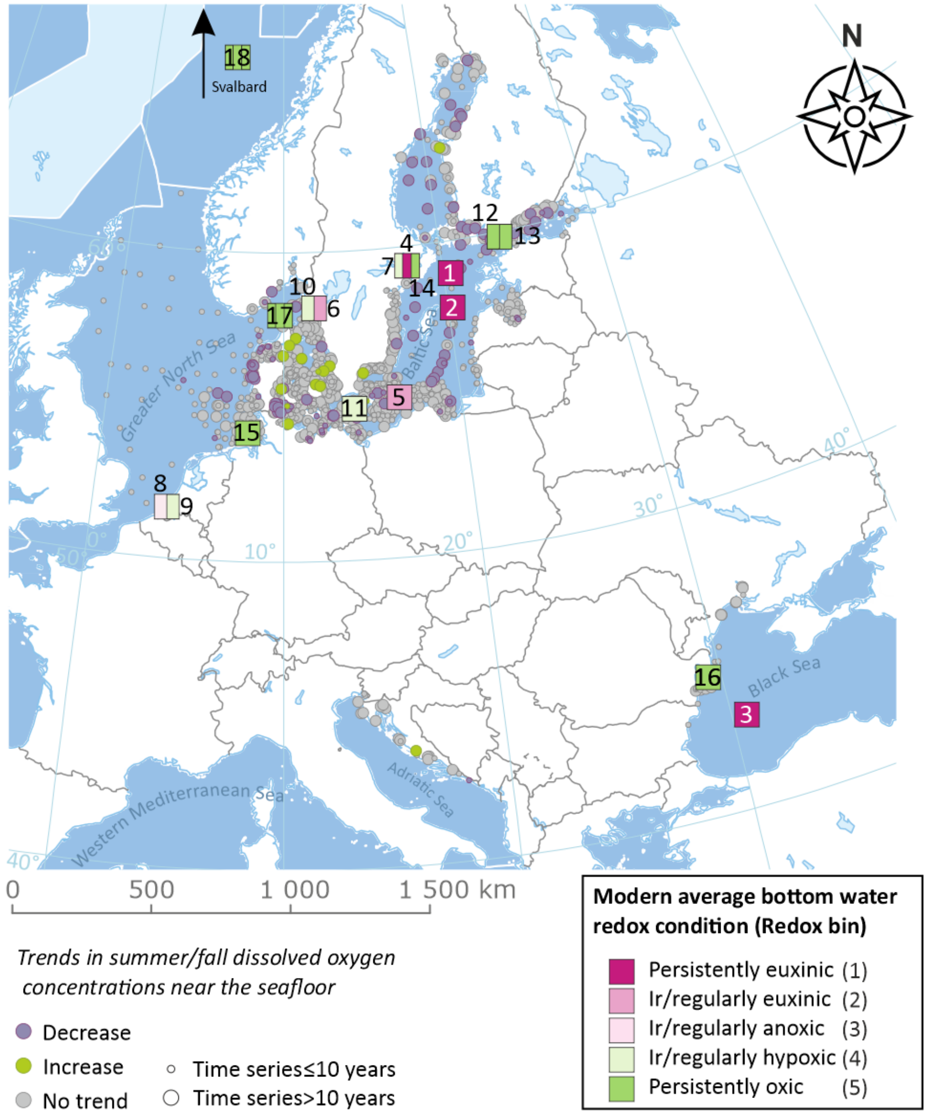


Fig. 1. The geographical location of the 18 study sites (filled squares) plotted together with the trends in summer/autumn dissolved oxygen concentration near the seafloor as determined by monitoring data (filled circles; European Environment Agency, EEA, 2019). The color of the squares corresponds to their modern average bottom water redox condition (redox bin, legend at the bottom right). Sites in close proximity are displayed as segmented squares. The number of segments corresponds to the number of sites. If the study sites have different redox bins, the segments have different colors. Modified from EEA (2019).

Deoxygenation is an increasing problem in many coastal European seas: (Fig. 1)

Causes:

- inflow of excess nutrients from land to sea (→ Eutrophication)
- rising water temperatures (→ Climate Change)

Consequences:

1. Increasing primary productivity & algal blooms
2. Increasing organic matter production
3. Increasing oxygen consumption in bottom waters (BW) due to aerobic microbial organic matter degradation
4. Oxygen consumption is exceeding oxygen demand
5. Extension of zones depleted in oxygen

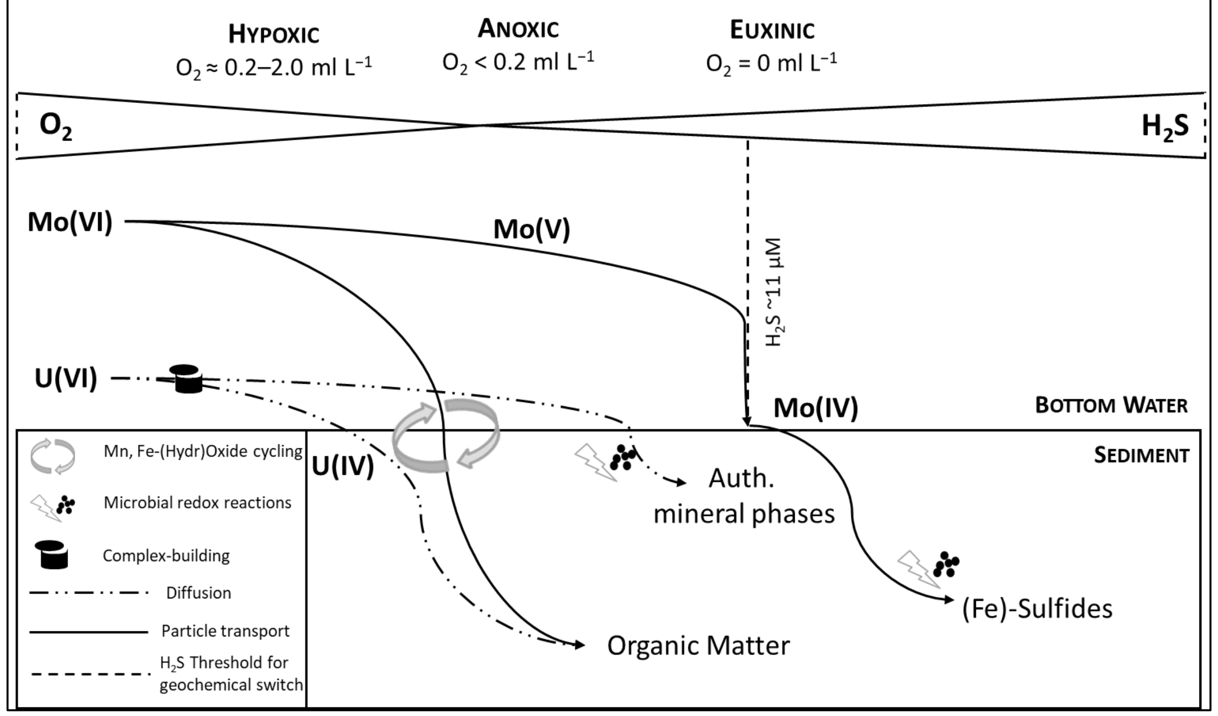


Fig. 2. Simplified overview of the sequestration mechanisms of U and Mo under different bottom water redox conditions.

Sedimentary trace metals have the potential to be useful indicator of coastal marine **deoxygenation.**

WHY?

Sedimentary trace metals are **unreactive** in **oxic waters** but **particle-reactive** under **oxygen-limiting conditions** (hypoxia – euxinia). Two of such "redox"-sensitive trace metals are **molybdenum (Mo)** and **uranium (U)**. Via different pathways (diffusion, or particle transport) they reach the seafloor, where they either form refractory complexes with host phases (e.g., organic matter or metal-sulfides) or transform into authigenic mineral phases (Fig. 2).

Funding

© Authors. All rights reserved

Sedimentary molybdenum and uranium sequestration in silled fjords on the Swedish West coast: implications for trace-metal based paleo redox proxies

Background information for talk (STUDY 1 – submitted)

EGU General Assembly 2022

Mareike Paul (mareike.paul@helsinki.fi)[1], Martijn Hermans[1], Sami A. Jokinen[2], Inda Brinkmann[3], Helena L. Filipsson[3], and Tom Jilbert[1]

[1]University of Helsinki, Helsinki, Finland (mareike.paul@helsinki.fi); [2]Geological Survey of Finland, Espoo, Finland; [43]und University, Lund, Sweden

Methods

Meta-analysis

1. Solid-phase and pore water trace metal data (ICP-MS, ICP-OES, C/N) from literature and new fieldwork data.
2. Categorizing different study sites according to their "recent" trends in bottom water redox conditions (**redox bins, see first slide**), based on monitoring and sediment geochemical data.
3. Normalization of trace metal enrichments against aluminum to account for detrital dilution using **enrichment factors (EF; see calculation below).**
4. Using **box and whisker plots** to test the sensitivity and applicability of various trace metals as indicators for redox changes.
5. Using the Mo-EF:U-EF – ratio approach (Tribovillard and Algeo, 2009) to further investigate the impact of secondary factors besides bottom water redox conditions on Mo- and U-EFs.
6. Making an assessment of the applicability of Mo- and U-EFs as proxies for deoxygenation in a range of depositional environments with contrasting bottom water redox conditions.

$$\text{TM–EF}=\left(\frac{\text{TM}}{\text{Al}}\right)_{\text{sample}}\Big/\left(\frac{\text{TM}}{\text{Al}}\right)_{\text{reference}}$$

Reference: global average **U**pper **C**ontinental **C**rust (UCC) Rudnick and Gao (2014)

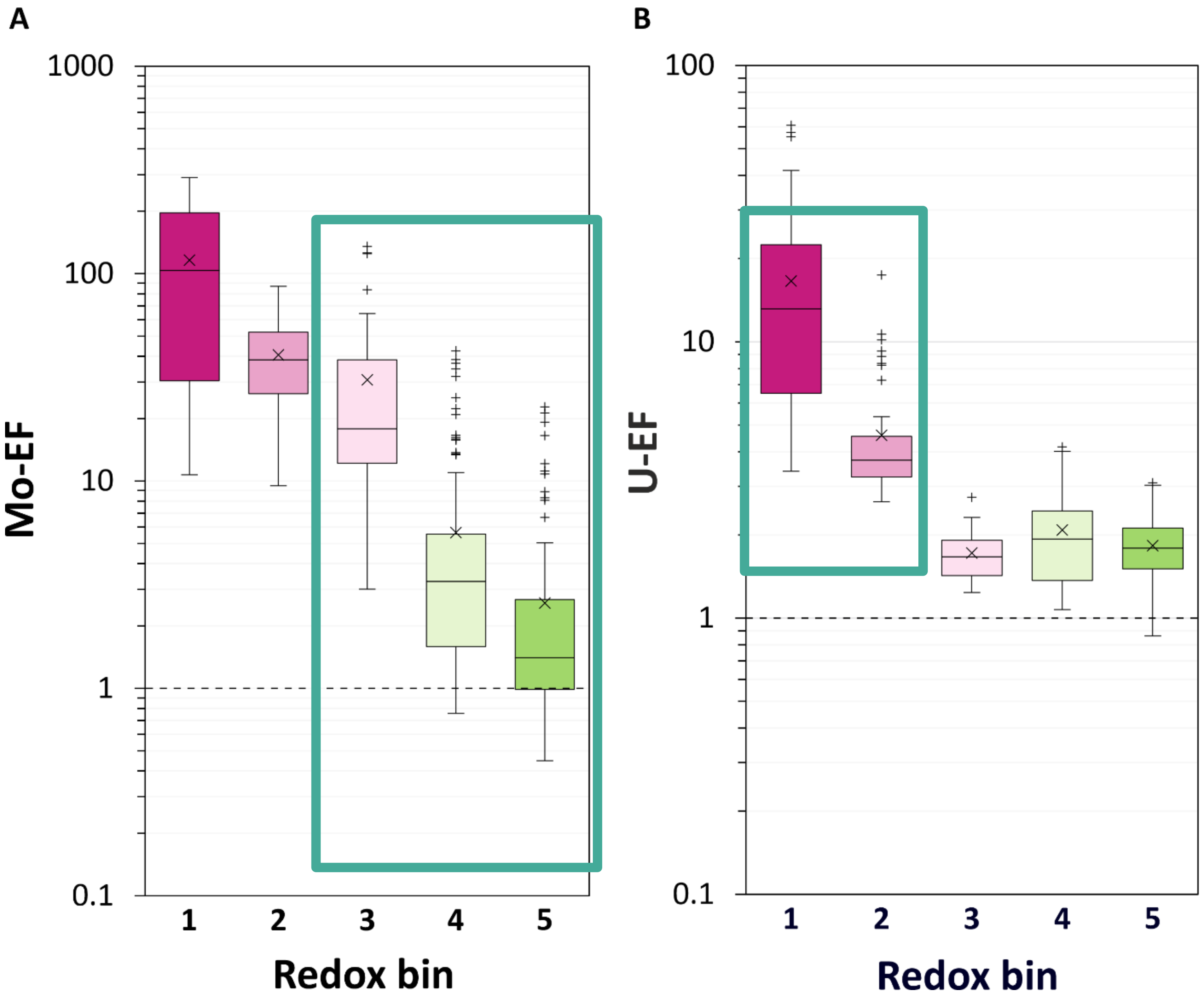


Fig. 3. Sedimentary Mo (panel A) and U (panel B) enrichment factors (EFs) among the bottom water redox conditions ('redox bins', Legend to the right), displayed on log10 scale. For detailed description of the box and whisker plots we refer the reader to the caption of Fig. 3. The horizontal dashed lines indicate the TM-EF value of 1, which is the threshold for authigenic Mo and U enrichments. Values below 1 indicate non-authigenic Mo and U concentrations.

Results 1

Mo-EF: there is a significant **difference** between **redox bins 3-5**

U-EF: there is a significant **difference** between **redox bin 1+2.**

\>> Mo and U have contrasting redox sensitivies.

---- $\text{TM/Al}_{\text{sample}} = \text{TM/Al}_{\text{UCC}}$
\>1: authigenic enrichment
<1: no authigenic enrichment (detrital)

Modern average bottom water redox condition (Redox bin)

■	Persistently euxinic	(1)
■	Ir/regularly euxinic	(2)
■	Ir/regularly anoxic	(3)
■	Ir/regularly hypoxic	(4)
■	Persistently oxic	(5)

Paul et al., submitted

© Authors. All rights reserved

Sedimentary molybdenum and uranium sequestration in silled fjords on the Swedish West coast: implications for trace-metal based paleo redox proxies

Background information for talk (STUDY 1 – submitted)

Mareike Paul (mareike.paul@helsinki.fi)[1], Martijn Hermans[1], Sami A. Jokinen[2], Inda Brinkmann[3], Helena L. Filipsson[3], and Tom Jilbert[1]

[1]University of Helsinki, Helsinki, Finland (mareike.paul@helsinki.fi); [2]Geological Survey of Finland, Espoo, Finland; [43]und University, Lund, Sweden

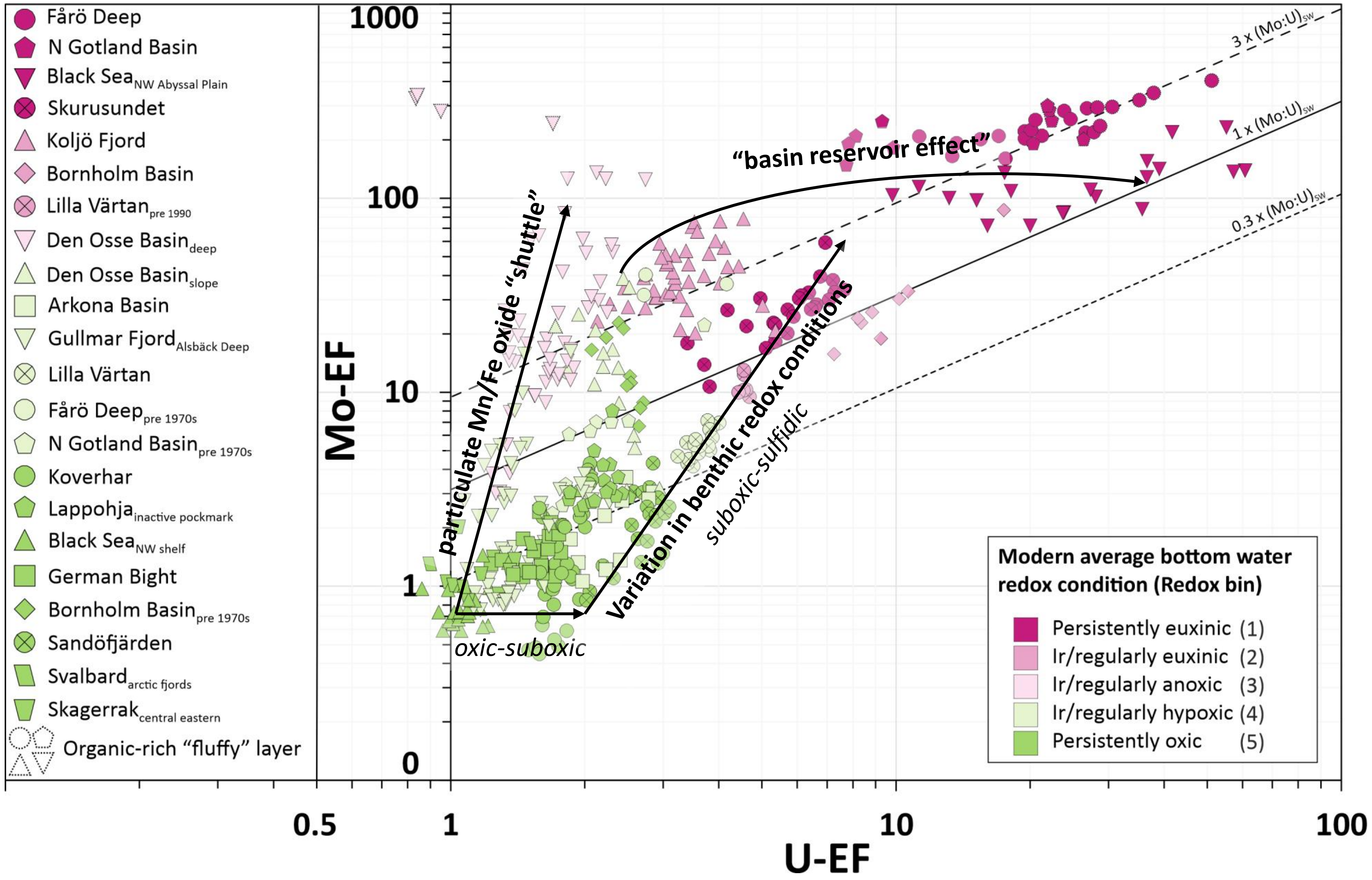


Fig. 4. Mo- and U-EF covariation patterns among the study sites based on whole core sediment samples (concept after Algeo and Tribovillard, 2009). The legend to the left shows all study sites with their corresponding bottom water redox color. The double arrow on the right shows the color coding of the redox bins 1-5. "Fluffy layer" refers to freshly deposited organic matter-rich layer.

Paul et al., submitted

Results

Mo and U sediment enrichments follow three key controls:

1. variations in **benthic redox conditions**,
2. **Fe/Mn particulate shuttling,** and
3. **The basin reservoir effect**

1. U responses more sensitive to shifts from oxic to suboxic conditions, as conditions become more sulfidic (e.g., due to increased organic matter degradation), Mo and U increase simultaneously.

2. The redox cycling of Fe and Mn accelerates shuttling and enrichment of Mo in the sediment. U is not affected by this

3. Strongly euxinic, (semi)-restricted basins can counteract Mo enrichment through imbalance of extremely efficient Mo sequestration but sluggish re-upply ("basin reservoir effect"). U is not affected by this, leading to the flattening of the enrichment pattern.

Conclusion

We confirm that **three controls** of **Mo-EF:U-EF covariations** are responsible for redox-sensitive **trace metal enrichments** in European coastal marine sea sediments.

Fe/Mn particulate shuttling and the **basin reservoir effect** are not first order redox controls, but **secondary factors** caused by the characteristics of the **depositional environment**.

Likely **more secondary factors** control Mo and U-EFs, which cannot be identified with the co-variation patterns.

© Authors. All rights reserved

Sedimentary molybdenum and uranium sequestration in silled fjords on the Swedish West coast: implications for trace-metal based paleo redox proxies

Further details (methods, results) for study presented (STUDY 2 – in prep)

Mareike Paul (mareike.paul@helsinki.fi)[1], Martijn Hermans[1], Sami A. Jokinen[2], Inda Brinkmann[3], Helena L. Filipsson[3], and Tom Jilbert[1]

[1]University of Helsinki, Helsinki, Finland (mareike.paul@helsinki.fi); [2]Geological Survey of Finland, Espoo, Finland; [43]und University, Lund, Sweden

Motivation: to better understand the mechanisms (secondary factors) that control Mo and U sequestration across a range of bottom water redox conditions and depositional environments

Methods: we conducted a 5 step sequential extraction of Mo and U, as well as Al, Ca, Fe, Mn, and S (Table 1), combined with pore water analyses (not shown). Enrichment patterns of Fe and Mn combined with Ca and S can provide us information about the formation of Fe/Mn carbonates or sulfides in relation to Mo and U sequestration. Al is an indicator for changes in the detrital background.

Table 1 Sequential extraction procedure for trace metals. Adapted from Jokinen et al. (2020a); an additional concentrated nitric acid step was added, designated as F5, in order to extract pyrite as described in Poulton and Canfield (2005).

	Code	Fraction	Solvent	Time	Targeted minerals phase	References
🟦	**F1**	Exchangeable	$MgCl_2$ (1 M), pH 8	0.5 h	Weakly-sorbed Me species	Tessier et al., 1979
🟦	**F2**	Acid-soluble	Na-acetate (1 M), pH 4.5	6 h	Carbonates AVS Mn(II) phosphates Labile Me-OM complexes	Tessier et al., 1979 Cornwell and Morse, 1987 Lenstra et al., 2021 Jilbert et al., 2018
🟦	**F3**	Reducible	Na-dithionite (5%), Acetic acid (0.35 M), Na-citrate (0.2 M), pH 4.8	4 h	Fe (oxyhydr)oxides Mn (oxyhydr)oxides Labile Me-OM complexes	Poulton and Canfield, 2005 Hermans et al., 2019 Lalonde et al., 2012
⬜	**F4**	Organic	Ashing at 550 °C HCl (1 M), pH 0	2 h 24 h	Refractory Me-OM complexes	Ruttenberg, 1992
🟥	**F5**	Strong-acid-soluble	HNO_3 (65-70%) MQ wash step[1]	2 h 0.5 h	Pyrite	Claff et al., 2010
🟧	**F6**	Residual	HF (40%) $HClO_4$:HNO_3 (3:2 vol%)	O/N[2]	Silicates	Poulton and Canfield, 2005
		Total	HF (40%) $HClO_4$:HNO_3 (3:2 vol%)	O/N[2]	Sum of all phases	

[1]An additional wash step was introduced here to remove residual concentrated nitric acid from the sample tubes. 2O/N = overnight.

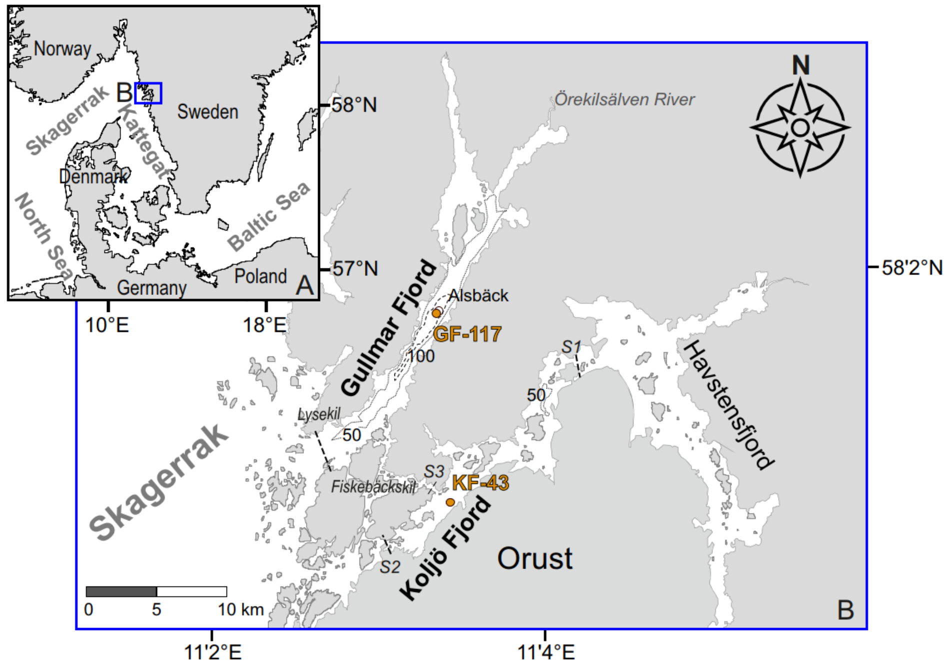


Fig. 5. Study locations of Koljö and Gullmar Fjord . Koljö Fjord is seasonally euxinic, and Gullmar Fjord seasonally hypoxic

© Authors. All rights reserved

Sedimentary molybdenum and uranium sequestration in silled fjords on the Swedish West coast: implications for trace-metal based paleo redox proxies

Further details (methods, results) for study presented (STUDY 2 – in prep)

Mareike Paul (mareike.paul@helsinki.fi)[1], Martijn Hermans[1], Sami A. Jokinen[2], Inda Brinkmann[3], Helena L. Filipsson[3], and Tom Jilbert[1]

[1]University of Helsinki, Helsinki, Finland (mareike.paul@helsinki.fi); [2]Geological Survey of Finland, Espoo, Finland; [43]und University, Lund, Sweden

- 1 Weakly-sorbed Me-species
- 2 Carbonates, AVS, Mn-phosphates, Labile Me-OM complexes
- 3 Labile Me-OM complexes Fe/Mn (oxy)(hydr)oxides
- 4 Refractory Me-OM complexes
- 5 Pyrite
- 6 Residual (Silicates)

Preliminary results: Sequential extraction of Mo, U, as well as Al, Ca, Mn, Fe at the more reducing site "KOLJÖ FJORD", which is a seasonally euxinic silled-fjord.

According to the Ca, Mn, and Fe data we find not evidence for Fe and/or Mn carbonate formation, which is in line with the sulfidic pore waters (Fig. 6).
Molybdenum is largely present as particle-reactive thio-molybdate intermediates, sulfidized organic matter, and associated with pyrite. Uranium is present as a mixture of labile and more refractory authigenic U mineral phases associates with organic matter and residual phases in the absence of carbonates.

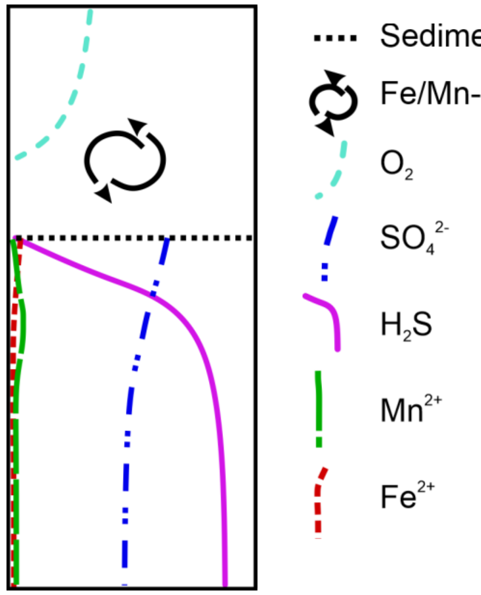
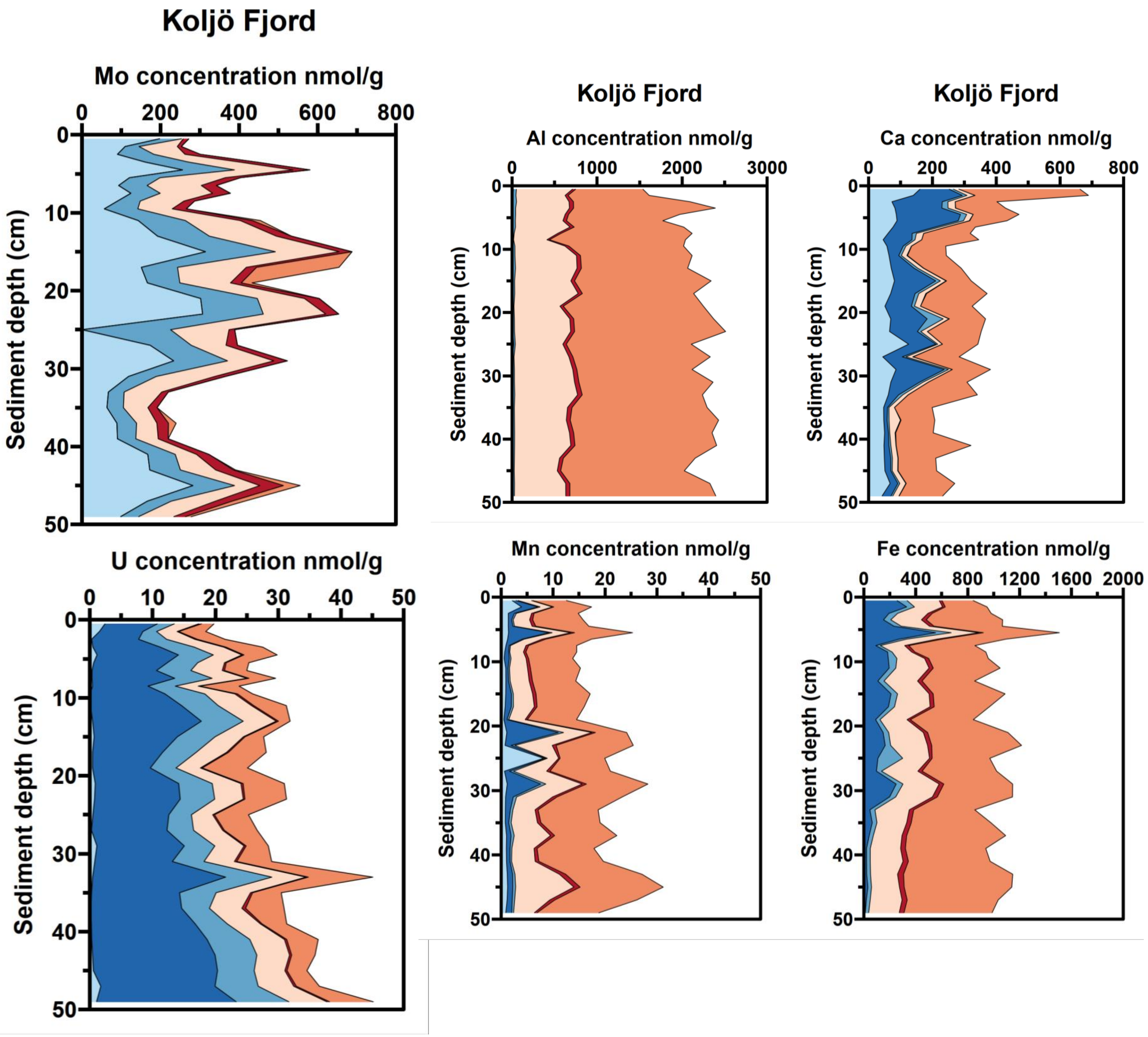


Fig. 6. Simplified drawing of the water column and pore water geochemical and redox processes at Koljö Fjord.



© Authors. All rights reserved

Sedimentary molybdenum and uranium sequestration in silled fjords on the Swedish West coast: implications for trace-metal based paleo redox proxies

Further details (methods, results) for study presented (STUDY 2 – in prep)

EGU General Assembly 2022

Mareike Paul (mareike.paul@helsinki.fi)[1], Martijn Hermans[1], Sami A. Jokinen[2], Inda Brinkmann[3], Helena L. Filipsson[3], and Tom Jilbert[1]

[1]University of Helsinki, Helsinki, Finland (mareike.paul@helsinki.fi); [2]Geological Survey of Finland, Espoo, Finland; [43]und University, Lund, Sweden

- 1 Weakly-sorbed Me-species
- 2 Carbonates, AVS, Mn-phosphates, Labile Me-OM complexes
- 3 Labile Me-OM complexes Fe/Mn (oxy)(hydr)oxides
- 4 Refractory Me-OM complexes
- 5 Pyrite
- 6 Residual (Silicates)

Preliminary results: Sequential extraction of Mo, U, as well as Al, Ca, Mn, Fe at the more reducing site "GULLMAR FJORD", which is a seasonally hypoxic silled-fjord.

According to the Ca, Mn, and Fe data we find evidence for Mn carbonate formation at depth, which is in line with strong Mn, and Fe shuttling at this site (Fig. 7).
Molybdenum shows the strongest enrichment at the top 5 cm in response to increased shuttling of Mo in association with Mn, and Fe oxides. The remaining Mo is likely associated with organic matter, but enrichments remain low.
Uranium increases with depth, likely in association with Mn carbonates. The remaining U is bound to organic matter, and residual phases.

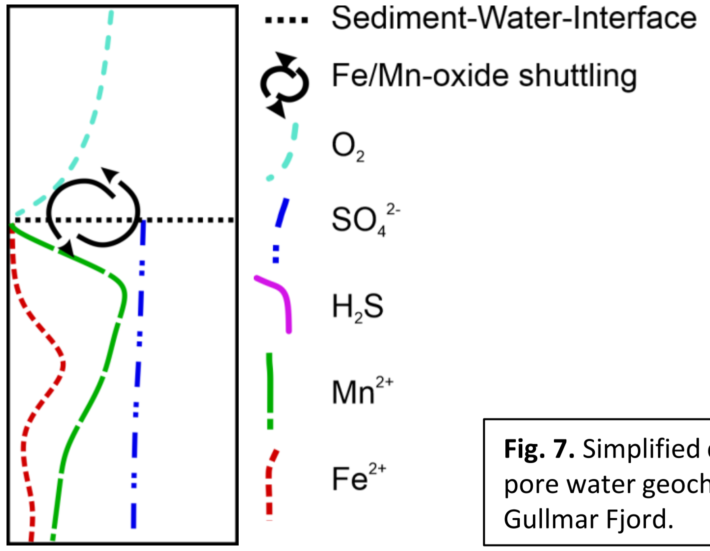
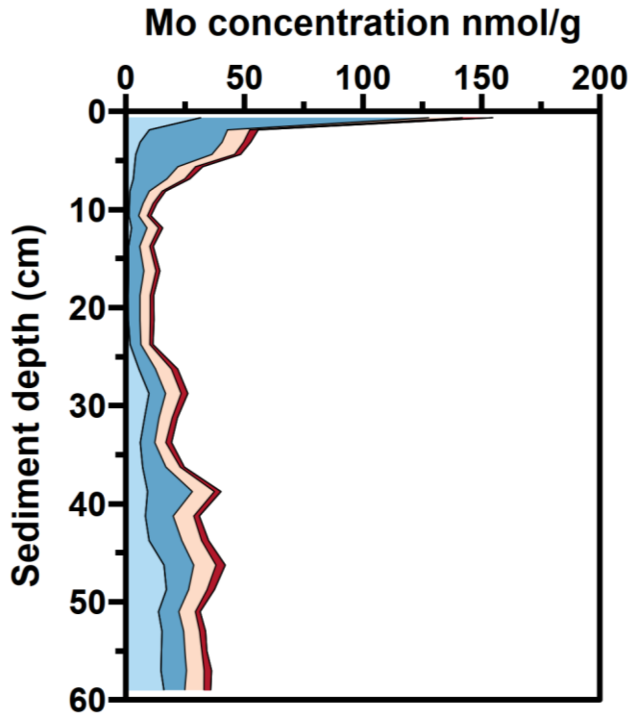
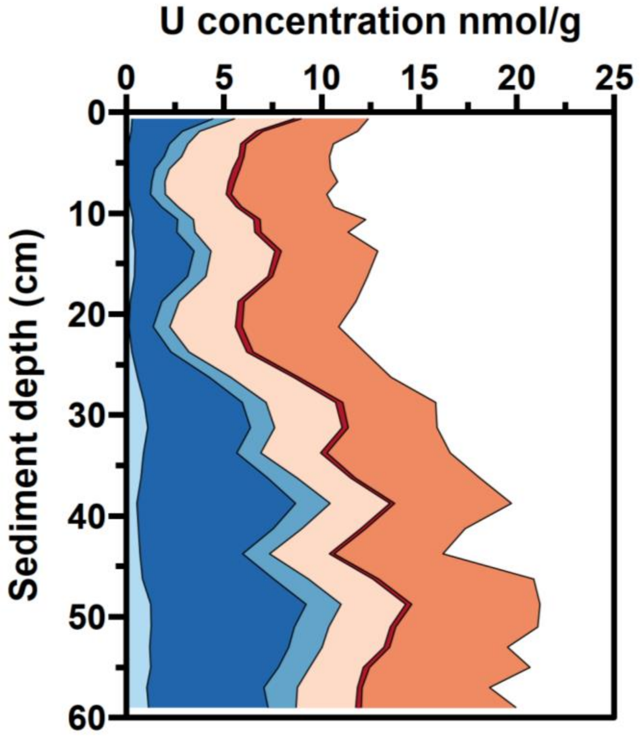
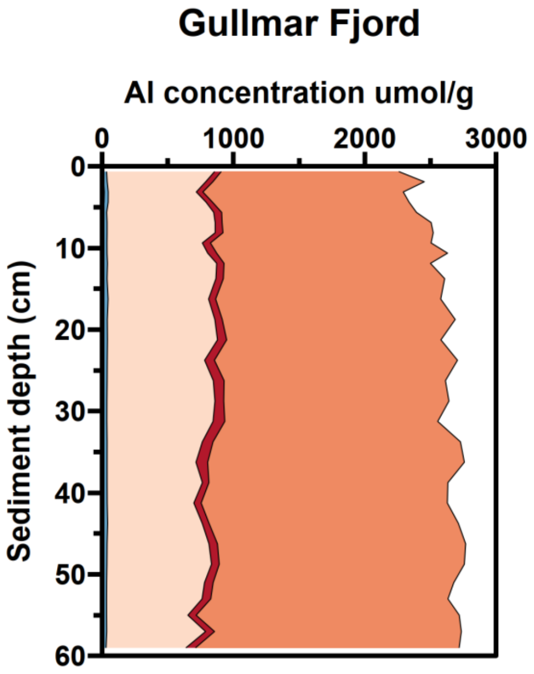


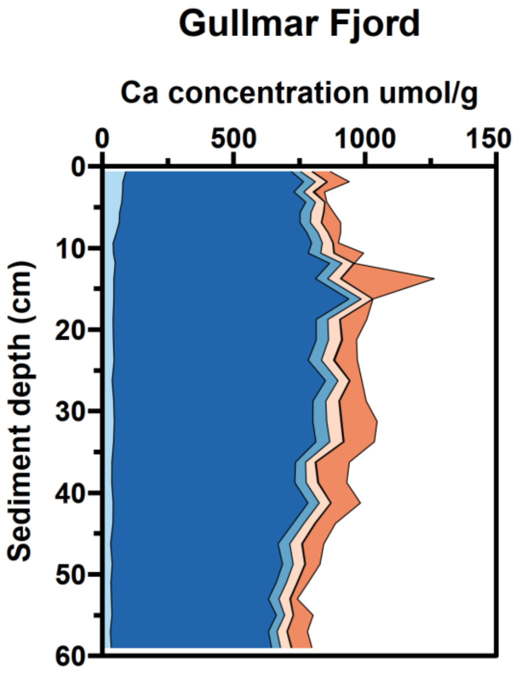
Fig. 7. Simplified drawing of the water column and pore water geochemical and redox processes at Gullmar Fjord.

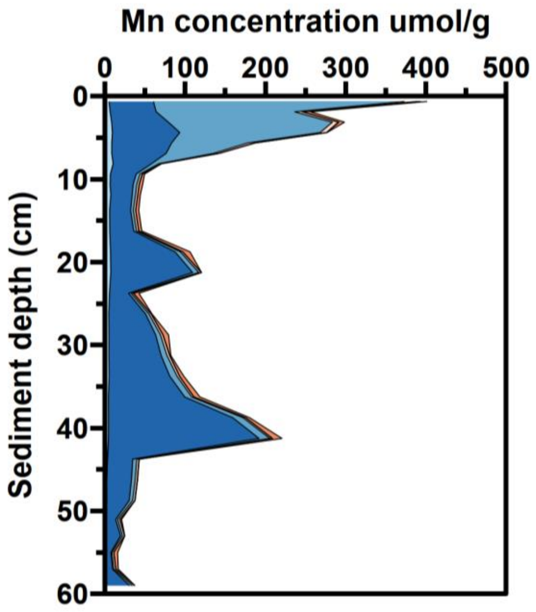
Gullmar Fjord

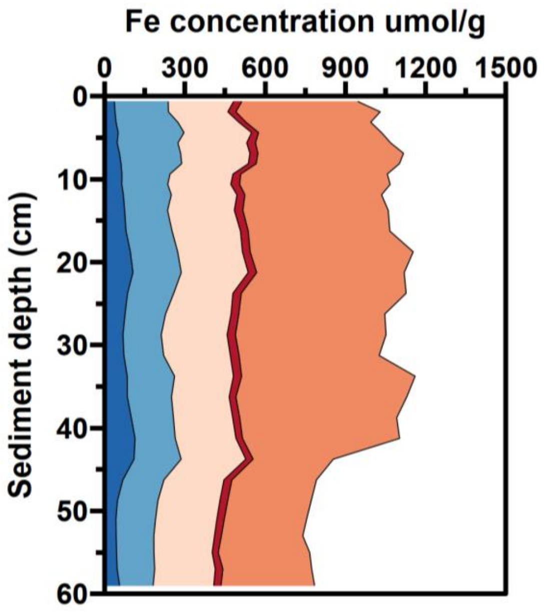












© Authors. All rights reserved