Sediments as the redox paleo-record

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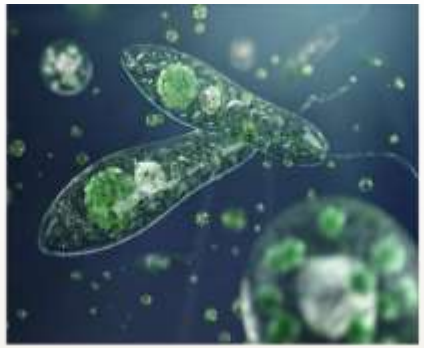
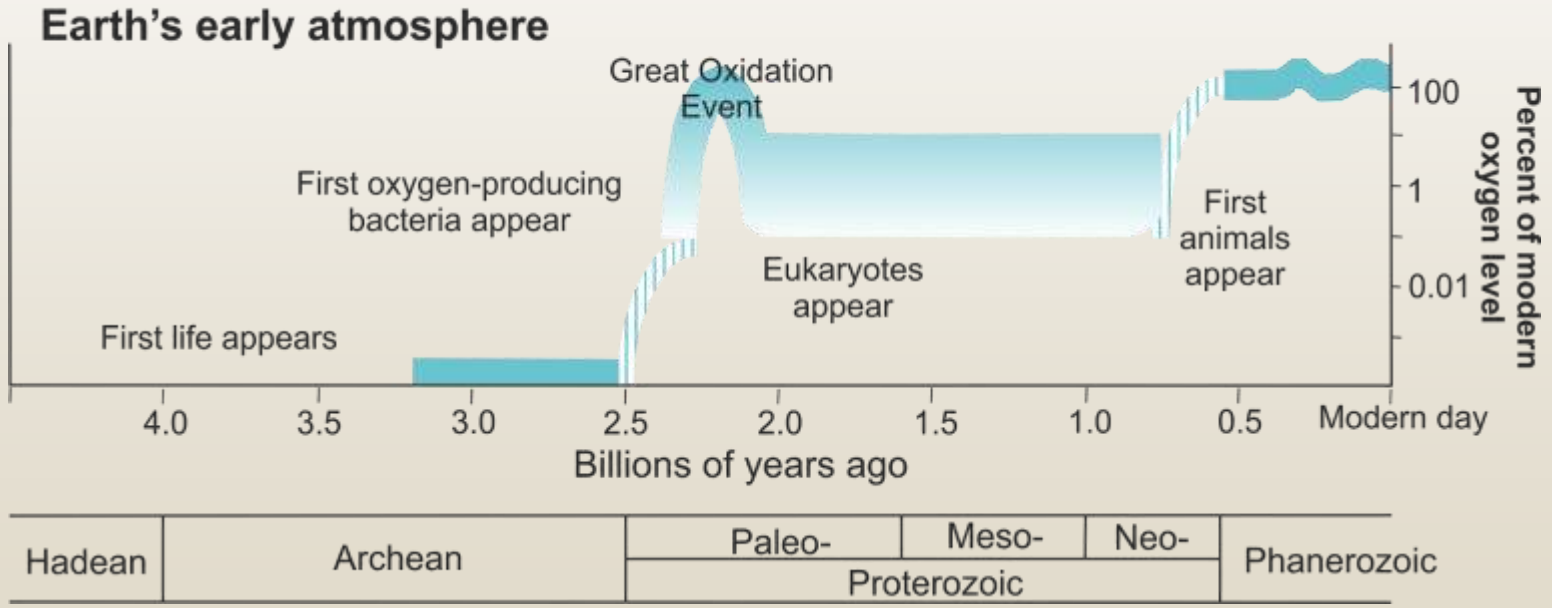
- Overview (state of the art in the research area)
- Results
- Future investigations

Evolution of Earth's atmosphere through time

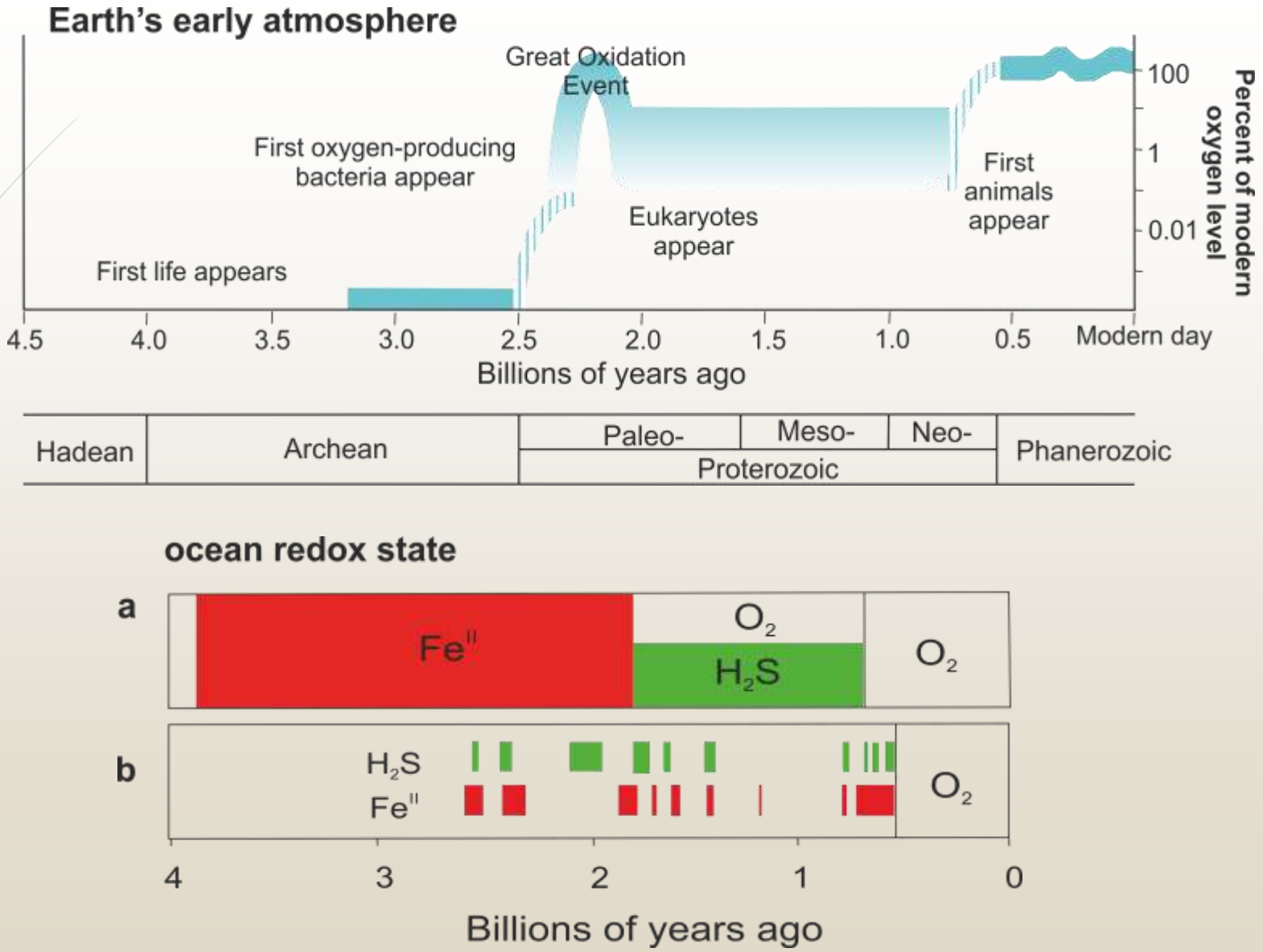




Modified after TW Lyons et al. Nature **506**, 307-315 (2014)

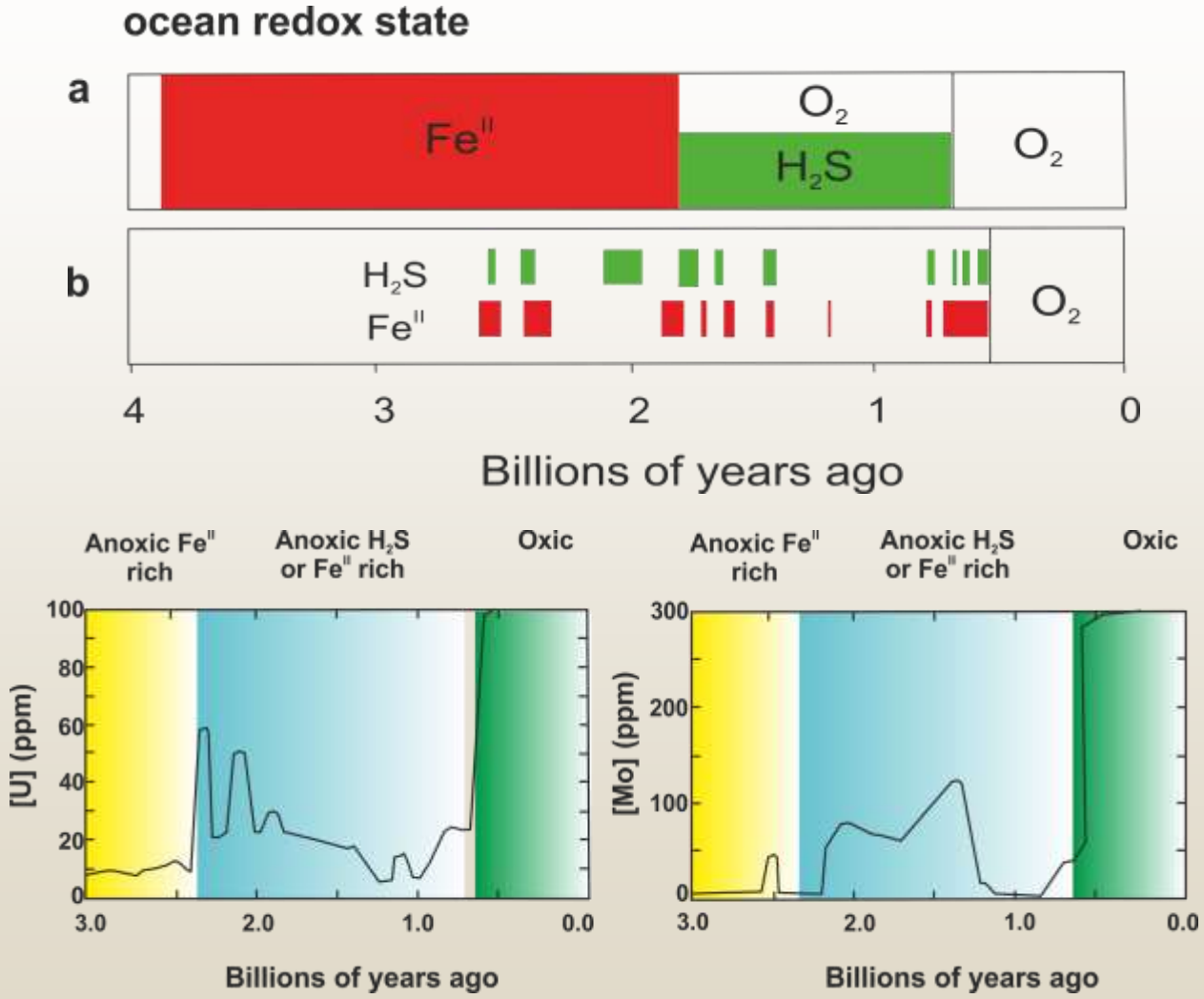
Map of ocean low oxygen - dead zones

Co-evolution of Earth's atmosphere and ocean redox state through time



Modified after *TW Lyons et al. Nature* **506**, 307-315 (2014)
and after *NJ Planavsky et al. Nature* **477**, 448-452 (2011)

Co-evolution of ocean redox state and Mo and U sedimentary concentrations through time



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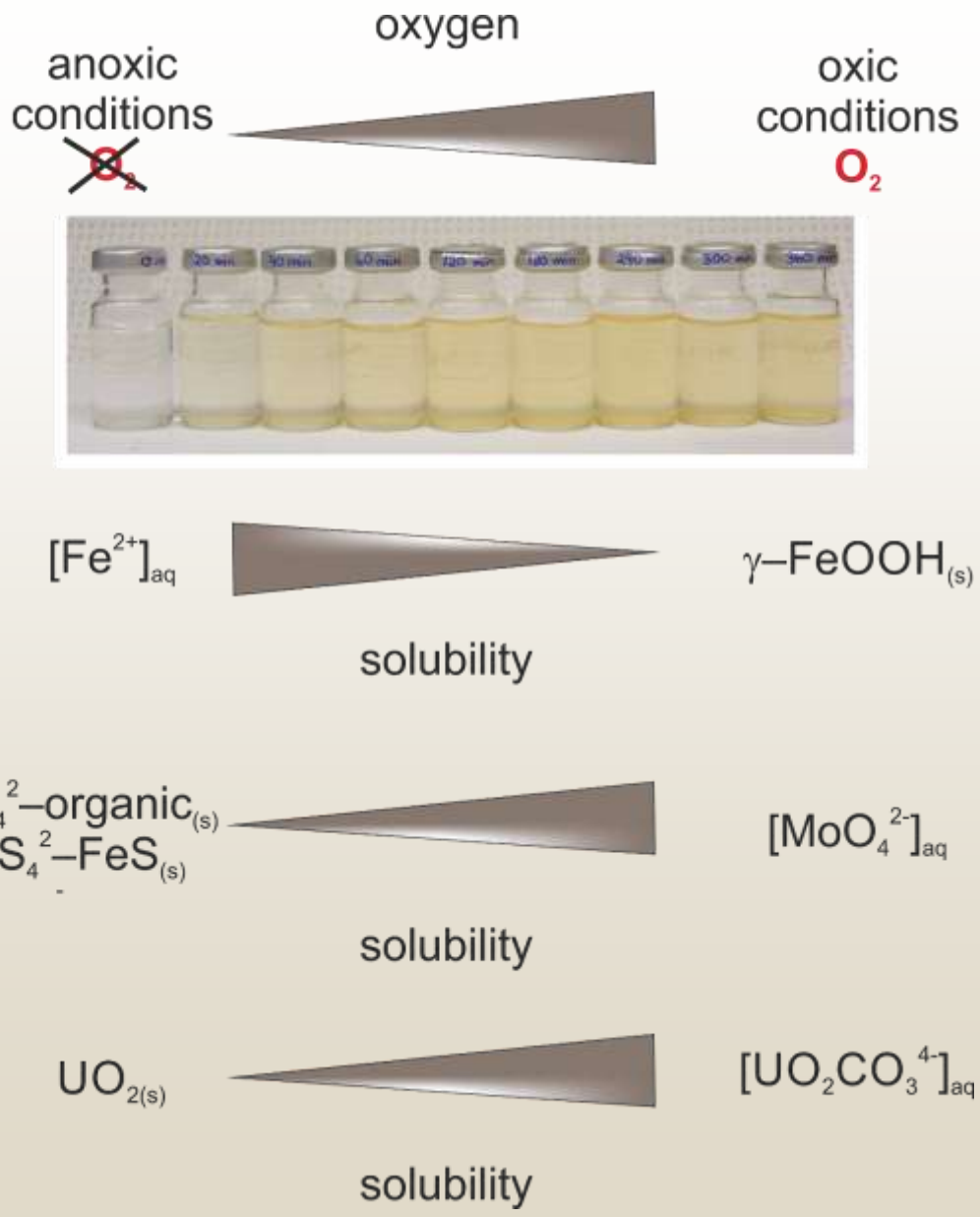
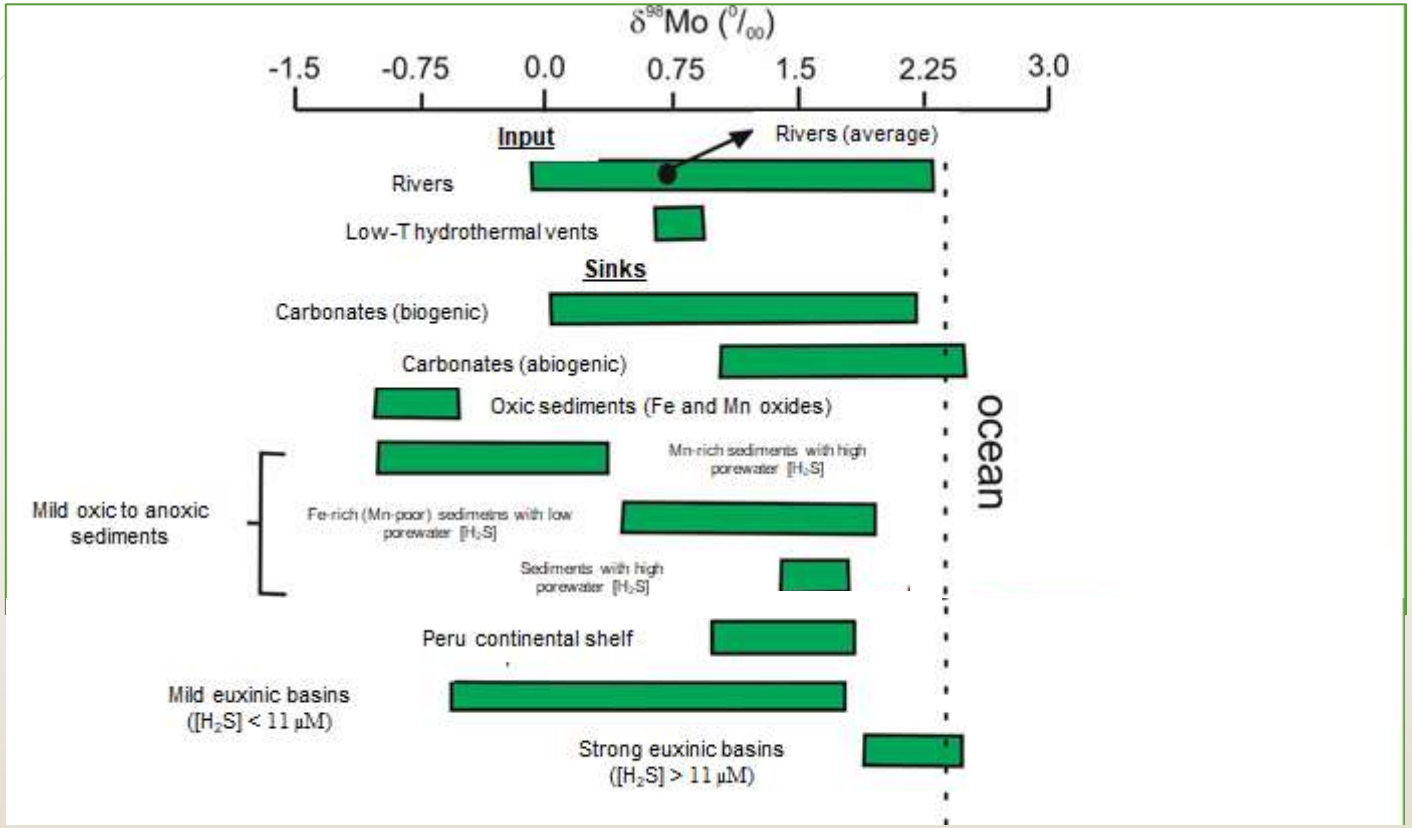
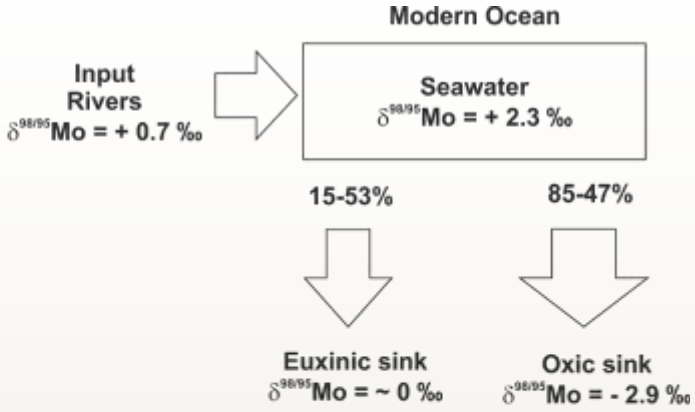
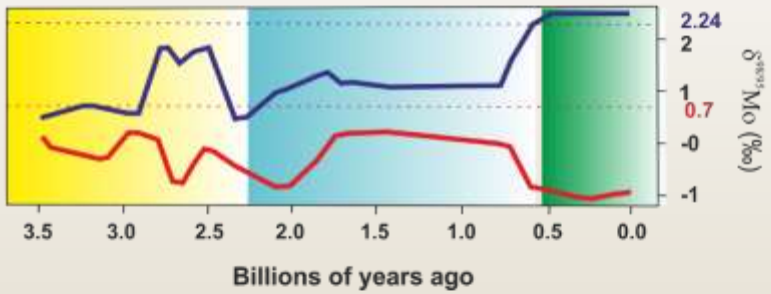
and after *NJ Planavsky et al. Nature* **477**, 448-452 (2011)

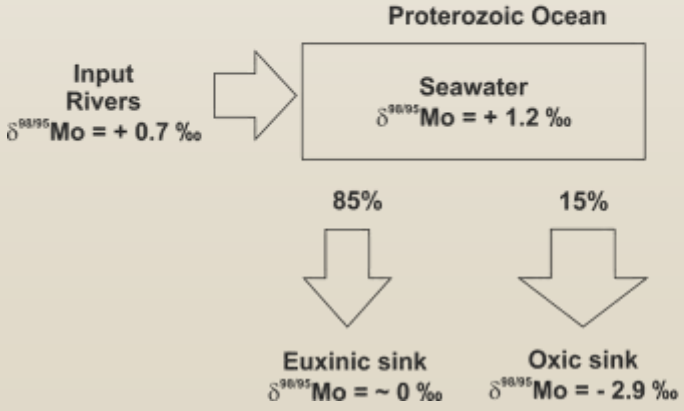

oxygen
anoxic conditions
O_2
oxic conditions
O_2
$[Fe^{2+}]_{aq}$
γ–$FeOOH_{(s)}$
solubility
MoS_4^{2-}–organic$_{(s)}$
MoS_4^{2-}–$FeS_{(s)}$
$[MoO_4^{2-}]_{aq}$
solubility
$UO_{2(s)}$
$[UO_2CO_3^{4-}]_{aq}$
solubility


δ98Mo (‰)
-1.5
-0.75
0.0
0.75
1.5
2.25
3.0
Input
Rivers (average)
Rivers
Low-T hydrothermal vents
Sinks
Carbonates (biogenic)
Carbonates (abiogenic)
Oxic sediments (Fe and Mn oxides)
Mn-rich sediments with high porewater [H2S]
Mild oxic to anoxic sediments
Fe-rich (Mn-poor) sediments with low porewater [H2S]
Sediments with high porewater [H2S]
Peru continental shelf
Mild euxinic basins ([H2S] < 11 μM)
Strong euxinic basins ([H2S] > 11 μM)
ocean



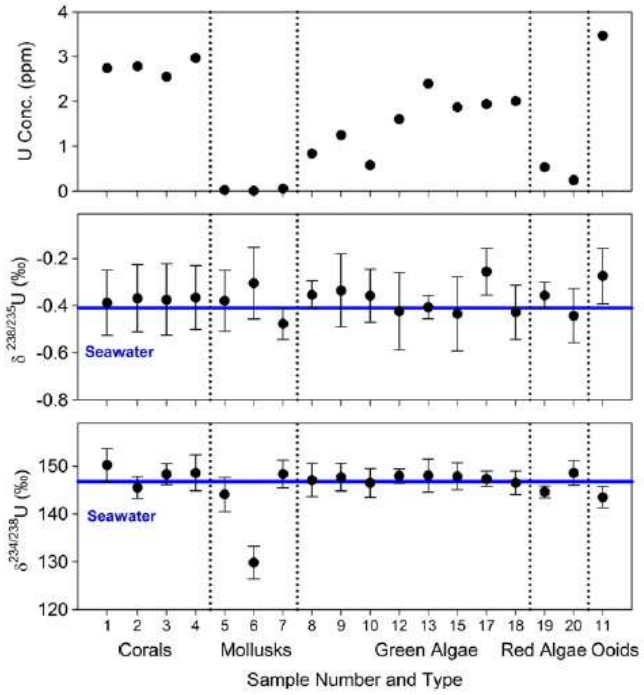
Oxic Mo sink predominates



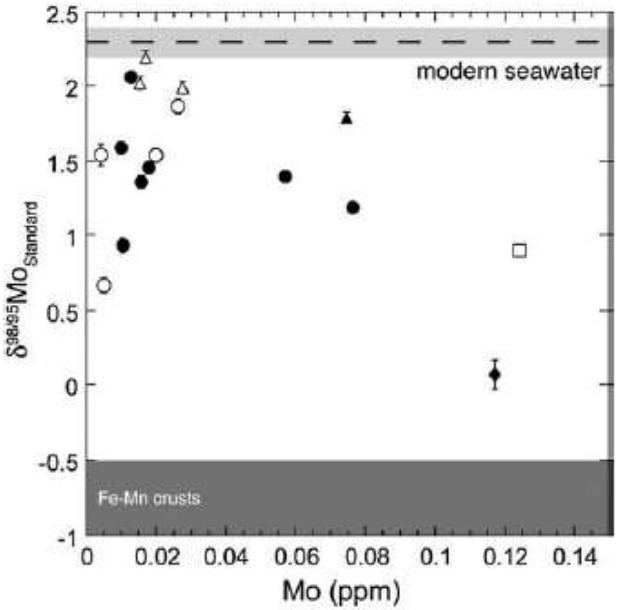


Euxinic Mo sink predominates

Modified after X Chen et al. Nature Commun.
DOI: 10.1038/ncomms8142 (2015)



U concentrations, $\delta^{238/235}U$, and $\delta^{234/238}U$ variations in primary carbonate precipitates. Error bars represent the 2σ precision of replicate analyses of the same solutions. Estimated U concentration errors are smaller than the symbol size. Horizontal solid lines indicate the composition of average seawater. Vertical dotted lines separate different sample types.

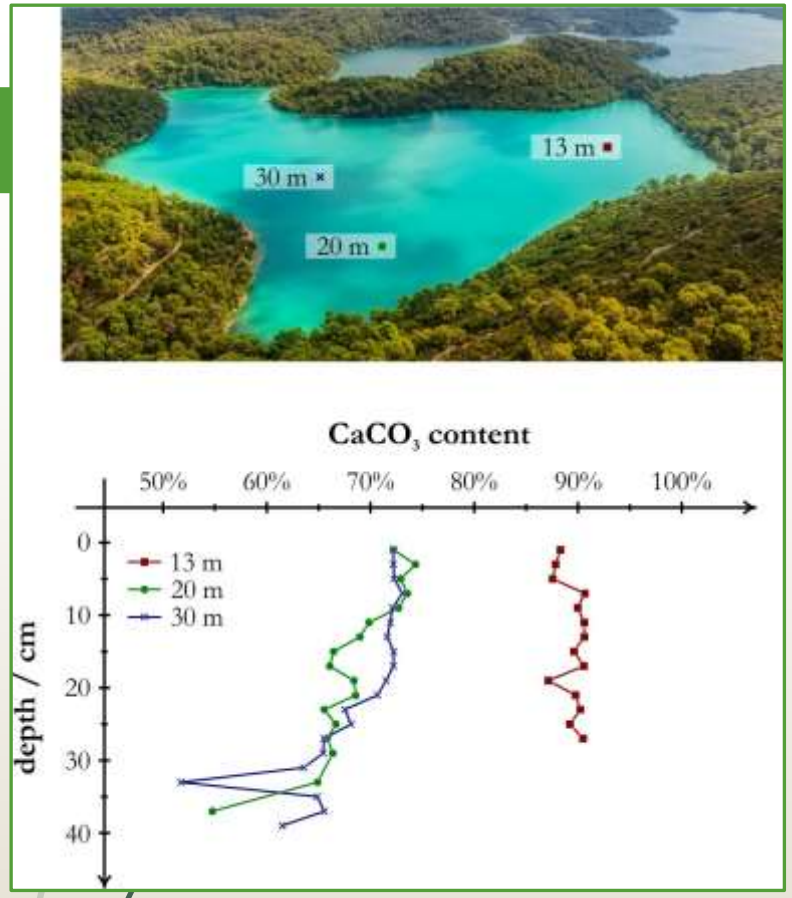


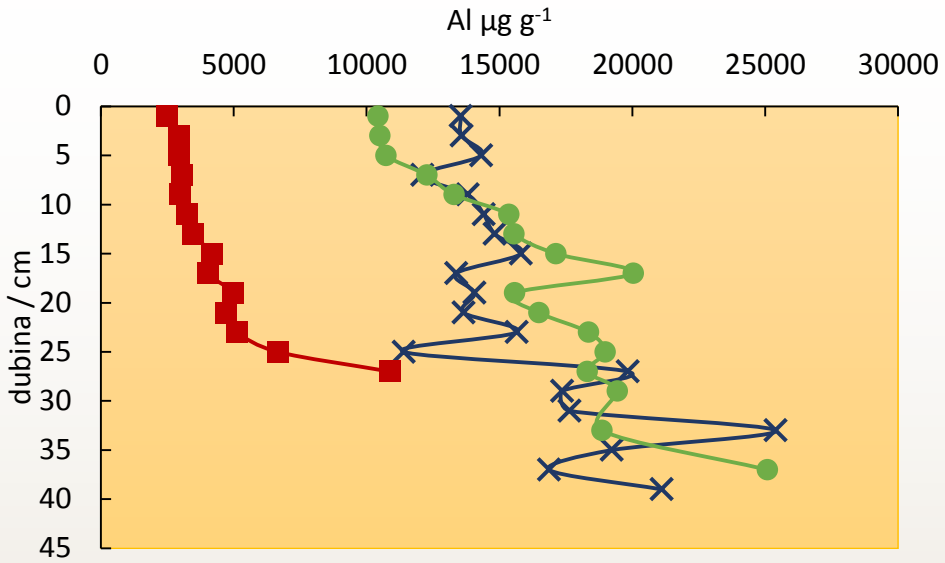
Mo isotope and concentration data of modern biologically precipitated carbonates. Open circles = gastropods, filled circles = bivalves, open triangles = corals, filled triangle = calcareous algae (*Halimeda*), diamond = brachiopod (*T. septentrionalis*), open square = serpulid tubes. All other labellings are as specified in Fig. 3.

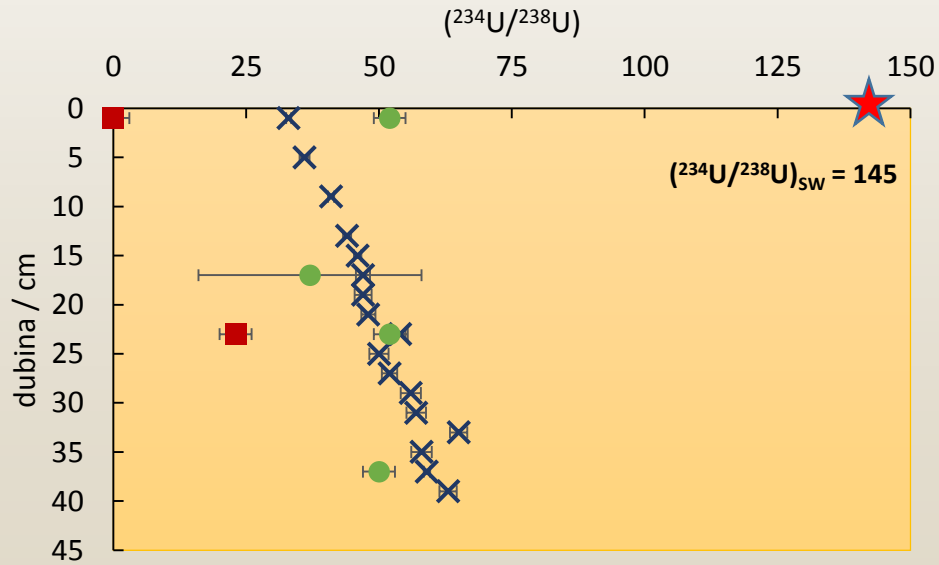
Romaniello, S.J., Hermann, A. and Anbar, A.D. (2013) Uranium concentrations and $^{238}U/^{235}U$ isotope ratios in modern carbonates from the Bahamas: Assessing a novel paleoredox proxy. *Chemical Geology* **362**, 305-316.

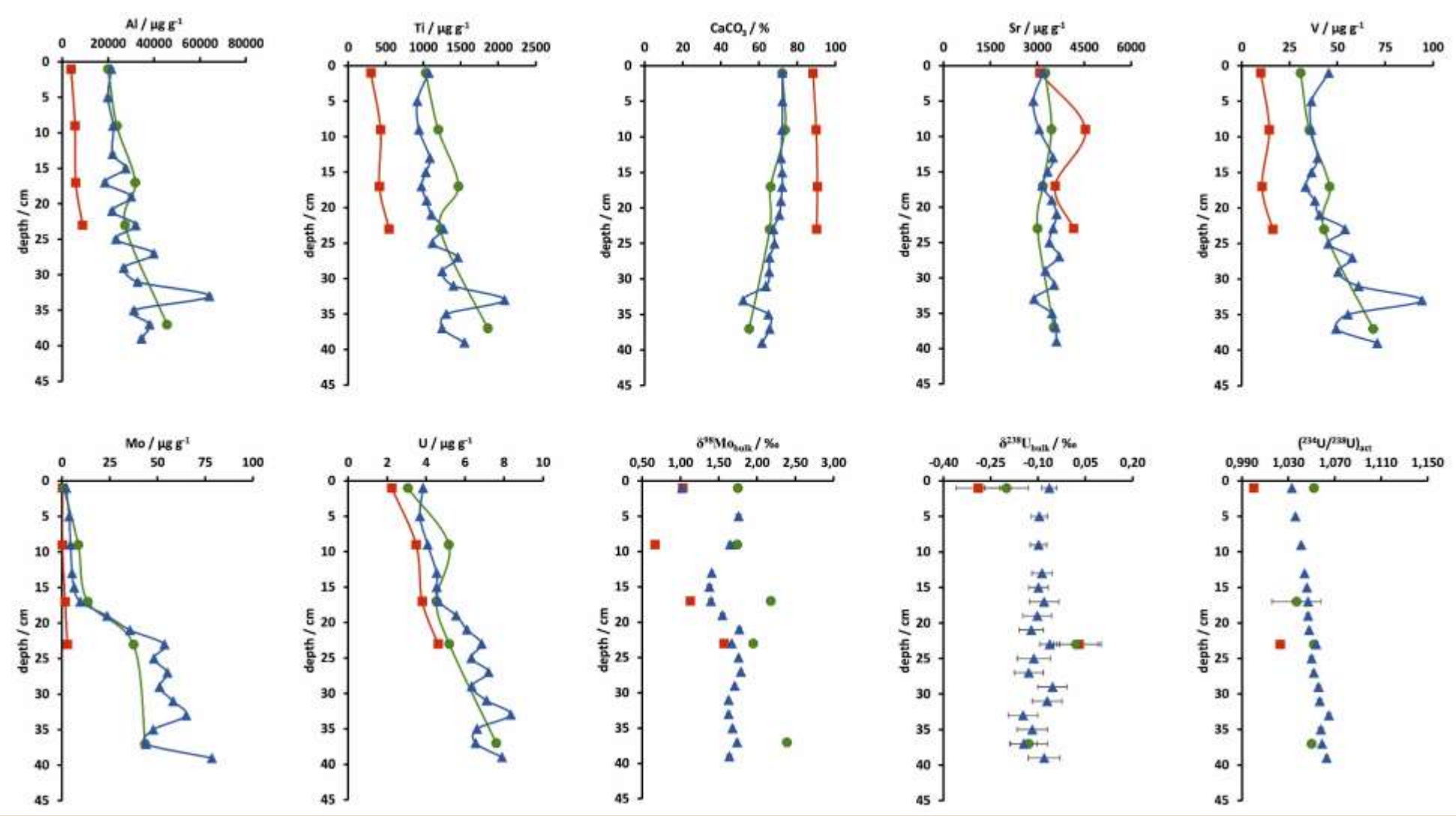
Vogelin, A.R., Nägler, T.F., Samankassou, E. and Villa, I.M. (2009) Molybdenum isotopic composition of modern and Carboniferous carbonates. *Chem. Geol.* **265**, 488-498


Mir Lake
Prokljan Lake
Krka River estuary
Rogoznica Lake
Mljet Lake


13 m
30 m
20 m
CaCO3 content
50%
60%
70%
80%
90%
100%
0
10
20
30
40
13 m
20 m
30 m
depth / cm


Al µg g-1
0
5000
10000
15000
20000
25000
30000
0
5
10
15
20
25
30
35
40
45
dubina / cm

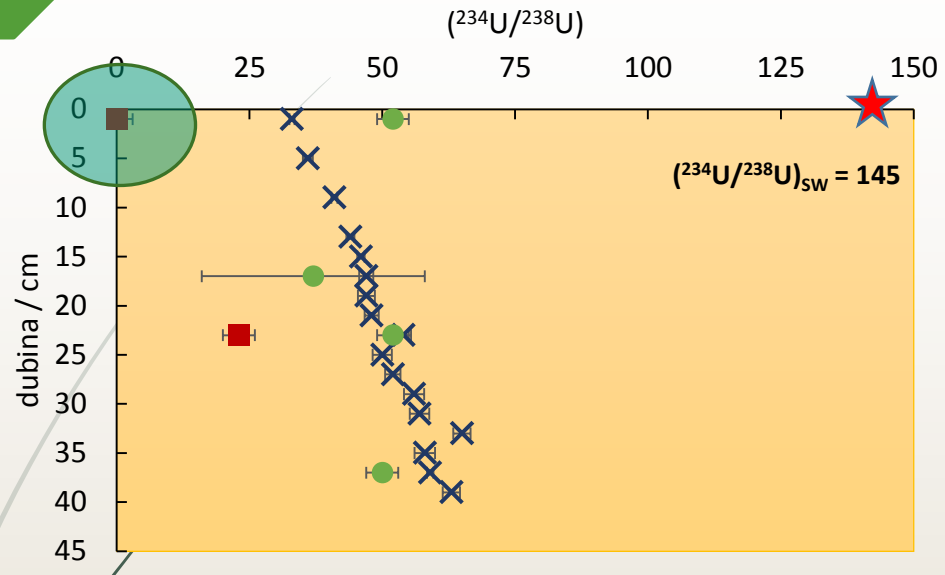

(234U/238U)
0
25
50
75
100
125
150
0
5
10
15
20
25
30
35
40
45
dubina / cm
(234U/238U)sw = 145


Al / µg g-1
Ti / µg g-1
CaCO3 / %
Sr / µg g-1
V / µg g-1
Mo / µg g-1
U / µg g-1
δ98Mobulk / ‰
δ238Ubulk / ‰
(234U/238U)act
depth / cm

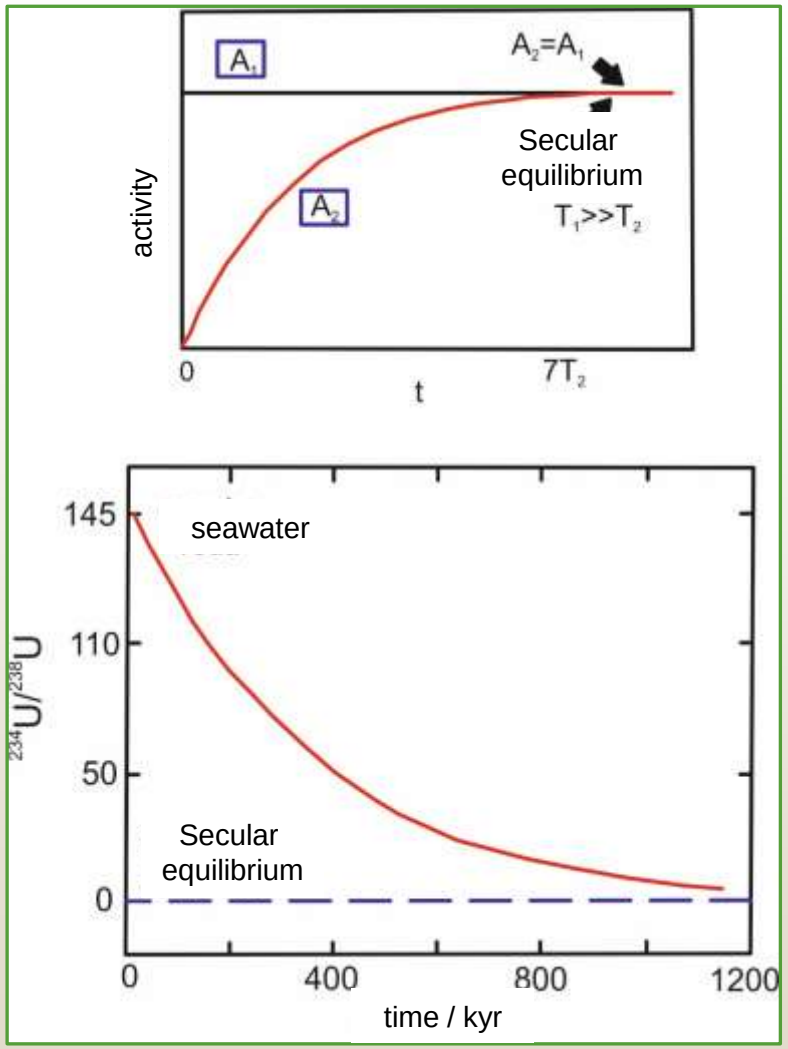
Year	Date	Lake depth / m		Lake depth / m	
		20	25	20 m	25 m
		H_2S / mg l^{-1}	H_2S / mg l^{-1}	H_2S / µmol l^{-1}	H_2S / µmol l^{-1}
1951	13.03.	not detected	1,86		58,13
	19.04.	not detected	3,72		116,25
	18.05.	not detected	2,21		69,06
	17.06.	not detected	2,22		69,38
	13.07.	0,61	3,31	19,06	103,44
	24.08.	0,33	2,96	10,3125	92,50
	04.10.	1,32	2,73	41,25	85,31
	07.11.	not detected	2,53		79,06
	13.12.	not detected	2,35		73,44
1952	15.01.	not detected	2,88		90,00
	21.02.	not detected	4,71		147,19
	06.03.	not detected	3,88		121,25
	31.03.	not detected	3,01		94,06
	02.04.	not detected	1,93		60,31
	05.05.	not detected	3,43		107,19
	07.05.	present	2,88		90,00
	08.06.	present	present		
	10.06.	present	present		
	15.07.	present	present		
	17.07.	present	present		
	19.08.	present	present		
	21.08.	not detected	present		
	25.09.	not detected	present		
	27.09.	not detected	3,17		99,06
	06.11.	1,28	2,33	40,00	72,81
	08.11.	not detected	traces		
	11.12.	4,84	4,95	151,25	154,69
	13.12.	3,83	3,68	115,00	115,00
1953	22.01.	not detected	traces		
	05.03.	not detected	2,93		91,56
	19.05.	pink water, not detected	not detected		
	21.05.	pink water, not detected	not detected		
	24.06.	red water, traces	no data		
	14.08.	present	no data		
	16.08.	present	present		
	23.09.	2,93	3,21	91,56	100,31
	24.11.	not detected	0,20		6,25
1954	20.01.	not detected	not detected		
	12.03.	not detected	not detected		
	27.05.	not detected	not detected		
	21.07.	not detected	not detected		
	20.08.	not detected	not detected		
	25.09.	not detected	not detected		
	24.11.	not detected	1,12		35,00
1955	13.02.	not detected	not detected		
	01.04.	not detected	not detected		
	25.09.	present	present		

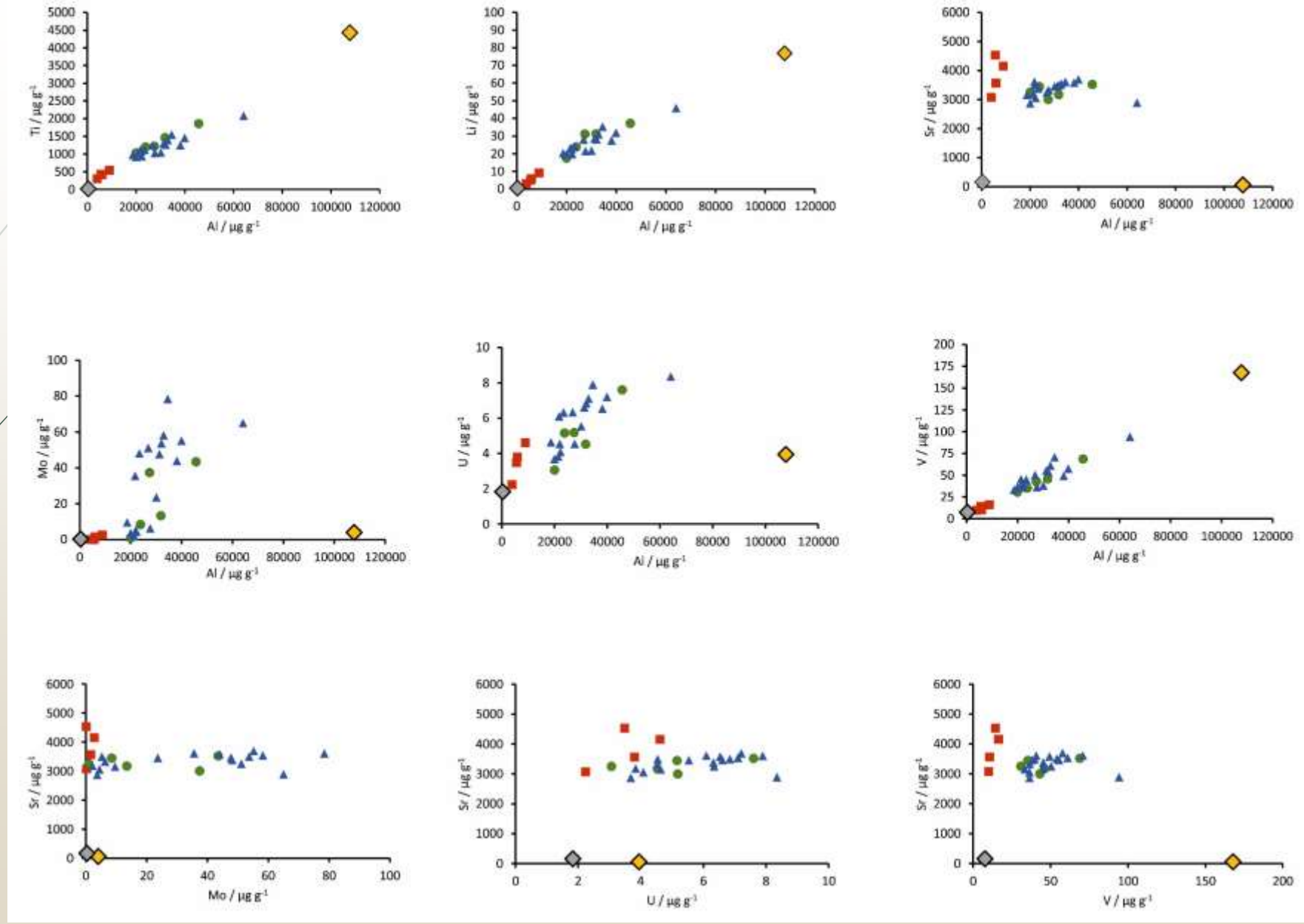
H_2S concentration in Malo Jezero water column from 1951 to 1961 (concentration were taken from Buljan and Špan, 1976).

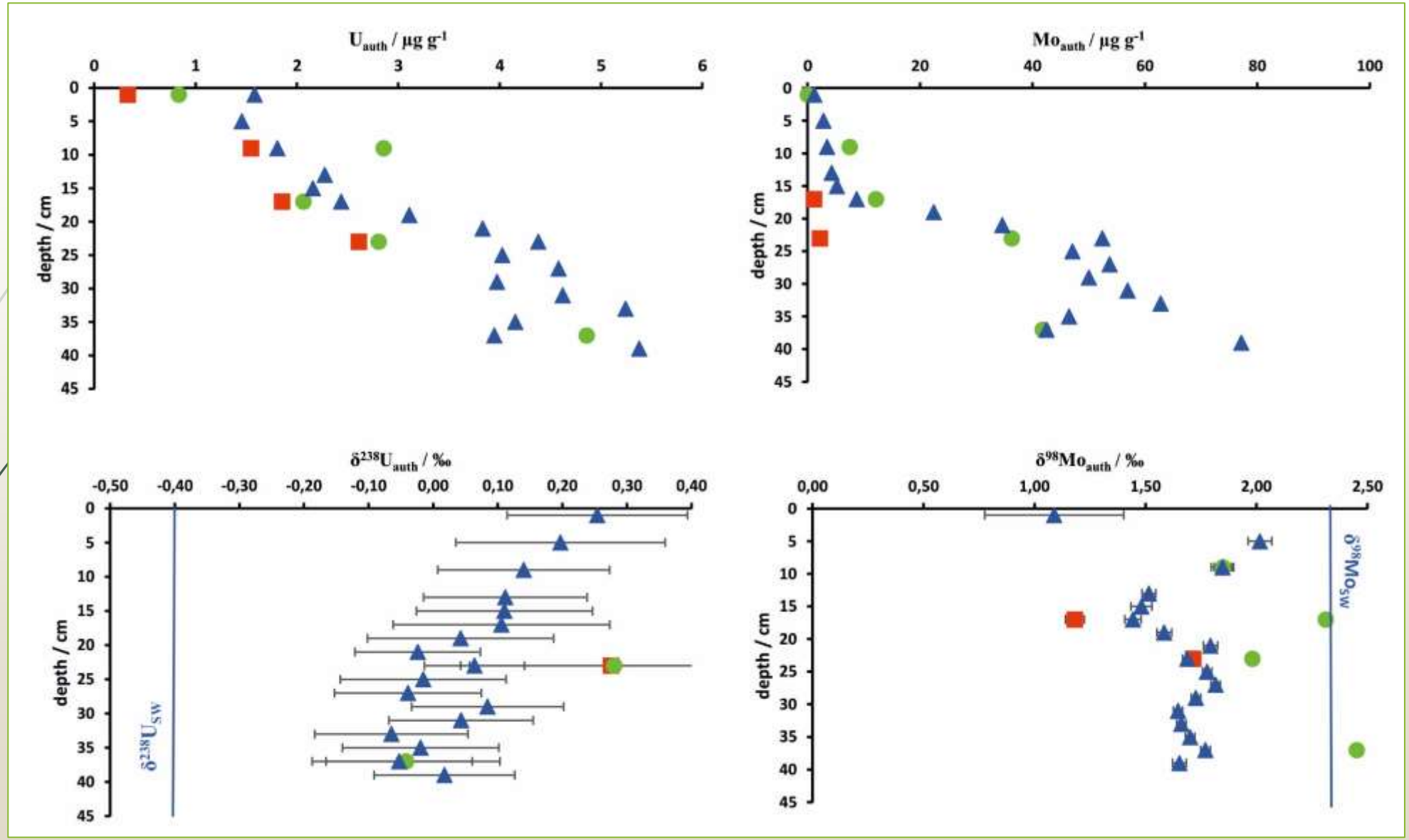
Velik udio terigenog materijala (karbonatni detritus)



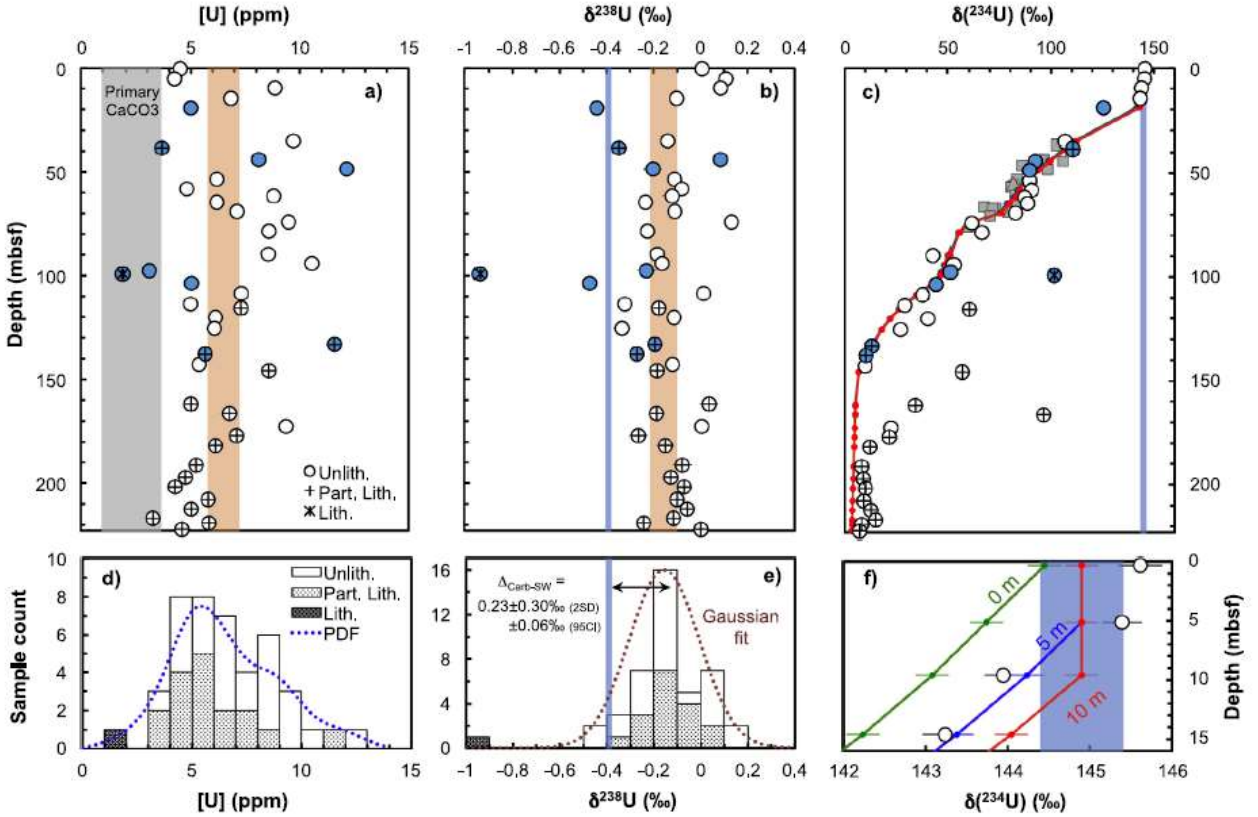
- **$^{234}U/^{238}U = 0$**
- **[U] = 3.30 µg g^{-1}**
- **$\delta^{238}U$ = -0.29‰ (±0.07).**




Ti / µg g-1
Al / µg g-1
Li / µg g-1
Al / µg g-1
Sr / µg g-1
Al / µg g-1
Mo / µg g-1
Al / µg g-1
U / µg g-1
Al / µg g-1
V / µg g-1
Al / µg g-1
Sr / µg g-1
Mo / µg g-1
Sr / µg g-1
U / µg g-1
Sr / µg g-1
V / µg g-1

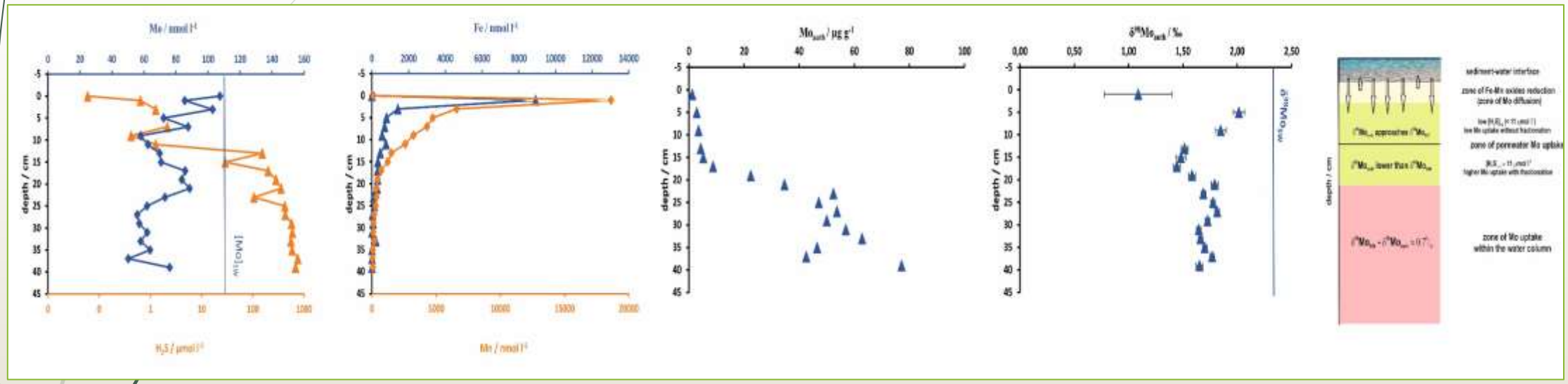

U_{auth} / µg g^{-1}
depth / cm
Mo_{auth} / µg g^{-1}
depth / cm
$\delta^{238}U_{auth}$ / ‰
depth / cm
$\delta^{238}U_{SW}$
$\delta^{98}Mo_{auth}$ / ‰
depth / cm
$\delta^{98}Mo_{SW}$

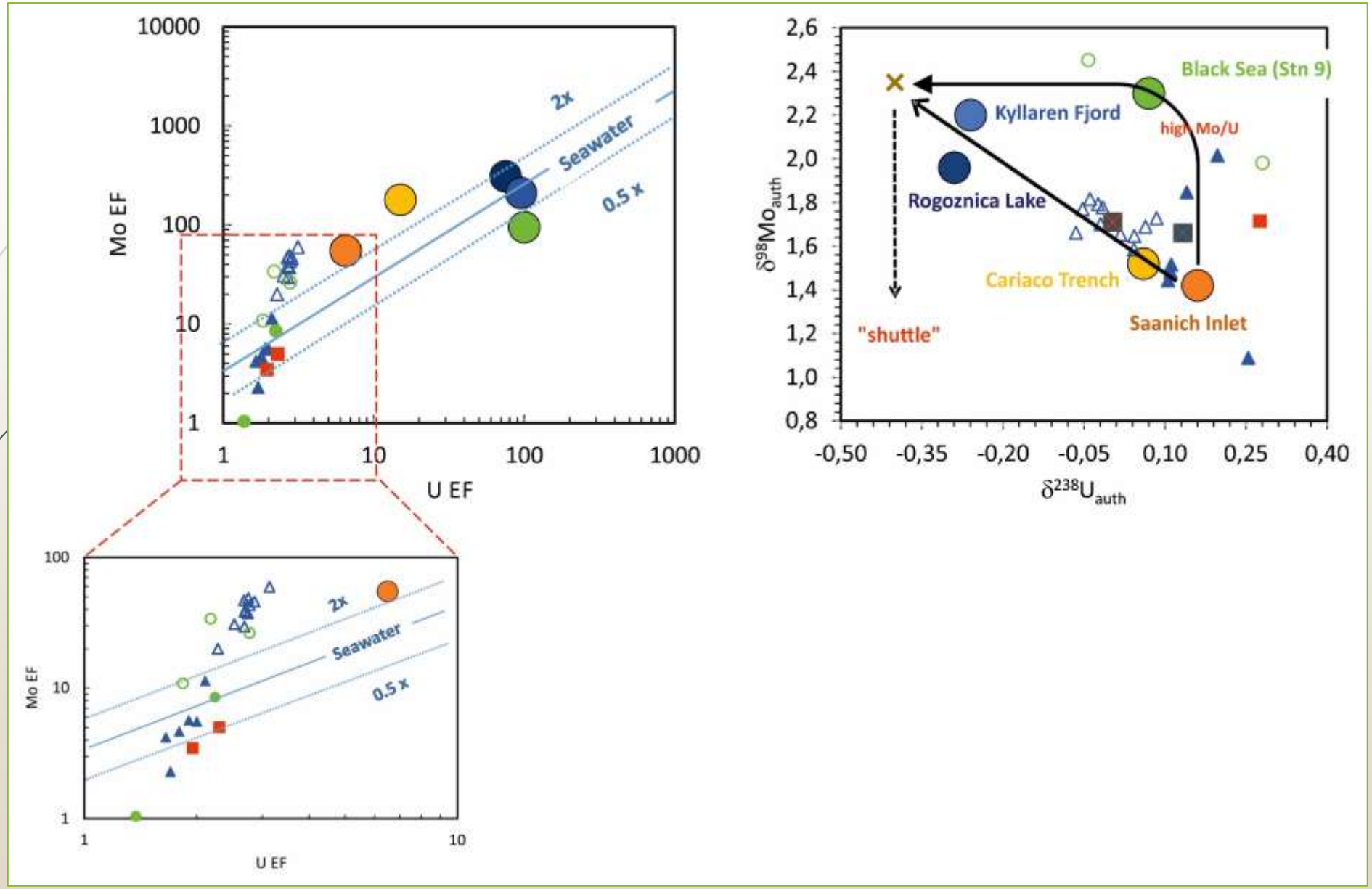
+0.24 ± 0.06‰

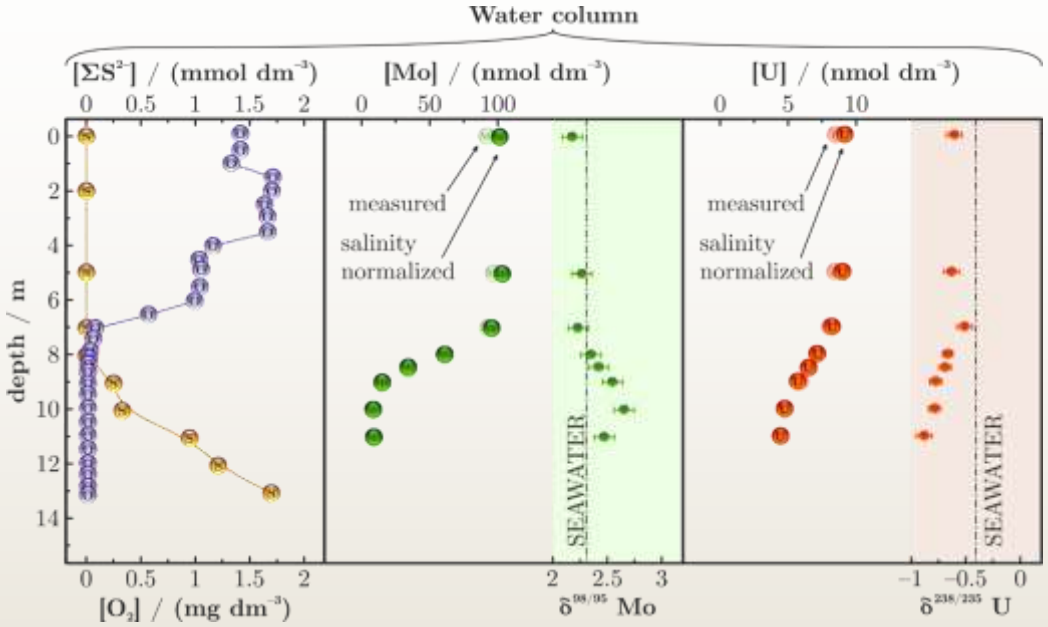


Concentration (a) and U isotope composition (b, c and f) depth profiles in the "central cut" (Step 2) of Site 1009 carbonates. Concentration and $\delta^{238}U$ histograms are also shown (d and e). Orange vertical bars represent the average of the dataset and blue vertical bars show the seawater value. Blue filled circles denote samples deposited during sea-level lowstands. Symbols: ○ = unlithified, ⊕ = partially lithified, ⊗ = lithified. On panel (c) and (f), the green, blue, and red curves show the expected $\delta(^{234}U)$ depth profiles calculated assuming that the samples formed with the seawater composition and closed, respectively, 0, 5, and 10 m below the water-sediment interface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

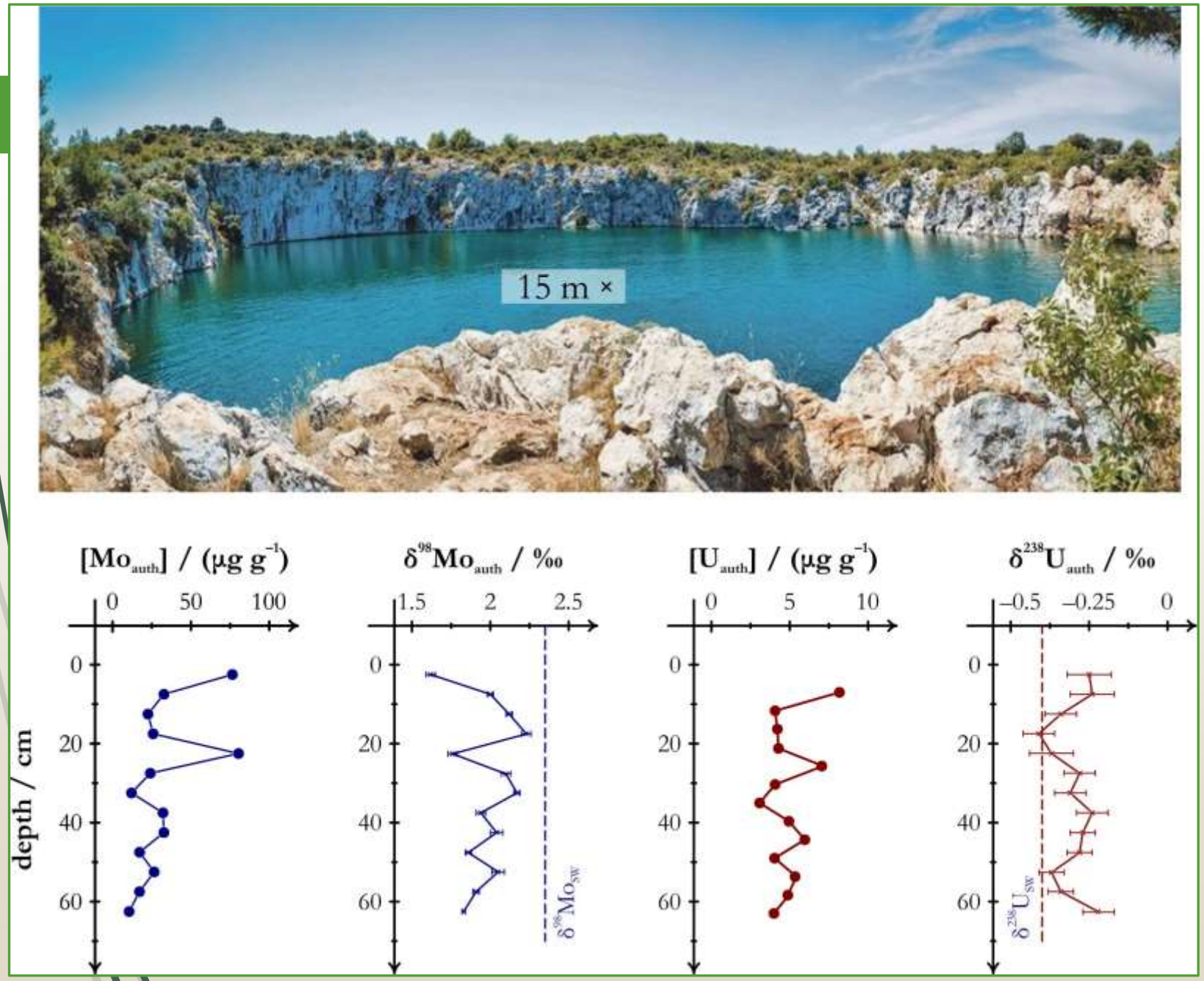
Tissot, F.L.H., Chen, C., Go, B.M., Nazeimiec, M., Healy, G., Bekker, A., Swart, P.L., Dauphas, N. (2018) Controls of eustasy and diagenesis on the $^{238}U/^{235}U$ of carbonates and evolution of the seawater ($^{234}U/^{238}U$) during the last 1.4 Myr. Geochimica et Cosmochimica Acta **242**, 233-265.


Mo / nmol l-1
depth / cm
H2S / µmol l-1
Fe / nmol l-1
Mn / nmol l-1
Mosolid / µg g-1
δ98Mosolid / ‰
sediment-water interface
zone of Fe-Mn oxides reduction (zone of Mo diffusion)
zone of porewater Mo uptake
zone of Mo uptake within the water column

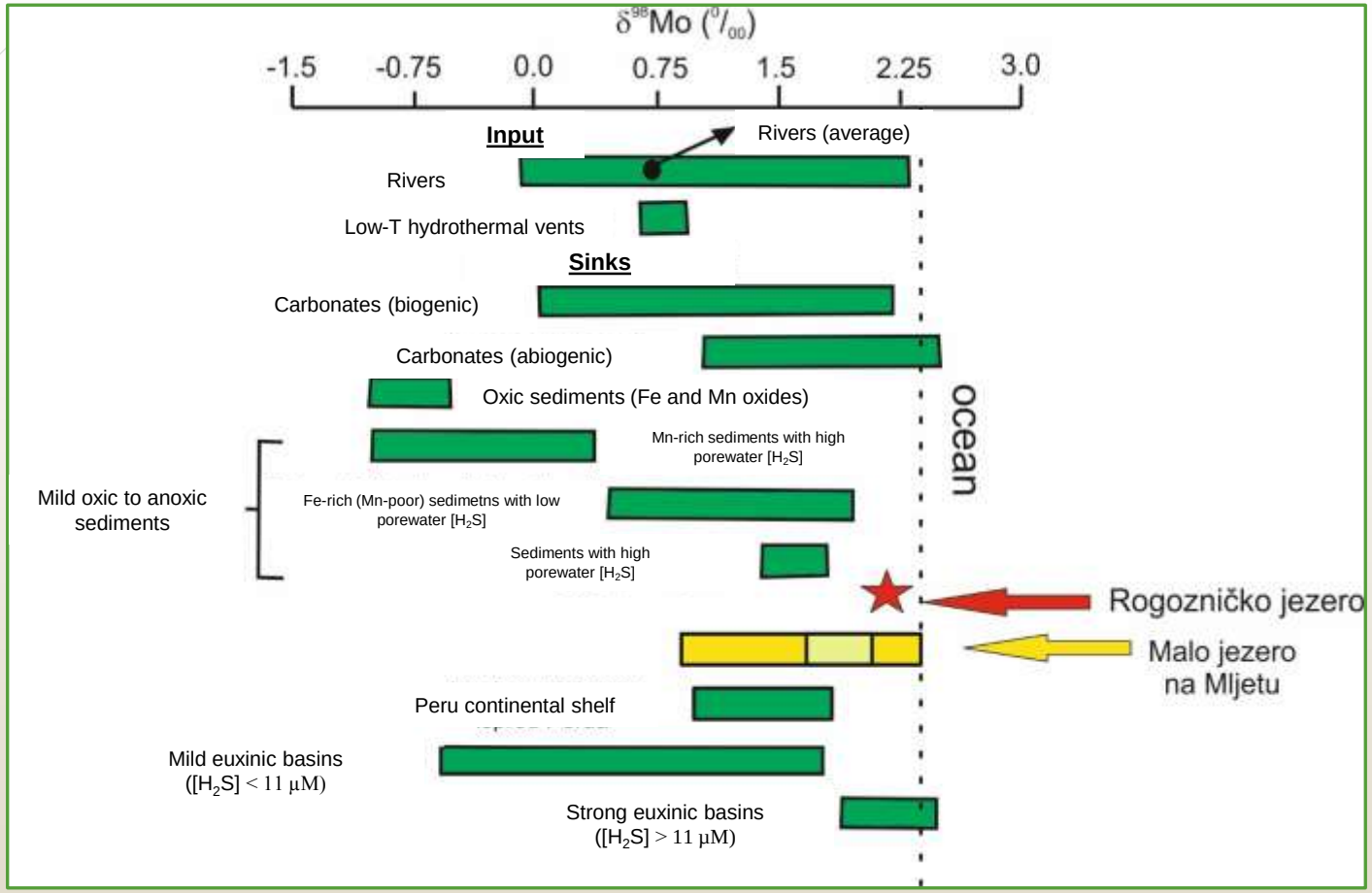

10000
1000
100
10
1
Mo EF
1
10
100
1000
U EF
2x
Seawater
0.5 x
100
10
1
Mo EF
1
10
U EF
2x
Seawater
0.5 x
2,6
2,4
2,2
2,0
1,8
1,6
1,4
1,2
1,0
0,8
$\delta^{98}Mo_{auth}$
-0,50
-0,35
-0,20
-0,05
0,10
0,25
0,40
$\delta^{238}U_{auth}$
Black Sea (Stn 9)
Kyllaren Fjord
high Mo/U
Rogoznica Lake
Cariaco Trench
Saanich Inlet
"shuttle"



Depth profiles of dissolved $\delta^{238}U$ and $\delta^{98}Mo$ at Rogoznica Lake in October 2013



Bura-Nakić, E., Andersen, M.B., Archer, C., de Souza, G.F., Marguš, M., Vance, D., 2017. Coupled Mo-U abundances and isotopes in a small marine euxinic basin: constraints on processes in euxinic basins. Submitirano u **Geochimica et Cosmochimica Acta**


δ98Mo (‰)
-1.5
-0.75
0.0
0.75
1.5
2.25
3.0
Input
Rivers (average)
Rivers
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Sinks
Carbonates (biogenic)
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Sediments with high porewater [H2S]
ocean
Rogozničko jezero
Malo jezero na Mljetu
Peru continental shelf
Mild euxinic basins ([H2S] < 11 μM)
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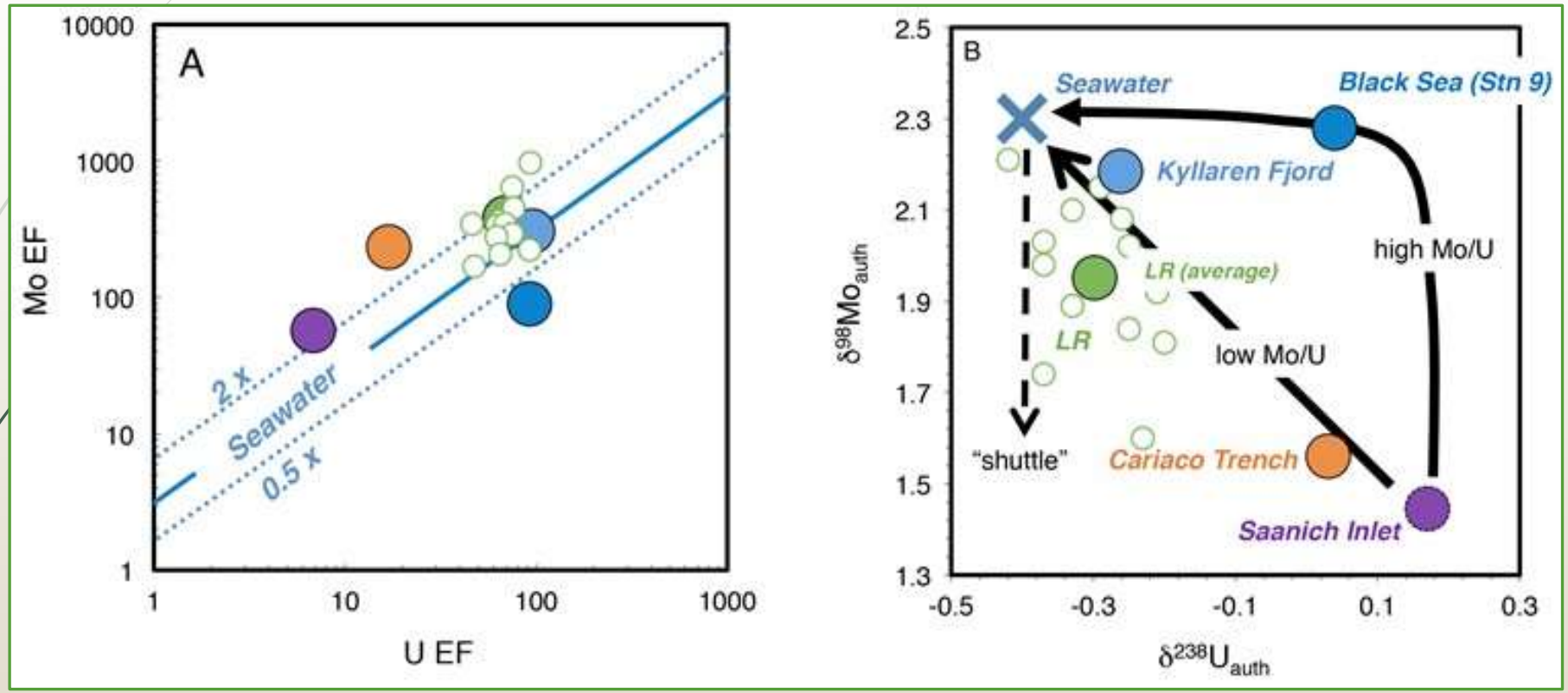
Bura-Nakić, E., Andersen, M.B., Archer, C., de Souza, G.F., Marguš, M., Vance, D., 2017. Coupled Mo-U abundances and isotopes in a small marine euxinic basin: constraints on processes in euxinic basins. Submitirano u **Geochimica et Cosmochimica Acta**

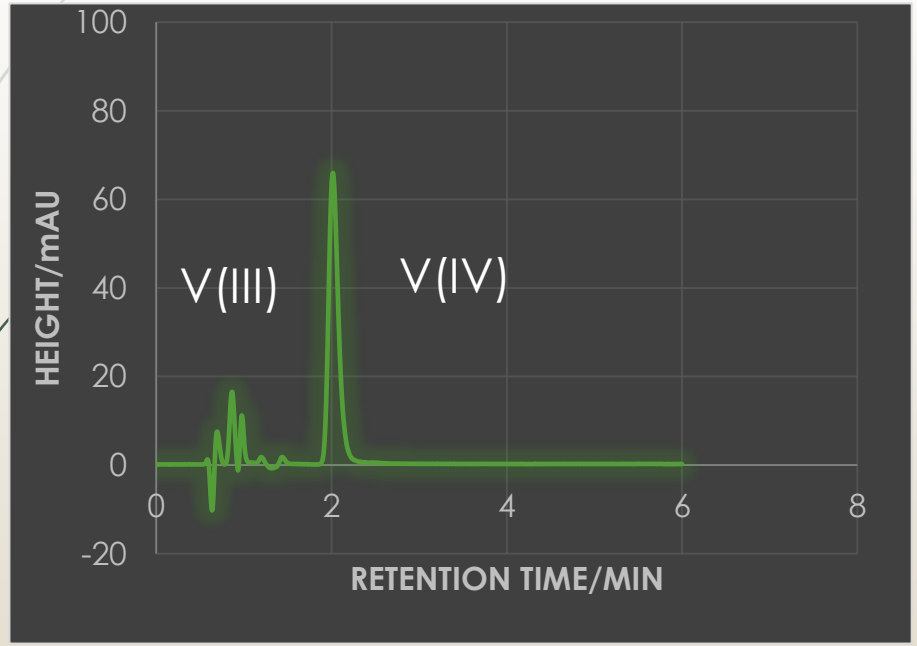


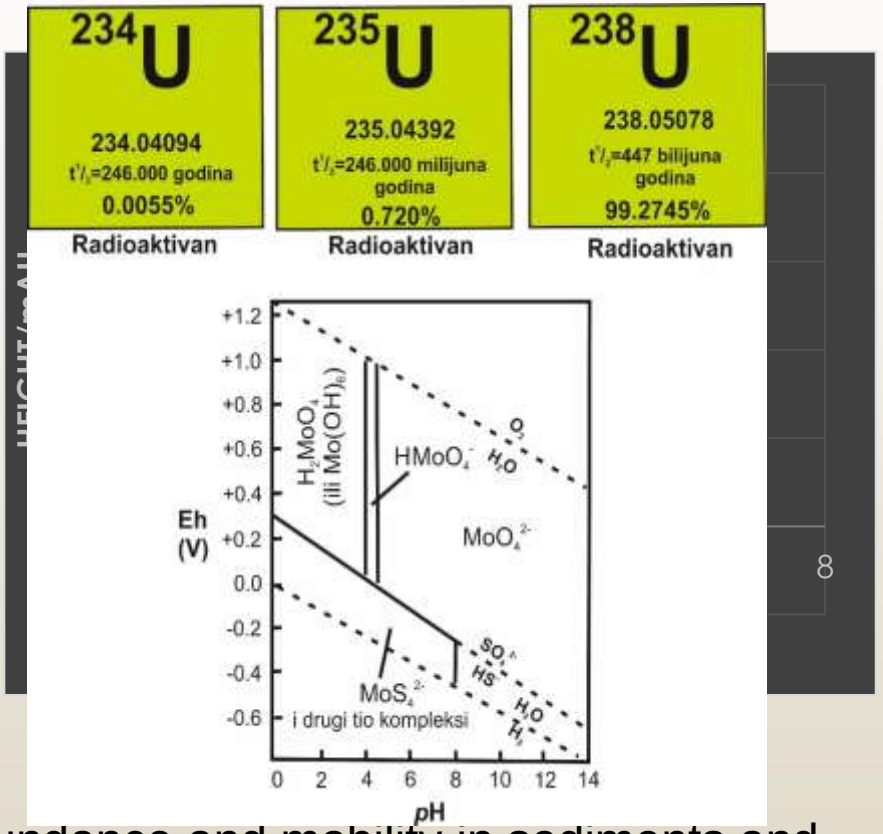
„Geochemistry and redox proxie's signature under the diverse environmental conditions: towards better understanding of the past redox"

REDOX

i.) improve the usage of coupled Mo-U abundance and isotopic composition as redox proxy;

ii.) development/implementation of specific analytical procedures for determining V redox speciation and Re pre-concentration;





iii.) determine the processes controlling Re and V abundance and mobility in sediments and overlying waters spanning oxic, hypoxic and anoxic conditions.

oxygen

anoxic conditions

oxic conditions

O_2

Black sea (H_2S~80 μM)

Rogoznica Lake (H_2S~1000 μM)

Prokljan Lake (seasonally anoxic)

Mir Lake (seasonally anoxic)

Mljet Lake (seasonally hypoxic)

ocean

Krka River estuary

Adriatic Sea

redox sensitive metals abundance

Thank you on your attention!

This work has been fully supported-supported in part by Croatian Science Foundation under the project IP-2018-01-7813

„Geochemistry and redox proxie's signature under the diverse environmental conditions: towards better understanding of the past redox" REDOX