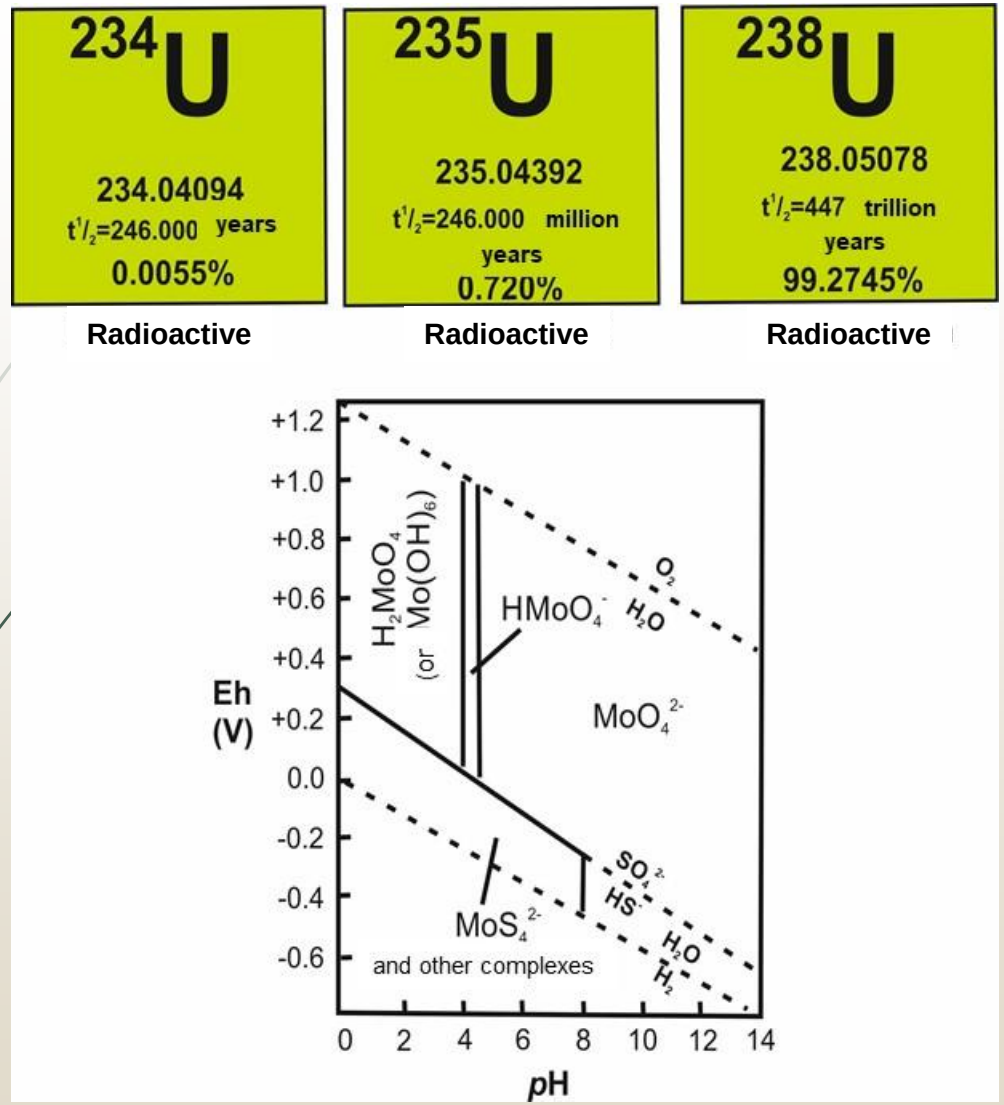

Isotopic and geochemical characteristics of uranium and molybdenum

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Bijenička 54, 10 000 Zagreb

MEBTRACE workshop - 13th July 2019, Šibenik, Croatia

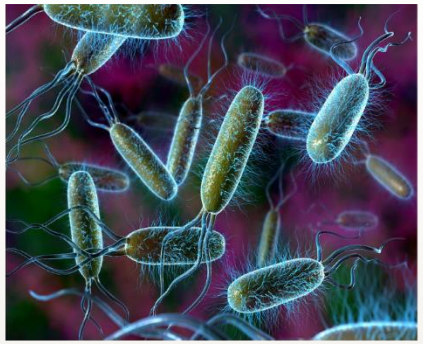
„Geochemistry and redox proxie's signature under the diverse environmental conditions: towards better understanding of the past redox"

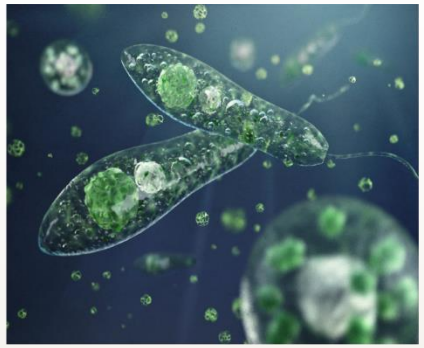
REDOX

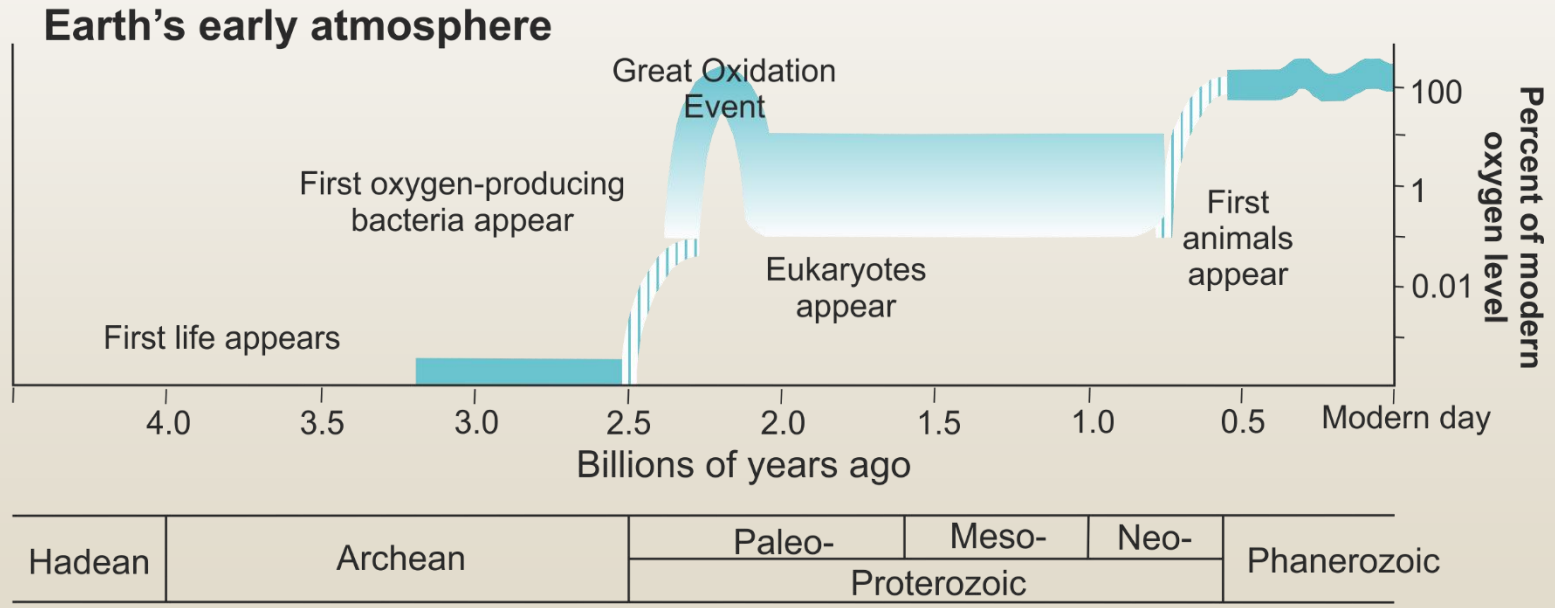
Research within this project is funded by Croatian Science Foundation, under the project number: IP-2018-01-7813, "REDOX"

- Overview (state of the art in the research area)

Evolution of Earth's atmosphere through time

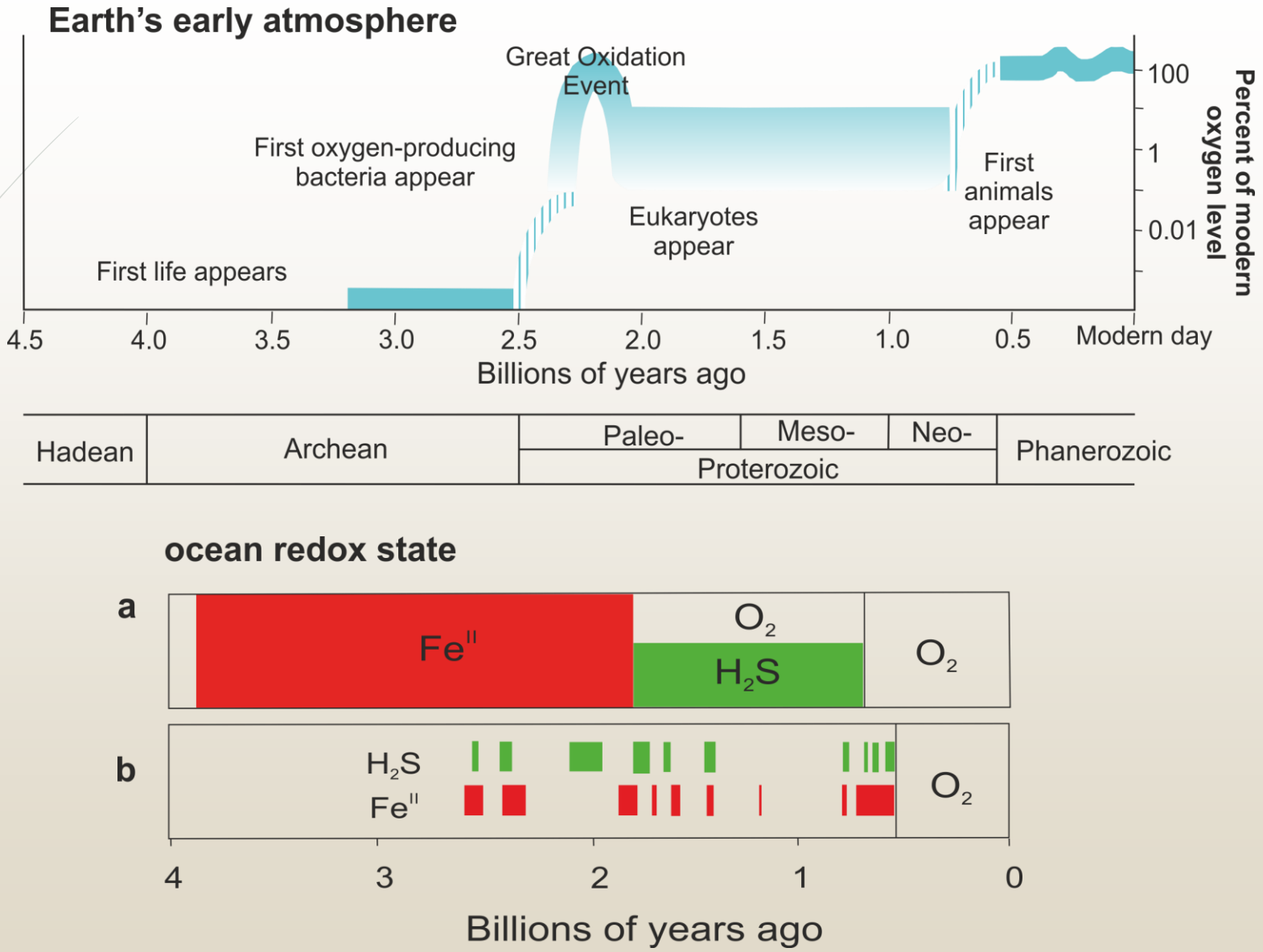






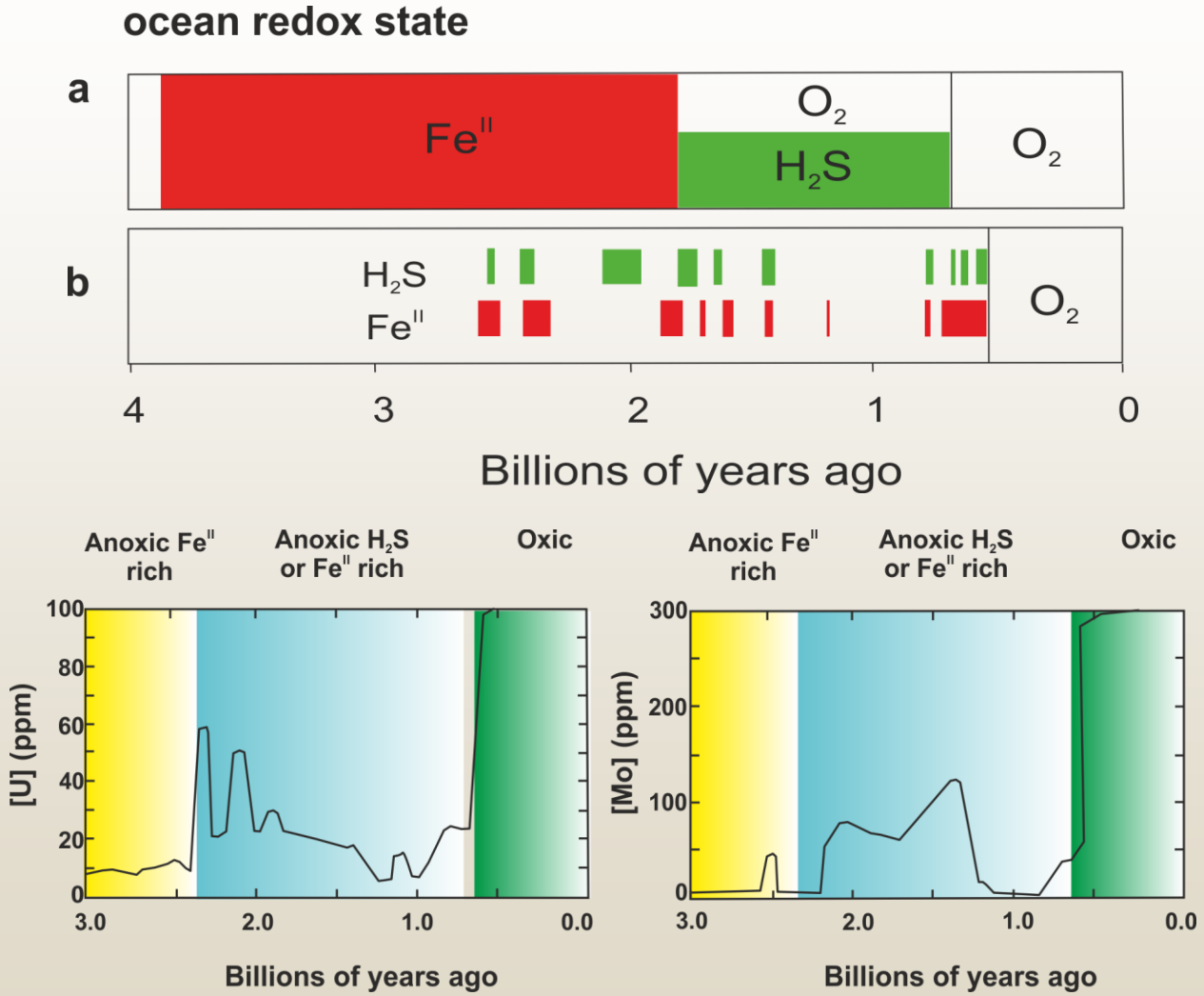
Modified after TW Lyons et al. Nature **506**, 307-315 (2014)

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

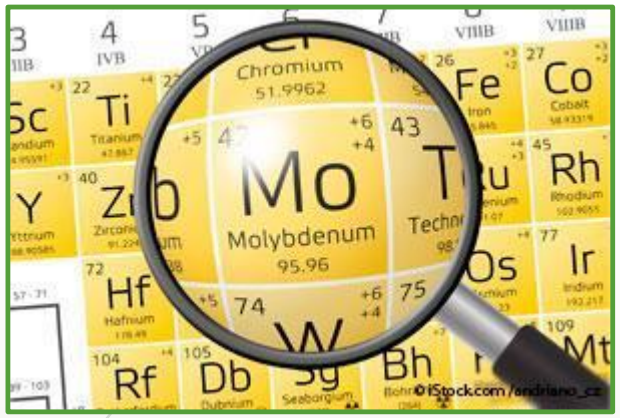


Modified after *TW Lyons et al. Nature* **506**, 307-315 (2014)
and after *NJ Planavsky et al. Nature* **477**, 448-452 (2011)

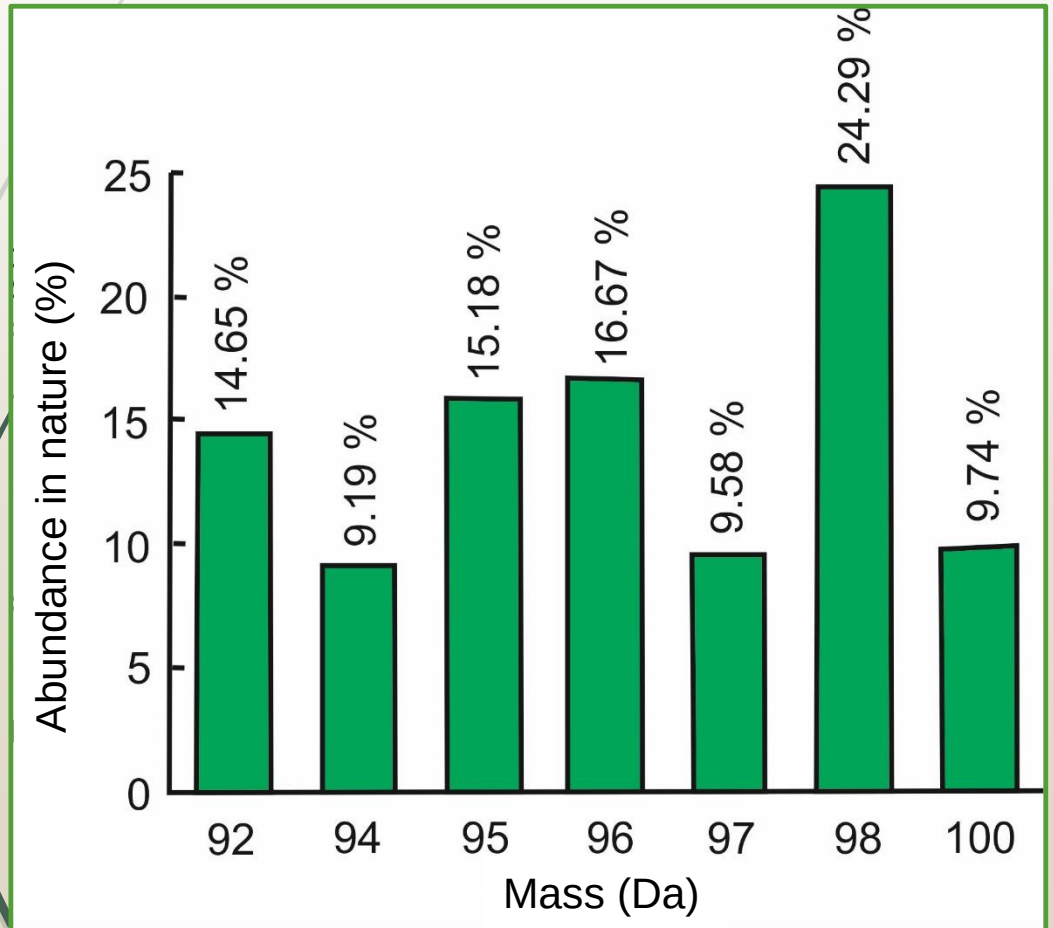
Co-evolution of ocean redox state and Mo and U sedimentary concentrations through time



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

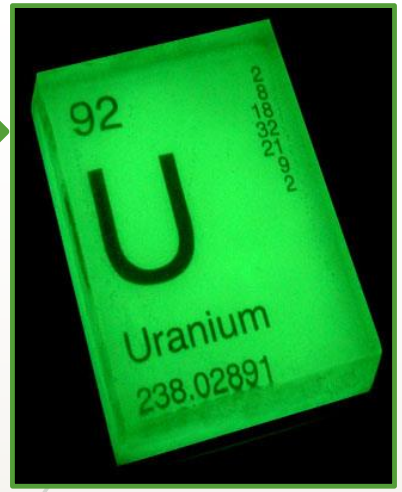


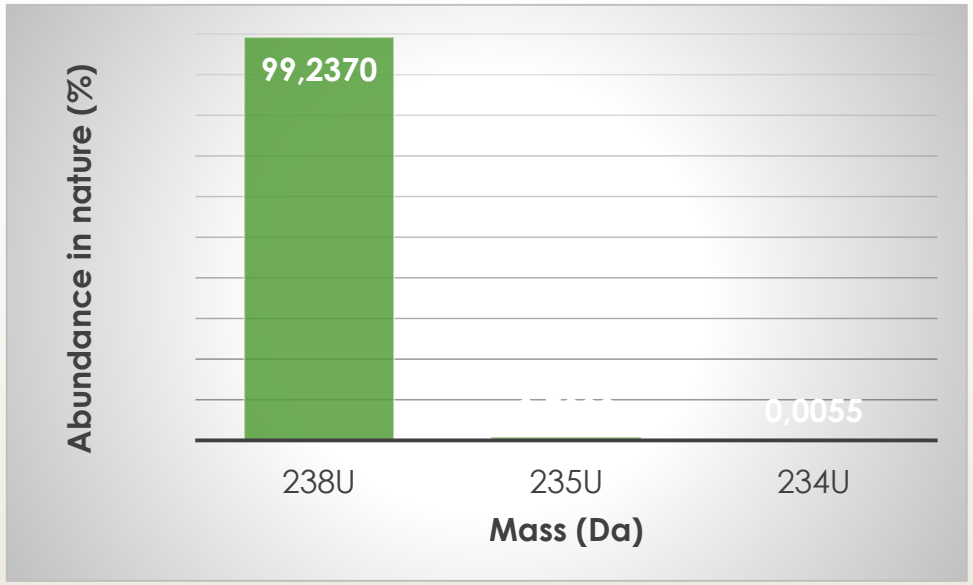
„molybdos" – simmilar to lead



$$\delta^{98}Mo_{sample}{}^{(‰)}=[{}^{98/95}Mo_{sample}/{}^{98/95}Mo_{standard}\ -1]\times 1000$$

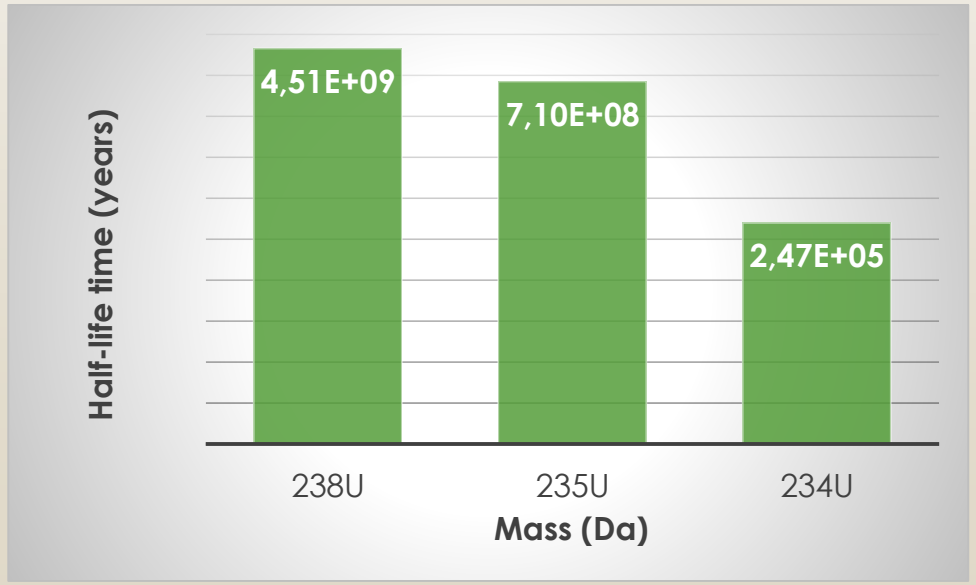
Uranium in nature – mixture of three long lived isotopes

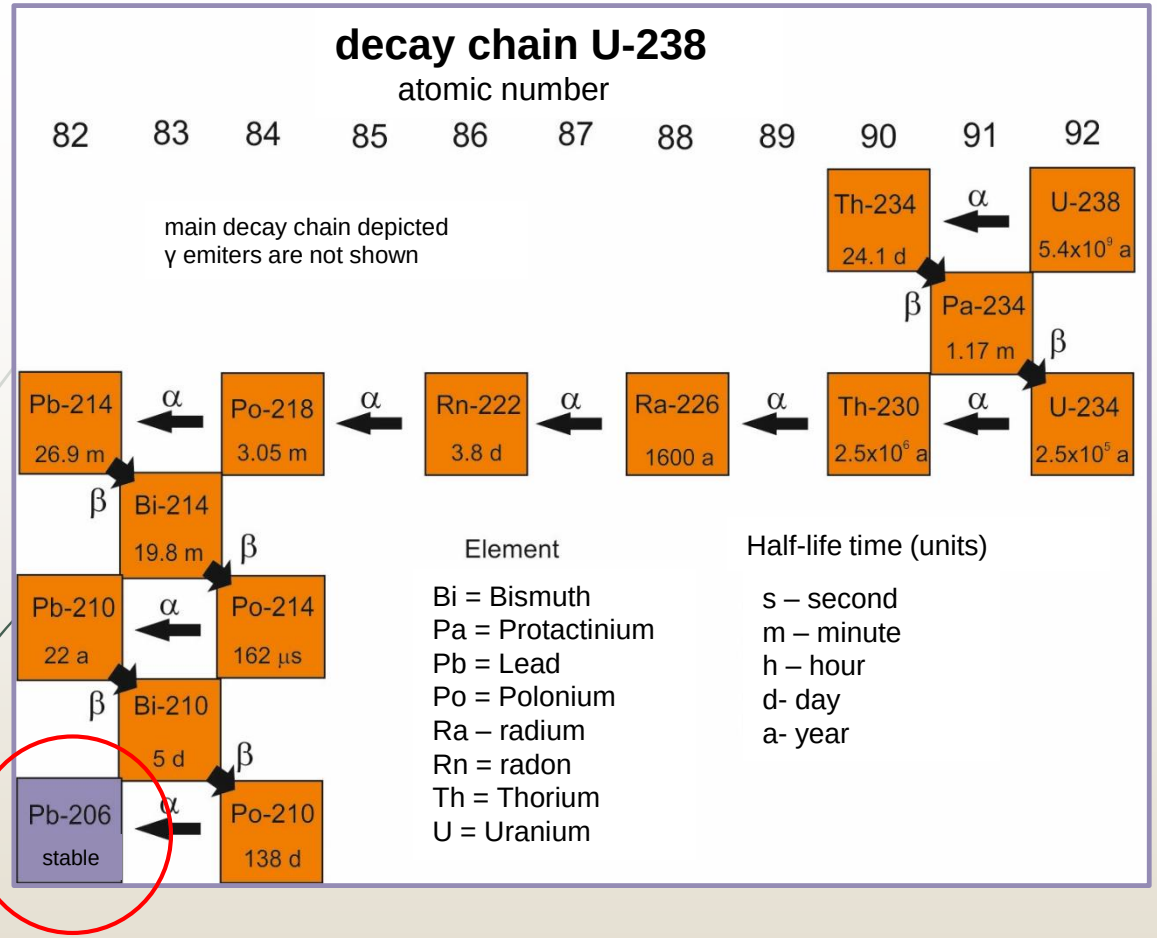


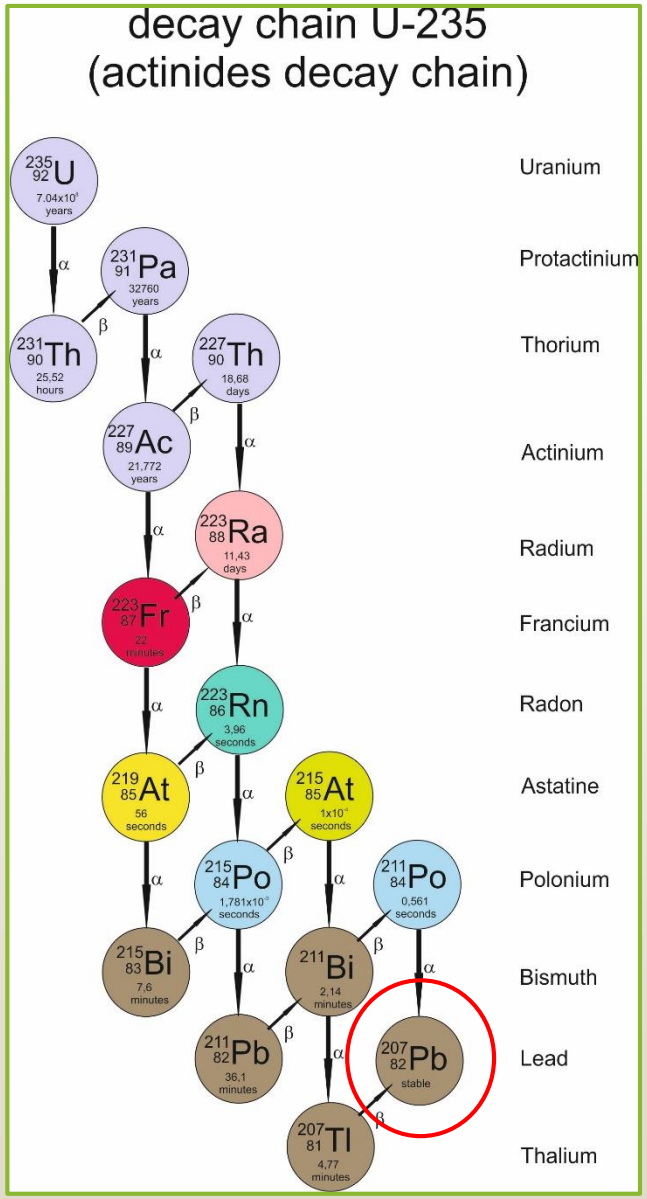


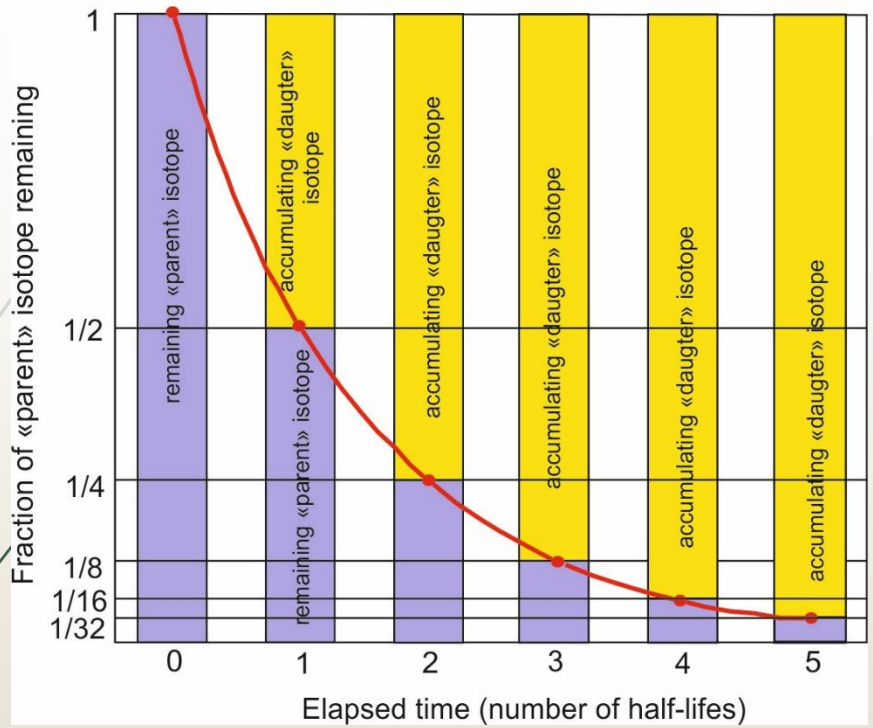
$$\delta^{238}U_{sample}(‰)=[^{238/235}U_{sample}/^{238/235}U_{standard} -1] \times 1000$$

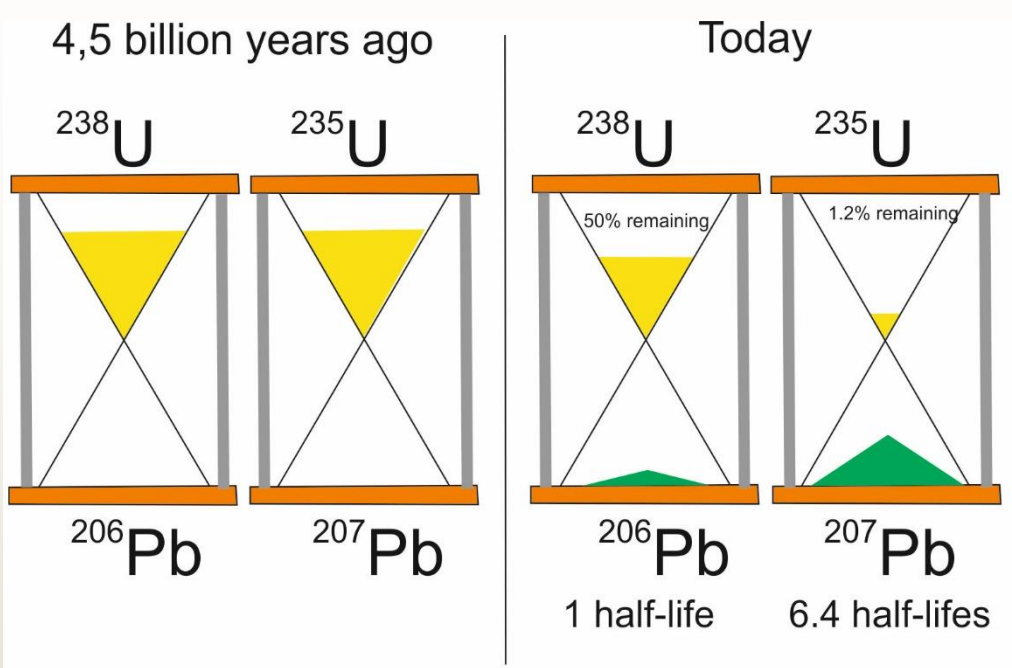
$$\delta^{234}U_{sample}(‰)=[^{234/238}U_{sample}/^{234/235}U_{sec.eq.} -1] \times 1000$$

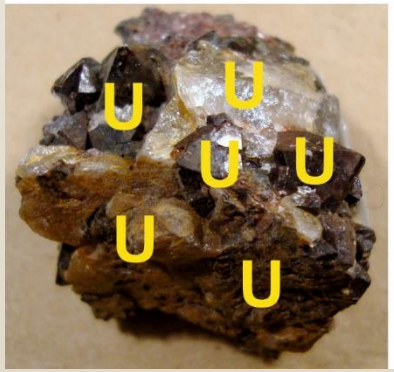


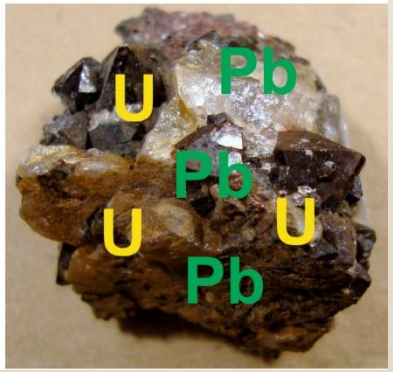

decay chain U-238
atomic number
82 83 84 85 86 87 88 89 90 91 92
main decay chain depicted
γ emitters are not shown
Th-234 24.1 d
U-238 5.4x10⁹ a
Pa-234 1.17 m
Pb-214 26.9 m
Po-218 3.05 m
Rn-222 3.8 d
Ra-226 1600 a
Th-230 2.5x10⁶ a
U-234 2.5x10⁵ a
Bi-214 19.8 m
Pb-210 22 a
Po-214 162 μs
Bi-210 5 d
Pb-206 stable
Po-210 138 d
α
β
Element
Bi = Bismuth
Pa = Protactinium
Pb = Lead
Po = Polonium
Ra – radium
Rn = radon
Th = Thorium
U = Uranium
Half-life time (units)
s – second
m – minute
h – hour
d- day
a- year


decay chain U-235
(actinides decay chain)
Uranium
Protactinium
Thorium
Actinium
Radium
Francium
Radon
Astatine
Polonium
Bismuth
Lead
Thalium

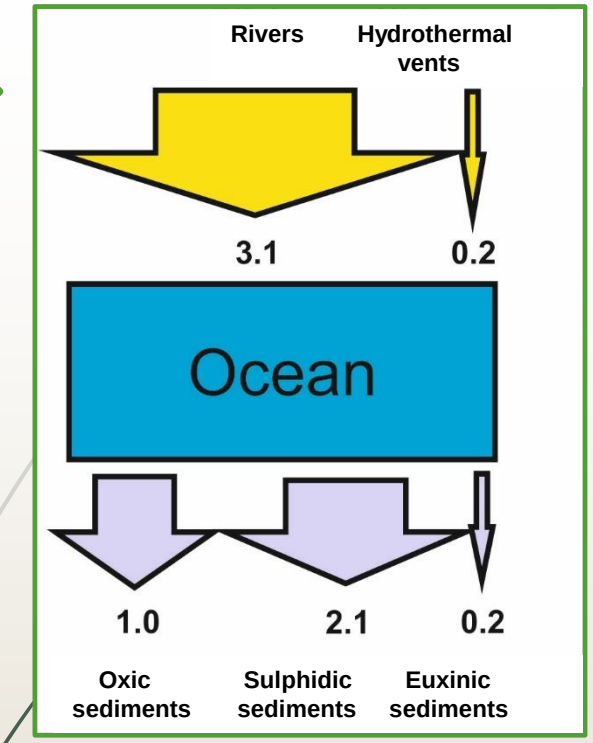

Fraction of «parent» isotope remaining
1
1/2
1/4
1/8
1/16
1/32
0
1
2
3
4
5
Elapsed time (number of half-lifes)
remaining «parent» isotope
accumulating «daugter» isotope
remaining «parent» isotope
accumulating «daugter» isotope
accumulating «daugter» isotope
accumulating «daugter» isotope
accumulating «daugter» isotope

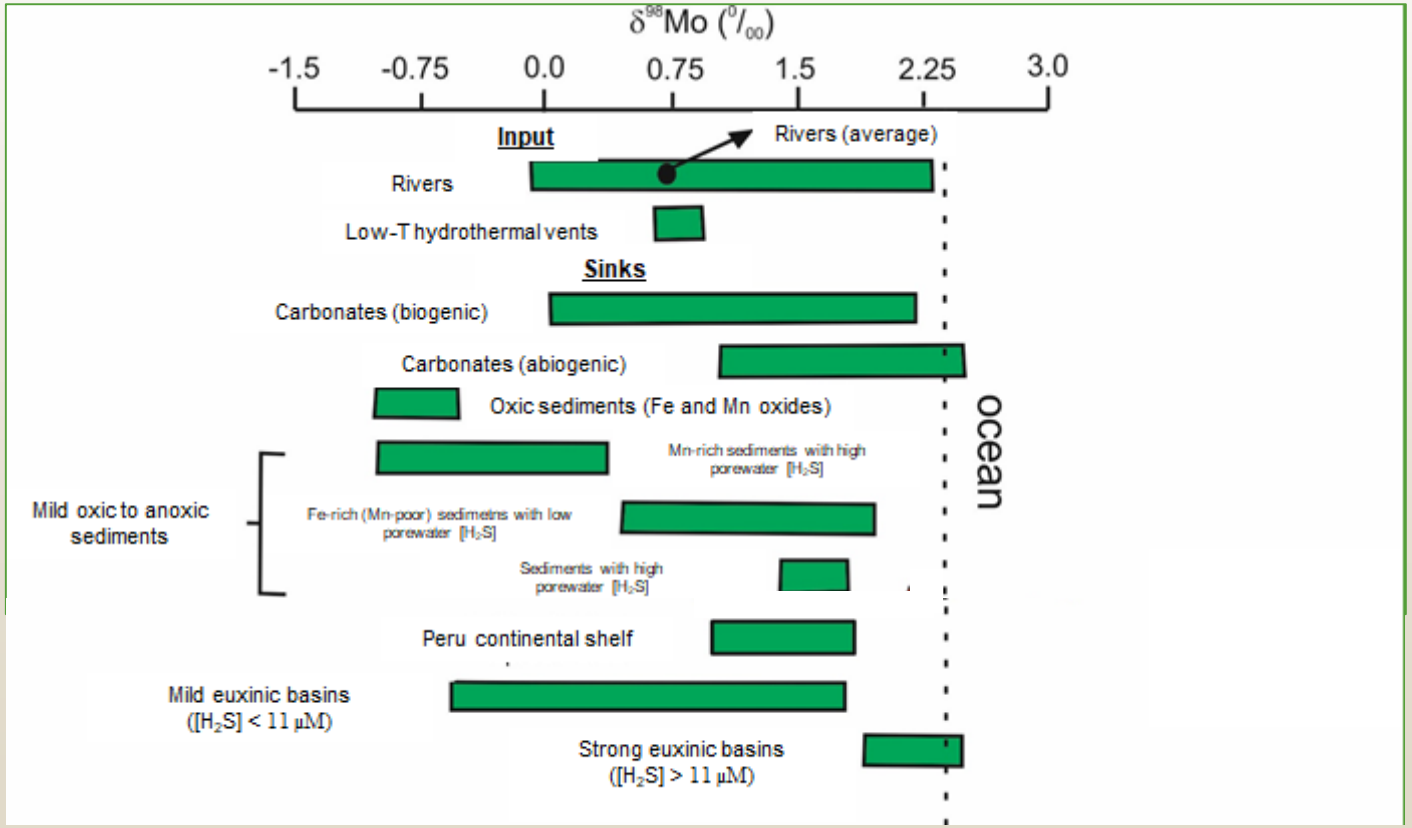

4,5 billion years ago
Today
238U
235U
206Pb
207Pb
238U
235U
50% remaining
1.2% remaining
206Pb
207Pb
1 half-life
6.4 half-lifes

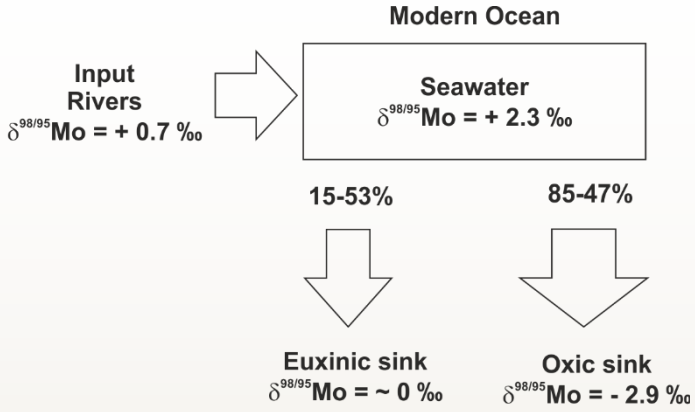

U
U
U
U
U
U


Pb
U
Pb
U
U
Pb

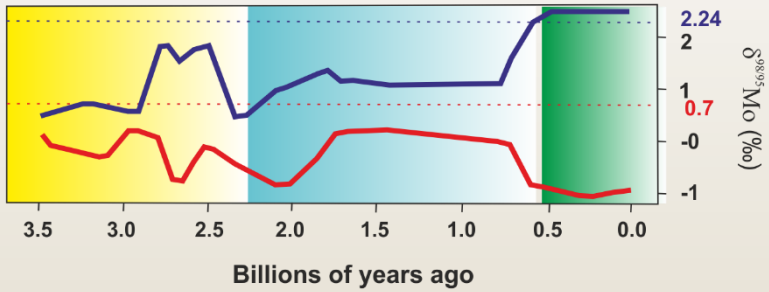
estimated Mo fluks (10^8 mol/year)

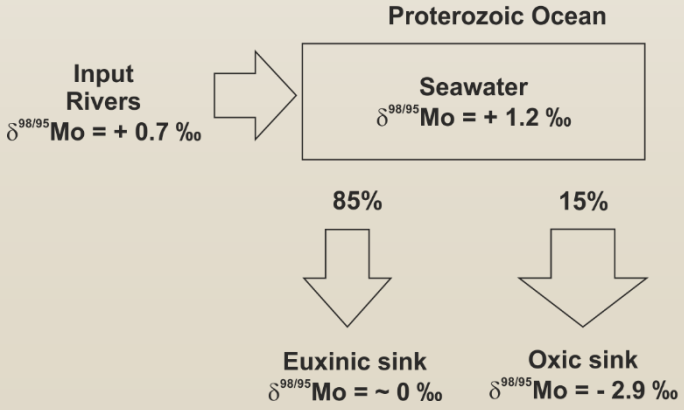






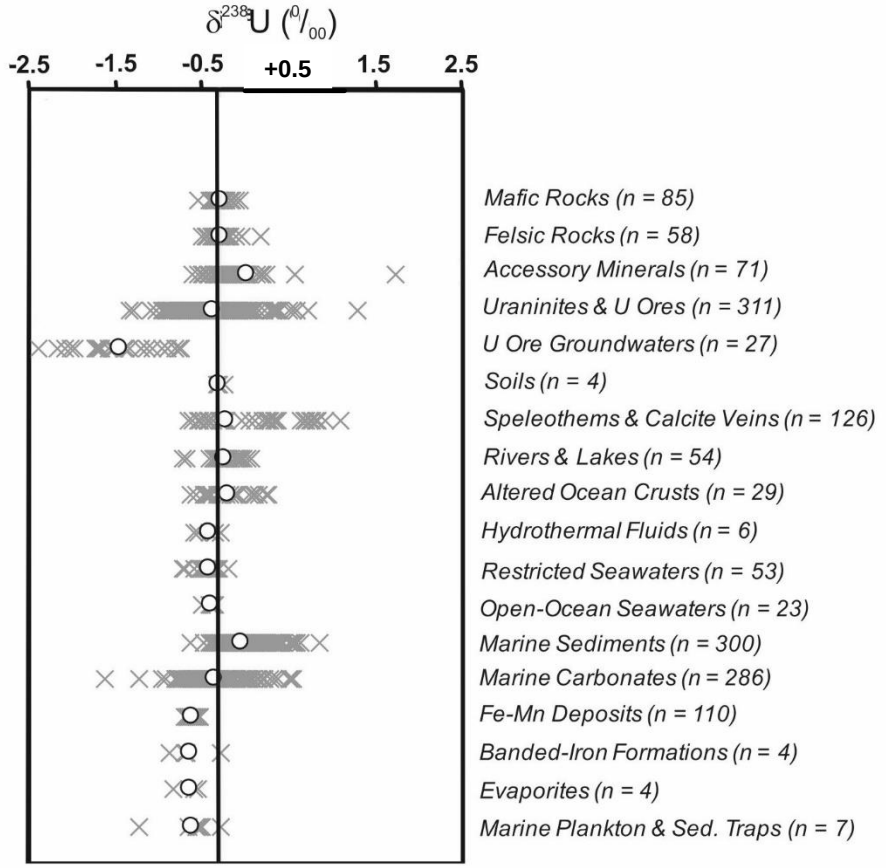
Oxic Mo sink predominates

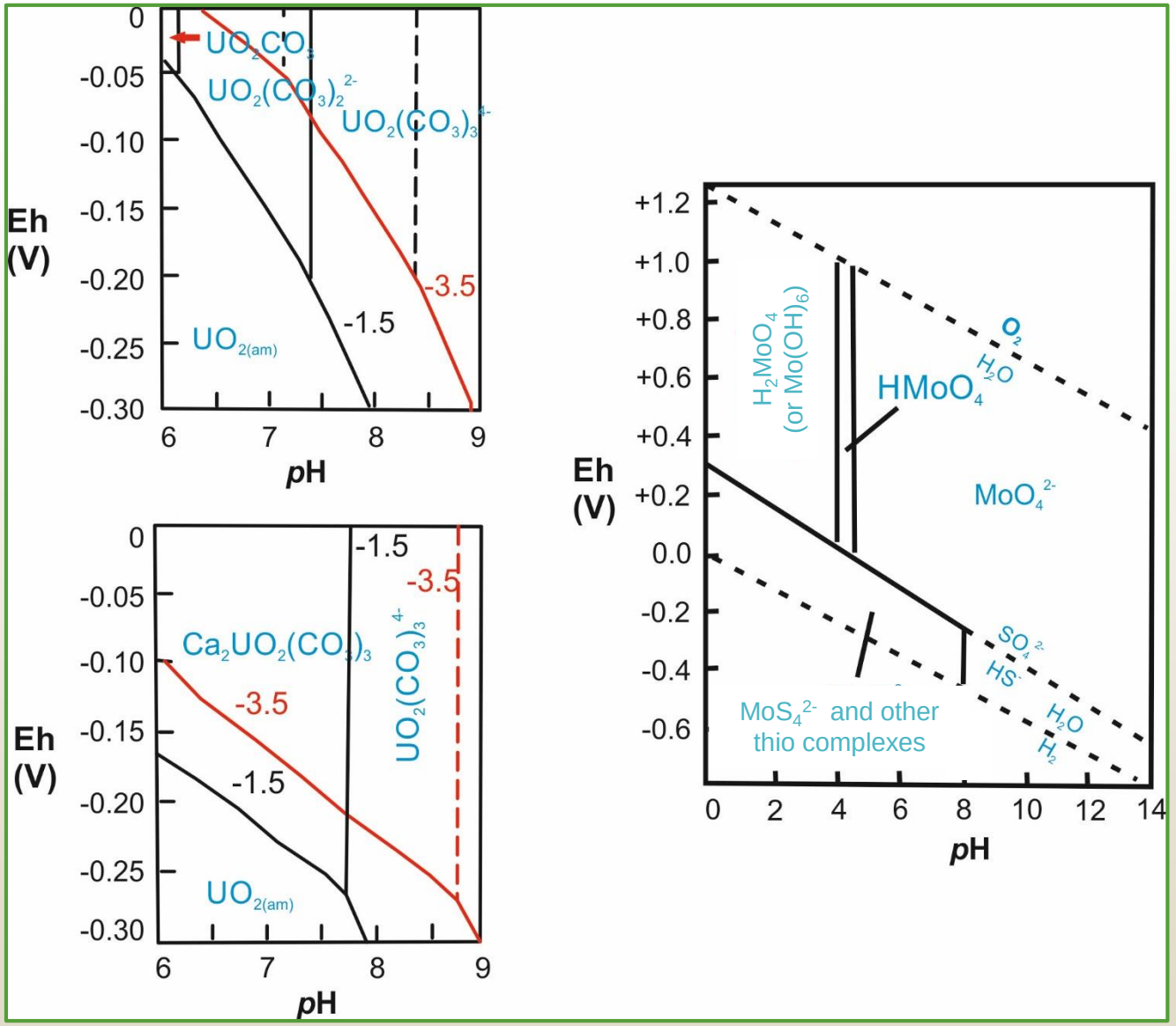




Euxinic Mo sink predominates

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


$\delta^{238}U$ ($^{0}/_{00}$)
-2.5
-1.5
-0.5
+0.5
1.5
2.5
Mafic Rocks (n = 85)
Felsic Rocks (n = 58)
Accessory Minerals (n = 71)
Uraninites & U Ores (n = 311)
U Ore Groundwaters (n = 27)
Soils (n = 4)
Speleothems & Calcite Veins (n = 126)
Rivers & Lakes (n = 54)
Altered Ocean Crusts (n = 29)
Hydrothermal Fluids (n = 6)
Restricted Seawaters (n = 53)
Open-Ocean Seawaters (n = 23)
Marine Sediments (n = 300)
Marine Carbonates (n = 286)
Fe-Mn Deposits (n = 110)
Banded-Iron Formations (n = 4)
Evaporites (n = 4)
Marine Plankton & Sed. Traps (n = 7)


Eh (V)
pH
UO_2CO_3
$UO_2(CO_3)_2^{2-}$
$UO_2(CO_3)_3^{4-}$
-3.5
-1.5
$UO_{2(am)}$
$Ca_2UO_2(CO_3)_3$
$UO_2(CO_3)_3^{4-}$
H_2MoO_4 (or $Mo(OH)_6$)
$HMoO_4^-$
MoO_4^{2-}
MoS_4^{2-} and other thio complexes
O_2
H_2O
SO_4^{2-}
HS^-
H_2

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

Results

Bura-Nakić, E., Sondi, I., Mikac, N., Morten B. Andersen. Investigating the molybdenum and uranium redox proxies in a modern shallow anoxic carbonate rich marine sediment setting of the Malo Jezero (Mljet Lakes, Adriatic Sea). Under rew **Chemical Geology**

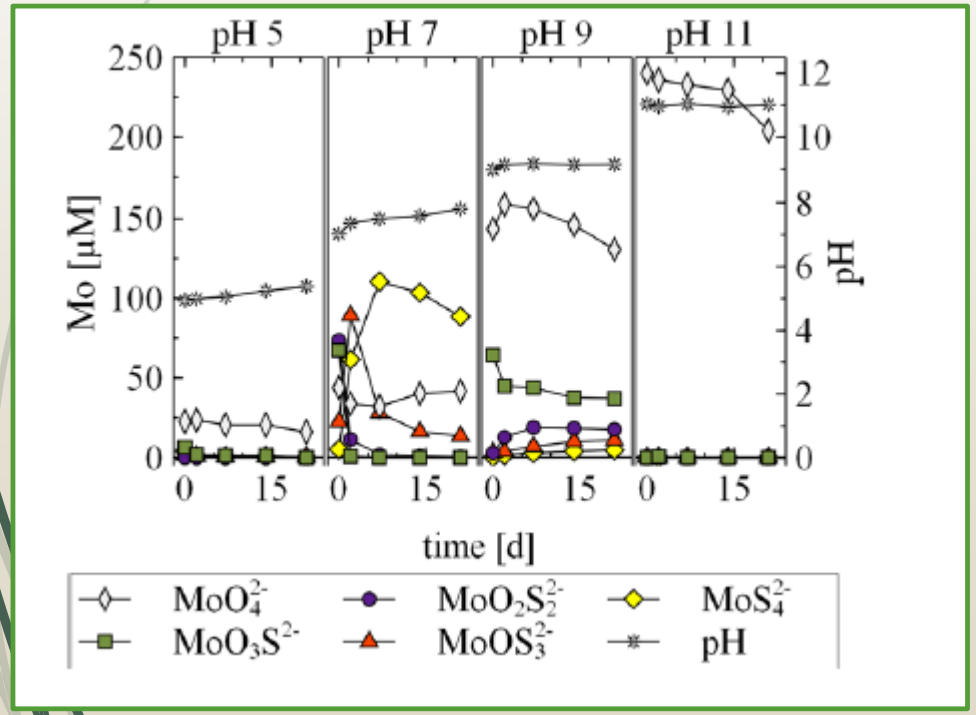
Bura-Nakić, E., Andersen, M.B., Archer, C., de Souza, G.F., Marguš, M., Vance, D., 2017. Coupled Mo-U abundances and isotopes in a small marine euxinic basin: constraints on processes in euxinic basins. Submitirano u **Geochimica et Cosmochimica Acta**

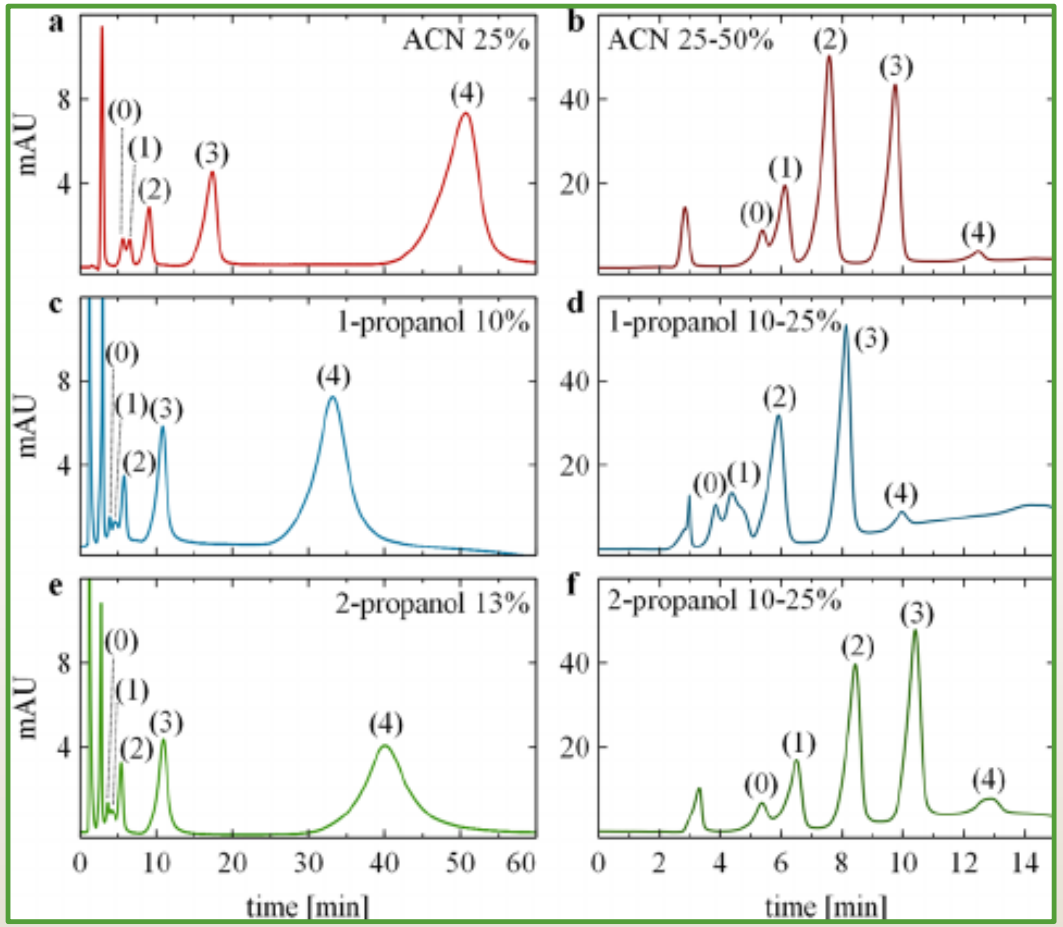
Kerl, C., Lohmayer, R., **Bura-Nakić, E.**, Vance, D., Planer-Friedrich, B., 2017. Experimental confirmation of isotope fractionation in thiomolybdates using ion chromatographic separation and detection by multicollector ICPMS. **Analytical Chemistry** 89, 3123-3129

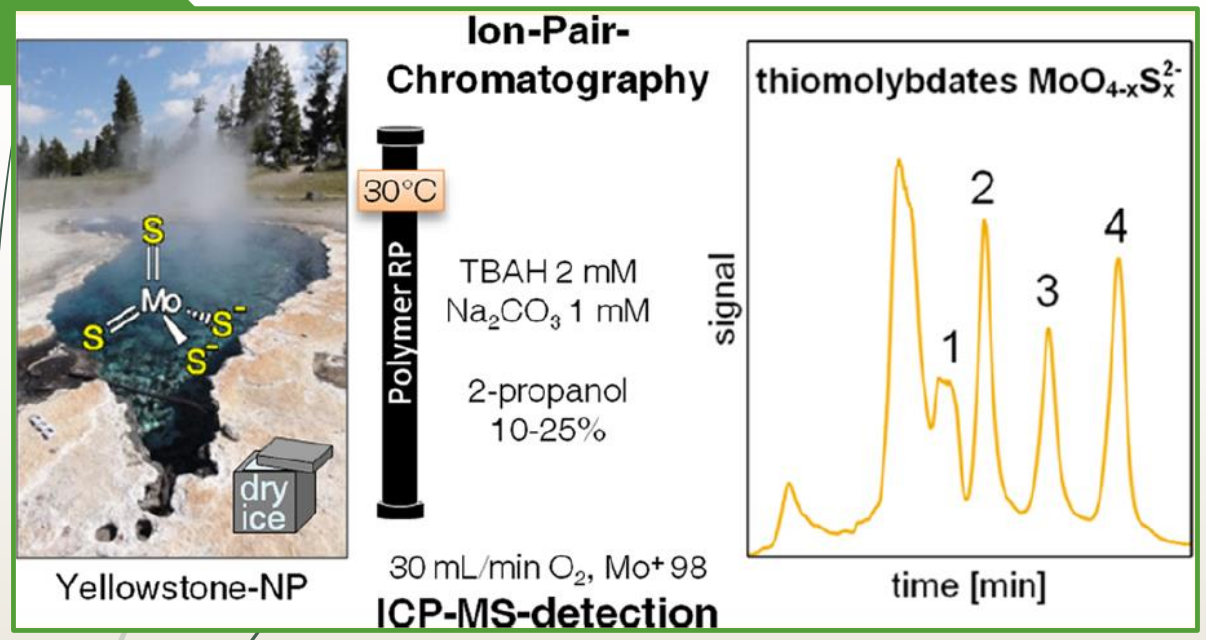
Andersen, M.B., Vance, D., Morford, J.L, **Bura-Nakić, E.**, Breitenbach, S.F.M., Och, L., 2016. Closing in on the marine 238/235U budget. **Chemical geology** 420, 11-22

Lohmayer, R., Reithmaier, G.M.S., **Bura-Nakić, E.**, Planer-Friedrich, B. Ion-Pair Chromatography Coupled to Inductively Coupled Plasma–Mass Spectrometry (IPC-ICP-MS) as a Method for Thiomolybdate Speciation in Natural Waters. **Analytical Chemistry** 87(6) (2015) 3388–3395

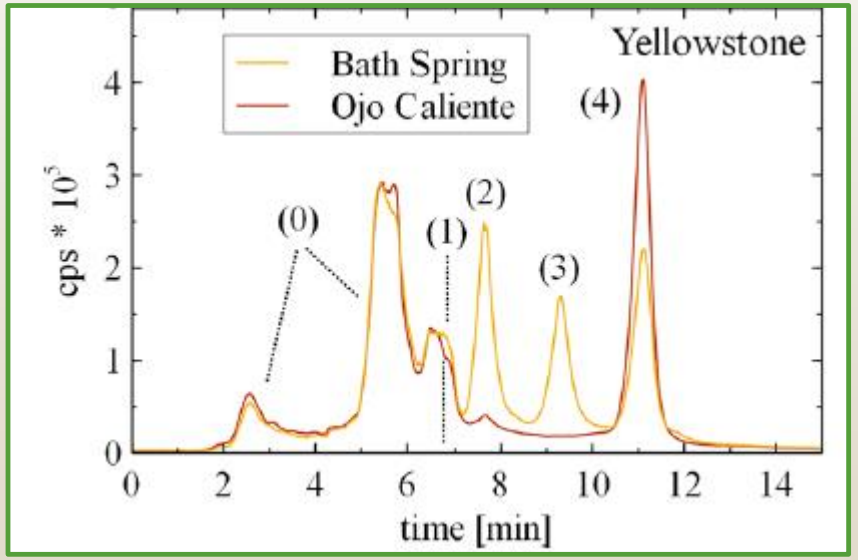
Lohmayer, R., Reithmaier, G.M.S., **Bura-Nakić, E.**, Planer-Friedrich, B. Ion-Pair Chromatography Coupled to Inductively Coupled Plasma–Mass Spectrometry (IPC-ICP-MS) as a Method for Thiomolybdate Speciation in Natural Waters. **Analytical Chemistry** 87(6) (2015) 3388–3395

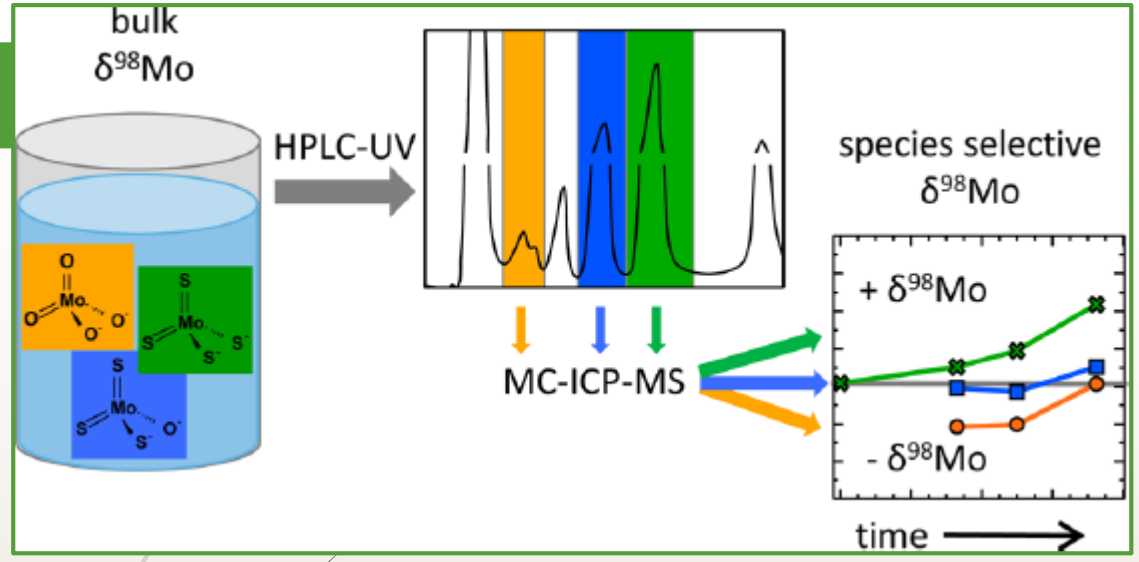




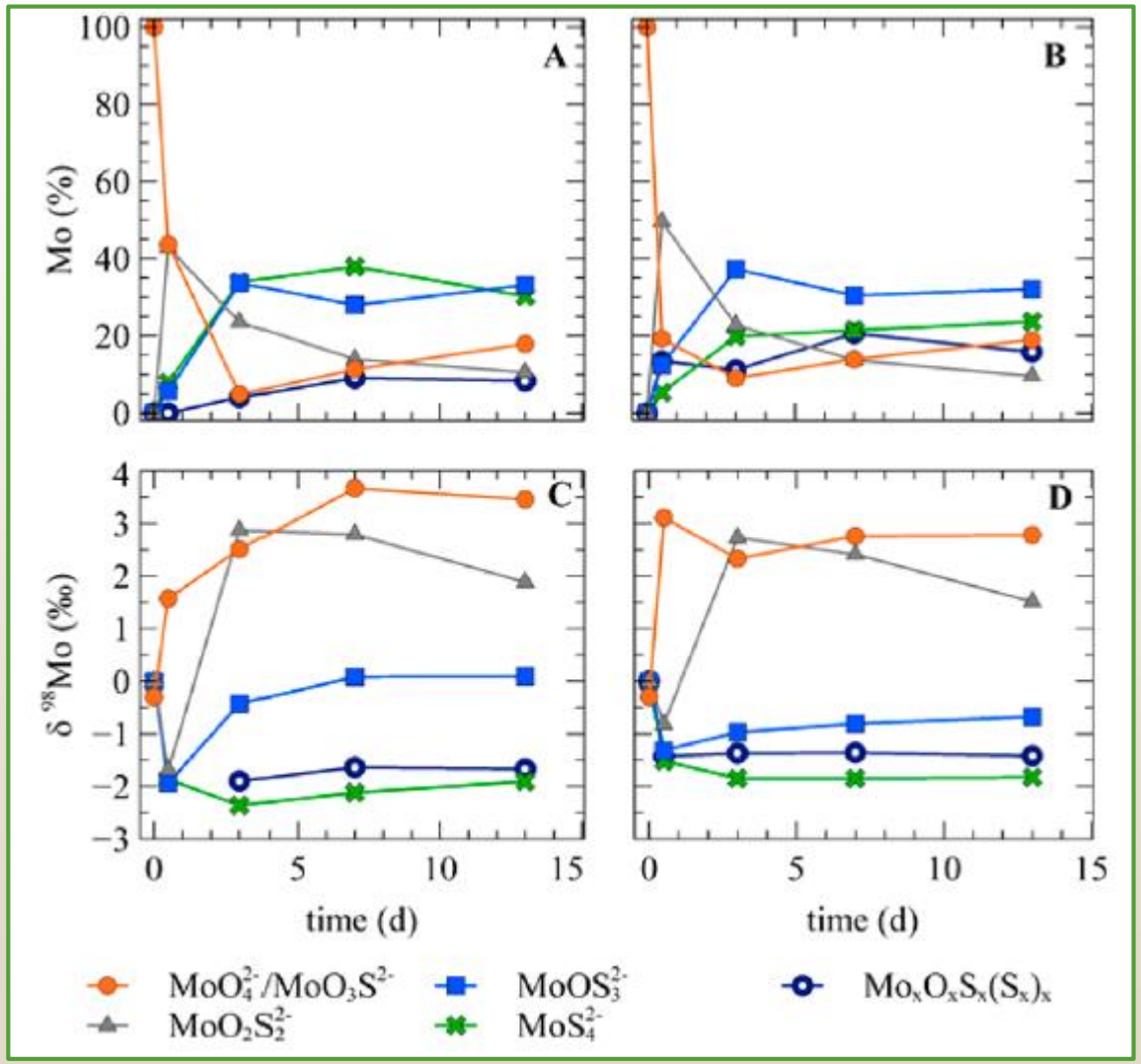


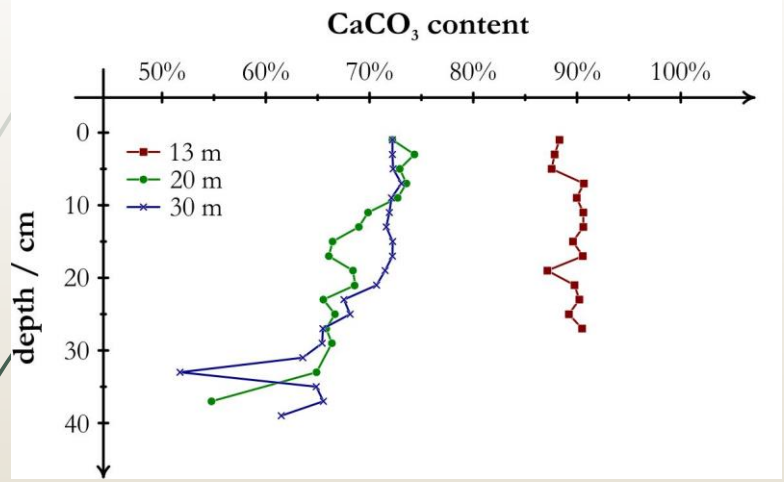
Lohmayer, R., Reithmaier, G.M.S., **Bura-Nakić, E.**, Planer-Friedrich, B. Ion-Pair Chromatography Coupled to Inductively Coupled Plasma–Mass Spectrometry (IPC-ICP-MS) as a Method for Thiomolybdate Speciation in Natural Waters. **Analytical Chemistry** 87(6) (2015) 3388–3395

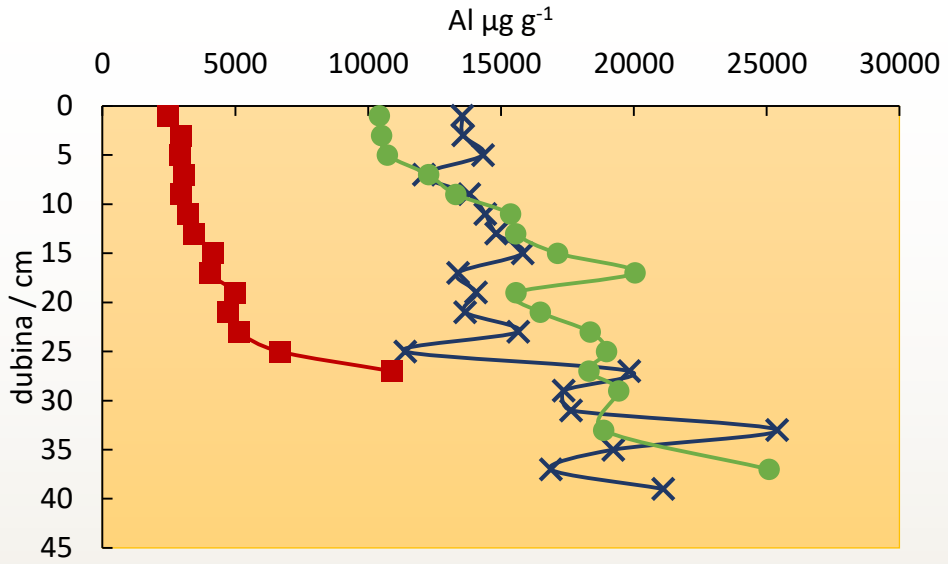


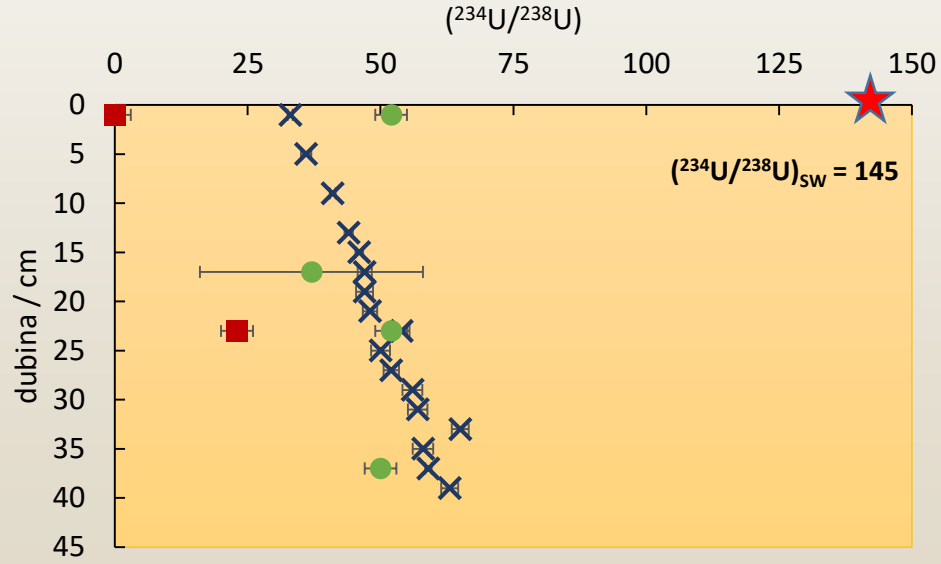


Kerl, C., Lohmayer, R., **Bura-Nakić, E.**, Vance, D., Planer-Friedrich, B., 2017. Experimental confirmation of isotope fractionation in thiomolybdates using ion chromatographic separation and detection by multicollector ICPMS. **Analytical Chemistry** 89, 3123-3129

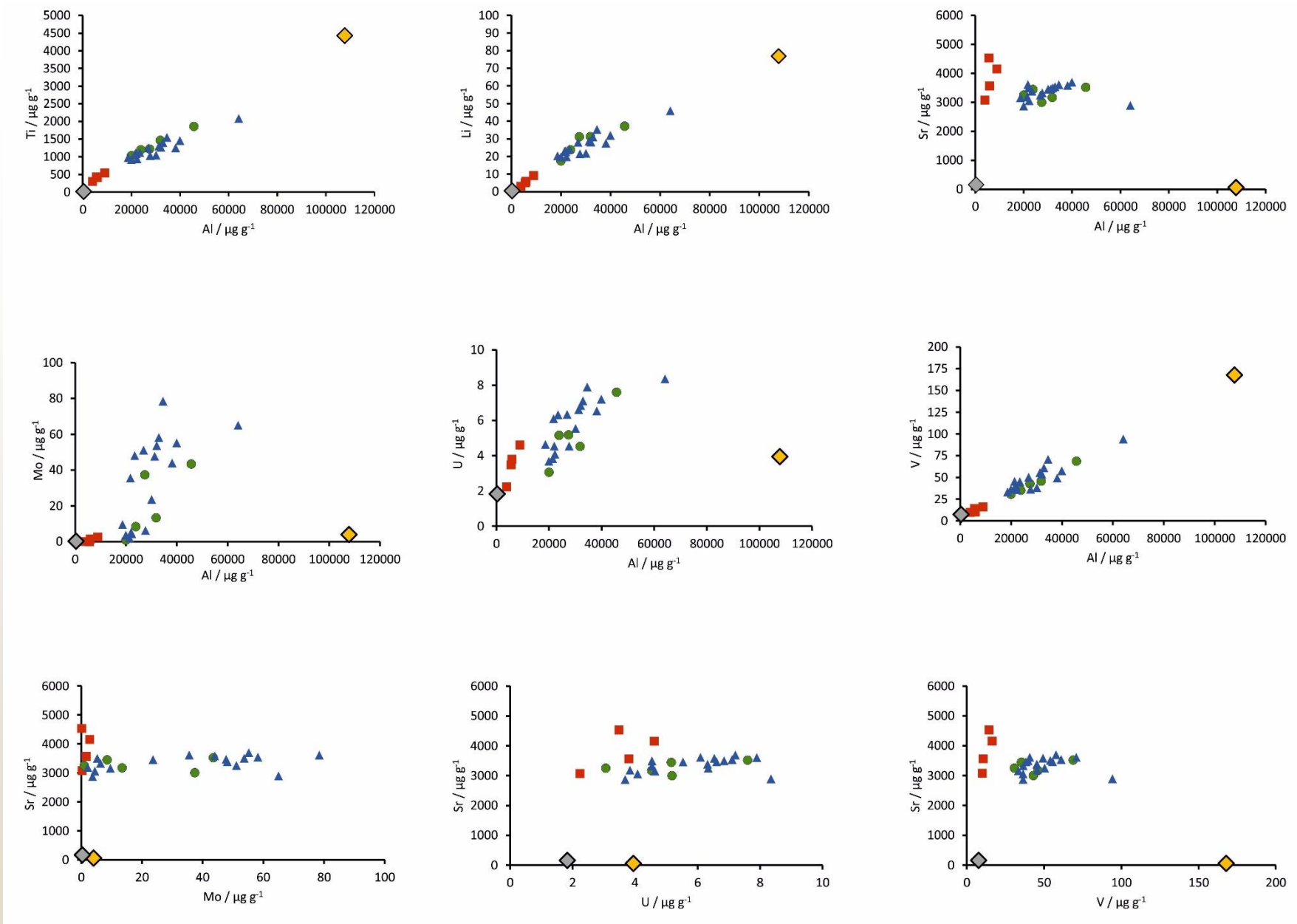






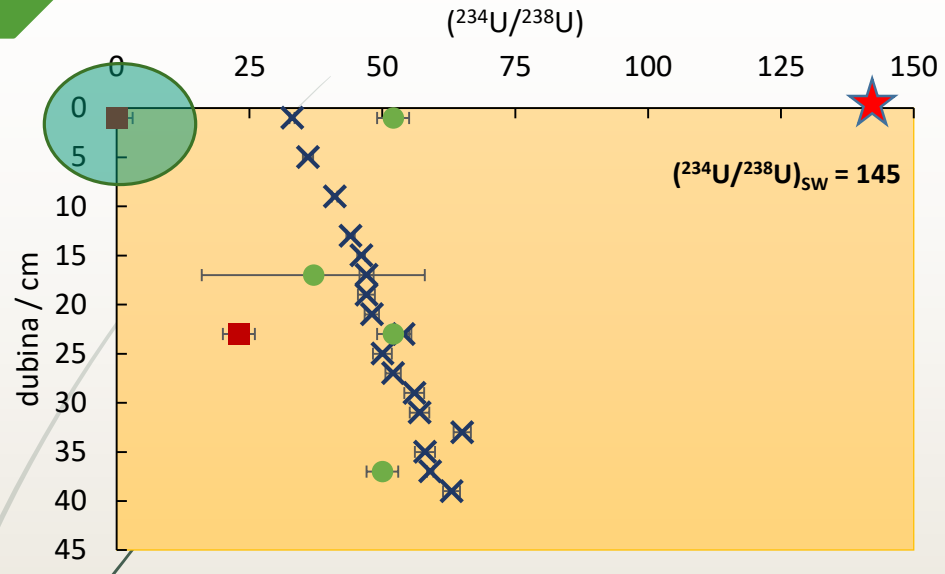


Bura-Nakić, E., Sondi, I., Mikac, N., Morten B. Andersen. Investigating the molybdenum and uranium redox proxies in a modern shallow anoxic carbonate rich marine sediment setting of the Malo Jezero (Mljet Lakes, Adriatic Sea). Under rew **Chemical Geology**

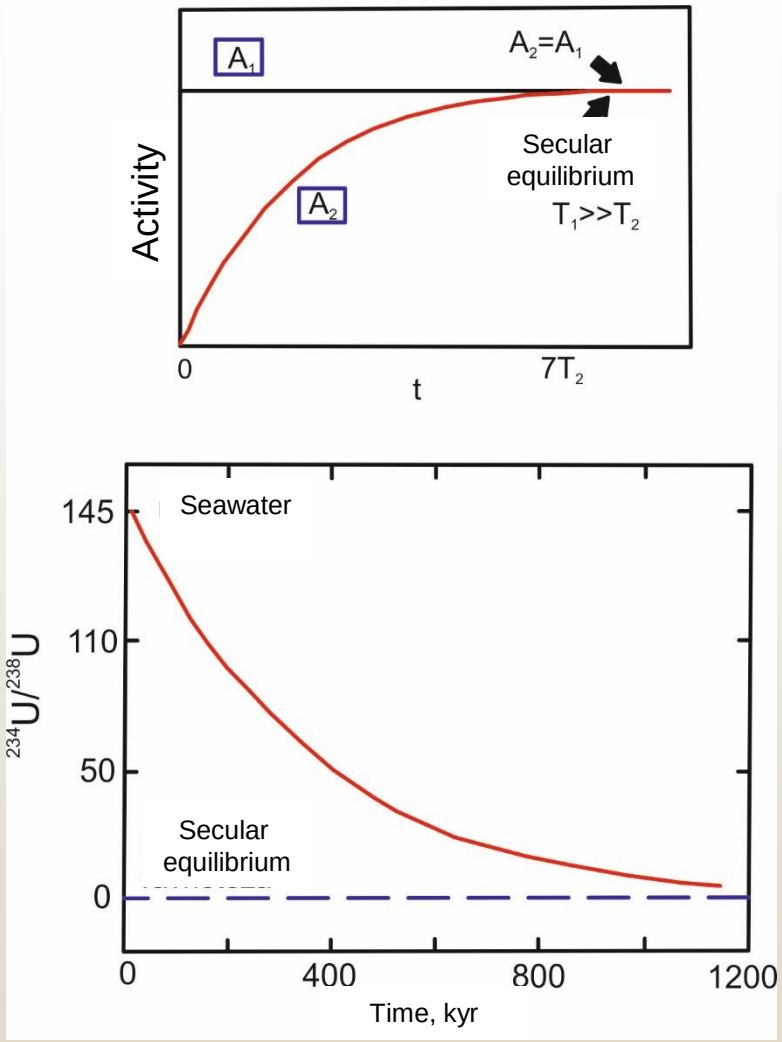


Bura-Nakić, E., Sondi, I., Mikac, N., Morten B. Andersen. Investigating the molybdenum and uranium redox proxies in a modern shallow anoxic carbonate rich marine sediment setting of the Malo Jezero (Mljet Lakes, Adriatic Sea). Under rew **Chemical Geology**

High amount of terrigenous material (carbonate detritus)



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



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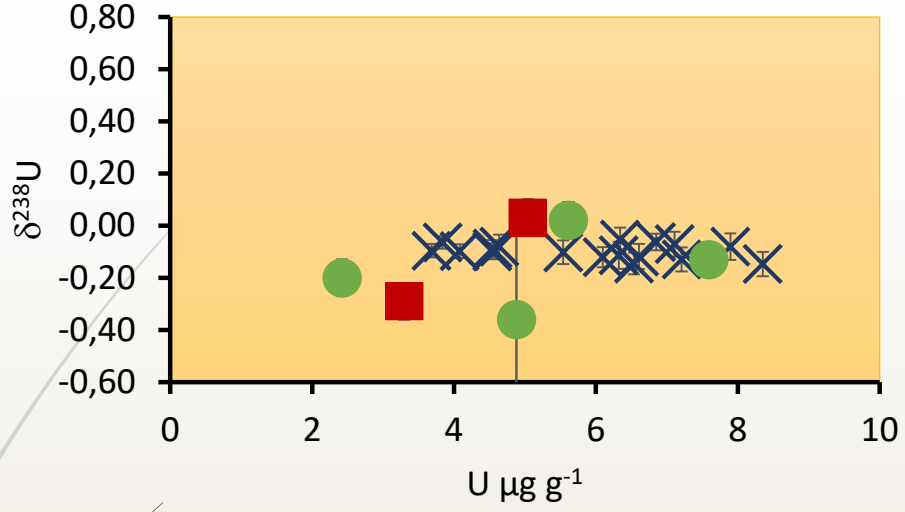
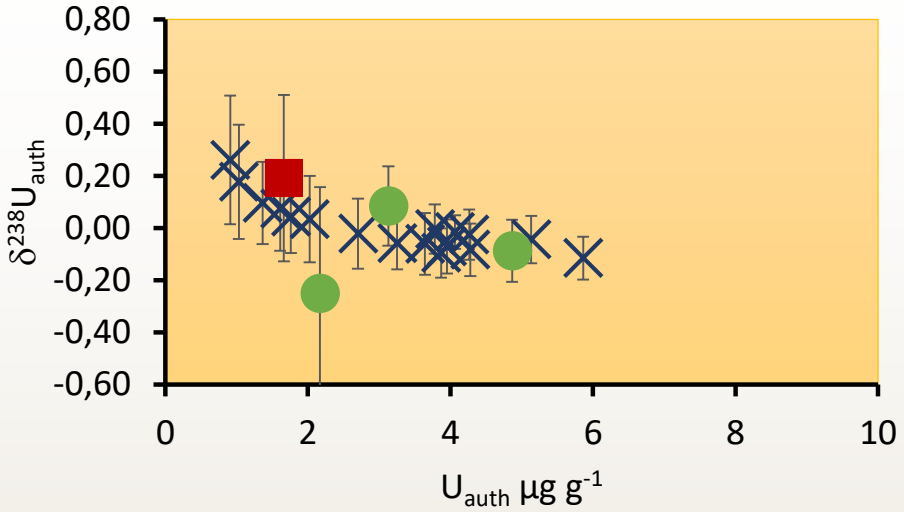
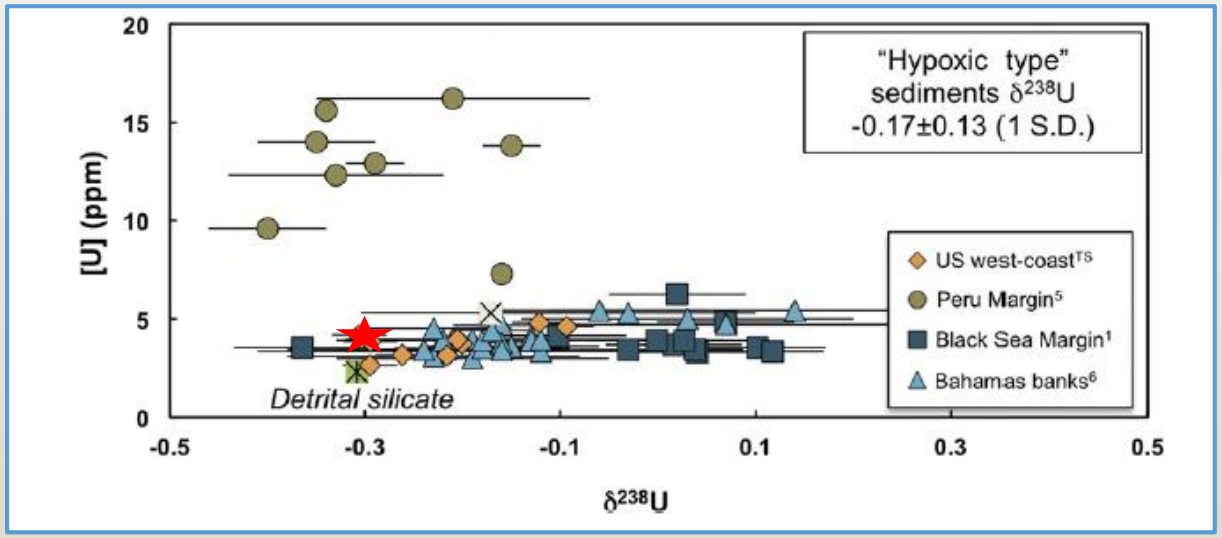
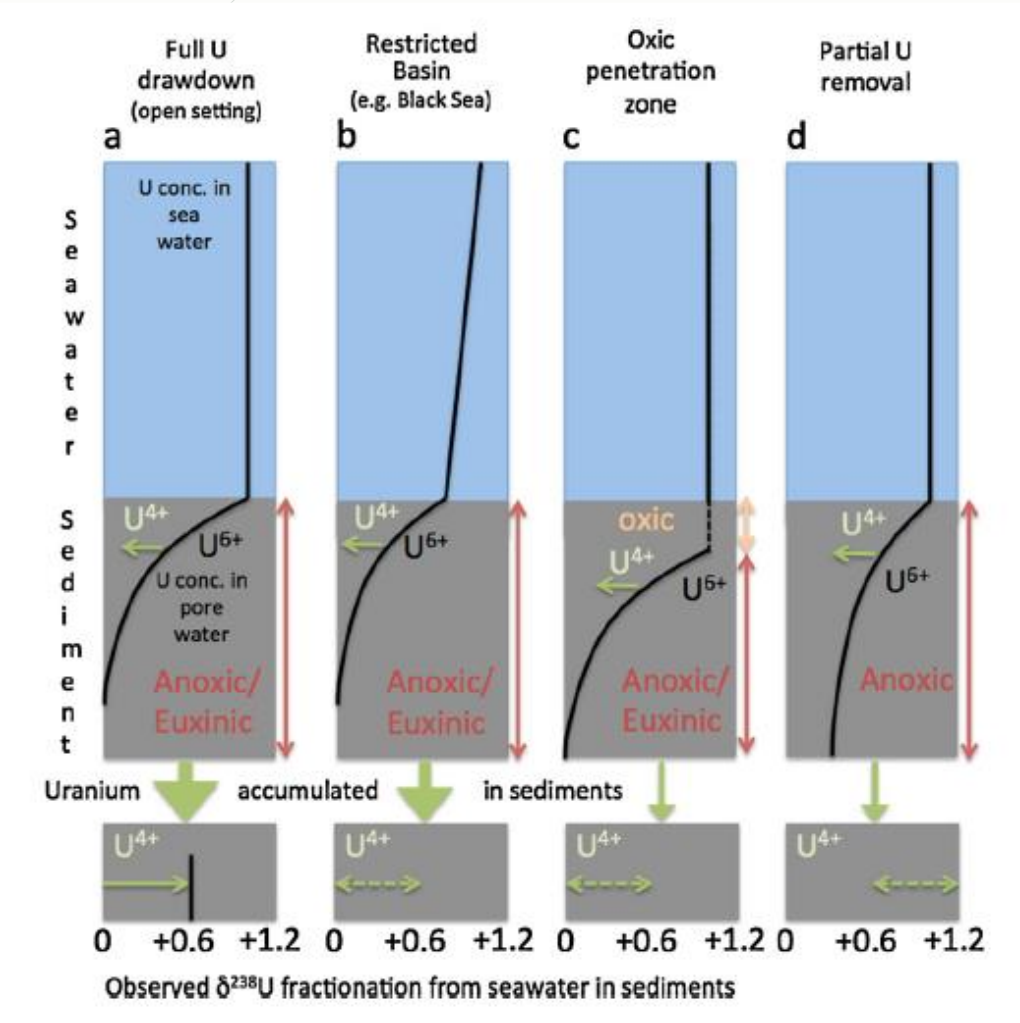




Andersen, M.B., Vance, D., Morford, J.L, **Bura-Nakić, E.**, Breitenbach, S.F.M., Och, L., 2016. Closing in on the marine 238/235U budget. **Chemical geology** 420, 11-22



Sedimentary δ^{238} U (‰)

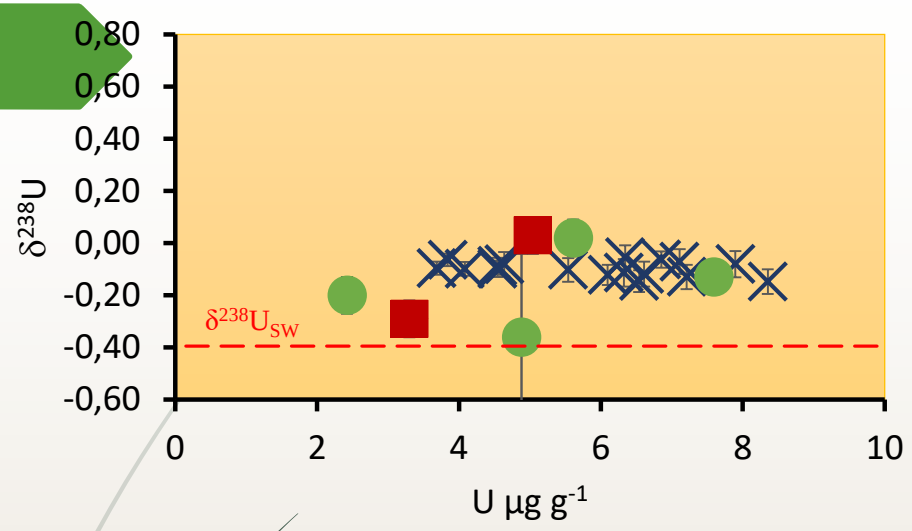


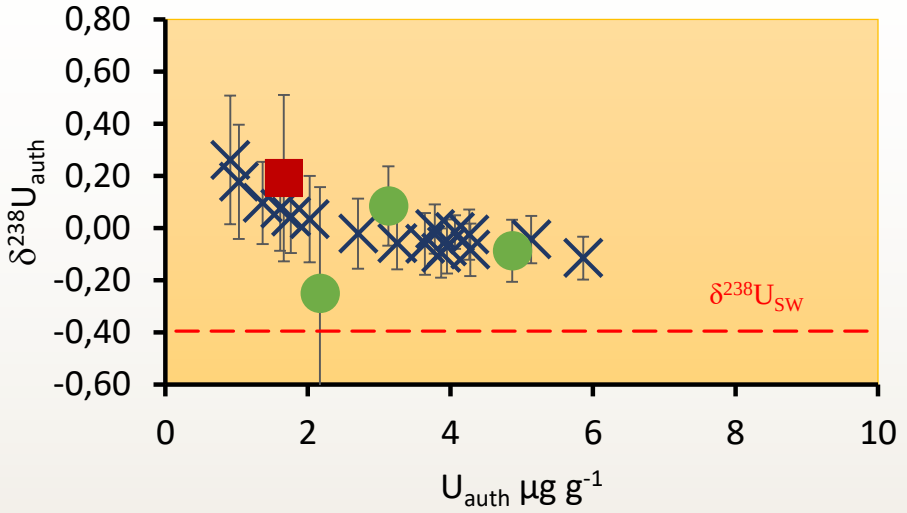
$\delta^{238}U_{open\ system}$ = from +0.8 to +0.2

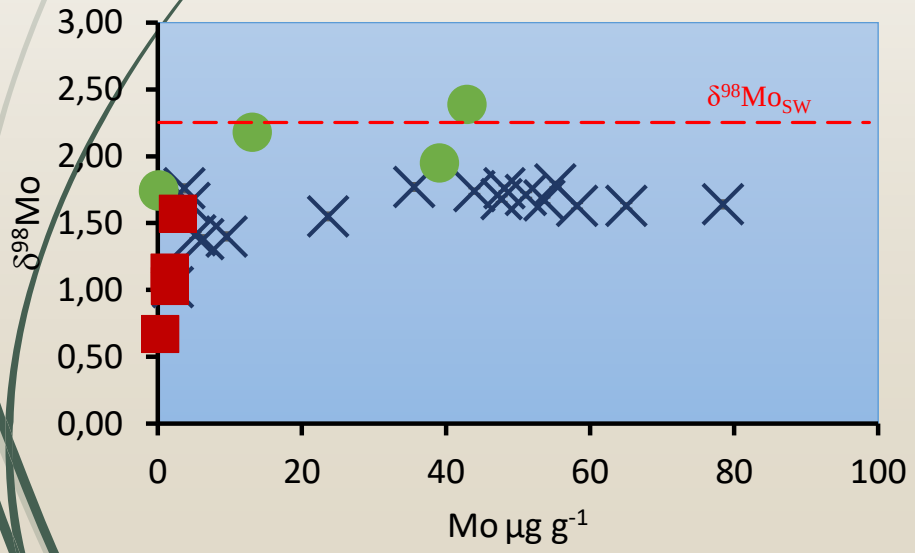
$\delta^{238}U_{open\ system}$ = +0.2

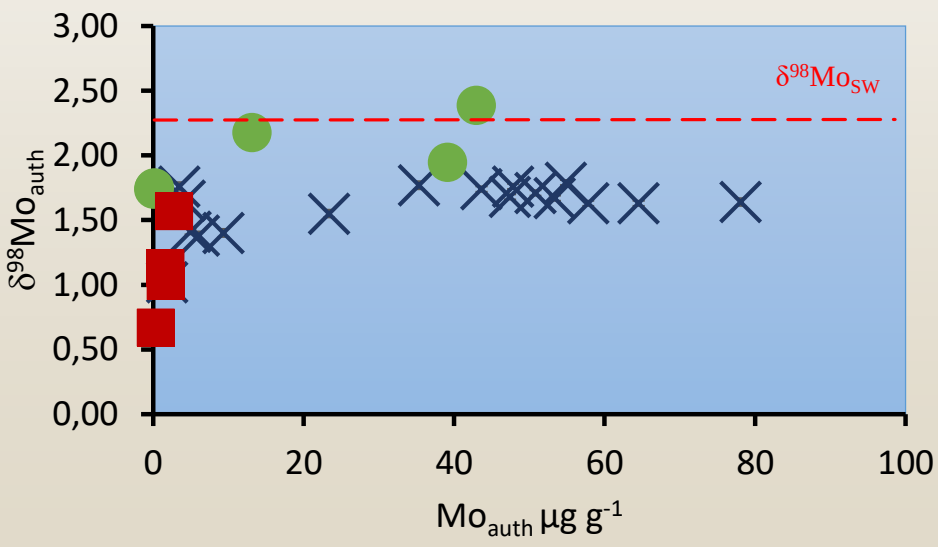
$\delta^{238}U_{open\ system}$ = from +0.2 to -0.4

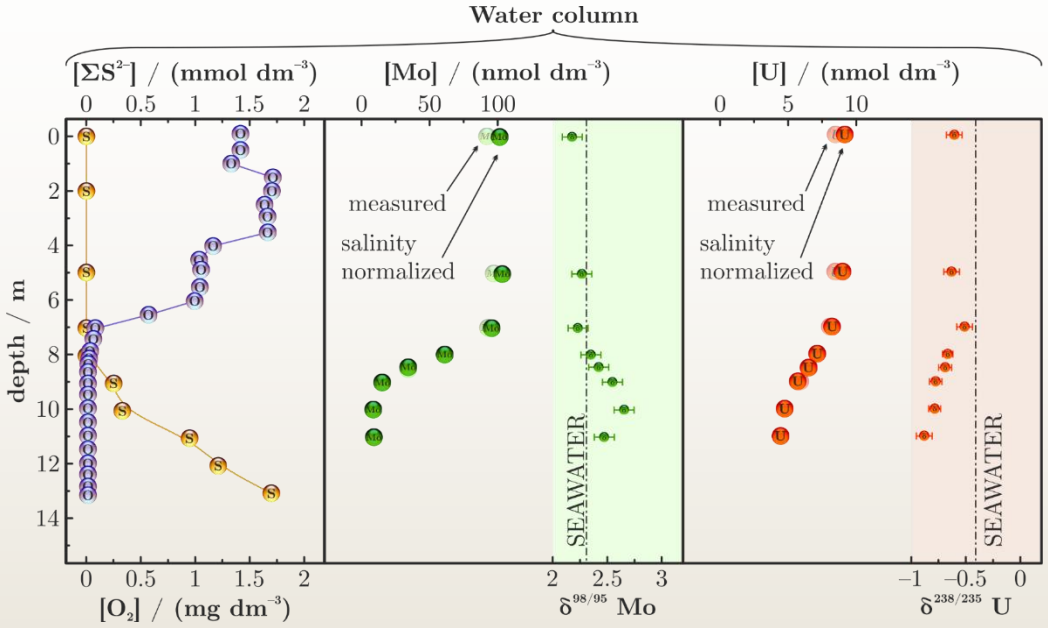
$\delta^{238}U_{closed\ system}$ = from +0.2 to -0.4


0,80
0,60
0,40
0,20
0,00
-0,20
-0,40
-0,60
δ238U
δ238USW
0
2
4
6
8
10
U µg g-1

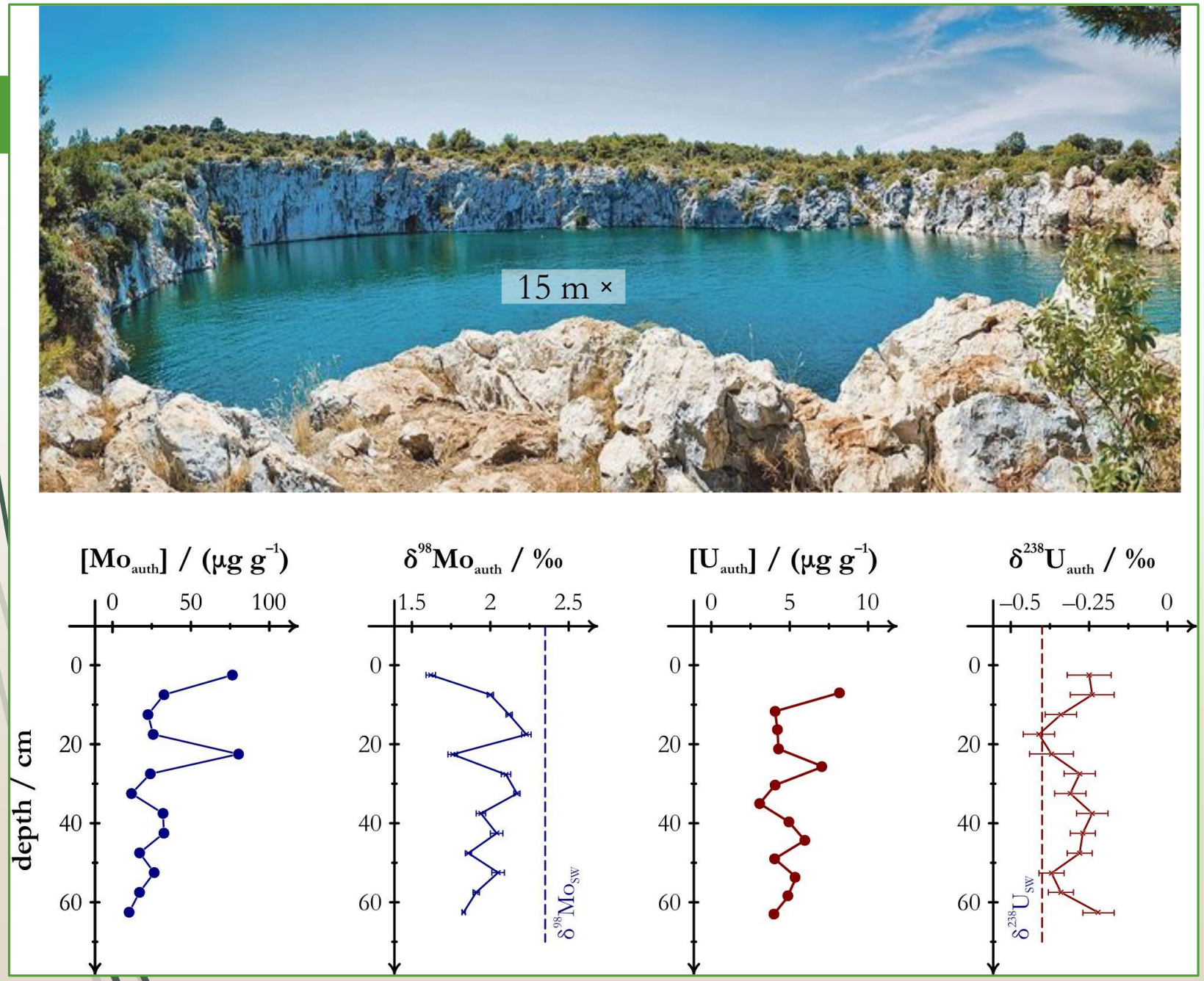

0,80
0,60
0,40
0,20
0,00
-0,20
-0,40
-0,60
δ238Uauth
δ238USW
0
2
4
6
8
10
Uauth µg g-1


3,00
2,50
2,00
1,50
1,00
0,50
0,00
δ98Mo
δ98MoSW
0
20
40
60
80
100
Mo µg g-1


3,00
2,50
2,00
1,50
1,00
0,50
0,00
δ98Moauth
δ98MoSW
0
20
40
60
80
100
Moauth µg g-1



Depth profiles of dissolved $\delta^{238}U$ and $\delta^{98}Mo$ at „Zmajevo oko” 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**

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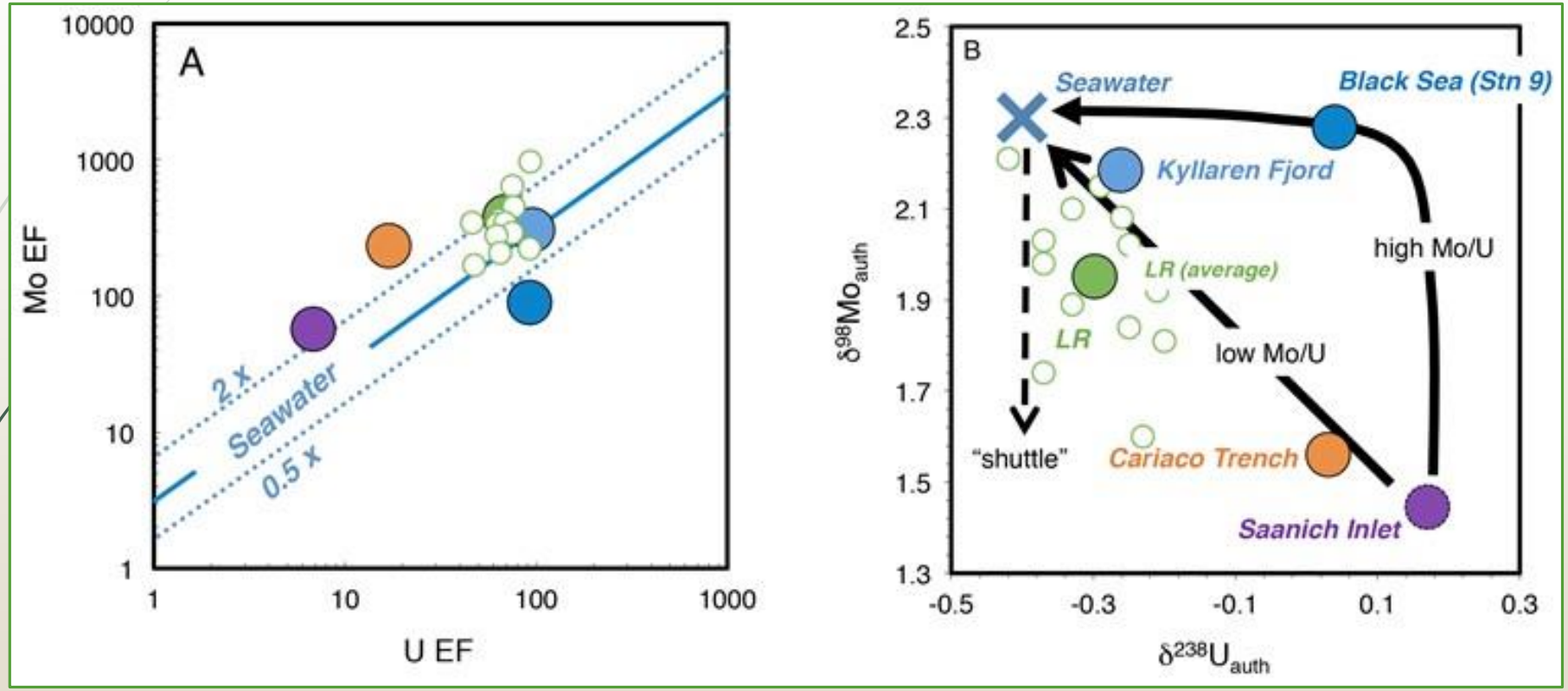
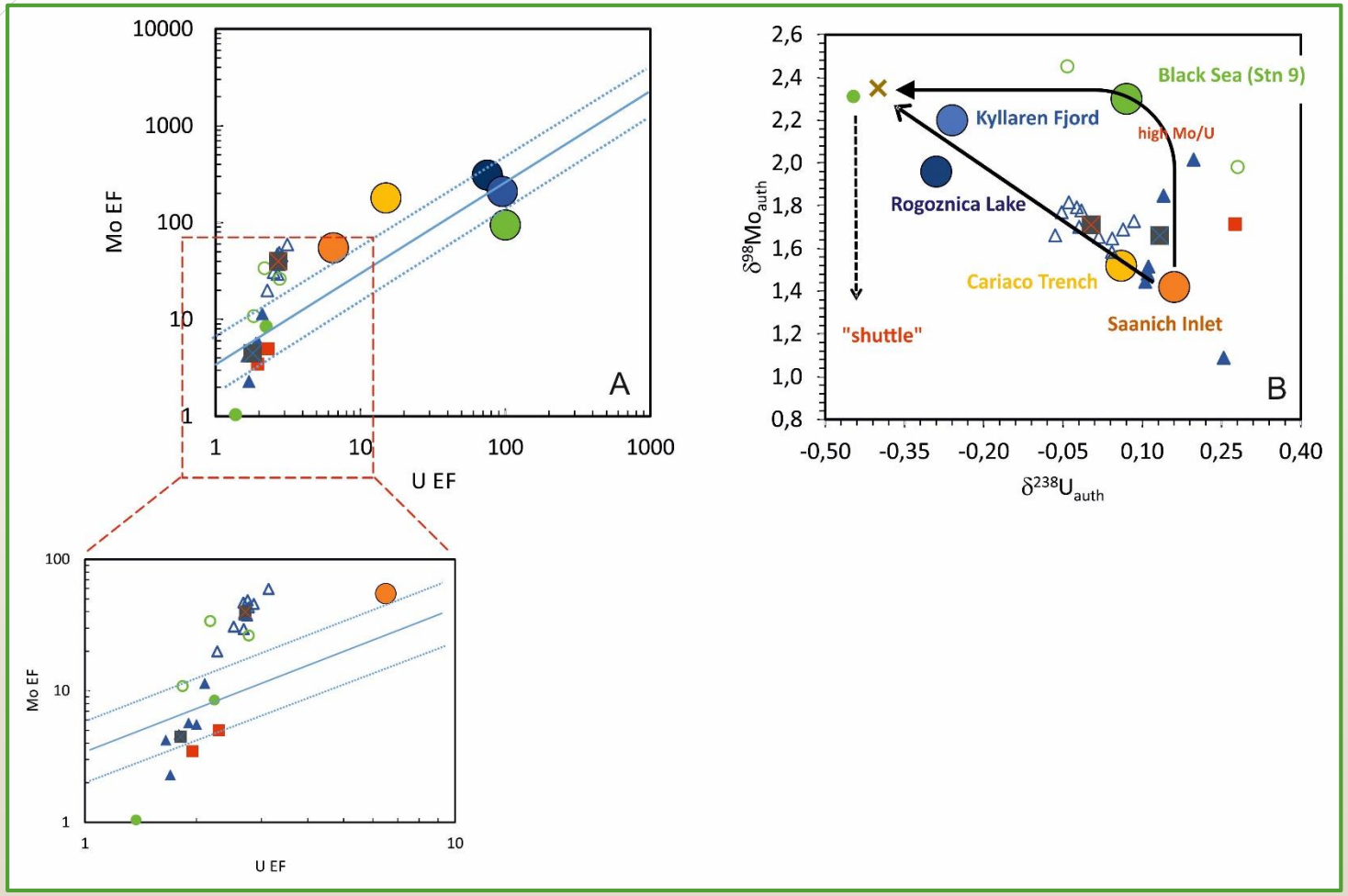
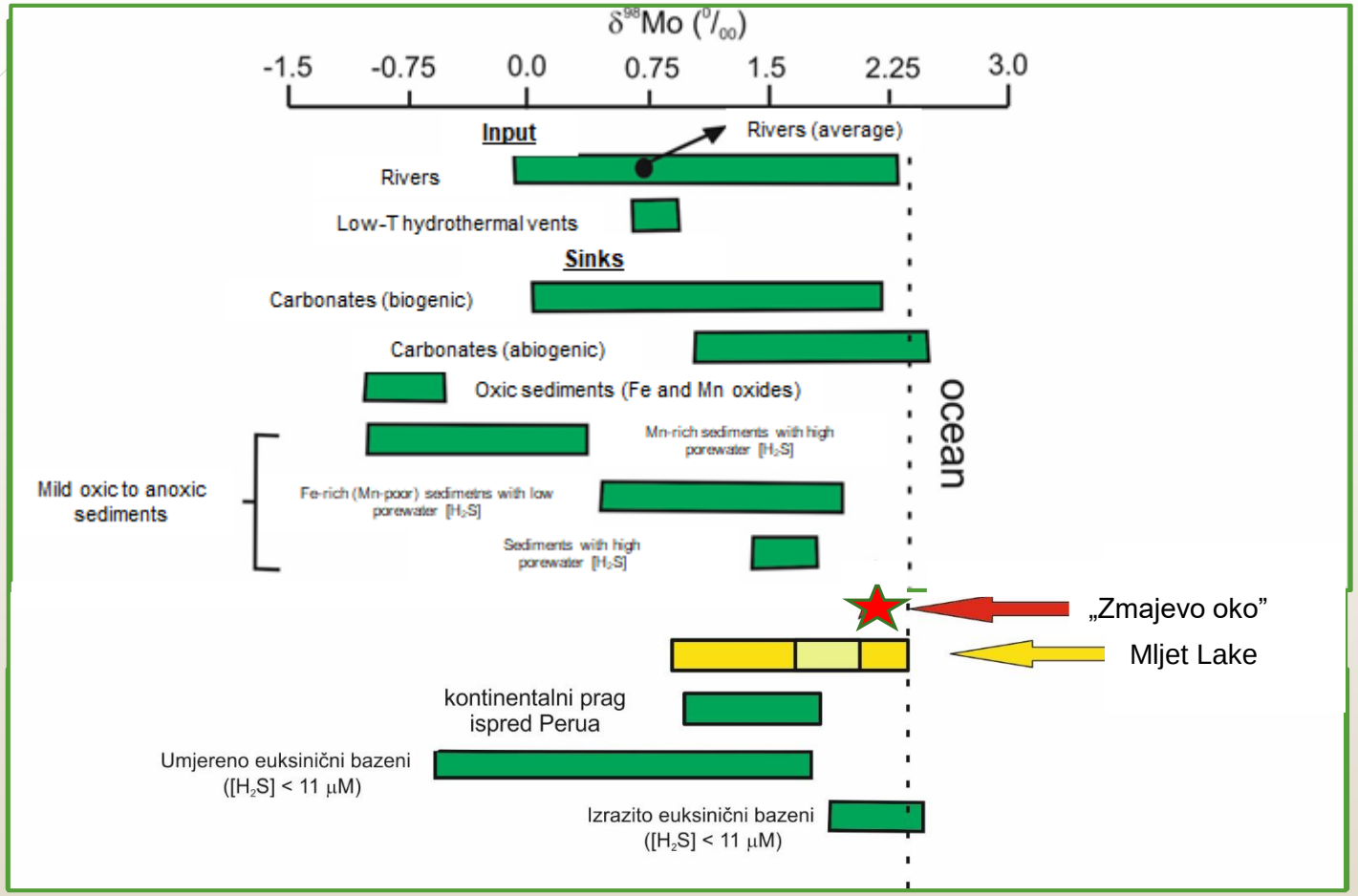


Bura-Nakić, E., Andersen, M.B., Archer, C., de Souza, G.F., Marguš, M., Vance, D., 2017. Coupled Mo-U abundances and isotopes in a small marine euxinic basin: constraints on processes in euxinic basins. Submitirano u **Geochimica et Cosmochimica Acta**




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) sedimetns with low porewater [H2S]
Sediments with high porewater [H2S]
ocean
„Zmajevo oko”
Mljet Lake
kontinentalni prag ispred Perua
Umjereno euksinični bazeni ([H2S] < 11 μM)
Izrazito euksinični bazeni ([H2S] < 11 μM)

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

Thank you on your attention!

Merci de votre attention!