Quest for the biogeochemical time machines:

Adriatic coast and beyond

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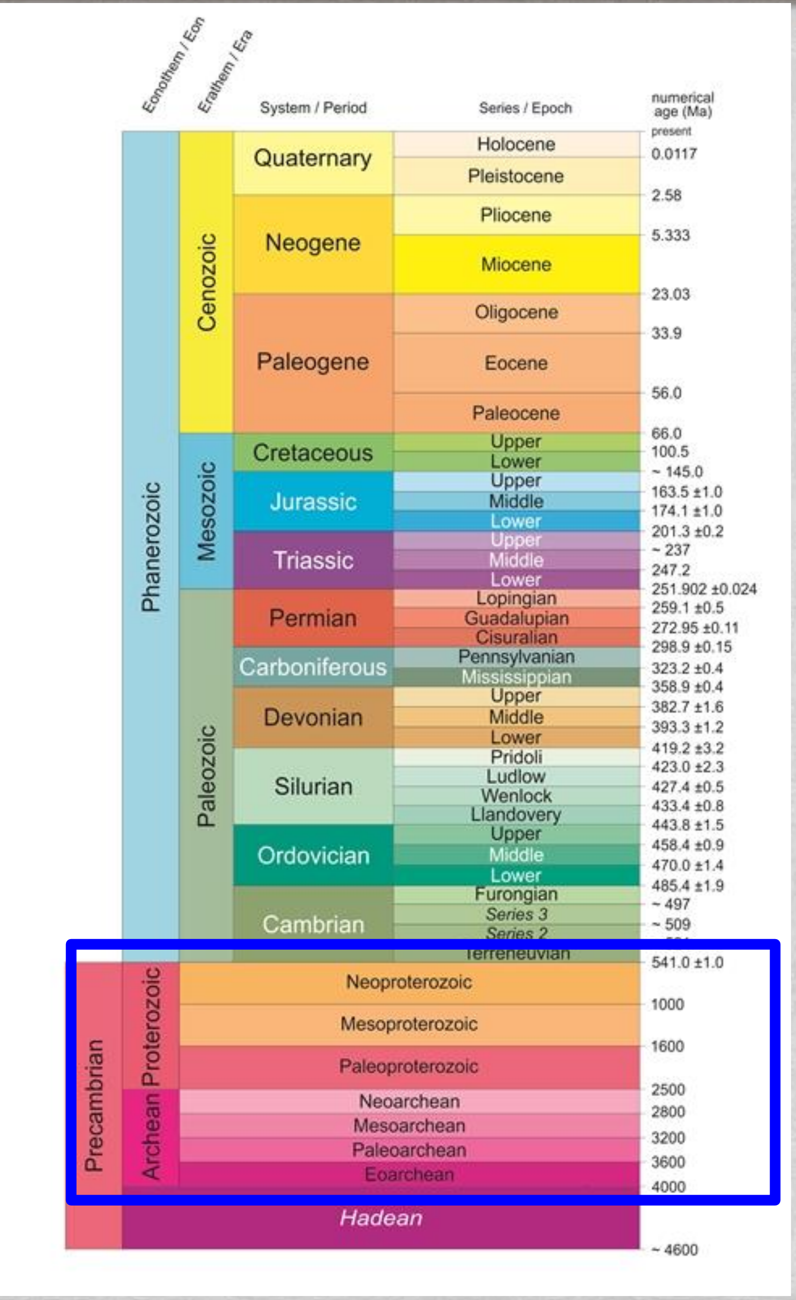
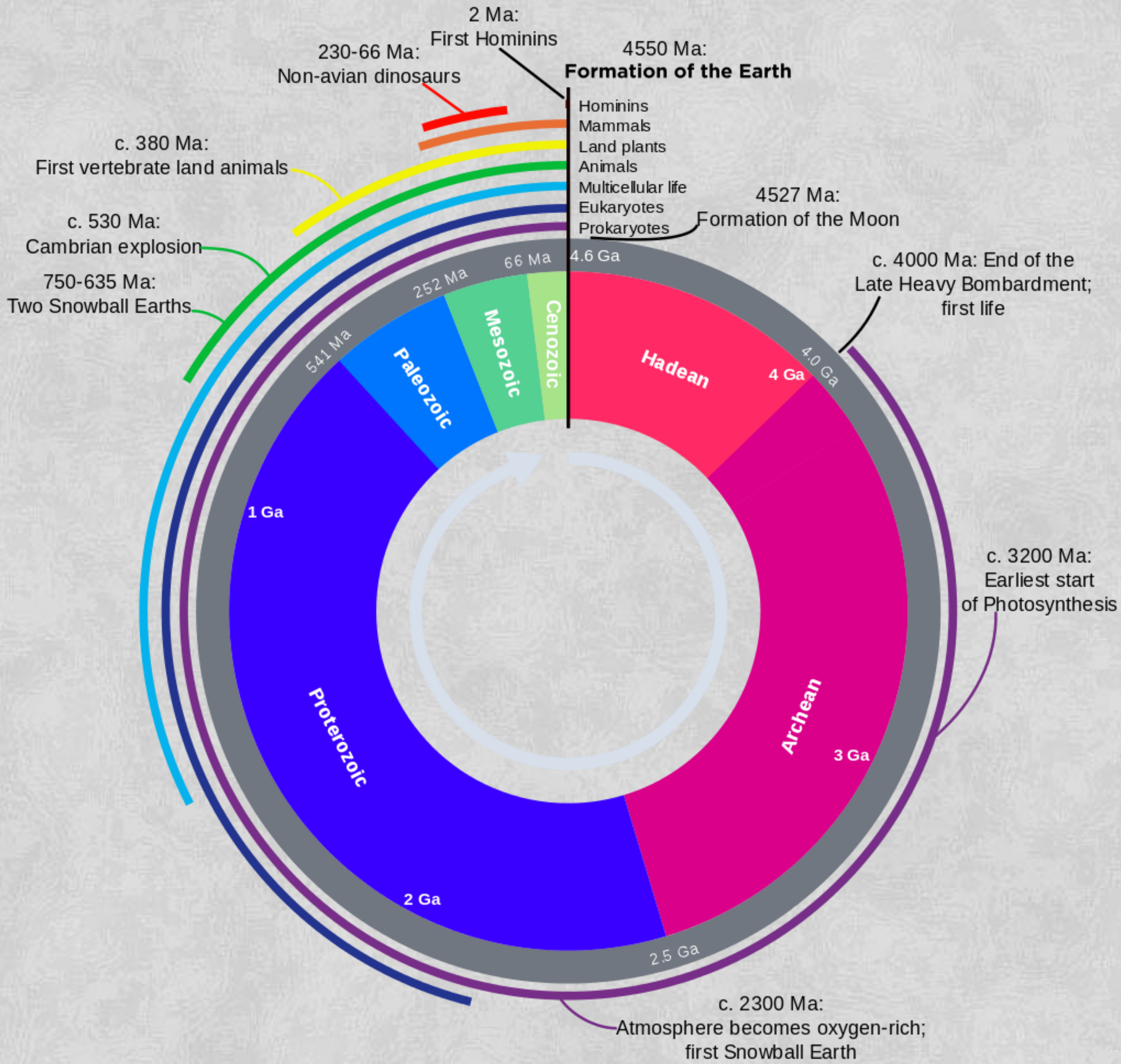
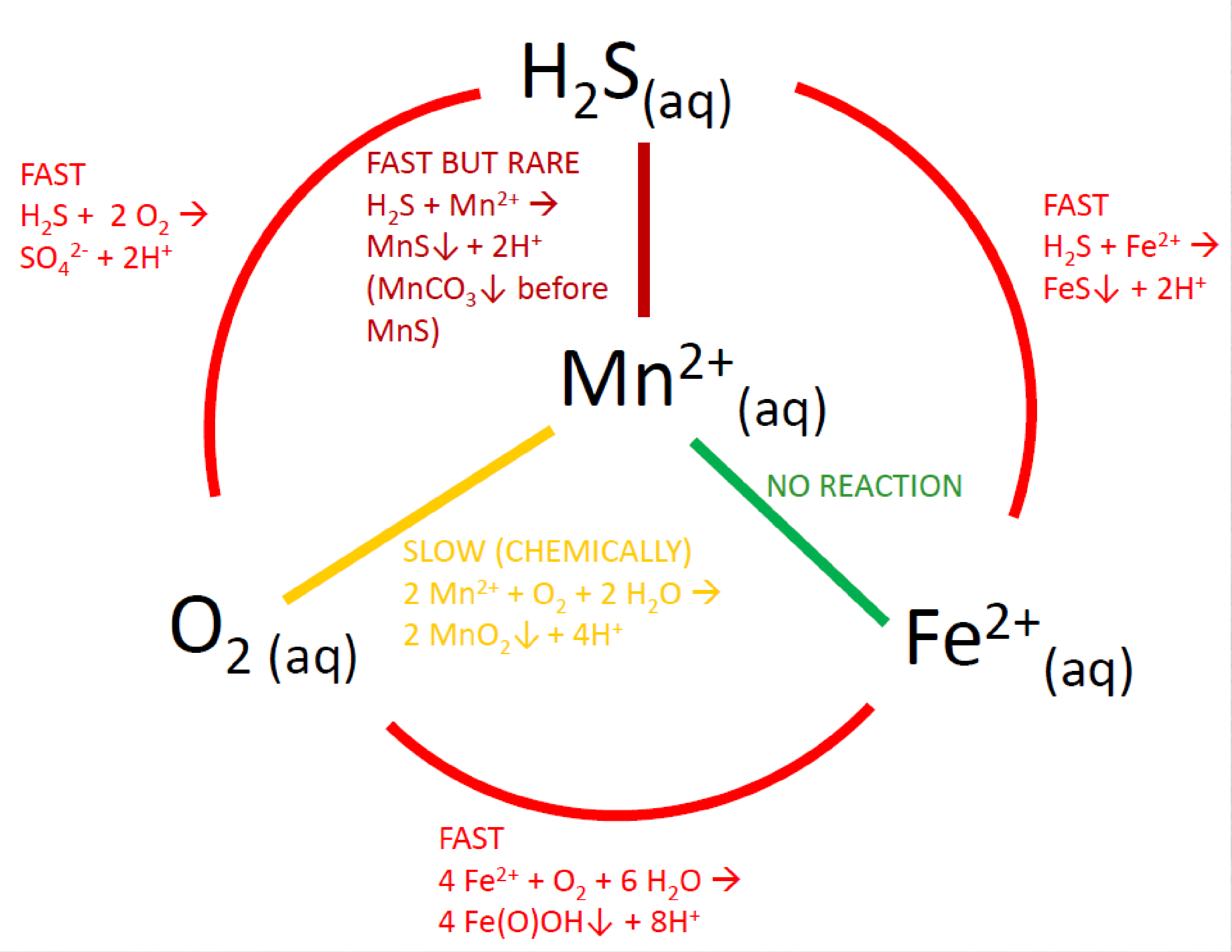
WHERE WOULD YOU GO?
THE TIME MACHINE
BE CAREFUL WHAT YOU WISH FOR.



Eonothem / Eon
Erathem / Era
System / Period
Series / Epoch
numerical age (Ma)
present
Phanerozoic
Cenozoic
Quaternary
Holocene
0.0117
Pleistocene
2.58
Neogene
Pliocene
5.333
Miocene
23.03
Paleogene
Oligocene
33.9
Eocene
56.0
Paleocene
66.0
Mesozoic
Cretaceous
Upper
100.5
Lower
~ 145.0
Jurassic
Upper
163.5 ±1.0
Middle
174.1 ±1.0
Lower
201.3 ±0.2
Triassic
Upper
~ 237
Middle
247.2
Lower
251.902 ±0.024
Paleozoic
Permian
Lopingian
259.1 ±0.5
Guadalupian
272.95 ±0.11
Cisuralian
298.9 ±0.15
Carboniferous
Pennsylvanian
323.2 ±0.4
Mississippian
358.9 ±0.4
Devonian
Upper
382.7 ±1.6
Middle
393.3 ±1.2
Lower
419.2 ±3.2
Silurian
Pridoli
423.0 ±2.3
Ludlow
427.4 ±0.5
Wenlock
433.4 ±0.8
Llandovery
443.8 ±1.5
Ordovician
Upper
458.4 ±0.9
Middle
470.0 ±1.4
Lower
485.4 ±1.9
Cambrian
Furongian
~ 497
Series 3
~ 509
Series 2
Terreneuvian
541.0 ±1.0
Precambrian
Proterozoic
Neoproterozoic
1000
Mesoproterozoic
1600
Paleoproterozoic
2500
Archean
Neoarchean
2800
Mesoarchean
3200
Paleoarchean
3600
Eoarchean
4000
Hadean
~ 4600


2 Ma:
First Hominins
4550 Ma:
Formation of the Earth
230-66 Ma:
Non-avian dinosaurs
Hominins
Mammals
Land plants
Animals
Multicellular life
Eukaryotes
Prokaryotes
c. 380 Ma:
First vertebrate land animals
4527 Ma:
Formation of the Moon
c. 530 Ma:
Cambrian explosion
750-635 Ma:
Two Snowball Earths
c. 4000 Ma: End of the
Late Heavy Bombardment;
first life
4.6 Ga
66 Ma
252 Ma
541 Ma
4.0 Ga
Cenozoic
Mesozoic
Paleozoic
Hadean
4 Ga
1 Ga
Proterozoic
Archean
3 Ga
2 Ga
2.5 Ga
c. 3200 Ma:
Earliest start
of Photosynthesis
c. 2300 Ma:
Atmosphere becomes oxygen-rich;
first Snowball Earth


H2S(aq)
FAST
H2S + 2 O2 →
SO4 2- + 2H+
FAST BUT RARE
H2S + Mn2+ →
MnS↓ + 2H+
(MnCO3↓ before
MnS)
FAST
H2S + Fe2+ →
FeS↓ + 2H+
Mn2+(aq)
NO REACTION
SLOW (CHEMICALLY)
2 Mn2+ + O2 + 2 H2O →
2 MnO2↓ + 4H+
O2 (aq)
Fe2+(aq)
FAST
4 Fe2+ + O2 + 6 H2O →
4 Fe(O)OH↓ + 8H+

Iron and Hydrogen Sulfide

Archean ocean

– [SO_4^{2-}] = <3 to 80 μM

– [H_2S] – very low, controlled by a solubility of FeS

– [Fe^{2+}] ≈ 100 μM

Proterozoic ocean

– [SO_4^{2-}] = 500 to >2,000 μM

– [H_2S] – lower or similar to [SO_4^{2-}] (coastal waters)

– [Fe^{2+}] ≤ 100 μM (deep waters)

Modern ocean

– [SO_4^{2-}] = 28,000 μM

– [H_2S] = <1 μM

– [Fe^{2+}] = <1 μM

Rational

In various modern aquatic systems some parameters, e.g., temperature, microbial communities, and especially chemical composition are similar to those that are believed to have existed in ancient oceans.

Research of chemical and microbial processes in such systems can be used to fill the gaps in our knowledge about the biogeochemical transformations of elements (especially nutrients and redox-sensitive elements) in the ancient oceans.

Isotopic approach

The most common approach to the evaluation of $[SO_4^{2-}]$ in the water columns of the ancient oceans is the measurement of the difference between isotopic compositions ($\delta^{34}S$) of sedimentary pyrite and seawater (evaporite) sulfate.

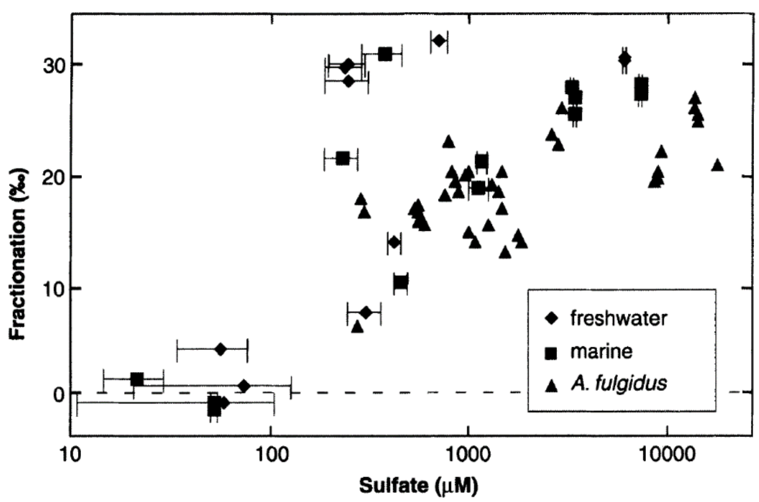


Fig. 1. Isotope fractionation as a function of sulfate concentration for freshwater (diamonds) and marine (squares) natural populations of sulfate reducers and for the hyperthermophile *A. fulgidus* (triangles). For the freshwater and marine populations, horizontal bars plot the range of sulfate concentrations within the reactor, with the higher concentration entering the reactor, and the low concentration exiting the reactor. The symbols are positioned on the bars at the average concentration in the reactor.

Problems of this approach:

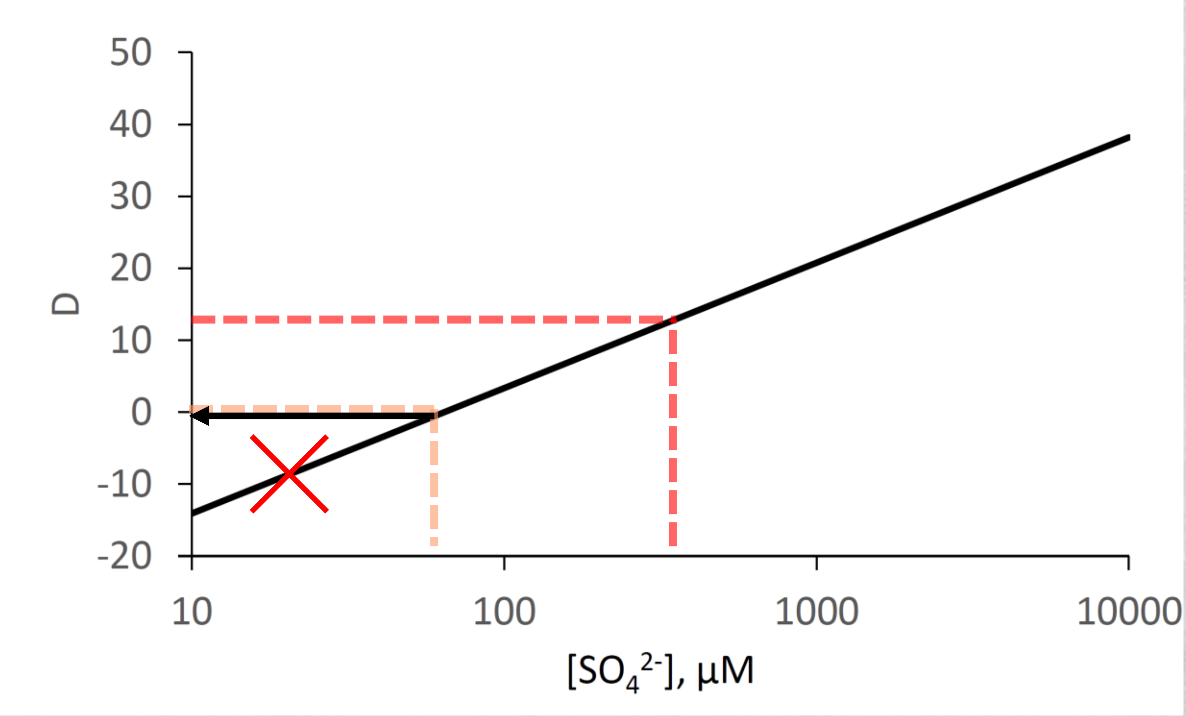
- precise quantitative calibration is impossible
- sulfate reduction cotinues in the sediemnts, all sulfate may be cosumed

Habicht, K.S., Gade, M., Thamdrup, B., Berg, P., Canfield, D.E. (2002) Calibration of sulfate levels in the Archean Ocean. Science, 298, 2372-2374.

Isotopic approach

Compilation of the data from numerous modern lakes leads to the following dependence:

$$D = \delta^{34}S_{water\ column\ sulfate} - \delta^{34}S_{sedimentary\ pyrite} = 7.57\ln([SO_4^{2-}], mM) + 20.76$$



Gomes, M.L., Hurtgen, M.T. (2015) Sulfur isotope fractionation in modern euxinic systems: Implications for paleoenvironmental reconstructions of paired sulfate–sulfide isotope records. Geochimica et Cosmochimica Acta, 157, 39-55.

Analogs of Prebiotic Ocean

Deep Sea Hydrothermal Vents

http://www.theecologist.org/siteimage/scale/800/600/158535.png

Analogs of Prebiotic Ocean

Yellowstone National Park

Kamyshny Jr., A., Druschel, G., Mansaray, Z.F., Farquhar, J. (2014) Multiple sulfur isotopes fractionations associated with abiotic sulfur transformations in Yellowstone National Park geothermal springs. Geochemical Transactions, 15:7.

Analogs of Archean Ocean

Lake Sihailongwan

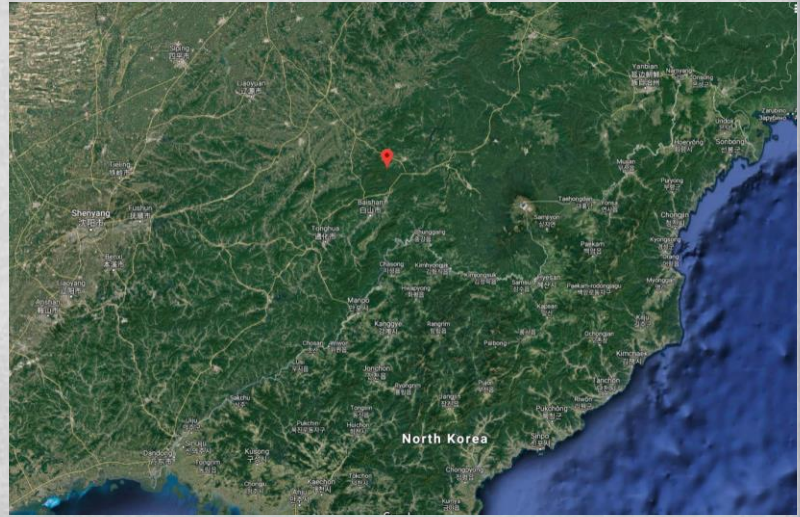
Iron rich hypolimnion

$[SO_4^{2-}]$ ≈ 80 μM

$[H_2S]$ up to 25 μM

$[Fe^{2+}]$ up to 60 μM

Boyko, V., Avetisyan, K., Findlay, A., Guo, Q., Yang, X., Pellerin, A., Kamyshny Jr., A. (2021) Biogeochemical cycling of sulfur, manganese and iron in ferruginous limnic analog of the Archean ocean. Geochimica et Cosmochimica Acta, 296, 56-74.



Analogs of Proterozoic Ocean

Lake Kinneret

$[SO_4^{2-}] \approx 500$ μM, sulfide rich hypolimnion

Knossow, N., Blonder, B., Eckert, W., Turchyn, A. V., Antler, G., Kamyshny Jr., A. (2015) Annual sulfur cycle in a warm monomictic lake with sub-millimolar sulfate concentrations. Geochemical Transactions, 16:7.

Analogs of Archean Ocean

Lake Sevan

$[SO_4^{2-}]$ ≈ 300 μM, sulfide rich hypolimnion

Avetisyan, K., Mirzoyan, N., Payne, R.B., Hayrapetyan, V., Kamyshny Jr., A. (2021) Eutrophication leads to formation of sulfide-rich deep-water layer in Lake Sevan (Armenia). Isotopes in Environmental and Health Studies, 57, 535-552.

In Search for Biogeochemical Time Machines in Croatia and Beyond

Croatia and the neighboring Balkan countries host a large number of lakes and artificial reservoirs with different hydrological settings.

Some of these lakes are promising candidates for the modern analogs of the Precambrian marine systems.

Other lakes are understudied and lacking the publications with detailed study of hydrology and chemistry (in English?).

The goal of this research is to evaluate lakes in Croatia and in other Balkan countries as the “Biogeochemical Time Machines”.

Examples of the Studied Lakes: Lake Rogoznica (Croatia)

Lake Rogoznica – stratified; sulfidic; not a good analog of the ancient ocean.
The reason – sulfate concentrations is too high (seawater lake).

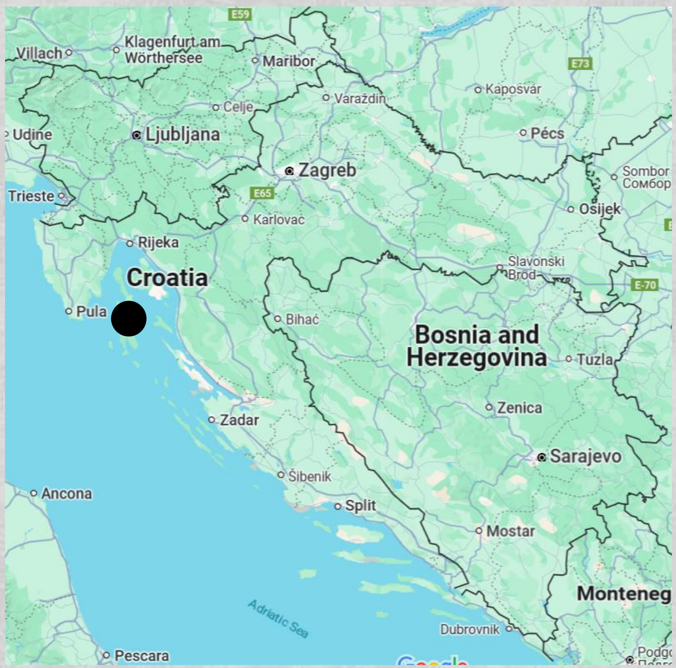
Kamyshny Jr., A., Zerkle, A.L., Mansaray, Z.F., Ciglenečki, I., Bura-Nakić, E., Farquhar, J., Ferdelman, T.G. (2011) Biogeochemical sulfur cycle in water column of shallow stratified sea-water lake: Speciation and quadruple sulfur isotope composition. Marine Chemistry, 127, 144-154.

Candidate Lakes in Croatia

Lake Vrana (Cres)

$[SO_4^{2-}] \approx$ 90-130 μM (calculated from $[Cl^-]$ and marine $[Cl^-]/[SO_4^{2-}]$ ratio).

Thermally stratified during the summer season.



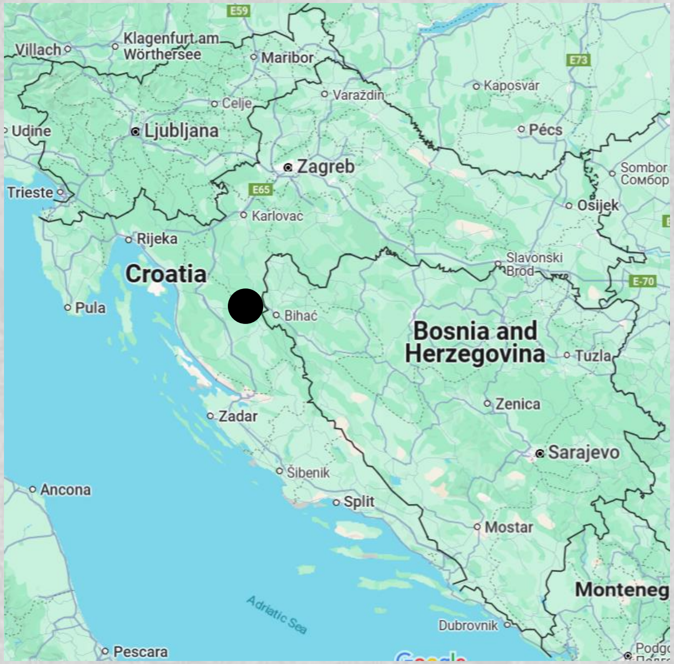
Katalanic, A., Rubinic, J., Buselic, J. (2008) Hydrology of two coastal karst cryptodepressions in Croatia: Vrana Lake *vs* Vrana Lake. Proceedings of TAAL2007, 732-743.

Candidate Lakes in Croatia

Lake Prošćansko (National Park Plitvička Jezera)

Reports on sulfate concentrations were not found.

Stratified, anoxic bottom (personal communication).

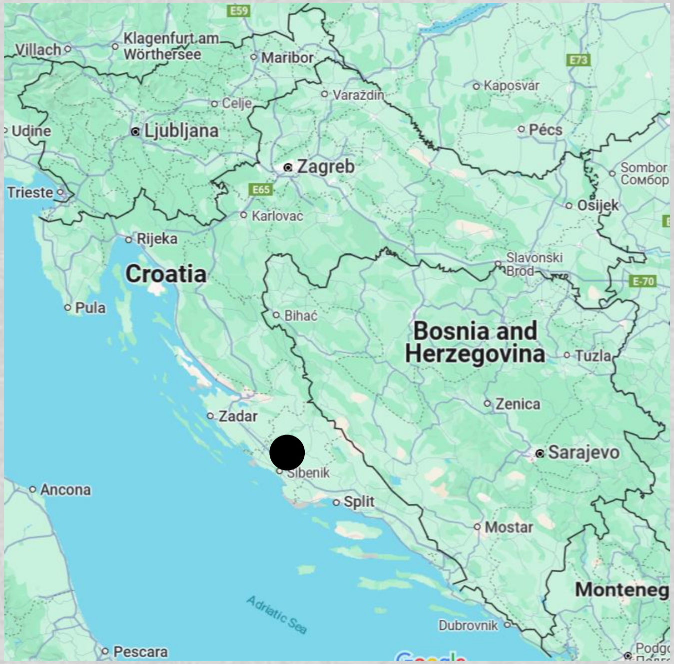


Candidate Lakes in Croatia

Lake Visovac (National Park Krka)

$[SO_4^{2-}]$ = 1000 – 2600 µM

Thermal stratification in the lake occurs from the spring to the late Autumn.



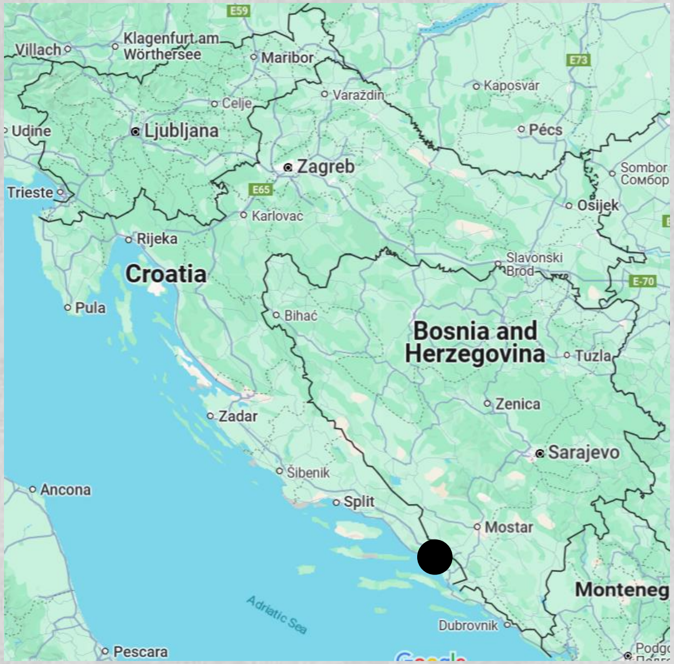
Udovič, M.G., Boroević, K.K., Žutinić, P., Šipoš, L., Plenković-Moraj, A. (2011) Net-phytoplancton species dominance in a travertine riverine lake Visovac, NP Krka. Natura Croatica, 20, 411-422.

Candidate Lakes in Croatia

Baćina Lakes

$[SO_4^{2-}] \approx 400 – 1100\ \mu M$

The lakes are stratified and anoxic until September, presence of hydrogen sulfide was not reported.



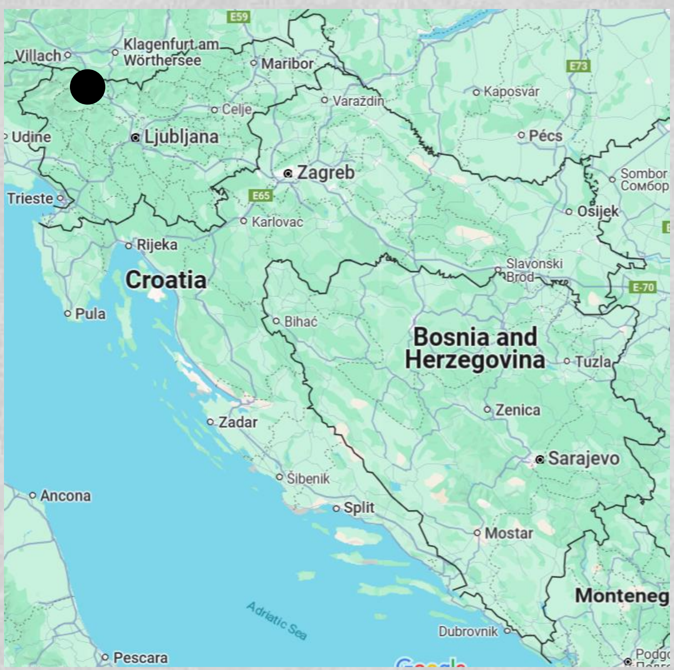
Ilijanić, N., Miko, S., Hasan, O., Čupić, D., Mesić, S., Širac, S., Marković, T., Miko, M.Š., Vlašić, A. (2015) Paleolimnological investigations of the Baćina Lakes - Crniševo Lake. Conference paper, Croatian Conference on Water. Croatian Waters on the Investment Wave, Opatija, May 20-23, 2015.

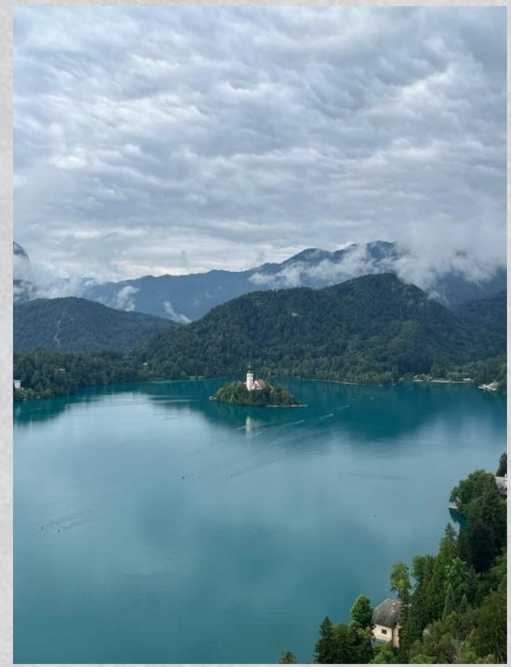
Candidate Lakes in Slovenia

Lake Bled

No reports on sulfate concentrations were found.

[H_2S] in the water column was reported to be up to 74 μM.



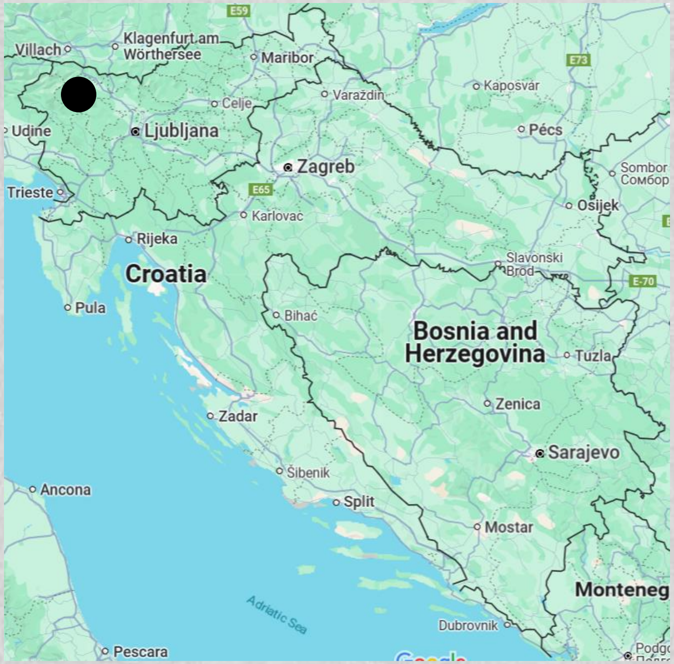


Molnar, F.M., Rothe, P., Förstner, U., Štern, J., Ogorelec, B., Šercelj, A., Culiberg, M. (1978) Lakes Bled and Bohinj: Origin, composition, and pollution of recent sediments. Geologija – Ljubljana, 21, 93-164.

Candidate Lakes in Slovenia

Lake Bohinj

Stratified, concentrations of sulfate and state of anoxia near the bottom were not found (although possibly known due to the monitoring program).

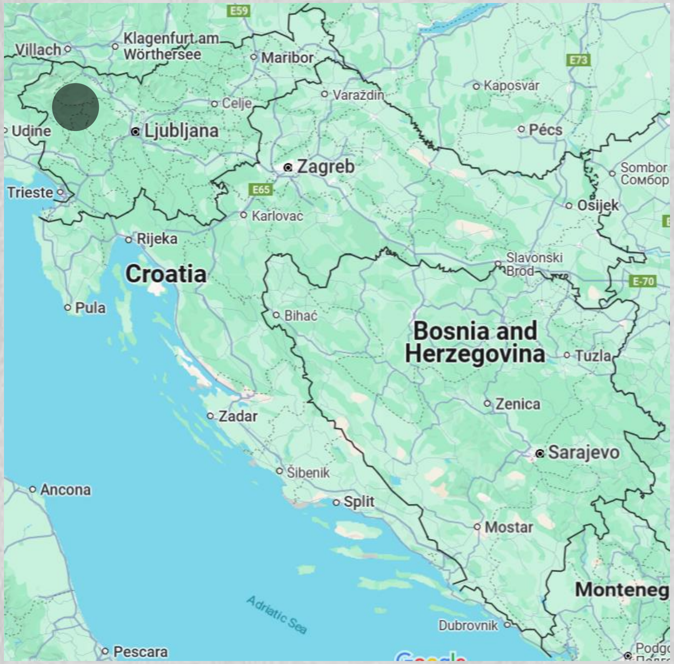


Candidate Lakes in Slovenia:
Three Small Alpine Lakes

Krnsko jezero, Jezero v Ledvicah, Jezero na Planini pri Jezeru

$[SO_4^{2-}]$ = 10-20 μM

Lakes are stratified in Summer – Autumn. Bottom waters may reach anoxia.



Muri, G., Brancelj, A. (2003) Seasonal water chemistry variations in three Slovenian mountain lakes. Acta Chimica Slovenica, 50, 137-147.

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QUESTIONS?

ANY TIME MACHINES TO SHARE?