



Institut
Ruđer
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Quest for the biogeochemical time machines: Adriatic coast and beyond

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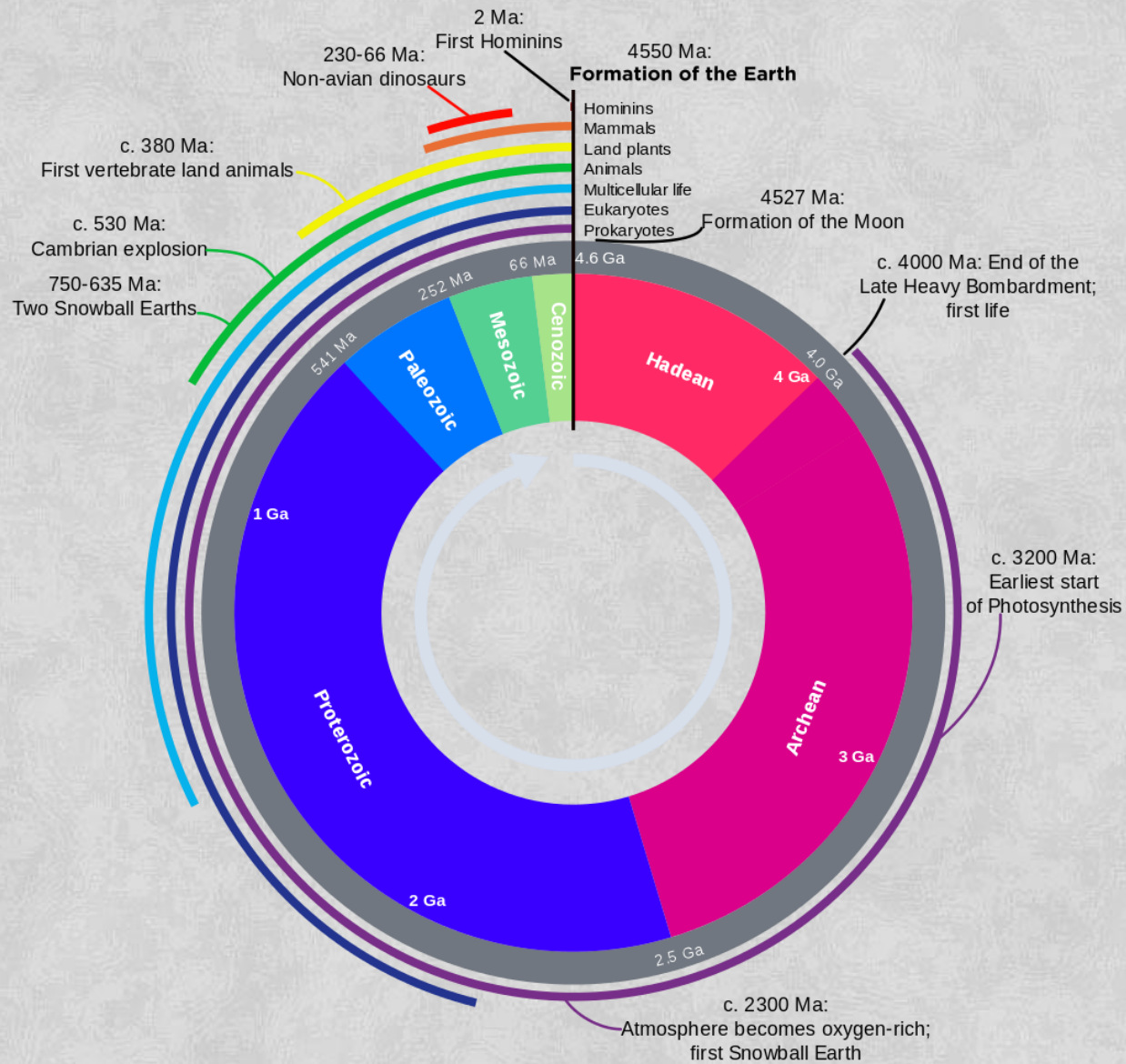
WHERE WOULD YOU GO?

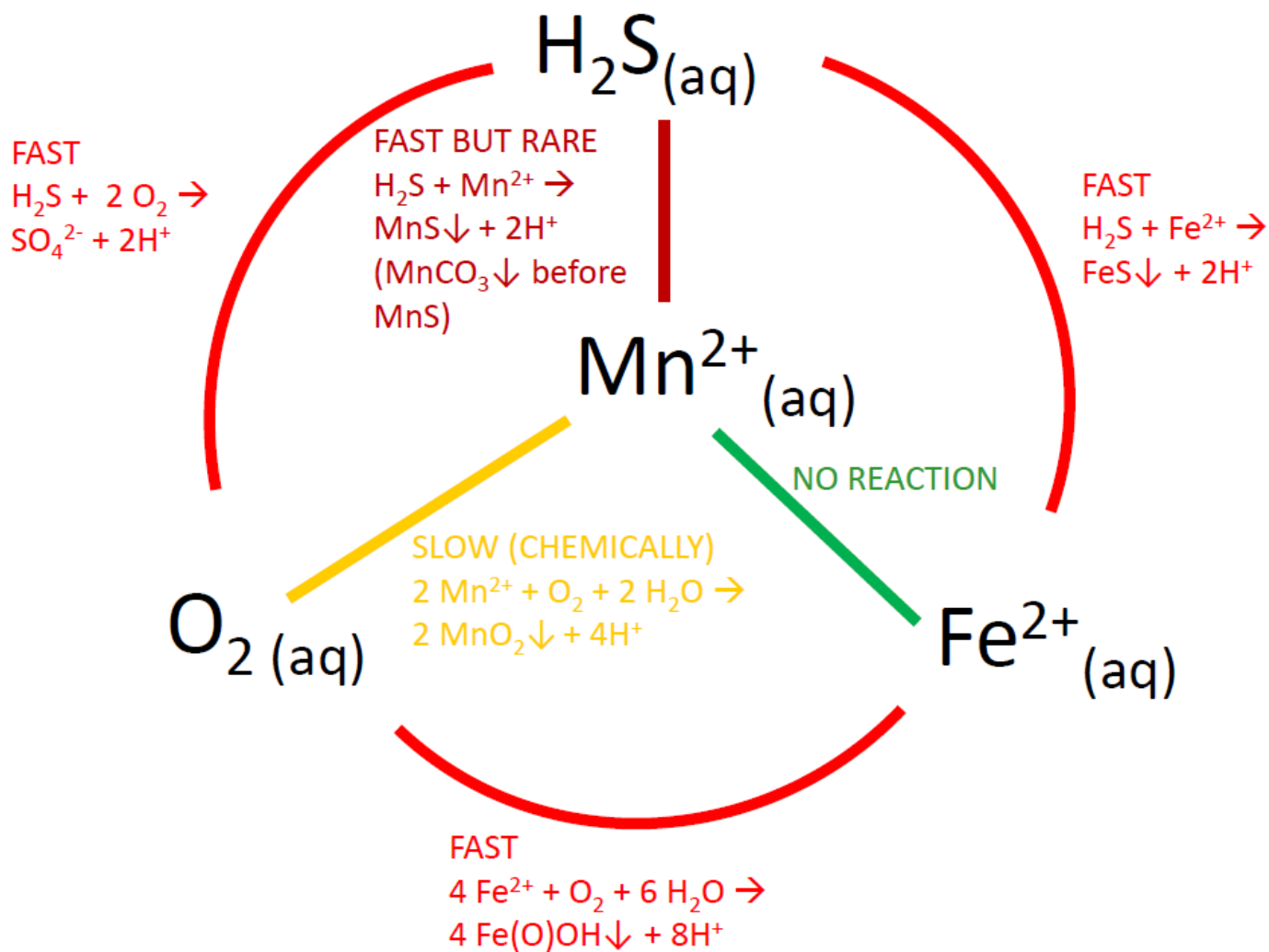


THE TIME MACHINE

BE CAREFUL WHAT YOU WISH FOR.

Eonothem / Eon		Erathem / Era		System / Period	Series / Epoch	numerical age (Ma)
Phanerozoic	Cenozoic	Quaternary		Holocene	present	
				Pleistocene	0.0117	
		Neogene		Pliocene	2.58	
				Miocene	5.333	
			Paleogene		Oligocene	23.03
					Eocene	33.9
				Paleocene	56.0	
		Mesozoic	Cretaceous		Upper	66.0
					Lower	100.5
			Jurassic		Upper	~ 145.0
				Middle	163.5 ± 1.0	
	Triassic			Lower	174.1 ± 1.0	
				Upper	201.3 ± 0.2	
	Paleozoic		Permian		Middle	~ 237
					Lower	247.2
					Lopingian	251.902 ± 0.024
			Carboniferous		Guadalupian	259.1 ± 0.5
				Cisuralian	272.95 ± 0.11	
		Devonian		Pennsylvanian	298.9 ± 0.15	
				Mississippian	323.2 ± 0.4	
				Upper	358.9 ± 0.4	
		Silurian		Middle	382.7 ± 1.6	
				Lower	393.3 ± 1.2	
			Pridoli	419.2 ± 3.2		
			Ludlow	423.0 ± 2.3		
			Wenlock	427.4 ± 0.5		
			Llandovery	433.4 ± 0.8		
			Upper	443.8 ± 1.5		
	Ordovician		Middle	458.4 ± 0.9		
			Lower	470.0 ± 1.4		
			Furongian	485.4 ± 1.9		
	Cambrian		Series 3	~ 497		
			Series 2	~ 509		
			Terreneuvian	~ 521		
	Precambrian	Archean Proterozoic	Neoproterozoic		541.0 ± 1.0	
Mesoproterozoic			1000			
Paleoproterozoic			1600			
Neoarchean			2500			
Hadean		Mesoarchean		2800		
		Paleoarchean		3200		
		Eoarchean		3600		
				4000		
Hadean						~ 4600





Iron and Hydrogen Sulfide

Archean ocean

- $[\text{SO}_4^{2-}] = <3 \text{ to } 80 \text{ } \mu\text{M}$
- $[\text{H}_2\text{S}]$ – very low, controlled by a solubility of FeS
- $[\text{Fe}^{2+}] \approx 100 \text{ } \mu\text{M}$

Proterozoic ocean

- $[\text{SO}_4^{2-}] = 500 \text{ to } >2,000 \text{ } \mu\text{M}$
- $[\text{H}_2\text{S}]$ – lower or similar to $[\text{SO}_4^{2-}]$ (coastal waters)
- $[\text{Fe}^{2+}] \leq 100 \text{ } \mu\text{M}$ (deep waters)

Modern ocean

- $[\text{SO}_4^{2-}] = 28,000 \text{ } \mu\text{M}$
- $[\text{H}_2\text{S}] = <1 \text{ } \mu\text{M}$
- $[\text{Fe}^{2+}] = <1 \text{ } \mu\text{M}$

Rational

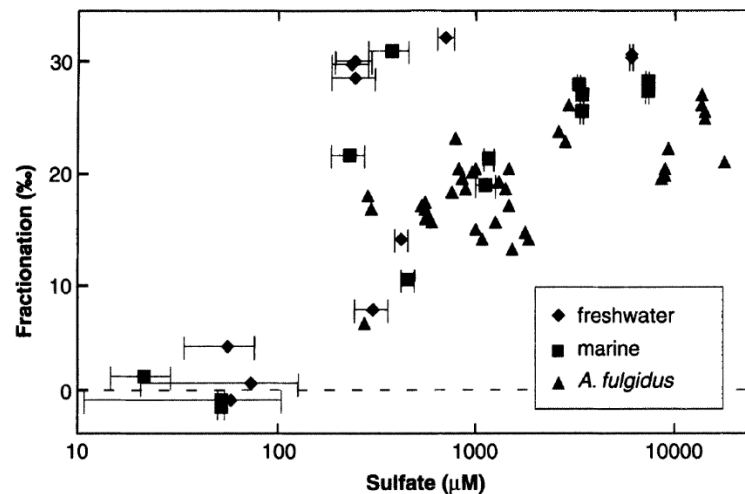
In various modern aquatic systems some parameters, e.g., temperature, microbial communities, and especially chemical composition are similar to those that are believed to have existed in ancient oceans.

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 $[\text{SO}_4^{2-}]$ in the water columns of the ancient oceans is the measurement of the difference between isotopic compositions ($\delta^{34}\text{S}$) 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:

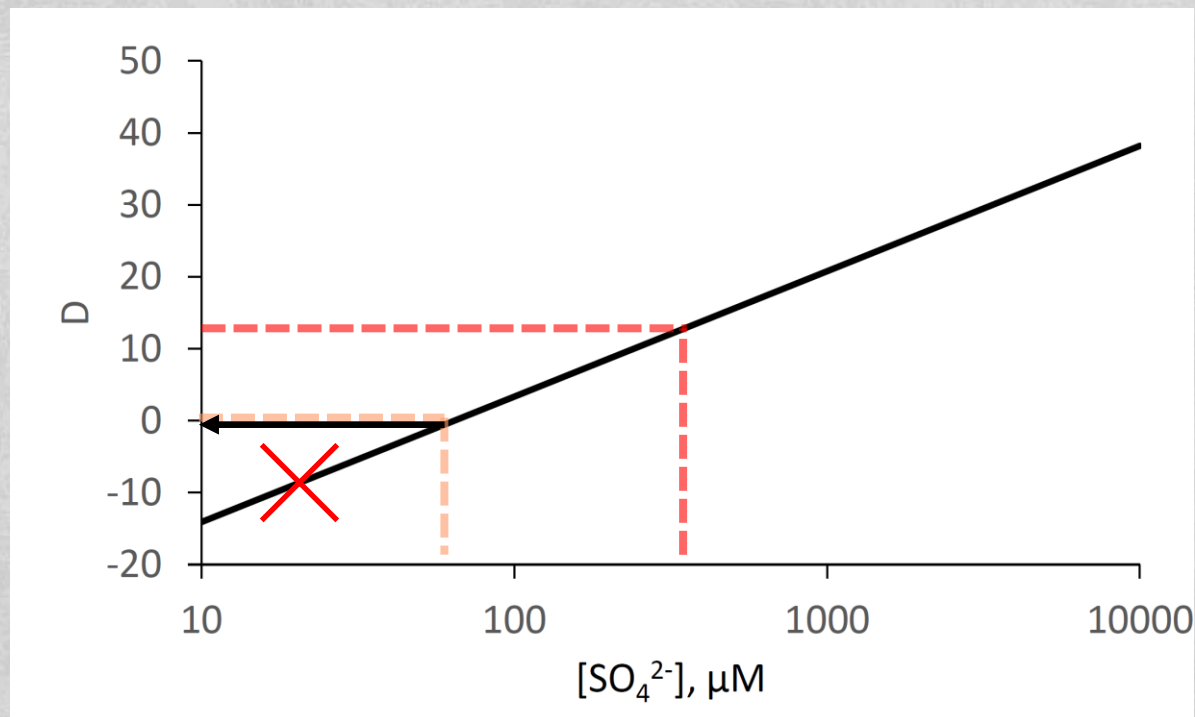
- precise quantitative calibration is impossible
- sulfate reduction continues in the sediments, all sulfate may be consumed

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:

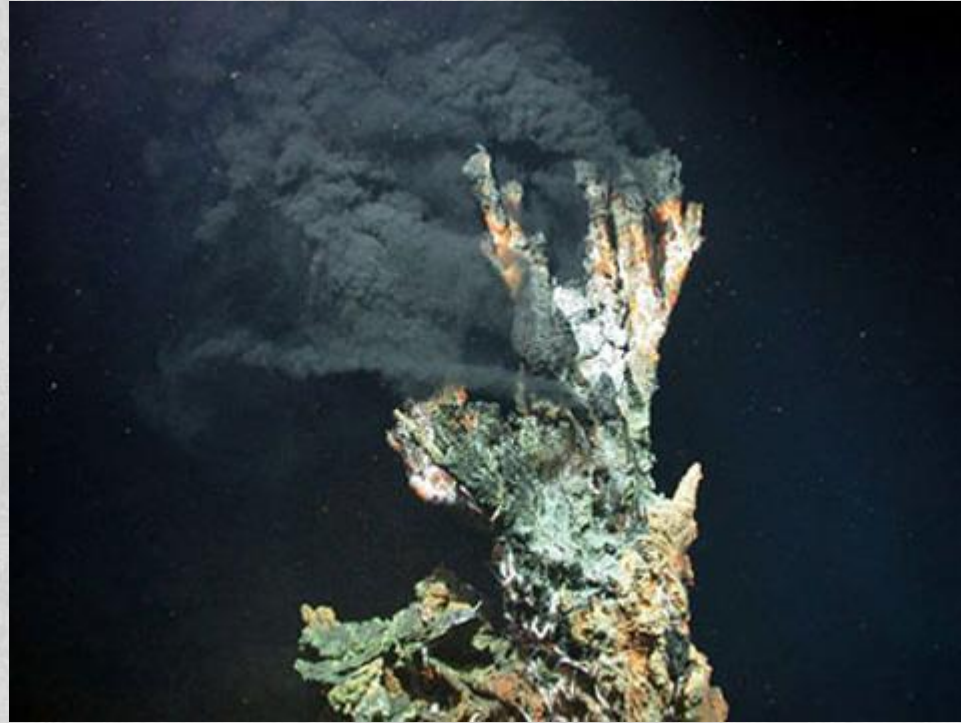
$$D = \delta^{34}S_{\text{water column sulfate}} - \delta^{34}S_{\text{sedimentary pyrite}} = 7.57 \ln([SO_4^{2-}], mM) + 20.76$$



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



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.

Analog of Archean Ocean

Lake Sihailongwan



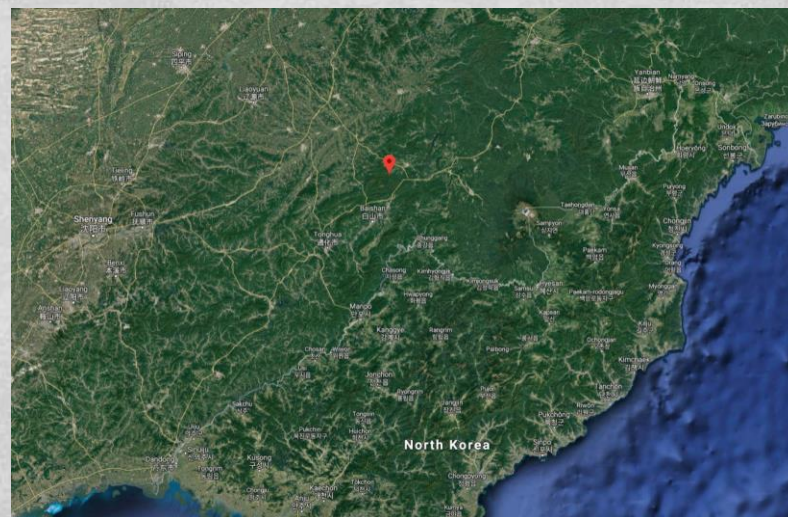
Iron rich hypolimnion

$[\text{SO}_4^{2-}] \approx 80 \mu\text{M}$

$[\text{H}_2\text{S}]$ up to $25 \mu\text{M}$

$[\text{Fe}^{2+}]$ up to $60 \mu\text{M}$

Boyko, V., Avetisyan, K., Findlay, A., Guo, Q., Yang, X., Pellerin, A., Kamysny 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

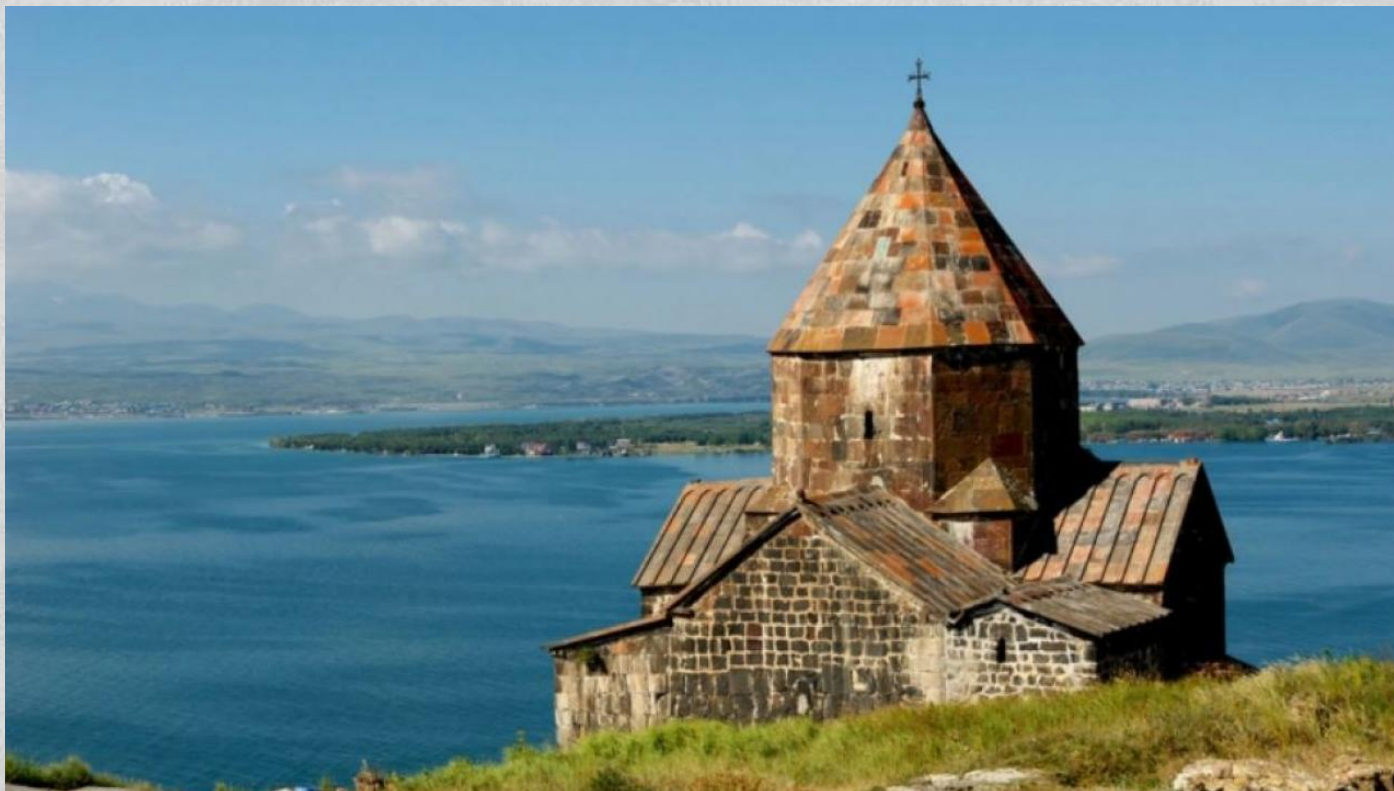


$[\text{SO}_4^{2-}] \approx 500 \mu\text{M}$, sulfide rich hypolimnion

Knossow, N., Blonder, B., Eckert, W., Turchyn, A. V., Antler, G., Kamysny 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



$[\text{SO}_4^{2-}] \approx 300 \mu\text{M}$, 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).

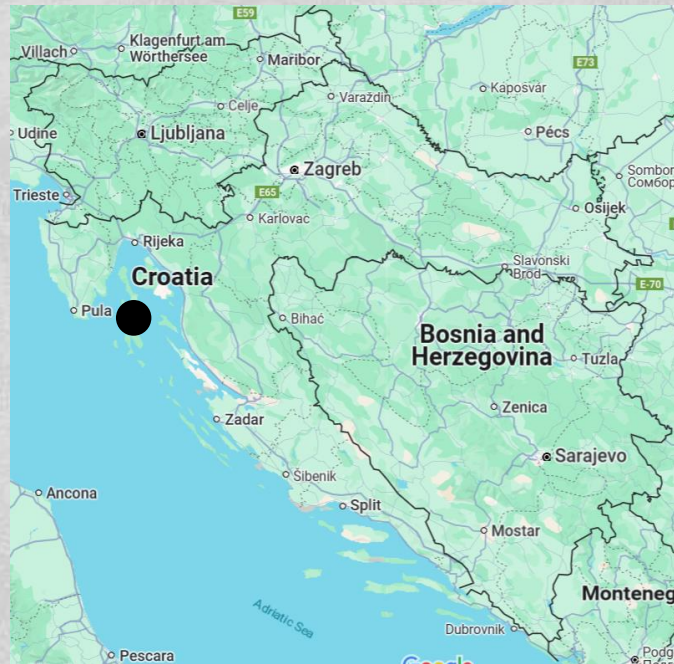
Kamyshny Jr., A., Zerkle, A.L., Mansaray, Z.F., Ciglencečki, I., Bura-Nakić, E., Farquhar, J., Ferdelman, T.G. (2011) Biogeochemical sulfur cycle in water column of shallow stratified sea-water lake: Speciation and quadruple sulfur isotope composition. *Marine Chemistry*, 127, 144-154.

Candidate Lakes in Croatia

Lake Vrana (Cres)

$[\text{SO}_4^{2-}] \approx 90\text{-}130 \mu\text{M}$ (calculated from $[\text{Cl}^-]$ and marine $[\text{Cl}^-]/[\text{SO}_4^{2-}]$ ratio).

Thermally stratified during the summer season.



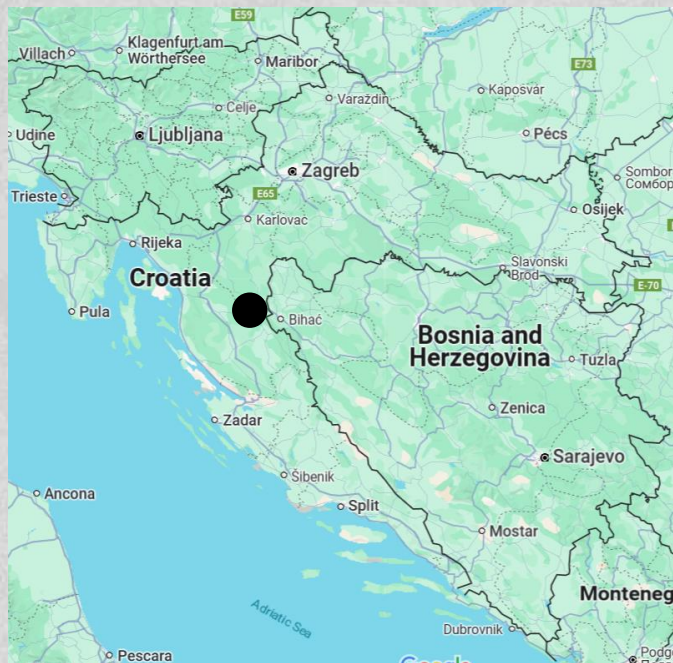
Katalanic, A., Rubinic, J., Buselic, J. (2008) Hydrology of two coastal karst cryptodepressions in Croatia: Vrana Lake vs Vrana Lake. Proceedings of TAAL2007, 732-743.

Candidate Lakes in Croatia

Lake Prošćansko (National Park Plitvička Jezera)

Reports on sulfate concentrations were not found.

Stratified, anoxic bottom (personal communication).

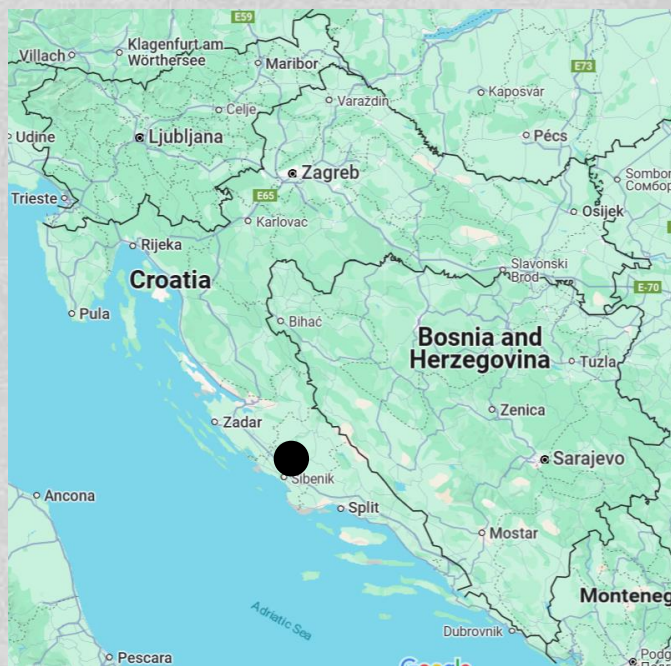


Candidate Lakes in Croatia

Lake Visovac (National Park Krka)

$$[\text{SO}_4^{2-}] = 1000 - 2600 \mu\text{M}$$

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



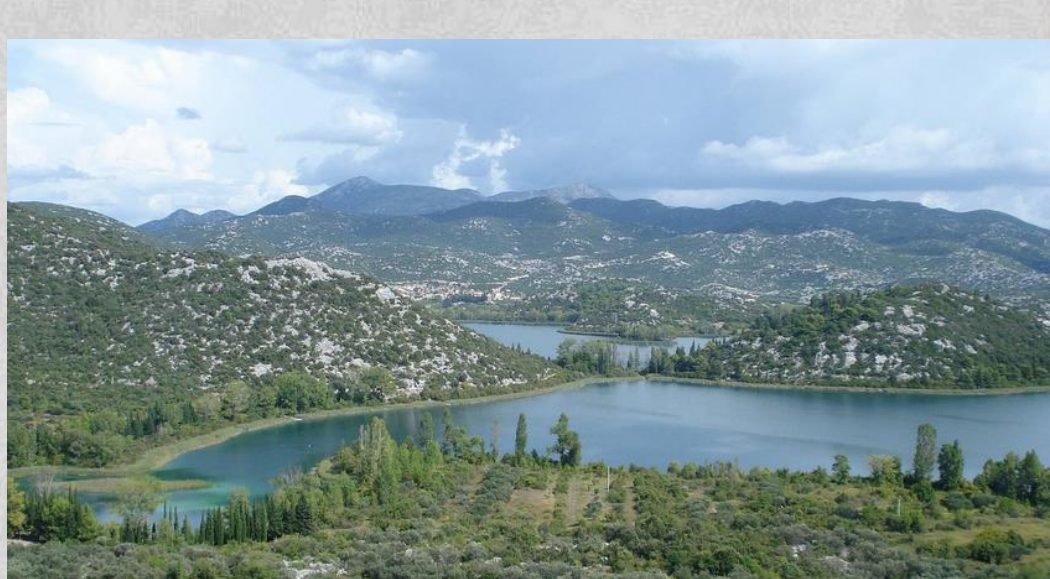
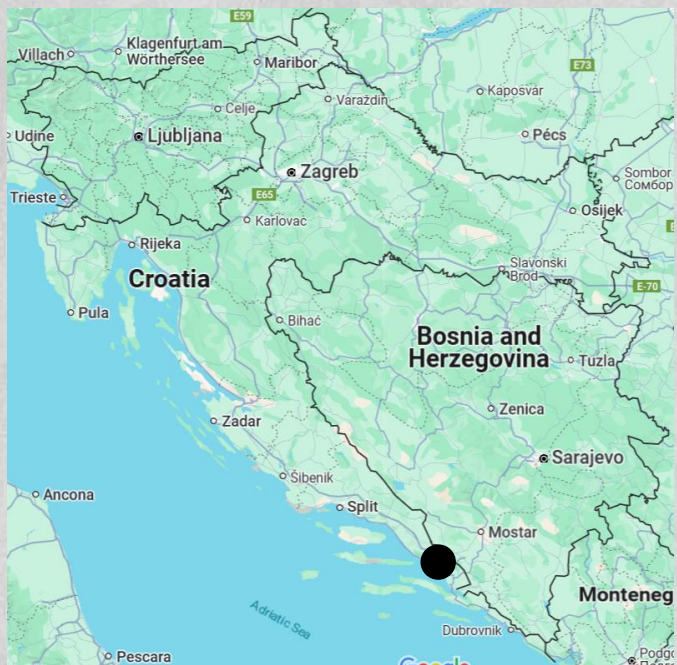
Udovič, M.G., Boroević, K.K., Žutinić, P., Šipoš, L., Plenković-Moraj, A. (2011) Net-phytoplankton species dominance in a travertine riverine lake Visovac, NP Krka. *Natura Croatica*, 20, 411-422.

Candidate Lakes in Croatia

Baćina Lakes

$[\text{SO}_4^{2-}] \approx 400 - 1100 \mu\text{M}$

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



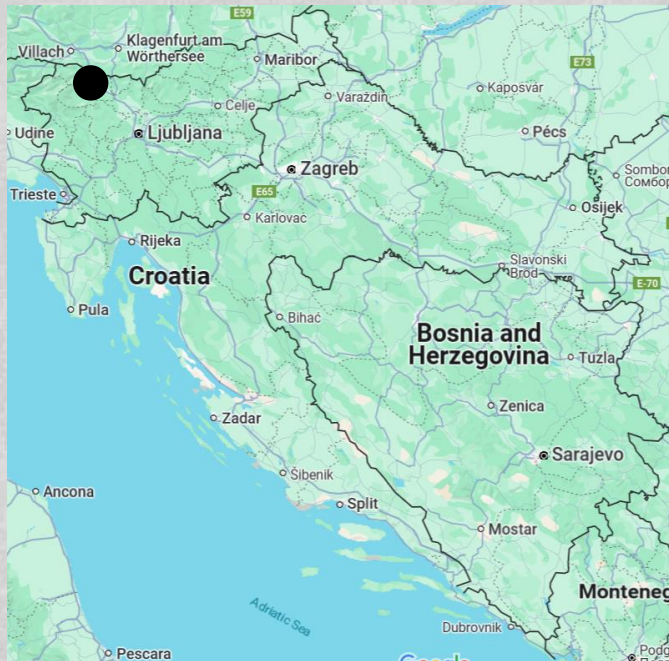
Ilijanić, N., Miko, S., Hasan, O., Čupić, D., Mesić, S., Širac, S., Marković, T., Miko, M.Š., Vlašić, A. (2015) Paleolimnological investigations of the Baćina Lakes - Crniševo Lake. Conference paper, Croatian Conference on Water. Croatian Waters on the Investment Wave, Opatija, May 20-23, 2015.

Candidate Lakes in Slovenia

Lake Bled

No reports on sulfate concentrations were found.

[H₂S] in the water column was reported to be up to 74 µM.

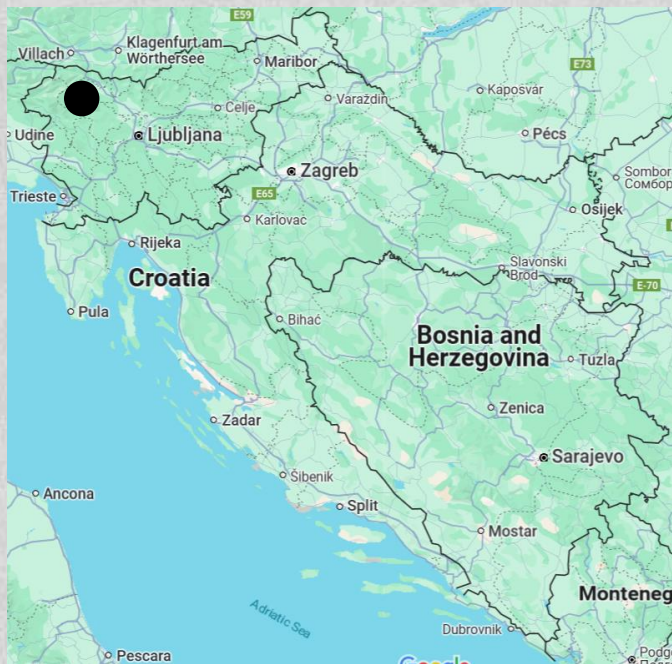


Molnar, F.M., Rothe, P., Förstner, U., Štern, J., Ogorelec, B., Šercelj, A., Culiberg, M. (1978) Lakes Bled and Bohinj: Origin, composition, and pollution of recent sediments. *Geologija – Ljubljana*, 21, 93-164.

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).



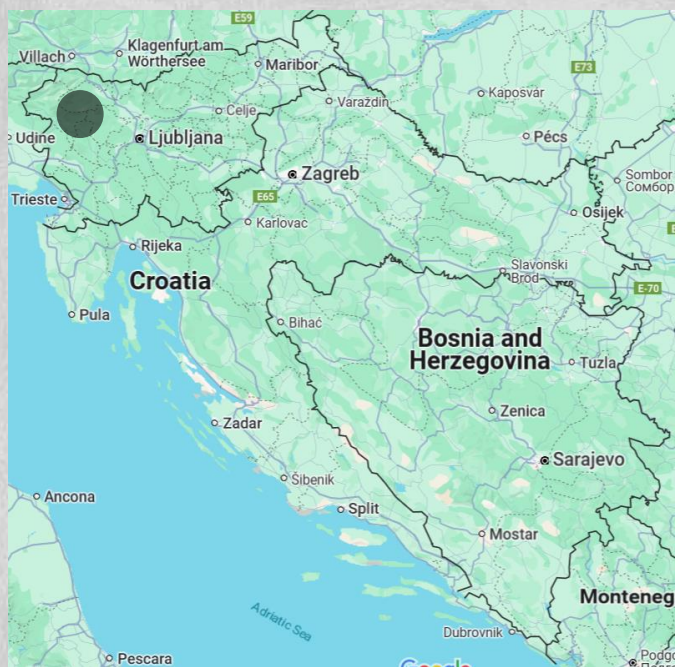
Candidate Lakes in Slovenia:

Three Small Alpine Lakes

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

$[\text{SO}_4^{2-}] = 10\text{-}20 \mu\text{M}$

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?