

## Dissolved molybdenum asymptotes in sulfidic waters

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### Supplementary Information

The Supplementary Information includes:

- Sources for Data Compiled in Table 1
- Note on Calculation of POC Values for Pore Waters in Table 1
- Derivation of Equation 4
- Supplementary Information References

### Sources of Data Compiled in Table 1

Location	Reference
<b>Euxinic marine waters</b>	
Black Sea (1991)	Emerson, S.R., Husted, S.S. (1991) Ocean anoxia and the concentrations of molybdenum and vanadium in seawater. <i>Marine Chemistry</i> 34, 177–196.
	Karl, D.M., Knauer, G.M. (1991) Microbial production and particle flux in the upper 350 m of the Black Sea. <i>Deep-Sea Research</i> 38(Supple 2), S921–S942.
Black Sea (2011)	Nägler, T.F., Neubert, N., Böttcher, M.E., Dellwig, O., Schnetger, B. (2011) Molybdenum isotope fractionation in pelagic euxinia: Evidence from the modern Black and Baltic Seas. <i>Chemical Geology</i> 289, 1–11.
Black Sea (2017)	Rolison, J.M., Stirling, C.H., Middag, R., Rijkenberg, M.J.A. (2017) Uranium stable isotope fractionation in the Black Sea: Modern calibration of the $^{238}\text{U}/^{235}\text{U}$ paleo-redox proxy. <i>Geochimica et Cosmochimica Acta</i> 203, 69–88.
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Black Sea (2019)	Dellwig, O., Wegwerth, A., Schnetger, B., Schulz, H., Arz, H.W. (2019) Dissimilar behaviors of the geochemical twins W and Mo in hypoxic-euxinic marine basins. <i>Earth-Science Reviews</i> 193, 1–23.

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- Rogoznica Lake (Sept.)  
Helz, G.R., Bura-Nakić, E., Mikac, N., Ciglencčki, I. (2011) New model for molybdenum behavior in euxinic waters. *Chemical Geology* 284, 323–332.
- Čanković, M., Žučko, J., Radić, D., Janeković, I., Petrić, I., Ciglencčki, I., Collins, G. (2019) Microbial diversity and long-term geochemical trends in the euxinic zone of a marine, meromictic lake. *Systematic and Applied Microbiology* 42, 126016.
- Sulfidic pore waters**
- Chesapeake Bay (2021)  
Cui, M., Luther, G.W. III, Gomes, M. (2021) Cycling of W and Mo species in natural sulfidic waters and their sorption mechanism on MnO<sub>2</sub> and implications for paired W and Mo records as a redox proxy. *Geochimica et Cosmochimica Acta* 295, 24–48.
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Eroglu, S., Scholz, F., Siebert, C. (2020) Influence of particulate versus diffusive molybdenum supply mechanisms on the molybdenum isotope composition of continental margin sediments. *Geochimica et Cosmochimica Acta* 273, 51–69.
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Hardisty, D.S., Lyons, T.W., Riedinger, N., Isson, T.T., Owens, J.D., Aller, R.C., Rye, D.M., Planavsky, N.J., Reinhard, C.T., Gill, B.C., Masterson, D.A., Johnston, D.T. (2018) An evaluation of sedimentary molybdenum and iron as proxies for pore fluid paleoredox conditions. *American Journal of Science* 318, 527–556.
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Northern Baltic  
Jokinen, S.A., Koho, K., Virtasalo, J.J., Jilbert, T. (2020) Depth and intensity of the sulfate-methane transition zone control sedimentary molybdenum and uranium sequestration in a eutrophic low salinity setting. *Applied Geochemistry* 122, 104767
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Mohajerin, T.J., Helz, G.R., Johannesson, K.H. (2016) Tungsten-molybdenum fractionation in estuarine environments. *Geochimica et Cosmochimica Acta* 177, 105–119.



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## Note on Calculation of POC Values for Pore Waters in Table 1

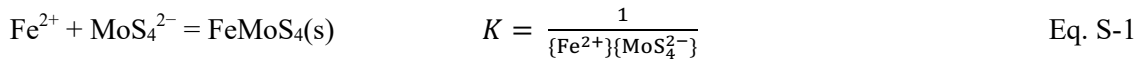
It is assumed that pore waters are in diffusive contact with all the organic carbon in sediments on the time scale of diagenesis. Therefore, POC aqueous concentrations (moles C/L) can be calculated from a sediment's dry TOC concentration, sediment porosity ( $\theta$ ) and solid phase density ( $\rho$ ) values:  $\text{POC} = [\text{C}_{\text{org}}/12.0][(1-\theta)\rho/\theta]$ , where  $\text{C}_{\text{org}}$  has units of g C/g dry sediment and 12.0 is the atomic mass of carbon. In a single core,  $\theta$  and  $\rho$  both will vary, but their ranges are not great. For calculations in Table 1, generic and constant values for porosity (0.8) and solid phase density



(2.3 g/cm<sup>3</sup>) were used. In nature, these values will differ from the generic values by as much as 15 %, but the error in POC arising from this simplification is negligible relative to the immense range in POC concentrations in the Table.

## Derivation of Equation 4

Precipitation of FeMoS<sub>4</sub> occurs by the following reaction (Vorlicek et al. 2018):

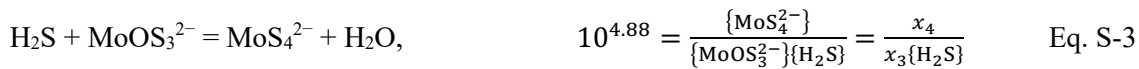


(Braces designate thermodynamic activities.) {MoS<sub>4</sub><sup>2-</sup>} is related to Mo<sub>aq</sub>, the total dissolved Mo concentration, by:

$$\{\text{MoS}_4^{2-}\} = (\gamma_{\text{MoS}_4})x_4\text{Mo}_{\text{aq}} \quad \text{Eq. S-2}$$

Where  $\gamma_{\text{MoS}_4}$  is the activity coefficient of the tetrathiomolybdate ion and  $x_4$  is its mol fraction in Mo<sub>aq</sub> (values plotted in Fig. 1).

Thiolation of MoOS<sub>3</sub><sup>2-</sup> to form MoS<sub>4</sub><sup>2-</sup> occurs by (Erickson and Helz, 2000):



At the very earliest stages of biological sulfate reduction in anoxic aquatic environments, before Mo<sub>aq</sub> precipitation begins, {Fe<sup>2+</sup>} becomes linked to pH and {H<sub>2</sub>S<sub>aq</sub>}, the non-ionized form of dissolved sulfide, by the solubility product constant of an iron monosulfide phase ( $K_{\text{FeS}}$ ):

$$\{\text{Fe}^{2+}\} = \frac{K_{\text{FeS}}(10^{-2\text{pH}})}{\{\text{H}_2\text{S}\}} \quad \text{Eq. S-4}$$

Substituting Equations S-2 to S-4 into S-1 yields:

$$\text{Mo}_{\text{aq}} = \frac{10^{-19.83}(10^{2\text{pH}})}{K_{\text{FeS}}(\gamma_{\text{MoS}_4})} x_3^{-1} \quad \text{Eq. S-5}$$

By replacing  $x_4$  with  $x_3$ , the explicit {H<sub>2</sub>S} term has been eliminated. In this form, Equation S-5 demonstrates that under conditions of relatively constant pH and ionic strength, rising sulfide concentrations produce a solubility minimum where  $x_3$  reaches a maximum.

Because FeMoS<sub>4</sub> precipitation is likely to occur in microniche hotspots where FeS nucleation and growth are active, Ostwald's Rule suggests that the relevant value of  $K_{\text{FeS}}$  is likely to be that of a metastable phase, such as FeS<sub>nano</sub> or FeS<sub>Amorph</sub>, rather than that of mackinawite. In Figure 2 in the main text, Wolthers' (2005) value of  $K_{\text{FeS}} = 10^{4.87}$  is assumed.

## Supplementary Information References

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