☒ **Talk** ☐ **Poster**

The Formation, Loss, and Speciation of Reduced Organic Sulfur

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Organic sulfur originates from biomolecules and abiotic transformations and influences major (e.g., sulfur, carbon) and trace (e.g., mercury) element cycles. Enduring questions remain on the sources, speciation, and stability of reduced organic sulfur, which controls elemental cycling and has disparate reactivity. A notable challenge is resolving thiols (R-SH) from thioethers (R-S-R') in complex natural mixtures due to limitations of XAS (e.g., similar absorption energies, wide variability in spectra of structurally diverse thiols)[1] and mass spectrometry approaches (e.g., lack of structural information). Here, we present three approaches using atomic- and molecular-level techniques that elucidate key environmental transformations and chemistries of reduced organic sulfur.

Abiotic sulfurization and photo-chemical desulfurization of dissolved organic matter (DOM) were investigated in the field and laboratory.[2, 3] Inorganic sulfide incorporated into unsaturated DOM molecules as primarily reduced sulfur species (86% of new sulfur formed thiols (R-SH) and/or thioethers (R-S-R')); the combined use of S XANES spectroscopy and ultrahigh-resolution mass spectrometry ruled out the prominence of disulfides in DOM. Reduced organic S species were recalcitrant under dark oxic conditions but the majority (~65%) rapidly oxidized to inorganic sulfate in the presence of sunlight.[3]

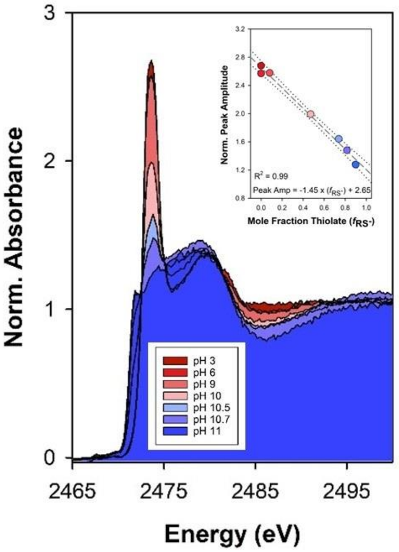

Fig. 1. S Kα_1 HERFD-XANES spectra of a model thiol from pH 3-11 (inset shows peak amp. vs fraction RS^-).

Next, we show that thiol and thioether moieties can be resolved by exploiting changes in S XANES spectra caused by thiol deprotonation (R-SH ↔ $R-S^- + H^+$). Using a tender X-ray emission spectrometer (TEXS) at ID26 of the ESRF,[4] S Kα_1 HERFD-XANES spectra were collected for model S compounds and DOM across the pH range of thiol pK_as. Model thiols exhibited systematic decreases in peak amplitude with deprotonation (**Figure 1**). DOM spectra exhibited marked and reversible decreases in reduced S peak amplitude between pH 7-11, permitting estimation of thiol vs. thioether contributions and thiol pK_as. We conclude with merits of the method, opportunities for optimization, and implications for environmental S cycling.

References

[1] Manceau & Nagy, *Geochim. Cosmochim. Acta*, **99**, 206-233 (2012). [2] Poulin et al. *Environ. Sci. Tech.*, **51**, 3630-3639 (2017) [3] Poulin. *Environ. Sci. Tech. Lett.*, **10**, 499-505 (2023) [4] Rovezzi et al. *J. Synchrotron Radiat.*, 27, 813-826. (2020).