

## Assessing the role of Holocene sapropels on the Black Sea methane cycle

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Sapropels, sedimentary intervals rich in organic matter, represent a substantial carbon source which directly affects the sedimentary redox conditions in marine sediments. While recently-deposited sapropels produce a shoaling of the redox zonation, the long term effect of sapropelic sediments once these become buried over several millennia and lose their most labile carbon fraction requires further addressing. In the northern Black Sea, the changing limnic to marine conditions due to the flooding of the Bosphorus straight and subsequent connection with the Mediterranean Sea circa 9.5 kyr before present (BP), led to local geochemical conditions which favored ocean stratification and an increase in the amount of organic matter reaching the sediment between 8.0 and 3.5 kyr BP. Through reactive transport models which focus on the methane cycle, we track the geochemical effects of the sapropel since its initial deposition up to present time. Our results reveal that, from the onset of their deposition, sapropels heavily influence the methane cycle by controlling the position of the sulfate-methane transition (SMT) through organoclastic sulfate reduction. Nevertheless, the influence of the sapropels on methanogenesis will ultimately depend on the time required for the sapropel to be buried below the SMT. Consequently, methane formation will be favored in locations with high sedimentation rates, or locations receiving turbidites and slumps, such that the sapropel can be quickly buried into the methanogenic zone.

## Determining thioitungstate stability constants for low temperature, low ionic strength aqueous solutions

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### Abstract

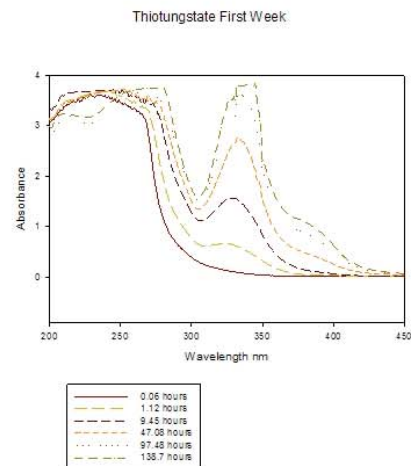
Due to recent findings that suggest childhood leukemia may be linked to exposure to tungsten in drinking water, a need has arisen to better understand geochemical reactions affecting W concentrations and speciation in groundwater flow systems. Preliminary data show that W has a strong and statistically significant positive correlation ( $p \leq 0.001$ ) with dissolved sulfide [i.e., S (-II)] concentration ( $r = 0.95$ ) in the Carrizo Sand aquifer where groundwaters become anoxic. We hypothesize that like Mo [1], W may form thioitungstate complexes in sulfidic groundwaters. In sulfidic waters the general form of the thioitungstate forming reaction is:



where x is 0 – 4, and the concentration product, Q, which is used to obtain the conditional equilibrium constants, is given as:

$$Q = [WO_{x-1}S_{5-x}^{2-}] / \{ [WO_xS_{4-x}^{2-}] [H_2S] \}$$

To better understand the geochemical behavior of thioitungstates, we are measuring the stability constants for these species in dilute, aqueous solutions. As the thioitungstate forming reaction occurs, sulfur replaces oxygen in the tungstate oxyanion. Changes in solution composition are measured by periodic scanning of the absorption spectrum ( $200 \text{ nm} \leq \lambda \leq 450 \text{ nm}$ ) by UV/Vis spectrophotometry. As shown in Figure 1, the wavelength pattern changes with time as different thioitungstate species are produced. Using the absorbance coefficients and absorption at the maximum spectra for each thioitungstate species, Beer's Law is employed to calculate the concentration of each thioitungstate species, from which Q for each reaction can be determined. The stability constants are then calculated from Q using a modified Debye-Hückel equation. Determination of the stability constants of each of thioitungstate species is then used in a geochemical model to predict their importance in groundwater systems. Preliminary data are presented for the stability constants of the thioitungstate complexes in dilute aqueous solutions.



**Figure 1:** Spectral changes occurring during the time interval when  $WO_4^{2-}$  changes to  $WO_3S^{2-}$ , and is beginning to form  $WO_2S_2^{2-}$

[1] Erickson & Helz (2000) *Geochemica et Cosmochimica Acta* **64**, 1149-1158