

## ACS-PRF Annual Report 2019

**Advancing the Vanadium Paleoredox Proxy:  
Defining the Chemistry Controlling Vanadium Speciation in Sulfidic and Polysulfidic Waters**

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**Project Objectives:** This project seeks to characterize experimentally the chemistry governing V speciation in initially  $S^0$ -free or  $S^0$ -rich euxinic waters. Taking a cue from known chemistries of elements (Mo, Re, W, and As) related to V, hypotheses posit the homogenous participation of thiovanadates ( $V^{(V)}O_{4-x}S_x^{3-}$ ), thiovanadyl ( $V^{(IV)}S^{2+}$ ), thiovanadites ( $V^{(III)}O_{3-x}S_x^{3-}$ ), and  $V^{(III \text{ or } IV)}$ -polysulfido complexes in euxinic speciation. According to LeChatelier's Principle,  $V^{(V)}O_{4-x}S_x^{3-}$  ought to be stabilized in  $S^0$ -rich solutions. These conditions may foster formation of  $V^{(III \text{ or } IV)}$ -polysulfido species via ligand-induced reduction. The presence of aquatic  $V^{(III \text{ or } IV)}$ -polysulfido complexes,  $V^{(IV)}S^{2+}$ , and/or  $V^{(III)}O_{3-x}S_x^{3-}$  may assist in explaining instances of elevated V solubility in sulfidic waters; preliminary evidence in initially  $S^0$ -free sulfidic solutions hints that  $V^{(IV)}S^{2+}$  and  $V^{(III)}O_{3-x}S_x^{3-}$  may be important. Various techniques are utilized to identify and quantify homogenous and heterogeneous phases. Ultimately, this work aims to identify reactions, quantify thermodynamic constants, and develop V speciation models.

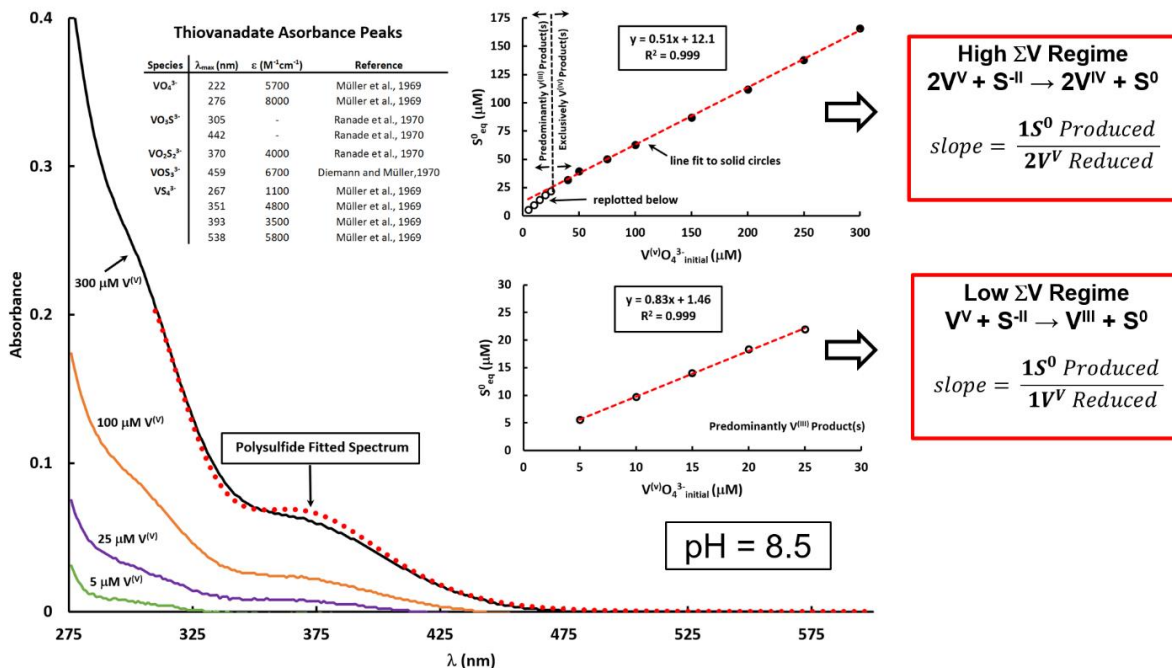
**Research Progress:**

**a.) At moderate alkalinity,  $V^{(III)}$  and  $V^{(IV)}$  phases are favored.**

Figure 1 shows the consequences of adding 5 to 300  $\mu\text{M}$   $VO_4^{3-}$  to solutions initially containing 3 mM  $\Sigma S^{2-}$  and 20 mM TRIS at pH = 8.5. The inset table of thiovanadate optical constants and UV-vis spectra shown in Fig. 1, demonstrates that  $V^{(V)}$ -thiovanadates are, at best, marginal species in these solutions. Rather, spectra are best fit using optical constants for polysulfide anions ( $S_n^{2-}$ ; n = 2-6), implying oxidation of  $S^{2-}$  to  $S^0$  and reduction of  $V^{(V)}$  occurs under these test conditions.  $\Sigma S^0$  concentrations formed in the test solutions were calculated from the fitted spectra and are plotted as a function of initial  $VO_4^{3-}$  concentrations in the inset graphs of Fig. 1. These plots appear to show two distinct reduction regimes. From  $\sim 40$  to 300  $\mu\text{M}$  initial  $VO_4^{3-}$ , the plot yields a slope of  $\sim 1/2$  (actual  $m=0.51$ ). Whereas, lower initial  $VO_4^{3-}$  concentrations give a distinctly higher slope of 0.83. These results infer that in the high  $\Sigma V$  regime, reduction of  $V^{(V)}$  to  $V^{(IV)}$  solely prevails. In the lower  $\Sigma V$  regime, reduction of  $V^{(V)}$  to  $V^{(III)}$  phase(s) becomes favored.

A Tyndall test was performed with a laser to confirm the presence or absence of any colloids in the test solutions of Fig. 1. These tests clearly showed the presence of scattered light through the high and low regime solutions, implying that heterogeneous  $V^{(III)}$  and/or  $V^{(IV)}$  products are formed in the test solutions. To remove the colloids prior to filtering and performing atomic absorption spectroscopy (AAS) analyses, 10 mM  $MgCl_2$  was added to the test solutions as a flocculation agent; Tyndall beams vanished after filtering test solutions with  $MgCl_2$  added. AAS data showed that  $>60\%$  of initial  $\Sigma V$

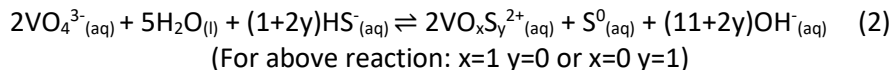
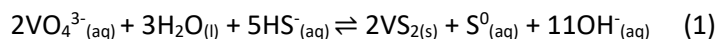
remained dissolved in the test solutions, demonstrating that homogenous  $V^{(III)}$  and/or  $V^{(IV)}$  phases are substantially present in the test solutions at equilibrium.



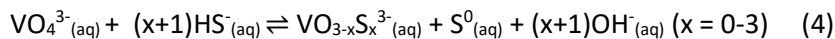
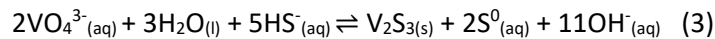
**Figure 1:** UV-vis spectra (solid lines; 1 cm cell) of filtered (0.45  $\mu m$ ) aliquots from test solutions initially containing 5-300  $\mu M VO_4^{3-}$ , 3 mM  $\Sigma S^{2-}$ , and 20 mM TRIS at pH = 8.50; spectra taken after 22 hours of reaction. Optical constants for the thiovanadates are found in the inset table. The red dotted curve is an example of a polysulfide spectrum obtained from fitting absorbance data using polysulfide optical constants. Inset graphs show the  $S^0$  solution concentrations, calculated from the fitted spectra.  $S^0$  data for test solutions with the lowest initial  $VO_4^{3-}$  are replotted in the lower inset graph.

Below are examples of plausible reactions to account for the data in Figure 1.

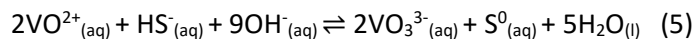
**Figure 1: One e<sup>-</sup> Reaction Examples ( $V^{(V)}$  to  $V^{(IV)}$ )**



**Figure 1: Two e<sup>-</sup> Reaction Examples ( $V^{(V)}$  to  $V^{(III)}$ )**



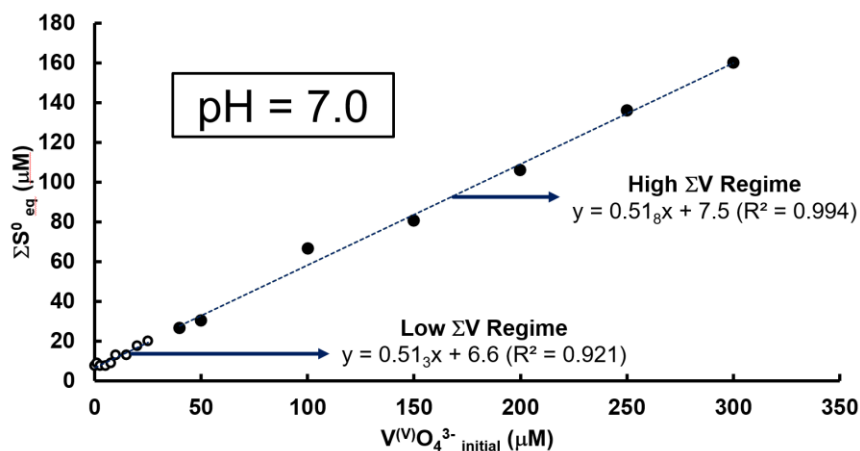
**Aquatic Equilibrium between  $V^{IV}$  and  $V^{III}$**



It should be noted that solutions similar to those used to construct Fig. 1 were prepared except elemental sulfur was added to saturation. As the above reactions attest,  $S^0$  in solution ought to promote formation of  $V^{(V)}$  species, like the thiovanadates, which Fig. 1 shows do not form significantly in the initially  $S^0$ -free solutions. The  $S^0$ -rich test solutions also did not yield observable thiovanadate concentrations. Thus, unlike various transition metals (e.g., Mo, Re, W), which all readily form thiometalates in the metal's highest oxidation state, V appears to resist the same outcome under the conditions of the test solutions here.

### b.) $V^{(IV)}$ products are solely formed at neutral pH.

Figure 2 displays the  $\Sigma S^0$  at equilibrium in test solutions with initial concentrations of  $VO_4^{3-}$  that span the low to high  $\Sigma V$  regimes implied in Fig. 1. Note that both regimes yield slopes of  $\sim 1/2$ , indicating that  $V^{(IV)}$  products are solely formed at neutral pH. Reaction 5 above shows that  $V^{(IV)}$  products ought to be favored with decreasing pH.

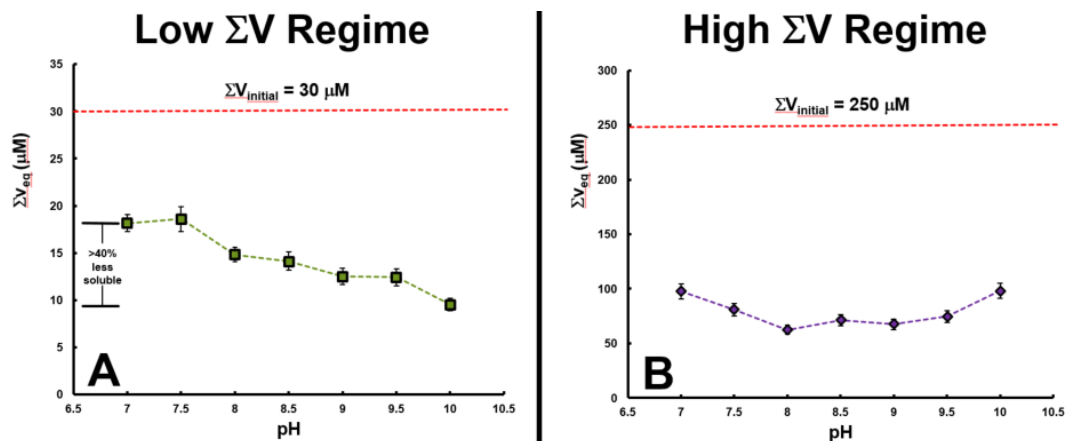


**Figure 2:**  $\Sigma S^0$  at equilibrium resulting from  $VO_4^{3-}$  reduction at pH = 7.0 and varying initial concentrations of  $VO_4^{3-}$ . Note slopes are consistent in the two concentration regimes; compare to Fig. 2 inset. At pH = 7.0,  $V^{(IV)}$  products are solely formed. Test solutions were filtered (0.45  $\mu m$ ) after 20 hours and initially contained 5-300  $\mu M$   $VO_4^{3-}$ , 3 mM  $\Sigma S^{2-}$ , and 20 mM TRIS at pH = 8.50.  $MgCl_2$  was not added to these solutions initially.

### c.) $\Sigma V$ solubility differs for test solutions in the low vs. high $\Sigma V$ reduction regime at pH 8.5.

Figure 3 displays the  $\Sigma V$  at equilibrium in filtered test solutions over a range of pH values and initial concentrations of  $VO_4^{3-}$  that span the low to high  $\Sigma V$  reduction regimes implied in Fig. 1;  $MgCl_2$  was initially added to these solutions to promote colloidal flocculation. In the low  $\Sigma V$  regime where  $V^{(III)}$  phases prevail at mild alkalinities, increasing pH lowers the solubility of V. As shown in reaction 5, decreasing solubility likely reflects a shift from  $V^{(IV)}$  to  $V^{(III)}$  products which are typically less soluble. In the high  $\Sigma V$  regime where reduction to  $V^{(IV)}$  solely occurs, V solubility shows a weak pH dependence over the tested range. However, both regimes indicate that unidentified solid V phases are significantly present at equilibrium. Solubilities in the low  $\Sigma V$  regime under mildly alkaline conditions suggest that presently unconfirmed thiovanadites ( $V^{(III)}O_{3-x}S_x^{3-}$ ) are significantly present in the test solutions.

These results hint that V may behave similarly to its main group cousin, As, which is known to form thioarsenites ( $\text{As}^{\text{(III)}}\text{O}_{3-x}\text{S}_x^{3-}$ ) in sulfidic solutions.



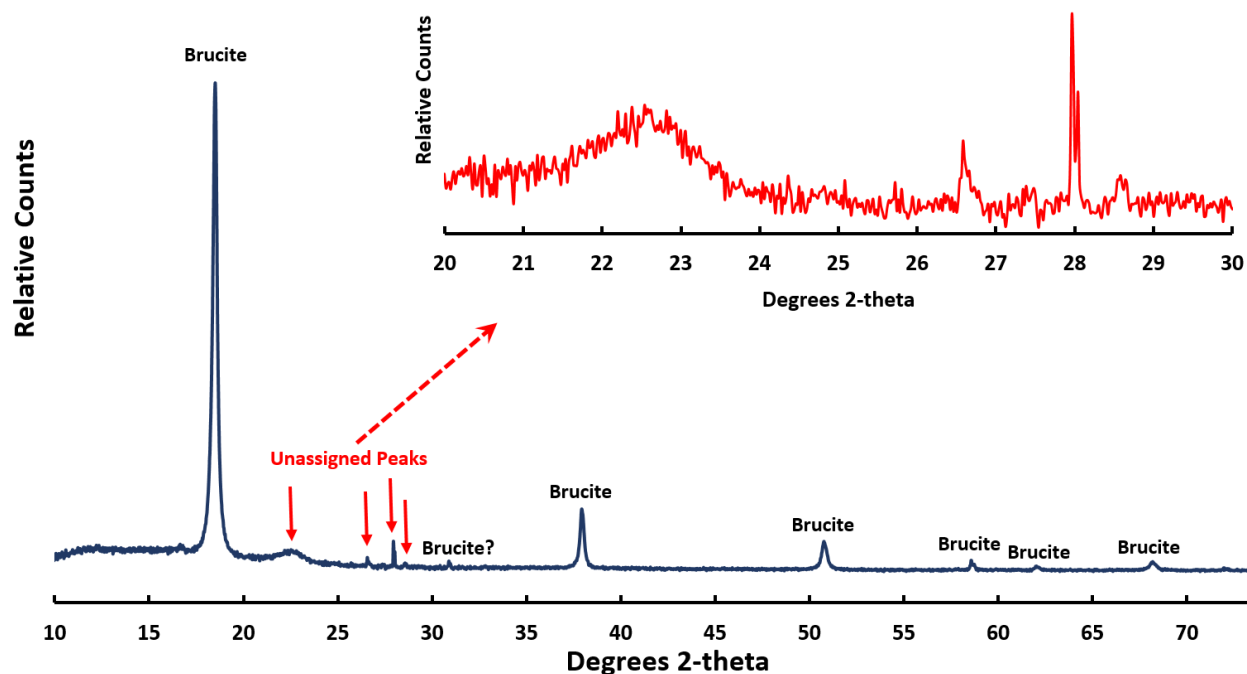
**Figure 3:** Panels A and B show  $\Sigma V$  at equilibrium in filtered (0.45  $\mu\text{m}$ ) test solutions at various pH values with initial  $\Sigma V$  set at concentrations within the low vs. high  $\Sigma V$  reduction regimes implied by Fig. 1. Test solutions initially contained 30 or 250  $\mu\text{M}$   $\text{VO}_4^{3-}$ , as well as 3 mM  $\Sigma\text{S}^{2-}$ , 10 mM  $\text{MgCl}_2$  and 20 mM TRIS at pH = 8.50.

**d.) XRD Spectrum shows  $\text{Mg}^{2+}$  is not a passive floc agent; unassigned peaks are present.**

As noted above,  $\text{Mg}^{2+}$  was added to our test solutions to promote flocculation of heterogeneous colloidal phases prior to filtering. Prior work with the Fe-Mo-S system, suggested that  $\text{Mg}^{2+}$  would act as a chemically passive floc agent, an ideal property of any floc agent. Fig. 4 shows an X-ray diffraction (XRD) spectrum for a precipitate harvested from a sulfidic mother solution initially containing 10  $\mu\text{M}$   $\text{VO}_4^{3-}$  and 10 mM  $\text{MgCl}_2$  under mildly alkaline conditions. The spectrum clearly demonstrates that brucite ( $\text{Mg}(\text{OH})_2$ ) is significantly present in the precipitate. However, there remains several unidentified reflections between 20 and 30° 2-theta, pointing to the presence of a V-S phase also in the precipitate. The precipitate was further analyzed using a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). EDS spectra showed a substantial Mg signal, but counts for x-rays associated with V and S were also significant.

**e.) Future work will find a passive floc agent and identify/quantify all equilibrium phases.**

Experiments discussed above that included  $\text{MgCl}_2$  in test solutions will need to be repeated once a suitable floc agent is found. Presently, tetraalkylammonium hydroxides appear to work well as floc agents at comparatively low (~1 mM) concentrations; chemical passivity still needs to be established. XRD and SEM-EDS will be repeated on precipitates from  $\text{MgCl}_2$ -free solutions. Dr. Anthony Chappaz (Central Michigan University) has agreed to analyze the precipitates using X-ray absorption techniques (XAFS, XANES). Chromatography, specifically reverse-phase ion pair chromatography will be utilized with mass spectroscopy to identify and quantify aqueous  $\text{V}^{\text{(III)}}$  or  $\text{V}^{\text{(IV)}}$  species formed in test solutions. These data will ultimately be used to quantify thermodynamic constants and model V speciation in natural waters.



**Figure 4:** XRD spectrum of the precipitate forming from solutions initially containing:  $10 \mu\text{M VO}_4^{3-}$ ,  $3 \text{ mM } \Sigma\text{S}^{2-}$ ,  $10 \text{ mM MgCl}_2$  and  $20 \text{ mM TRIS}$  at  $\text{pH} = 8.50$ .  $\text{MgCl}_2$  was added with the intention that it serve as a passive flocc agent. Unfortunately, XRD shows brucite ( $\text{Mg(OH)}_2$ ) precipitated from the test solution. Several unassigned peaks, highlighted in the inset graph, may be due to the presence of a V-S solid(s) in the precipitate as well.

#### e.) Student participation, publications, and presentations

A total of three undergraduates participated in the project over the past year. One student, Samantha Weston ('18, BS ACS Chemistry), presented project results at the Spring 2019 ACS national meeting.

Weston S., Medina M. and Vorlicek T.P. (2019) Ion Pair Chromatographic Separation of  $\text{V}^{\text{V}}$ ,  $\text{VI}^{\text{V}}$ , and  $\text{V}^{\text{III}}$  Ions in Sulfidic Waters. Presented at the Chemical Education Undergraduate Poster Session, Geochemistry, Spring 2019 American Chemical Society National Meeting, Orlando, FL.