

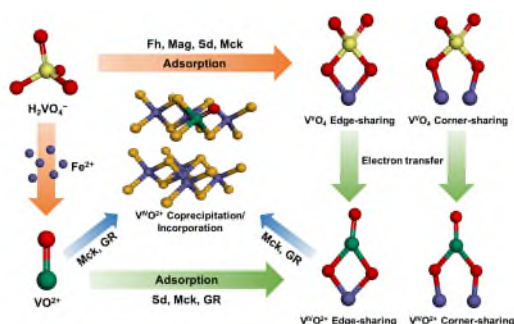
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Aqueous vanadate removal by iron(II)-bearing phases under anoxic conditions

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**TOC/Abstract Art.**

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ABSTRACT.

Vanadium contamination is a growing environmental hazard worldwide. Aqueous vanadate ($\text{H}_x\text{V}^{\text{V}}\text{O}_4^{(3-x)-}(\text{aq})$) concentrations are often controlled by surface complexation with metal (oxyhydr)oxides in oxic environments. However, the geochemical behaviour of this toxic redox-sensitive oxyanion in anoxic environments is poorly constrained. Here we describe results of batch experiments to determine kinetics and mechanisms of aqueous $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ (100 μM) removal under anoxic conditions in suspensions (2.0 g L^{-1}) of magnetite, siderite, pyrite, and mackinawite. We present results of parallel experiments using ferrihydrite (2.0 g L^{-1}) and $\text{Fe}^{2+}(\text{aq})$ (200 μM) for comparison. Siderite and mackinawite reached near complete removal (46 $\mu\text{mol g}^{-1}$) of aqueous vanadate after 3 h and kinetic rates were generally consistent with ferrihydrite. Whereas magnetite removed 18 $\mu\text{mol g}^{-1}$ of aqueous vanadate after 48 h and uptake by pyrite was limited. Uptake by $\text{Fe}^{2+}(\text{aq})$ was observed after 8 h, concomitant with precipitation of secondary Fe phases. X-ray absorption spectroscopy revealed V(V) reduction to V(IV) and formation of bidentate corner-sharing surface complexes on magnetite and siderite, and with $\text{Fe}^{2+}(\text{aq})$ reaction products. These data also suggest that V(IV) is incorporated into the mackinawite structure. Overall, we demonstrate that Fe(II)-bearing phases can promote aqueous vanadate attenuation and, therefore, limit dissolved V concentrations in anoxic environments.

INTRODUCTION.

Vanadium contamination of terrestrial and aquatic ecosystems is a growing environmental hazard due to increased releases from mining, steel making, energy production, and other anthropogenic activities.¹⁻⁴ Dissolved V concentrations typically range from 0.5 to 2.4 $\mu\text{g L}^{-1}$ in surface waters due to natural weathering of geologic materials. Elevated aqueous concentrations may result from leaching of V-enriched waste materials, including steel slag and mine wastes generated at coal, bauxite, uranium, phosphate and oil sands operations.^{2,4-10} At higher concentrations, vanadate oxyanions ($\text{H}_x\text{V}^{\text{V}}\text{O}_4^{(3-x)-}(\text{aq})$) can be acutely toxic to aquatic organisms,^{11,12} bacteria,¹³ and humans¹⁴⁻¹⁶ due to similarities with phosphate inhibiting Ca-, Na- and K-ATPase ion pumps and cellular uptake through ion mimicry. Despite its inclusion on the USEPA contaminant candidate list, few jurisdictions have established soil or water quality guidelines for V.¹⁷⁻¹⁹ Recent research has presented a hazardous concentration endangering 5% of species (HC5) to be 50 $\mu\text{g L}^{-1}$ for freshwater aquatic organisms.²⁰ Canada established a criterion for V in soil of 130 mg kg^{-1} and recently instituted water quality guidelines of 120 $\mu\text{g L}^{-1}$ and 5 $\mu\text{g L}^{-1}$ for freshwater and marine waters, respectively.^{18,21}

Aqueous V speciation is highly dependent on solution chemistry (i.e., ionic strength), $[\text{V}]_{\text{T}}$, pH, and redox conditions, which strongly affect surface complexation and the solubility of discrete V phases. While V exists in a range of oxidation states from V(-I) to V(V), the most prevalent in near-surface environments are V(V), V(IV), and V(III).^{2,3,22} Under oxic conditions, $\text{H}_2\text{V}^{\text{V}}\text{O}_4^{-}(\text{aq})$ is the predominant species at circum-neutral pH, while $\text{V}^{\text{V}}\text{O}_2^{+}$ dominates under acidic (i.e., pH < 3) conditions. Reduction of V(V) to V(IV) or V(III) can limit solubility through precipitation of V (hydr)oxides or enhanced sorption at mineral surfaces.^{8,23-25} Vanadium(V) reduction to V(IV) leads to the formation of aqueous vanadyl species VO^{2+} , VOOH^{+} , and $\text{VO}(\text{OH})_3^{-}$, and further

reduction produces aqueous V(III) as V^{+3} , VOH^{2+} , and $V(OH)_2^+$.^{26–28} Removal of aqueous V(V) or V(IV) by reduction to V(IV) and V(III) has been observed in laboratory and field settings through reaction with $H_2S_{(aq)}$, Fe(II)-oxide surfaces, organic compounds, and anaerobic microbial respiration.^{23–25,29,30}

Iron (oxyhydr)oxides and sulfides in natural soils, sediments, and aquifers play a key role in the sequestration of organic and inorganic contaminants.^{31–33} Previous studies have established how surface reactions and redox processes affect the environmental mobility of oxyanion forming metal(loid)s (e.g., As, Se, and Cr) with Fe (oxyhydr)oxides^{34,35} and Fe sulfide minerals.^{36,37} In comparison, aqueous V reactions have received less attention with the current literature being limited to sorption onto metal (oxyhydr)oxides^{26,38–41} and clay minerals^{42,43} under oxic conditions. Wehrli and Stumm (1989) showed the adsorption of V(V) onto TiO_2 and $\delta-Al_2O_3$ surfaces with the formation of inner sphere monodentate complexes at low pH (< 3) as $V^VO_2^+$, while at higher pH (i.e., 4 to 8) $H_2V^VO_4^-$ sorption occurred via inner sphere complexes similar to phosphate. These authors also found that $V^{IV}O^{2+}_{(aq)}$ removal by TiO_2 and $\delta-Al_2O_3$ results from formation of bidentate surface complexes. Recent EXAFS studies demonstrated that $H_2V^VO_4^-$ uptake by 2-line ferrihydrite^{38,40} and goethite³⁹ at circum-neutral pH occurs via formation of inner sphere edge- and corner-sharing surface complexes, respectively. Under anoxic conditions, White and Peterson (1996) found enhanced reduction of vanadate in the presence of magnetite and ilmenite at pH 3 related to dissolved aqueous Fe^{2+} , whereas at pH 5 and 7 these authors observed decreased aqueous V(V) reduction and limited removal, as a result of increased sorption at magnetite and ilmenite surfaces. Reducing conditions are known to limit V mobility within aquifers,⁴⁴ contaminated sites,⁸ and marine systems;⁴⁵ however, molecular mechanisms of V removal by Fe(II)-phases remain poorly constrained.

The objectives of this study are to determine $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ (aq) removal kinetics and mechanisms during reaction with the Fe(II)-bearing phases magnetite [Fe_3O_4], pyrite [FeS_2], mackinawite [FeS], and siderite [FeCO_3] under anoxic conditions. We conducted parallel experiments to examine $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ (aq) removal during reaction with 2-line ferrihydrite [$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$], as a comparison for adsorption processes, and Fe^{2+} (aq), to assess the affects of aqueous Fe^{2+} on V removal as a result of Fe(II)-bearing mineral dissolution. Solid-phase V associations were examined by transmission electron microscopy–energy dispersive X-ray spectroscopy (TEM–EDX), X-ray absorption spectroscopy near edge structure (XANES) spectroscopy, and extended X-ray absorption fine structure (EXAFS) spectroscopy. Our results improve understanding of V mobility in anoxic conditions and provides new insight into environmental V geochemistry.

MATERIALS AND METHODS.

Batch experiments and all associated sample preparation occurred under an anoxic atmosphere ($\leq 5\%$ H_2 , balance N_2) in an anaerobic chamber (Coy Laboratory Products, USA) with O_2 concentrations remaining below 10 ppm. All solutions were prepared using ultra-pure water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$ resistivity) that was first purged with $\text{N}_{2(\text{g})}$ for at least 24 h. Prior to use, all glassware and the polytetrafluoroethylene (PTFE) paddle mixers were soaked for 24 h in 10% (v/v) oxalic acid, then soaked for 24 h in 10% (v/v) HCl, and rinsed thoroughly with deionized (DI) water.

Experimental solids. Ferrihydrite, siderite, mackinawite, and $\text{V}^{\text{IV}}\text{O}(\text{OH})_{2(\text{s})}$ were synthesized using modified versions of methods described by Cornell and Schwertmann (2003), Qu et al. (2011), Wolthers et al. (2003), and Chen et al. (2018), respectively (Supporting Information). Commercially-available magnetite (<5 nm, 95% purity; Sigma-Aldrich, USA) and pyrite (<44 nm, 99.8% purity; Sigma-Aldrich, USA) was washed in 10 % (v/v) HCl and 0.001M HCl,

respectively, and then rinsed with N_{2(g)}-purged ultra-pure water and freeze dried. The mineralogy of synthesized and purchased solids was confirmed by powder X-ray diffraction (XRD) and Raman spectroscopy (Supporting Information). Particle size was estimated from TEM images and specific surface area (SSA) was determined using the Brunauer-Emmett-Teller N₂ sorption method (Table S1).

Batch Experiments. Batch experiments were conducted in the anaerobic chamber using 2000 mL glass beakers. The final background electrolyte solution was 0.05 M NaCl and 0.005 M MOPS adjusted to pH 7.0 ± 0.1. The MOPS buffer was chosen based on previous studies showing it does not significantly affect oxyanion sorption between pH 6 and 8.5.^{36,49,50} A vanadate stock solution was prepared by dissolving 13.9 mg of Na₃V^VO₄ (99.98%, Sigma-Aldrich, USA) into 500 mL of ultra-pure water. Mineral suspensions were prepared by adding 2.0 g of a given phase to a separate 500 mL of background electrolyte. For reactions involving only Fe²⁺_(aq), solutions were prepared by dissolving 25.4 mg of FeCl₂ (> 98.0 %, Sigma-Aldrich, USA) into 500 mL of the background electrolyte solution. Prior to initiating the experiments, the 500 mL mineral suspensions or Fe²⁺_(aq) solution were stirred continuously with an overhead mixer (RW 20 digital, IKA Works, Inc., USA) fitted with a PTFE paddle. After 3 h of equilibration, 500 mL of the aqueous vanadate solution was quickly added, bringing the total volume to 1000 mL. This method produced an initial V concentration of 100 μM (5.0 mg L⁻¹), which is relevant to mining-impacted sites,⁵⁻⁸ yet low enough to limit formation of polynuclear V species (Figure S1). Redox potential (Eh) and pH were continuously measured during the experiments. The Eh ranged from -70 to -350 mV depending on mineral phase, whereas pH was consistently 7.0 ± 0.1 during the 3 h experiments and adjusted as needed at late time during the 48 h experiments using 0.1 M HCl and NaOH.

Two different experimental durations were used (3 h, 48 h) to obtain high-resolution aqueous-phase data for kinetic modeling and solid-phase samples for examining V removal mechanisms. Samples were collected from triplicate 3 h experiments at the following times: 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 10, 20, 30, 40, 60, 120, 180 min ($n = 19$). Samples were collected from the 48 h experiment at the following times: 0, 1.0, 2.5, 5.0, 10, 20, 30, 40, 60, 120, 180, 240, 480, 1080, 1440, and 2880 min ($n = 16$). Each 4 mL sample was collected into an all-plastic syringe (Norm-Ject, HSW GmbH, Germany) and passed through a sterile 0.1 μm polyethersulfone syringe filter membrane (Minisart, Sartorius AG, Germany) into high-density polyethylene bottles (Nalge Nunc International Corp., USA). Samples for ICP-MS (Nexion 300D, Perkin Elmer, Inc., USA) analysis were acidified to $\text{pH} < 2$ with 25 μL of trace-metal grade HNO_3 acid (OmniTrace, Millipore Sigma, USA). Following the final sample time, each experiment was terminated by vacuum filtering remaining solution through 8 μm cellulose filter paper (Whatman Grade 2, GE Healthcare, USA). Retained solids were transferred into 2 mL cryogenic polypropylene tubes, flash frozen in liquid nitrogen and stored cryogenically (i.e., $\sim 80\text{K}$) until analysis by TEM-EDX-SAED (Supporting Information) and XAS. Sample names referenced herein correspond to experiment reaction times (3 and 48 h) and reaction phases used, including ferrihydrite (3-Fh and 48-Fh), magnetite (3-Mag and 48-Mag), siderite (3-Sd and 48-Sd), mackinawite (3-Mck and 48-Mck), pyrite (3-Py and 48-Py), and aqueous Fe^{2+} (3- Fe^{2+} and 48- Fe^{2+}).

X-ray Absorption Spectroscopy. Synchrotron based powder X-ray absorption spectroscopy was performed at the Canadian Light Source (CLS) on beamline 06-B1-1 (SXRMB). Solid-phase samples from each batch were thawed and dried overnight in a vacuum desiccator within the anaerobic chamber. These samples were homogenized using an agate mortar and pestle, and

approximately 0.05 g of each sample was mounted to a conductive Cu plate using two-sided adhesive C tape. Several reference materials including sodium orthovanadate [$\text{Na}_3\text{V}^{\text{V}}\text{O}_4$], vanadyl hydroxide [$\text{V}^{\text{IV}}\text{O}(\text{OH})_2$], vanadyl sulfate [$\text{V}^{\text{IV}}\text{OSO}_4$] ($\geq 99.99\%$, Sigma Aldrich, Inc., USA), and V(III) chloride [$\text{V}^{\text{III}}\text{Cl}_3$] ($> 99\%$, Sigma Aldrich, Inc., USA) were also prepared for analysis. The samples were sealed in a vacuum desiccator under an anoxic atmosphere for transport to the CLS (< 15 min).

The Cu plates were quickly transferred from the vacuum desiccator to the solid state end station, which was operated at high vacuum ($10^{-8.7}$ Torr) and ambient temperature during collection of fluorescence spectra with a 7-element Si drift detector (RaySpec Ltd., UK). Incident X-ray energy was selected using a monochromator fitted with paired Si(111) crystals and the beam spot size was focused to 1 mm (vertical) by 4 mm (horizontal). This beamline setup gives an energy resolution of ~ 0.55 eV at the V K-edge. Triplicate V K-edge spectra were obtained for all samples and reference materials by scanning incident energy from 100 eV below the theoretical absorption edge (5465 eV) to $k = 14 \text{ \AA}^{-1}$ at steps of 0.25 eV in the XANES region and $0.05 \text{ \AA}^{-1}$ in the EXAFS region.

Data processing and analysis was performed using Athena software (Version 0.9.26), which is a component of the Demeter software package.⁵¹ Data reduction, energy calibration, pre-edge background subtraction, post-edge normalization, and background removal were performed prior to EXAFS modeling. Non-linear least squares fitting of EXAFS data were performed using ARTEMIS by generating amplitude and phase functions with FEFF 6.0 for all reference V compounds, and a modified $\text{Na}_3\text{V}^{\text{V}}\text{O}_4$ and $\text{V}^{\text{IV}}\text{OSO}_4$ structure with Fe(III) substitution.

Pseudo-radial distribution functions were obtained through Fourier transform of $\chi(k) \cdot k^3$ functions

over varying k -ranges depending on data quality. Due to crystal glitches above $\sim 10.5 \text{ \AA}^{-1}$, all EXAFS models were constrained between 2.5 and $10.5 \text{ \AA}^{-1}$.

Kinetic Reaction Modeling. Rate constants were initially determined by fitting first, pseudo first, and second order models to aqueous concentration data averaged for replicate batches (Figure S2). However, similar to other oxyanion-forming elements (e.g., As), V removal may proceed through multiple reaction pathways including adsorptive equilibrium, incorporation into mineral structures, and reduction. We therefore used a mixed-reaction modeling approach for V removal that integrates (i) fast, reversible uptake via outer sphere complexation represented by K_{eq} , (ii) slow, rate-controlled reversible uptake, corresponding to diffusion of vanadate to sorption sites or formation of inner-sphere complexation represented by rate constants k_f (adsorption) and k_b (desorption), and (iii) slow, irreversible uptake by intra- or interparticle diffusion or the formation of surface precipitates represented by k_i .^{36,52} Both the initial kinetic (Table S2) and mixed-reaction model (Table 1) parameters were fit to the 3 h and 48 h kinetic batch experiment data by inverse modeling to minimize the root-mean-square error (RMSE).

RESULTS AND DISCUSSION

Vanadate Removal Kinetics. Similar to other metal(loid) oxyanions, $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ sorption onto ferrihydrite (3-Fh, 48-Fh) is a fast process reaching 90% removal ($42 \text{ \mu mol g}^{-1}$) by 40 min and near complete removal ($46 \text{ \mu mol g}^{-1}$) after 3 h (Figure 1a). These results agree with previous experiments performed at pH 7.0, which reported $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ adsorption *via* inner sphere complexation at Fe(III) (oxyhydr)oxide surfaces.^{38–40} In comparison, $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ uptake by magnetite (3-Mag, 48-Mag) plateaued within 10 min at $15 \text{ \mu mol g}^{-1}$ ($\sim 33\%$ removal) and increased to $19 \text{ \mu mol g}^{-1}$ (42% removal) after 48 hr (Figure 1a).

Vanadate removal by siderite varied slightly due to variations in crystallite size and, therefore, surface area (Table S1). Uptake of $\text{H}_2\text{V}^{\text{VO}_4^-}$ by siderite (3-Sd-avg, 48-Sd) reached $42 \mu\text{mol g}^{-1}$ (90% removal) after 3 h and increased to $46 \mu\text{mol g}^{-1}$ (~100% removal) following 48 h (Figure 1b). Partial dissolution of siderite during equilibration released aqueous Fe into solution with an initial concentration of $114 \mu\text{M}$, which decreased to $94 \mu\text{M}$ over the first 4 h, and subsequently increased to $620 \mu\text{M}$ after 48 h (Figure S3). The V removal rate and capacity for siderite correlated to SSA, where above $10 \text{ m}^2 \text{ g}^{-1}$ (3-Sd-b, 3-Sd-c, 3-Sd-d) kinetic rates are similar with an average K_{eq} value of 0.63, compared to 3-Sd-a ($5.8 \text{ m}^2 \text{ g}^{-1}$) with a K_{eq} of 0.30 (Table 1).

Table 1. Initial ($[\text{V}]_0$) and final ($[\text{V}]_f$) aqueous V concentrations along with estimated equilibrium constant (K_{eq}), rate constants, forward (k_f), backward (k_b), and irreversible (k_i), and goodness of fit parameters, R^2 and RMSE, obtained from multi-reaction modeling. Sample names correspond to experiment duration and mineral abbreviations including ferrihydrite (Fh), magnetite (Mag), mackinawite (Mck), and siderite (Sd).

Sample	Time (h)	$[\text{V}]_0$ (μM)	$[\text{V}]_f$ (μM)	$\log$ K_{eq}	k_f (h^{-1})	k_b (h^{-1})	k_i (h^{-1})	R^2	RMSE
3-Fh	3	93.7	0.55	-0.2	29.2	17.3	0.01	0.997	1.60
48-Fh	48	90.2	0.08	-0.4	15.9	5.8	0.0007	0.998	0.64
3-Mag	3	92.1	61.5	-0.6	665.8	159.7	0.02	0.963	0.33
48-Mag	48	89.5	51.7	-0.4	525.8	189.5	0.003	0.90	0.57
3-Mck	3	91.1	0.13	0.4	69.1	178.2	0.03	0.985	0.44
48-Mck	48	89.9	0.0	0.5	28.0	79.7	0.00	0.972	0.64
3-Sd-a	3	87.0	31.2	-0.5	77.3	22.1	0.08	0.986	0.72
3-Sd-b	3	94.0	7.4	-0.2	118.1	81.8	0.05	0.994	0.64
3-Sd-c	3	92.1	13.6	-0.4	134.0	59.4	0.08	0.995	0.59
3-Sd-d	3	91.6	5.3	-0.1	115.5	86.9	0.06	0.991	0.69
3-Sd-avg	3	92.6	8.77	-0.2	121.3	75.4	0.06	0.995	0.58
48-Sd	48	92.7	0.04	-0.2	27.3	16.9	0.0007	0.997	0.64

Mackinawite is a highly reactive metastable Fe(II) sulfide phase with the potential for sorption and reduction of metal(loid)s.^{53,54} Attenuation of $\text{H}_2\text{V}^{\text{VO}_4^-}$ by mackinawite (3-Mck, 48-Mck)

was rapid and 100% removal ($45 \mu\text{mol g}^{-1}$) was observed after 1 h (Figure 1c). During the 48 h experiment aqueous Fe concentrations, as a result of mineral dissolution during equilibration, increased from $265 \mu\text{M}$ to $804 \mu\text{M}$ (Figure S3). In contrast to mackinawite, $\text{H}_2\text{V}^{\text{VO}_4^-}$ removal by pyrite under the experimental conditions was limited (Figure 1d). We attribute this result to the low SSA of authigenic pyrite (Table S1), and limited aqueous Fe in solution due to the low solubility of pyrite at circumneutral pH. Vanadium removal during reaction with only aqueous Fe^{2+} (48- Fe^{2+}) was limited after 3 h, but increased to $22 \mu\text{mol g}^{-1}$ (47% removal) after 48 h (Figure 1d). This decrease in aqueous V concentrations corresponded to a decrease in aqueous Fe concentrations from 200 to $143 \mu\text{M}$ after 48 h (Figure S3) and the appearance of visible precipitates.

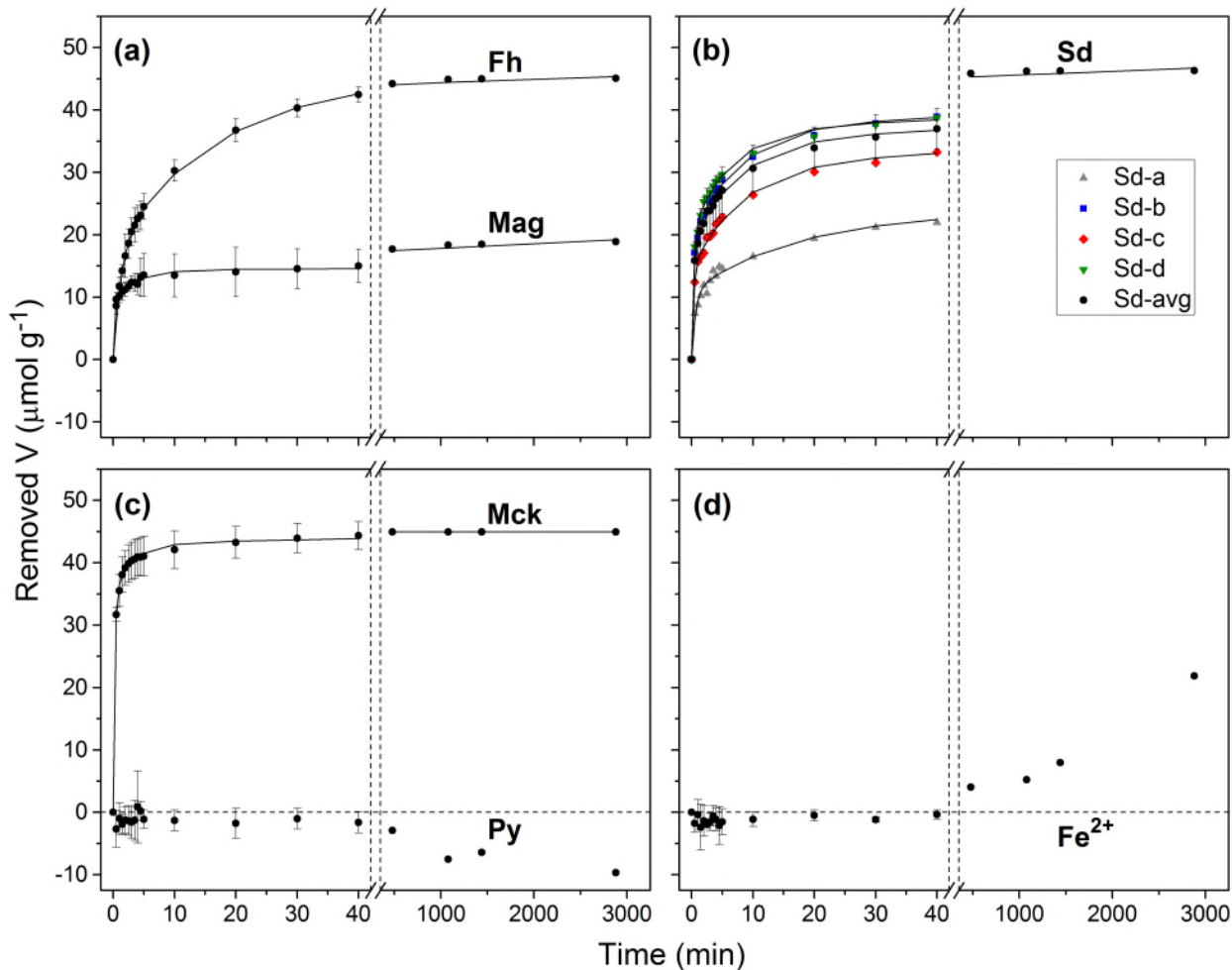


Figure 1. Measured (closed circles) and multi-reaction modeled (solid lines) concentrations of aqueous V during batch experiments with (a) ferrihydrite (Fh) and magnetite (Mag), (b) siderite (Sd), (c) mackinawite (Mck) and pyrite (Py), and (d) aqueous Fe^{2+} . Siderite kinetic experiments corresponding to Sd-a, Sd-b, Sd-c, and Sd-d (b) and demonstrate the effect of SSA on removal rates.

Spectroscopic Analyses. Vanadium oxidation states were assessed using V K-edge XANES

collected for experimental samples and reference materials (Figure 2; Figure 3). Pre-edge

intensity and energy position were compared to previously-reported values for $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ (aq) and

$\text{V}^{\text{IV}}\text{O}^{2+}$ (aq).³⁸ Vanadium pre-edge peak height, energy position and area correlate to oxidation

state and are sensitive to coordination changes.^{45,55-57} As expected, normalized pre-edge peak

height and area decreased with oxidation state in the reference materials following the order:

$\text{Na}_3\text{V}^{\text{V}}\text{O}_4$, 48-Fh > $\text{VO}^{\text{IV}}(\text{OH})_2$, $\text{VO}^{\text{IV}}\text{SO}_4 \gg \text{V}^{\text{III}}\text{Cl}_3$ (Table S3). Based on methods developed by

Chaurand et al. (2007), Levina et al. (2014) and Bennett et al. (2018), V oxidation states were

estimated using a linear regression ($R^2 = 0.980$) of the normalized pre-edge peak area (Figure 2a;

Table S4). Using this approach on reference spectra yielded averaged oxidation states of +5.13

($\text{Na}_3\text{V}^{\text{V}}\text{O}_4$), +4.95 (48-Fh), +3.96 ($\text{V}^{\text{IV}}\text{O}(\text{OH})_2$), +3.88 ($\text{V}^{\text{IV}}\text{OSO}_4$), and +3.08 ($\text{V}^{\text{III}}\text{Cl}_3$) for the

reference materials (Table S3).

Vanadium associated with reacted ferrihydrite and magnetite samples are consistent with

$\text{Na}_3\text{V}^{\text{V}}\text{O}_4$ spectra, which exhibits a smooth XANES feature and large normalized pre-edge peak

(Figure 2b; Figure 3a), with an average oxidation state of approximately +5. Spectra obtained for

reacted siderite and aqueous Fe^{2+} displayed a slightly elevated near-edge region and dampened

pre-edge peak height similar to $\text{V}^{\text{IV}}\text{O}(\text{OH})_{2(\text{s})}$, and $\text{V}^{\text{IV}}\text{O}^{2+}$ (aq). Estimated oxidation states yielded

+4.37 (3-Sd-a), +4.33 (3-Sd-b), +4.14 (48-Sd) and +4.31 (48- Fe^{2+}) indicating that sorbed V(IV)

is the dominant oxidation state associated with reactions (Figure 2b). Similarly, V K-edge

pre-edge peak height and area for mackinawite samples indicated oxidation states of +3.80

(3-Mck) and +3.65 (48-Mck), suggesting the presence of V(IV) and possibly minor amounts of

V(III) (Table S3). In addition, V in reacted mackinawite samples show a distinct XANES features consistent with the $V^{IV}OSO_4$ reference (Figure 3).

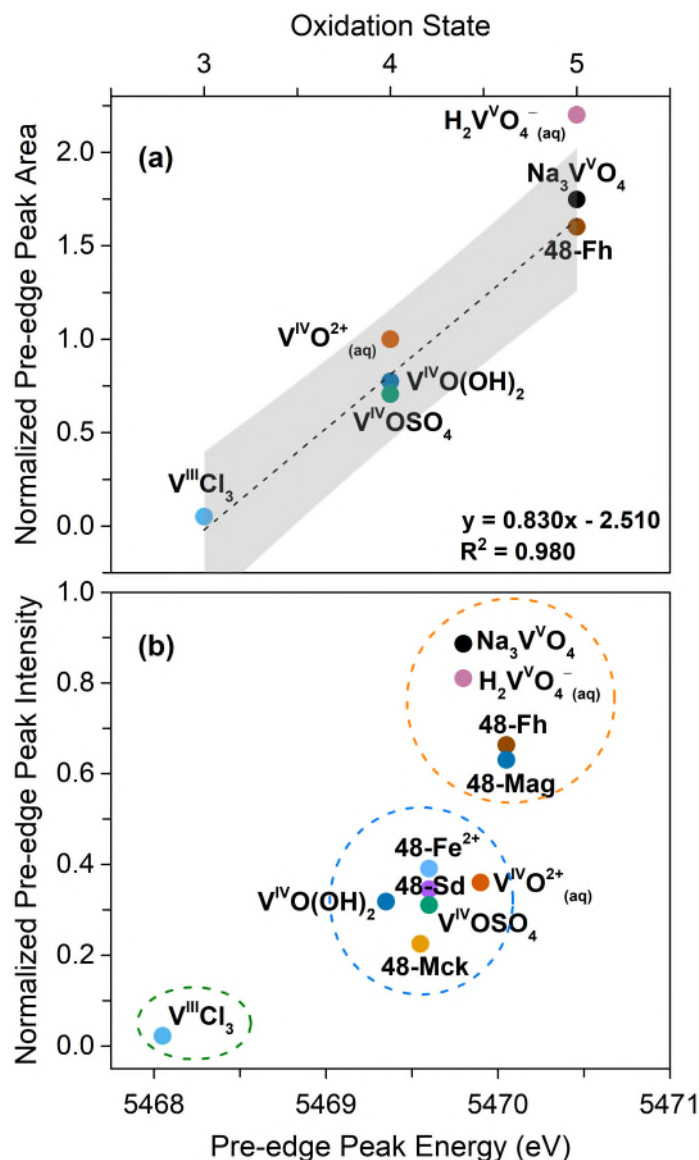


Figure 2. (a) Normalized pre-edge peak area and oxidation state with linear regression (dashed line) of V oxidation states in reference materials used to estimate average V oxidation state in experimental samples. Gray shaded area is the 95% confidence interval for the linear regression fit. (b) Normalized pre-edge peak intensity plotted against pre-edge energy position for standards and 48 h reacted samples. Dashed circles group V(V) (orange), V(IV) (blue), and V(III) (green) oxidation states. Data for $H_2V^{VO}_4_{(aq)}$ and $V^{IV}O^{2+}_{(aq)}$ from Larsson et al. (2017), these points were not included in the linear regression fit.

Non-linear least squares modeling was performed for V K-edge EXAFS spectra of all references and experimental samples to determine bonding environments, and assess vanadate removal mechanisms under anoxic conditions (Figure 3; Table S4). Vanadium reference spectra were fit to tetrahedral ($\text{Na}_3\text{V}^{\text{V}}\text{O}_4$) and octahedral ($\text{V}^{\text{IV}}\text{O}(\text{OH})_{2(\text{s})}$, $\text{V}^{\text{IV}}\text{OSO}_4$, $\text{V}^{\text{III}}\text{Cl}_3$) coordination environments. The V(V) reference, $\text{Na}_3\text{V}^{\text{V}}\text{O}_4$, was consistent with previous fitting parameters^{38,40} and exhibited a first shell V-O coordination number of 4 at 1.713 Å and a multiple scattering path around the VO_4 tetrahedron (3.14 Å). The $\text{V}^{\text{IV}}\text{O}(\text{OH})_2$ reference was fit based on structural parameters from Krakowiak et al. (2012) and Besnardiere et al. (2016), where V(IV) is in a distorted octahedral coordination with the first shell V-O being a characteristic, singly coordinated short double bond ($\text{V}=\text{O}$) at 1.614 Å, followed by 4 coordinate *trans* V-O bonds at 2.000 Å, and an elongated V-O_{eq} bond at 2.527 Å. Long range photoelectron interactions in the $\text{V}^{\text{IV}}\text{O}(\text{OH})_2$ structure were fit to 4 coordinate V-V backscatters at 3.04 Å, 3.24 Å, and 3.43 Å. Similarly, $\text{V}^{\text{IV}}\text{OSO}_4$ exhibits octahedral coordination with a single $\text{V}=\text{O}$ bond, 4 coordinate $\text{V-O}_{\text{trans}}$, and singly coordinated V-O_{eq} at 1.597 Å, 2.018 Å, and 2.52 Å, respectively.^{58,60} Following the V-O bonds, 2 coordinate V-S is fit at 3.27 Å, similar to $\text{V}^{\text{IV}}\text{OPO}_4$ structure.⁶¹ Lastly, $\text{V}^{\text{III}}\text{Cl}_3$ was fit with V-Cl, $\text{V-Cl}_{\text{trans}}$, and V-Cl_{eq} at 2.03 Å, 2.27 Å, and 2.41 Å, respectively, followed by repeating crystal structural units of 3 coordinate V-V backscatters at 3.41 Å and V-Cl backscatters at 4.80 Å in six-fold coordination.

Consistent with previous literature on vanadate sorption, we observed bidentate complexes with tetrahedral V-O shell at 1.71 Å and a $\text{V}^{\text{V}}\text{O}_4$ tetrahedron multiple scattering path (3.17 Å) in 3 and 48 h ferrihydrite samples (3-Fh, 48-Fh).^{38,40} A single Fe backscattering atom at 2.68 Å was fit similar to Larsson et al. (2017); however, we excluded the V-O-Fe multiple scattering path included by these authors. Rather, we fit a second V-Fe scattering path, with a coordination

number of 2.0, at 3.32 and 3.29 Å to 3-Fh and 48-Fh, respectively. The two V-Fe backscatters represent the concurrent formation of bidentate edge- and corner-sharing bonds, which has previously been reported for other sorbed oxyanion forming metal(loid)s (e.g., As) on Fe (oxyhydr)oxide phases (Figure 4).⁶² The addition of a bidentate corner-sharing complex could be a result of higher ionic strength background electrolyte used in this study (0.05 M NaCl) compared to Larsson et al. (2017). Vanadium removal by magnetite followed a similar mechanism to ferrihydrite and other oxyanion metal(loid)s (e.g., Jönsson and Sherman, 2008). A tetrahedral V-O shell was fit at 1.701 Å to the 3 h magnetite sample (3-Mag) with a V-Fe scattering path (corner-sharing) at 3.33 Å with a coordination number of 2.0. Reduced V species were not apparent at magnetite surface following 3 h of reaction time (3-Mag) indicated by a first shell V^{VO_4} tetrahedron at 1.701 Å. In contrast, after 48 h (48-Mag) a first shell V-O with a coordination number of 3.1 at 1.673 Å was fit, suggesting a mix of V(V) (as V^{VO_4}) and V(IV) (as $V^{IVO^{2+}}$). The fit for 48-Mag was further improved by including a second V-O shell at an interatomic distance of 2.24 Å with a coordination of 2.1, which is consistent with bidentate $V^{IVO^{2+}}$ adsorption (Figure 4). Similar to ferrihydrite fits, two V-Fe paths were fit at 2.65 and 3.31 Å indicative of bidentate edge- and corner-sharing complexation. Although White and Peterson (1996) observed limited capacity for $H_2V^{VO_4^-}$ reduction by magnetite at pH 7.0, our EXAFS fits indicate reduction of V(V) to V(IV) through electron transfer at magnetite surfaces. However, the surface reactivity of magnetite is known to decrease with ageing or adsorption of redox-sensitive elements (e.g., Cr(VI) or N(V)).^{31,64,65} While the synthetic magnetite used in this study was rinsed with weak HCl to remove oxidized surface products (i.e., Fe(III) (oxyhydr)oxides), there is the potential for residual Fe(III) products to remain. Likewise, active redox sites at magnetite surfaces may be further passivated following electron transfer with

adsorbed $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$.⁶⁴ While V-Fe edge-sharing distances for ferrihydrite (2.68 Å) and magnetite (2.65 Å) are shorter than V-Fe backscattering path (2.78 Å) modeled by Larsson et al. (2017), edge-sharing distances presented here are consistent with *ab initio* calculations and modeling performed by Peacock and Sherman (2004).

Siderite is a highly reactive mineral that actively sorbs^{63,66} and reduces^{54,67} trace metal(loid)s. Aqueous V removal by siderite (Figure 1b) suggests rates are dependent on surface area. Therefore, 3-Sd-a and 3-Sd-b V K-edge EXAFS spectra were separately modeled and compared to assess potential differences in removal mechanisms based on surface area. Secondary precipitates were apparent in the siderite (3-Sd, 48-Sd) and aqueous Fe^{2+} (48- Fe^{2+}) batch experiments attributed to $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ reduction coupled with surficial or aqueous Fe^{2+} oxidation (Eqs. 1–3). Combined XRD and TEM-EDX-SAED results revealed minor amounts of mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ green rust and Fe(III) (oxyhydr)oxide in the siderite (3-Sd, 48-Sd) and Fe^{2+} (48- Fe^{2+}) solids (Figure S4). Green rust was identified in 48- Fe^{2+} by the hexagonal platy morphology and confirmed by SAED analysis with calculated d-spacings of 8.00 and 5.34 Å corresponding to the 003 and 006 lattice planes, respectively (Figure S4-d).⁶⁸ Needle-like morphologies consistent with lepidocrocite and goethite were noted in reacted siderite samples (3-Sd, 48-Sd), but were not apparent for precipitates from the Fe^{2+} experiment (48- Fe^{2+}). Vanadium co-precipitation, as $\text{H}_2\text{V}^{\text{V}}\text{O}_4^-$ or $\text{V}^{\text{IV}}\text{O}^{2+}$, with the secondary phases was not directly observed but was previously reported by Kaur et al. (2009) and Schwertmann and Pfab (1994).

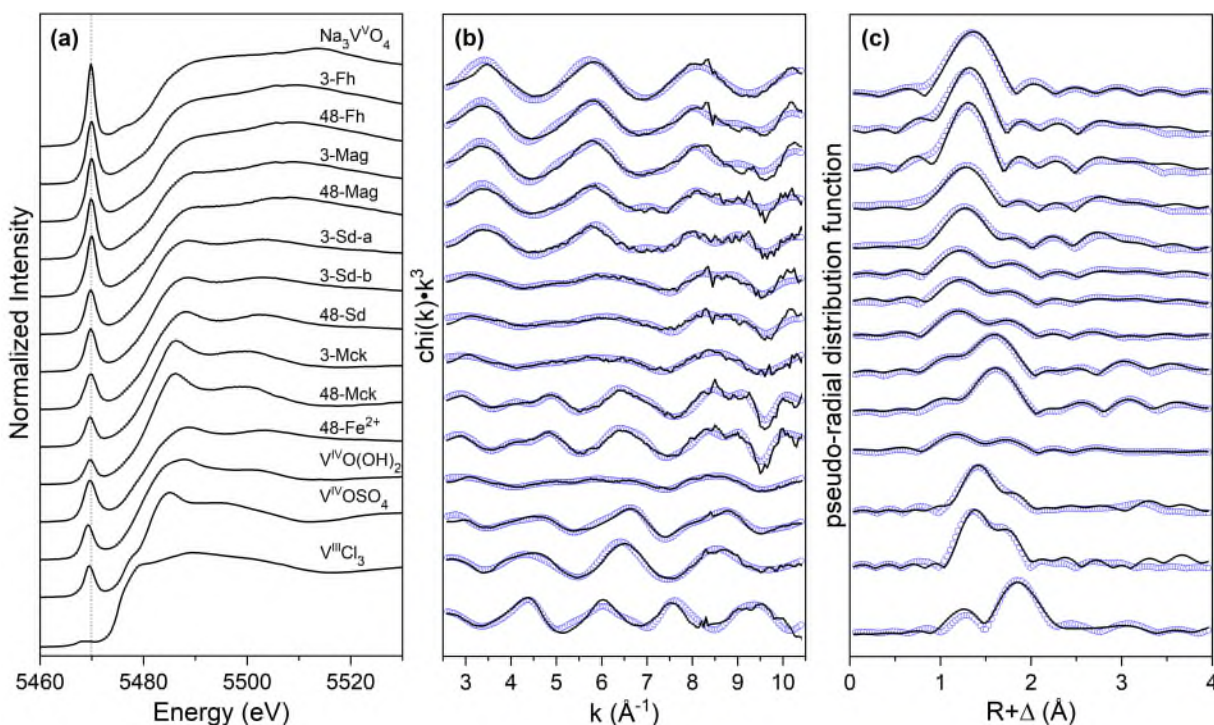
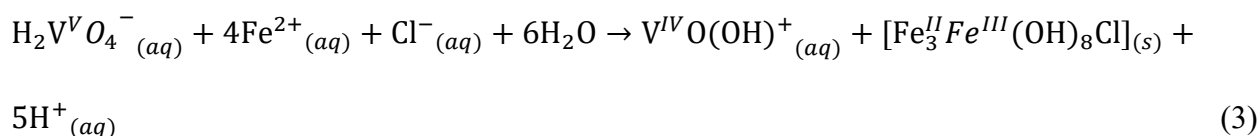
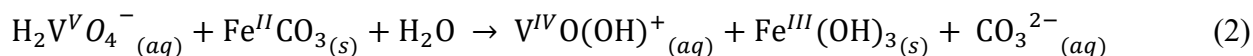
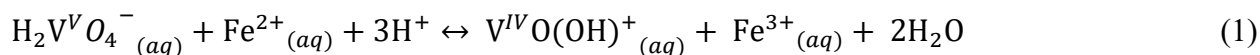


Figure 3. (a) Normalized absorbance of V K-edge XANES spectra for selected reference compounds and samples. Vertical dashed line indicates the theoretical V pre-edge peak position (5468.9 eV). (b) Measured (solid black lines) and modeled EXAFS (open blue circles) k^3 -weighted EXAFS spectra. (c) Pseudo-radial distribution functions for reference compounds and samples. Reference and sample spectra in panels (b) and (c) are ordered for consistency with panel (a).

Variations in EXAFS parameters for reacted siderite samples (3-Sd-a, 3-Sd-b, 48-Sd) were not apparent. The first shell V-O was fit to interatomic distances of 1.660 Å, 1.651 Å, and 1.662 Å, with second shells (V-O) and third shells (V-Fe) consistent between the three samples (Table S4). A second V-Fe scattering path was included for 3-Sd-a (3.66 Å) and 3-Sd-b (3.60 Å) with coordination numbers of ~ 1 , which are indicative of monodentate sorption. This monodentate V-Fe complex was not apparent after 48 h, suggesting conversion to more energetically favorable bidentate corner-sharing complex. The formation of bidentate and monodentate surface complexes simultaneously on metal (oxyhydr)oxide surfaces has been demonstrated to be thermodynamically favourable.^{26,39} Similar to reacted siderite samples, aqueous Fe^{2+} reactions with vanadate produced precipitates with similar EXAFS parameters. Specifically, these

precipitates exhibited a first shell V-O at 1.660 Å, followed by 2 O atoms at 1.955 Å and 2 coordinate Fe backscatters at 3.60 Å. Based on the Fe coordination and interatomic distances for the V-Fe backscatters (3.31-3.38 Å), the V K-edge EXAFS spectra indicate a bidentate corner-sharing complex forming on siderite, and secondary green rust or Fe (oxyhydr)oxides (Figure 4), and is consistent with previous studies of other oxyanion forming metal(loid)s.^{63,66,70,71} First shell V-O distances for 3-Sd-a, 3-Sd-b, 48-Sd, and 48-Fe²⁺ are indicative of mixed sorbed V(V) and V(IV) species at approximately 25% and 75%, respectively. The presence of mixed V oxidation states helps explain the slightly elongate first shell V-O (1.651 - 1.662 Å) and larger than expected first shell coordination compared to the first shell of V^{IV}O(OH)₂ reference (1.614 Å).



V K-edge spectra for reacted mackinawite (3-Mck, 48-Mck) samples revealed the presence of V(IV) and, possibly, V(III) incorporated into the tetragonal structure (Figures 2, 3). The incorporation of metal(loid)s *via* coprecipitation with mackinawite has been previously been demonstrated with metal cations (e.g., Ni²⁺), selenium, (thio)arsenic, and technetium.^{36,70,72–76} EXAFS fitting for V in reacted mackinawite samples were first attempted through V^{IV}O²⁺ sorption and V^{IV}O(OH)₂ precipitation (octahedral coordination); however, X²_{red} and R factor goodness of fit parameters for 3-FeS and 48-FeS were optimized by fitting a single V=O bond at

1.57 and 1.58 Å, respectively, and S atoms with a coordination of ~3 at 2.16 and 2.18 Å, respectively. Following the first two shells repeating V-Fe and V-S backscatters were fit corresponding to the structure of mackinawite similar to Ikogou et al. (2017). Incorporation of V(IV) and V(III) into mackinawite may proceed through coprecipitation reactions or atom rearrangement at the FeS surface (Figure 4).^{72,74} The low solubility product of mackinawite can enhance dissolution-precipitation reactions allowing for the incorporation of dissolved V constituents.^{32,77} However, reduction pathways for V(V) during these experiments cannot be distinguished between surface electron transfer or by dissolved Fe^{2+} as a result of mackinawite dissolution.

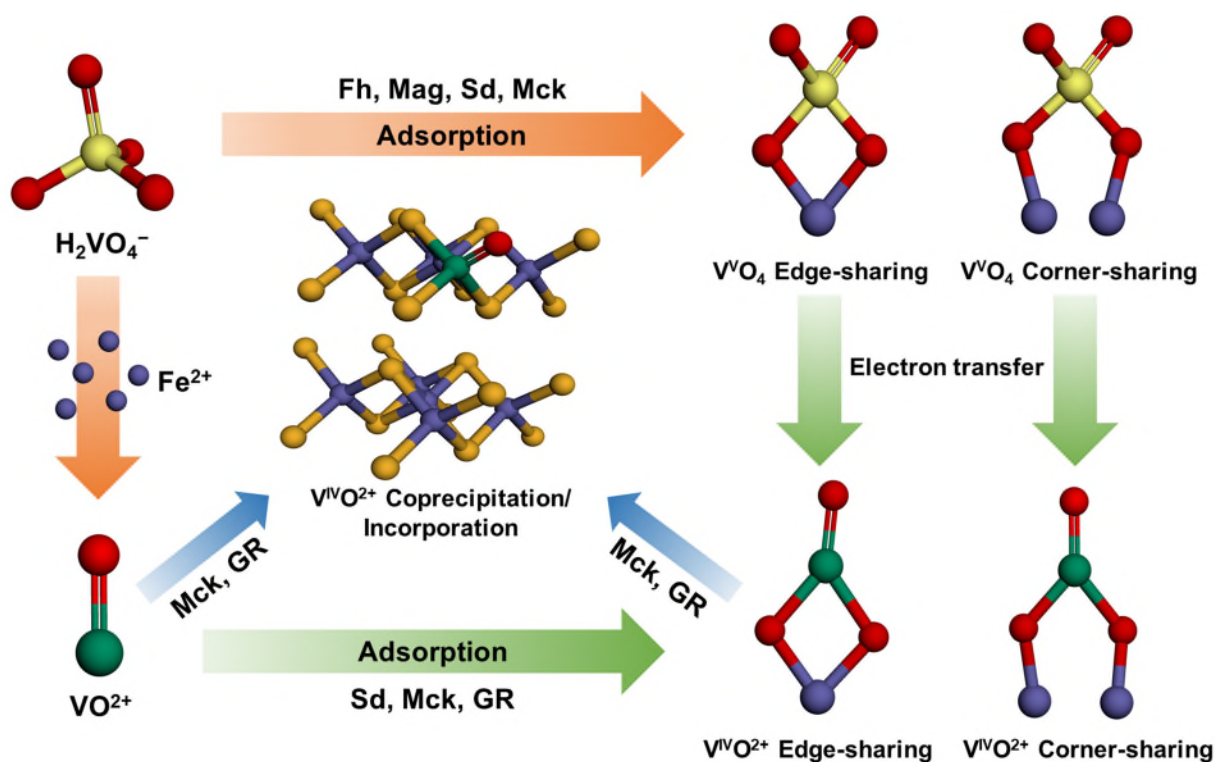


Figure 4. Schematic diagram of vanadate adsorption, reduction, and coprecipitation mechanisms. Atoms colours indicate Fe(II) (purple), O (red), S(-II) (orange), V(V) (yellow), and V(IV) (green). Mineral abbreviations correspond to ferrihydrite (Fh), magnetite (Mag), siderite (Sd), mackinawite (Mck), and secondary green rust (GR).

Environmental Implications. Vanadate removal at circumneutral pH under anoxic conditions by Fe(II)-bearing minerals can involve sorption, reduction, and, in the case of mackinawite, structural incorporation. Although reaction rates differ between Fe(II) mineral phases, V(V) removal and reduction to V(IV) occurs during reaction with magnetite, siderite, and mackinawite. Relative removal rates and V sorption capacity under anoxic conditions follow the general order: mackinawite > ferrihydrite $\geq$ siderite > magnetite >> pyrite. Structural incorporation of V(IV) and, possibly, V(III) into mackinawite is another potential removal mechanism. Despite slower kinetics, reaction with $\text{Fe}^{2+}_{(\text{aq})}$ in anoxic systems can also promote V(V) reduction and subsequent association of V(V) with resulting precipitates. Each of these reactions can remove V(V) from solution under anoxic conditions, thereby limiting aqueous concentrations and, potentially, decreasing bioavailability and toxicity.^{ref}

Our findings suggest that redox cycling associated with oxic-anoxic interfaces, for example the water-sediment interface in lakes or saturated-unsaturated interface in soils, may have important implications for environmental V mobility.^{8,22,44} Although adsorption onto Fe(III) (oxyhydr)oxides can limit aqueous V(V) mobility under oxic conditions,^{38–40} our results demonstrate that Fe(II)-bearing phases can promote extensive V attenuation under anoxic conditions *via* coupled V(IV) adsorption and reduction. These results may have important implications for surface water and groundwater impacted by V leaching from mining and industrial wastes.¹ For example, this information could be used to improve predictions of V(V) mobility at mining and industrial sites and to support development of management and reclamation strategies for associated waters.

ASSOCIATED CONTENT**Supporting Information**

Additional details on synthesis methods and analysis by XRD and Raman spectroscopy are provided. In addition, four additional tables and three additional figures referenced in the text.

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Notes

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